

UNIVERSIDADE ESTADUAL PAULISTA

“Júlio de Mesquita Filho”

Alexandre Zirpoli Simões

**CERÂMICAS E FILMES FINOS COM PROPRIEDADES
ELETROELETRÔNICAS E MULTIFERRÓICAS: UMA ABORDAGEM
MULTIDISCIPLINAR EMPREGANDO MÉTODOS QUÍMICOS.**

GUARATINGUETÁ

2016

UNIVERSIDADE ESTADUAL PAULISTA

“Júlio de Mesquita Filho”

Alexandre Zirpoli Simões

**CERÂMICAS E FILMES FINOS COM PROPRIEDADES
ELETROELETRÔNICAS E MULTIFERRÓICAS: UMA ABORDAGEM
MULTIDISCIPLINAR EMPREGANDO MÉTODOS QUÍMICOS.**

Texto apresentado a Faculdade de Engenharia
de Guaratinguetá, Universidade Estadual
Paulista - UNESP, para o concurso de Livre
Docência.

GUARATINGUETÁ

2016

Simões, Alexandre Zirpoli

S593c

Cerâmicas e filmes finos com propriedades eletroeletrônicas e multiferróicas: uma abordagem multidisciplinar empregando métodos químicos / Alexandre Zirpoli Simões – Guaratinguetá, 2016.

293f.: il.

Bibliografia: f. 109-119

Tese (Livre-Docência) – Universidade Estadual Paulista, Faculdade de Engenharia de Guaratinguetá, 2016.

1. Ferroeletricidade. 2. Cerâmica. 3. Filmes finos. 4. Cristalização.

I. Título

CDU 537.226.4

**Aos co-autores deste trabalho, citados ou não,
Todos igualmente importantes.**

MEUS ORIENTADOS

AGRADECIMENTOS

Gostaria de expressar meus sinceros agradecimentos a todos que direta ou indiretamente contribuíram para realização deste trabalho. Embora reconheça que tivesse que nomeá-los, eu certamente esqueceria muitos de vocês, confio que cada um será capaz de se reconhecer nas palavras que seguem:

Aos mestres, que em momento difíceis de minha vida souberam mostrar o caminho correto a seguir;

Os alunos, e especialmente aos alunos de iniciação científica, mestrado, doutorado e pós-doutorado que estiveram presente, e que tornaram possível desenvolver este trabalho, embora apenas alguns de vocês sejam citados explicitamente. Sem vocês tudo continuaria na forma de idéias e projetos.

Aos Docentes do Departamento de Materiais e da Faculdade de Engenharia de Guaratinguetá, que me ensinaram a caminhar e permitiram que eu crescesse.

A todos os funcionários desta instituição, da UFSCar e do IQ-UNESP-Araraquara que colaboraram diretamente na execução deste trabalho.

A minha família pelo amor e carinho, e pela compreensão em todos os momentos que deixei de participar.

Aos amigos sempre presentes, mesmo ausentes.

Não posso deixar de expressar ainda meus agradecimentos aos órgãos de apoio ao desenvolvimento das pesquisas que permitiram o crescimento científico: CAPESP, CNPq, FAPESP e FUNDUNESP, financiando as pesquisas, a formação de recursos humanos e a divulgação dos resultados científicos.

Finalmente, quero agradecer a DEUS pelo dom da vida e pela capacidade de acreditar no futuro como um mundo melhor.

**Professores corrigem os erros,
Mestres ensinam a pensar.
Augusto Cury**

RESUMO

O objetivo central desta tese foi obter sistemas cerâmicos com estruturas perovskitas ferroelétricos e multiferróicos do tipo $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ e observar a influência dos métodos químicos de processamento na capacidade de formador da rede cristalina atuar na estabilidade dos complexos polióxidos. Para esse propósito, cerâmicas e filmes finos com composição complexa foram estudados e permitiram respostas elétricas que demonstram sem dúvida o avanço da tecnologia em eletroeletrônica e como guias de onda planar. O método dos precursores poliméricos que considera a capacidade de fixar metais de forma que estes utilizem sua memória química foi elucidado. Avanços consideráveis foram alcançados na formação de fases como $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ sem a cristalização de fases deletérias, livre de aglomerados, distribuição homogênea do tamanho de partículas, elevada pureza e cristalinidade. Vale destacar que a concentração dos reagentes formadores da cadeia polimérica, a temperatura de decomposição e a atmosfera utilizada durante a combustão do polímero determinam a reatividade dos óxidos dos metais que se formam inicialmente complexados. Em específico para os pós cerâmicos, o controle da cristalização das fases secundárias e da morfologia permite ampliar o universo de aplicação dos desde sua compactação e sinterização em temperaturas menores com menor variação da estequiometria até sua aplicação em filmes espessos, capacitores, catalisadores, sensores, etc. Para obtenção de filmes finos por métodos químicos, por dip-coating ou spin-coating, um número muito grande de variáveis devem ser controlados como: composição, concentração, viscosidade, temperatura e tempo de tratamento do filme. As características das soluções são determinantes na morfologia, superfície, densidade e cristalinidade dos filmes. A vantagem desse método é a possibilidade de se trabalhar com concentração mínima de aditivos, de poder depositar camadas de diferentes materiais, tipo heteroestruturas, de poder tratar todas as camadas de uma só vez ou tratá-las separadas, permitindo obter filmes com características ferroelétricas, piezoelétricas e multiferróicas de interesse da comunidade científica em diferentes segmentos de aplicações. Portanto, a versatilidade do método em temperatura relativamente baixa, garante um controle sobre a estrutura, estequiometria e morfologia destes filmes permitindo utilizar substratos menos nobres e obter filmes texturizados ou orientados preferencialmente, utilizando o artifício da camada semente. No que refere-se às propriedades para guias de onda planar, filmes com espessura superiores a 500 nm são capazes de suportar vários modos TE (elétrico transversal) e TM (magnético transversal) com mínima perda óptica. As propriedades dos filmes finos usados para memórias de múltiplos estados e memórias não voláteis dependem da espessura, eletrodo inferior, atmosfera e tipo de cristalização, tipo de dopante, nível de textura, microestrutura, interação filme-substrato. O acoplamento magnetoelétrico foi determinado para filmes obtidos pelo método dos precursores poliméricos por intermédio da interação ferroelástica entre uma camada ferromagnética e uma adjacente antiferromagnética. Portanto, podemos dizer que independente do custo, tempo e rendimento, a qualidade, a flexibilidade e a eficiência dos processos químicos são indiscutíveis.

PALAVRAS CHAVES: Perovskita. Síntese Química. Ferroeletricidade.

ABSTRACT

The main goal of the present work was to obtain ceramic systems with perovskite structure based on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ with ferroelectric and multiferroic properties and observe the influence of chemical processing methods in the capacity of the crystal lattice network providing stability of polyoxides complex. For this purpose, ceramics and thin films with complex composition were studied and allowed electrical responses that demonstrate the technology advances in electroelectronics and as planar waveguides. The polymeric precursor method that considers the ability to fix metal using its chemical memory has been elucidated. Considerable advances have been achieved in the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT $\text{CaBi}_2\text{Nb}_2\text{O}_9$ phases without deleterious phases crystallization, free from agglomerates, homogeneous distribution of particle size, high purity and crystallinity. It is noted that the concentration of the polymer chain forming reactants, the decomposition temperature and atmosphere employed during combustion of the polymer determine the reactivity of the metals oxides initially complexed. In particular for the ceramic powders, controlling the crystallization of secondary phases and the morphology allows to extend the application universe from compaction and sintering at lower temperatures with less variation in stoichiometry allowing its application in thick films, capacitors, catalysts, sensors, etc. To obtain thin films by chemical methods, by dip-coating or spin-coating, some variables must be controlled such as: composition, concentration, viscosity, temperature and time of annealing. The solutions characteristics are crucial in morphology, surface, density and crystallinity of the films. The advantage of this method is the possibility to work with a minimum concentration of additives in order to deposit layers of different materials, heterostructure architecture, able to deposit all layers at once or treat them apart, allowing to obtain films with ferroelectric piezoelectric and multiferroics characteristics of enormous interest in the scientific community in different segments of applications. Therefore, the versatility of the method at relatively low temperatures, ensures control over the structure, stoichiometry and morphology of these films allowing to use less noble substrates and to obtain textured films or preferentially oriented using the seed layer. Films obtained by the polymeric precursor method and used as planar waveguides with a thickness greater than 500 nm are capable of supporting multiple modes TE (transverse electric) and TM (transverse magnetic) with minimal optical loss. The properties of thin films used for multi-state nonvolatile memories and non-volatile memories depend on the thickness, the bottom electrode, atmosphere, type of crystallization and dopants, texture level, microstructure, film-substrate interaction. The magnetoelectric coupling was determined from films obtained by the polymeric precursors by the ferroelastic interaction between a ferromagnetic layer and an adjacent antiferromagnetic layer. Therefore we can say that regardless of the cost, time and performance, quality, flexibility and efficiency of chemical processes are unquestioning

KEYWORDS: Perovskite. Chemical Syntheses. Ferroelectrics.

SUMÁRIO

1 CONSIDERAÇÕES GERAIS	12
2 CERÂMICAS E FILMES FINOS COM APLICAÇÕES ELETROELETRÔNICAS: VISÃO GERAL	17
3 COMPILAÇÃO DOS RESULTADOS OBTIDOS PARA SISTEMAS ELETROELETRÔNICOS (CERÂMICAS)	25
4 COMPILAÇÃO DOS RESULTADOS OBTIDOS PARA SISTEMAS ELETROELETRÔNICOS (FILMES FINOS)	48
4.1 FILMES FINOS OBTIDOS POR MÉTODO QUÍMICO VIA SOLUÇÃO	48
4.2 SISTEMA CAMADA DE BISMUTO (FAMÍLIA DOS AURIVILLIUS)	48
4.3 SISTEMA MULTIFERRÓICO A BASE DE FERRITA DE BISMUTO	77
4.4 COMPARAÇÃO ENTRE AS MEMÓRIAS DE ACESSO ALEATÓRIO (RANDOM ACCESS MEMORIES- RAM)	79
5 CONSIDERAÇÕES FINAIS	107
REFERÊNCIAS	109
ANEXO A - Preparation of lanthanum doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics by the polymeric precursor method	120
ANEXO B - Niobium doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics obtained by the polymeric precursor method	125
ANEXO C - Rietveld Analyses and Piezoelectric Properties of Niobium Doped Bismuth Titanate Systems	129
ANEXO D - Piezoresponse force microscopy behaviour of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics with various excess bismuth	138
ANEXO E - Electrical Properties of Textured Niobium-Doped Bismuth Titanate Ceramics	150

ANEXO F - Mechanically activating formation of layered structured bismuth titanate	157
ANEXO G - Effect of processing route on the phase formation and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics	163
ANEXO H - Synthesis and electrical characterization of tungsten doped $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ceramics obtained from a hybrid process	169
ANEXO I - Lanthanum doped BiFeO_3 powders: Syntheses and characterization	173
ANEXO J - Low-temperature synthesis of nanosized bismuth ferrite by the soft chemical method	178
ANEXO K - Influence of temperature on the dielectric and ferroelectric properties of bismuth titanate thin films obtained by the polymeric precursor method	186
ANEXO L- Characterization of lanthanum-doped bismuth titanate thin films prepared by polymeric precursor method	192
ANEXO M - The influence of crystallization route on the properties of lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared from polymeric precursors	198
ANEXO N - Ferroelectric and Dielectric Properties of Lanthanum-Modified Bismuth TitanateThin Films Obtained by the Polymeric Precursor Method	206
ANEXO O - Influence of the solution pH on the morphological, structural and electrical properties of $\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{12}$ thin films obtained by the polymeric precursor method	212
ANEXO P - Fatigue-free behavior of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films grown on several bottom eletrodes by the polymeric precursor method	218
ANEXO Q - Retention characteristics in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films prepared by the polymeric precursor method	221
ANEXO R - Electromechanical properties of calcium bismuth titanate films: A potential candidate for lead-free thin-film piezoelectrics	224
ANEXO S - Effect of the microwave oven on structural, morphological and electrical properties of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ thin films grown on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates by a soft chemical method	227
ANEXO T - Synthesis and electrical characterization of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films	

deposited on Pt/Ti/SiO ₂ /Si substrates by polymeric precursor method	233
ANEXO U - High Curie point CaBi ₂ Nb ₂ O ₉ thin films: A potential candidate for lead-free thin-film piezoelectrics	237
ANEXO V - Ferroelectric characteristics of BiFeO ₃ thin films prepared via a simple chemical solution deposition	241
ANEXO W - Improvement of fatigue resistance on La modified BiFeO ₃ thin films	247
ANEXO X – Strain behavior of lanthanum modified BiFeO ₃ thin films prepared via soft chemical method	251
ANEXO Y - Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films	258
ANEXO Z - Effect of niobium dopant on fatigue characteristics of BiFeO ₃ thin films grown on Pt electrodes	264
ANEXO A1 - Structure, ferroelectric/magnetoelectric properties and leakage current density of (Bi _{0.85} Nd _{0.15})FeO ₃ thin films	270
ANEXO B1 - Magnetoelectric Coefficient in Strontium Ruthenate Buffered Lanthanum Modified Bismuth Ferrite Thin Films Grown by Chemical Method	280
ANEXO C1 - Experimental evidence of enhanced ferroelectricity in Ca doped BiFeO ₃	286

1 CONSIDERAÇÕES GERAIS

O desenvolvimento da sociedade humana tem estado condicionado, em muitos aspectos, ao desenvolvimento de novos materiais artificiais e de novas tecnologias de fabricação de dispositivos. Quando se trata de materiais eletroeletrônicos, a evolução tecnológica passa pela preparação de materiais multi-componentes com características especiais. No entanto, a busca desse desenvolvimento tem gerado o aumento do consumo das reservas naturais e de energia. A destruição do meio ambiente e a perspectiva de escassez de reservas têm levado os pesquisadores a concentrar mais esforços no desenvolvimento de métodos alternativos que consumam menos energia, dispensem o uso de vácuo e/ou alta pressão e não causem alterações climáticas pela liberação de gases na atmosfera. Observando a natureza, podemos ver os contrastes entre os métodos utilizados por plantas e animais e os utilizados pelos engenheiros, para sintetizar materiais similares. Por exemplo, a casca do arroz assim como as paredes das células das diatomáceas, contêm sílica, que é produzida a temperatura ambiente por meios químicos naturais. Considerando a sua capacidade de imitar a natureza, como alternativa, para obtenção de materiais avançados em condições menos agressivas ao meio ambiente, os processos químicos têm atraído os pesquisadores. Assim, novos métodos de síntese, baseados na química de via úmida, têm sido desenvolvidos nas últimas décadas.

Na realidade, pode se constatar que os métodos químicos eram utilizados na síntese de materiais já no século XVII, quando von Helmont preparou o vidro líquido, que se tornou rapidamente um produto de importância industrial pela baixa energia exigida e por oferecer sílica na forma solúvel (1-2). Em 1797, Valquelin publicou a produção de zircônia a partir de hidróxido de zircônio (3). No início do século XIX, Berthier se reportava à síntese de zirconato de cobre obtido pela reação de sais de cobre e de zircônio precipitados com hidróxido de amônio (4). A síntese de alcoxido de silício foi reportada pela primeira vez por Ebelmen (5), e meio século depois, Ohring reportou pela primeira vez a síntese de sílica por intermédio da hidrólise do alcoxido de silício (6). Definitivamente, constatamos que os métodos químicos, desde a apresentação inicial como métodos alternativos, foram sendo viabilizados desde o século XVII e são hoje amplamente utilizados na indústria.

Temos atualmente o Processo Bayer, para produção de alumina, que envolve dissolução do minério, em meio básico, seguida de precipitação. A produção de zeólitas, para catálise de petróleo, obtida por síntese hidrotérmica. A produção de óxido de zircônio, livre de háfnio, para reatores nucleares, ou estabilizado com ítria, para fabricação de refratários baseada na

dissolução de zirconita em meio básico, seguida de precipitação e purificação. Esses exemplos ilustram os processamentos utilizados quando os processos envolvem o uso de minerais. Nos casos acima, são exigidos métodos químicos para se obter matérias-primas purificadas e com características específicas para a aplicação de alto desempenho. Na sua maioria, os materiais inorgânicos são óxidos simples ou complexos, que constituem os chamados materiais cerâmicos, mas têm os minerais como fonte de matéria-prima. Portanto, têm estado sujeitos a processos especiais, que envolvem alta energia, para extração, moagem, fusão, obtenção do intermediário, purificação sinterização, prensagem a quente, etc. Esses processos são necessários para obtenção e conformação de um material de forma que o dispositivo exiba características específicas. Entretanto, as cerâmicas tradicionalmente preparadas a partir de mistura dos óxidos individuais apresentam aglomerados grandes e fortes, o que dificulta o processo de sinterização. Em função da necessidade de temperaturas elevadas acontece a perda de componentes voláteis, acarretando diferentes fenômenos como: cristalização de fases secundárias, crescimento anormal dos grãos, baixa reprodutibilidade e perda estequiométrica. Como consequência, tem-se um produto final com propriedades elétrica e mecânicas muito inferiores às desejadas.

Apesar de a utilização dos métodos químicos já estar presente na preparação de materiais há muitos anos, somente no século XX verificou-se um crescente interesse por parte da indústria de alta tecnologia. Esse interesse deve-se às propriedades especiais exibidas pelos materiais, quando as partículas atingem um intervalo de tamanho nanométrico, entre os estados molecular e sólido, podem gerar propriedades únicas devido aos efeitos de confinamento quântico ou de superfície. Essas nanoestruturas e os materiais nanoestruturados de um modo geral, estão dentro das necessidades de miniaturização de circuitos eletrônicos integrados devido as novas aplicações de nanodispositivos eletrônicos. O desenvolvimento de circuitos integrados, memórias de computador e outros dispositivos caminham com a pesquisa em nanomateriais, pois equipamentos mais potentes e versáteis ajudam na pesquisa de novos processos e na descoberta de novos materiais nanoestruturados, que por sua vez permitem o aperfeiçoamento dos referidos componentes eletrônicos, ópticos, etc. No esforço de se obter pós-cerâmicos e filmes nanoestruturados têm-se desenvolvido inúmeras pesquisas direcionadas à otimização de métodos não tradicionais, que permitam obter compostos cristalinos com um único passo de processamento. Processos químicos em solução, síntese hidrotérmica, eletrodeposição, “templates”, deposição por evaporação de sólidos ou líquidos ou mesmo métodos que utilizem multi-etapas, como precipitação por ajuste de pH, sol-gel, síntese por dupla troca ou reação de estado sólido podem ser utilizados desde que viabilizem a

síntese de fases complexas. As características especiais dos materiais, consequência de processamento diferenciado, resultam em comportamento e propriedades também diferenciados, quando de sua utilização. A importância da obtenção dos materiais nanoestruturados está em possibilitar cerâmicos de melhor sinterabilidade (6), maior resistência, a exemplo dos revestimentos de alta dureza, como os fabricados a partir do WC/Co (7). De um modo geral, as cerâmicas nanoestruturadas são mais resistentes e tenazes. Incontáveis exemplos de materiais nanoestruturados estão disponíveis, como: dispositivos multicamadas magnéticas que apresentam maior poder de armazenamento, membranas cerâmicas com poros na faixa de 2,5 nm, usadas na separação de líquidos e gases ou em catálise (8) filmes finos aplicados em junções “tunnel” e “quantum wells” e memórias de acesso aleatório dinâmica (DRAM) (9). Já temos a oferta de processadores de tamanho reduzido com capacidade superior a 1 Gbyte. Isso só foi possível com a manufatura e a engenharia em escala nanométricas. Nos EUA, o interesse pelos materiais nano-estruturados tem crescido 30% ao ano e os processos químicos via úmida, ou seja, o processo em solução, têm sido uma alternativa promissora para alcançar o controle tridimensional (tamanho e forma) e em escala atômica (composição estequiométrica e de dopantes) dos materiais (10).

A crescente demanda por materiais com melhor desempenho e funcionalidade tem acelerado o desenvolvimento de técnicas de síntese para produzir pós com partículas bem definidas em tamanho, forma e cristalinidade. As eletrocerâmicas, na forma de filmes finos ou corpo cerâmico, têm seu desempenho determinado pela composição e características dos pós utilizados e pelo processo de preparação. Portanto, propriedades físicas e químicas dos pós, tais como: controle da estequiometria, pureza química, homogeneidade, tamanho e forma de partícula, devem ser considerados quando da escolha dos métodos de síntese.

Há uma vasta literatura sobre a síntese de materiais ferroelétricos com composição complexa, particularmente os de estrutura perovskita (11-17), devido ao interesse nas propriedades piezelétricas, dielétricas e ópticas de monocristais ou materiais ferroelétricos policristalinos. Impurezas, tamanho e morfologia das partículas são características importantes a serem controladas pela escolha do método de síntese, particularmente em materiais cujas propriedades estão relacionadas à anisotropia dos cristais. O crescimento da indústria eletrônica está associado ao desenvolvimento dos materiais ferroelétricos tipo perovskita baseados em óxidos multicomponentes (composições com 4 ou mais cátions), incluindo os dopantes usualmente adicionados para melhorar as propriedades. Esses óxidos multicomponentes são usualmente utilizados para produzir cerâmicas eletroeletrônica de alta tecnologia, alto desempenho e com reprodutibilidade.

Atualmente, esses materiais não estão disponíveis comercialmente com as características necessárias, portanto a indústria tem enorme necessidade de produzi-los. Aliado a isso, durante as últimas duas décadas, o interesse pela síntese de materiais nanoestruturados resultou em um aumento significativo dos métodos de preparação das partículas. Algumas dessas técnicas podem ser utilizadas na síntese de um vasto número de materiais. Dentre os métodos destacam-se:

Síntese por micro emulsões: (18-21). Osseo-Asare (22) tem estudado os materiais e as condições usadas para sintetizar óxidos de metal obtidos por microemulsão. A maioria dessas partículas são classificadas como nanométricas, por causa da natureza da síntese nos nano-reatores auto-controlados. A maioria das partículas produzidas em micro-reatores é esférica.

Síntese Hidrotérmica: É uma técnica rápida e pode obter alto rendimento do produto. Essa técnica permite produzir pós com alta pureza, alta cristalinidade, tamanho médio de partículas de 3 nanômetros até micrometros, estreita distribuição de partículas e bom controle estequiométrico, em baixas temperaturas. Adair e colaboradores (19) têm estudado a síntese de partículas de tamanho nanométrico, em particular a síntese de partículas nanométricas em forma de placas. Por exemplo, Moon e colaboradores (12-13) desenvolveram estudos específicos para controle morfológico especialmente em PbTiO_3 (PT), BaTiO_3 (BT) e $(\text{Pb,Zr})\text{TiO}_3$ (PZT).

Método sol gel (23-26): Dentre os métodos químicos em solução, é um dos mais conhecidos. Utiliza predominantemente alcoóxidos de metal como precursores e produz partículas estequiométricas com tamanho de ordem de 50-1000 Å, com estreita distribuição de tamanho. As principais desvantagens desse método são: o baixo rendimento, as matérias-primas mais caras e o longo tempo de processamento.

Processo Pechine (18): Produz uma matriz polimérica, que pode ser utilizada para preparar pós ou ser depositada na forma de filmes finos. A resina polimérica, contendo os cátions imobilizados e homogeneamente distribuídos, é convertida termicamente em óxidos inorgânicos. Esse método permite sintetizar partículas na faixa de nanômetros a micrômetros, utilizando precursores mais baratos. A desvantagem desse método, principalmente para a preparação de pós, é a dificuldade em inibir a formação de aglomerados devido à elevada reatividade superficial das partículas. No caso de filmes, a desvantagem está no alto teor de matéria orgânica a ser eliminada.

Biomimetismo (27-28); **Self-Assembly** (29-30); **Templating** (31-32) são alguns dos outros métodos ainda pouco conhecidos e pouco utilizados, mas também aplicáveis na fabricação de materiais com características específicas. O uso de uma determinada técnica ou

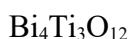
associação de duas ou mais delas pode ser a chave do sucesso. Na obtenção do material, considera-se a pureza de fase, morfologia, cristalinidade, homogeneidade química, etc. Dependendo do material a ser fabricado das características desejadas, algumas técnicas podem apresentar limitações, portanto a diversidade de técnicas disponíveis é um fator muito importante que sempre impulsiona as pesquisas por novos caminhos.

2 CERÂMICAS E FILMES FINOS COM APLICAÇÕES ELETROELETRÔNICAS: VISÃO GERAL

Recentemente tem havido uma crescente demanda por eletrocerâmicas com melhor desempenho e funcionalidade. Essa demanda tem acelerado o desenvolvimento de técnicas de síntese para produzir pós com partículas bem definidas em tamanho, forma e cristalinidade. A eletrocerâmicas, na forma de “bulk” e filmes finos, têm seu desempenho determinado pelas características dos pós-utilizados e pelo processo de preparação das soluções. Portanto, propriedades físicas e químicas dos pós, tais como: controle da estequiometria química, pureza, homogeneidade, tamanho e forma de partícula devem ser observados quando da escolha do método de síntese.

A síntese de materiais ferroelétricos com composição complexa, particularmente perovskita, tem despertado interesse pelas propriedades piezoelétricas, dielétricas e ópticas desses materiais, mono ou policristalinos. Impurezas, tamanho e morfologia de partícula são características importantes que podem ser controladas pela escolha do método de síntese. As cerâmicas ferroelétricas com estrutura perovskita compõem uma família de materiais com amplo horizonte de aplicações tanto na forma de corpo cerâmico como na forma de filmes finos. Dentre as aplicações estão ultra-sonografia médica, atuadores, sensores e transdutores piezoelétricos (34), filmes finos aplicados a circuitos integrados, capacitores de multicamadas (35), memórias FERAM e DRAM (36), atuadores eletrostrictivos (37), detetores piroelétricos (38), componentes eletroópticos (39), guias de onda (40). Esse amplo espectro de aplicações realimenta o interesse por novos dispositivos mais eficientes e viáveis economicamente (41).

$\text{Pb}(\text{Zr,Ti})\text{O}_3$	Piezoelétrico
$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$	Dielétrico
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	Dielétrico Relaxor
BaTiO_3 , SrTiO_3	Capacitor /semiconductor
$\text{SrBi}_2\text{Nb}_2\text{O}_8$	Capacitor de multicamadas
$\text{SrBi}_2\text{Ta}_2\text{O}_8$	Capacitor de multicamadas
$\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{65}\text{Ti}_{35})\text{O}_3$	Eletroóptico
LiNbO_3 e KNbO_3	Eletroóptico



Capacitor Ferroelétrico



Multiferróico

Os resultados disponíveis na literatura em processamento de cerâmicas perovskita com propriedades ferroelétricas indicam que existem dificuldades em se obter as fases ferroelétricas sem a presença de outras fases deletérias, como é o caso da fase pirocloro. Essa fase pode nuclear como precursora da fase perovskita ou como resultado de sua decomposição. Por exemplo, uma fase pirocloro deficiente em magnésio aparece em temperaturas inferiores a de formação do PMN indicando que a reação de difusão não está completa, enquanto a fase pirocloro $\text{Pb}_3\text{Nb}_2\text{O}_8$ aparece como resultado da decomposição da fase PMN durante a sinterização. A dificuldade em se obter a fase perovskita pura é mais preponderante em compostos com estrutura contendo chumbo, pois durante a sinterização ocorre a volatilização do óxido de chumbo, o que torna difícil controlar a estequiometria dessas cerâmicas (42-47). Como consequência pode haver formação de fases não ferroelétricas gerando heterogeneidade. O uso de métodos químicos tem por objetivo diminuir a temperatura de formação da fase cristalina desejada, aumentar a reatividade superficial do pó obtido, controlar a homogeneidade química e assim baixar a temperatura de sinterização, o que possibilita controlar a estequiometria das fases cerâmicas e minimizar a cristalização de fases secundárias.

O titanato de bário (BaTiO_3) foi a primeira cerâmica ferroelétrica a ser explorada extensivamente, nos últimos 50 anos, para utilização como dielétrico, como capacitores de multicamadas, transdutores eletromecânicos e para fabricação de termistores devido às suas propriedades (48). No entanto, desde o estabelecimento do diagrama de equilíbrio entre as fases PbTiO_3 e PbZrO_3 indicando uma extensa região de solução sólida com propriedades ferroelétricas, as cerâmicas perovskitas à base de chumbo passaram a receber uma atenção muito grande devido às suas excelentes propriedades dielétricas, piezoelétricas, piroelétricas, etc. Essa classe de cerâmicas engloba desde as composições mais simples tipo ABO_3 (PbTiO_3) até composições complexas tipo $\text{A}(\text{B}', \text{B}'')\text{O}_3$, $\text{Pb}(\text{Mg}_{0.5}\text{Nb}_{0.66})\text{O}_3$, em que B' e B'' são alcalinos terrosos ou metais de transição. Geralmente, os cátions do sítio B' apresentam baixa valência, por exemplo íons Mg^{+2} , Zn^{+2} , Fe^{+2} , Ni^{+2} , enquanto os cátions do sítio B'' apresentam valência maior, por exemplo Ti^{+4} , Nb^{+5} , Ta^{+5} , W^{+6} (49).

Os mais recentes desenvolvimentos na área de cerâmicas ferroelétricas, tais como ultrasonografia médica, atuadores piezoelétricos, filmes finos aplicados a circuitos integrados,

entre outros, realimentam o interesse em novos dispositivos mais eficientes e viáveis economicamente. Basicamente duas cerâmicas formam o eixo principal das pesquisas em materiais ferroelétricos: PZT e PMN-PT.

O Titanato Zirconato de Chumbo (PZT) é a cerâmica piezoelétrica mais amplamente estudada e aplicada comercialmente. A fase PZT de interesse pode apresentar uma gama de composições segundo a fórmula $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$. No limite morfotrópico de fases (LMF), para $x=0,52$, há uma otimização nas propriedades piezoelétricas, operando na temperatura ambiente (50,51). Na prática, as cerâmicas PZTs são frequentemente modificadas para permitir a diversidade de aplicações ou melhorar o desempenho do dispositivo final. Dependendo da demanda por diferentes aplicações, podem ser adicionados modificadores, fazendo com que o PZT possa operar em condições drásticas (“PZT Hard”), devido aos baixos valores de permissividade elétrica, fator de dissipação e coeficiente piezoelétrico, fazendo com que seja de difícil polarização e despolarização. Para fabricação de um “PZT Hard” adicionam-se convencionalmente íons receptores de elétrons, como K^+ ou Na^+ no sítio A, ou Fe^{+3} , Al^{+3} ou Mn^{+3} no sítio B da estrutura perovskita. Um “PZT Soft”, no entanto, é usado em condições que exijam forte propriedade piezoelétrica e é obtido ao se adicionar íons doadores de elétrons, como La^{+3} no sítio A, ou Nb^{+5} ou Sb^{+5} no sítio B da estrutura (52-55).

O Niobato de Chumbo e Magnésio (PMN) possui estrutura perovskita $\text{A}(\text{B}',\text{B}'')\text{O}_3$ com composição $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. É uma cerâmica relaxora amplamente estudada devido ao grande potencial tecnológico. Apresenta propriedades eletrostrictivas, que possibilitam sua utilização em sensores de deslocamento de alta precisão e alta constante dielétrica ($K_m > 20.000$), conferindo eficiência volumétrica nos capacitores. Essas características tornam o PMN especialmente vantajoso na fabricação de capacitores cerâmicos de multicamadas, pois permitem aumentar a capacitância por um custo menor, possibilitando ainda a operação em baixa voltagem (56,57). Uma limitação de seu potencial é a temperatura de máxima constante dielétrica, T_m , que está intrinsecamente entre -7 e -15 °C. O uso de dopantes ou de uma outra cerâmica ferroelétrica como PT, com T_m elevada são alternativas intrinsecamente pesquisadas. A adição de PT faz com que a T_m da cerâmica PMN se eleve em torno de 5°C para cada 1 mol % de PT adicionado (58). As excelentes propriedades eletromecânicas alcançadas para a cerâmica PMN-PT viabilizaram sua aplicação como transdutores piezoelétricos e eletrostrictivos (59-65). No entanto, as propriedades relaxoras, típicas do PMN, são diminuídas proporcionalmente com o aumento da concentração da fase PT. Cerâmicas eletrostrictivas como PMN-PT exibem um efeito de conversão eletromecânica

similar às piezocerâmicas tipo PZT, onde o sinal elétrico é convertido em movimento mecânico ou força geradora. As cerâmicas eletrostrictivas mostram ainda algumas vantagens sobre os atuadores PZT durante o controle de movimento simples. Uma comparação do coeficiente piezoelétrico dos sistemas $\text{Pb}(\text{Zr}_{0,5}\text{Ti}_{0,5})\text{O}_3$ (PZT) e $0,60 \text{ Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 + 0,40 \text{ PbTiO}_3$ (PMN-PT) feito por Beillaiche e Vanderbilt (66) mostrou que o coeficiente piezoelétrico do PMN-PT pode ser de 2,7 melhor que o coeficiente piezoelétrico do PZT.

Estudos já realizados indicam que o sistema $(1-x)\text{PMN}-x\text{PT}$ tem natureza piezoeletrica para composições com $x > 0,30$, enquanto que para valores de $x < 0,15$ o sistema $(1-x)\text{PMN}-x\text{PT}$ apresenta propriedades eletrostrictivas. O sistema PMN-PT tem um limite morfotrópico de fase (LMF) separando as fases tetragonal e romboédrica, muito similar ao LMF encontrado no sistema titanato zirconato de chumbo (PZT). Assim como neste sistema, as propriedades piezoelétricas são maximizadas na região do LMF, que se localiza no intervalo onde $0,30 < x < 0,40$, para o sistema $(1-x)\text{PMN}-x\text{PT}$ (67).

Embora as cerâmicas perovskitas, à base de chumbo tenham um grande potencial de aplicações, possuem também os inconvenientes da formação de fases deletérias e consequentemente baixa reprodutibilidade. Esses fatores têm um peso muito grande quando se trata de produção em larga escala. Novas fases ferroelétricas perovskita que exibem propriedades comparáveis com o PZT, que não apresentam chumbo na composição têm se apresentado como opção para substituir os materiais que apresentam problemas de estabilidade e os filmes que apresentam o fenômeno de fadiga. Nesse sentido, nos últimos anos foram sintetizadas novas fases cerâmicas principalmente niobatos e tantalatos de camadas de bismuto da família de Aurivilius. Dentre essas novas fases, destacam-se $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) e $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN). A estrutura dos ferroelétricos de camada de bismuto foi investigada por Aurivilius em 1949 (68). Mais recentemente Smolenski estudou a ferroeletricidade desses óxidos complexos (69) e verificou que são excelentes para serem usados em capacitores de filmes finos devido à ausência de fadiga (mesmo após 10^{12} ciclos de polarização-despolarização), boas características de retenção e baixa corrente de fuga. Essas propriedades são observadas mesmo para filmes mais finos que 100 nm (70,71).

A formação da fase pirocloro no SBT e SBN tem sido constatada em várias publicações e muitas vezes tem sido também citada a formação de uma fase intermediária fluorita, durante a cristalização da fase perovskita (72-74). Acredita-se que essa fase seja controlada pela difusão do bismuto. Desta forma, se a difusão do bismuto for controlada, será possível obter fases SBT ou SBN em menores temperaturas. A fase pirocloro é deletéria às propriedades ferroelétricas e apresentam grãos pequenos e de forma arredondada (75). Para confirmar a

presença dessa fase, normalmente utiliza-se a microscopia eletrônica de varredura. As cerâmicas e filmes de camada de bismuto apresentam também dois problemas sérios que são a volatilização do bismuto e o crescimento de grãos com anisotropia. A formação de partículas com morfologia de placas, especialmente se não forem nanométricas dificulta o empacotamento e a densificação a verde. Portanto, o processo de sinterização a temperaturas relativamente baixas (900 a 1000 °C) torna-se ineficiente pois os poros do compacto a verde são de tamanho muito grande e de forma irregular. O fenômeno de crescimento irregular das partículas, no entanto, tem sido controlado com sucesso, pelo uso de processos químicos. Uma das rotas que permite controlar o tamanho das partículas é introduzir dopantes que controlem a morfologia das partículas ou dos grãos quando da sinterização (76).

A obtenção de filmes finos é outra conquista recente da tecnologia que tem permitido progressos no desenvolvimento de novos materiais com estrutura perovskita com propriedades otimizadas. Considerando o grande potencial de cerâmicas e filmes finos ferroelétricos em aplicações eletrônicas e na microeletrônica, é necessário conhecer bem tanto a síntese como o controle da estabilidade dessas fases, durante o seu processamento. A reprodutibilidade das propriedades de filmes finos está diretamente ligada à homogeneidade química, à microestrutura e à composição de fases. Dos filmes finos ferroelétricos, além do controle estequiométrico e estabilidade das fases, é necessário conhecer bem a interface substrato-filme para o crescimento de filmes policristalinos ou epitaxiais. Portanto, existem vários desafios, tanto na síntese como no processamento de filmes finos visando a otimização das propriedades ferroelétricas e dielétricas.

Para aplicações, o filme fino deve apresentar características bem definidas: homogeneidade, densidade, ausência de interação filme-substrato, cristalinidade acentuada, apresentando-se policristalino, texturizado e epitaxial ou completamente amorfo, dependendo de sua aplicação. Além disso, o filme deve apresentar uma baixa rugosidade de superfície, parâmetro muito importante, especialmente para aplicações em óptica eletrônica. Por exemplo, a fabricação de um guia de onda óptico com perda inferior a 1 dB-cm, requer que a rugosidade seja menor que 1,0 nm. O espalhamento óptico, devido a uma superfície rugosa, pode levar a perdas ópticas de até 50% (77). Por outro lado, para aplicações ópticas os filmes ferroelétricos devem ser epitaxiais orientados com o substrato. Dessa forma, a obtenção de filmes finos de grandes dimensões para aplicações ópticas não é trivial e as variáveis de processamento devem ser otimizadas e controladas.

A obtenção de filme fino de PZT com excelente qualidade é muito difícil, considerando que o chumbo (Pb), componente principal do PZT, evapora-se facilmente a temperaturas de

500°C ou maiores, o controle da composição e da sinterização é muito difícil, pois a razão superfície-massa é muito grande. Por outro lado, as reações entre o filme e o metal do substrato podem causar a fadiga nas propriedades ferroelétricas, tornando a vida útil da memória FeRAM muito curta. Para uso em memórias FeRAM em filme deve ter: alta polarização remanescente, campo coercitivo baixo, constante dielétrica alta e fadiga ferroelétrica baixa. Várias soluções foram propostas, incluindo a utilização de "buffer layer" para aumentar a resistência à fadiga desses materiais. Filmes finos amorfos de cerâmicas do tipo BaTiO₃ ou SrTiO₃ também pode ser processados visando obter alta constante dielétrica (> 40), baixa perda dielétrica, baixa dispersão das propriedades em função da frequência e baixa corrente de fuga. Essas condições são fundamentais para a construção de memórias do tipo DRAM.

Qualquer que seja o método empregado para a obtenção dos filmes ferroelétricos com propriedades para memórias FeRAM, busca-se sempre obter uma microestrutura com grãos grandes no sentido de obter valores altos de polarização remanescente (P_r) e baixo campo coercitivo (E_c). Tratamento térmico para crescimento de grãos não é uma solução, visto que há um limite de temperatura de sinterização e a cinética é muito lenta. Na otimização das propriedades também é importante obter estruturas cristalinas com orientação preferencial (78-80). Da mesma forma, o controle da estequiometria, bem como o estado de oxidação exercem grande influência nas propriedades ferroelétricas (81). Para melhorar a orientação preferencial dos cristais no filme, tem-se usado controle de atmosfera e tratamentos térmicos rápidos dos filmes (RTA). Assim, atmosferas de oxigênio devem ser utilizadas nos tratamentos térmicos (82-83).

A bibliografia disponível sobre filmes de SBT e SBN cresceu rapidamente nos últimos anos. Foram várias publicações sobre os métodos de síntese (84-87), com variações do tratamento térmico (convencional e/ou RTA) (88), e também com variações da composição: com excesso de Bi (89), com deficiência de Sr (90) ou mesmo a conjugação de ambos (91-92), e ainda com variação do substrato utilizado (93). A atmosfera de cristalização também foi estudada, e normalmente, utiliza-se a cristalização sob atmosfera de O₂ (94). Filmes de Aurivillius, quando processados convenientemente, podem apresentar excelentes propriedades para memórias FeRAM, incluindo baixa perda por fadiga. Métodos físicos como "RF Sputtering" e "ablação a laser" têm sido muito utilizados para depositar filmes de SBT e SBN e estudar o efeito de tratamento térmico e concentração de Bi nas propriedades ferroelétricas desses filmes (95-99). A perda do Bi durante a preparação dos filmes de SBT ou SBN leva à perda da estequiometria e, conseqüentemente, a uma drástica alteração nas propriedades

elétricas e microestruturais. Para contornar esse problema, as medidas tomadas têm sido a utilização de precursores e alvos com excesso de Bi, além da utilização concomitante de alvos enriquecidos e alvos de Bi_2O_3 .

Os materiais ferroelétricos também podem exibir propriedades ópticas não lineares como alto coeficiente eletroóptico o que os qualifica para várias aplicações incluindo guias de onda. Para tais aplicações é indispensável fabricar filmes finos epitaxiais para eliminar contornos de grãos que espalham luz e para guiar ondas ópticas com baixa perda. Várias técnicas (deposição com laser pulsado, processo de decomposição de organometálicos) têm sido usadas para fazer crescer filmes finos de PbTiO_3 em diferentes substratos e baixa temperatura para evitar a interação entre o filme e o substrato (100).

O niobato de lítio também apresenta excelentes propriedades eletroópticas e piezoelétricas (101-102). Por isso, esse material ferroelétrico é um bom candidato para a fabricação de vários dispositivos ópticos e acústicos, tais como guia de onda, moduladores de fase, moduladores de amplitude e filtros acústicos. Diferentes métodos são atualmente utilizados para preparar filmes finos de LiNbO_3 tais como o processo sol-gel (103-104), os processos CVD (Chemical Vapor Deposição) e MOCVD (Metallo-Organic Chemical Vapor Deposition) (105) a deposição por "sputtering" (106) e a ablação a laser (107).

Para ser utilizado, o filme fino deve ser homogêneo, denso e apresentar uma qualidade quase monocristalina. Além disso, o filme deve apresentar uma baixa rugosidade de superfície, parâmetro muito importante, especialmente para aplicações em óptica eletrônica. Por exemplo, a fabricação de um guia de ondas ópticas, com perdas inferiores a 1 dB/cm, requer que a rugosidade seja menor que 1,0 nm. O espalhamento óptico, devido a uma superfície rugosa, pode levar a perdas ópticas de até 50% (108). Por outro lado, para aplicações ópticas os filmes ferroelétricos devem ser epitaxialmente orientados com o substrato. Dessa forma, a obtenção de filmes finos de grandes dimensões para aplicações ópticas não é trivial e as variáveis de processamento devem ser otimizadas e controladas.

Considerando o grande potencial de cerâmicas e filmes finos ferroelétricos para aplicações em eletrocerâmicas e na microeletrônica, é necessário conhecer bem tanto a síntese dessas fases ferroelétricas perovskita, como o controle da estabilidade dessas fases durante o seu processamento, levando a uma microestrutura homogênea. A reprodutibilidade das propriedades dessas cerâmicas ou filmes finos está diretamente ligada à homogeneidade química, à microestrutura e à composição de fases. No caso dos filmes finos ferroelétricos, além do controle estequiométrico e estabilidade das fases, é necessário conhecer bem a interface substrato-filme para o crescimento de filmes epitaxiais. Portanto, existem vários

desafios, tanto na síntese como no processamento de cerâmicas e filmes finos, visando a otimização das propriedades ferroelétricas e dielétricas.

O titanato zirconato de chumbo e lantânio, PLZT com composição de 9/65/35 tem estrutura cúbica e, portanto, não é ferroelétrico. Essas cerâmicas exibem alta transparência óptica para composições próximas do contorno morfotrópico de fases entre as fases ferroelétricas e paraelétricas, correspondendo a uma variação de 1 mol% de lantânio. A maioria das composições para uso como cerâmicas eletroópticas correspondem de 8,8 a 9,5 mol% de lantânio, 65 mol% de zircônio e 35 mol% de titânio. Da mesma forma, para utilização em memórias ferroelétricas, as composições localizadas na região de fase ferroelétrica romboédrica devem ser usadas, correspondendo à faixa de 7 a 8 mol% de lantânio.

Os materiais ferroelétricos à base de bismuto têm recebido recentemente atenção, principalmente por apresentarem excelentes propriedades piezoelétricas, magnéticas dielétricas e por serem livres de chumbo. Embora esses compostos tenham sido estudados em forma de filmes, pouca informação existe sobre a sua sinterização e utilização como cerâmicas. A síntese de pós de BIT, BFO, SBT, SBN, BBT e BBN com tamanhos nanométricos, utilizando o método dos precursores poliméricos, foi estudada. As fases cristalinas foram caracterizadas por difração de raios X empregando-se o método quantitativo de análise de fases por Rietveld. Como as partículas dessas fases são em forma de placas, o processamento a verde e a sinterização das cerâmicas merecem um estudo especial. Para evitar o crescimento de partículas durante a síntese, dopantes do tipo doadores, que segregam na superfície das partículas, foram empregadas. Visando obter cerâmicas homogêneas e com alta densidade foram empregadas conformação por colagem e prensagem a quente. O controle da microestrutura é fundamental para otimizar as propriedades dielétricas, piezoelétricas e magnéticas.

Pode-se dizer que o controle de fatores como reatividade superficial e morfologia das partículas, formação de fases deletérias nas propriedades desejáveis; temperaturas elevadas para formação da fase perovskita, instabilidade da fase formada, perda de componentes por volatilização gerando segregação de fases, heterogeneidade química no interior da cerâmica, grão e contorno de grão; heterogeneidade da microestrutura da cerâmica, tamanho e distribuição de grãos, e aparecimento de mais de uma fase cristalina tornam o processo de obtenção dessa classe de cerâmicas reprodutível, além de permitir o ajuste da microestrutura e das propriedades, segundo as demandas da indústria eletroeletrônica.

3 COMPILAÇÃO DOS RESULTADOS OBTIDOS PARA SISTEMAS ELETROELETRÔNICOS (CERÂMICAS)

Iniciei meu pós-doutoramento na utilização de processos, via úmida, para preparação de materiais compostos por diferentes óxidos, que apresentavam problemas com controle de estequiometria e de homogeneidade. O sistema titanato de bismuto foi o primeiro da família dos Aurivillius a ser obtido e caracterizado por método químico pelo nosso grupo. Esse sistema é uma cerâmica ferroelétrica largamente usada como material piezoelétrico em sensores, atuadores, ressonadores, pois possui altos valores de coeficiente de acoplamento eletromecânico, K_p , e piezoelétrico, d_{33} , alta resistência à despolarização, alta temperatura de transição de fase, T_c . A síntese do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) pelo método convencional de mistura de óxidos requer altas temperaturas para formação da fase, o que causa perda de chumbo, heterogeneidade química e alto grau de aglomeração. Os métodos químicos são uma alternativa para se obter pós mais reativos em temperaturas mais baixas e com maior homogeneidade química. Coprecipitação e sol-gel são as opções mais populares utilizadas em síntese cerâmica. Uma variação do processo sol-gel é o método de complexação de metais por um ácido orgânico polifuncional, conhecido por método Pechine (18). O complexo metal-citrato é esterificado com um poliálcool, mediante aquecimento, obtendo-se um poliéster viscoso. A combustão do poliéster, eliminando a matéria orgânica, gera a fase cristalina. Quando se usa método químico para obtenção de óxidos cristalinos, a transição amorfo-cristalina requer alta energia de cristalização; tal processo pode dificultar a formação de algumas fases em detrimento de outras, dependendo do valor dessa energia de nucleação. Uma alternativa para diminuir essa barreira de energia é o uso de núcleos cristalinos isomorfos que funcionam como superfície de menor energia para nucleação (109). Para que esses núcleos sejam considerados eficientes, os parâmetros da rede cristalina dos núcleos devem ser semelhantes aos da rede cristalina da fase que desejamos cristalizar; a segunda exigência é que as partículas estejam desaglomeradas e apresentem uma estreita faixa de distribuição de tamanho. As características morfológicas dos pós obtidos a partir de uma solução nucleada dependem da frequência e do tamanho dos núcleos. Os núcleos devem ser adicionados e distribuídos homogeneamente na massa precursora da amostra. A mistura precursor-sementes deve ser suficientemente viscosa para garantir que os núcleos não sejam sedimentados durante a decomposição. Considerando as características do método dos precursores poliméricos, optamos por usá-lo para obter a fase BIT e estudar a influência dos

íons La, nas propriedades estruturais, microestruturais e elétricas. Alexandre Zirpoli Simões desenvolveu seu pós-doutoramento e obteve dados muito interessantes, pois as pesquisas revelaram que o comportamento observado, quando se usa mistura de óxidos, não é válido para a mesma composição obtida por processo químico. Por exemplo, o efeito dos íons La é diferente quando se parte de um processo em solução comparado ao método de mistura os óxidos. A utilização de La trouxe uma indicação muito interessante, foi verificado que esse íon atua de diferentes modos. Para baixas concentrações de La, os elétrons deixados pela vacância de Bi aumentam a resistência elétrica e o tamanho de grão. Quando a concentração é alta, o La atua como gerador de vacâncias baixando a resistência, quando a concentração atinge o limite de solubilidade, o lantânio migra para o contorno de grão, controlando o crescimento do grão do BIT. Esses efeitos são possíveis porque a utilização de métodos em solução permite maior homogeneidade de distribuição dos íons na rede do material.

Para verificar qual a melhor temperatura e tempo de tratamento térmico para a obtenção de filmes finos com alta cristalinidade e boa morfologia, realizou-se um estudo sistemático com os pós de BIT e BLT. É necessário estabelecer as condições de cristalização das fases trabalhando com os pós, porque nos filmes pode haver problemas de interação entre o precursor e o substrato, gerando fases secundárias, orientação preferencial e epitaxia, que interferem na caracterização da fase cristalina, pois apresentam picos de difração diferentes aos da ficha cristalográfica da fase ortorrômbica $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (73-2181), JCPDS-International Centre for Diffraction Data. O comportamento térmico dos pós obtidos pela calcinação das resinas a 300°C, por 4 horas, foi avaliado pela perda de massa em função da temperatura, representada na curva termogravimétrica (TG). As curvas termogravimétricas indicam que a decomposição dos precursores ocorre basicamente em duas etapas: (1) degradação dos polímeros com decomposição em CO_2 e H_2O e perda de grande parte do material orgânico e (2) perda do restante do material orgânico, com decomposição das carboxilas ligadas aos metais com consequente formação de uma fase estável metal-oxigênio. As curvas DSC para o pó preparado pela calcinação das resinas a 300°C por horas indicam a presença de uma banda exotérmica bastante intensa entre 340 e 540°C, verificando-se um máximo de calor liberado referente à decomposição das carboxilas complexadas com metal e à combustão da cadeia polimérica; Nessa etapa ocorre o início do processo de cristalização da fase BIT. A partir de 580°C é estabelecido um patamar até 1000°C, mostrando que não há mais qualquer tipo de reação ocorrendo. Os pós de BIT e BLT, tratados no intervalo de 500°C a 800°C, apresentam picos característicos da fase cristalina para os pós calcinados a partir de 500°C, identificada

como titanato de bismuto ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$). Observa-se que, com o aumento da temperatura, a fase Bi_2O_3 localizada em $2\theta = 28^\circ$ e em grande quantidade no pó calcinado a 500°C , por 4 horas, é eliminada devido à sua difusão para a matriz de $\text{Bi}_2\text{Ti}_2\text{O}_7$ com conseqüente formação da fase cristalina $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. Os difratogramas indicam também que o aumento da temperatura entre 500 e 700°C melhora a cristalinidade do material devido ao estreitamento do pico de máxima intensidade, localizado em $2\theta = 30^\circ$. Para os pós calcinados a 700°C , por 4 horas, os picos relativos à fase BIT já estão bem definidos. Verifica-se, também, que os picos de difração apresentados estão perfeitamente de acordo com os dados da ficha cristalográfica da fase BIT (73-2181), JCPDS-International Centre for Diffraction Data. A fim de avaliar o efeito da adição de lantânio sobre a cristalinidade do BIT puro, foram preparados pós com $x = 0,25, 0,5$ e $0,75$, os quais foram calcinados na temperatura de 750°C . A adição de lantânio não provoca alterações nos picos de difração da fase estequiométrica de titanato de bismuto, indicando a formação de solução sólida substitucional sem a presença de fases indesejáveis. A influência da quantidade de La^{+3} na estrutura do BIT, assim como a determinação dos parâmetros de rede e as estruturas cristalinas destes materiais, foram avaliadas mediante refinamento pelo Método de Rietveld. Os dados de difração para os pós-cerâmicos foram obtidos em amostras calcinadas a 750°C por 4 horas. O grupo espacial encontrado para o material em estudo foi o FMMM com as posições atômicas referentes à ficha ICSD de número 24735. A dopagem com La^{3+} alonga o eixo c drasticamente. Esse fato caracteriza que a densidade de carga é bem diferente do bismuto, havendo uma maior densidade eletrônica por parte dos íons lantânio. Por outro lado, o alongamento do eixo c pode ser devido não somente à simples inclusão de lantânio que tem um efeito radial maior, estabilizando as vacâncias de oxigênio, e, como conseqüência a estrutura. Outra observação é que, com a adição de lantânio, há uma tendência dos parâmetros a e b tornarem-se iguais fazendo com que a estrutura ortorrômbica mude para estrutura tetragonal. O refinamento das vacâncias de oxigênio indica que os átomos nas posições O2 e O4 são os que contribuem para formação de vacâncias. Não foi possível realizar o refinamento nas posições O1 e O5, pois elas estão ligadas ao titânio formando um quadrado planar. O refinamento do átomo na posição O3 também não foi realizado com êxito, pois esse oxigênio liga-se ao átomo de Bi1, que não tem vacância, pelo fato de que o lantânio está ligado a ele. Logo, ambos os átomos nas posições O2 e O4 contribuem para a origem das vacâncias, pois o Bi2, o que apresenta vacância, está mais livre na estrutura para migrar sendo composto por camadas alternadas de Bi2 e O2 e O4. Estudos ainda em andamento mostram que a quantidade de vacâncias para baixos valores de lantânio ocorre na razão 30,9% de O2

para 69,1% de O₄, uma razão bem lógica, uma vez que o arranjo em camadas com os átomos de Bi₂ possui 4 átomos de O₂ e 9 átomos de O₄. O parâmetro de rede *c* encontrado para a amostra pura de 32,78 Å significa hipoteticamente que a ligação Ti₂-O₄ seria de 1,5 Å, muito menor que o mínimo possível de 1,955 Å, que é a simples soma dos raios iônicos do titânio (0,605 Å) e oxigênio (1,35 Å). Esse fato só pode ser explicado pela existência de vacâncias na posição O₄, ocorrendo migração dos átomos de Bi₂ e O₄, em um rearranjo complexo da estrutura, talvez com perda de simetria. No cômputo de várias celas unitárias, isso faz com que a ligação Ti₂-O₄ calculada se apresente com esse valor médio tão pequeno. Essa hipótese se baseia na posição que os átomos de Ti₂, Bi₂ e O₄ ocupam na estrutura, com ângulo de 180° e posicionados na aresta da cela unitária (108,109). Os resultados destes estudos estão publicados no artigo que consta no ANEXO A (SIMÕES, A. Z., QUILENATO, C, RIES, A., STOJANOVIC, B. D., LONGO, E., VARELA, J A., Preparation of Lanthanum doped Bi₄Ti₃O₂ Ceramics by the polymeric precursor method. **Materials Chemistry and Physics**. v.98, p.481 - 485, 2006).

Com a adição de um dopante doador, os efeitos elétricos de cerâmicas de BIT puras e dopadas com Nb, foram avaliados pelo método dos precursores poliméricos. As resinas pré-calcinadas de titanato de bismuto puro foram submetidas a um estudo de calcinação em várias temperaturas desde 400 até 800° C por 4h para verificar a formação da fase. Na temperatura de calcinação escolhida, variou-se o excesso de bismuto de 0 a 30%. As medidas de difração de raios X dos pós e das cerâmicas sinterizadas mostram a evolução na formação da fase de titanato de bismuto desde a menor até a maior temperatura. Para calcinação na temperatura 400° C verifica-se a formação de óxido de bismuto (Bi₂O₃). A partir de 500° C, a fase Bi₄Ti₃O₁₂ já pode ser identificada, principalmente pelo pico de difração (117), mas ainda há presença do Bi₂O₃. Nas demais temperaturas, a fase cristalina do titanato de bismuto é mais definida com seus respectivos picos indexados. Após esse estudo, escolheu-se a temperatura de 700° C como mais adequada para calcinação devido à formação bem definida da fase Bi₄Ti₃O₁₂, assim como a 800° C; porém nessa temperatura pode já ocorrer perda de bismuto e consequente variação na estequiometria. Quando se analisa o comportamento da variação do excesso de bismuto na composição a 700°C - 4h, observa-se que o BIT puro apresenta a maioria dos picos correspondentes ao Bi₄Ti₃O₁₂. Nas demais composições também foram identificadas as fases do titanato de bismuto, porém, acima de 10% do excesso de Bi, nota-se a presença de fases indesejáveis. A composição BIT-10% excesso de nióbio foi escolhida como sendo a melhor, pois resultou em uma fase cristalina. Ocorre solubilização do óxido de bismuto (Bi₂O₃) na matriz do BIT, de tal modo que exista um máximo dessa solubilidade na

rede cristalina. Verifica-se também a presença de uma estrutura ortorrômbica: perovskita com camada de bismuto, característica do material (133). Os gráficos de difração de raios X dos pós e cerâmicas sinterizadas em forno convencional e microondas permitem quantificar os planos ($h\ k\ l$) e as fichas cristalográficas (padrão de $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - 73-2181 e padrão de α - Bi_2O_3 27-50). Os dados de difração de raios X respectivos aos pós de partida, obtidos pelo método dos precursores poliméricos seguidos de calcinação a 700°C -4h, indicam a presença da fase principal do titanato de bismuto com bom ordenamento a longa distância, caracterizada principalmente pelos picos (111), (117), (200), (208), (220), (2014) e (317). Para os pós de BIT-0,2 e BIT-0,4 foram identificadas fases de óxido de bismuto, caracterizadas pelos picos (201) e (203) respectivamente. A presença dessa fase pode ser explicada pela quantidade em excesso desse modificador da rede, levando a formação de uma fase deletéria. Observa-se a formação da fase principal de titanato de bismuto, tanto para os pós quanto para os compactos densos sinterizados em forno convencional ou microondas. Um detalhe é a presença dos picos (201) e (203) nas composições de BIT-0,2 e BIT-0,4 dos pós, característicos da fase do óxido de bismuto beta (ficha cristalográfica 27-50). Nota-se também que após sinterização das amostras, estes picos diminuem ou desaparecem devido à liberação de óxido de bismuto durante o processo de sinterização.

Para se investigar o comportamento da adição do nióbio nas cerâmicas com 10% excesso de Bi e dopadas com 0,1; 0,2 e 0,4 mol % de Nb, foram realizadas medidas de difração de raios X dos pós. Os resultados obtidos foram comparados com padrões de difração e indicaram a formação de uma só fase. Verifica-se, para todas as composições a fase bem definida do BIT, implicando em boa cristalinidade e organização a longa distância. O dopante não permitiu a formação de fases secundárias e também não mudou os picos de difração. O pico de maior intensidade relativa significa orientação preferencial na direção a - b . Esses valores são condizentes com resultados obtidos para medidas de raios X do titanato de bismuto dopado com nióbio em outras concentrações. Percebe-se que ocorreu um acréscimo na área superficial com a adição de nióbio. O dopante atua de modo a favorecer a diminuição do tamanho de partícula e muito provavelmente melhorando a densificação. As cerâmicas dopadas com nióbio apresentaram maior superfície específica quando comparadas às cerâmicas puras e com excesso de bismuto; isso demonstra que as composições dopadas podem favorecer a etapa de sinterização. O comportamento dos valores de área de superfície específica em função do nióbio não segue uma linearidade com relação ao acréscimo do dopante. Todos os valores são próximos uns dos outros, à exceção da composição contendo maior quantidade de nióbio. Pelo procedimento de moagem em moinho de bolas durante 4h

foi possível identificar uma diminuição significativa no tamanho de partícula quando comparadas às cerâmicas moídas e não moídas. Os resultados obtidos demonstram que houve otimização do pó de titanato de bismuto, muito importante para obtenção por método químico dos precursores poliméricos. Esses resultados são concordantes com os resultados obtidos por microscopia eletrônica de transmissão.

Os valores das bandas observados representam os modos vibracionais permitidos para excitação das ligações no titanato de bismuto. Medidas de espectroscopia Raman dos pós de BIT puro e com excesso de Bi implicaram em modos vibracionais idênticos aos do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. As bandas 127, 227, 269, 323, 536 e 846 cm^{-1} são características do titanato de bismuto puro e estão presentes em todas as cerâmicas. A banda em 45 cm^{-1} pode ser atribuída às vibrações Bi-Bi; já os modos vibracionais relativos aos maiores e menores valores do número de onda correspondem às vibrações de ligações Ti-O e Bi-O, respectivamente (135). Os picos correspondentes às bandas 226 e 269 cm^{-1} indicam as vibrações das ligações do TiO_6 octaédrico. Nota-se, portanto, uma organização a média e curta distância na estrutura do material. O acréscimo do excesso de Bi resultou na diminuição do número de bandas presentes, provavelmente devido à distorção da estrutura ortorrômbica característica do titanato de bismuto. A adição do dopante não modificou substancialmente as bandas, quando comparadas às do BIT puro; praticamente as mesmas bandas são verificadas na cerâmica dopada. Verifica-se que os modos vibracionais das ligações Ti-O e Bi-O são respectivos aos maiores e menores comprimentos de onda dos espectros de Raman, porém as bandas neste primeiro caso podem ser também atribuídas às ligações Nb-O. O papel do nióbio como dopante é de substituir parte do titânio no octaedro TiO_6 , fato explicado pela observação do decréscimo na banda 226 cm^{-1} no BIT dopado, quando comparado ao BIT puro. É também provável que as vibrações da rede sejam afetadas por causa do pequeno raio iônico e da maior valência do nióbio comparada ao titânio (+5 e +3 respectivamente), segundo comportamento semelhante para o vanádio como dopante.

Medidas de espectroscopia de ultravioleta na região do visível foram realizadas nos pós-obtidos por calcinação a 700°C -4h, para determinar a concentração de defeitos e a relação com o “band gap” do material em função do excesso de bismuto e dopante. Nota-se um comportamento similar para todas as amostras com excesso de bismuto. Em contrapartida, as amostras dopadas com nióbio apresentam um ligeiro desvio, em função da quantidade de defeitos na estrutura cristalina do composto. A composição BIT-0,4 apresenta um maior tamanho de partícula quando comparada às demais composições. É evidente que a adição de dopante na matriz provoca essa desordem, ocasionando redução das vacâncias de oxigênio. O

desvio entre os valores encontrados deve ter sido causado pelo excesso de bismuto que provoca aumento nos defeitos da rede cristalina do material.

Para se avaliar o tamanho das partículas das cerâmicas de BIT puro e com excesso de Bi, calcinadas a 700°C – 4h foi empregada à técnica de microscopia eletrônica de varredura. Todas as composições em estudo apresentaram aglomerados das partículas, com tamanho das partículas entre 200-300 nm. A morfologia dos pós não foi alterada pela adição do excesso de Bi, porém os aglomerados aumentaram de tamanho. Uma etapa posterior de moagem como, por exemplo, em moinho de bolas de alta energia, pode favorecer a diminuição desses e permitir o aumento da área superficial. Quanto menor o tamanho das partículas, maior pode ser a densidade a verde e isso deve refletir no aumento da densificação da cerâmica. A análise por microscopia eletrônica de varredura (MEV) da superfície dos pós de BIT dopados com nióbio foi realizada para avaliar o tamanho das partículas e a morfologia dos pós. Nota-se que a presença do nióbio como dopante aparentemente não modificou a morfologia inicial dos aglomerados, porém o tamanho de partícula aumentou até por volta de 300 nm. Esses aglomerados possivelmente dificultam a sinterização das cerâmicas policristalinas, que provavelmente serão diminuídas com a moagem. Observa-se que os valores encontrados para densidade a verde dos discos cerâmicos são relativamente bons, entre 47 e 58% do valor da densidade teórica do BIT; no entanto, para amostras sinterizadas, o melhor resultado corresponde a 80% de densificação, considerado baixo. Já o efeito da adição do nióbio nas densidades revela que o máximo valor para concentração de dopante resultou em aumento da densidade a verde, mas diminuição da densidade após sinterização, embora não exista um comportamento direto para essa tendência. Conseqüentemente houve melhora na densidade dos compactos à verde devido à redução no tamanho de partícula que associada à melhor condição de prensagem uniaxial (1,1 ton) apresentou densidade de 60%. Os compactos sinterizados apresentaram variação na densificação em função do excesso de bismuto ou da adição de nióbio nas amostras sinterizadas. Porém, verificou-se que esses são convenientes apenas para o titanato de bismuto preparado por mistura mecânica dos óxidos. A porcentagem de densificação diminui com o aumento do excesso de Bi ou concentração do Nb, pois isso contribui para perda de massa. Uma tendência verificada é que o excesso de Bi dificulta a densificação do titanato de bismuto; contudo, para 5% em excesso, obteve-se melhor resultado na densificação do BIT sem dopante. Talvez seja possível aumentar a densificação do titanato de bismuto, utilizando esse valor do excesso de bismuto na matriz dopada com nióbio. Após sinterização dos compactos cerâmicos em forno convencional, na temperatura de 800°C sem atmosfera de compensação, investigou-se a microestrutura das amostras para

determinação da forma e compactação tanto na superfície polida e atacada termicamente como na fratura de cada uma delas. Verifica-se que todas as amostras apresentaram grãos alongados na forma de placas com distribuição mais homogênea e empacotada para o BIT, estrutura essa típica dos compostos em camadas de bismuto (110). Para as demais composições observa-se um empacotamento não muito denso, com uma microestrutura porosa. A adição do nióbio na estrutura do material reduz significativamente o tamanho de grão. Formas alongadas dos grãos com tamanho aproximado de 600 nm (BIT) foram obtidos, sendo que com adição de nióbio estes reduziram drasticamente para 400 e 200nm aproximadamente. As amostras dopadas com nióbio e com excesso de bismuto apresentam distribuição mais homogênea dos grãos. Os resultados de densidade relativa para ambas as composições são concordantes com os resultados de micrografias eletrônicas de varredura, que podem estar relacionados à formação de fase líquida no sistema. Os valores da densidade relativa determinada pelo método de Arquimedes foram razoavelmente bons para as amostras sinterizadas em forno convencional a 800°C-1h sem atmosfera de compensação e 800°C-15 min para amostras sinterizadas em forno microondas. Os valores de densidade relativa obtidos foram baseados na densidade teórica do titanato de bismuto puro de 8,04 g/cm³ (111) e ficha cristalográfica do Bi₄Ti₃O₁₂ (73-2181). Dos compostos com camada de bismuto, esse material destaca-se como um dos mais densos, visto a grande dificuldade do empacotamento desse material devido ao fato de às camadas de bismuto não terem sido totalmente empacotadas. Um estudo mais detalhado da sinterização em função da atmosfera de compensação, tempo e temperatura para as cerâmicas com excesso e dopadas com Bi foi realizado. Verificou-se que a atmosfera de compensação (5% em massa BIT) durante a sinterização suprime a perda de massa do bismuto e inibe a densificação, para temperaturas de 800°C até 900°C e com variação do tempo. O fenômeno que pode ter ocorrido é a saturação da atmosfera, uma vez que esse processo foi realizado em barquinha de alumina fechada ao meio externo. Para amostras sinterizadas em temperaturas variando de 850 até 800°C, nota-se um acréscimo na densidade com a diminuição da temperatura e tempo. Após variação dos parâmetros de sinterização das cerâmicas, foi possível obter densidades relativas entre 87 e 92% da teórica, na temperatura de 800°C-1h em sistema fechado. Nessa temperatura ocorre um máximo de densificação, tendo a amostra BIT apresentado melhor densidade. A adição de nióbio provoca uma queda na densidade até BIT-0,2 e aumenta novamente para BIT-0,4 até valor próximo da composição sem dopante e, como as amostras apresentam tamanho de partícula semelhante (à exceção de BIT-0,4), o responsável por esse comportamento deve ser a reorganização da estrutura em função da distorção provocada pela quantidade reduzida de nióbio. A formação

de um eutético entre bismuto e titanato de bismuto ocorre nesse caso. Em temperaturas acima desse valor, ocorre difusão do bismuto, de modo que o aspecto de “infladas” e porosas é verificado. Desse modo, para investigar o efeito da rápida taxa de aquecimento no processo de sinterização e perda de massa, propôs-se à sinterização em forno microondas para avaliar o efeito desta na densidade e cristalinidade. Para as amostras sinterizadas na melhor condição, 800°C-1h em forno convencional e 800°C-15 min em forno microondas, a perda de massa foi pouco significativa com máximo valor em torno de 1%. Normalmente, a temperatura de sinterização do BIT obtida via método químico é diminuída consideravelmente quando comparada à por via mecanoquímica. Esses resultados são coerentes com os obtidos na literatura (112) e comparados com a reação do estado sólido (113). No BIT obtido também por método químico, por exemplo, dos hidróxidos precursores e sol-gel, a densidade encontrada é bem menor que a obtida via método físico (114); variando de 85 a 88% no primeiro caso, de 85 a 95% no segundo caso. A explicação para redução na densidade deve-se à menor quantidade de energia despendida no processo químico por consequência de menor temperatura para sinterização, que é favorecida devido ao tamanho reduzido das partículas ($< 1\mu\text{m}$). A grande diferença entre esses dois métodos é exatamente na diferença do tamanho de partícula. A diminuição do tamanho de partícula implica obrigatoriamente em um decréscimo da temperatura de sinterização, podendo assim explicar a diferença entre os métodos químico e físico. O comportamento tensão-corrente não linear das amostras de titanato de bismuto puro e dopado, obtidas por sinterização a 800°C-1h em forno convencional e 800°C-15min em forno microondas foram avaliadas. Sabe-se que o BIT é uma cerâmica de condutividade eletrônica tipo *p*. Nesse material os defeitos são gerados pelo Bi^{+3} , segundo equação de defeito 1:



A equação acima indica que defeitos do tipo buraco existem em materiais ferroelétricos com estrutura em camadas de bismuto. Quando o material é dopado com íons doadores (valência do íon dopante é maior que a valência do íon da rede), como nesse caso o nióbio, ocorre a seguinte equação de defeitos 2:



Para o Nb^{+5} substituindo o Ti^{+4} ocorre o fornecimento de $1e^-$ na rede, um centro positivo no sítio do titânio e um elétron são criados sob restrições de neutralidade de carga. Os elétrons fornecidos pelo dopante neutralizam o efeito dos buracos (cargas positivas) e conseqüentemente a concentração dos portadores torna-se menor, diminuindo a condutividade do material. Observa-se que todas composições apresentam baixa condutividade, mesmo em valores altos de campo elétrico aplicado. Como já observado na literatura, a adição do nióbio e conseqüentemente a substituição do titânio por esse metal na rede cristalina causa decréscimo na condutividade (115). Nota-se também uma redução da condutividade em amostras sinterizadas em forno microondas possivelmente devido à maior perda de bismuto causada pela maior taxa de aquecimento. A perda de bismuto provocaria menor formação de portadores de carga, segundo a equação 1.

Dados de histerese ferroelétrica para as cerâmicas sinterizadas em forno convencional e microondas indicam que a adição do nióbio (Nb^{+5}) como substituinte do titânio (Ti^{+4}) em cerâmicas de BIT diminuiu eficientemente a concentração de $\text{V}_{\text{O}}^{\bullet}$, impedindo o aprisionamento dos domínios ferroelétricos. O decréscimo da densidade espacial de carga (vacâncias de oxigênio) leva ao aumento da polarização remanescente. Conseqüentemente, o decréscimo do tamanho de grão e a mudança da estrutura dos domínios pode ser o fator preponderante para o elevado campo coercitivo (116). Todas amostras apresentaram baixo valor de polarização remanescente (aproximadamente $0,2 \mu\text{C}/\text{cm}^2$) e alto campo coercitivo ($3\text{KV}/\text{cm}$ respectivamente). O aumento das vacâncias de oxigênio e as tensões geradas no cristal ferroelétrico podem ser os grandes causadores da forma da curva de histerese (baixos valores de P_r e altos valores de campo coercitivo). Para as amostras sinterizadas em forno de microondas, a adição de nióbio proporcionou uma melhora nas propriedades ferroelétricas desse material; tal fenômeno pode ser explicado pela diminuição da condutividade pelo preenchimento das cargas positivas (buracos) após fornecimento de cargas negativas (é) pelo dopante. De acordo com a literatura, conclui-se que dentro da estrutura da camada perovskita do BIT, as vacâncias do oxigênio estão situadas preferencialmente na vizinhança dos íons do bismuto, isto é, confinadas o mais provavelmente na camada Bi_2O_2 . A constante e perda dielétrica em função da temperatura a 100 kHz revela um aumento da constante dielétrica com acréscimo da temperatura. Uma transição de fase característica do material ocorre na temperatura de Curie, onde a constante dielétrica é máxima e depois diminui gradativamente. Determinou-se a temperatura de Curie para o titanato de bismuto na frequência de 1 MHz para todas as composições; nessa temperatura ocorre mudança da fase ferroelétrica a paraelétrica com alteração abrupta no valor da permissividade dielétrica. A temperatura de

transição de fase desse material puro é 675°C (117), praticamente não havendo variação dessa temperatura quando da adição do nióbio no sítio do titânio. A adição de dopante na matriz reduz a perda dielétrica devido à substituição dos sítios de titânio pelos átomos de nióbio, dificultando o movimento das cargas. O comportamento da permissividade e perda dielétrica não foi afetado pelo tipo de tratamento térmico e pela adição de nióbio. A baixa perda dielétrica medida no mesmo intervalo de temperatura que a constante dielétrica indica maior capacidade de armazenamento de dados, visando aplicações em dispositivos que se baseiam em memórias FeRAMs. Os valores obtidos para constante dielétrica e perda ficaram entre 170 e 0,02 aproximadamente, semelhantes aos encontrados na literatura (118). Verificou-se um acréscimo da perda dielétrica com aumento da temperatura e com adição de nióbio houve decréscimo da perda. Os filmes espessos de titanato de bismuto preparados por Tape Casting foram obtidos a partir dos pós cerâmicos sintetizados pelo método dos precursores poliméricos. Filmes espessos e empacotados nas composições: BIT, BIT-0,1Nb, BIT-0,2Nb e BIT-0,4Nb foram prensados em 20 camadas, calcinados e sinterizados, e sua espessura final foi de aproximadamente 0,4 mm. O preparo consistiu na diluição dos pós do BIT em 20% de água deionizada, seguida de adição do dispersante, ligante e plastificante. A moagem com bolas de zircônia foi realizada durante 24h, logo após agitação e aquecimento para concentração da solução, baseando-se no trabalho reportado na literatura de obtenção de barbotinas aquosas (119). A deposição dos filmes foi realizada em temperatura ambiente e vazão de ar constante equivalente a 40Psi, para secagem do solvente. A velocidade de deposição foi de aproximadamente 0,18 cm/s com abertura da lâmina “doctor blade” entre 100 - 120 µm. Filmes flexíveis com espessura definida e aparentemente sem trincas foram soltos do substrato polietileno tereftalato. Em seguida foram cortados em forma circular com diâmetro de 6 mm, empacotados e prensados uniaxialmente. Notou-se uma mudança na coloração de cinza mais escuro para branco e posteriormente cinza claro. A calcinação em 500°C -3h, taxa de aquecimento de 2°C/min, foi necessária para eliminação dos componentes orgânicos da barbotina inicial. Os compactos sinterizados a 800°C -1h em atmosfera ambiente apresentaram visualmente redução volumétrica frente aos compactos à verde, principalmente nas amostras com dopante. Em outro estudo, cerâmicas de titanato de bismuto obtidas pelo método tape-casting foram processadas mediante adição de partículas templates. As partículas templates sintetizadas pelo método dos sais fundidos tiveram como material de partida o titanato de bismuto com 10% excesso Bi, obtido por mistura de óxidos, moído durante 4h e calcinado a 700°C -4h. Quantidades equivalentes de sulfato de sódio e potássio foram adicionadas à mesma quantidade em massa do BIT de partida e “fundidas” em cadinho de

alumina fechado. O pó resultante da síntese foi lavado diversas vezes com água deionizada para eliminação dos sais, e originou a semente de cor cinza. As partículas templates (semente) obtidas foram caracterizadas quanto à fase por difratometria de raios X e morfologia por microscopia eletrônica de varredura. O difratograma de raios X da semente sintetizada e os respectivos picos encontram-se indexados, correspondendo ao titanato de bismuto com orientação preferencial na direção c : (008), (0010), (0012), (0014), (0016), (0018), diferente da fase ortorrômbica encontrada nas cerâmicas policristalinas e filmes espessos no presente trabalho. A ficha cristalográfica (n° 50-300) corresponde ao padrão do composto. Nesse mesmo difratograma, pode ser visto o pico pouco intenso de difração (117) que corresponde ao máximo de orientação no eixo c para o caso das cerâmicas policristalinas investigadas. Os resultados obtidos para microscopia eletrônica de varredura da semente indicaram partículas epitaxiais de tamanho micrométrico (da ordem de aproximadamente 2 a 5 μm), com morfologia bastante diferenciada daquela observada para o BIT policristalino.

Em outro estudo, cerâmicas de $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ foram preparadas com sucesso a partir de pós de tamanho nano obtidos por ambos os métodos utilizados : síntese mecanoquímica através de um processo de moagem de alta energia e por síntese química via método dos precursores poliméricos. As diferenças nos parâmetros de rede cristalina, a área de superfície específica e densidades de dados para BIT preparados por ambos os métodos são causadas por várias razões. O mais importante é o empacotamento dos átomos do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ na rede cristalina e a menor aglomeração dos pós preparados pelo método químico quando comparados ao método de síntese assistida mecanicamente. A cerâmica BIT obtida a partir de pós preparados pelo método dos precursores poliméricos apresenta uma mistura de grãos na forma de placas e em forma de hastes, comparando-se a forma em placas semelhante a estrutura de BIT preparado pelo processo de moagem. O processo mecanoquímico tem uma vantagem sobre o método do precursor polimérico, porque usa óxidos de baixo custo e amplamente disponíveis como materiais de partida e ignora a etapa de calcinação a uma temperatura intermediária, conduzindo a um processo simplificado. Em outro trabalho o mesmo sistema foi preparado por um processo de moagem de alta energia directamente a partir de óxido por meio de síntese mecanoquímica assistida. BIT monofásico foi formado após 180 minutos de tempo de moagem. O excesso de 3% em peso de Bi_2O_3 não melhora significativamente a cristalinidade do pó obtido. O sistema possui estrutura cristalina tetragonal, com pequeno tamanho de cristalito, menor do que 20 nm e microstrains inferiores a 2%. O BIT formado é uma mistura de fase amorfo/cristalino com ligeira alteração com o aumento do tempo de moagem e o excesso de Bi_2O_3 na mistura inicial. Não foi observada uma redução significativa do tamanho

das partículas após 720 minutos de tempo de moagem, no entanto, a tendência para a aglomeração foi aumentada. Os resultados estão concordantes com os encontrados. Esses resultados foram publicados e constam nos anexos B, C, D, E, F e G (SIMÕES, A. Z., AGUIAR, E.C., RIES, A., LONGO, E., VARELA, J.A., Niobium doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics obtained by the polymeric precursor method. *Materials Letters* (General ed.). v.61, p.588 - 591, 2007; AGUIAR, E.C., SIMÕES, A. Z., VARELA, J A, LONGO, E. Rietveld Analyses and Piezoelectric Properties of Niobium doped Bismuth Titanate Systems. *Journal of Advanced Microscopy Research*. v.5, p.1 - 9, 2010. AGUIAR, E.C., VARELA, J A, LONGO, E. MOURA, F., SIMÕES, A. Z. Piezoresponse force microscopy behaviour of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics with various excess bismuth. *Processing and Application of Ceramics*. v.5, p.1 - 12, 2011; AGUIAR, E.C., FOSCHINI, CESAR, SIMÕES, A. Z., VARELA, J. A., LONGO, E. MISTLER, R. Electrical Properties of Textured Niobium doped Bismuth Titanate Ceramics. *Journal of the American Ceramic Society*. v.95, p.1 - 7, 2012; STOJANOVIC, B. D., SANTOS, C. O. P., JOVALEKIC, C., SIMÕES, A. Z., FILHO, F.M., LAZAREVIC, V., VARELA, J. A., Mechanically Activating Formation of Layered Structured Bismuth Titanate. *Materials Chemistry and Physics*., v.96, p.471 - 476, 2006; STOJANOVIC, B. D., SIMÕES, A. Z., SANTOS, C. O. P., LONGO, E., VARELA, J.A., Effect of processing route on the phase formation and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. *Ceramics International*. v.32, p.707 - 712, 2006).

Avanços também foram realizados em cerâmicas de PZT dopado com W sintetizado pela rota conjugada dos métodos Pechini e Oxalato Parcial. A formação da fase ZT, a partir da resina polimérica (carvão) até a fase estabilizada, foi acompanhada por análises TG, DSC e raios X, de forma que permitisse relacionar resultados, e a partir deles, definir-se a temperatura de calcinação do mesmo. As três amostras mostraram uma perda de massa em uma única etapa até 150 °C referente à saída de água existente na resina polimerizada (carvão), em correspondência com o pico a 70 °C observado na curva DTG. Após a desidratação todas as curvas apresentaram perdas de massa em uma única etapa entre 300 e 490 °C (ZT2W) e 300-570°C (ZTp e ZT8W), apesar de a curva DTG sugerir duas etapas para as composições ZTp e ZT8W e uma única etapa para o ZT2W. A fim de evidenciarmos as alterações sofridas pelas amostras de ZT que foram submetidas à análise termogravimétrica, as curvas termogravimétricas derivadas (DTG) ilustram o primeiro pico que é observado a 70 °C, devido à eliminação de água contida nas amostras. As curvas indicam, com um pequeno ombro, que a decomposição da resina, para as amostras ZTp e ZT8W, ocorre em duas etapas. Para o ZTp e o ZT8W, as temperaturas de máxima velocidade de perda de massa estão em

torno de 380 °C e 480 °C respectivamente. Para a amostra ZT2W, tal decomposição se dá em uma única etapa com a máxima velocidade de perda em torno de 430 °C. As curvas DSC apresentaram picos eventos endotérmicos a 70 °C atribuídos a desidratação e picos exotérmicos a 430 °C com um ombro em 335 °C (ZT2W); 477 °C (ZTp) e 495 °C (ZT8W), sendo que os dois últimos apresentaram um pequeno evento exotérmico em 380°C. Todos os eventos térmicos observados nas curvas DSC estão de acordo com as perdas de massa observadas nas curvas TG/DTG. Para as amostras ZTp e ZT8W, a primeira etapa, referente à decomposição da cadeia poliéster ocorre entre 200 °C e 400 °C (200 °C e 350 °C para amostra ZT2W). Na segunda etapa, correspondente ao segundo pico, situado entre 400 °C e 600 °C (350 °C e 530 °C para amostra ZT2W), verifica-se um máximo de calor liberado referente à decomposição das carboxílas complexadas com metal e à combustão da cadeia polimérica. Observam-se também picos exotérmicos de cristalização entre 650°C e 730°C para todas as amostras. Podemos concluir que, para as três composições, a partir de 570°C temos a fase ZT estabilizada, podendo definir a temperatura de calcinação do pó no intervalo de 730°C a 800°C. Isso mostra que um aumento na concentração de tungstênio causa um aumento na temperatura de cristalização do ZT. As resinas referentes às amostras ZTp, ZT2W e ZT8W foram, cada uma, calcinadas a diferentes temperaturas (450; 550; 650; 750 °C) por 3 horas e analisados por difração de raios X, no intuito de mostrar a evolução da fase ZT (puro e dopado). Observa-se que o aparecimento da fase cristalina ZT para todas as composições só ocorre à temperatura superior a 550 °C, concordando com o que foi observado nas curvas de análises térmicas. As composições ZTp e ZT2W apresentam uma única fase ZrTiO_4 , identificada como JCPDS (International Centre for Diffraction Data) número 34-415. Enquanto que a composição ZT8W apresenta uma segunda fase, que é identificada como sendo a WO_3 , de acordo com a ficha JCPDS número 24-747*. A ação do dopante é evidente quando observamos que para a composição ZT2W ocorre uma nucleação para a temperatura de 550 °C, indicando início de cristalização, o que não foi observado para as amostras ZTp e ZT8W. Tal resultado confirma o observado nas curvas de análises térmicas, que mostram que para a amostra ZT2W a fase é estabilizada em menor temperatura. O aumento na concentração do dopante provocou uma diminuição na área superficial específica, conseqüentemente uma elevação no diâmetro equivalente esférico.

As micrografias das suspensões dos pós ZTp, ZT2W e ZT8W calcinados a 750 °C/3 h mostraram que os mesmos se encontravam bastante finos, porém em estado de alta aglomeração. A seqüência de reação entre o oxalato de chumbo precipitado e o pó ZT, para a formação da fase PZT foi acompanhada por análise térmica (TG, DTA, DSC) e por difração

de raios X para diferentes temperaturas de calcinação (450, 550, 650, 750 °C por 3 horas), de forma que permitisse relacionar os resultados e, a partir deles, definir-se a temperatura de calcinação. Dados de difração de raios X, cada um deles relativo a uma composição PZT calcinada a 800 °C/3 h., com exceção da PZT8W, apresentaram apenas a fase cristalina PZT, quando calcinados a 800 °C/3 h, enquanto que a exceção apresentou uma fase secundária identificada como ZrO_2 (ICSD 89426). Fase essa que deve ser resultado tanto da volatilização do PbO quanto da maior valência do W, que desestabiliza o PZT, fazendo com que o zircônio seja segregado da rede, a fim de ser mantida a neutralidade de cargas. O conjunto de difratogramas revelou a manutenção da fase ZrO_2 , mesmo com o aumento da temperatura de calcinação, porém, permitiu observar que a quantidade dessa fase nas amostras deve diminuir consideravelmente devido à maior volatilização do Pb, o que proporciona a reentrada do Zr na estrutura a fim de ser mantida a neutralidade cristalina. Para a composição PZT2W, a fase cristalina não se manteve estável para temperaturas de calcinação superiores a 650 °C. O ZT8W utilizado nesse trabalho para obtenção do PZT8W apresentou uma fase secundária WO_3 , enquanto que o PZT8W calcinado apresentou uma fase secundária ZrO_2 . A introdução do W na rede, formando a estrutura PZT favorece a expulsão do Zr da rede. As micrografias dos pós de PZTp, PZT2W, PZT8W derivados do método do oxalato parcial calcinados a 800 °C/3 h indicam fortes aglomerados de pequenas partículas esféricas. O PZTp foi o que apresentou maior aglomeração de pequenas partículas que se mostraram com um tamanho médio inferior a 100 nm. Os pós de PZT preparados pelo método do oxalato parcial foram submetidos ao ensaio de dilatometria, a fim de definir-se a temperatura adequada de sinterização para cada composição. Para tanto, compactos foram preparados prensados e ensaiados. A retração linear $\Delta L / L_o$, juntamente com taxa de retração $d(\Delta L / L_o) / dT$, em função da temperatura ilustra as características das curvas dilatométricas que direcionaram a respeito da temperatura de sinterização a ser adotada para os compactos: temperatura de início de retração linear (T_{ir}) e a temperatura de máxima taxa de retração linear (T_{mr}). Pretendeu-se adotar como temperatura de sinterização (T_s) dos compactos um valor de ~ 30 °C acima da temperatura de máxima taxa de retração linear. A partir de dados dilatométricos adotou-se uma temperatura de sinterização geral de 1130°C, no intuito de eliminar-se mais uma variável, quando da comparação de resultados (temperatura). As amostras de PZTp, PZT2W e PZT8W mostraram uma provável formação de fase líquida na faixa de temperatura de 700 a 900 °C, evidenciada pela presença de um pequeno ombro. A introdução do W elevou um pouco a T_{ir} , embora o aumento de concentração não tenha mostrado variação expressiva. A microestrutura

do PZTp apresentou-se uniforme, com sinais de formação de fase líquida, que atua com inibidor do crescimento do grão. A ação do dopante W se deu de forma a elevar o tamanho dos grãos, além de mostrar uma forma menos arredondada. O que deve inibir a densificação, que se expressa pela grande quantidade de poros. O Ca alterou muito pouco a homogeneidade dos grãos, sem alterar muito o seu tamanho médio, porém aumentando a densificação. Em geral, o tamanho de grão para as composições aqui analisadas encontra-se no intervalo de 1-5 μm . A análise estrutural e quantitativa de fases da cerâmica PZT descrita neste trabalho foi realizada fazendo-se uso do método Rietveld. Os difratogramas de raios X observados, calculados, residuais (observado-calculado) e as posições dos picos de Bragg para as fases presentes nas amostras PZTp, PZT2W, PZT8W, sinterizadas a 1130 °C/3 h. Nas composições PZT2W e PZT8W pôde-se observar a coexistência das fases tetragonal e romboédrica (r), sendo esta última de grupo espacial R3c. A adição do tungstênio levou ao aparecimento de uma fase romboédrica, característica de PZT rico em Zr. Tal formação pode ser evidenciada com a apresentação dos difratogramas do PZTp, PZT2W e do PZT8W, onde observou-se (em *zoom*) o surgimento da fase romboédrica, ascendente com a concentração de W representada pelas reflexões R. O PZT dopado com W quando apenas calcinado mostrou uma fase segregada identificada como ZrO_2 , cuja ocorrência é atribuída à volatilização do PbO . A sinterização dos compactos ocorreu fazendo-se uso de uma atmosfera rica em PbO , o que promoveu uma queda na criação de vacâncias de Pb. Isso permitiu a incorporação do Zr pela estrutura do PZT, daí então, os difratogramas dos PZT dopados com W não mostraram a fase ZrO_2 segregada. A introdução do tungstênio na concentração de 2 % reduziu o volume da cela na fase tetragonal, apesar do aumento no parâmetro a , pois houve redução acentuada do parâmetro c . Isso nos leva a sugerir que tal fenômeno se deu decorrente da maior carga efetiva do W, que promove maior repulsão entre íons W e pares de mesma carga, em relação ao Ti e seus pares. É de se supor que devido ao raio iônico do W ser levemente menor que o do Ti, exista uma tendência para diminuição do parâmetro c , o que se confirma com a amostra dopada com 8 % de W. Nota-se que houve um aumento ainda maior do parâmetro a (repulsão) e uma redução ainda maior, do parâmetro c , levando à expansão do volume de cela, que se deu, principalmente, devido ao crescimento do parâmetro a . Pode-se imaginar que a estrutura está tendendo ao equilíbrio (tendendo à cúbica), com relação a tal repulsão. Com a adição de tungstênio houve o surgimento da fase romboédrica. Para a concentração de 2 % de W, o percentual de tal fase foi de 26 %. E quando a concentração foi de 8 % de W, esse percentual subiu para 60 %. Ou seja, o aumento na concentração de dopante promove o aumento no percentual de fase romboédrica. Com a adição do dopante W, o volume da fase

tetragonal diminui e em seguida aumenta, enquanto o volume da fase romboédrica diminui. O que nos leva a considerar que a ação repulsiva do W é mais eficiente na estrutura tetragonal do que na estrutura romboédrica, pois o volume da estrutura tetragonal tende a crescer com a concentração de W, logicamente, pelo aumento do parâmetro a e o volume da estrutura romboédrica tende a diminuir, pela redução no parâmetro a . Tal redução de volume de cela da estrutura romboédrica pode ser devido ao tungstênio possuir menor raio iônico, sugerindo a substituição ao titânio. A variação dos parâmetros de rede da estrutura tetragonal e o fator de tetragonalidade para o PZT dopado com W em comparação ao PZT puro. Isso mostra que o fator de tetragonalidade apresenta uma diminuição com a adição de W. Mas, o que chama a atenção é que tal diminuição ocorre realmente, devido a um grande aumento do parâmetro a , em concorrência com a diminuição do parâmetro c . O que mais uma vez sugere que o W promove mesmo, a repulsão com os seus vizinhos mais próximos (vizinhos com carga de mesmo sinal). Enquanto o parâmetro c diminui, o parâmetro a aumenta, como se o equilíbrio para tal estrutura fosse a fase cúbica. O mecanismo de compensação de carga que deve estar presente nessa fase tetragonal ocorre pelo fato de o tungstênio poder estar presente em outro estado de oxidação, ocorrendo a compensação de carga pela redução do elemento dopante. Considerando que a possível criação de vacâncias de Pb promoveria a retração da rede, resultaria em uma redução do volume de cela unitária, enquanto que uma redução do elemento dopante levaria ao aumento do raio iônico e, conseqüentemente, ao aumento do volume da cela unitária. Para a fase romboédrica acredita-se que o mecanismo de compensação de carga, devido à introdução do W, se dá pela geração de vacâncias de Pb, uma vez que ocorre uma redução de volume da fase romboédrica com o aumento da concentração de W, decorrente principalmente da diminuição do parâmetro a . Visando à análise dos deslocamentos dos átomos a partir de suas posições de origem, e no intuito de relacionar tais deslocamentos com propriedades elétricas experimentalmente determinadas, descreveremos a seguir as posições atômicas fracionárias dos átomos. O esquema de distribuição dos átomos para a estrutura tetragonal sugere deslocamentos do Zr/Ti/W e dos oxigênios (O_2) os quais serão considerados positivos se estiverem localizados abaixo do plano (002). Todos os deslocamentos $\delta Z_{Zr/Ti}$, δZ_{O_1} e δZ_{O_2} ocorreram no mesmo sentido do eixo c , daí considerar-se o mesmo sinal para todos eles. As composições PZT2W e PZT8W apresentaram a coexistência das fases tetragonal e romboédrica, portanto, apresenta-se um esquema da distribuição dos átomos na cela unitária da fase romboédrica. Nele pode-se observar o octaedro formado pelos oxigênios que envolvem o cátion B (Zr/Ti/W), em verde. A partir dos

valores de parâmetros de rede e dos deslocamentos atômicos $\delta Z's$ (acompanhados dos seus respectivos sinais) pôde-se determinar os valores de polarização espontânea para todas as composições aqui estudadas. A polarização espontânea sofre a influência do dopante, sugerindo que a simples substituição de um cátion por outro de valência superior não favorece a melhora nessa propriedade. O momento de dipolo esperado seria maior, e a polarização espontânea aqui determinada foi menor, mostrando que tal aumento de polarização deve-se muito mais aos deslocamentos atômicos e ao parâmetro de rede a . O tungstênio, quando adicionado ao PZT, promoveu uma redução da distância média Zr/Ti/W-O₁, o que resultou na redução de c . Mas o que deveríamos esperar é que a distância O₂-O₂, que é a base do octaedro que envolve o cátion B, diminuísse. Isso não aconteceu, levando-nos mais uma vez a concluir que a força de repulsão é privilegiada com o aumento da concentração de W, sendo responsável pelo aumento de volume da cela tetragonal, não influenciando muito no valor teórico da polarização espontânea da cerâmica. A influência junto à polarização espontânea deve-se principalmente ao maior deslocamento atômico do cátion B, ocorrido na fase romboédrica ($t = 0,0435$). Para a concentração de 8% de W, a fase tetragonal apresentou um aumento de volume, com redução do percentual de fase., enquanto a fase romboédrica apresentou uma redução de volume, seguida de um aumento do percentual de fase. O efeito repulsivo do W é mais efetivo na fase tetragonal, daí o aumento de volume com redução do parâmetro c . Com o aumento do percentual de fase romboédrica, a ação do W favoreceu a polarização espontânea média. A adição de 2 % de W ao PZT promoveu uma leve redução do volume dos poliedros da fase tetragonal (V_A e V_B). Dando-se nesse momento o surgimento da fase romboédrica. Tal redução de volume dos poliedros da fase tetragonal, aprisionou ainda mais o cátion B e reduziu a polarização espontânea ($11 \mu\text{C}/\text{cm}^2$), enquanto a fase romboédrica apresentou uma polarização espontânea elevada ($77 \mu\text{C}/\text{cm}^2$). Na concentração de 8 % de W, o PZT apresentou aumento de volume dos poliedros para a fase tetragonal e, para a fase romboédrica, houve uma diminuição do volume de tais poliedros (nesse caso deve-se observar que a razão V_A/V_B se manteve, mas o volume da cela unitária diminuiu). O aumento do percentual de fase romboédrica, acompanhado de uma redução na polarização espontânea, pode ser entendido com vistas à diminuição do volume do octaedro que envolve o cátion B e do volume do pseudocubo que envolve o Pb. Isso restringe o espaço para seus deslocamentos, daí menores valores de t e s .

Com a adição de 8 % W houve redução de volume da cela romboédrica, que ocorreu principalmente devido à redução do parâmetro a , apesar de pequena elevação do parâmetro c . Tal efeito pode ser relacionado à polarização espontânea, quando se observa que a estrutura

foi rearranjada inibindo a polarização. Isso se confirma com a redução do ângulo ω , que passou de 45,70 para 41,32°. Com um menor ângulo de inclinação do octaedro em relação ao eixo c, o cátion B possui menor possibilidade de deslocamento, pois a aproximação com outros cátions tende a centralizá-lo no octaedro, daí menor distorção do octaedro. As medidas da constante dielétrica relativa (k) e do fator de dissipação ou perda dielétrica ($\tan\delta$) foram realizadas no intervalo de 50 a 500 °C, resultando em curvas que possibilitaram o conhecimento da constante dielétrica relativa à temperatura ambiente (k_a), da constante dielétrica relativa máxima (k_c), da temperatura de Curie (T_c) e da perda dielétrica ou fator de dissipação ($\tan\delta$). As medidas mais representativas foram realizadas em frequências de 100 kHz e 1 MHz. A constante dielétrica à temperatura ambiente k_a atinge um máximo de 1018 (1 MHz) para a amostra PZT2W. A constante dielétrica na temperatura de Curie ou constante dielétrica máxima k_c aumenta com a concentração de dopante.

E com relação ao fator de dissipação, vê-se que o mesmo se encontra fluando em torno de 0,04 %, que é um valor característico dos dielétricos cerâmicos. Os maiores valores de fator de dissipação são referentes às amostras dopadas com W, pois nelas portadores de carga foram gerados devido à diferença de valência entre W e Ti. Esses portadores migram para o contorno de grão, sendo que as perdas se associam em parte à acumulação de cargas nos contornos de grão, propiciando perdas referentes ao movimento desses portadores de carga. O tungstênio reduziu a temperatura de Curie T_c , sendo que tal ação se deu pela desestabilização do octaedro de oxigênios ao seu redor. E ainda como resposta à adição de W, tem-se a elevação da constante dielétrica máxima do PZT o que confirma a ação de dopantes que levam a cerâmicas do tipo *soft* (120). A adição do tungstênio W, quando considerado em substituição ao Ti, promove a instabilidade do octaedro, já que possui menor raio iônico que o substituído. Novamente percebe-se que os maiores valores de perda dielétrica são referentes às amostras dopadas com W, visto que propiciam a geração de portadores de carga nos contornos de grão, propiciando perdas referentes ao movimento desses portadores de carga. Tais portadores de carga seriam gerados devido ao mecanismo de compensação de carga através da redução de parte do W introduzido na rede. Mesmo assim tais perdas são consideradas normais, pois não atingem 0,1%. As curvas de histerese (polarização *versus* campo, ou P - E) das composições PZTp, PZT2W, PZT8W revelam curvas típicas de memória ferroelétrica com forma quadrática. O aumento da concentração de W promove a diminuição do campo coercitivo E_c e o aumento da polarização P_r , fato que não condiz com o resultado obtido para a polarização espontânea através dos resultados dos refinamentos da estrutura cristalina, onde a polarização tende a diminuir com a adição de W. Esse comportamento pode

ser assumido devido ao fato de a adição de um dopante doador, em substituição ao íon Ti ou Zr, induzir a formação de vacâncias de Pb, reduzindo assim o “stress” entre os domínios, facilitando a mobilidade dos mesmos. Isso sugere que a adição do W aumenta a polarização determinada experimentalmente, pelo fato de melhorar a reorientação dos domínios e não pelo simples fato de substituir um cátion por outro de valência superior. O aumento da concentração de W leva a uma redução no volume da cela unitária, seguida de uma elevação do percentual de fase romboédrica. As amostras de PZT2W e PZT8W mostram maiores valores de P_s e P_r , o que sugere que o surgimento de uma segunda fase favorece a polarização. A fase PZT8W, que possui maior percentual de fase romboédrica (60 %), apresenta maiores valores de polarização. O mecanismo de compensação de carga dominante, na fase romboédrica é a criação de vacâncias de Pb, que difundem para o contorno de grão e aumentam ainda mais a possibilidade de reorientação dos domínios com o campo de polarização, levando a valores de polarização ainda maiores. Para a amostra dopada com W, fica a impressão de que a saturação atingiria níveis mais altos, uma vez que os valores de polarização de saturação evoluem plenamente com o aumento do campo. O d_{33} e o K_p aumentam de forma linear com o teor de W, visto que os mesmos estão relacionados diretamente à reorientação dos domínios quando da polarização. O movimento das paredes de domínios ou mobilidade dos domínios, que é elevado com a adição de W, favorece a melhoria em tais propriedades piezoelétricas. Os resultados estão concordantes com o encontrado em que é apresentado no anexo H (SANTOS, D., **SIMÕES, A.Z.**, ZAGHETE, M.A., SANTOS, C. O. P., VARELA, J.A., LONGO, E., Synthesis and electrical characterization of tungsten doped $Pb(Zr_{0.53}Ti_{0.75})O_3$ ceramics obtained from a hybrid process. **Materials Chemistry and Physics**. v.103, p.371 - 374, 2007).

Com o intuito de desenvolver materiais magnetoelétricos, novos estudos foram iniciados com o método dos precursores poliméricos na fabricação de pós de ferrita de bismuto pura e modificada com lantânio. Para verificar qual a melhor temperatura e tempo de tratamento térmico necessários para a obtenção de filmes finos com alta cristalinidade e boa morfologia, realizou-se um estudo sistemático com os pós de BFO e BLF. É necessário estabelecer as condições de cristalização das fases trabalhando com os pós, porque nos filmes pode haver problemas de interação entre o precursor e o substrato, o que gera fases secundárias, orientação preferencial e epitaxia, que interferem na caracterização da fase cristalina, pois apresentam picos de difração diferentes aos da ficha cristalográfica da fase hexagonal $BiFeO_3$ (86-1518), JCPDS-International Centre for Diffraction Data. O comportamento térmico dos pós obtidos pela calcinação das resinas a 300°C, por 4 horas, foi

avaliado pela perda de massa em função da temperatura. As curvas termogravimétricas indicam que a decomposição dos precursores ocorre basicamente em duas etapas: (1) degradação dos polímeros com decomposição em CO_2 e H_2O e perda de grande parte do material orgânico e (2) perda do restante do material orgânico, com a decomposição das carboxilas ligadas aos metais e consequente formação de uma fase estável metal-oxigênio. Nessa etapa ocorre o início do processo de cristalização da fase BFO. A partir de 800°C é estabelecido um patamar até 1000°C , mostrando que não há mais qualquer tipo de reação ocorrendo. A técnica de difração de raios-X (DRX) possibilitou acompanhar a formação de fases e cristalização em função da temperatura de calcinação das amostras. Os pós de BFO puro tratados no intervalo de 700°C a 800°C foram analisados por DRX. Os picos característicos da fase cristalina foram observados para os pós calcinados a partir de 600°C e identificados como ferrita de bismuto (BFO). Observa-se que, com o aumento da temperatura, a fase Bi_2O_3 localizada em $2\theta = 28^\circ$ e em grande quantidade no pó calcinado a 600°C , por 2 horas, é diminuída devido à sua difusão para a matriz com consequente formação da fase cristalina de ferrita de bismuto. Os difratogramas indicam também que o aumento da temperatura entre 600 e 800°C melhora a cristalinidade do material devido ao estreitamento do pico de máxima intensidade localizado em $2\theta = 32^\circ$. Para os pós calcinados a 800°C , os picos relativos à fase BFO já estão bem definidos, indicando melhor organização à longa distancia (periodicidade). Entretanto, a presença de algumas fases adicionais ainda é observada no pó calcinado a 800°C por 2 horas. Verifica-se também que a maioria dos picos de difração estão de acordo com os dados da ficha cristalográfica da fase BiFeO_3 (86-1518), JCPDS-International Centre for Diffraction Data. Com o intuito de avaliar o efeito da adição de lantânio sobre a cristalinidade dos pós de BFO, prepararam-se amostras com $x = 0$, $x = 0,08$, $x = 0,15$ e $x = 0,30$, as quais foram calcinadas na temperatura de 800°C . Pela análise dos difratogramas, observa-se que a adição de lantânio provoca alterações nos picos de difração da fase estequiométrica de ferrita de bismuto, indicando a formação de solução sólida substitucional sem a presença de fases indesejáveis. Uma característica que deve ser notada é que, com aumento da quantidade de lantânio, alguns picos tendem a desaparecer e outros a surgir na forma de dubletes. Isso está associado ao caráter iônico apresentado pelo lantânio, que leva o sistema a se organizar reduzindo a quantidade de picos de difração e consequentemente levando a uma estrutura mais simétrica. A perda de bismuto na forma de óxido também é minimizada quando da adição de lantânio, levando a pós-livres de fases indesejáveis. Os pós de BFO e BLF calcinados a 800°C por 2 horas foram avaliados pela

técnica de espectroscopia Raman. Os modos vibracionais podem ser classificados a partir das transições de rede envolvidas no deslocamento dos cátions e dos modos internos do octaedro de FeO_6 . Considerando o efeito da massa atômica nos modos vibracionais do BFO, os modos de baixa frequência podem ser atribuídos ao movimento dos átomos de Bi. Simultaneamente, os modos vibracionais internos do octaedro de FeO_6 são esperados acima de 200 cm^{-1} . Os picos localizados a 212, 316, 377, 445, 537, 635 cm^{-1} são causados por modos de vibração internos do octaedro FeO_6 , enquanto que abaixo de 200 cm^{-1} são devidos aos diferentes sítios ocupados pelo Bi, dentro das unidades perovskita. Os picos localizados em 97, 120 e 145 cm^{-1} são relacionados com os átomos de Bi da perovskita e correspondem a um modo de camada rígida que se origina do deslocamento do átomo de Bi. Comparando com o espectro de Raman do BFO, os picos referentes aos modos no BLF são menos intensos e se deslocam para altas frequências. O primeiro pico localizado em 97 cm^{-1} é muito difuso para se determinar com precisão sua posição. Entretanto, os picos localizados em 118 e 147 cm^{-1} para o BIT nitidamente se deslocam para altas frequências (127 e 168 cm^{-1} no BLF). Esse deslocamento indica que o átomo de lantânio por possuir pequeno peso atômico, foi substituído no BFO. Portanto, o aumento do número de onda no BLF sugere que o sítio de substituição preferido pelos átomos de La é o sítio atômico do Bi da camada perovskita. O lantânio tem um caráter iônico mais marcante que o ferro, logo tem a tendência de localizar-se em um sítio com densidade de carga semelhante à do bismuto, comportando-se como modificador de rede. As mudanças que ocorrem acima de 200 cm^{-1} no BLF são causadas pela relaxação da distorção estrutural e redução das vibrações do octaedro de FeO_6 causadas pela substituição com lantânio. Os modos localizados em 90 e 118, 150 e 186 cm^{-1} estão associados com átomos de Bi localizados no sítio A da perovskita e explicam o comportamento ferroelétrico do material. O modo localizado a 118 cm^{-1} diminui de intensidade, com alargamento do pico e aumento da frequência com a concentração de lantânio. A frequência do modo é governada por fatores locais, como a constante de força e a massa atômica do elemento a ser substituído. Se o fator local predomina, a frequência do modo será proporcional à raiz de k/m em que k é a constante de força e M a massa reduzida. Uma vez que a densidade de carga do La^{3+} é semelhante ao do bismuto Bi^{3+} , a constante de força é praticamente independente da substituição. De acordo com estudos prévios em óxidos perovskitas, ocorre estiramento do octaedro de FeO_6 exibindo característica de A_{1g} . As frequências dos modos são insensitivas à substituição pelo lantânio. Localmente, a energia da ligação é covalente (FeO), logo o FeO_6 tem muito maior energia de ligação no cristal, de forma que a frequência do modo é principalmente determinada pela ligação no Fe-O. O espectro de Xanes da pré-borda K do átomo de Fe dessas amostras foi

avaliado. Por comparação, os espectros do FeO e do Fe₂O₃ também são mostrados. O espectro evidencia que os átomos de ferro apresentam valência 3+, uma vez que estão superpostos ao composto Fe₂O₃. O pico A corresponde a transição proibida por dipolo elétrico 1s-3d, onde o pico C significa a transição permitida por dipolo para um orbital 4p desocupado. O pico B, que apresenta um ombro, é causado por um processo de perturbação no qual um elétron do orbital 2p do oxigênio transfere carga parcialmente ao orbital do Fe 3d, num processo chamado transferência de carga metal-ligante. A média distância (7-8 Å), a borda de absorção dos espectros é muito similar. A região da pré-borda de absorção retirada do background e normalizada está associada a uma transição 1s-3d, que é formalmente proibida por dipolo, mas torna-se permitida quando o átomo de ferro está simetricamente distorcido. Os átomos de ferro apresentam a mesma simetria nas amostras de BFO e BFO08 enquanto que nas amostras BLF015 e BLF030 apresentam simetria baixa e intermediária. Nesse sentido, ocorre uma mudança estrutural entre as amostras BFO e BLF08 e BLF015 e BLF030. Os resultados deste trabalho estão contidos nas referências que constam nos anexos I e J (GARCIA, F.G. RICCARDI, C.S., **SIMÕES, A. Z.** Lanthanum doped BiFeO₃: Syntheses and characterization. **Journal of Alloys and Compounds**. v.501, p.25 - 29, 2010) e (AGUIAR, E. CARLOS, MOURA, F, RAMIREZ, M A, VARELA, J.A., LONGO, E. **SIMÕES, A. Z.** Low-temperature synthesis of nanosized bismuth ferrite by the soft chemical method. **Ceramics International**. v.39, p.13 - 20, 2013).

4 COMPILAÇÃO DOS RESULTADOS OBTIDOS PARA SISTEMAS ELETROELETRÔNICOS (FILMES FINOS)

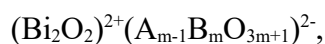
4.1 FILMES FINOS OBTIDOS POR MÉTODO QUÍMICO VIA SOLUÇÃO

O estudo de filmes finos de compostos ferroelétricos e multiferróicos tiveram seu início motivado pelos bons resultados obtidos na síntese de óxidos complexos via solução orgânica de citratos. A literatura disponível na década de 1990 não contemplava o uso do método Pechine para obtenção de filmes finos, especialmente porque as dificuldades são muitas na obtenção das fases cristalinas na forma de cerâmicas. No caso de filmes finos, essa dificuldade se acentua, pois, a relação área-massa é muito grande e as perdas de voláteis ocorrem muito mais intensamente. Encontramos, na literatura de filmes, a predominância de métodos físicos ou químicos usando fase de vapor, portanto, usar o método Pechine era um desafio que merecia ser tentado. Vários foram os sistemas estudados, faremos um compilado de cada um separadamente, pois, ao longo dos experimentos, encontramos características e particularidades que são bem mais entendidas se tratadas em separado. Portanto, optamos por apresentar numa introdução, os objetivos buscados e os pontos atingidos em cada sistema. Embora o objetivo central seja a preparação e caracterização de filmes finos, o início da pesquisa em cada sistema sempre foi desenvolvido usando o pó cerâmico, pois a quantidade de massa envolvida em filme é muito pequena e às vezes não é possível observar ou analisar o efeito de aditivos e fases secundárias que se cristalizam nos sistemas, por limite de detecção. Portanto, adotou-se como critério estabelecer a melhor condição para os materiais na forma de pós e depois obter os filmes.

4.2 SISTEMA CAMADA DE BISMUTO (FAMÍLIA DOS AURIVILLIUS)

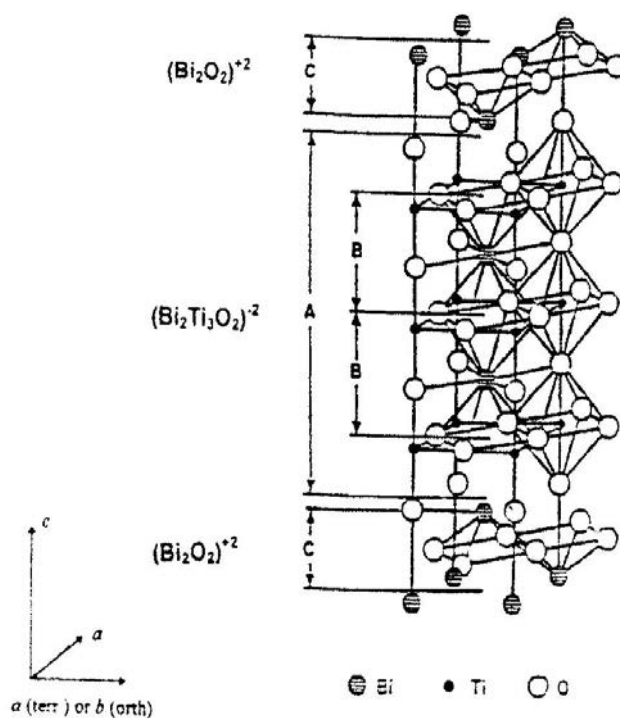
O material mais explorado para aplicação em memórias ferroelétricas tem sido o PZT, devido à sua alta constante dielétrica e baixa temperatura de cristalização, compatível com a tecnologia do silício. A desvantagem desse composto é a presença de chumbo que, devido a sua alta volatilidade, pode causar danos ao meio ambiente além de tornar mais difícil o controle composicional. No entanto, o maior problema apresentado pelo PZT tem sido sua alta degradação após diversos ciclos de polarização e despolarização, ou seja, a fadiga por

polarização (ou fadiga ferroelétrica) quando depositado sobre eletrodo de platina. Na busca de materiais alternativos, os materiais pertencentes à família dos óxidos com estruturas de camadas de bismuto (“bismuth layer oxide”) têm sido muito pesquisados. Esses materiais foram primeiramente estudados por Aurivillius & Fang (110) e podem ser considerados como estruturas do tipo peroviskitas intercaladas com camadas de óxido de bismuto. Podem ser representados por:



em que **A** pode ser Bi^{3+} , Ba^{2+} , Sr^{2+} , Pb^{2+} , K^+ ou Na^+ ; **B** pode ser Ti^{4+} , Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+} ou Fe^{3+} e *m* é um número inteiro, de 1 a 8, ou uma fração como 2 (1/2) ou 3 (1/2) (121). **A** é o cátion de coordenação 12 na sub-rede de peroviskita e **B** é o sítio octaédrico. O Bi forma a camada de $(\text{Bi}_2\text{O}_2)^{2+}$ entre os blocos de peroviskita $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, em que *m* é igual ao número de camadas octaédricas no interior da estrutura de sub-rede de peroviskita. Dentre os compostos acima citados, os mais comuns são o $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), o $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) e o $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT). Na Figura 1 pode ser visualizada uma representação esquemática da estrutura do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ indexado ao sistema ortorrômbico (JCPDS – 35795).

Figura 1 - Estrutura representativa do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, mostrando alternância entre as peroviskita e as camadas de bismuto. **A** significa a altura da camada múltipla peroviskita, **B** significa unidades estruturais de peroviskita hipotética e **C** camadas de $(\text{Bi}_2\text{O}_2)^{+2}$.



O arranjo atômico na estrutura cristalina do $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ favorece a obtenção de filmes com orientação preferencial na direção do eixo c . Conforme pode ser visto na Figura 3, o $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ consiste de camadas de $(\text{Bi}_2\text{O}_2)^{+2}$ intercaladas com camadas de $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{-2}$. O eixo c é perpendicular a essas camadas. No estágio inicial do crescimento do filme, a alta quantidade de camadas de $(\text{Bi}_2\text{O}_2)^{+2}$ paralelas ao substrato induz à orientação do filme no eixo c .

Existem vários trabalhos na literatura sobre a preparação de filmes finos de titanato de bismuto por diferentes métodos, tais como deposição de laser pulsado (PLD) (123), processamento sol-gel (sol-gel) (124), crepitação (sputtering) (125), ablação a laser (laser ablation) (126), laser MBE (127), feixe molecular epitaxial (BEM) (128), deposição de vapor químico (CVD) (129), e decomposição de vapor químico de metalorgânico (MOCVD) (130). Esse material tem apresentado boas propriedades ferroelétricas e dielétricas, sendo bastante atrativo para aplicações em memórias ferroelétricas. No entanto, suas propriedades são frequentemente afetadas por parâmetros do processo de fabricação, tais como: adição de dopante, temperatura de tratamento térmico, natureza do substrato, efeito da atmosfera utilizada, entre outros. Por isso, estabelecer os melhores parâmetros durante o processamento se torna fundamental e preparar filmes da família dos Aurivillius a partir de soluções químicas foi mais um desafio encarado em minha pesquisa no pós-doutoramento. Esses filmes foram preparados pelo método dos precursores poliméricos e depositados pelo processo “spin-coating”. Mais de 40 artigos indexados foram publicados nestes últimos anos nessa temática, demonstrando a importância desses filmes na fabricação de dispositivos de memórias.

Visando conhecer o efeito da temperatura na obtenção de filmes finos com boas características morfológicas, realizou-se um estudo sistemático de preparação de filmes finos de BIT e BLT e depositados em substratos de silício recoberto com platina. Inicialmente, fez-se um estudo utilizando-se solução com $\text{pH} = 3$ para deposição dos filmes. Primeiramente, prepararam-se filmes em diferentes temperaturas (600 a 700°C) utilizando tratamento térmico em forno convencional e o método “spin-coating” para deposição. O controle dessa etapa é muito importante, porque a mudança volumétrica envolvida para diferentes temperaturas pode conduzir à formação de defeitos superficiais do tipo trincas e bolhas após tratamento térmico. Manteve-se constante a velocidade de rotação do substrato da solução em 5000 rpm. Fixou-se a viscosidade da solução em 20 cPs (1,20 g/cm³), a concentração iônica em 0,1 mol. L⁻¹. Os filmes foram tratados termicamente com taxa de aquecimento lenta de 3°C/min até a temperatura de decomposição térmica dos orgânicos (400°C) para evitar a formação de trincas e taxa de 5°C/min entre 600 e 700°C. Os difratogramas de raios X para os filmes de BIT

puros e tratados termicamente em várias temperaturas indicam que, embora os picos de difração correspondentes à estrutura perovskita tenham sido detectados a baixas temperaturas (600°C), eles são bastante alargados indicando a baixa cristalinidade do filme obtido. Para temperaturas superiores a 650°C, picos de difração bem estreitos foram observados sendo sua intensidade bem dependente da temperatura de tratamento térmico. Observa-se também que para baixas temperaturas o crescimento dos grãos no plano (0100) é favorecido, enquanto que com o aumento da temperatura os grãos estão orientados no plano (117). Esta observação é importante pois algumas propriedades elétricas como constante dielétrica, polarização remanescente e campo coercitivo, variam com a mistura de orientações que difere de um filme para o outro. As morfologias das superfícies dos filmes, com cinco deposições, tratadas termicamente conforme as condições experimentais descritas anteriormente indicam que o aumento da temperatura de tratamento térmico influencia na morfologia do filme obtido. Essa observação sugere que mantendo-se constante viscosidade e velocidade de rotação, o aumento da temperatura de tratamento térmico elevam a mobilidade iônica dentro da célula unitária causando um aumento no tamanho de grão e uma diminuição da porosidade. Os grãos estão homogeneamente distribuídos com tamanho médio de grão variando de 80 a 179 nm, o que é comparado com os resultados obtidos por MFA.

O tamanho médio de grão e a rugosidade superficial dos filmes de BIT foram estimados por microscopia de força atômica (MFA) usando modo contato. Observa-se que a morfologia obtida é livre de trincas e de baixa porosidade. Outro parâmetro importante a ser controlado é a rugosidade, uma vez que as propriedades dielétricas e ferroelétricas dependem não somente de uma morfologia bem definida, mas também das interações que ocorrem na interface filme-substrato. A variação da constante dielétrica em função da frequência para esses filmes revela forte dependência da constante dielétrica com a temperatura de tratamento térmico. Essa observação sugere que o eixo polar é mais próximo do plano (117) que do (0100), o que é consistente com os resultados obtidos para filmes epitaxiais. Idêntico comportamento foi observado para monocristais de titanato de bismuto, nos quais a constante dielétrica medida ao longo do eixo *a* é aproximadamente o dobro da medida ao longo do eixo *c* com deslocamento de 4,5° do eixo polar para o titanato de bismuto em relação ao eixo *a*. A dependência da capacitância-voltagem para filmes de BIT puro obtidos a 100 kHz e com voltagem de varredura de + 10 a -10 V. A relação entre a voltagem e a capacitância é bem linear, confirmando as propriedades ferroelétricas do filme resultante da reversão dos domínios. A curva *C-V* para o filme tratado termicamente a 700°C por 2 horas indica simetria nos valores máximos de capacitância, que podem ser observados na reversão da polarização espontânea.

A curva é simétrica próximo à voltagem zero, indicando que o filme contém poucas cargas espaciais acumuladas na interface filme-substrato. Para filmes tratados termicamente a temperaturas de 600 e 650°C uma pequena variação da capacitância é observada indicando que existem cargas espaciais localizadas próximas à interface filme-substrato. Dados de histerese ferroelétrica para os filmes de BIT tratados termicamente entre 600 e 700° indicam polarização remanescente e o campo coercitivo medido para o filme tratado termicamente a 700°C é de 23,7 $\mu\text{C}/\text{cm}^2$ e 3,1 V, respectivamente, sob uma voltagem máxima aplicada de 14V. A polarização remanescente e a o campo coercitivo diminuem para 11,8 $\mu\text{C}/\text{cm}^2$ e 2,4V. A maior polarização remanescente e o maior campo coercitivo obtidos para a temperatura de tratamento térmico de 700°C é consistente com os filmes epitaxiais de BIT relatados na literatura (171). Em contrapartida, a polarização remanescente para o filme orientado no plano (0100)-excede o valor de ($P_r = 1,1 \mu\text{C}/\text{cm}^2$) provavelmente devido à contribuição de grãos orientados no plano (117).

Os testes de fadiga para os filmes de BIT em função dos ciclos de polarização foram examinados pela aplicação de pulsos bipolares de largura de 8,6 μs com amplitude de 10 mV. A polarização remanescente foi calculada a partir da diferença entre as polarizações reversa e não reversa. Para os filmes tratados termicamente a altas temperaturas a polarização reversa apresenta-se livre de degradação até 10^{10} ciclos de polarização. Esse resultado é um pouco surpreendente, pois geralmente filmes de BIT puros apresentam baixa resistência à fadiga, devido à presença de cargas espaciais na interface filme-substrato que causam aprisionamento dos domínios ferroelétricos. Porém, conforme observado na curva $C-V$ o filme tratado a 700°C por 2 horas contém pequena quantidade de cargas espaciais, devido a simetria nos valores de capacitância para diferentes voltagens gerando um filme livre de fadiga e com alto valor de polarização remanescente. O filme tratado a 650°C também não apresenta fadiga ferroelétrica, porém sua polarização é muito menor que a do filme tratado a 700°C, o que para aplicação em memórias FeRAMs não é bastante desejável. Em contrapartida, os filmes tratados termicamente a 600°C por 2 horas não apresentaram resistência a fadiga, devido ao aumento local da corrente causada pela baixa cristalinidade, que eventualmente destrói a interface filme-eletrodo causando uma diminuição da polarização remanescente. Dessa forma, a partir desses resultados podemos definir a temperatura de 700°C como a mais apropriada para obtenção de filmes finos de BIT, com alta cristalinidade, morfologia livre de defeitos, e com maiores valores de constante dielétrica, polarização remanescente e livre de fadiga, que são características ideais para obtenção de circuitos integrados baseados nesses filmes. As

principais informações obtidas estão no artigo que consta no anexo K (SIMÕES, A. Z., RAMIREZ, M. A., RICCARDI, C. S., RIES, A., LONGO, E., VARELA, J.A., Influence of temperature on the dielectric and ferroelectric properties of bismuth titanate thin films obtained by the polymeric precursor method. **Materials Chemistry and Physics**. v.92, p.373 - 378, 2005).

Após otimizado que a temperatura de 700°C, por 2 horas, era a mais apropriada para obtenção de filmes finos de BIT, fez-se um estudo variando a quantidade de lantânio e a rota de cristalização dos filmes visando a obtenção de boas propriedades elétricas como alta polarização remanescente, baixo campo coercitivo e resistência a fadiga. Um novo conjunto de filmes foi preparado visando compreender a influência do dopante e da rota de cristalização. É bem sabido que a rota de cristalização afeta a microestrutura dos filmes. Os filmes tratados pela rota da camada intermediária cristalina (RCIC), consistem em pequenos grãos da fase perovskita isolados, que possuem tamanhos uniformes. Essa rota favorece uma alta taxa de nucleação conduzindo a um elevado número de sítios cristalinos. Como consequência, o tamanho de grão diminui levando a uma microestrutura com grãos pequenos. No caso do filme tratado pela rota da camada intermediária amorfa (RCIA), a menor taxa de nucleação promove um número menor de núcleos de cristalização conduzindo a um aumento do tamanho de grão. Uma possível explicação para o aumento no tamanho de grão, para as diferentes rotas de cristalização, pode ser a história térmica da primeira camada. O núcleo formado no tratamento térmico da primeira camada pode crescer durante o tratamento térmico das próximas camadas, portanto, a cristalização do filme muda conduzindo a um aumento no tamanho de grão. Para a RCIA a formação de menos núcleos conduz a um aumento no tamanho de grão. Basicamente nesse caso, a nucleação inicia-se da superfície do filme em direção ao substrato. Dois conjuntos de filmes com cinco camadas foram preparados por rotas diferentes. Os filmes foram tratados a 400°C, por 2 horas, até que o número de camadas fosse alcançado. Posteriormente, todas camadas amorfas foram tratadas termicamente a 700°C por 2 horas. Essa rota é denominada RCIA. Na RCIC cada camada foi cristalizada a 700°C por 2 horas antes da próxima deposição. A difração de raios X mostra que os filmes de BIT foram tratados termicamente por ambas as rotas e dopados com diferentes quantidades de lantânio. Observam-se somente picos relacionados às fases cristalinas BIT e BLT, sugerindo que a substituição do Bi pelo La não conduz à formação de fases secundárias. A transformação dos picos (0100) e (200) em dois dubletes indica mudança de estrutura cristalina de ortorrômbica

para tetragonal. Além da fase BIT, um pico de alta intensidade pertencente ao substrato de platina recoberto com silício (111) em $2\theta = 40^\circ$ foi identificado.

Comparando as intensidades dos picos de BIT com dados da literatura, observa-se que a adição de lantânio ($x = 0,75$) resulta em orientação preferencial em $2\theta = 16^\circ$, devido à mudança de sistema cristalino ortorrômbico-tetragonal. Independente da rota utilizada, somente os picos referentes à fase BIT foram detectados, sugerindo que a rota de cristalização não conduz ao aparecimento de fases secundárias. Verificou-se pelo filme tratado pela RCIA, que independente da fração de lantânio adicionada conduz a um filme policristalino. Em contraste, para a RCIC, o aumento da fração de lantânio conduz à orientação preferencial na direção (006). Considerando que a espessura do filme obtido pela RCIC é menor quando comparada com o filme obtido pela RCIA o aparecimento de orientação preferencial devido à nucleação interfacial foi observado. Para os filmes tratados pela RCIA, a maior espessura pode dar origem a outro fenômeno como a nucleação superficial originando um filme policristalino. As micrografias dos filmes de BIT puro e dopados com lantânio e tratados termicamente por diferentes rotas de cristalização foram analisadas. Morfologias na forma de placas foram observadas para o filme de BIT e BLT ($x = 0,25$) e tratado pela RCIC. O tamanho médio de grão obtido por SEM representa um valor médio de várias medidas realizadas em diversas posições de cada grão individual. O tamanho médio de grão aumenta até a fração de lantânio igual a ($x = 0,5$). Após este limite, uma larga diminuição no tamanho de grão é observada, indicando a forte dependência da fração de lantânio nas propriedades morfológicas dos filmes, resultante da diminuição da quantidade de bismuto do sistema. Dados de microscopia revelam que as superfícies dos filmes são densas, lisas e livres de trincas. Os grãos estão distribuídos homogeneamente, com tamanho de grão médio variando de 140 a 210 nm. Uma significativa diferença na morfologia do filme pode ser observada pelas diferentes rotas de cristalização. Para a RCIC um filme denso com grãos alongados em forma de placas foi observado. Os filmes tratados termicamente pela RCIA apresentam uma microestrutura densa e granular com grãos esféricos. A ausência de trincas indica que o filme apresenta uma morfologia homogênea. A diferença na forma dos grãos está relacionada com a quantidade de material depositado na superfície do substrato para cristalização dos filmes. Considerando que o filme tratado pela RCIC possui menos material para ser cristalizado camada por camada, os grãos tendem a assumir a forma energética mais favorável (forma arredondada). Em contrapartida, os filmes tratados pela RCIA possuem uma maior quantidade de material a ser cristalizado em uma única etapa conduzindo a uma forma energética menos favorável (grãos alongados). Independente da rota de cristalização utilizada,

observa-se uma microestrutura livre de trincas e com baixa porosidade. O tamanho de grão aumenta com a fração de lantânio até limite de $x = 0,5$, reduzindo para $x = 0,75$, indicando que a substituição do bismuto pelo lantânio causa uma mudança na morfologia dos filmes. Além disso, a quantidade de lantânio adicionada reduz as vacâncias de oxigênio, que agem como centros aprisionadores dos domínios facilitando o processo de reversão dos dipolos elétricos. A espessura e a rugosidade não foram significativamente dependentes da fração de lantânio adicionada no sistema; em contrapartida, influem fortemente na forma e no tamanho dos grãos. A rugosidade medida está entre 10 e 17 nm. Esses resultados são comparados com outros métodos químicos (17 nm) e aos obtidos por métodos físicos (9 nm). Os resultados mostram que as diferentes rotas de cristalização conduzem a filmes com diferentes microestruturas. Os filmes cristalizados usando a RCIC apresentam uma estrutura típica de camada de bismuto. Em contrapartida, os filmes cristalizados usando a RCIA apresentam grãos esféricos com tamanho variando de 180 a 250 nm. Considerando ambas as rotas de cristalização, a RCIA parece favorecer a elevada taxa de nucleação conduzindo a um elevado número de núcleos cristalinos. Cada camada intermediária cristalina age como uma semente de nucleação para a próxima camada a ser cristalizada. No caso da RCIC, a taxa de nucleação pode ser menor, promovendo um menor número de núcleos cristalinos, o que conduz a grãos alongados na forma de placas. Basicamente a nucleação ocorre na superfície e na interface filme-substrato. A constante dielétrica e o fator de dissipação foram medidos à temperatura ambiente em função da frequência no intervalo de 10 kHz a 1 MHz. Os filmes apresentaram boas propriedades dielétricas, uma constante dielétrica de 148 com perda de $(\tan \delta) = 0,013$ a 1 MHz para o filme tratado pela RCIC e dopado com lantânio ($x = 0,5$). A constante dielétrica mostra pouca dispersão com a frequência indicando que os filmes possuem baixa quantidade de defeitos na interface filme-substrato. A baixa dispersão da constante dielétrica e a ausência de qualquer pico de relaxação em $\tan \delta$ indicam que a polarização interfacial do tipo Maxwell Wagner e aquela causada pela barreira do eletrodo são desprezadas nesses filmes. Também se observa que a adição de lantânio aumenta a constante dielétrica e diminui a perda dielétrica, indicando que esse elemento tem um papel crucial nas propriedades elétricas de filmes finos de BIT obtidos pela RCIC. A dopagem, mesmo em baixas concentrações, tem uma forte influência nas propriedades dielétricas do sistema BIT. A constante dielétrica do filme dopado lantânio ($x = 0,75$) e orientado no eixo c é maior que a do monocristal de BIT observado na literatura ($\epsilon = 130$). A diferença na magnitude pode ser atribuída à mudança no tamanho de grão causado pela modificação estrutural quando da

adição de lantânio. O menor tamanho de grão conduz a um aumento na constante dielétrica e diminuição da perda dielétrica, resultado este que pode ser explicado pela redução da tensão residual e do volume da célula unitária do filme durante resfriamento devido à mudança de estrutura cristalina quando da dopagem com lantânio ($x = 0,75$). Foi observado que os filmes tratados por diferentes rotas de cristalização conduzem a propriedades dielétricas semelhantes. Esse resultado não é surpresa porque embora o filme tratado pela RCIC favoreça a orientação preferencial na direção (006) não conduz a um maior valor na constante dielétrica uma vez que o filme está orientado no mesmo plano da fase policristalina. Os resultados de constante dielétrica e perda dielétrica obtidos são consistentes com os dados microestruturais e cristalográficos apresentados até o presente momento. As medidas ferroelétricas desses filmes foram investigadas com um analisador ferroelétrico para frequência de 100 Hz e uma voltagem aplicada da ordem de 20 V. Observam-se curvas bem saturadas com uma polarização remanescente, que variam de 15 a 22 $\mu\text{C}/\text{cm}^2$ e voltagem de operação de 1,35 a 3,36 V. A saturação dessas curvas em baixas frequências indica que as perdas são mínimas sugerindo um filme altamente resistivo. A rota de cristalização afeta ligeiramente as propriedades ferroelétricas dos filmes. As curvas de histerese para os filmes tratados pela RCIC e dopados com lantânio apresentam-se mais simétricas. Pode ser observado que a adição de lantânio até a fração de $x = 0,75$ para o filme tratado pela RCIC conduz à orientação preferencial, que resulta numa menor voltagem de operação do filme ferroelétrico. Verifica-se que a polarização remanescente é muito maior que aquela esperada para filmes orientados no eixo c do BIT e pode ser atribuída à presença de componentes de polarização no eixo a conforme visto por DRX. Pode se notar que as curvas de histerese do filme tratado termicamente pela RCIA apresentam um deslocamento ao longo do eixo do campo coercitivo em direção ao lado positivo, fenômeno esse conhecido com imprint. A variação na voltagem pode causar uma falha do capacitor devido a aparente perda de polarização em um dos estados remanescentes. Conseqüentemente, um aumento no campo, coercitivo em uma direção pode ocorrer. Esses dois efeitos podem causar falha de memória do capacitor e são compatíveis com os dados apresentados de medidas $C-V$. Para os filmes de BIT puro e dopado com lantânio e tratados termicamente por diferentes rotas de cristalização, observa-se que a dependência da voltagem é fortemente não linear indicando as propriedades ferroelétricas dos filmes, resultado das reversão dos domínios. Pelo fato de a curva ser simétrica ao redor da voltagem nula, pode-se dizer que esses filmes apresentam poucos íons móveis e cargas acumuladas na interface filme-substrato. As curvas de $C-V$ para os filmes tratados termicamente pela RCIC indicam simetria nos valores máximos de

capacitância os quais podem ser observados pelo mecanismo de reversão de domínios ferroelétricos. As curvas são simétricas ao redor da voltagem zero, indicando que os filmes contêm pequena quantidade de cargas espaciais acumuladas na interface filme-eletrodo. Em contrapartida, o filme tratado termicamente pela RCIA apresenta uma pequena mudança nos valores de capacitância, indicando que existem cargas aprisionadas na interface filme-eletrodo. Vale a pena destacar que para algumas curvas de histereses a saturação dos domínios ocorre em menores voltagens quando comparada às curvas de $C-V$. Esse fato pode ser explicado pela diferença nas frequências de medida das curvas de histerese e capacitância em função da voltagem. Considerando que a polarização e a capacitância dependem da frequência, pode-se atribuir uma diferente cinética de reversão dos domínios ferroelétricos, o que reflete fortemente no formato das curvas. As medidas de $J-V$ desses filmes foram realizadas usando o equipamento radiant technology no modo de voltagem-corrente variando de 0 a + 10V, e +10 a -10V, voltando novamente a 0V. As curvas para esses filmes foram medidas com passos de voltagem de 0,1 V e tempo de 1,0 s para cada voltagem. Independente da rota de cristalização utilizada observam-se duas regiões distintas. Na primeira região a densidade de corrente aumenta linearmente com o campo elétrico externo na região de baixa voltagem sugerindo uma condução ôhmica. Para altas voltagens a densidade de corrente aumenta exponencialmente o que implica que pelo menos uma parte da condutividade resulta do mecanismo de emissão do tipo Schottky ou Poole-Frenkel. A densidade de corrente a 1,0 V diminui com o aumento da concentração de lantânio para ambas as rotas de cristalização. Alguns fatores podem ter contribuído para essa melhora. Primeiramente a redução da rugosidade superficial com o aumento da concentração de lantânio; considerando que a condutividade é fortemente afetada pela característica da interface filme-substrato, a morfologia dos filmes de BIT puro e dopados com lantânio é uma das maiores causas do aumento da densidade de corrente em capacitores ferroelétricos. Outro fator pode ser a redução das microtrincas causadas pela tensão residual. Uma vez que a estrutura ortorrômbica e a transição de fase diminuem com o aumento na concentração de lantânio, o volume da célula unitária durante o resfriamento diminui e a tensão residual aumenta. A ligeira diminuição nos valores de densidade de corrente observados para o filme tratado pela RCIA pode ser atribuída a diferenças de tamanho e forma dos grãos, densidade e estrutura de superfície, devido às diferenças nos procedimentos de cristalização. As características da interface filme-eletrodo e da morfologia de superfície dos filmes de BIT são os principais fatores que determinam a densidade de corrente para capacitores do tipo metal-ferroelétrico-metal. A resistência à fadiga para os filmes de BIT em função dos ciclos de polarização foi

observada pela aplicação de pulsos bipolares de largura 8,6 μ s com 10 mV de amplitude. Independente da rota de cristalização utilizada, elevada resistência à fadiga foi observada até 10^{10} ciclos para filmes de BIT dopados com lantânio ($x = 0,50$ e $0,75$). A substituição do La por Bi pode mudar o meio químico das camadas perovisquitas e resolver o problema de fadiga dos filmes puros de BIT, pois reduz vacâncias de oxigênio. Entretanto, não fica claro onde o La muda o ambiente químico das camadas perovisquita. É provável que o lantânio substitua íons bismuto próximos às camadas octaédricas do TiO_6 reduzindo a quantidade de vacâncias de oxigênio presente na estrutura. Outra justificativa é o papel de compensação de cargas das camadas de $(\text{Bi}_2\text{O}_2)^2$. As principais informações obtidas estão nos artigos que constam nos anexos L e M (SIMÕES, A. Z., S, Riccardi C.S., FILHO, F.M., RIES, A., ZAGHETE, M. A., STOJANOVIC, B. D., LONGO, E., VARELA, J. A., Characterization of lanthanum-doped bismuth titanate thin films prepared by polymeric precursor method. **Materials Letters** (General ed.). v.58, p.2842 - 2847, 2004) e (SIMÕES, A. Z., RICCARDI, C. S., QUINELATO, C., RAMIREZ, M. A., RIES, A., CILENSE, M., LONGO, E., VARELA, J. A., The influence of crystallization route on the properties of lanthanum doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared from polymeric precursors. **Materials Science and Engineering. B, Solid State Materials for Advanced Technology**. v.113, p.207 - 214, 2004).

Embora as melhores condições de tratamento térmico, rota de cristalização e concentração de lantânio tenham sido anteriormente otimizadas, o controle da rugosidade superficial torna-se importante para obter propriedades elétricas desejáveis. Dessa forma, a concentração iônica teve seu valor ajustado de 0,1 para 0,05 mol.L^{-1} e o pH da solução de 3 para 9, visando obter uma superfície mais homogênea e com menor rugosidade. É bem sabido que o poder de complexação dos metais pelos grupos carboxílicos é dependente dos valores de pH do meio. Por exemplo, a complexação do bismuto pelo ácido cítrico conduz a um polímero linear, levando à formação de filmes com morfologia preferencialmente na forma de placas. Em contrapartida, a adição de etilenodiamina compete com o ácido cítrico para complexação do bismuto, tornando o efeito volumétrico mais acentuado e modificando a morfologia do filme para grãos arredondados. Obviamente, as condições estabelecidas para a solução com concentração iônica maior e $\text{pH} = 3$ não são as mesmas para a solução com menor concentração iônica (0,05 mol.L^{-1}) e $\text{pH} = 9$. Portanto, antes de medir as propriedades elétricas dos filmes de BIT, foi necessário aumentar o número de depósitos visando à obtenção de filmes finos com boas características morfológicas que permitem obter propriedades elétricas satisfatórias. Sabe-se que a espessura do filme influencia no tamanho de grão, e nas propriedades ferroelétricas e dielétricas. Para filmes finos a interação entre as

camadas existentes na interface filme-substrato, denominadas “dead layers”, pode ocorrer de forma mais acentuada que no caso de filmes mais espessos, prejudicando o desempenho do dispositivo. Essas camadas surgem através da interdifusão de oxigênio, reações químicas ou defeitos estruturais na interface e podem ser suprimidas se o filme apresentar espessura superior a 200 nm. Esta espessura crítica pode ser obtida através de multi-deposições. A fim de evitar a formação de trincas, manteve-se constante a velocidade de rotação do substrato em 5000 rpm e a taxa de aquecimento em 3°C/min. Fixaram-se também os parâmetros como: a viscosidade da solução em 20 cPs (1,20 g/cm³) e a concentração iônica em 0,05 mol.L⁻¹. Filmes com 10 camadas foram depositados em substratos de silício recoberto com platina por spin-coating e tratados termicamente em atmosfera de oxigênio e atmosfera de ar (estática), visando obter espessuras superiores a 200 nm. Realizou-se um estudo com o tratamento do filme em atmosfera de oxigênio e ar estático (ambiente) cristalizando camada por camada a 700°C por 2 horas. A vazão de oxigênio foi mantida constante a 100 mL/min.

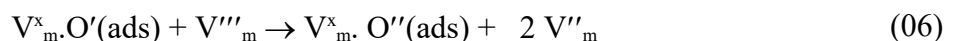
Analisando os resultados de DRX pode-se observar que a atmosfera utilizada durante o tratamento térmico influencia diretamente na nucleação da fase cristalina BIT. A atmosfera de ar (ambiente) favoreceu a cristalização da fase BIT policristalina, com pico de máxima intensidade em (117) $2\theta = 30^\circ$. Em atmosfera de oxigênio, a decomposição da matéria orgânica é mais rápida, e sendo uma reação exotérmica, libera maior quantidade de calor, promovendo a cristalização da fase BIT a partir do substrato que é a superfície de menor energia de ativação para cristalização, pois tem superfície com planos orientados. Essa cristalização rápida a partir do substrato impede a formação de fases secundárias na interface filme-substrato, embora não aumente a concentração de BIT que cristaliza com heterotopaxia orientada no plano (117). Observa-se que, independente da quantidade de lantânio adicionada, não houve formação de fases secundárias tanto para atmosfera estática como dinâmica.

Verifica-se uma superfície mais homogênea, uniforme e densa para os filmes de BIT tratados em atmosfera de oxigênio. Independente da quantidade de lantânio utilizada, os filmes calcinados em atmosfera de oxigênio apresentam menor espessura quando comparados à atmosfera de ar (ambiente). Isso ocorre devido à vazão de oxigênio aumentar a taxa de nucleação, favorecendo uma distribuição mais homogênea do material depositado na superfície do substrato com baixa porosidade. Observa-se que os filmes tratados termicamente em atmosfera de oxigênio apresentam uma superfície mais homogênea quando comparados aos tratados em atmosfera de ar. Isso pode ser explicado em função da diferente taxa de

nucleação que ocorre para os filmes tratados termicamente em atmosfera de oxigênio, comparados aos tratados em atmosfera estática de ar (ambiente). O tamanho de grão diminuiu para os filmes tratados em oxigênio, pois, em atmosfera dinâmica, o crescimento do grão na direção *a-b* tornando-se um grão arredondado é favorecido. Em atmosfera de ar (ambiente), o tamanho de grão é maior quando comparado à atmosfera dinâmica de oxigênio. Embora o filme tratado em atmosfera de oxigênio apresente menor rugosidade e porosidade, espera-se que suas propriedades elétricas sejam inferiores a dos filmes tratados em atmosfera estática, uma vez que essas propriedades dependem fortemente do tamanho médio de grão. Considerando que somente os filmes dopados com lantânio ($x = 0,5$ e $0,75$) apresentaram-se livres de fadiga, realizaram-se medidas elétricas desses filmes visando compreender a influência da atmosfera de tratamento térmico. É bem sabido que a constante dielétrica e o fator de dissipação dependem da temperatura de tratamento térmico, tipo de eletrodo, defeitos, paredes de domínios e composição da fase. A amostra tratada termicamente em atmosfera de oxigênio apresenta uma intensa queda na constante dielétrica no intervalo de frequência de 10 a 100 kHz. É possível que essa diminuição na constante dielétrica nesse intervalo de frequência seja causada pela polarização de carga espacial ou polarização interface do tipo Maxwell Wagner. A polarização de carga espacial está relacionada com o acúmulo de cargas não uniformes, que podem ter sido originadas durante o tratamento em atmosfera de oxigênio. Verifica-se que o formato das curvas de histerese ferroelétrica depende fortemente de um bom controle da interface filme/substrato, que pode ser notado pela dependência entre a constante dielétrica com a frequência. Em geral, quanto maior a dispersão entre a constante dielétrica e a frequência, mais defeitos interfaciais são verificados e as curvas de histerese apresentarão os seguintes problemas: insaturação, maior gap de polarização, falta de reversibilidade dos domínios ferroelétricos e o fenômeno de “imprint”, que é a tendência de uma camada ferroelétrica reverter a direção de polarização para um estado mais estável. Quando os filmes foram tratados em atmosfera estática, uma redução na dispersão da constante dielétrica com a frequência foi observada indicando que houve uma diminuição no efeito de carga espacial, confirmando que a relaxação dielétrica não é um fenômeno de bulk, mas está relacionada com a interface. A partir dos resultados obtidos observa-se uma diferença na constante dielétrica para os filmes tratados em atmosfera estática, devido a diferenças em tamanho de grão, cristalinidade e defeitos estruturais.

As curvas de histerese para os filmes tratados termicamente em atmosfera estática indicam que o processo de polarização é mais acentuado. Entretanto, para os filmes tratados termicamente em atmosfera de oxigênio as cargas carregadas (O_2^-) associadas a outros

defeitos ($V_0^{\bullet\bullet}$ ou até mesmo dipolos complexos) tais como vacâncias de oxigênio associadas com vacâncias de bismuto ($V'''_{Bi} - V_0^{\bullet\bullet}$) localizadas no contorno de grão e na interface filme-substrato podem promover um deslocamento na curva de histerese. Ferroeletricidade nos filmes foi observada com polarização remanescente de 15 e 21, 5 $\mu\text{C}/\text{cm}^2$ com voltagem de 1,75 e 1,44 V para filmes recozidos em atmosfera estática ($x = 0,5$ e $0,75$) e 10 e 13 $\mu\text{C}/\text{cm}^2$ com voltagem de 1,05 e 1,46V para filmes recozidos em atmosfera de oxigênio ($x = 0,5$ e $0,75$), respectivamente. O valor de polarização espontânea para um monocristal de titanato de bismuto é 50 $\mu\text{C}/\text{cm}^2$, que é maior que os valores correspondentes aos filmes. Isso pode ser atribuído aos componentes de vetores de polarização orientados no plano c que apresentam polarização remanescente baixa. A curva de histerese para o filme tratado termicamente em atmosfera de oxigênio mostra uma diferença no campo coercitivo em direção ao lado positivo, definido como imprint. A mudança de voltagem pode causar uma falha no capacitor devido à perda de polarização em um dos estados remanescente. Consequentemente, pode ocorrer um aumento no campo coercitivo em uma direção, causando uma falha na memória. Esses resultados são consistentes com as medidas $C-V$ e podem ser causados pela alta concentração de vacâncias de bismuto e oxigênio localizadas na interface filme-substrato. Novamente, observa-se uma relação não linear indicando propriedades ferroelétricas resultado da reversão dos domínios ferroelétricos. Para os filmes tratados em atmosfera estática, a curva é simétrica para valores de voltagem baixos indicando que os filmes contêm poucas cargas espaciais acumuladas na interface filme-substrato. Em contrapartida, uma dispersão nos valores de capacitância foram observadas para os filmes tratados termicamente em atmosfera de oxigênio, indicando que existem cargas espaciais acumuladas na interface filme-substrato. Essas cargas podem ter sido originadas durante o processo de tratamento térmico para decomposição do polímero precursor. As cargas negativas podem estar associadas com a presença de espécies de oxigênio negativamente carregadas localizadas no contorno de grão e na interface filme-substrato. As cargas negativas do oxigênio podem ser causadas pela transferência de carga entre a vacância do metal e o oxigênio, de acordo com seguintes equações:



onde O^x , V'''_m , V^x_m , e O'' representam os íons oxigênicos neutros em suas posições normais, vacâncias de metal triplamente carregadas negativamente, vacâncias de metal neutras, e íons oxigênicos duplamente carregados negativamente. As propriedades isolantes dos filmes são bem dependentes da atmosfera de tratamento térmico. A densidade de corrente é bastante reduzida para os filmes tratados em atmosfera estática devido à melhor cristalinidade e completa formação da fase perovisquita. As propriedades elétricas para baixos campos são geralmente de natureza ôhmica, o que significa que a densidade de corrente J é função linear da voltagem V . Para altos campos esses filmes exibem comportamento não linear o qual pode ser expresso pela lei de potência empírica $J = KV^\alpha$. Usualmente, as características elétricas para campos elevados não podem ser descritas por um simples processo de condução; geralmente num intervalo de voltagem podem manifestar comportamento elétrico distintos. Pode ser visualizada duas regiões distintas. A densidade de corrente aumenta linearmente com o campo elétrico na região de baixo campo sugerindo uma condução ôhmica. Para campos elevados a densidade aumenta exponencialmente, o que implica que pelo menos uma parte da condutividade resulta do mecanismo de emissão do tipo Schottky ou Poole- Frenkel. A densidade de corrente a 1,0 V diminui quando os filmes são tratados termicamente em atmosfera estática devido a diferenças no tamanho de grão, densidade e superfícies estruturais devido às diferenças na cristalinidade. A corrente de fuga para o filme tratado em ar é menor que para o filme tratado em oxigênio, o que indica que o filme cristalizado em oxigênio é menos isolante que o cristalizado em ar, o que explica o valor mais baixo obtido para polarização remanescente para esse filme. Com o aumento do campo elétrico, as vacâncias de oxigênio interagem fortemente com os domínios influenciando o processo de condução. Supõe-se que as vacâncias móveis de Bi e O localizadas próximo do contorno de grão contribuem para um aumento na densidade de corrente. As características da interface filme-eletrodo e a morfologia da superfície dos filmes de BIT são os principais fatores que determinam a densidade de corrente dos capacitores. A resistência à fadiga para os filmes de BIT em função dos ciclos de polarização foi observada para as diferentes atmosferas de tratamento térmico e concentração de lantânio. Independente da quantidade de lantânio adicionada filmes de BIT tratados em atmosfera de oxigênio apresentaram fadiga ferroelétrica. Esse resultado sugere que as cargas carregadas (O_2'') associadas a outros defeitos (V_0'' ou até mesmo dipolos complexos, tais como vacâncias de oxigênio associados com vacâncias de bismuto ($V'''_{Bi} - V_0''$) localizadas no contorno de grão na interface filme-substrato podem aumentar a condutividade do filme para elevados ciclos de polarização,

causando uma destruição no contato eletrodo-filme ferroelétrico. A densidade de armazenamento de carga dos filmes livres de fadiga foi estimada a partir das curvas $C-V$, usando a relação $Q_c = \varepsilon_0 \varepsilon_r E$, onde ε_0 é a permissividade do vácuo, ε_r é a permissividade relativa e E é o campo aplicado. A maior capacidade de armazenamento de carga observada para o filme dopado com 0,75 mol em La indica que essa composição é a mais apropriada para desenvolvimento de memórias DRAMS com 256 Mb. Quanto maior esta constante, maior a quantidade de elétrons que podem ser arquivados na memória. Esse parâmetro mede quanto o material permite o deslocamento da carga elétrica através de sua superfície para outras camadas internas dos componentes.

As micrografias obtidas por microscopia de transmissão dos filmes de $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0, 75$), calcinados a 700°C por 2 horas em atmosferas de ar (estática) e de oxigênio bem como a análise por difração de elétrons evidenciam policristalinidade dos grãos no plano do filme para ambas as atmosferas. Os grãos possuem forma regular e o tamanho estimado de 100 e 50 nm respectivamente como observado por MFA. Poros com tamanho menor que 10 nm estão presentes dentro dos grãos e ao longo do contorno de grão. Observa-se também que o filme tratado em atmosfera de oxigênio apresenta cristalitos pequenos e menor cristalinidade que o filme tratado em atmosfera estática, em virtude de a análise por difração de elétrons apresentar uma distribuição mais desordenada dos planos cristalográficos.

Visando conhecer o efeito do lantânio na obtenção de materiais com boas características morfológicas, realizou-se um estudo sistemático de preparação de filmes finos de BIT e BLT, depositados em substratos de silício recoberto com platina. Fez-se um estudo utilizando-se solução com $\text{pH} = 10$ para deposição dos filmes. Prepararam-se filmes a 700°C por 2 horas utilizando tratamento térmico em forno convencional e o método “spin-coating” para deposição. O controle dessa etapa é muito importante, porque a mudança volumétrica envolvida para diferentes temperaturas pode conduzir à formação de defeitos superficiais do tipo trincas e bolhas após tratamento térmico. Manteve-se constante a velocidade de rotação do substrato da solução em 5000 rpm. Fixou-se a viscosidade da solução em 20 cPs ($1,20 \text{ g/cm}^3$), a concentração iônica em $0,1 \text{ mol. L}^{-1}$. Os filmes foram tratados termicamente com taxa de aquecimento lenta de 3°C/min até a temperatura de decomposição térmica dos orgânicos (400°C) para evitar a formação de trincas e taxa de 5°C/min entre 600 e 700°C . Dados de difração de raios-X obtidos para os filmes de BIT tratados termicamente com diferentes quantidades de lantânio revelam somente picos relacionados às fases cristalinas

BIT e BLT, sugerindo que a substituição do Bi pelo La não conduz à formação de fases secundárias. A transformação dos picos (0100) e (200), em dois dubletes indicam mudança de estrutura cristalina de ortorrômbica para tetragonal. Além da fase BIT, um pico de alta intensidade pertencente ao substrato de platina recoberto com silício (111) em $2\theta = 40^\circ$ foi identificado. Comparando as intensidades dos picos de BIT com dados da literatura, observa-se que a adição de lantânio ($x = 0,75$) resulta em orientação preferencial em $2\theta = 16^\circ$ devido à mudança de sistema cristalino ortorrômbico-tetragonal. As micrografias dos filmes de BIT puro e dopados com lantânio mostram morfologias na forma de placas para os filmes de BIT e BLT ($x = 0,25$). O tamanho médio de grão aumenta até a fração de lantânio igual a ($x = 0,5$). Após esse limite, uma larga diminuição no tamanho de grão é observada, indicando a forte dependência da fração de lantânio nas propriedades morfológicas dos filmes, resultante da diminuição da quantidade de bismuto do sistema. Também se observa que a adição de lantânio aumenta a constante dielétrica e diminui a perda dielétrica, indicando que o elemento lantânio tem um papel crucial nas propriedades elétricas de filmes finos de BIT, obtidos pelo método dos precursores poliméricos. A dopagem com lantânio mesmo em baixas concentrações tem uma forte influencia nas propriedades dielétricas do sistema BIT. A diferença na magnitude pode ser atribuída à mudança no tamanho de grão causado pela modificação estrutural quando da adição de lantânio. O menor tamanho de grão conduz a um aumento na constante dielétrica e diminuição da perda dielétrica, resultado esse que pode ser explicado pela redução da tensão residual e do volume da célula unitária do filme durante resfriamento devido à mudança de estrutura cristalina quando da dopagem com lantânio ($x = 0,75$). As medidas ferroelétricas destes filmes mostram curvas bem saturadas com uma polarização remanescente que varia de 15 a 22 $\mu\text{C}/\text{cm}^2$ e voltagem de operação de 1,35 a 3,36 V. A saturação dessas curvas em baixas frequências indica que as perdas são mínimas, sugerindo um filme altamente resistivo. Pode ser observado que a adição de lantânio até a fração de $x = 0,75$ conduz a orientação preferencial que resulta numa menor voltagem de operação do filme ferroelétrico. Verifica-se que a polarização remanescente é muito maior que aquela esperada para filmes orientados no eixo c do BIT e pode ser atribuída à presença de componentes de polarização no eixo a conforme visto por DRX. A densidade de corrente dos filmes a 1,0 V diminui com o aumento da concentração de lantânio devido à redução da rugosidade superficial com o aumento da concentração de lantânio, redução das microtrincas causadas pela tensão residual. A resistência à fadiga para os filmes de BIT em função dos ciclos de polarização revela elevada resistência à fadiga até 10^{10} ciclos para filmes de BIT dopados com lantânio ($x = 0,50$ e $0,75$). A substituição do La por Bi pode mudar o meio

químico das camadas perovisquitais e resolver o problema de fadiga dos filmes puros de BIT, pois reduz vacâncias de oxigênio. Entretanto, não fica claro onde o La muda o ambiente químico das camadas perovisquita. É provável que o lantânio substitua íons bismuto próximos às camadas octaédricas do TiO_6 reduzindo a quantidade de vacâncias de oxigênio presente na estrutura. Outra justificativa é o papel de compensação de cargas das camadas de $(\text{Bi}_2\text{O}_2)^2$. As principais informações obtidas estão nos artigos que constam nos anexos N e O (SIMÕES, A. Z., GONZÁLEZ, A.H.M., RICCARDI, C.S., SOUZA, E.C.F., FILHO, F.M., ZAGHETE, M. A., LONGO, E., VARELA, J.A., *Ferroelectric and Dielectric Properties of Lanthanum Modified Bismuth Titanate Thin Films Obtained by the Polymeric Precursor Method*. **Journal Of Electroceramics**. , v.13, p.65 - 70, 2004) e (SIMÕES, A. Z., RIES, A, MOURA, F., RICCARDI, C. S., VARELA, J. A., *Influence of the solution pH on the morphological, structural and electrical properties of $\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{12}$ thin films obtained by the polymeric precursor method*. **Materials Letters** (General ed.), v.59, p.2759 - 2764, 2005).

Devido à estrutura anisotrópica do titanato de bismuto com parâmetros de rede iguais: $a = 0,545 \text{ nm}$, $b = 0,541 \text{ nm}$ e $c = 3,283 \text{ nm}$, filmes finos de $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ podem crescer perpendicularmente ao plano do filme, com orientação na direção do eixo c , quando depositados em substrato de silício recoberto com platina. Porém, filmes de camada de bismuto orientados no eixo c têm componente de polarização remanescente e constante dielétrica menor que ao longo do eixo a . Dessa forma, o crescimento de filmes orientados na direção do eixo a é um pouco complicado e a alternativa para melhorar as propriedades ferroelétricas e dielétricas do material é a deposição de eletrodos condutores de LaNiO_3 , $\text{La}_{0,5}\text{Sr}_{0,5}\text{CoO}_3$ e RuO_2 .

Foram depositados eletrodos óxidos de LaNiO_3 , $\text{La}_{0,5}\text{Sr}_{0,5}\text{CoO}_3$ e RuO_2 a partir de soluções de precursores poliméricos, com viscosidade controlada, em substrato de SiO_2/Si tratando-se os filmes no forno de microondas. Os filmes foram pré-tratados a 400°C , por 2 horas, para eliminação da matéria orgânica e cristalizados a 700°C por 10 minutos em forno de microondas. Observam-se picos bem estreitos indicando a alta cristalinidade devido à utilização da energia por microondas. A utilização do microondas se mostra um efetivo método para reduzir a resistividade e evitar reações interfaciais que são prejudiciais para propriedades desejadas, além de controlar a orientação cristalográfica dos filmes. O forno de microondas é de baixo custo de aquisição, e de baixo consumo de manutenção. A camada passivadora de óxido de silício deve ser utilizada para evitar a difusão dos eletrodos no silício,

o que pode afetar o contato com o filme ferroelétrico. Posteriormente, depositaram-se filmes da fase ferroelétrica desejada (lantânio modificado com titanato de bismuto) sobre os eletrodos óxidos. Os filmes depositados sobre o RuO_2 e LaNiO_3 apresentam grãos arredondados, enquanto os depositados em substratos de LSCO grãos alongados na forma de placas. A rugosidade superficial é bem maior nos filmes depositados em LSCO, pois o crescimento em placas aumenta a distância da base ao topo do filme elevando, portanto, a rugosidade. Observa-se que, independente do eletrodo utilizado, os grãos estão uniformemente distribuídos, indicando que o forno de microondas é apropriado para cristalização de filmes obtendo-se boas características morfológicas. As curvas de histerese, para o titanato de bismuto modificado com lantânio, indicam que o processo de polarização pode ser facilmente obtido independente do eletrodo utilizado. As curvas de histereses para os filmes depositados em LaNiO_3 e RuO_2 mostram uma pequena diferença no campo coercitivo em direção do lado positivo, que é definido como “imprint”. A mudança de voltagem pode causar uma falha no capacitor devido à perda de polarização em um dos estados remanescentes. Conseqüentemente, um aumento no campo coercitivo, em uma direção, pode ocorrer causando uma falha na memória. Esses resultados são consistentes com as medidas $C-V$ e podem ser causados pela presença de vacâncias de bismuto e oxigênio, localizadas na interface filme-substrato. Os íons (O_2^- e O^-) localizados no contorno de grão e na interface filme-eletrodo podem promover um desvio na estequiometria do material. Esses íons associados a outros defeitos ($V_0^{\bullet\bullet}$ e $V_0^\bullet$) ou até mesmo a defeitos de dipolos complexos, tais como vacâncias de oxigênio associadas a vacâncias de bismuto ($V_{\text{Bi}}''' - V_0^{\bullet\bullet}$) localizadas próximo ao contorno de grão, alteram a simetria da curva de histerese. Para os filmes depositados em eletrodo de LSCO observam-se curvas de histerese mais simétricas, indicando que esse material pode atingir o equilíbrio de defeitos de forma mais efetiva, como as vacâncias de oxigênio pela mudança do oxigênio não estequiométrico, gerado durante tratamento térmico impedindo sua migração para a interface filme-eletrodo. O elevado valor de polarização remanescente e a baixa voltagem de operação permitem dizer que esses filmes são apropriados para memórias FeRAMs. Uma vez que eletrodos, como RuO_2 , LSCO, LaNiO_3 , resultam em filmes livres de fadiga, supõe-se que, se as vacâncias de oxigênio se acumulam na interface filme-eletrodo, estas são consumidas pela mudança de oxigênio não estequiométrico inibindo, portanto, a presença desses defeitos na interface. Dentre os eletrodos estudados, o LSCO se mostrou o mais promissor no sentido de evitar o acúmulo de vacâncias de oxigênio, na interface filme-eletrodo provavelmente porque possui uma alta afinidade com o oxigênio, sendo um dos principais critérios na escolha de um material para

uso como óxido condutor. Os resultados de fadiga ferroelétrica, em função do número de ciclos de polarização, foram examinados para os filmes de titanato de bismuto modificado com lantânio. Independente do eletrodo utilizado, observou-se excelente resistência à fadiga até 10^{10} ciclos. Esses resultados indicam que a fabricação de eletrodos condutores pelo método dos precursores poliméricos, embora não tenha permitido a obtenção de filmes orientados, possibilitou obter filmes livres de fadiga ferroelétrica, o que, do ponto de vista de aplicação em circuitos integrados, já é bastante interessante. As principais informações obtidas estão no artigo que consta no anexo P (SIMÕES, A. Z., RIES, A., FILHO, F.M., RICCARDI, C.S., VARELA, J.A., LONGO, E., Fatigue-free behavior of $\text{Bi}_{3,25}\text{La}_{0,75}\text{Ti}_3\text{O}_{12}$ thin films grown on several bottom electrodes by the polymeric precursor method. *Applied Physics Letters*. v.85, p.5962 - 5964, 2004).

Outro fator que limita a vida do dispositivo de memória ferroelétrica é o fenômeno de retenção, que na verdade é a medida da mudança de tempo em função do estado de polarização do filme ferroelétrico. As propriedades de retenção desses filmes foram medidas em temperatura ambiente empregando-se a seqüência de pulsos relatada a seguir: O pulso triangular de - 5 V foi aplicado para escrever um estado lógico conhecido, depois de um determinado tempo, o estado lógico foi sequencialmente lido pela aplicação de dois pulsos triangulares de + 5 V e - 5 V. A largura para todos os pulsos triangulares foi de 1,0 ms. O capacitor polarizado com um pulso de voltagem negativa corresponde ao dígito binário “1”. De forma semelhante, o estado “0” foi escrito polarizando o capacitor com um pulso positivo, seguido de leitura depois de um intervalo de tempo com um pulso negativo. As curvas de retenção para longos períodos para os filmes de BIT puro e dopados com lantânio permitem inferir que, quando se aumenta a concentração de lantânio, a dependência do tempo de retenção com a polarização é bastante satisfatória. Após um tempo de retenção de 1×10^4 s, a perda de polarização é de somente 6% para um tempo de $t = 1$ s e campo elétrico de 150 kV/cm. Campos de despolarização gerados por redistribuição de cargas espaciais, defeito e dipolos complexos podem ser a razão para o decaimento da polarização após o processo de escrita. Para os primeiros 10 s, campos de despolarização podem ser a principal causa para a perda de polarização. O campo de despolarização aumenta com o aumento da polarização, sendo dependente do tempo. A perda de retenção para longos períodos pode ser atribuída a efeitos de redistribuição de cargas. Esse efeito conduz a uma pequena redução na polarização pela compensação de cargas de polarização quando a redistribuição de defeitos de cargas é governada pela polarização. Devido à relaxação dielétrica, a carga retida é geralmente menor que a carga medida na curva de histerese, e a diferença entre elas deve ser a menor possível

para manter uma diferença significativa entre os dígitos “1” e “0”. O fenômeno de retenção é similar à fadiga, pois depende da espessura do filme, natureza do eletrodo, morfologia dos grãos, temperatura e detalhes experimentais. O entendimento e melhora da degradação, em filmes finos ferroelétricos, terá um impacto essencial no sucesso destes filmes para aplicações em dispositivos. Outra propriedade avaliada nesse filmes foi a estabilidade dos domínios ferroelétricos, as propriedades piezoelétricas e os defeitos gerados durante a formação da fase cristalina BIT e BLT. Essa análise visa a utilização em memórias DRAM/FeRAMs, “smart cards” e circuitos integrados. Para tal finalidade utilizou-se um microscópio de força atômica acoplado a um modo piezoelétrico, que permite a visualização dos domínios, em escala nanométrica. Essas medidas permitiram diferenciar se os domínios estão dentro ou fora do plano, dependendo do contraste observado na imagem de MFP e de como contribuem para a polarização total do sistema. Investigou-se o efeito causado pelo lantânio na disposição dos domínios ferroelétricos do sistema $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ puro (BIT), depositando filmes em substratos de silício recoberto com platina, seguido de tratamento térmico em atmosfera estática. Foram medidas imagens de topografia e de resposta piezoelétrica dos filmes de BIT e BLT, com voltagem dc aplicada de polaridade negativa igual a 12 V. Nesse caso, aplicou-se nas amostras somente uma voltagem de polaridade negativa, com a finalidade de se verificar quais eram piezoelectricamente ativas. Observa-se pelas micrografias, resposta no plano, duas regiões com diferentes contrastes: uma mais clara que corresponde ao filme como foi crescido e outra quadrática mais escura que foi produzida aplicando-se uma voltagem dc negativa, resultando em vetor polarização direcionado para fora do plano do filme. Com aumento do campo elétrico, alguns domínios são favorecidos, em relação aos outros com respeito à direção de crescimento. Esse processo continua até que os domínios menos favoráveis revertam à direção polar próximo à direção do campo elétrico. Finalmente, após remoção do campo elétrico os contornos de grãos podem nuclear novos domínios reversos. Na imagem fora do plano, os contrastes de cor representam polarizações, em direção ao eletrodo inferior e à ponta do MFA, sendo que a região mais escura tem o vetor polarização orientado na direção do “tip”. Em geral, a maior parte do filme se encontra num estado simples de polarização com cristalitos não revertidos (regiões claras) e que se encontram preferencialmente dentro das regiões quadráticas escuras exibindo um pequeno sinal piezoelétrico. Esse resultado é bastante comum para materiais ferroelétricos da família de camada de bismuto, em que se observa uma grande polarização ao longo do eixo, a , enquanto uma pequena polarização é observada ao longo do eixo c , refletindo-se em regiões com diferentes contrastes. Quando uma voltagem inferior a 12 V foi aplicada na amostra um sinal de mesma característica, mas

de menor intensidade, foi observado indicando que o filme não estava completamente polarizado. Pela análise dos resultados supõe-se que as regiões com pouco contraste estão orientadas no eixo c e são, portanto, não reversíveis. Essas regiões apresentam uma fraca resposta piezoelétrica, causada por um desvio do vetor polarização, a partir da direção normal ao plano do filme. Considerando que o sinal piezoelétrico muda de sentido, sob aplicação de uma voltagem positiva no “tip”, observa-se que as regiões claras correspondem a domínios negativos (polarização fora do plano do filme), enquanto que as regiões escuras são representadas por domínios positivos (polarização no plano do filme). Outra causa pode ser a baixa frequência ac usada para determinar a reversão da polarização em nossos experimentos, levando a imagens com regiões de baixos contrastes, devido à presença de grãos complexos polarizados. A partir de uma análise cuidadosa dos resultados supõe-se que as propriedades piezoelétricas do titanato de bismuto são fortemente afetadas pela adição de lantânio no sistema. Observa-se que a piezoeletricidade diminui significativamente, a partir da concentração de 0,50 em lantânio, resultando em nenhuma resposta para concentração de 0,75. A redução da resposta piezoelétrica, com o aumento na concentração de lantânio, deve-se provavelmente à redução da polarização principalmente ao longo do eixo a , que contribui significativamente para as propriedades ferroelétricas do titanato de bismuto. Nas imagens no plano observa-se que os grãos mais claros têm o vetor polarização orientado na direção positiva do eixo y , enquanto os grãos escuros na direção oposta do mesmo eixo. Os grãos que apresentam contraste intermediário possuem resposta piezoelétrica nula, sendo, portanto não reversíveis. Supõe-se que esses grãos que não mudam de contraste têm os domínios aprisionados. Paralelamente, a análise de disposição dos domínios, estudou-se como o lantânio atua sobre os defeitos cristalinos, que surgem durante a cristalização da fase ferroelétrica. Esses defeitos interferem nas propriedades piezoelétricas e ferroelétricas do sistema, indicando que estas dependem não somente de uma morfologia bem definida, mas também da qualidade da interface filme-substrato. Embora o lantânio leve a uma redução das propriedades piezoelétricas, auxilia a estabilizar as paredes de domínios carregadas fortemente, que interagem com as vacâncias de oxigênio, inibindo a fadiga ferroelétrica e a perda de retenção de dados nos filmes. Esses resultados podem ser comprovados quando se analisam as curvas de retenção da polarização, em função do tempo de retenção. Portanto, o lantânio tem como principal função suprimir a volatilização do óxido de bismuto reduzindo tensões internas na rede, além de reduzir os defeitos presentes no plano c do BIT, como resultado do “mismatch” entre a camada de Bi_2O_3 e a camada perovskita. A substituição do bismuto pelo lantânio reduz a energia livre do sistema, prevalecendo às interações dipolo-

dipolo e a energia eletrostática, o que afeta a estrutura e o tamanho dos domínios. Ocorre nesse sentido um grande movimento dos domínios de 90° , devido à rotação dos octaedros de oxigênio com o eixo vertical, levando a tensões na rede e alguns espaços propícios para acúmulo de cargas. No sistema puro, devido à alta volatilidade do bismuto, grandes deformações na rede resultam do acúmulo de defeitos, que provavelmente aprisionam os domínios de 90° mais que no sistema dopado. Esses defeitos reduzem fortemente a mobilidade dos domínios, com conseqüentes interações com os deslocamentos, o que leva à fadiga ferroelétrica e ao fenômeno de retenção. Supõe-se, portanto, que paredes de domínios de 90° estão presentes nos filmes e sua reversão necessita de tempos de relaxação maiores devido à presença de tensões na rede cristalina. No sistema puro não se observa nenhuma tensão para as paredes de domínios de 180° , indicando que as tensões externas induzidas pela relaxação dos domínios de 90° aprisionam os domínios de 180° , durante o processo de reversão. Nos filmes dopados nenhuma tensão é produzida no movimento dos domínios de 90° , devido à redução das tensões causadas pelo movimento dos domínios opostos. Portanto, o aprisionamento dos domínios de 180° pelas tensões é reduzido. Porém, devido à complexidade da distribuição dos domínios nesse sistema, um estudo mais detalhado de dinâmica de domínios deve ser realizado visando à compreensão de tal comportamento e, também, a possível distinção entre as possíveis orientações dos domínios presentes nos filmes. O fraco sinal causado pela adição de lantânio sugere que um forte campo de despolarização aparece na área polarizada abaixo do “tip”. Esse campo de despolarização deve suprimir a reversão da polarização espontânea durante o “poling”. Além disso, deve acelerar a reversão da polarização com a remoção do campo externo, sendo evidente pela redução do d_{33} , quando a voltagem de “poling” reduz de máximo a zero. Os resultados dessa pesquisa estão elucidados no artigo que consta no anexo Q (SIMÕES, A. Z., RAMIREZ, M. A., PARUCCI, N. A., RICCARDI, C. S., LONGO, E., VARELA, J.A., Retention characteristics in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin Films Prepared by the polymeric precursor method. *Applied Physics Letters*. v.86, 112909-112911, 2005).

Adicionalmente, outras classes de materiais da família de camadas de bismuto ($\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ – SBTi, $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ – CBT144 e $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO)) que possuem temperaturas de transição de fase elevadas foram estudadas. Essas classes, mostram-se bastante promissoras na construção de memórias ferroelétricas. Filmes de $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ foram depositados em substratos de platina, realizando a caracterização estrutural, morfológica e também as propriedades ferroelétricas desenvolvidas por esses filmes. Observa-se que o filme de CBTi144 apresenta-se monofásico e livre de orientação preferencial. Os picos de difração

da família (00 l) apresentam intensidade superior, quando comparados com os outros picos de difração presentes no sistema. A morfologia obtida para os filme de CBTi144 apresenta-se livre de trincas e com baixa porosidade. O valor da rugosidade encontrado foi de 3,2 nm, enquanto o tamanho de grão que apresenta morfologia arredondada é da ordem de 46 nm. O controle da rugosidade é extremamente importante já que as propriedades ferroelétricas não dependem apenas de uma excelente microestrutura, mas também da qualidade da interface filme-eletrodo. A medida de densidade de corrente logarítmica ($\log J$) em função da voltagem (V) revela duas regiões distintas: na primeira a densidade de corrente aumenta com o campo elétrico externo na região de baixas voltagens, sugerindo uma condução ôhmica. Esse comportamento ôhmico ocorre em filmes isolantes, indicando que o filme é quase neutro, ou seja, a corrente gerada no filme excede a corrente devido ao mecanismo de condução devido às cargas livres injetadas a partir do eletrodo. Esta corrente deve-se ao mecanismo de condução para baixo campo elétrico, pois a excitação térmica dos elétrons aprisionados a partir de um sítio para outro domina o transporte nos filmes. Para altos campos, a densidade de corrente aumenta exponencialmente, o que implica que uma parte da condutividade resulta dos mecanismos de condução tipo Schottky ou Poole-Frenkel. A densidade de corrente a 1,0 V é igual a 10^{-7} A/cm². A baixa densidade de corrente observada nesses filmes pode ser um efeito do pequeno tamanho de grão, o que implica em vários contornos de grão, de forma que a corrente possa fluir agindo como barreira de potencial e também devido à pequena rugosidade superficial, como observado pelas imagens de MFA. Observa-se uma curva simétrica para ambas as polaridades indicando que as propriedades do “bulk” controlam o sistema uma vez que foram utilizados eletrodos superiores e inferiores de materiais diferentes e também condições de processamento distintas. Observou-se ferroeletricidade no filme fino de titanato de bismuto e cálcio com polarização remanescente igual a 12 μ C/cm² e campo coercitivo igual a 77 kV/cm. Nota-se a ausência de “imprint”, o que causa um deslocamento da curva ao longo do eixo do campo elétrico, indicando que os filmes apresentam uma pequena concentração de cargas espaciais na interface filme-eletrodo. Estes resultados são consistentes com as medidas de C-V, em que se observou simetria ao redor do zero do eixo, indicado que os filmes contem poucos íons móveis ou acúmulo de cargas na interface filme eletrodo. A resistência à fadiga do filme de CBTi144 foi testada a 1 MHz em função dos ciclos de polarização aplicando 8,6 μ s pulsos bipolares com amplitude máxima de ± 9 V. Excelente resistência à fadiga foi observada até 1×10^{10} ciclos, sugerindo que o CBTi144 é promissor para aplicações em memórias. A ausência de fadiga ferroelétrica se deve à redução das vacâncias de oxigênio, que estabiliza as cargas aprisionadas na parede

do domínio, dificultando sua reversão. Estas também podem se acumular próximo aos eletrodos aumentando a injeção do elétron. Isso ocorre devido à metalicidade da ligação do cálcio nos blocos de Ca–Ti–O ser muito estável, conduzindo a uma menor concentração de vacâncias de oxigênio e, portanto, levando a um não aprisionamento das paredes dos domínios. As medidas de retenção desses filmes mostram pouca variação da polarização em função do tempo de retenção, sendo que após 1×10^4 s, a perda de polarização medida é de aproximadamente 2,0 % do valor inicial. A causa para o decaimento da polarização depois do processo de escrita pode ser causada por campos de despolarização gerados pela redistribuição das cargas espaciais, defeitos e dipolos. O campo de despolarização aumenta com o acréscimo da polarização da retenção, sendo dependente do tempo. A perda de retenção por longos períodos pode ser atribuída aos efeitos de redistribuição e defeitos de carga. A natureza dos defeitos envolvidos na polarização é provavelmente neutralizada inserindo-se vacâncias no lugar do oxigênio. Isso compensa a divergência de valências introduzidas substituindo Bi^{3+} por Ca^{2+} . Estudos de microscopia de força piezoelétrica para os filmes de CBTi144 depositados em atmosfera estática foram realizados. Imagens fora do plano (OP) e no plano (IP) dos filmes como crescidos, depois de aplicar-se uma voltagem de -12V, em uma área de $2 \mu\text{m} \times 2 \mu\text{m}$, e depois um bias oposto de + 12V na área central $1 \mu\text{m} \times 1 \mu\text{m}$ foram realizadas. As regiões claras nas imagens de MFP fora do plano correspondem a domínios com vetor polarização orientados em direção ao eletrodo inferior, sendo denominados com polarização para baixo enquanto as regiões que correspondem aos domínios orientados para cima se denominam polarização para cima. Alguns grãos que não mudam de contraste estão associados a polarização nula fora do plano, enquanto que outros exibem contraste associado a componente de polarização em direção ao eletrodo inferior. Em contrapartida, nas imagens de MFP no plano, as mudanças de contraste são associadas às mudanças na componente de polarização no plano. Nesse caso, o contraste mais claro indica polarização na direção positiva do eixo y, enquanto o contraste mais escuro é dado pelos componentes de polarização direcionados à parte negativa do eixo y. O filme de CBTi144 possui uma curva de histerese bem acentuada com máximo valor de d_{33} , ~ 65 pm/V. O aumento da polarização pode ser causado pela orientação do eixo *a/b* do filme ferroelétrico devido à orientação preferencial do substrato de Pt. A curva de histerese mostra um deslocamento na direção vertical, que pode estar diretamente relacionada ao efeito de clamping com o substrato e a existência de um gap ultrafino de ar entre o tip e a amostra, que pode reduzir a voltagem atual no filme. Detalhes deste artigo podem ser encontrados no artigo que consta no anexo R (SIMÕES, A.Z. RAMIREZ, M.A., PERUCCI, N.A., ZAGHETE,

M.A., VARELA, J.A., LONGO, E., Electromechanical properties of calcium bismuth titanate films: A Potential candidate for lead-free thin-film piezoelectrics, **Applied Physics Letters**, v.88, p.916-1 - 916-3, 2006).

Foi avaliada a influência da energia das microondas para controlar a orientação cristalográfica, reduzir a resistividade e também evitar reações interfaciais que são prejudiciais para as propriedades desejadas. O forno de microondas é de baixo custo para aquisição e manutenção e consome pouca energia. Os filmes foram pré-tratados a 400°C, por 2 horas, para eliminação da matéria orgânica e cristalizados a 700°C por 10 minutos. A utilização da energia por microondas conduz à elevada cristalinidade devido à presença de picos bem estreitos. Observam-se somente picos relacionados à fase policristalina, sugerindo que a energia de microondas não conduz à formação de fases deletérias. A ausência de orientação preferencial pode ser atribuída aos defeitos gerados na primeira camada do filme. Dessa forma, as demais camadas são depositadas sobre uma superfície policristalina, que não se assemelha a um monocristal, gerando então um filme policristalino. Portanto, se o objetivo é obter um filme orientado utilizando método químico deve-se observar se o filme é orientado desde o início, para que se possa depositar as camadas seguintes mantendo alto grau de orientação, além de utilizar materiais com parâmetro de rede semelhantes ao do material ferroelétrico em estudo. Dessa forma, a fabricação de filmes de camadas de bismuto, orientados na direção do eixo *a* que permita obter propriedades elétricas superiores as obtidas pela orientação na direção do eixo *c* por métodos químicos de deposição exige que alguns parâmetros sejam controlados. Entre esses se destacam a diferença de parâmetro de rede entre o filme e o substrato e também o coeficiente de expansão térmica que deve ser o menor possível em relação ao filme visando satisfazer as mínimas condições para obtenção de estruturas altamente orientadas. Filmes ferroelétricos de SBTi foram depositados sobre substrato de Pt/Ti/SiO₂/Si e cristalizados a 700°C, por 10 minutos, em forno de microondas. Observa-se que a morfologia dos filmes cristalizados em forno de microondas consiste de grãos grandes circundados por grãos pequenos arredondados, além de elevada porosidade. Isso ocorre porque a elevada taxa de aquecimento faz com que o material passe de um regime de baixa temperatura, em que a difusão superficial é mais rápida e uma microestrutura com grãos pequenos é evidente, para um regime de alta temperatura onde a difusão da rede via contorno de grão predomina sobre a difusão superficial. Portanto, o tempo disponível para o crescimento do grão é substancialmente reduzido neste processo levando a uma microestrutura global constituída de grãos pequenos. Uma vez que o susceptor foi colocado

abaixo do substrato, o filme se cristaliza por um fluxo de calor vindo da interface filme-substrato, gerando tensões causadas por diferenças de coeficiente de expansão térmica entre o filme e o substrato. A energia das microondas provavelmente exerce um papel importante, além do simples aquecimento do susceptor, mas o seu papel ainda não é totalmente compreendido. Supõe-se que os choques térmicos causados pelo rápido aquecimento do SiC favoreçam o acúmulo de cargas estáticas na interface filme-substrato. Como consequência, a temperatura real no susceptor pode ser maior, que aliado ao efeito da energia das microondas pode causar degradação da interface filme-eletrodo e, portanto, levar à perda das propriedades ferroelétricas e piezoeletricas. Uma alternativa para minimizar o efeito drástico dos choques térmicos é colocar uma lâmina cerâmica entre o susceptor e o substrato para prevenir surtos elétricos. Como conclusão, o tempo exigido para obtenção de filmes bem cristalinos é bastante reduzido, quando da utilização de energia de microondas. Isto é vantajoso, pois inibe reações indesejáveis entre o filme e o substrato evitando perdas de estequiometria do filme. A constante dielétrica e o fator de dissipação para os filmes de SBTi indicam boas propriedades dielétricas, com constante dielétrica de 185, com perda de $(\tan \delta) = 0,025$ a 1 MHz para o filme de SBTi. A constante dielétrica mostra pouca dispersão com a frequência indicando baixa quantidade de defeitos na interface filme-substrato. Esses resultados mostram que o tratamento térmico em forno de microondas suprime a formação de uma camada de pequena constante dielétrica na interface filme-eletrodo, que causa a pequena constante dielétrica relacionada a materiais ferroelétricos. A energia de microondas pode danificar a interface devido às descargas elétricas entre o susceptor de SiC e o termopar causado pelo campo elétrico elevado da energia das microondas. A dependência entre a capacitância e a voltagem revela uma relação não linear indicando propriedades ferroelétricas, resultado da reversão dos domínios ferroelétricos. Uma dispersão nos valores de capacitância foi observada para os filmes cristalizados em forno de microondas. Isso pode ter sido originado pelos choques térmicos causados pelo rápido aquecimento do susceptor de SiC que favorece o acúmulo de cargas estáticas na interface filme-substrato. O estreitamento nas curvas $C-V$ indica que o processo de reversão dos domínios é mais rápido e a saturação ocorre às custas de menor energia para o alinhamento dos domínios ferroelétricos. As curvas de histerese ilustram um campo coercitivo elevado, indicando que a energia das microondas afeta as características de reversão dos domínios pela presença de defeitos localizados na interface filme-substrato. A temperatura real no susceptor é de alguns graus superiores, a qual, aliada ao efeito da energia das micro-ondas, pode causar degradação da interface filme-eletrodo e perda das propriedades ferroelétricas. Nenhuma resistência à fadiga foi observada para os filmes cristalizados em

forno de microondas, indicando aumento da corrente local que danifica a interface filme-eletrodo e reduz a polarização remanescente. O aparecimento de defeitos, tais como vacâncias de oxigênio, nessas regiões pode resultar no aparecimento de cargas espaciais na vizinhança o que dificulta a mobilidade dos domínios. Os resultados deste artigo estão na referência e consta no anexo S (**SIMÕES, A.Z., RAMIREZ, M.A., RICCARDI, C.S., VARELA, J.A., LONGO, E.,** Effect of microwave oven on structural, morphological and electrical properties of $\text{SrBiTi}_4\text{O}_{15}$ thin films grown on Pt/Ti/SiO₂/Si substrates by a soft chemical method, **Materials Characterization.** v.59, p.675 - 680, 2008).

Filmes de $\text{CaBi}_2\text{Nb}_2\text{O}_9$ foram depositados em substratos de platina, realizando a caracterização estrutural, morfológica e também as propriedades ferroelétricas desenvolvidas por esses filmes. Observa-se que o filme de CBNO apresenta-se monofásico com estrutura cristalina ortorrômbica e orientação aleatória com pico de máxima intensidade em $2\theta = 29^\circ$. A morfologia obtida para os filme de CBNO apresenta-se livre de trincas e com baixa porosidade. O valor da rugosidade encontrado foi de 16 nm, enquanto o tamanho de grão que apresenta morfologia arredondada e isotropico é da ordem de 120 nm. O controle da rugosidade é extremamente importante já que as propriedades ferroelétricas não dependem apenas de uma excelente microestrutura, mas também da qualidade da interface filme-eletrodo. A medida de densidade de corrente logarítmica ($\log J$) em função da voltagem (V) revela duas regiões distintas: Na primeira a densidade de corrente aumenta com o campo elétrico externo na região de baixas voltagens, sugerindo uma condução ôhmica. Este comportamento ôhmico ocorre em filmes isolantes, indicando que o filme é quase neutro, ou seja, a corrente gerada no filme excede a corrente devido ao mecanismo de condução devido as cargas livres injetadas a partir do eletrodo. Esta corrente deve-se ao mecanismo de condução para baixo campo elétrico, pois a excitação térmica dos elétrons aprisionados a partir de um sítio para outro domina o transporte nos filmes. Na segunda região, para altos campos, a densidade de corrente aumenta exponencialmente, o que implica que uma parte da condutividade resulta dos mecanismos de condução tipo Schottky ou Poole-Frenkel. A densidade de corrente a 1,0 V é igual a 10^{-7} A/cm^2 . Medidas de $C-V$ indicam que o processo de reversão dos domínios é mais rápido e a saturação ocorre às custas de menor energia para o alinhamento dos domínios ferroelétricos. A curva de histerese apresenta uma voltagem de 1,7 V e polarização remanescente de $4,2 \mu\text{C/cm}^2$. O baixo valor da polarização indica crescimento do filme na direção c onde as características de reversão dos domínios pela presença de defeitos localizados na interface filme-substrato são acentuadas. Resistência à fadiga foi observada até 1×10^8 ciclos de

polarização indicando baixa corrente local, o que danifica a interface filme-eletrodo e reduz a polarização remanescente. O aparecimento de defeitos, tais como vacâncias de oxigênio, nessas regiões podem resultar no aparecimento de cargas espaciais na vizinhança, o que dificulta a mobilidade dos domínios. Portanto, a polarização remanescente tende a diminuir com o aumento da polarização. Maiores detalhes desta pesquisa são encontrados no artigo que consta no anexo T (**SIMÕES, A.Z., RAMIREZ, M.A., RICCARDI, C.S., GONZÁLEZ, A. H. M., VARELA, J.A., LONGO, E., Synthesis and electrical characterization of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films deposited on Pt/Ti/SiO₂/Si substrates by polymeric precursor method, *Materials Chemistry and Physics*. v.98, p.203 - 206, 2006).**

Na continuação sobre o potencial dos filmes de $\text{CaBi}_2\text{Nb}_2\text{O}_9$ depositados por método químico, avaliou-se a dependência da temperatura nas propriedades dielétricas a 100 kHz. A temperatura de transição de fase foi de $(944 \pm 2^\circ\text{C})$. Medidas de piezoelectricidade no plano e fora do plano revelam diferentes contrastes indicando aprisionamento dos domínios em determinada direção. As regiões claras nas imagens de MFP fora do plano correspondem a domínios com vetor polarização orientados em direção ao eletrodo inferior, sendo denominados com polarização para baixo, enquanto as regiões que correspondem aos domínios orientados para cima se denominam polarização para cima. Alguns grãos que não mudam de contraste estão associados à polarização nula fora do plano, enquanto outros exibem contraste associado a componente de polarização em direção ao eletrodo inferior. Em contrapartida, nas imagens de MFP no plano, as mudanças de contraste são associadas às mudanças na componente de polarização no plano. Nesse caso, o contraste mais claro indica polarização na direção positiva do eixo y, enquanto o contraste mais escuro indica componentes de polarização direcionados à parte negativa do eixo y. O filme de CBNO possui uma curva de histerese bem acentuada com máximo valor de d_{33} , ~ 58 pm/V. O aumento da polarização pode ser causado pela melhor distribuição de planos na direção do eixo a/b do filme ferroelétrico devido à orientação preferencial do substrato de Pt. Como pode ser visto, a curva de histerese mostra um deslocamento na direção vertical que pode estar diretamente relacionada ao efeito de clamping com o substrato e à existência de um gap ultrafino de ar entre o tip e a amostra, o que pode reduzir a voltagem atual no filme. Detalhes deste artigo podem ser encontrados no anexo U (**SIMÕES, A.Z., RAMIREZ, M.A., RICCARDI, C.S., GONZÁLEZ, A. H. M., VARELA, J.A., LONGO, E., High Curie point $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films: A Potential candidate for lead-free thin films piezoelectrics, *Journal of Applied Physics* v. 100, p. 074110-074114, 2006).** A partir desses resultados fica evidente que o tipo de tratamento térmico é necessário para garantir a formação de filmes com

boa qualidade morfológica, uma estrutura mais organizada, mais densa, menos rugosa. A substituição de íons isovalentes e aceptores no sítio do bismuto afetam a densidade de defeitos e a resposta global do capacitor. Eletrodos óxidos são uma alternativa para compensação de cargas espaciais na interface, melhorando drasticamente as propriedades ferroelétricas e piezelétricas e tornando os filmes com potencial uso em memórias não voláteis.

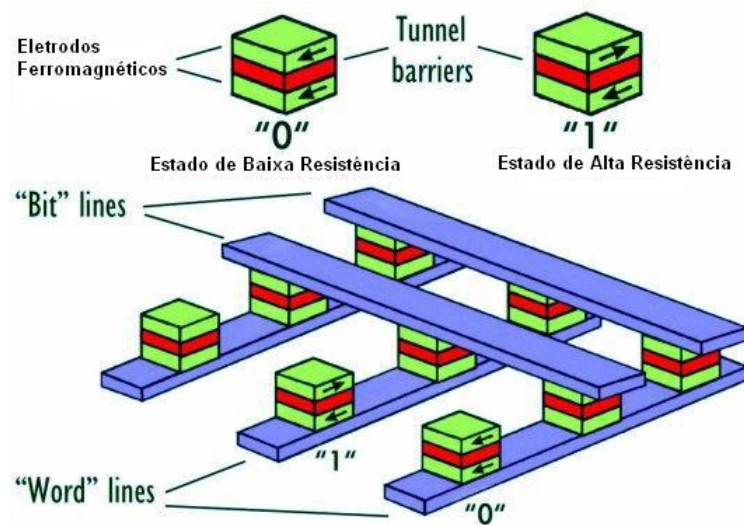
4.3 SISTEMA MULTIFERRÓICO A BASE DE FERRITA DE BISMUTO

Multiferróicos são uma classe de materiais com coexistência de parâmetros de ordem. Existe um grande interesse em multiferróicos nos quais coexistem ferroeletricidade e ordenamento magnético direcionado em grande parte pela potencial aplicação na spintrônica, cuja implementação requer a habilidade de manipular o estado magnético de um material pela aplicação de um campo elétrico. A exploração do efeito spintrônico tem permitido a criação de memórias não-voláteis (que não perdem dados na ausência de energia). A próxima geração de computadores será “instantânea” no sentido de que não necessitarão passar pelo processo de boot, no qual as informações têm que ser movidas do disco rígido para a memória. Os computadores também armazenarão dados em espaços menores e acessarão esses dados mais rapidamente, tudo isso consumindo menos energia do que os atuais. Isso, em parte, graças ao desenvolvimento de memórias de acesso aleatórias magnéticas (MRAM – Magnetoresistive Random Access Memory), que armazenarão dados utilizando o spin dos elétrons (estado magnético), o que lhes dá uma enorme vantagem sobre as memórias atuais que utilizam a carga dos elétrons.

A célula básica da MRAM é chamada de “Magnetic Tunnel Junction” (MTJ), e é formada por duas placas de filmes finos ferromagnéticos (cada uma podendo ser magnetizada em direções específicas) separadas por uma camada espaçadora ultrafina isolante. Uma das placas tem sua direção de magnetização fixa, similar a um magneto permanente, enquanto a magnetização da outra placa pode ser mudada entre duas direções opostas (placa livre). As duas diferentes direções de magnetização da placa livre são usadas para representar 0 e 1. Um circuito de memória é constituído de uma rede dessas células, e dados são escritos pela passagem de corrente através das linhas de escrita acima e abaixo da célula, criando campos magnéticos que mudam a magnetização da placa livre. (Figura 2). Para determinar o estado da placa livre, uma voltagem é aplicada na célula para que elétrons atravessem a camada

espaçadora isolante (por tunelamento), criando uma corrente de tunelamento. Uma vez que materiais ferromagnéticos produzem uma corrente de tunelamento polarizada, a resistência de tunelamento depende da direção magnética da placa livre em direção a placa fixa. A resistência é maior quando a magnetização aponta em direções opostas e é menor quando a magnetização é paralela.

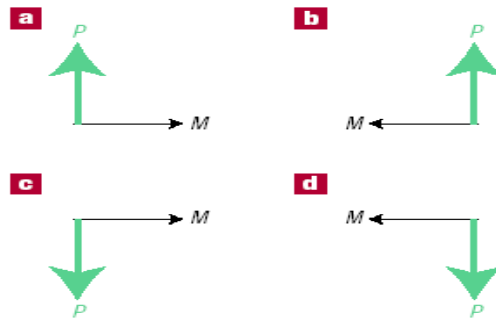
Figura 2: Ilustração esquemática de uma memória de acesso aleatório magnética (MRAM)



Fonte: (<http://www.ece.nus.edu.sg/isml/ResearchArea.htm>).

Camadas de filmes finos multiferróicos podem ser usadas como “Tunnel Junction”, permitindo que o dispositivo MRAM opere como um sistema resistivo de quatro estados, ou seja, é possível codificar informações de quatro estados através do acoplamento dos parâmetros de ordem ferromagnética e ferroelétrica e ler estas informações não-destrutivamente utilizando uma medida de resistência (Figura 3).

Figura 3: Os quatro graus de ordenamento dos multiferróicos: **a-d**, polarização elétrica (P) e a magnetização (M) podem assumir quatro estados não-colineares em um cristal multiferróico. Neste esquema com magnitudes arbitrárias, as direções estão no espaço real. Para muitos materiais os spins e as polarizações estão altamente correlacionados, então somente os pares **a** e **d** ou alternativamente **b** e **c** estão realmente acessíveis.



Fonte: (<http://www.ece.nus.edu.sg/isml/ResearchArea.htm>).

4.4 Comparação entre as memórias de acesso aleatório (Random Access Memories – RAM)

Os parâmetros técnicos mais importantes a serem considerados para aplicação de um dispositivo de memória estão listados comparativamente na Tabela 1 para os diferentes tipos de RAMs.

Tabela 1 – Parâmetros técnicos de vários tipos de memórias de acesso aleatório: Dinâmico (DRAM), Estático (SRAM) e Flash são baseados em semicondutores enquanto que Ferroelétrica (FeRAM), Fase-Carga (PCRAM) e Magnética (MRAM) são novos conceitos

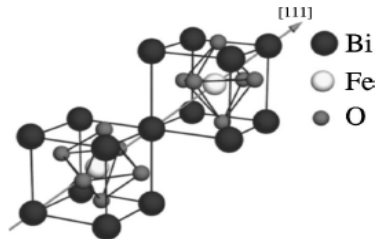
	DRAM	SRAM	FLASH	FeRAM	OUM	MRAM
Velocidade de escrita	Moderada	Rápida	Lenta	Moderado	Moderada	Rápida
Velocidade de leitura	Moderada	Rápida	Rápida	Moderado	Rápida	Rápida
Densidade	Alta	Baixa	Alta	Média	Alta	Alta
Suportabilidade de (Endurability)	Boa	Boa	Pobre	Pobre	Boa	Boa
Potencia (power)	Alta	Baixa	Baixa	Baixa	Baixa	Baixa
Restauração (refresh)	Sim	Não	Não	Não	Não	Não
Retenção	Não	Não	Sim	Parcialmente	Sim	Sim
Scalability	Ruim	Boa	Boa	Média	Boa	Boa
Write/Erase	Carga (Capacitância)	CMOS Logic	Carga (Tunelamento)	Ferroeletricidade	Transição de fase	Magnetização

Fonte: (<http://www.spintec.fr/Magnetic-Random-Access-Memories-M.html>).

Entretanto, antes que a revolução da spintrônica possa começar, será necessário um entendimento científico muito mais aprofundado das propriedades dos materiais muliferróicos. A Ferrita de Bismuto (BiFeO_3 ou apenas BFO) apresenta características raras (e potencialmente úteis) com relação ao seu comportamento multiferróico, ou seja, suas propriedades ferroelétricas e antiferromagnéticas são bem estabelecidas à temperatura ambiente. O BFO tem uma estrutura perovskita distorcida em um sistema romboédrico (parâmetros de rede: $a = 3,958 \text{ \AA}$, $\alpha = 89,30^\circ$) (Figura 4). O BFO também tem uma temperatura de transição de fase paraelétrica-ferroelétrica de aproximadamente 820°C , que é maior em relação aos outros materiais ferroelétricos, e que sugere que o BFO tem potencial para exibir um grande valor de polarização espontânea (P_s). Embora somente valores de P_s de aproximadamente ($6 \mu\text{C}/\text{cm}^2$) (131) tenham sido reportados para cerâmicas de BFO, os

primeiros estudos previram valores teóricos de polarização remanescente (P_r) de 90-100 $\mu\text{C}/\text{cm}^2$.

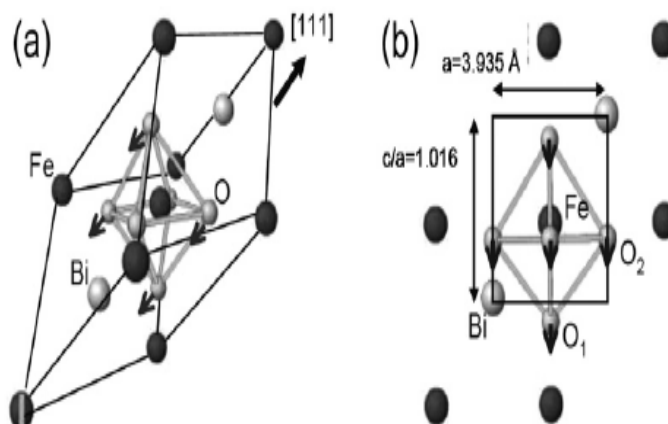
Figura 4: Vista esquemática da estrutura R3c construída a partir de duas celas unitárias perovskita cúbica. Os cátions estão deslocados na direção [111] em relação aos ânions, e o oxigênio octaédrico girando com direção alternada em torno do eixo [111] (132).



Fonte: Ederer, C.; Spaldin, N. A. (2005)

Wang et al. (133) obtiveram filmes texturizados de BFO em substrato de Si, recobertos com uma camada template de SrTiO_3 (STO) [100] por deposição de laser pulsado (PLD), utilizando o SrRuO_3 (SRO) como eletrodo condutor, que apresentavam valores de P_r de 50-60 $\mu\text{C}/\text{cm}^2$ e campo coercitivo (E_c) de 150 KV/cm, ou seja, valores de polarização com mais de uma ordem de magnitude em comparação aos sistemas cerâmicos de BFO. A origem dessa melhora está relacionada ao stress compressivo no plano imposto pelo eletrodo de SRO, que leva a uma distorção tetragonal da estrutura perovskita para os filmes, em oposição à distorção romboédrica observada no bulk (Figura 5).

Figura 5: Estrutura Cristalina do BFO: (a) Cella unitária romboédrica no bulk e (b) cela unitária tetragonal do filme.



Fonte: Wang, J. et al. (2003)

Yun et al. (134) também depositaram filmes tetragonais de BFO com uma polarização ferroelétrica gigante superior a $150 \mu\text{C}/\text{cm}^2$ e campo coercitivo de até $250 \text{ KV}/\text{cm}$ em substratos de $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ por PLD. Apesar das excelentes propriedades, dois sérios problemas são comumente encontrados para imediata aplicação desse material em memórias multiferróicas: alta densidade de corrente, resultado da flutuação de valência dos íons Fe (Fe^{3+} para Fe^{2+}) com conseqüente criação de vacâncias de oxigênios e da existência de fases secundárias (135-138) e elevado campo coercitivo causado pelo grande número de contornos de domínios ferroeletromagnéticos, que restringem a reversão da polarização.

Visando conhecer o efeito da temperatura na obtenção de filmes finos com boas características morfológicas, realizou-se um estudo sistemático de preparação de filmes finos de BFO, que foram depositados em substratos de silício recoberto com platina. Inicialmente, fez-se um estudo utilizando-se solução com $\text{pH} = 8-9$ para deposição dos filmes. Primeiramente, preparou-se filmes em diferentes temperaturas (500 a 700°C) utilizando tratamento térmico em forno convencional e o método “spin-coating” para deposição. O controle dessa etapa é muito importante, porque a mudança volumétrica envolvida para diferentes temperaturas pode conduzir à formação de defeitos superficiais do tipo trincas e bolhas após tratamento térmico. Manteve-se constante a velocidade de rotação do substrato da solução em 5000 rpm . Fixou-se a viscosidade da solução em 20 cPs ($\sim 1,20 \text{ g}/\text{cm}^3$), a concentração iônica em $0,1 \text{ mol. L}^{-1}$. Os filmes foram tratados termicamente com taxa de aquecimento lenta de $3^\circ\text{C}/\text{min}$ até a temperatura de decomposição térmica dos orgânicos (400°C) para evitar a formação de trincas e taxa de $5^\circ\text{C}/\text{min}$ entre 500 e 700°C . Observa-se que a formação de fase perovskita livre de fases indesejáveis é formada a 500°C . Os picos de difração foram identificados de acordo com a estrutura pseudo-cúbica. A intensidade dos picos de difração nos planos (100) e (200) é mais intensa com relação ao pico (110). Esta observação é importante, pois algumas propriedades elétricas como permissividade dielétrica, polarização remanescente e campo coercitivo variam com a mistura de orientações que difere de um filme para o outro. Observa-se que com o aumento da temperatura de tratamento térmico conduz à formação de fases indesejáveis do tipo Bi_2O_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$ e $\text{Bi}_{36}\text{Fe}_{24}\text{O}_{57}$ devido à flutuação composicional causada pela volatilização do bismuto. Outras fases secundárias não identificadas estão presentes nos filmes recozidos a 700°C por 2 horas. O tamanho médio de grão e a rugosidade superficial foram estimados por microscopia de força atômica (MFA) usando modo contato. Observa-se que o aumento da temperatura de tratamento térmico influencia na morfologia do filme obtido. Essa observação sugere que o aumento da

temperatura de tratamento térmico mantendo-se constante viscosidade e velocidade de rotação, aumenta a mobilidade iônica dentro da célula unitária, causando um aumento no tamanho de grão e uma diminuição da porosidade. A fim de verificar a ligação química nos filmes de BFO, realizaram-se análises de XPS. Os dados de XPS dos filmes de BFO recozidos a 500°C mostram-se monofásicos com ferro no estado de valência Fe^{3+} , sendo consistentes com os resultados de DRX mostrados anteriormente. Os dupletos 3/2 e 1/2 spin-órbita da fotoemissão do Fe 2p localizados em 711.1 e 724.6 eV foram identificados como Fe^{3+} , respectivamente. Não há evidências de Fe^{2+} e Fe no sistema. O estado de oxidação do ferro é puramente 3+, o que é uma vantagem para produção de filmes de BFO com baixa corrente de fuga. A ausência de íons Fe^{2+} sugere a redução de vacâncias de oxigênio em nossos filmes, o que pode ser uma das razões para a melhora significativa das propriedades ferroelétricas. Embora o filme tratado termicamente a 600°C apresente uma pequena quantidade de fases adicionais, íons Fe^{2+} e Fe não foram vistos no espectro devido à sua presença estar abaixo do limite de detecção do XPS ou à sua fotoemissão coincidir com as energias de ligação dos outros dois picos. Não há evidências de fotoemissão do Fe 2p para o filme tratado termicamente a 700°C. Este é um resultado surpreendente e indica que o poder de penetração de poucos nanômetros do XPS não foi suficiente para excluir a possível diferença entre a superfície e o interior do filme. Medidas de $C-V$ para filmes de BFO obtidos a 100 kHz e com voltagem de varredura de + 10 a - 10 V foram realizadas. A dependência entre a voltagem e a capacitância é bem linear, confirmando as propriedades ferroelétricas do filme resultante da reversão dos domínios. A curva $C-V$ para o filme tratado termicamente a 500°C por 2 horas indica simetria nos valores máximos de capacitância que podem ser observados na reversão da polarização espontânea. A curva é simétrica ao redor do zero de voltagem, indicando que o filme contém poucas cargas espaciais acumuladas na interface filme-substrato. Para filmes tratados termicamente a temperaturas de (600 e 700°C) uma pequena variação da capacitância é observada, indicando que existem cargas espaciais localizadas próxima à interface filme substrato. A corrente de fuga do filme recozido a 500°C é de aproximadamente 10^{-7} A/cm^2 , demonstrando a qualidade do filme obtido. A corrente de fuga do filme recozido a 600°C e 700°C foi somente de 10^{-6} A/cm^2 at 1,0 V. O aumento da corrente de fuga com a temperatura deve-se à presença de fases adicionais e do aumento do tamanho de grão uma vez que este torna-se não-uniforme. A forte dependência da corrente de fuga e do tamanho médio de grão sugere que o contorno de grão domina o processo de condução nesses filmes. Curvas de histerese para os filmes de BFO tratados termicamente em

diferentes temperaturas foram medidas. Os filmes tratados termicamente a 600 e 700° C exibem histerese ferroelétrica insaturada, tipicamente observada em ferroelétricos condutores. A dificuldade de saturação está provavelmente associada à presença de fases adicionais que aprisionam os domínios ferroelétricos impedindo a saturação da curva de histerese. Em contraste, os filmes de BFO tratado termicamente a 500°C apresenta histerese bem saturada com uma polarização remanescente de (P_r) $31 = \mu\text{C}/\text{cm}^2$ e campo coercitivo de (E_c) 560 kV/cm para um campo elétrico aplicado de 1000 kV/cm. O valor de P_r é atribuído à intensa orientação na direção (100). O elevado campo coercitivo deve-se à dificuldade de reversão da polarização em filmes com tamanho de grão reduzido, conforme observado por MFA. Os testes de fadiga para os filmes de BFO em função dos ciclos de polarização foram examinados pela aplicação de pulsos bipolares de largura de 8,6 μs com amplitude de 10 mV. A polarização remanescente foi calculada a partir da diferença entre as polarizações reversa e não reversa. Para os filmes tratados termicamente em baixa temperatura, a polarização reversa apresenta-se livre de degradação até 10^{10} ciclos de polarização. Esse resultado é um pouco surpreendente, pois geralmente filmes de BFO apresentam elevada corrente de fuga e baixa resistência a fadiga, devido a presença de cargas espaciais aprisionadas na interface filme-substrato que causam dificuldade de reversão dos domínios ferroelétricos. Porém, conforme observado na curva $C-V$, o filme tratado a 500°C por 2 horas contém pequena quantidade de cargas espaciais, devido à simetria nos valores de capacitância para diferentes voltagens o que gera um filme livre de fadiga. Os filmes tratados a 600°C e 700°C por 2 horas não apresentaram fadiga ferroelétrica, o que para aplicação em memórias FeRAMs não é muito desejável. Isso se deve ao aumento local da corrente causada pela larga presença de fases indesejáveis, que eventualmente prejudicam a qualidade da interface filme-eletrodo. A partir desses resultados podemos definir a temperatura de 500°C como a mais apropriada para obtenção de filmes finos de BFO monofásicos, com alta cristalinidade, morfologia livre de defeitos e com maiores valores de permissividade dielétrica, polarização remanescente e livre de fadiga que são características ideais para obtenção de memórias de múltiplos estados baseadas em filmes multiferróicos. Os resultados estão descritos no artigo que consta no anexo V (GONZALEZ, A. H. M., CAVALCANTE, L. S., RICCARDI, C. S., LONGO, E., VARELA, J.A., **SIMÕES, A. Z.**, Ferroelectric characteristics of BiFeO₃ thin films prepared via a simple chemical solution deposition, **Journal of Applied Physics.**, v.101, p.074108 074112- , 2007).

Apesar das excelentes propriedades, dois sérios problemas são comumente encontrados para imediata aplicação deste material em memórias multiferróicas: alta densidade de corrente, resultado da flutuação de valência dos íons Fe (Fe^{3+} para Fe^{2+}) com consequente criação de vacâncias de oxigênios, o que acarreta a formação de fases secundárias e elevado campo coercitivo causado pelo grande número de contornos de domínios ferroeletromagnéticos, que restringe a reversão da polarização. Para reduzir a corrente de fuga do BFO foram feitas várias tentativas na preparação de soluções sólidas com outros materiais de estrutura perovskita como BaTiO_3 e $\text{Pb}(\text{Ti,Zr})\text{O}_3$ e adição de alguns dopantes aos filmes finos de BFO, como Cr, Nb, La e Nd. Para reduzir a condução elétrica de filmes finos ferroelétricos com estrutura perovskita sugere-se substituição iônica, uma vez que esta diminui a formação de vacâncias de oxigênio que atuam como portadores de carga. A substituição do Bi por cátions terras-raras com o objetivo de diminuir a condução elétrica mostrou-se efetiva para outros sistemas ferroelétricos à base de Bi, como SBT e BIT.

Após otimizado que a temperatura de 500°C , por 2 horas, era a mais apropriada para obtenção destes filmes, fez-se um estudo variando a quantidade de lantânio, visando a obtenção de boas propriedades elétricas como alta polarização remanescente, baixo campo coercitivo e corrente de fuga e resistência à fadiga. Um novo conjunto de filmes foi preparado visando compreender a influência do dopante. Dados de DRX obtidos para os filmes de BFO modificados com diferentes quantidades de lantânio revelam somente picos relacionados à fase cristalina BFO, sugerindo que a substituição do Bi pelo La não conduz à formação de fases secundárias. Além da fase multiferróica, um pico de alta intensidade pertencente ao substrato de platina recoberto com silício (111) em $2\theta = 40^\circ$ foi identificado. Verificou-se também que, independente da fração de lantânio adicionada, o filme apresenta natureza policristalina. As imagens obtidas por MEV mostram que as superfícies dos filmes são densas, lisas e livres de trincas, levando a um filme homogêneo. Porém, não foi possível a observação dos grãos em virtude da pequena magnitude. Em contrapartida, as imagens de MFA mostram diferenças de morfologia quando da adição de lantânio. O tamanho médio de grão diminui com o aumento da fração de lantânio, resultante da diminuição da quantidade de bismuto do sistema. Os grãos estão distribuídos homogeneamente, com tamanho de grão médio variando de 60 a 100 nm. Além disso, a quantidade de lantânio adicionada reduz as vacâncias de oxigênio, que agem como centros aprisionadores dos domínios, facilitando o processo de reversão dos dipolos elétricos. A espessura e a rugosidade não foram significativamente dependentes da fração de lantânio adicionada no sistema, em contrapartida, influem fortemente na forma e no tamanho dos grãos. A rugosidade medida está entre 3 e 4

nm. Os dados de caracterização dielétrica apresentados são valores médios de pelo menos três amostras. A permissividade dielétrica e o fator de dissipação também foram determinados à temperatura ambiente em função da frequência no intervalo de 10 kHz a 1 MHz. Os filmes apresentaram boas propriedades dielétricas, uma permissividade dielétrica de 148 com perda de $(\tan \delta) = 0,013$ a 1 MHz para o filme de BLF030. A permissividade dielétrica mostra pouca dispersão com a frequência, indicando baixa quantidade de defeitos na interface filme-substrato. A baixa dispersão da permissividade dielétrica e a ausência de qualquer pico de relaxação em $\tan \delta$ indicam que a polarização interfacial do tipo Maxwell Wagner e aquela causada pela barreira do eletrodo são desprezadas nesses filmes. Também se observa que a adição de lantânio aumenta a permissividade dielétrica e diminui a perda dielétrica indicando que o elemento lantânio tem um papel crucial nas propriedades elétricas de filmes finos de BFO. A dopagem com lantânio mesmo em baixas concentrações tem uma forte influência nas propriedades dielétricas do sistema BFO. Como pode ser visto, o menor tamanho de grão conduz a um aumento na permissividade dielétrica e diminuição da perda dielétrica, resultado esse que pode ser explicado pela redução da tensão residual e do volume da célula unitária do filme durante resfriamento devido à mudança de estrutura cristalina quando da dopagem com lantânio. As medidas ferroelétricas desses filmes foram investigadas por um analisador ferroelétrico para frequência de 100 Hz e uma voltagem aplicada da ordem de 20 V. Observam-se curvas bem saturadas com uma polarização remanescente que varia de 15 a 30 $\mu\text{C}/\text{cm}^2$ e voltagem de operação de 1,35 a 3,36 V. A saturação dessas curvas em baixas frequências indica que as perdas são mínimas, sugerindo um filme altamente resistivo. Pode ser observado que a adição de lantânio até a fração de $x = 0,30$ para o filme resulta numa menor voltagem de operação do filme ferroelétrico. Nota-se que as curvas de histerese dos filmes não apresentam um deslocamento ao longo do eixo do campo coercitivo em direção ao lado positivo, fenômeno este conhecido com imprint. A ausência de imprint evita a falha do capacitor devido à aparente perda de polarização em um dos estados remanescentes. O significativo aumento nas propriedades dielétricas, ferroelétricas resultam da melhora de cristalinidade e aumento do volume de rede com a substituição por lantânio. Considerando-se que a polarização e a capacitância dependem da frequência, pode-se atribuir uma diferente cinética de reversão dos domínios ferroelétricos, o que reflete fortemente no formato das curvas. As medidas de J-V destes filmes foram realizadas usando o equipamento radiant technology no modo de voltagem-corrente, variando de 0 a + 10V, e +10 a -10V voltando novamente a 0V. As curvas para estes filmes foram medidas com passos de voltagem de 0,1 V e tempo de 1,0 s para cada voltagem. Duas regiões distintas são observadas nas curvas. Na

primeira região, a densidade de corrente aumenta linearmente com o campo elétrico externo na região de baixa voltagem sugerindo uma condução ôhmica. Para altas voltagens, a densidade de corrente aumenta exponencialmente o que implica que pelo menos uma parte da condutividade resulta do mecanismo de emissão do tipo Schottky ou Poole-Frenkel. A densidade de corrente a 1,0 V diminui com o aumento da concentração de lantânio. Alguns fatores podem contribuir para essa melhora. Primeiramente a redução da rugosidade superficial com o aumento da concentração de lantânio. Considerando que a condutividade é fortemente afetada pela característica da interface filme-substrato, a morfologia dos filmes de BFO e BLF é uma das maiores causas do aumento da densidade de corrente em capacitores ferroelétricos. Outra explicação pode ser a redução das microtrincas causadas pela tensão residual. Uma vez que a ocorre transição de fase com o aumento na concentração de lantânio, o volume da célula unitária durante o resfriamento diminui e a tensão residual aumenta. A possível explicação para este comportamento está associada à diferenças de tamanho e forma dos grãos, densidade e estrutura de superfície devido às diferenças nos procedimentos de cristalização. As características da interface filme-eletrodo e da morfologia de superfície dos filmes são os maiores fatores que determinam a densidade de corrente para capacitores do tipo metal-ferroelétrico-metal. A resistência à fadiga para os filmes de BFO em função dos ciclos de polarização foi observada pela aplicação de pulsos bipolares de largura 8,6 μ s com 10 mV de amplitude. Observa-se que o aumento na concentração de lantânio conduz resistência à fadiga até 10^{10} ciclos de polarização. A substituição do La por Bi pode mudar o meio químico das camadas perovisquitas e resolver o problema de fadiga dos filmes puros de BFO, pois reduzem vacâncias de oxigênio. Entretanto, não fica claro onde o La muda o ambiente químico das camadas perovisquita. É provável que o lantânio substitua íons bismuto próximos às camadas octaédricas do FeO_6 , reduzindo a quantidade de vacâncias de oxigênio presente na estrutura. É de grande interesse nesta pesquisa avaliar como alguns parâmetros de processamento, concentração de dopante, atmosfera e tipo de tratamento térmico, e natureza do eletrodo inferior afetam a estrutura e estabilidade dos domínios ferroelétricos, as propriedades piezoelétricas e os defeitos gerados durante a formação da fase cristalina BFO e BLFO. Essa análise visa a utilização em memórias DRAM/FeRAMs, “smart cards” e circuitos integrados. Sabe-se que a formação de estruturas multi-domínios resulta do processo de relaxação da energia interna, em filmes ferroelétricos. Portanto, torna-se importante compreender como a estrutura dos domínios varia com o campo elétrico aplicado, visando utilização em memórias não voláteis. Para tal finalidade utilizou-se de um microscópio de força atômica acoplado a um modo piezoelétrico, que permite a visualização dos domínios,

em escala nanométrica. Essas medidas permitiram diferenciar se os domínios estão dentro e fora do plano, dependendo do contraste observado na imagem de MFP e de como contribuem para a polarização total do sistema. Considerando que os materiais a base de bismuto têm coeficientes piezoelétricos relativamente baixos ($d_{33} \approx 19$ pm/V), torna-se difícil obter uma imagem de alto contraste na resposta piezoelétrica, principalmente, na contribuição dentro do plano. Outra dificuldade é que geralmente filmes de BLFO depositados em substrato de platina são policristalinos, tornando difícil a obtenção de informações dos domínios dentro e fora do plano, devido à complexidade da estrutura dos domínios para filmes não orientados. Desse modo, para obtenção de uma imagem de alto contraste, uma voltagem que exceda o campo coercitivo e mude a estrutura dos domínios deve ser aplicada durante a varredura. Numa primeira etapa, investigou-se o efeito causado pelo lantânio na disposição dos domínios ferroelétricos do sistema BFO, depositando filmes em substratos de silício recoberto com platina, seguido de tratamento térmico em atmosfera estática. A resposta piezoelétrica dos filmes de BFO e BLFO foi medida com voltagem dc aplicada de polaridade negativa igual a 12 V. Nesse caso, aplicou-se somente uma voltagem de polaridade negativa nessas amostras, com a finalidade de se verificar quais eram piezoelectricamente ativas. Observam-se duas regiões com diferentes contrastes: uma mais clara que corresponde ao filme como foi crescido e outra quadrática mais escura que foi produzida aplicando-se uma voltagem dc negativa, resultando em vetor polarização direcionado para fora do plano do filme. Com aumento do campo elétrico, alguns domínios são favorecidos, em relação aos outros com respeito à direção de crescimento. Este processo continua até que os domínios menos favoráveis revertam a direção polar próxima à direção do campo elétrico. Finalmente, após remoção do campo elétrico, os contornos de grãos podem nuclear novos domínios reversos. Na imagem fora do plano, os contrastes de cor representam polarizações, em direção ao eletrodo inferior e à ponta do MFA, sendo que a região mais escura tem o vetor polarização orientado na direção do “tip”. Em geral, a maior parte do filme se encontra num estado simples de polarização com cristalitos não revertidos (regiões claras) e que se encontram preferencialmente dentro das regiões quadráticas escuras exibindo um pequeno sinal piezoelétrico. Esse resultado é bastante comum para materiais ferroelétricos em que se observa uma grande polarização ao longo de uma determinada direção específica, refletindo em regiões com diferentes contrastes. Quando uma voltagem inferior a 12 V foi aplicada na amostra um sinal de mesma característica, mas de menor intensidade foi observado indicando que o filme não estava completamente polarizado. Da análise dos resultados, supõe-se que as regiões com pouco contraste estão orientadas numa direção de baixa polarização e são,

portanto, não reversíveis. Essas regiões apresentam uma fraca resposta piezoelétrica, causada por um desvio do vetor polarização, a partir da direção normal ao plano do filme. Considerando que o sinal piezoelétrico muda de sentido, sob a aplicação de uma voltagem positiva no “tip”, observa-se que as regiões claras correspondem a domínios negativos (polarização fora do plano do filme), enquanto as regiões escuras são representadas por domínios positivos (polarização no plano do filme). Outra causa pode ser a baixa frequência *ac* usada para determinar a reversão da polarização, em nossos experimentos levando a imagens com regiões de baixos contrastes, devido à presença de grãos complexos polarizados. A partir de uma análise cuidadosa dos resultados supõe-se que as propriedades piezoelétricas da ferrita de bismuto são fortemente afetadas pela adição de lantânio. Observa-se que a piezoeletricidade diminui significativamente a partir da concentração de 0,15 em lantânio, resultando em nenhuma resposta para concentração de 0,30. A redução da resposta piezoelétrica, com o aumento na concentração de lantânio, deve-se provavelmente à redução da polarização principalmente ao longo da direção (111), que contribui significativamente para as propriedades ferroelétricas da ferrita de bismuto. Nas imagens no plano observa-se que os grãos mais claros têm o vetor polarização orientado na direção positiva do eixo y, enquanto os grãos escuros na direção oposta do mesmo eixo. Os grãos que apresentam contraste intermediário possuem resposta piezoelétrica nula, sendo, portanto, não reversíveis. Supõe-se que estes grãos que não mudam de contraste têm os domínios aprisionados. Paralelamente, à análise de disposição dos domínios, estudou-se como o lantânio atua sobre os defeitos cristalinos, que surgem durante a cristalização da fase ferroelétrica. Esses defeitos interferem nas propriedades piezoelétricas e ferroelétricas do sistema, indicando que estas dependem não somente de uma morfologia bem definida, mas também da qualidade da interface filme-substrato. O lantânio embora leve a uma redução das propriedades piezoelétricas, auxilia a estabilizar as paredes de domínios carregadas fortemente, que interagem com as vacâncias de oxigênio, inibindo a fadiga ferroelétrica e a perda de retenção de dados nos filmes. Portanto, o lantânio tem como principal função suprimir a volatilização do óxido de bismuto reduzindo tensões internas na rede, além de reduzir os defeitos como resultado do “mismatch” entre a camada de Bi_2O_2 e a camada perovskita. A substituição do bismuto pelo lantânio reduz a energia livre do sistema, prevalecendo as interações dipolo-dipolo e a energia eletrostática, o que afeta a estrutura e o tamanho dos domínios. Ocorre nesse sentido um grande movimento dos domínios de 90° , devido à rotação dos octaedros de oxigênio com o eixo vertical, levando a tensões na rede e alguns espaços propícios para acúmulo de cargas. No sistema puro, devido à elevada volatilidade do bismuto grandes deformações na rede resultam do acúmulo de

defeitos, que provavelmente aprisionam os domínios de 90° mais que no sistema dopado. Esses defeitos reduzem fortemente a mobilidade dos domínios, com conseqüente interações com os deslocamentos, o que leva à fadiga ferroelétrica e ao fenômeno de retenção. Supõe-se, portanto, que paredes de domínios de 90° estão presentes nos filmes e sua reversão necessita de tempos de relaxação maiores devido à presença de tensões na rede cristalina. No sistema puro não se observa nenhuma tensão para as paredes de domínios de 180° , indicando que as tensões externas, induzidas pela relaxação dos domínios de 90° , aprisionam os domínios de 180° , durante o processo de reversão. Nos filmes dopados nenhuma tensão é produzida no movimento dos domínios de 90° , devido à redução das tensões causadas pelo movimento dos domínios opostos. Portanto, o aprisionamento dos domínios de 180° pelas tensões é reduzido. Porém, devido à complexidade da distribuição dos domínios neste sistema, um estudo mais detalhado de dinâmica de domínios deve ser realizado visando à compreensão de tal comportamento e, também a possível distinção entre as possíveis orientações dos domínios presentes nos filmes. O fraco sinal causado pela adição de lantânio sugere que um forte campo de despolarização aparece na área polarizada abaixo do “tip”. Este campo de despolarização deve suprimir a reversão da polarização espontânea durante o “poling”. Além disso, deve acelerar a reversão da polarização com a remoção do campo externo, sendo evidente pela redução do d_{33} , quando a voltagem de “poling” reduz de máximo a zero. A curva de deformação em função do campo elétrico indica deformação máxima em 5 kV/cm, enquanto o regime de saturação atinge 10 kV/cm. A adição de lantânio reduz a deformação devido à reorientação dos domínios. Além disso, é possível que o bias aplicado resulte numa transição de fase assimétrica para simétrica. Essa transição de fase pode estar associada à redução de energia livre entre as fases polimórficas presente no sistema. Uma análise cuidadosa da curva S-E revela duas regiões distintas: uma a baixo campo ($E < 5$ kV/cm) e outra a alto campo ($E > 10$ kV/cm), além de uma região de transição de fase que corresponde à reorientação dos domínios induzidas pelo campo elétrico. A deformação em forma de curva de histerese está associada à reorientação dos domínios. Para campos maiores que 5 kV/cm, a deformação é livre de histerese, indicando uma estável relação entre domínio simples/estado de reversão dos domínios induzido por campos elétricos externos elevados. Além disso, a partir da curva S vs E , nenhuma transição de fase induzida é observada para campos elétricos elevado. A adição de lantânio reduz a deformação quando comparado ao filme puro, à deformação obtida é de ($S = 0,16, 0,12$ e $0,11\%$) e ($S = 0,17\%$) para os filmes modificados com lantânio e BFO puro, respectivamente. A redução da deformação e da energia livre após adição do dopante pode estar associada à diminuição da polarizabilidade e do efeito de

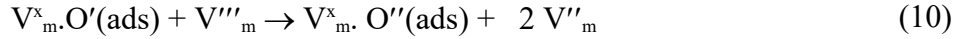
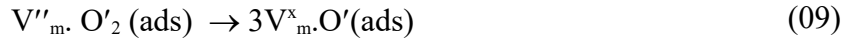
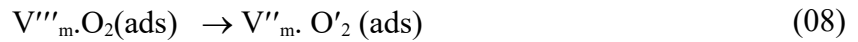
aprisionamento dos domínios ferroelétricos. Os resultados desta pesquisa são encontrados nos artigos que constam nos anexos W e X (L. S. CAVALCANTE, L.S., RICCARDI, C. S., LONGO, E. VARELA, J.A., **SIMÕES, A. Z.**, Improvement of fatigue resistance on La modified BiFeO₃ thin films, **Current Applied Physics.**, v.9, p.520 - 523, 2009) e (ANDRES, J., AGUIAR, E. C., GONZALEZ, A. H. M. RICCARDI, C. S., LONGO, E., VARELA, J.A., **SIMÕES, A. Z.**, Strain Behaviour of Lanthanum Modified BiFeO₃ Thin Films Prepared Via Soft Chemical Method. **Journal of Applied Physics.** v.104, p.104115-1 - 104115-6, 2008).

Embora as melhores condições de tratamento térmico, concentração de lantânio tenham sido anteriormente otimizadas, o controle da rugosidade superficial torna-se importante para obter propriedades elétricas desejáveis. Dessa forma, foram depositados filmes com 10 camadas em substratos de silício recoberto com platina por spin-coating, tratando-os termicamente em atmosfera de oxigênio e atmosfera de ar (estática). Realizou-se um estudo com o tratamento do filme em atmosfera de oxigênio e ar estático (ambiente), cristalizando camada por camada a 500°C por 2 horas. A vazão de oxigênio foi mantida constante a 100 mL/min. Considerando que somente os filmes BLF015 e BLF030 não apresentam fadiga ferroelétrica, esses foram caracterizados quanto às propriedades elétricas quando tratados em atmosfera oxidante. Dados de DRX revelam que a atmosfera utilizada durante o tratamento térmico influencia diretamente na nucleação da fase cristalina. A atmosfera de ar (ambiente) favoreceu a cristalização da fase BFO policristalina, com pico de máxima intensidade em (100) $2\theta = 22^\circ$. Observa-se que, para o filme de BLF015, os picos estão deslocados em relação às outras composições. Esse fato pode estar associado à colocação da amostra durante a análise de DRX. Nota-se também um pico em $2\theta = 28^\circ$ referente à fase deletéria de óxido de bismuto. A presença dessa fase provavelmente está associada a substituição do lantânio pelo bismuto na estrutura cristalina do BFO. Além da fase multiferróica, um pico de alta intensidade pertencente ao substrato de platina recoberto com silício (111) em $2\theta = 40^\circ$ foi identificado. Verificou-se também que, independente da fração de lantânio adicionada, o filme apresenta natureza policristalina. Em atmosfera de oxigênio, a decomposição da matéria orgânica é mais rápida e sendo uma reação exotérmica, libera maior quantidade de calor promovendo a cristalização da fase BFO a partir do substrato que é a superfície de menor energia de ativação para cristalização, pois tem superfície com planos orientados. Essa cristalização rápida conduz à formação de fases indesejáveis do tipo Bi₂O₃, Bi₂Fe₄O₉ e Bi₃₆Fe₂₄O₅₇ devido à flutuação composicional causada pela volatilização do bismuto. Outras fases secundárias não identificadas estão presentes, principalmente no filme BLF030. Embora

os filmes tratados termicamente em atmosfera oxidante possuam fases deletérias, sua superfície é mais homogênea, uniforme e densa. Independente da quantidade de lantânio utilizada, os filmes calcinados em atmosfera de oxigênio apresentam menor espessura quando comparados à atmosfera de ar (ambiente). Isso ocorre devido à vazão de oxigênio aumentar a taxa de nucleação favorecendo uma distribuição mais homogênea do material depositado na superfície do substrato com baixa porosidade. Dados de MFA indicam que os filmes tratados termicamente em atmosfera de oxigênio apresentam uma superfície mais homogênea quando comparados aos tratados em atmosfera de ar. Isso pode ser explicado em função da diferente taxa de nucleação que ocorre para os filmes tratados termicamente em atmosfera de oxigênio comparados aos tratados em atmosfera estática de ar (ambiente). O tamanho de grão diminuiu para os filmes tratados em oxigênio, pois em atmosfera dinâmica o crescimento do grão na direção *a-b* tornando-se um grão arredondado é favorecido. Em atmosfera de ar (ambiente) o tamanho de grão é maior quando comparado à atmosfera dinâmica de oxigênio. Embora o filme tratado em atmosfera de oxigênio apresente menor rugosidade e porosidade espera-se que suas propriedades elétricas sejam inferiores aos filmes tratados em atmosfera estática uma vez que essas propriedades dependem fortemente da magnitude do tamanho médio de grão e da presença de fases deletérias. Considerando que somente os filmes dopados com lantânio ($x = 0,15$ e $0,30$) apresentaram-se livres de fadiga realizaram-se medidas elétricas desses filmes, visando compreender a influência da atmosfera de tratamento térmico. O filme tratado termicamente em atmosfera de oxigênio apresenta uma intensa queda na constante dielétrica no intervalo de frequência de 10 a 100 kHz. É possível que esta diminuição na constante dielétrica nesse intervalo de frequência seja causado pela polarização de carga espacial ou polarização interface do tipo Maxwell Wagner. A polarização de carga espacial está relacionada com o acúmulo de cargas não uniformes, as quais podem ser originadas durante o tratamento em atmosfera de oxigênio. Verifica-se que o formato das curvas de histerese ferroelétrica depende fortemente de um bom controle da interface filme-substrato, que pode ser notado pela dependência da constante dielétrica com a frequência. Em geral, quanto maior a dispersão entre a constante dielétrica e a frequência, mais defeitos interfaciais são verificados e as curvas de histerese apresentarão os seguintes problemas: insaturação, maior gap de polarização, falta de reversibilidade dos domínios ferroelétricos e o fenômeno de "imprint", que é a tendência de uma camada ferroelétrica reverter a direção de polarização para um estado mais estável. Quando os filmes foram tratados em atmosfera estática, uma redução na dispersão da constante dielétrica com a frequência foi observada indicando que houve uma diminuição no efeito de carga espacial confirmando que a relaxação dielétrica não

é um fenômeno de bulk, mas sim relacionado com a interface. A partir dos resultados obtidos observa-se uma diferença na constante dielétrica para os filmes tratados em atmosfera estática devido a diferenças em tamanho de grão, cristalinidade e defeitos estruturais. As curvas de histerese para os filmes tratados termicamente em atmosfera estática indicam que o processo de polarização é mais acentuado. Entretanto, para os filmes tratados termicamente em atmosfera de oxigênio as cargas carregadas ($O_2^{\bullet\bullet}$) associadas com outros defeitos ($V_0^{\bullet\bullet}$ ou até mesmo dipolos complexos tais como vacâncias de oxigênio associadas com vacâncias de bismuto ($V'''_{Bi} - V_0^{\bullet\bullet}$) localizados no contorno de grão na interface filme-substrato pode promover um deslocamento na curva de histerese. Ferroeletricidade nos filmes foram observadas com polarização remanescente de 14,5 e 16, 5 $\mu C/cm^2$ com voltagem de 1,75 e 1,64 V para filmes recozidos em atmosfera estática ($x = 0,15$ e $0,30$) e 7,3 e 14,5 $\mu C/cm^2$ com voltagem de 1,4 e 1,6V para filmes recozidos em atmosfera de oxigênio ($x = 0,15$ e $0,30$), respectivamente. A curva de histerese para o filme tratado termicamente em atmosfera de oxigênio mostra uma diferença no campo coercitivo em direção do lado positivo, o que é definido como imprint. A mudança de voltagem pode causar uma falha no capacitor devido à perda de polarização em um dos estados remanescente. Consequentemente, pode ocorrer um aumento no campo coercitivo em uma direção, causando uma falha na memória. Esses resultados são consistentes com as medidas $C-V$ e podem ser causadas pela alta concentração de vacâncias de bismuto e oxigênio localizadas na interface filme-substrato. A dependência entre a capacitância e voltagem mostra uma relação não linear indicando propriedades ferroelétricas como resultado da reversão dos domínios ferroelétricos. Para os filmes tratados em atmosfera estática, a curva é simétrica para valores de voltagem baixos, indicando que os filmes contêm poucas cargas espaciais acumuladas na interface filme-substrato. Em contrapartida, uma dispersão nos valores de capacitância foi observada para os filmes tratados termicamente em atmosfera de oxigênio indicando que existem cargas espaciais acumuladas na interface filme-substrato. Essas cargas podem ser originadas durante o processo de tratamento térmico para decomposição do polímero precursor. As cargas negativas podem estar associadas com a presença de espécies de oxigênio negativamente carregadas localizadas no contorno de grão e na interface filme-substrato. As cargas negativas do oxigênio podem ser causadas pela transferência de carga entre a vacância do metal e o oxigênio, de acordo com seguintes equações:





Onde O^x , V'''_m , V^x_m , e O'' representam os íons oxigênicos neutros em suas posições normais, vacâncias de metal triplamente carregadas negativamente, vacâncias de metal neutras, e íons oxigênicos duplamente carregados negativamente. As propriedades isolantes dos filmes são bem dependentes da atmosfera de tratamento térmico. A densidade de corrente é bastante reduzida para os filmes tratados em atmosfera estática devido a melhor cristalinidade e completa formação da fase perovskita. As propriedades elétricas para baixos campos são geralmente de natureza ôhmica, o que significa que a densidade de corrente J é função linear da voltagem V . Para altos campos esses filmes exibem comportamento não linear, que pode ser expresso pela lei de potência empírica $J = KV^\alpha$. Usualmente, as características elétricas para campos elevados não podem ser descritas por um simples processo de condução; geralmente num intervalo de voltagem pode manifestar comportamento elétrico distinto. Duas regiões distintas são visualizadas. A densidade de corrente aumenta linearmente com o campo elétrico na região de baixo campo sugerindo uma condução ôhmica. Para campos elevados a densidade aumenta exponencialmente o que implica que pelo menos uma parte da condutividade resulta do mecanismo de emissão do tipo Schottky ou Poole- Frenkel. A densidade de corrente a 1,0 V diminui quando os filmes são tratados termicamente em atmosfera estática devido a diferenças no tamanho de grão, densidade e superfícies estruturais devido às diferenças na cristalinidade. A corrente de fuga para o filme tratado em ar é menor que para o filme tratado em oxigênio, o que indica que o filme cristalizado em oxigênio é menos isolante que o cristalizado em ar, o que explica o valor mais baixo obtido para polarização remanescente para esse filme. Com o aumento do campo elétrico, as vacâncias de oxigênio interagem fortemente com os domínios influenciando no processo de condução. Supõe-se que as vacâncias móveis de Bi e O localizadas próximo do contorno de grão contribuem para um aumento na densidade de corrente. As características da interface filme-eletrodo e a morfologia da superfície dos filmes são os principais fatores que determinam a densidade de corrente dos capacitores. A resistência à fadiga para os filmes de BFO em função dos ciclos de polarização foram observados para as diferentes atmosferas de tratamento térmico e concentração de lantânio. Independente da quantidade de lantânio adicionada filmes de BFO tratados em atmosfera de oxigênio apresentaram fadiga

ferroelétrica. Esse resultado sugere que as cargas carregadas ($O_2^{\bullet}$) associadas com outros defeitos ($V_O^{\bullet\bullet}$ ou até mesmo dipolos complexos tais como vacâncias de oxigênio associados com vacâncias de bismuto ($V_{Bi}^{\bullet\bullet\bullet} - V_O^{\bullet\bullet}$) localizados no contorno de grão na interface filme-substrato podem aumentar a condutividade do filme para elevados ciclos de polarização, causando uma destruição no contato eletrodo-filme ferroelétrico. Os resultados desse artigo estão elucidados na referência que constam no anexo Y (RICCARDI, C. S., DOS SANTOS, M. L., LONGO, E., VARELA J.A., SIMÕES, A. Z., Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films. **Materials Research Bulletin.**, v.44, p.1747 - 1752, 2009).

Filmes de BFO também foram dopados com Nb no sítio do Fe visando o controle de flutuação composicional. A adição de Nb minimiza a presença da fase secundária $Bi_2Fe_4O_9$, pois auxilia no controle de vacâncias de oxigênio e evita o aparecimento de Fe^{3+} e Fe^{2+} . A adição do dopante doador reduz o tamanho de grão de 70 nm para o sistema BFO e 50 nm para o sistema levemente dopado. O papel do dopante é minimizar a formação de vacâncias de oxigênio que agem como defeitos pontuais e reduzem a heterogeneidade superficial. A redução no tamanho de grão é uma forte evidência da inibição do transporte de massa e traz como consequência baixa taxa de difusão de oxigênio pelos contornos de grão. As medidas ferroelétricas destes filmes foram investigadas por um analisador ferroelétrico para frequência de 100 Hz e uma voltagem aplicada da ordem de 20 V. Observa-se curvas bem saturadas com uma polarização de saturação (P_s) de $40 \mu C/cm^2$ e remanescente de $32 \mu C/cm^2$. A curva de histerese do filme puro indica menor grau de anisotropia, embora a curva não sature devido ao elevado campo elétrico aplicado (1000 kV/cm) na frequência de 1 kHz. Os filmes dopados com Nb apresentam pior comportamento ferroelétrico, embora menores voltagens sejam exigidas para saturação da curva de histerese. Isto pode ser um indicativo da redução de vacâncias de oxigênio de acordo com a química de defeitos.

As propriedades de retenção desses filmes foram medidas em temperatura ambiente, empregando-se a seguinte sequência de pulsos: pulso triangular de - 5 V foi aplicado para escrever um estado lógico conhecido, depois de um determinado tempo, o estado lógico foi sequencialmente lido pela aplicação de dois pulsos triangulares de + 5 V e - 5 V. A largura do pulso foi de 1,0 ms. O capacitor polarizado com um pulso de voltagem negativa corresponde ao dígito binário “1”. De forma semelhante, o estado “0” foi escrito polarizando-se o capacitor com um pulso positivo seguido de leitura, depois de um intervalo de tempo com um pulso negativo. As curvas de retenção para longos períodos para os filmes de BFO puro e

dopados com nióbio permitem inferir que quando se aumenta a concentração de nióbio, a dependência do tempo de retenção com a polarização é bastante satisfatória. Após um tempo de retenção de 1×10^4 s, a perda de polarização é de somente 6% para um tempo de $t = 1$ s e campo elétrico de 150 kV/cm. Campos de despolarização gerados por redistribuição de cargas espaciais, defeito e dipolos complexos podem ser a razão para o decaimento da polarização após o processo de escrita. Para os primeiros 10 s, campos de despolarização podem ser a principal causa para a perda de polarização. O campo de despolarização aumenta com o aumento da polarização, sendo dependente do tempo. A perda de retenção para longos períodos pode ser atribuída a efeitos de redistribuição de cargas. Esse efeito conduz a uma pequena redução na polarização pela compensação de cargas de polarização quando a redistribuição de defeitos de cargas é governado pela polarização. Devido à relaxação dielétrica, a carga retida é geralmente menor que a carga medida na curva de histerese, e a diferença entre elas deve ser a menor possível para manter uma diferença significativa entre os dígitos “1” e “0”. O fenômeno de retenção é similar à fadiga, pois depende da espessura do filme, natureza do eletrodo, morfologia dos grãos, temperatura e detalhes experimentais. O entendimento e melhoria da degradação, em filmes finos ferroelétricos, terá um impacto essencial no sucesso desses filmes para aplicações em dispositivos. Os resultados deste artigo estão apresentados na referencia, consta no anexo Z (PIANNO, R.F.C., AGUIAR, E.C., LONGO, E., VARELA J.A., **SIMÕES, A. Z.**, Effect of niobium dopant on fatigue characteristics of BiFeO_3 thin films grown on Pt Electrodes. **Journal of Alloys and Compounds.** , v.479, p.274-279, 2009).

O efeito de outro dopante nas propriedades estruturais, isolantes e ferroelétricas de filmes de BiFeO_3 (BFO) foi investigado. Filmes de BFO com a seguinte composição $(\text{Bi}_{1.00-x}\text{RE}_x\text{Fe}_{1.00}\text{O}_3$ ($x = 0.15$), $\text{RE} = \text{Nd}$ foram depositados sobre substrato de Pt (111)/Ti/SiO₂/Si usando-se solução química. A adição de Nd nos filmes de BFO não levou ao aparecimento de orientação preferencial, embora tenha reduzido a fase parasita $\text{Bi}_2\text{Fe}_4\text{O}_9$, presente no filme puro. A natureza policristalina do filme pode ser atribuído às diferenças de energia entre o material de nucleação e o substrato. De acordo com o padrão, o filme tem uma estrutura de perovskita tetragonal. Mudanças na morfologia da superfície dos filmes também foram avaliadas por MFA. A adição de terras raras tende a suprimir o crescimento de grãos. Esses resultados são consistentes com os resultados de DRX, com uma redução na intensidade dos picos quando da adição do Nd. O filme puro exibe uma microestruturaa heterogênea que consistem em grãos pequenos e grandes com rugosidade de 6,2 nm. A adição de Nd leva a uma morfologia na forma de placas, que pode ser explicada pela complexação

dos íons Nd^{3+} pelos grupos carboxílicos, que conduz a um polímero linear e uma morfologia do tipo em placas. A rugosidade superficial desse filme é de 4,6 nm. O papel dos terras raras é o de eliminar as cargas espaciais que atuam como defeitos pontuais e, portanto, diminuir a heterogeneidade da superfície dos filmes. A diminuição do tamanho de grão dos filmes de terras raras dopados com BFO pode ser interpretada pela supressão da concentração de vacâncias de oxigênio, o que resulta em mais lento movimento de íons de oxigênio e, conseqüentemente, menor taxa de crescimento dos grãos. Medidas de densidade de corrente de fuga (J) versus campo elétrico (E) foram medidas à temperatura ambiente. A densidade de corrente dos filmes não substituídos de BFO foi maior do que a do filme modificado com Nd, especialmente acima de 4V. As diferenças nas características de J - E foram atribuídas à supressão das vacâncias de oxigênio nos filmes BFO pela substituição do íon terra rara no sítio do Bi volátil. A densidade de corrente de fuga desses filmes tinha menos de 10^{-8} A/cm^2 para o filme modificado e de 10^{-6} A/cm^2 para o filme puro. Resultados de medidas de histerese indicam que o valor da polarização remanescente reduziu com a adição do íon Nd. Esse comportamento pode ser atribuído a uma estreita correlação existente entre a anisotropia cristalina, temperatura Curie, e polarização espontânea. Ferroelétricos baseados em perovskita com maior anisotropia cristalina à temperatura ambiente geralmente possuem altas temperaturas de Curie. A temperatura de Curie (isto é, mudança de fase ferroelétrica-paraelétrica temperatura de transição de fase) é também considerada como a temperatura em que a anisotropia do cristal desaparece durante o aquecimento ou o resfriamento. As temperaturas de transição de fase aumentam com a anisotropia de cristal devido à anisotropia cristalina degradada progressivamente com o aumento da temperatura, da atmosfera. A adição de Nd no BFO afeta significativamente a temperatura de Curie, gerando tensões bidimensionais no filme que degrada a anisotropia cristalina do BFO, baixando a temperatura de Curie e a polarização espontânea. Curvas de histerese magnética Magnetização (M) em função do campo magnético (H) foram registradas as 300 K. Filmes de BFO puro apresentam um campo magnético de 1,3 emu/g. Essa fraca resposta ferromagnética sugere que a distribuição estatística de íons Fe^{3+} no octaedros ou a criação de defeitos de rede pode levar à magnetização ou ligeiro ferromagnetismo. O fraco caráter ferromagnético neste composto pode ser atribuído tanto à inclinação dos spins antiferromagnéticos causados por distorção estrutural ou à ruptura do equilíbrio entre a magnetização de sub-rede antiparalela aos íons Fe^{3+} , devido à substituição de íons de metal com valências diferentes. A magnetização aumenta linearmente com o campo magnético aplicado, que é característica de um material antiferromagnético. A alteração nas propriedades magnéticas, nesse caso, é

explicada, não só por diferentes momentos magnéticos e raios dos íons neodímio (Nd não possui qualquer momento magnético intrínseco), mas também pela anisotropia dos momentos magnéticos dos íons Nd. A maior magnetização surge devido ao ordenamento magnético da substituição com Nd. Essa melhoria pode ser atribuída a diferentes fatores tais como (1) a distorção estrutural devido à substituição, (2) variações na estequiometria de oxigênio ou concentração de íons Fe^{2+} , (3) redução do tamanho dos grãos e (4) alterações na anisotropia magnética. Os resultados deste artigo são encontrados no anexo A1 (MOURA, F., CAVALCANTE, L.S., LONGO, E., VARELA J.A., **SIMÕES, A. Z.**, Structure, ferroelectric/magnetoelectric properties and leakage current density of $(\text{Bi}_{0.85}\text{Nd}_{0.15})\text{FeO}_3$ thin films. **Journal of Alloys and Compounds.**, v.509, p.5326 - 5335, 2011).

O efeito do eletrodo inferior foi verificado para filmes de BFO dopados com La. O padrão de DRX do filme de BLFO015 em substrato de LSCO/Pt/Ti/SiO₂/Si (100) e BLFO015/Pt/Ti/SiO₂/Si (100) (100) foi indexado de acordo com a ficha ICSD 72-2035. O filme se cristaliza com picos extremamente intensos e finos e livre de fases impuras como $\text{Bi}_2\text{Fe}_4\text{O}_9$ e $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$. De acordo com o padrão, o filme tem uma estrutura romboédrica tipo perovskita. Além disso, é orientada aleatoriamente. O pico mais intenso do filme corresponde ao plano (110) LSCO não orientado com grãos com estrutura tipo perovskita, sendo a sua posição no padrão coincidente com a orientação BLFO015 (012). Verificou-se que todos os filmes consistem de uma única fase com orientação preferencial nos planos (012) e (111). Os resultados de DRX mostram claramente que os filmes depositados no eletrodo de LSCO favorecem o crescimento no plano (111) enquanto que os grãos dos filmes depositados sobre Pt crescem no plano (012). Algumas propriedades físicas sensíveis à orientação tais como permissividade dielétrica e tensão de polarização remanescente rígida variam de acordo com o grau de orientações diferentes, que são diferentes para os filmes desenvolvidos em diferentes eletrodos. No entanto, esse comportamento não foi observado para os filmes com conteúdo de lantânio superior a 15,0 %. Essa distorção estrutural pode ser responsável pela elevada corrente de fuga e menor polarização remanescente do sistema $\text{Bi}_{0.7}\text{La}_{0.30}\text{FeO}_3$. As orientações preferenciais podem ser causadas por diferenças de parâmetros de rede e os coeficientes de expansão térmica entre o eletrodo óxido e o filme e elas indicam que o eixo polar está mais próximo do plano (111) do que do (012). Para confirmar a morfologia da superfície, a MFA foi realizada. As alterações na morfologia da superfície dos filmes de BLFO015 foram avaliadas. Independentemente do filme, observou-se que o eletrodo óxido possui uma superfície homogênea indicando que o método do precursor polimérico permite a preparação de materiais com a morfologia controlada. O valor médio de

rugosidade da superfície é de 4,3 nm para o filme depositado sobre o eletrodo de Pt e 7,5 nm para o filme depositado sobre LSCO. O tamanho de grão médio é de 58 nm e 85 nm, respectivamente. Verificou-se também que o eletrodo de Pt tende a suprimir o crescimento de grãos. Esses resultados são consistentes com os resultados de DRX, com uma diminuição da intensidade de pico para o eletrodo de Pt. A substituição com La mostra-se eficiente no melhoramento da morfologia da superfície de filmes de BFO, porque o filme precursor passa por um processo de nucleação e o crescimento otimizado para a produção de filmes com uma microestrutura homogênea e densa. Além disso, a microestrutura homogênea do filme de BLFO015 pode afetar as propriedades ferroelétricas, porque a tensão pode ser aplicada uniformemente sobre o filme. De modo a avaliar o papel exercido pelo eletrodo óxido sobre a morfologia do filme de BLFO015, imagens de MET e padrões de difração de área selecionada mostram grãos no plano dos filmes com forma regular e tamanho estimado de 80 nm para o filme de BLFO015, depositado sobre o eletrodo de LSCO e 60 nm para o filme de BLFO015, depositado sobre eletrodo de Pt. Poros minúsculos menores do que 10 nm de tamanho estão presentes nos grãos e ao longo das fronteiras de grão. O papel do eletrodo óxido é o de eliminar vacâncias que atuam como defeitos pontuais e, portanto, diminuir a heterogeneidade superficial nos filmes. A diminuição do tamanho de grão dos filmes de BLFO015 depositados sobre em Pt pode ser interpretado pelo lento movimento dos íons oxigênio e, consequentemente, menor taxa de crescimento dos grãos. Desta forma, o tamanho de grão inferior pode ser um reflexo de aumento da temperatura de cristalização, devido as diferenças de força de ligação química entre Fe -O, La - O com átomos de Pt. Dessa forma, assumimos que o eletrodo inferior tem forte efeito sobre a estrutura cristalina de filmes de BLFO015. Estudos de XPS permitem identificar a ligação química nos filmes de BLFO015. O espectro expandido a partir de 700 eV a 745 eV revela componentes spin-órbita 3/2 e 1/2 da fotoemissão do Fe 2p localizada em 711,1 e 724,6 eV, respectivamente, identificados como Fe³⁺. Não há evidência de Fe²⁺ e Fe nos espectros de XPS, indicando que os filmes finos de BLFO015, em ambos os eletrodos inferiores, têm uma única fase com um estado de valência de Fe³⁺, o que é consistente com os resultados de DRX, sendo vantajoso para a produção de BLFO015 com baixa corrente de fuga. Os espectros Raman de filmes finos de BLFO015 depositados sobre ambos eletrodos mostram o grau de ordem-desordem da estrutura atômica a curta distância. Os modos são divididos em componentes longitudinais e transversais, devido às intensas forças eletrostáticas associadas ao caráter iônico. Átomos de lantânio que substituem o bismuto dentro da estrutura perovskita tem influência nas interações entre as camadas e (Bi₂O₂)²⁺ e a fase perovskita. Os modos de vibração localizados em 224, 355, 385,

531, e 564 cm^{-1} a partir do resultado octaédrico FeO_6 ($\text{Fe} = 5$ ou $\text{Fe} = 6$). A banda localizada abaixo de 200 cm^{-1} é devido aos diferentes locais ocupados por bismuto na fase de perovskita. Pequenas alterações que ocorrem acima de 200 cm^{-1} no BLFO015 podem ser associadas à distorção estrutural e redução de vibrações nos octaedros FeO_5 . Os modos de vibração do filme depositado no eletrodo de Pt tendem a desaparecer quando comparadas com o filme depositado sobre LSCO. Durante o processo de transferência de energia rearranjos estruturais específicos podem ter lugar e distorções em clusters octaédricos (FeO_6) e dodecaédricos (BiO_{12}) podem ser evidenciados. Deste modo, existe uma quebra do processo de simetria ao longo da rede de ambos os clusters $[\text{FeO}_6]$ e $[\text{BiO}_{12}]$ levando à baixa simetria. Isso pode estar relacionado com desordenamento estrutural em curto alcance, bem como a uma transição de fase para uma estrutura cristalina ordenada. As mudanças estruturais desenvolvidas na interface Pt criam níveis localizados nas bandas e uma distribuição de carga não homogênea entre bandas de valência e de condução. Curvas de C - V para filmes de BLFO015 obtidos a 100 kHz e tensão de varredura DC de + 10 para -10 V ilustram dependência fortemente não-linear, o que confirma as propriedades ferroelétricas do filme resultantes da reversão dos domínios. Filmes de BLFO015 depositados sobre eletrodo inferior de LSCO apresentam uma curva C - V simétrica em torno do eixo zero de polarização, indicando que os filmes contêm apenas alguns íons móveis com cargas acumuladas na interface filme-eletrodo. Embora as curvas de histerese sejam saturadas a $\geq 5\text{V}$, a curva C - V se estende até $\pm 10\text{V}$ porque ambas as medidas foram realizadas em diferentes frequências em que o alinhamento de domínio é um processo dependente do tempo e desempenha um papel importante no comportamento de reversão dos domínios. Portanto, as faixas de varredura diferem grandemente (5V) e, conseqüentemente, também o valor de (dC/dV) por unidade de tempo, leva a diferentes cinéticas de alinhamento de domínio. O estreitamento da curva de C - V obtido para o filme depositado sobre o LSCO indica que o processo de reversão dos domínios é mais rápido e a saturação ocorre com baixo consumo de energia para o alinhamento do domínio ferroelétrico. Por outro lado, para os filmes depositados sobre Pt uma ligeira alteração nos valores de capacitância é observada, indicando que existem portadores de carga (vacâncias de oxigênio) presos próximos da interface filme-eletrodo. Essas cargas podem ser originadas durante o processo de tratamento térmico devido à decomposição do precursor polimérico. Pode-se supor que se durante o tratamento térmico ocorre acúmulo de vacâncias de oxigênio perto da interface do eletrodo oxidado, o condutor LSCO pode consumir essas vacâncias, alterando a estequiometria do oxigênio e, assim, o acúmulo de vacâncias de oxigênio próximas da interface é evitado ou reduzido. A densidade de corrente de fuga, como

uma função da tensão, medida à temperatura ambiente, mostra claramente duas regiões diferentes. As propriedades de isolamento dos filmes são dependentes do eletrodo inferior. A densidade de corrente de fuga diminuiu para os filmes depositados sobre o eletrodo inferior. Uma redução na densidade de corrente de fuga pode ser atribuída à elevada afinidade do oxigênio pelo LSCO de forma que o oxigênio do material do eletrodo seja consumido pelo material ferroelétrico, deixando assim uma camada deficiente em oxigênio do eletrodo na interface e aumentando a resistência. Uma vez que a condutividade é fortemente influenciada pelas características da interface filme - eletrodo, a corrente de fuga inferior observada nesse caso, pode provavelmente ser atribuída a diferenças no tamanho de grãos, densidade e orientação preferida devido a diferenças no material ferroelétrico e a interface. A densidade de corrente aumenta linearmente com a tensão externa na região de baixa tensão o que sugere uma condução ôhmica. A densidade de corrente aumenta exponencialmente o que implica que pelo menos uma parte da condutividade é do tipo Schottky ou Poole - Frenkel. A densidade de corrente de fuga a 5,0 V é de 10^{-10} (LSCO) e de 10^{-8} A/cm² (Pt). A principal razão para um valor tão pequeno pode ser atribuída às alterações da rugosidade da superfície e à redução de microfissuras, devido a modificações na estabilidade da interface no eletrodo óxido. Assim, o eletrodo inferior de LSCO reduz as vacâncias de oxigênio, melhorando o processo de reversão dos domínios ferroelétricos. Curvas de histerese em temperatura ambiente para filmes de BLFO015 depositados sobre LSCO e Pt revelam uma curva bem saturada para o filme depositado em LSCO com $P_r \sim 34 \mu\text{C} / \text{cm}^2$ após a aplicação de uma tensão de 10 V. Nenhum sinal de corrente de fuga foi observado. No entanto, para o filme depositado sobre o eletrodo de Pt, a carga presa (O_2) associada a outros defeitos ($V_0 \dots$) ou dipolos complexos, como vacâncias de oxigênio associadas a vacâncias de bismuto ($V'''_{\text{Bi}} - V_0 \bullet\bullet$) localizadas no controno de grão e na interface filme - eletrodo pode promover um desvio da estequiometria local e influenciar na forma das curvas de histerese. Como consequência destas cargas espaciais, uma mudança significativa ao longo do eixo do campo elétrico para a polarização positiva, que é definida como “imprint”, pode levar a uma falha do capacitor. Um ciclo de histerese mais simétrico é observado para o filme depositado sobre LSCO, indicando que a alta afinidade desse óxido pelo oxigênio deste material evita a migração das cargas espaciais para a interface do filme. Esse comportamento pode ser atribuído aos grãos maiores dos BLFO015 depositados sobre LSCO. As paredes de domínios em grãos maiores são mais fáceis de serem ligadas em campo externo. A reversão da polarização em filmes com pequenos grãos é geralmente mais difícil, como é o caso do eletrodo de Pt. Portanto, o crescimento do filme numa direção não coincidente com a orientação preferencial no eixo *c*

vai favorecer grãos maiores como os observados para o LSCO, conduzindo a um E_c inferior quando comparado com o filme sobre Pt. O filme fino de BLFO015 depositado sobre Pt exibe um ciclo de histerese pouco saturado, que tipicamente é observado para cerâmicas condutoras, devido a uma grande corrente de fuga. As propriedades ferrelétricas do filme fino de BLFO015 podem estar ligadas a dois fatores principais: aumento no espaçamento entre os octaedros de oxigênio devido ao maior tamanho do átomo de La, e diminuição do tamanho do grão com o eletrodo de Pt, uma vez que a força de polarização é fortemente relacionada com o tamanho de grão. Verificou-se que a polarizabilidade em perovskitas (ABO_3) está parcialmente relacionada com os tamanhos dos cátions A e B. Em geral, um cátion grande permite um aumento na polarizabilidade, uma vez que leva a um maior espaçamento e afetando os octaedros de oxigênio. O aumento da polarização remanescente para os filmes finos de BLFO015 depositados sobre LSCO eletrodo inferior pode ser explicado pela substituição do La (1,172 Å) por parte do íon Bi (1,03 Å). No caso do filme depositado sobre Pt, a fração volumétrica diminui a polarização dielétrica com a redução do tamanho dos grãos afetando a polarização remanescente. Resistência à fadiga foi observada em até 10^8 ciclos para o eletrodo inferior de LSCO, sugerindo um bom potencial para aplicações em memórias ferroelétricas. Este resultado indica que se há acúmulo de vacâncias de oxigênio perto da interface filme - eletrodo durante a fadiga, o óxido condutor pode fornecer o oxigênio para essas vacâncias, alterando sua estequiometria e, assim, o acúmulo de vacâncias de oxigênio próximos da interface é evitado ou reduzido. Por outro lado, os filmes baseados em BLFO015 depositados sobre eletrodo de Pt revelam um aumento na corrente local em torno dos locais de nucleação, o que pode danificar a interface filme - eletrodo e suprimir a nucleação dos domínios orientadas opostamente à superfície. Nesse filme um aumento na polarização de comutação leva a um aumento local da condutividade na região de interface. A polarização comutável do filme de BLFO015 depositado sobre Pt mostra 25,0% de decaimento após 10^8 ciclos de polarização. Esse filme também apresentou boas características de retenção, retendo 94% dos valores medidos em $t = 1 \times 10^4$ s para um campo elétrico aplicado de 150 kV/cm. A redistribuição de cargas de polarização pelos defeitos deve ser considerada para explicar essa pequena perda de retenção. O coeficiente magnetolétrico em função do campo magnético de polarização nas direções longitudinais e transversais revela comportamento histerético, conforme observado nos ciclos de campo magnético. O coeficiente máximo magnetoelétrico de 12V / cmOe na direção longitudinal é muito maior do que o previamente relatado para filmes finos (3 V/cmOe) na mesma direção, a campo nulo (139). Essa é uma consequência do eixo antiferromagnético do BLFO que gira através do cristal, com um período de

comprimento de onda incomensurável de $\sim 620 \text{ \AA}$ (140). A magnetização para o filme foi observada com um campo magnético de $2,5 \text{ emu / g}$, sugerindo que a propriedade magnética de filmes finos de BLFO é aumentada não apenas pela restrição epitaxial, mas também pela homogeneização do arranjo espacial de rotação induzido pelo La (141). Como pode ser visto, a magnetização do nosso filme cresce linearmente com o campo magnético aplicado. Esse comportamento é característico de um material antiferromagneto e pode ser alterado através da introdução de uma pequena fração de terras raras que irá alterar a estrutura magnética do BFO. As alterações que ocorrem nas propriedades magnéticas podem ser explicadas não só por diferentes momentos magnéticos e raio do íon lantânio (o átomo de La não possui qualquer momento magnético intrínseco), como também pela anisotropia dos momentos magnéticos dos íons lantânio. A presença de um leve momento ferromagnético deve estar relacionada a um mecanismo de troca de spins que causa supressão induzida por modulação espiral. O momento magnético do lantânio pode não contribuir para magnetização remanescente e coercitividade. Os baixos campos magnéticos coercitivos do filme de BLFO são indicativos de sua natureza magneticamente suave (142). As estruturas de domínios ferroelétricas observadas no filme por microscopia de força piezoelétrica (MFP) sugerem que esses domínios consistem de uma mistura de um estado de múltiplos domínios dispostos de 71° e 180° . O fato de os domínios crescerem em vários estados é uma consequência da espessura de filmes, que é perto de 300 nm . Dessa forma, o lantânio age reduzindo a energia de deformação e os defeitos carregados. Os resultados da pesquisa foram publicados no artigo que consta no anexo B1 (SIMÕES, A. Z., Filiberto Gonzalez Garcia, MOURA, F. Magnetoelectric Coefficient in Strontium Ruthenate Buffered Lanthanum Modified Bismuth Ferrite Thin Films Grown by Chemical Method. **Journal of Scanning Probe Microscopy**., v.4, p.1 - 6, 2010).

É bem sabido que o tipo de dopante afeta a morfologia dos filmes e consequentemente as propriedades elétricas. Nesse sentido, filmes de ferrita de bismuto dopadas com Ca foram estudadas visando aplicação em memórias de múltiplos estados. A adição de Ca fase multiferróica leva à mudança no comportamento semicondutor no contorno de grão levando ao efeito resistivo. Dados de difração de raios X para os filmes de BFO puro e dopados com Ca sugerem somente picos relacionados as fases cristalinas BFO indicando que a substituição do Bi pelo Ca não conduz à formação de fases secundárias. A transformação dos picos (100) e (200), em dois dubletes indica mudança de estrutura cristalina de romboédrica para tetragonal. Essa fase foi identificada utilizando a ficha cristalográfica JCPDS (International Centre for Diffraction Data - 86-1518), o que leva a presença da fase referente ao BiFeO_3 . Além da fase

BFO, um pico de alta intensidade pertencente ao substrato de platina recoberto com silício (111) em $2\theta = 40^\circ$ foi identificado. Independente da rota utilizada, somente os picos referentes à fase BFO foram detectados, sugerindo que a rota de cristalização não conduz ao aparecimento de fases secundárias conduzindo a um filme policristalino. A espessura dos filmes não variou significativamente em função da adição de cálcio, mostrando que o método empregado na preparação das resinas permite controle dos parâmetros de processamento, como viscosidade, concentração iônica e densidade das soluções. A morfologia da superfície do filme de BFO puro e dopado com Ca mostra que o aumento da concentração de Ca promove a densificação dos filmes pela redução dos poros intergranulares, levando a um filme com grãos na forma de placas típicos da estrutura de camadas de bismuto e com morfologia homogeneamente distribuída. Os filmes de BiFeO_3 puros e dopados com Ca, depositados sobre substrato de $\text{Pt/TiO}_2/\text{SiO}_2/\text{Si}$ e tratados a 500°C por 2 horas foram caracterizados por microscopia de força atômica quanto à morfologia e à rugosidade superficial. A adição de Ca ao BiFeO_3 puro conduz a um tamanho de grão homogêneo com distribuição uniforme na superfície, reduzindo sua magnitude. Os filmes de BFO puro e dopado com concentrações menores que 10 mol % apresentam partículas com morfologia esférica, para concentrações acima de 0,10 de Ca apresentam grãos alongados. As medidas ferroelétricas desses filmes foram investigadas com um analisador ferroelétrico para frequência de 100 Hz e uma voltagem aplicada da ordem de 40 V. Observam-se curvas pouco saturadas com uma polarização remanescente que varia de 0,05 a $60 \mu\text{C}/\text{cm}^2$ e voltagem de operação de 1,0 a 30 V. A ausência de saturação dessas curvas em baixas frequências indicam que as perdas são elevadas sugerindo um filme altamente condutor. As curvas de histerese para os filmes dopados com cálcio apresentam-se mais saturadas. Pode ser observado que a adição de cálcio até a fração de $x = 0,30$ conduz a uma maior polarização remanescente a uma menor voltagem de operação do filme ferroelétrico. Verifica-se que a polarização remanescente é muito maior que aquela esperada para filmes orientados no eixo c do BFO e pode ser atribuída à presença de componentes de polarização no eixo a conforme visto por DRX. Pode-se notar que as curvas de histerese apresentam um deslocamento ao longo do eixo do campo coercitivo em direção ao lado positivo, fenômeno esse conhecido com “imprint”. A variação na voltagem pode causar uma falha do capacitor devido à aparente perda de polarização em um dos estados remanescentes. Consequentemente, pode ocorrer um aumento no campo coercitivo em uma direção. Esses dois efeitos podem causar falha de memória do capacitor e são compatíveis com os dados apresentados de medidas $C-V$. A origem da condução elétrica se deve às vacâncias de oxigênio criadas para manter a neutralidade de carga, que são críticas para

compreender o comportamento de condução. A ionização de vacâncias de oxigênio em amostras de BiFeO_3 dopados com Ca surge para compensar as lacunas introduzidas pelo dopante para manter o estado de valência $3+$ dos íons de ferro. As vacâncias de oxigênio são cargas móveis positivas, que podem mover-se pela amostra sob campos elétricos elevados, visando atingir o equilíbrio termodinâmico. Por exemplo, vacâncias de oxigênio podem mover-se e se acumulam perto da superfície para as condições de polarização de íons negativos. Como resultado, o oxigênio doador e os íons de cálcio aceitadores são localmente desequilibrados; assim, a região da superfície tem caráter semicondutor tipo n , enquanto que a região próxima ao eletrodo de base torna-se tipo p . Aplicando-se um campo elétrico oposto ao fluxo de vacâncias de oxigênio, estas se movem para as lacunas, formando assim um isolante eletrônico.

As curvas C - V obtidas para os filmes de BFO puro e dopado com cálcio e tratados a 500°C por 2 horas, contendo 10 camadas indicam dependência não linear da voltagem o que confere propriedades ferroelétricas dos filmes, resultado da reversão dos domínios. Pelo fato de a curva para o filme de BFO ser simétrica ao redor da voltagem nula, pode-se dizer que estes filmes apresentam poucos íons móveis e cargas acumuladas na interface filme-substrato, embora os defeitos cristalinos dificultem a reversão dos domínios levando à saturação da polarização. As curvas são simétricas ao redor da voltagem zero indicando que os filmes contem pequena quantidade de cargas espaciais acumuladas na interface filme-eletrodo. As curvas de C - V para os filmes dopados indicam assimetria nos valores máximos de capacitância, que podem ser observados pelo mecanismo de reversão de domínios ferroelétricos. Isso sugere a presença de cargas aprisionadas na interface filme-eletrodo. Novos estudos dos filmes depositados em eletrodos óxidos estão em andamento visando inibir a formação de cargas espaciais na interface filme-eletrodo. Vale a pena destacar que, para algumas curvas de histerese, a saturação dos domínios ocorre em menores voltagens, quando comparadas às curvas de C - V . Este fato pode ser explicado pela diferença nas frequências de medida das curvas de histerese e capacitância em função da voltagem. Considerando que a polarização e a capacitância dependem da frequência pode-se atribuir uma diferente cinética de reversão dos domínios ferroelétricos o que reflete fortemente no formato das curvas. As medidas de J - V desses filmes foram realizadas usando o equipamento *radiant technology* no modo de voltagem-corrente, variando de 0 a $+10\text{V}$, e $+10$ a -10V , voltando novamente a 0V . As curvas para estes filmes foram medidas com passos de voltagem de $0,1\text{ V}$ e tempo de $1,0\text{ s}$ para cada voltagem. Na primeira região a densidade de corrente aumenta linearmente com o campo elétrico externo na região de baixa voltagem, sugerindo uma condução ôhmica.

Para altas voltagens a densidade de corrente aumenta exponencialmente, o que implica que pelo menos uma parte da condutividade resulta do mecanismo de emissão do tipo Schottky ou Poole-Frenkel. A densidade de corrente a 1,0 V diminui com o aumento da concentração de cálcio. Alguns fatores podem contribuir para essa melhora. Primeiramente a redução do tamanho médio de grão com o aumento da concentração de cálcio. Considerando que a condutividade é fortemente afetada pela característica da interface filme-substrato, a morfologia dos filmes de BFO puros e dopados com Ca é uma das maiores causas do aumento da densidade de corrente em capacitores ferroelétricos. Outra explicação pode ser a redução das microtrincas causadas pela tensão residual. Uma vez que a estrutura ortorrômbica e a transição de fase diminuem com o aumento na concentração de cálcio, o volume da célula unitária durante o resfriamento diminui e a tensão residual aumenta (143). J. Liu et al. (144) depositaram filmes de BFO com Ce e Zr e observaram que a adição dos dopantes reduz a corrente de fuga drasticamente devido à co-substituição no sítio do Bi e do Fe. Os autores constataram uma corrente de fuga da ordem de $7.99 \times 10^{-5} \text{ A/cm}^2$ para um campo elétrico de 150 kV/cm. Em outra pesquisa X.J. Meng et al. (145) reportou uma redução na densidade de corrente de 10^{-3} para o BFO para 10^{-6} para filmes dopados com Sm e Cr pelo método de deposição de solução química. A ligeira diminuição nos valores de densidade de corrente pode ser atribuída a diferenças de tamanho e forma dos grãos, densidade e estrutura de superfície devido às diferenças durante a adição do dopante. As características da interface filme-eletrodo e da morfologia de superfície dos filmes de BFO são os maiores fatores que determinam a densidade de corrente para capacitores do tipo metal-ferroelétrico-metal. (216)

Os resultados deste artigo são encontrados no anexo C1 (COSTA, L.V., DEUS, R.C., FOSCHINI, C.R., Longo, E., CILENSE, M., **SIMÕES, A.Z.** Experimental evidence of enhanced ferroelectricity in Ca doped BiFeO₃. **Materials Chemistry and Physics**. v.144, p.476 - 483, 2014).

5 CONSIDERAÇÕES FINAIS

Considerando todos os aspectos analisados durante estes anos trabalhando com síntese química de cerâmicas e filmes finos com composição complexa, podemos apresentar a opinião bastante otimista de que, sem dúvida o avanço da tecnologia eletroeletrônica está na otimização de sistemas hoje tidos como potencialmente aplicáveis.

Analisando os sistemas perovskitas ferroelétricos e multiferróicos com os quais mais trabalhamos, como $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ podemos observar que o método químico permite usar as características dos elementos com sua eletronegatividade e sua capacidade de ser formador da rede cristalina, como elementos básico, para atuar na estabilidade dos complexos polióxidos. Essa capacidade química dos elementos não pode ser utilizada se o processo de síntese for via óxidos ou mesmo por um método químico que não permita ao pesquisador de atuar modificando suas características individuais. A precipitação química não permite controlar características como Kps dos sais ou hidróxidos individuais, o que gera heterogeneidade. Nesse caso, trabalhar com materiais de composição complexa se torna inviável. Podemos afirmar que é necessário respeitar as características de cada elemento e podemos fazer isso utilizando um método que mantém todos os elementos presos a uma única molécula de forma estável. Quando pensamos nesse sentido, temos que considerar um polímero que tenha a capacidade de fixar metais de forma que estes utilizem sua memória química, estruturando-se no polímero com estabilidade e posições diferentes. Isso é formar fases como $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BiFeO_3 , PZT, $\text{CaBi}_2\text{Nb}_2\text{O}_9$ e outras sem a cristalização de fases deletérias, que se formam preferencialmente quando usamos mistura de óxidos ou coprecipitação.

Quanto às características morfológicas e à reatividade superficial, também podemos interferir e, portanto, controlar segundo nossas necessidades ou objetivos. A concentração dos reagentes formadores da cadeia polimérica, a temperatura de decomposição e a atmosfera utilizada durante a combustão do polímero determinam a reatividade dos óxidos dos metais que se formam inicialmente complexados. O controle da cristalização das fases secundárias e da morfologia permite ampliar o universo de aplicação dos pós cerâmicos desde sua compactação e sinterização em temperaturas menores com menor variação da estequiometria até sua aplicação em filmes espessos, catalisadores, sensores, etc.

Quanto ao uso de métodos químicos para obtenção de filmes, por dip-coating ou spin-coating, o sucesso passa por um número muito grande de variáveis que exigem o controle rígido de parâmetros como: composição, concentração, viscosidade, temperatura e tempo de

tratamento do filme. As características das soluções são determinantes na morfologia, superfície, densidade e cristalinidade dos filmes. A vantagem que queremos destacar está na possibilidade de se trabalhar com concentração mínima de aditivos, de poder depositar camadas de diferentes materiais, tipo heteroestruturas, de poder tratar todas as camadas de uma só vez ou tratá-las separadas. Essas variáveis permitem obter filmes com características diferentes segundo suas aplicações. A versatilidade do método permite inclusive utilizar substratos menos nobres e obter filmes texturizados ou orientados preferencialmente, utilizando o artifício da camada semente.

Mesmo os materiais mais complexos e instáveis como a ferrita de bismuto foram formados com o controle do processamento e a flexibilidade dos métodos químicos. A estequiometria, a morfologia e a reprodutibilidade se mostraram controláveis. Portanto, podemos dizer que independente do custo, tempo e rendimento, a qualidade, a flexibilidade e a eficiência dos processos químicos são indiscutíveis.

REFERÊNCIAS

- (1) HELMONT, J. B., **Opuscula medica inaudita**. Amsterdam: Elzevir, 1648, 313p.
- (2) ORDWAY, J. M., Waterglass. **American Journal of Science**, New Haven, v. 32, p. 153-165, nov. 1861.
- (3) VAUQUELIN, L. N., Mémoire sur une nouvelle substance métallique, contenue dans le plomb rouge de Sibérie, et qu'on propose d'appeler chrome, **Annales de chimie et de physique**, Paris, v. 22, p. 179, 1797.
- (4) BERTHIER, M. P., Sur la Préparation de la Zircône et du Titane, **Annales de chimie et de physique**, Paris, v. 50, p. 362-375, 1832.
- (5) EBELMEN, J. J., Sur les éthers siliciques, **Comptes rendus de l'Académie des Sciences**, Paris, v. 19, p. 398-400, 1844.
- (6) GRIMAUUX, M. E. Sur l'éthylate ferrite et l'hydrate ferrite colloïdal **Comptes rendus de l'Académie des Sciences**, Paris, v. 98, p. 105-106, 1884.
- (7) RING, T. **Fundamentals of Ceramic Powder Processing and Synthesis**. San Diego: Academic Press, 1996. 961 p.
- (8) CAHN, R. W. Nanostructures come of age. **Nature**, London, v. 359, p. 591-592, out. 1992.
- (9) BURGGRAAF, A. J., KEIZER, K., VAN HASSEL, B. A. Ceramic nanostructure materials, membranes and composite layers. **Solid State Ionics**, Amsterdam, v. 32-33, p. 771-782, feb./mar. 1989.
- (10) LUTH, H. Nanostructures and semiconductor electronics. **Physica Status Solidi B**, Weinheim, v. 192, n.2, p. 287-299, sept. 1995.
- (11) HENCH, L. L., WEST, J. K., **Chemical processing of advanced materials**, New York: John Wiley & Sons, 1992, 513 p.
- (12) MOON, J. *et al.* Particle-shape control and formation mechanisms of hydrothermally derived lead titanate. **Journal of Materials Research**, New York, v. 14, n. 3, p. 866-875, mar. 1999.
- (13) MOON, J. *et al.* Hydrothermal synthesis of perovskites from chemically modified titanium isopropoxide and acetate salts. **Journal of Materials Research**, Cambridge, v. 14, n. 2, p. 425-435, feb. 1999.
- (14) PETERSON, C. R., SLAMOVICH, E. B., Effect of processing parameters on the morphology of hydrothermally derived PbTiO₃ powders. **Journal of the American Ceramic Society**, Westerville, v. 82, n. 7, p. 1702-1710, jul. 1999.

- (15) ROEDER, R. K., SLAMOVICH, E. B., Stoichiometry control and phase selection in hydrothermally derived $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ powders. **Journal of the American Ceramic Society**, Westerville, v. 82, n. 7, p. 1665-1675, jul. 1999.
- (16) QI, J. Q. *et al.* Direct large-scale synthesis of perovskite barium strontium titanate nano-particles from solutions. **Journal of Solid State Chemistry**, Amsterdam, v. 178, n.1, p. 279-284, jan. 2005.
- (17) MOULSON, A. J., HERBERT, J. M., **Electroceramics: Materials, Properties and Applications**, London: Chapman & Hall, 1993, 576 p.
- (18) UNITED STATE PATENTS (USA) Pechini Maggio P. Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor, U. S. Patent 3.330.697, 26 aug. 1963, 11 jul. 1967.
- (19) MESSING, G. L. *et al.* **Ceramic Transactions: Ceramic Powder Science II**, Westerville: American Ceramic Society, 1987, 592 p.
- (20) RAVAINÉ, S. *et al.* Photochemical generation of gold nanoparticles in Langmuir–Blodgett films. **Langmuir**, Washington DC, v. 14, n. 3, p. 708-713, jan. 1998.
- (21) WHIPPS, S. *et al.* Growth of calcium oxalate monohydrate at phospholipid Langmuir monolayers, **Journal of Crystal Growth**, Amsterdam, v. 192, n. 1-2, p. 243-249, aug. 1998.
- (22) BONANNI, A. *et al.* Control of morphology changes in self-assembled Mn-based nanostructures overgrown with mismatched material, **Applied Physics Letters**, Melville, v. 74, n. 24, p. 3732, jun. 1999.
- (23) OSSEO-ASARE, K. *et al.* Microemulsion-mediated synthesis of nanosize Molybdenum sulfide coal liquefaction catalysts. In: Marcel Dekker Inc., P. **Handbook of Microemulsion Science and Technology**. New York: CRC Press, 1999, p. 549-603.
- (24) LEV, O. *et al.* Sol–Gel Materials in Electrochemistry, **Chemistry of Materials**, Washington DC, v. 9 n. 11, p. 2354-2375, nov. 1997.
- (25) KLEIN, L. C., **Sol-gel Optics: Processing and Applications**. New York: Springer Science & Business Media, 1994, 592 p.
- (26) EDELSTEIN, A. S., CAMMARATRA, R. C., **Nanomaterials: Synthesis, Properties and Applications**. Bristol: CRC Press, 1996, 616p.
- (27) LANGE, F. F., Chemical Solution Routes to Single-Crystal Thin Films, **Science**, Washington DC, v. 273, n. 5277, p. 903-909, aug. 1996.
- (28) MANN, S. **Biomimetic Materials Chemistry**. Nova Iorque: Wiley, 1995, 400 p.

- (29) BUNKER, B. C. *et al.* Ceramic thin-film formation on functionalized interfaces through biomimetic processing, **Science**, Washington DC, v. 264, n. 5155, p. 48-55, mar. 1994.
- (30) PHILP, D., STODDART, J. F., Self-assembly in natural and unnatural systems, **Angewandte Chemie International Edition in English**, Weinheim, v. 35, n. 11, p. 1155-1196, jun. 1996.
- (31) LIU, J. *et al.* Self-assembly in the synthesis of ceramic materials and composites, **Advances in Colloid and Interface Science**, Amsterdam, v. 69, n. 1-3, p. 131-180, dec. 1996.
- (32) OZIN, G. A., Nanochemistry: Synthesis in diminishing dimensions, **Advanced Materials**, Weinheim, v. 4, n. 10, p. 612-649, oct. 1992.
- (33) MANN, S., Molecular tectonics in biomineralization and biomimetic materials chemistry, **Nature**, London, v. 365, p. 499-505, oct. 1993.
- (34) TAKAHASHI, S. *et al.* Internal Electrode Piezoelectric Ceramic Actuators, **Ferroelectrics**, London, v. 50, n. 1, p. 181-190, 1983.
- (35) SMOLENSKII, G. A., AGRANOVSKAYA, A. I., Dielectric polarization of a number of complex compounds, **Soviet Physics-Solid State**, St. Petersburg, v. 1, n.10, p. 1429-1437, 1960.
- (36) KANEGAE, T. SAKATA, K., TAKENAKA, T., $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -Based Piezoelectric and Electrostrictive Ceramics, **Japanese Journal of Applied Physics**, Tokyo, v. 30, n. 9B, p. 2232-2235, sept. 1991.
- (37) UCHINO, K., Electrostrictive actuators: materials and applications, **American Ceramic Society Bulletin**, Westerville, v. 65, n. 4, p. 647-652, 1986.
- (38) WHATMORE, R. W., OSBOND, P. C., SHORROCKS, N. M., Ferroelectric materials for thermal IR detectors, **Ferroelectrics**, London, v. 76, n. 1, p. 351-367, 1987.
- (39) HAERTLING, G. H., PLZT reflective displays, **Ferroelectrics**, London, v. 50, n. 1, p. 63-72, 1983.
- (40) BUTCHER, S. J., THOMAS, N. W., Ferroelectricity in the system $\text{Pb}_{(1-x)}\text{Ba}_x(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, **Journal of Physics and Chemistry of Solids**, Amsterdam, v. 52, n. 4, p. 595-601, 1991.
- (41) HAERTLING, G. H., Ferroelectric ceramics: History and Technology, **Journal of the American Ceramic Society**, Westerville, v. 82, n. 4, p. 797-818, april 1999.
- (42) KIM, N. K., Synthesis chemistry of MgNb_2O_6 and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, **Materials Letters**, Amsterdam, v. 32, n. 2-3, p. 127-130, aug. 1997.

- (43) CAVALHEIRO, A. A. *et al.* Influence of Synthesis and Processing Parameters of the Columbite Precursor on the Amount of Perovskite PMN, **Materials Research**, São Carlos, v. 2, n. 4, p. 255-260, oct. 1999.
- (44) CAVALHEIRO, A. A., BERTOCHI, M. A. Z., VARELA, J. A., Efeito da adição de dopantes durante a síntese do precursor columbita para a preparação da cerâmica ferroelétrica relaxora PMN, **Cerâmica**, São Paulo, v. 45, n. 296, p. 188-192, dec. 1999.
- (45) MAZON, T., *et al.* Influence of seed particle frequency on the phase formation and on the microstructure of 0.88 PZN-0.07 BT-0.05 PT ceramic, **Ceramics International**, Amsterdam, v. 26, n. 7, p. 727- 731, aug. 2000.
- (46) SPAGNOL, P. D., ZAGHETE, M.A., VARELA, J.A., LONGO, E., Evidence of hetero-epitaxial growth of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ on the BaTiO_3 seed particles of a citrate solution, **Materials Chemistry and Physics**, Amsterdam, v. 77, n.3, p 918-923, jan. 2003.
- (47) KHAN, A. *et al.* Growth of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -35mol% PbTiO_3 Single Crystals from (111) Substrates by Seeded Polycrystal Conversion, **Journal of the American Ceramic Society**, Westerville, v. 82, n. 11, p. 2958-2962, nov. 1999.
- (48) FOUSEK, J. Ferroelectricity: Remarks on historical aspects and present trends, **Ferroelectrics**, London, v. 113, n.1, p. 3-20, 1991.
- (49) LARBOT, A. *et al.* Elaboration and characterization of lead perovskites from colloidal solution, **Journal of Non-Crystalline Solids**, Amsterdam, v. 147-148, p. 74-79, 1992.
- (50) NOHEDA, B. *et al.* New features on the morphotropic phase boundary in the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ system, **Ferroelectrics**, London, v. 237, n.1, p. 237-244, 2000.
- (51) YAMAZAKI, T. *et al.* Thermal Behavior and Phase Transition in PZT near the Morphotropic Phase Boundary, **Ferroelectrics**, London, v. 266, n.1, p. 139-151, 2002.
- (52) KULCSAR, F. Electromechanical Properties of Lead Titanate Zirconate Ceramics with Lead Partially Replaced by Calcium or Strontium, **Journal of the American Ceramic Society**, Westerville, v. 42, n.1, p. 49-51, jan. 1959.
- (53) WESTON, T. B., WEBSTER, A. H., MCNAMARA, V. M. Lead zirconate-lead titanate piezoelectric ceramics with iron oxide addition, **Journal of the American Ceramic Society**, Westerville, v. 52, n. 5, p. 253-257, may 1969.
- (54) ATKIN, R. B., HOLMAN, R. L., FULRATH, R. M., Substitution of Bi and Nb ions in lead zirconate-titanate, **Journal of the American Ceramic Society**, Westerville, v. 54, n. 2, p. 113-115, feb. 1971.
- (55) UCHIDA, N., IKEDA, T., Studies on $\text{Pb}(\text{Zr-Ti})\text{O}_3$ ceramics with addition of Cr_2O_3 , **Japanese Journal of Applied Physics**, Tokyo, v. 6, n.11, p. 1292-1299, jun. 1967.

- (56) SMITH, J. W., CROSS, L. E., A macroscopic theory for the dielectric properties of lead magnesium niobate, **Ferroelectrics**, London, v. 1, n. 1, p. 137-140, 1970.
- (57) DAVIES, P. K., AKBAS, M. A., Chemical order in PMN-related relaxors: structure, stability, modification and impact on properties, **Journal of Physics and Chemistry of Solids**, Amsterdam, v. 61, n. 2, p. 159-166, feb. 2000.
- (58) HUANG, J., CHASTEEN, N. D., FITZGERALD, J. J., X-band EPR studies of ferroelectric lead titanate (PT), piezoelectric lead magnesium niobate (PMN), and PMN/PT powders at 10 and 85 K, **Chemistry of Materials**, Washington DC, v. 10, n. 12, p. 3848-3855, nov. 1998.
- (59) ZHAO, J. *et al.* Neutron diffraction study of electrostrictive coefficients of prototype cubic phase of relaxor ferroelectric $(\text{PbMg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, **Applied Physics Letters**, Melville, v. 72, n.9, p. 1048-1050, marc. 1998.
- (60) COLLA, E. V., YUSHIN, W. K., VIEHLAND, D., Dielectric properties of $(\text{PMN})_{1-x}(\text{PT})_x$ single crystals for various electrical and thermal histories, **Journal of Applied Physics**, Melville, v. 83, n. 6, p. 3298, marc. 1998.
- (61) HAN, K., SKIM, S., KOO, H. J., New preparation method of low-temperature-sinterable perovskite $0.9 \text{ Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.1 \text{ PbTiO}_3$ powders and its dielectric properties, **Journal of the American Ceramic Society**, Westerville, v. 81, n. 11, p. 2998-3000, nov. 1998.
- (62) BROWN, S. A. *et al.* Electromechanical testing and modeling of a $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{PbTiO}_3 - \text{BaTiO}_3$ relaxor ferroelectric, **Journal of the American Ceramic Society**, Westerville, v. 79, n. 9, p. 2271-2282, sept. 1996.
- (63) ZHANG, Q. M. *et al.* An X-ray diffraction study of superlattice ordering in lead magnesium niobate, **Solid State Communications**, Amsterdam, v. 97, n. 8, p. 693-698, feb. 1996.
- (64) HUANG, J., CHASTEEN, N. D., FITZGERALD, J. J., X-band EPR studies of ferroelectric lead titanate (PT), piezoelectric lead magnesium niobate (PMN), and PMN/PT powders at 10 and 85 K, **Chemistry of Materials**, Washington DC, v. 10, n. 12, p. 3848-3855, nov. 1998.
- (65) BELLAICHE, L., VANDERBILT, D., Intrinsic piezoelectric response in perovskite alloys: PMN-PT versus PZT, **Physical Review Letters**, Ridge, v. 83, n. 7, p. 1347-1350, aug. 1999.
- (66) KELLY, J. *et al.* Effect of composition on the electromechanical properties of $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3$ ceramics, **Journal of the American Ceramic Society**, Westerville, v. 80, n. 4, p. 957-964, apr. 1997.
- (67) VILLEGAS, M. *et al.* Perovskite phase formation in the $\text{Pb Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3 - \text{PbZrO}_3 - \text{PbTiO}_3$ system by the columbite route, **Journal of Materials Science**, Heidelberg, v. 30, n. 5, p. 1391-1396, jan. 1995.

- (68) AURIVILLIUS, B., Mixed bismuth oxides with layer lattices. 1. Structure type of $\text{CaNb}_2\text{Bi}_2\text{O}_9$, **Arkiv foer Kemi**, v. 1, p. 463-480, 1949.
- (69) SMOLENSKY, G. A., ISUPOV, V. A., AGRANOVSKAYA, A. I., A new group of ferroelectrics (with layered structure), **Soviet Physics-Solid State**, St. Petersburg, v. 1, n.1, p. 149-150, 1959.
- (70) ARAUJO, C. A. P. *et al.* Fatigue-free ferroelectric capacitors with platinum electrodes, **Nature**, London, v. 374, p. 627-629, Apr. 1994.
- (71) SYMETRIX CORPORATION (USA). Carlos A. Paz de Araújo, Joseph D. Cuchiaro, Michael C. Scott, Larry D. McMillan. Layered superlattice materials applications. Geneva Switzerland. World Intellectual Property Organization Patent Publication No. WO 93/12542, 12 dec. 1991, 24 jun. 1993.
- (72) TANAKA, M. *et al.* The Crystallization Path of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ from Sr-Bi-Ta-O MOD Precursors, **Materials Research Bulletin**, Amsterdam, v. 33, n. 5, p. 789-794, may 1998.
- (73) ZHANG, Z. G. *et al.* Fatigue characteristics of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by metalorganic decomposition, **Applied Physics Letters**, Melville, v. 73, n. 6, p. 788-790, aug. 1998.
- (74) ZHANG, Z. G. *et al.* Structure and voltage dependence of ferroelectric properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Journal of Applied Physics**, Melville, v. 85, n. 3, p. 1746-1749, feb. 1999.
- (75) OSAKA, T. *et al.* Phase transition in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films with change of heat-treatment temperature, **Japanese Journal of Applied Physics**, Tokyo, v. 37, n. 2, p. 597-601, feb.1998.
- (76) OSAKA, T. *et al.* Control of crystal orientation of ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films with multi-seeding layers, **Japanese Journal of Applied Physics**, Tokyo, v. 39, n. 9B, p. 5476- 5480, sept. 2000.
- (77) FORK, D. K. *et al.* Thin film epitaxial oxide optical waveguides, In: **MRS Proceedings**. Cambridge University Press, Cambridge, v. 392, p. 189, jan. 1995.
- (78) HU, G. D. *et al.* Structure control and characterization of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films by a modified annealing method, **Applied Physics Letters**, Melville, v. 74, n. 9, p. 1221-1223, feb. 1999.
- (79) KIM, J. S. *et al.* The low temperature processing for removal of metallic bismuth in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Applied Surface Science**, Amsterdam, v. 140, n. 1-2 p. 150-155, feb. 1999.
- (80) Yi, J. H. *et al.* $\text{SrBi}_2\text{Nb}_2\text{O}_9$ Ferroelectric Powders and Thin Films Prepared by Sol-Gel, **Journal of Sol-Gel Science and Technology**, New York, v. 13, n. 1, p. 885-888, jan. 1998.

- (81) HU, G. D. *et al.* Structure control and characterization of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films by a modified annealing method, **Applied Physics Letters**, Melville, v. 74, n. 9, p. 1221-1223, feb. 1999.
- (82) ZHOU, Q. F., CHAN, H. L. W., CHOY, C. L., Synthesis and properties of ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ powder and films prepared by a sol-gel process, **Journal of Non-Crystalline Solids**, Amsterdam, v. 254, n. 1-3, p. 106-111, sept.1999.
- (83) OSAKA, T. *et al.* Structural defects in $\text{Sr}_{0.7}\text{Bi}_{2.3}\text{Ta}_2\text{O}_9$ thin film for ferroelectric memory, **IEICE Transactions on Electronics**, Tokyo, v. E81-C, n. 4, p. 545-551, apr. 1998.
- (84) YANG, P. *et al.* Pulsed laser ablation synthesis and ferroelectric properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Integrated Ferroelectrics: An International Journal**, Philadelphia, v. 20, n. 1-4, p. 79-86, 1998.
- (85) OGATA, N. *et al.* Fine-Grained $\text{SrBi}_2\text{Ta}_2\text{O}_9$ Thin Films by Low Temperature Annealing, **Japanese Journal of Applied Physics**, Tokyo, v. 37, n. 6A, p. 3481-3486, jun. 1998.
- (86) DINU, R. *et al.* Film structure and ferroelectric properties of in situ grown $\text{SrBi}_2\text{Ta}_2\text{O}_9$ films, **Applied Physics A**, Heidelberg, v. 69, n. 1, p. 55-61, jul. 1999.
- (87) NAGAHAMA, T. *et al.* Epitaxy of (106)-oriented $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin films, **Thin Solid Films**, Amsterdam, v. 353, n. 1-2, p. 52-55, sept.1999.
- (88) KOIWA, I. *et al.* Effect of Annealing Method to Crystallize on $\text{Sr}_{0.9}\text{Bi}_{2.3}\text{Ta}_2\text{O}_{9+\alpha}$ Thin Film Properties Formed from Alkoxide Solution, **Japanese Journal of Applied Physics**, Tokyo, v. 37, n. 1, p. 192-197, jan. 1998.
- (89) YEON, D. J., PARK, J. D., OH, T. S., Preferred orientation and ferroelectric properties of $\text{SrBi}_{2x}\text{Ta}_2\text{O}_9$ thin-films prepared by mod process, **Journal of Korean Physical Society**, Seoul, v. 32, n. 94, p. 1445-1447, jan.1998.
- (90) ZHU, J. *et al.* Size effects of $0.8\text{SrBi}_2\text{Ta}_2\text{O}_9 - 0.2\text{Bi}_3\text{TiNbO}_9$ thin films, **Journal of Applied Physics**, Melville, v. 83, n. 3, p. 1610-1612, feb. 1998.
- (91) ISHIKAWA, K., FUNAKUBO, H. Electrical properties of (001)- and (116)-oriented epitaxial $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by metalorganic chemical vapor deposition, **Applied Physics Letters**, Melville, v. 75, n. 13, p. 1970-1972, sept. 1999.
- (92) BAE, C. *et al.* Ex situ growth of the c-axis preferred oriented $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films on Pt/Ti/SiO₂/Si substrates, **Journal of Vacuum Science & Technology A**, Melville, v. 17, n. 5, p. 2957-2962, sept.1999.
- (93) RASTOGI, A. C., TIRUMALA, S., DESU, S. B., Plasma-assisted pulsed laser deposition of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films of improved ferroelectric and crystalline properties, **Applied Physics Letters**, Melville, v. 74, n. 23, p. 3492-3494, jun.1999.

- (94) YANG, C. H. *et al.* The Correlation Between Composition and Preferred Orientation of Ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ Thin Films, **Electrochemical and Solid-State Letters**, Pennington, v. 2, n. 1, p. 39-42, 1999.
- (95) BATTACHARYYA, S., JAMES, A. R., KRUPANIDHI, S. B., Role of growth conditions and Bi-content on the properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Solid State Communications**, Amsterdam, v. 108, n. 10, p. 759-763, nov. 1998.
- (96) LEE, J. K. *et al.* Electrical characterization of $\text{Pt/SrBi}_2\text{Ta}_2\text{O}_9/\text{Pt}$ capacitors fabricated by the pulsed-laser ablated deposition technique, **Journal of Vacuum Science & Technology A**, Melville, v. 14, n. 3, p. 900-904, may 1996.
- (97) PARK, Y. B. *et al.* Bismuth composition control of $\text{SrBi}_2\text{TaNbO}_9$ thin films by heat treating Bi_2O_3 -inserted heterostructure, **Journal of Materials Research**, Cambridge, v. 14, n. 7, p. 2986-2992, jul. 1999.
- (98) TANAKA, M. *et al.* The Crystallization Path of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ from Sr–Bi–Ta–O MOD Precursors, **Materials Research Bulletin**, Amsterdam, v. 33, n. 5, p. 789-794, may 1998.
- (99) ZHANG, Z. G. *et al.* Fatigue characteristics of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by metalorganic decomposition, **Applied Physics Letters**, Melville, v. 73, n. 6, p. 788-790, aug. 1998.
- (100) ZHANG, Z. G. *et al.* Structure and voltage dependence of ferroelectric properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Journal of Applied Physics**, Melville, v. 85, n. 3, p. 1746-1749, feb. 1999.
- (101) OSAKA, T. *et al.* Phase transition in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films with change of heat-treatment temperature, **Japanese Journal of Applied Physics**, Tokyo, v. 37, n. 2, p. 597-601, feb. 1998.
- (102) PISANI, C. *et al.* *Ab initio* Hartree–Fock perturbed cluster treatment of local defects in crystals, **The Journal of Chemical Physics**, Melville, v. 92, n. 12, p. 7448-7460, jun. 1990.
- (103) ABOUELLEIL, M. M., LEONBERGER, F. J., Waveguides in lithium niobate, **Journal of the American Ceramic Society**, Westerville, v. 72, n. 8, p. 1311-1321, aug. 1989.
- (104) MARSH, A. M. *et al.* Pulsed laser deposition of high quality LiNbO_3 films on sapphire substrates. **Applied Physics Letters**, Melville, v. 62, n. 9, p. 952-954, mar. 1993.
- (105) BOUQUET, V. *et al.* Epitaxially grown LiNbO_3 thin films by polymeric precursor method, **Journal of Materials Research**, Cambridge, v. 15, n. 11, p. 2446-2453, nov. 2000.
- (106) CHENG, S. D. *et al.* C-axis oriented sol-gel derived $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ thin films of Si(111) substrates, **Thin Solid Films**, Amsterdam, v. 365, n. 1, p. 77-81, apr. 2000.

- (107) MAJIMA, T. *et al.* High-rate deposition of $\text{LiNb}_{1-x}\text{Ta}_x\text{O}_3$ films by thermal plasma spray CVD, **Journal of Crystal Growth**, Amsterdam, v. 220, n. 3, p. 336-340, dec. 2000.
- (108) BORNAND, V. *et al.* LiNbO_3 and LiTaO_3 thin films deposited by chemical and/or physical processes. **Annales de Chimie Science des Materiaux**, Amsterdam, v. 26, n. 1, p. 49-54, jan.- feb. 2001.
- (109) BOUQUET, V. *et al.* LiNbO_3 Thin Films prepared from a Polymeric Precursor Method, **Key Engineering Materials**, Zurich, v. 132-136, p. 1143-1146, apr. 1997.
- (110) AURIVILLIUS, B., FANG, P. H., Ferroelectricity in the Compound $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$, **Physical Review**, Ridge, v. 126, n. 3, p. 893-896, may 1962.
- (111) RODRIGUEZ, M. A. *et al.* Formation of $\text{SrBi}_2\text{Ta}_2\text{O}_9$: Part II. Evidence of a bismuth-deficient pyrochlore phase, **Journal of Materials Research**, Cambridge, v. 11, n. 9, p. 2282-2287, sept. 1996.
- (112) NEWNHAM, R. E., WOLF, R. W., DORRIAN, J. F., Structural basis of ferroelectricity in the bismuth titanate family, **Materials Research Bulletin**, Amsterdam, v. 6, n. 10, p. 1029 - 1039, oct. 1971.
- (113) RAMESH, R. *et al.* Epitaxial Cuprate Superconductor/Ferroelectric Heterostructures, **Science**, Washington DC, v. 252, n. 5008, p. 944-946, may 1991.
- (114) NAGAHAMA, T. *et al.* Epitaxy of (106)-oriented $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin films, **Thin Solid Films**, Amsterdam, v. 353, n. 1-2, p. 52-55, sept. 1999.
- (115) WU, S. Y. *et al.* Domain structure and polarization reversal in films of ferroelectric bismuth titanate, **Ferroelectrics**, London, v. 3, n. 1, p. 217-224, may 1972.
- (116) RAMESH, R. *et al.* Epitaxial Cuprate Superconductor/Ferroelectric Heterostructures, **Science**, Washington DC, v. 252, n. 5008, p. 944-946, may 1991.
- (117) CHOOPUN, S., MATSUMOTO, T., KAWAI, T. Low temperature growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ epitaxial films on $\text{SrTiO}_3(001)$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8(001)$ single crystals by laser molecular beam epitaxy, **Applied Physics Letters**, Melville, v. 67, n. 8, p. 1072-1074, aug. 1995.
- (118) THEIS, C. D. *et al.* Adsorption-controlled growth of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by reactive MBE, **Applied Physics Letters**, Melville, v. 72, n. 22, p. 2817-2819, jun. 1998.
- (119) MITSUYA, M., NUKAGA, N., FUNAKUBO, H. Direct Preparation of Crystalline $\text{SrBi}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_9$ Thin Films by Thermal Metalorganic Chemical Vapor Deposition at Low Temperature, **Japanese Journal of Applied Physics**, Tokyo, v. 39, n. 8A, p. L822-L824, aug. 2000.
- (120) ISHIKAWA, K., FUNAKUBO, H. Electrical properties of (001)- and (116)-oriented epitaxial $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by metalorganic chemical vapor deposition, **Applied Physics Letters**, Melville, v. 75, n. 13, p. 1970 -1972, sept. 1999.

- (121) CUMMINS, S. E., CROSS, L. E., Electrical and Optical Properties of Ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Single Crystals, **Journal of Applied Physics**, Melville, v. 39, n. 5, p. 2268-2273, apr. 1968.
- (122) BUHAY, H. *et al.* Pulsed laser deposition and ferroelectric characterization of bismuth titanate films, **Applied Physics Letters**, Melville, v. 58, n. 14, p. 1470-1472, apr.1991.
- (123) ZANETTI, S. M. *et al.* An alternative chemical route for synthesis of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films, **Journal of Materials Research**, Cambridge, v. 15, n.10, p. 2091-2095, oct. 2000.
- (124) TAKENAKA, T., SAKATA, K., Electrical properties of grain-oriented ferroelectric ceramics in some lanthanum modified layer-structure oxides, **Ferroelectrics**, London, v. 38, n. 1, p. 769 -772, oct. 1981.
- (125) KIM, J. P. *et al.* Microstructure and Dielectric Properties of Lanthanum Bismuth Titanate Thin Films, **Journal of Korean Physical Society**, Seoul, v. 35, n. 95, p. S1202-S1205, dec. 1999.
- (126) ITO, Y. *et al.* New Low Temperature Processing of Sol-Gel $\text{SrBi}_2\text{Ta}_2\text{O}_9$ Thin Films, **Japanese Journal of Applied Physics**, Tokyo, v. 35, n. 9B, part 1, p. 4925 -4929, sept. 1996.
- (127) LEE, J. K. *et al.* Electrical characterization of $\text{Pt/SrBi}_2\text{Ta}_2\text{O}_9/\text{Pt}$ capacitors fabricated by the pulsed-laser ablated deposition technique, **Journal of Vacuum Science & Technology A**, Melville, v. 14, n. 3, p. 900-904, may 1996.
- (128) SCOTT, J. F., ARAUJO, C. A. P., Ferroelectric Memories, **Science**, Washington DC, v. 246, n. 4936, p. 1400-1405, dec.1989.
- (129) BUCHANAN, R. C. *et al.* Orientation effects on polarization and pyroelectric properties of ferroelectric thin films on Si, **Journal of the European Ceramic Society**, Amsterdam, v. 21, p. 1577-1580, aug. 2001.
- (130) WU, T. B., SHY, H. J., Deposition and properties of highly (100)-oriented barium titanate thin films on LaNiO_3 electrode, **Ceramics International**, Amsterdam, v. 26, n.6, p. 599-603, jul. 2000.
- (131) TEAGUE, J. R., GERSON, R., JAMES, W. J., Dielectric hysteresis in single crystal BiFeO_3 , **Solid State Communications**, Amsterdam, v. 8, n. 13, p. 1073-1074, jul. 1970.
- (132) NEATON, J. B. *et al.* First-principles study of spontaneous polarization in multiferroic BiFeO_3 , **Physical Review B**, Ridge, v. 71, n. 1, p. 014113-1 - 014113-8, jan. 2005.
- (133) WANG, J. *et al.* Epitaxial BiFeO_3 thin films on Si, **Applied Physics Letters**, Melville, v. 85, n. 13, p. 2574- 2576, sept. 2004.

- (134) YUN, K. Y., NODA, M., OKUYAMA, M. Prominent ferroelectricity of BiFeO₃ thin films prepared by pulsed-laser deposition, **Applied Physics Letters**, Melville, v. 83, n. 19, p. 3981-3983, nov. 2003.
- (135) PALKAR, V. R., JOHN, J., PINTO, R. Observation of saturated polarization and dielectric anomaly in magnetoelectric BiFeO₃ thin films, **Applied Physics Letters**, Melville, v. 80, n. 9, p. 1628-1630, mar. 2002.
- (136) QI, X. *et al.* Greatly reduced leakage current and conduction mechanism in aliovalent-ion-doped BiFeO₃, **Applied Physics Letters**, Melville, v. 86, n.6, p. 062903, feb. 2005.
- (137) LI, J. *et al.* Dramatically enhanced polarization in (001), (101), and (111) BiFeO₃ thin films due to epitaxial-induced transitions, **Applied Physics Letters**, Melville, v. 84, n. 25, p. 5261-5263, jun. 2004.
- (138) YUN, K. Y. *et al.* Giant ferroelectric polarization beyond 150 $\mu\text{C}/\text{cm}^2$ in BiFeO₃ thin film, **Japanese Journal of Applied Physics**, Tokyo, v. 43, n. 5A, part 2, p. L647, may 2004.
- (139) SINGH, S. K., ISHIWARA, H., MARUYAMA, K. Room temperature ferroelectric properties of Mn-substituted BiFeO₃ thin films deposited on Pt electrodes using chemical solution deposition, **Applied Physics Letters**, Melville, v. 88, n. 26, p. 262908, jun. 2006.
- (140) HU, G. D. *et al.* Effects of Gd substitution on structure and ferroelectric properties of BiFeO₃ thin films prepared using metal organic decomposition, **Applied Physics Letters**, Melville, v. 91, n. 23, p. 232909, dec. 2007.
- (141) UCHIDA, H. *et al.* Crystal structure and ferroelectric properties of rare-earth substituted BiFeO₃ thin films, **Journal of Applied Physics**, Melville, v. 100, n.1, p. 014106, jul. 2006.
- (142) WANG, Y., NAN, C. W., Enhanced ferroelectricity in Ti-doped multiferroic BiFeO₃ thin films, **Applied Physics Letters**, Melville, v. 89, n. 5, p. 052903, jul. 2006.
- (143) LUO, X. J. *et al.* The trap state relaxation related polarization in CaCu₃Ti₄O₁₂, **Journal of Applied Physics**, Melville, v. 108, n. 1, p. 014107, jul. 2010.
- (144) LIU, H., LIU, Z., YAO, K., Improved electric properties in BiFeO₃ films by the doping of Ti, **Journal of Sol-Gel Science and Technology**, New York, v. 41, n. 2, p. 123-128, feb. 2007.
- (145) MENG, X. J. *et al.* Growth of (1 0 0)-oriented LaNiO₃ thin films directly on Si substrates by a simple metalorganic decomposition technique for the highly oriented PZT thin films, **Journal Crystal Growth**, Amsterdam, v. 220, n. 1-2, p. 100-104, nov. 2000.
- (146) EDERER, C., SPALDIN, N. A., Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite. **Physical Review B**, Ridge, v 71, p . 060401-1-060401-4, feb. 2005.

Preparation of lanthanum doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics by the polymeric precursor method

A.Z. Simões^{a,*}, C. Quinelato^a, A. Ries^a, B.D. Stojanovic^a, E. Longo^b, J.A. Varela^a

^a Chemistry Institute, UNESP - Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

^b Chemistry Department, UFSCar - Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil

^c Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Serbia and Montenegro

Received 18 August 2005; received in revised form 27 September 2005; accepted 29 September 2005

Abstract

Lanthanum-modified bismuth titanate, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT) ceramics, with x ranging from 0 to 0.75 were prepared by the polymeric precursor method. Orthorhombicity of the system is decreased with the increase of lanthanum content in the bismuth titanate (BIT) crystal lattice. No secondary phases were evident after lanthanum addition. Increasing lanthanum content causes a structural distortion in the bismuth titanate lattice. The shape of the grains is strongly influenced by the lanthanum added to the system.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Crystal structure; Sintering

1. Introduction

Ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) ceramics are potential candidates for device applications due to their high dielectric constant, Curie temperature and breakdown strength [1–3]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were conventionally prepared by solid-state reaction process, where an oxide mixture of Bi_2O_3 and TiO_2 was ball milled, calcinated at intermediate temperature and finally sintered at elevated temperature [4]. The conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The presence of hard particle agglomerates will also result in poor microstructure and properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature. The methods reported in the literature to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics include co-precipitation [5–7] and sol–gel processing [8]. The sol–gel process utilizes expensive precursors and the drying process is a critical operation. The co-precipitation process is limited to cation solutions with similar solubility constants. The polymeric precursor method, which employs complexing of cations in organic media, makes use of low cost precursors resulting in

a homogeneous ion distribution at molecular level [9]. Because of the formation of a polyester resin during the synthesis, there is no segregation of cations during the thermal decomposition of the organic matter.

The substitution of bismuth by lanthanum influences the ferroelectric properties of this material dramatically. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies ($V_{\text{Bi}}^{\prime\prime\prime}$) accompanied by oxygen vacancies ($V_{\text{O}}^{\circ\circ}$) [10–11]. In order to minimize these defects, the substitution of Bi by La on A-site is required [12]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies acting as space charges. Recently, it has been reported that ferroelectric properties were improved by ion doping on A- or B-site [13]. Effects of ion doping on ferroelectric properties and electric conduction have been widely studied [14]. In this work, the effect of lanthanum substitution on the phase formation, crystal structure as well as the morphology of BIT ceramics prepared by polymeric precursor method was investigated. To the best of our knowledge, this method has not been used for pure and lanthanum doped BIT.

2. Experimental procedure

The procedure of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT) synthesis, based on the polymeric precursor method, also called Pechini method [15], starts from the fact that

* Corresponding author. Tel.: +55 16 3301 6600; fax: +55 16 3322 7932.
E-mail address: alezipo@yahoo.com (A.Z. Simões).

certain α -hydroxycarboxylic organic acids can form polybasic, acid chelates with a wide range of cations. After addition of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneous cation distribution. Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. In this work, an excess of 5 wt% Bi was added to the solution aiming at compensating some unavoidable bismuth oxide loss during the thermal treatment. Without this additional bismuth, the pure phase could not be obtained. Most of the organic matter is subsequently eliminated at temperatures as low as 300 °C, forming a dark residue containing reactive oxides with well-controlled stoichiometry. Pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and lanthanum-modified bismuth titanate ceramics with $x = 0.25, 0.50$ and 0.75 were prepared from the metal–citrate complex which was polyesterified in ethylene glycol. Appropriate quantities of Bi, Ti and La solutions were mixed and homogenized by stirring at 90 °C for 3 h. Next, the temperature was increased to 130–140 °C, yielding to a highly viscous polyester resin.

TG and DSC analyses of resins prepared at 140 °C were carried out in atmosphere of synthetic air with heating rate of 10 °C min⁻¹ (SDT2960).

Most of the organic material was decomposed during thermal treatment from room temperature up to 400 °C for 3 h. The formed porous product was crushed and heated in an alumina crucible at 750 °C for 2 h to eliminate residues of organic material. The resulting powder was milled in an attritor with zirconia balls in an acetone medium for 40 min using a procedure according to the literature [16].

Powders were analyzed by X-ray diffraction (XRD) for phase determination. The powders were isostatically pressed (210 MPa) into pellets. For Rietveld analyses, X-ray diffraction data were collected with a Rigaku 20–2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, $20^\circ \leq 2\theta \leq 120^\circ$, $\Delta 2\theta = 0.02^\circ$, $\lambda_{\text{CuK}\alpha}$ monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 [17]. The profile function used was the modified Thompson–Cox–Hasting pseudo-Voigt, in which η (the lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum.

The pellets were sintered inside a box furnace with heating rate of 10 °C min⁻¹ from room temperature up to 1000 °C for 4 h using a closed system containing 3 wt% of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, relative to the pellets' mass, to generate a bismuth oxide rich atmosphere. The density of the pellets was determined by the water displacement method (Archimedes). A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains.

3. Results and discussion

In order to determine the best annealing conditions and to evaluate the crystallization temperature necessary to obtain a single bismuth titanate phase, thermal analyses were performed. Figs. 1 and 2 show the TG and DSC curves of the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ resins obtained from room temperature up to 1000 °C using a heating rate of 10 °C min⁻¹ with x equal to 0 and 0.75, respectively. In these figures, the existence of two stages corresponding to the weight and energy change can be observed. The first characterized stage (25–230 °C) with small weight loss is related to elimination of excess ethylene glycol and water formed during the process of esterification (Fig. 1). The second stage (380–500 °C) is related to the decomposition of the polymeric metal–carboxylate complexes and to the formation of a metal oxide phase. In the low temperature range (25–230 °C), the DSC curve (Fig. 2) presents a slow increase compared to a horizontal baseline which ends later in the large peak. This is attributed to further organic degradation reactions (whereby

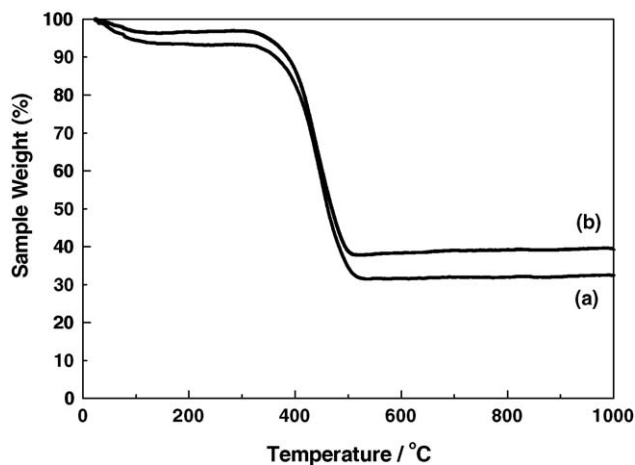


Fig. 1. Thermal analyses for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 300 °C, for 4 h, in dependence of temperature for the lanthanum contents: (a) $x = 0$ and (b) $x = 0.75$.

forming CO, C, H_2O) followed by an exothermic oxidation of C and CO to CO_2 . This occurs to some extent already at such low temperatures. The exothermic effect (380–500 °C) is associated with the main decomposition of organic ligands and crystallization of the BIT phase. The maximum of this exothermic peak was observed around the 440 °C in the DSC curve. Above 580 °C, only for the BLT sample, a very low exothermic effect was noticed, which could be ascribed to released surface tension from a further grain growth. The addition of lanthanum results in a lower weight loss and smaller exothermic peak because lanthanum reduces the bismuth oxide loss during the sintering process.

The influence of lanthanum addition on the crystallinity of BIT powders calcinated at 750 °C for 4 h was studied by XRD analyses (Fig. 3). Four different compositions were investigated ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, where $x = 0, 0.25, 0.5$ and 0.75). No strong influence of lanthanum addition was noted indicating the formation of solid solution free of secondary phases. A shift of the peaks position was noted after the addition of lanthanum

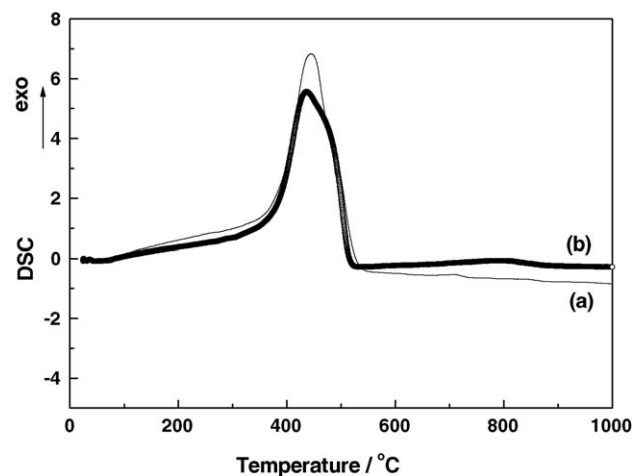


Fig. 2. Differential scanning calorimetry analyses for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 300 °C, for 4 h, in dependence of temperature for the lanthanum contents: (a) $x = 0$ and (b) $x = 0.75$.

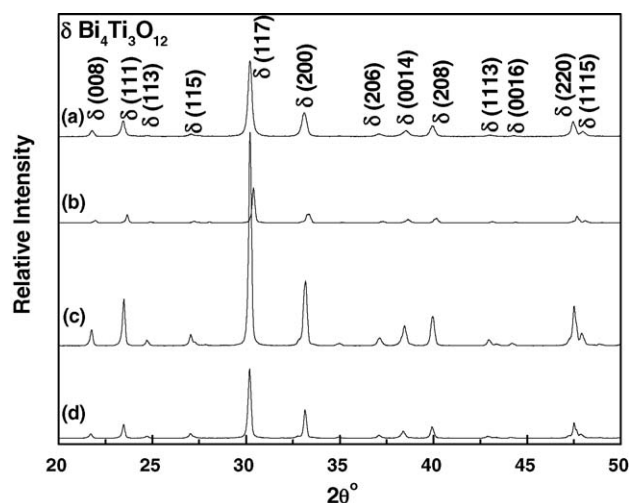


Fig. 3. X-ray data for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 750°C for 4 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.50$ and (d) $x = 0.75$.

and can be ascribed to the change of crystal structure as already discussed in reference [18].

Infrared spectra for the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 750°C for 4 h with x equal to 0 and 0.75, respectively, were recorded (Fig. 4). The typical band characteristics of oxygen–metal bonds were observed in the $450\text{--}640\text{ cm}^{-1}$ region. It was also noted that the powders are free of carbonates independent from the investigated composition. This result is satisfactory from a technological point of view since the electrical properties are dependent on the purity of the raw powders used to fabricate the ceramics. Especially carbonate traces may cause porous ceramics due to CO_2 elimination. The O–H bond stretching near 3400 cm^{-1} could be attributed to adsorbed water due to the contact of the sample with the environment.

The influence of lanthanum on the properties of BIT ceramic materials was evaluated by means of weight loss, green and sintered densities. The addition of La^{3+} causes a decrease in the weight loss because it stabilizes mainly the $(\text{Bi}_2\text{O}_2)^{2+}$ phase

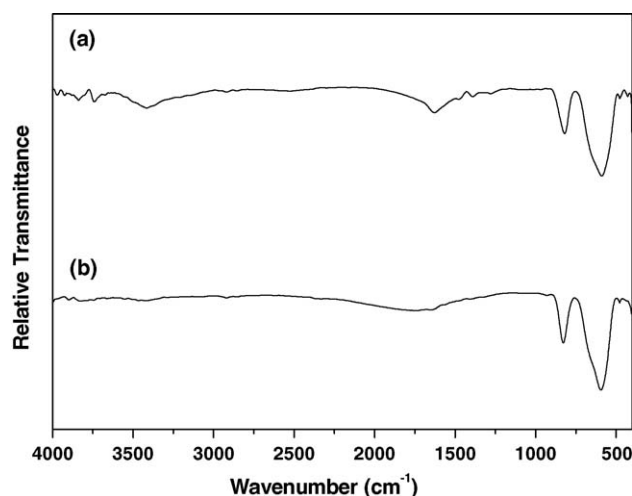


Fig. 4. Infrared data for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 750°C for 4 h as a function of lanthanum content: (a) $x = 0$; (b) $x = 0.75$.

Table 1

Physical characterization for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000°C for 4 h in dependence of the lanthanum content

Samples	Δm (%)	Green density (g cm^{-3})	Sintered density (g cm^{-3})
BIT	0.3234	71.32	95.6
BLT025	0.2114	69.45	95.5
BLT050	0.1268	67.46	95.9
BLT075	0.1974	69.56	95.4

layer where defects, such as oxygen vacancies, are formed avoiding the bismuth loss during the sintering process (Table 1). Therefore, the role of lanthanum is to suppress the volatilization of bismuth oxide and to increase the stability of the metal–oxygen octahedra in BIT. This trend was also observed by Watanabe et al. in the preparation of pure and lanthanum doped BIT thin films [19].

The BIT system has already been investigated from a fundamental point of view, regarding the role of dopant in the crystal structure of the pure material [20]. In the present study, we have adopted the Rietveld refinement technique to investigate the crystal structure of the BIT and BLT systems, and have obtained adequate evidence for the preferred site for lanthanum substitution. The data were collected from the powders calcinated at 750°C for 4 h. Table 2 illustrates the R_{WP} , R_{exp} and S indexes, as well as the lattice parameters (a , b and c) and the unit cell volume (V). The space group obtained from the Rietveld analyses was FMMM with the atomic positions belonging to the ICSD card (number 24735). The quantitative phase analyses of powders for the orthorhombic phase were calculated according to the reference of Young et al. [17]. The obtained results confirmed that the Bi^{3+} ion was substituted by the La^{3+} ion in the orthorhombic BIT phase and no changes occurred in the refinements. It was observed that La^{3+} substitutes Bi^{3+} only in a perovskite-type unit cell, causing a distorted structure whereby distortion increases with raising lanthanum content. The covalent interaction, which originates from the strong hybridization between Ti 3d and O 2p orbitals, plays an important role in the structural distortion of these materials. It can be assumed that doping with La improves oxygen ion stability in the lattice because some of the Bi ions in the pseudo-perovskite layers containing Ti–O octahedra were substituted by La ions.

From the low S values ($S = R_{\text{WP}}/R_{\text{exp}}$), it can be assumed that the refinement was successfully performed with all the investigated parameters close to literature data [21]. It can be inferred that the c -axis is more elongated after lanthanum addition. This is caused by differences in charge density of lanthanum and bismuth atoms. Also, the addition of lanthanum that has a radial substitution effect higher than bismuth, is to stabilize the oxygen vacancies, and consequently the structure. As a consequence, the a and b parameters became closer indicating a change from orthorhombic to tetragonal structure.

In order to evaluate the effect of the lanthanum addition on the morphology and shape of the grains, the pellets doped with 0.25, 0.50 and 0.75 were sintered at 1000°C for 4 h. As it can be seen from Fig. 5, there is a tendency for the plate-like morphology to be more evident in the doped samples suggesting that the

Table 2

Index refinements for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders calcinated at 750° for 4 h with different lanthanum contents: (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$ and (d) $x=0.75$

Parameter	BIT	BTL25	BTL50	BTL75
Refinement index				
R_{WP} (%)	11.12	12.57	10.78	10.19
R_{EXP}	7.06	9.00	6.60	7.02
S	1.57	1.39	1.62	1.44
Lattice parameters				
a (Å)	5.4175	5.4141	5.4151	5.4208
b (Å)	5.4403	5.4377	5.4310	5.4213
c (Å)	32.7862	32.8409	32.8578	32.8924
V (Å ³)	966.30	966.85	966.33	966.64
D (g cm ⁻³)	8.02	7.89	7.78	7.67
Perovskite (mol%)	97.5 ± 0.5	97.1 ± 0.4	98.4 ± 0.4	97.7 ± 0.4
Stoichiometry	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_{3.75}\text{La}_{0.25}\text{Ti}_3\text{O}_{12}$	$\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{12}$	$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$
Refinement	$\text{Bi}_4\text{Ti}_3\text{O}_{11.6}$	$\text{Bi}_{3.75}\text{La}_{0.25}\text{Ti}_3\text{O}_{11.6}$	$\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{11.6}$	$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{11.8}$

lanthanum caused a structural distortion in the system leading to a different grain shape. On the other hand, the pure system presents a mixture of rod-like and plate-like grains. The rod-like grains might be originated from an anisotropic behaviour of bismuth titanate. Table 1 shows the percentual weight loss for the

investigated compositions. As expected, La-doping significantly decreases the weight loss during sintering, which is actually due to the bismuth oxide volatilization. Although the sintering process starts from fairly different green densities, the obtained final densities are almost identical, i.e. not influenced by the La

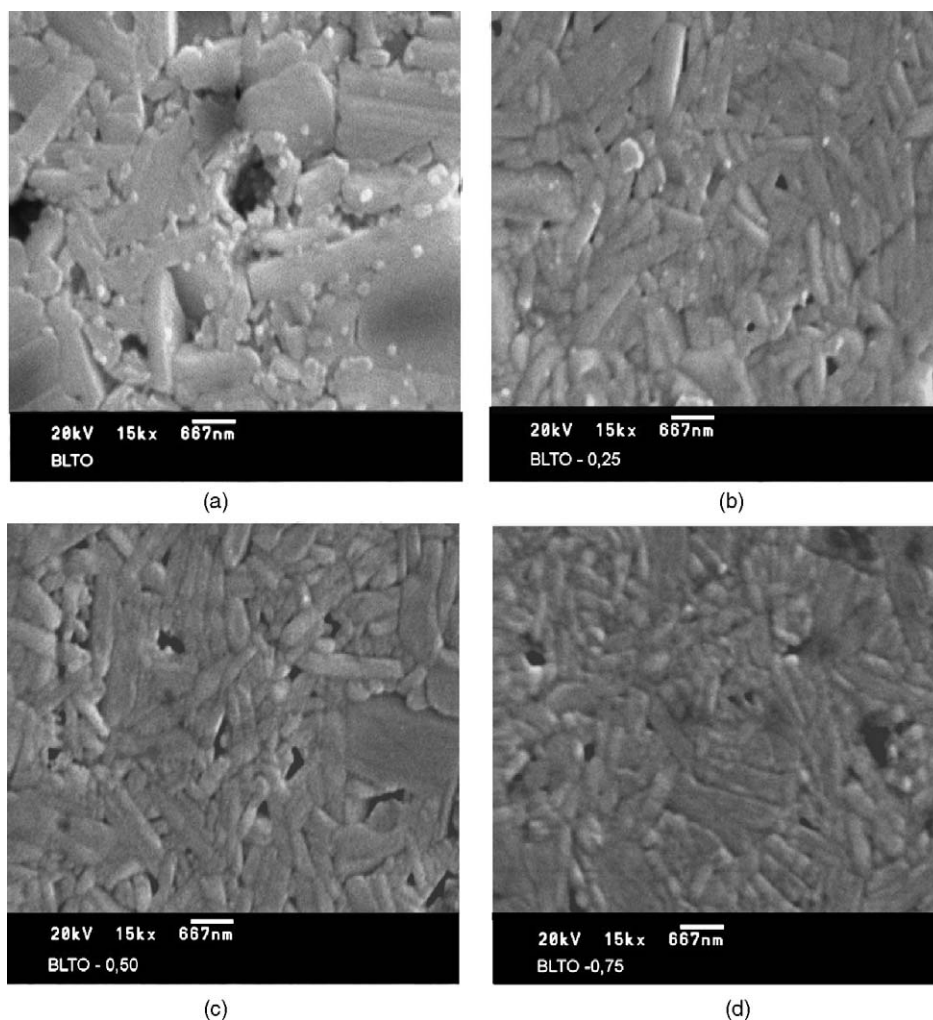


Fig. 5. SEM micrographs for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ powders sintered at 1000°C for 4 h for different lanthanum contents: (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$ and (d) $x=0.75$.

content. This fact is also well-reflected in the SEM micrographs, which do not reveal a clear trend in porosity. Either a few large or many smaller pores can be seen.

4. Conclusions

In summary, it was shown for the first time the successful preparation of pure and lanthanum doped BIT ceramics by the polymeric precursor method. The addition of lanthanum reduces significantly the volatilization of bismuth oxide. Our results support that a single phase, free of carbonates was obtained. A structural distortion is evident with the increase in lanthanum content. Finally, the lanthanum causes a change in the grain morphology which can be explained by the structural distortion of the lattice parameters leading to a more tetragonal symmetry.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

References

- [1] J.F. Dorrian, R.E. Newnham, K.K. Smith, *Ferroelectrics* 3 (1971) 17.
- [2] S.E. Cummings, L.E. Cross, *J. Appl. Phys.* 39 (1968) 2268.
- [3] H.S. Shulman, M. Testorf, D. Damjanovic, N. Setter, *J. Am. Ceram. Soc.* 79 (1996) 3214.
- [4] M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, *J. Am. Ceram. Soc.* 82 (1999) 2411.
- [5] A.Q. Jiang, H.G. Li, L.D. Zhang, *J. Appl. Phys.* 83 (1998) 4878.
- [6] S.H. Hong, J.A. Horn, S. Trolier-McKinstry, G.L. Messing, *J. Mater. Sci. Lett.* 19 (2000) 1661.
- [7] J.A. Horn, S.C. Zhang, U. Selvaraj, G.L. Messing, S. Trolier-McKinstry, *J. Am. Ceram. Soc.* 82 (1999) 921.
- [8] G. Tomandl, A. Stiegelschmitt, R. Bohner, *Proceedings in Science of Ceramic Chemical Processing*, John Wiley & Sons, New York, 1986.
- [9] A.Z. Simões, A.H.M. Gonzalez, M.A. Zaghete, B. Stojanovic, A.A. Cavallheiro, P. Moeckli, N. Setter, J.A. Varela, *Ferroelectrics* 271 (2002) 33.
- [10] W.C. Stewart, L.S. Cosentino, *Ferroelectrics* 1 (1970) 149.
- [11] R. Lohkamper, H. Neumann, G. Arlt, *J. Appl. Phys.* 68 (1990) 4220.
- [12] B.H. Park, B.S. Kang, S.D. Bu, W. Jo, *Nature* 401 (1999) 682.
- [13] A.Q. Jiang, Z.X. Hu, L.D. Zhang, *Appl. Phys. Lett.* 74 (1999) 114.
- [14] Y.P. Wang, W.I. Lee, T.Y. Tseng, *Appl. Phys. Lett.* 69 (1996) 1807.
- [15] M.P. Pechini, US Patent 3,330,697 (11 July 1967).
- [16] M.A. Zaghete, C.O. Paiva-Santos, J.A. Varela, E. Longo, Y.P. Mascarenhas, *J. Am. Ceram. Soc.* 75 (1992) 2088.
- [17] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, *J. Appl. Cryst.* 28 (1995) 366.
- [18] A.Z. Simões, C.S. Riccardi, F. Moura, E. Longo, J.A. Varela, *Mater. Lett.* 22 (2004) 2842.
- [19] T. Watanabe, Hiroshi Funakubo, M. Mizuhira, M. Osada, *J. Appl. Phys.* 90 (2001) 6533.
- [20] J.F. Scott, C.A. Paz de Araujo, B.M. Melnick, *J. Alloys Compd.* 211 (1994) 451.
- [21] S. Luo, Y. Noguchia, M. Miyayamab, T. Kudo, *Mater. Res. Bull.* 36 (2001) 531.

Niobium doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics obtained by the polymeric precursor method

A.Z. Simões*, E.C. Aguiar, A. Ries, E. Longo, J.A. Varela

Chemistry Institute, UNESP — Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

Received 14 December 2005; accepted 10 May 2006

Available online 5 June 2006

Abstract

Pure and niobium doped bismuth titanate ceramics ($\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ (BTN)), with x ranging from 0 to 0.4 were prepared by the polymeric precursor method. X-ray diffraction showed no secondary phases. Increasing niobium content leads to more resistive ceramics. The shape and size of the grains are strongly influenced by the niobium added to the system. The dielectric constant is not influenced by the niobium addition while hysteresis loops are significantly narrowed.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Powder technology; Sintering

1. Introduction

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) ceramics are potential candidates for ferroelectric device applications due to their high dielectric constant, high Curie temperature and high breakdown strength [1–3]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were conventionally prepared by solid-state reaction process, where a mixture containing Bi_2O_3 and TiO_2 was ball milled, calcinated and finally sintered at high temperature [4]. This conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder. The presence of hard particle agglomerates will also result in poor microstructure and properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature. The methods reported in the literature to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics include co-precipitation [5–7], and sol–gel processing [8]. The sol–gel process utilizes expensive precursors and the drying process is critical operation. The co-precipitation process is limited to cation solutions with similar solubility constants. However, the polymeric precursor method, which employs complexing of cations in an organic media, makes use of low cost precursors resulting in a homogeneous ion distribution at a molecular level [9]. Because of the formation of

a polyester resin during the synthesis, there is no segregation of cations during the thermal decomposition of organic matter.

The applications of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics have been limited because of its high electrical conductivity, which is maximum in the a – b plane. It is difficult to polarize $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ to obtain high piezoelectric activity. It is well known that donor dopants decrease the conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ which is a p-type semiconductor. There have been correlative investigations in the literature about a modified electrical conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ when Ti^{4+} was substituted by Nb^{5+} or W^{6+} [8–12]. Obtaining high resistivity makes it possible to observe pronounced piezoelectric properties. In the present study, phase purity, microstructure, electrical conductivity, dielectric and ferroelectric properties of Nb(V)-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prepared by polymeric precursor method have been investigated. To the best of our knowledge, this is the first time that the polymeric precursor method has been used for the preparation of niobium doped bismuth titanate.

2. Experimental procedure

The procedure of the $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ synthesis, based on the polymeric precursor method, starts from fact that certain organic α -hydroxycarboxylic acids can form stable chelate complexes with several cations, including Bi, Ti and Nb. During heating of the mixture containing a polyhydroxylic alcohol and the metal

* Corresponding author. Tel.: +55 16 3301 6600; fax: +55 16 3322 7932.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

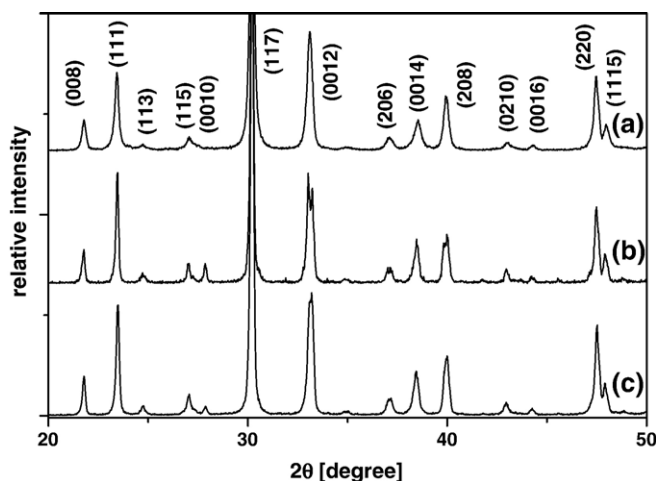


Fig. 1. X-ray data for $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ powders calcinated at 750°C for 4 h and different niobium content: (a) $x=0$; (b) $x=0.02$; (c) $x=0.04$.

chelates, these complexes transform into a polymer, with a completely homogeneous cation distribution. Titanium isopropoxide (Hulls AG, 97% purity), hydrated lanthanum carbonate (Aldrich, 99.9% purity), niobium(V) oxide (Alfa Aesar, 99.9985% purity) and bismuth nitrate (Aldrich, 99.99% purity) were used as raw materials. The precursor solutions of bismuth, titanium and niobium were prepared by adding the raw materials to ethylene glycol (Synth, 99% purity) and concentrate aqueous citric acid (Synth, 99% purity) under heating and stirring. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16 in all precursor solutions. Appropriate quantities of solutions of Ti-, Bi- and Nb-precursors were mixed and homogenized by stirring at 90°C for 3 h. In this work, an excess of 5 wt.% Bi was added to the ideal stoichiometric mixture aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Next, the temperature was increased to $130\text{--}140^\circ\text{C}$, yielding a high viscous polyester resin. Most of the organic material was decomposed by thermal treatment at 400°C for

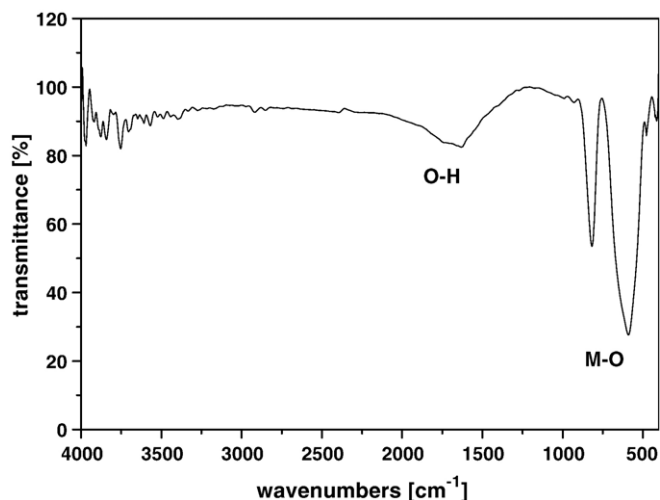


Fig. 2. Infrared data for $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ powder with $x=0.02$ after calcination at 750°C for 2 h.

3 h. The formed porous product was crushed and heated in a crucible alumina at 750°C for 4 h to eliminate residues of organic material. The resulting material was milled in an attritor

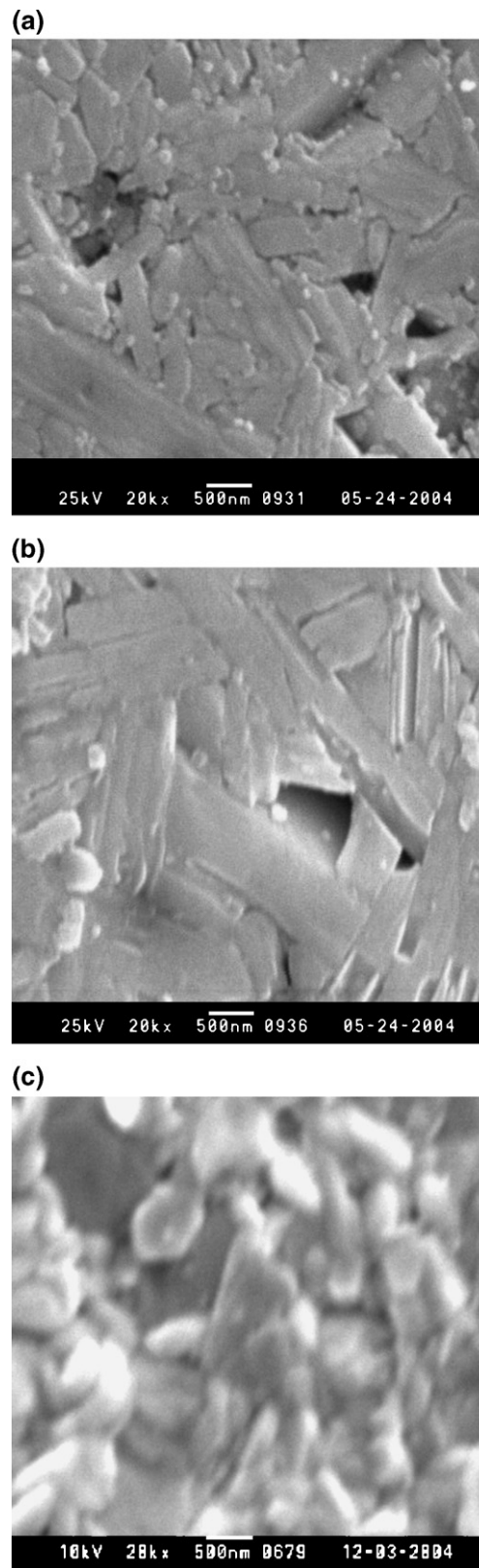


Fig. 3. SEM micrographs for $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ ceramics sintered at 1000°C for 4 h as a function of niobium content: (a) $x=0$; (b) $x=0.02$ and (c) $x=0.04$.

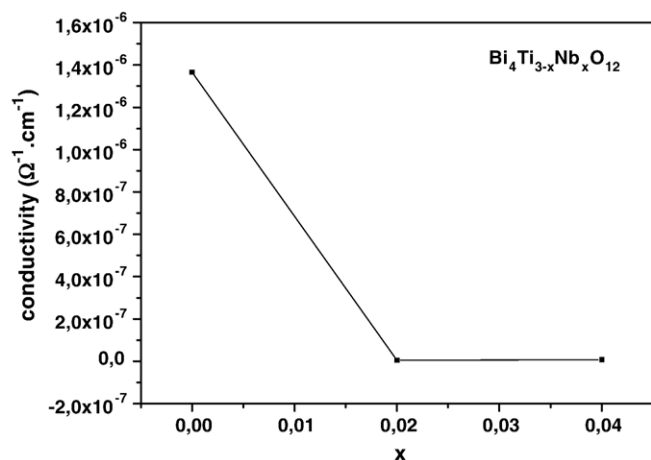


Fig. 4. Conductivity as a function of niobium content for bismuth titanate ceramics sintered at 1000 °C for 4 h.

with zirconia balls in acetone medium for 40 min using a procedure according to the literature [13].

Pure $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and niobium modified bismuth titanate, $\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$, ceramics with x equal to 0, 0.02 and 0.04 were prepared as described above. Powders were first analyzed by X-ray diffraction (XRD) for phase determination. The powders were isostatically pressed (210 MPa) into pellets. The pellets were sintered inside a box furnace (heating and cooling rate of 10 °C/min) at 1000 °C for 4 h using a closed system containing 3 wt.% of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ relative to the pellets' mass, to generate a bismuth oxide rich atmosphere. The density of the pellets was determined by the water displacement method (Archimedes). A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains (Topcom SM-300).

Gold electrodes for electrical measurements were deposited to the polished surface of sintered discs by evaporation through a sputtering system. A high resistance meter (KEITHLEY 6517A) was used to measure electrical conductivity in a direct current

circuit. The relative dielectric constant, ϵ_r , in dependence of frequency was measured using an impedance analyzer (model 4192 A, Hewlett-Packard). Ferroelectric properties were measured on a Radiant Technology RT6600A tester equipped with a micrometer probe station in a virtual ground mode.

3. Results and discussion

The influence of niobium addition on the crystallinity of BIT powders calcinated at 750 °C for 4 h were observed by XRD analyses (Fig. 1). Among the three different investigated compositions ($\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$, where $x=0; 0.02$ and 0.04), all diffraction data showed the existence of a single orthorhombic phase, without any detectable secondary phase.

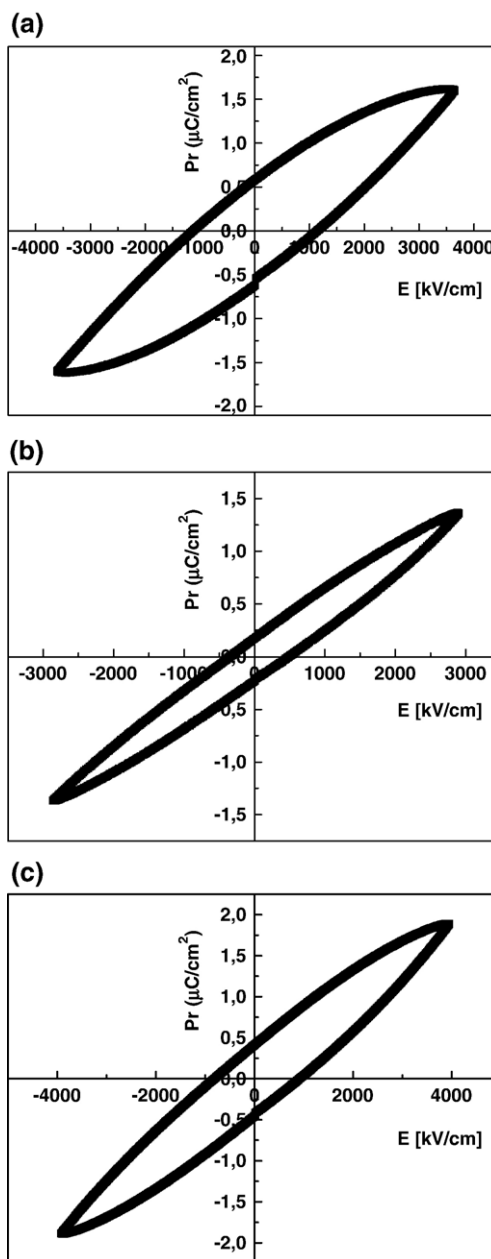


Fig. 6. Hysteresis loops for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ceramics sintered at 1000 °C for 4 h as a function of niobium content: (a) $x=0$; (b) $x=0.02$ and (c) $x=0.04$.

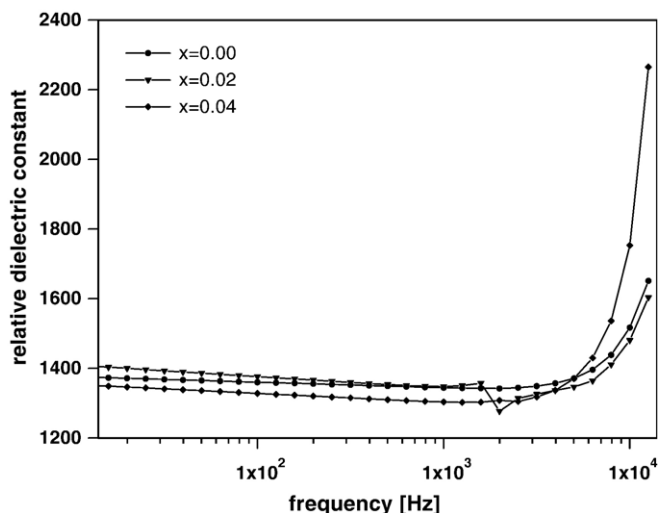


Fig. 5. Dielectric constant as a function of frequency and niobium content for BIT ceramics sintered at 1000 °C for 4 h.

Finally, niobium at low concentrations does not change the crystal structure of the undoped system.

Fig. 2 shows the IR spectrum of the ceramic powder for the $x=0.02$ composition. The main band characteristic of the oxygen–metal bond was observed in the region $450\text{--}640\text{ cm}^{-1}$. Due to the absence of a $\text{C}=\text{O}$ vibration around 1450 cm^{-1} , it follows that the powders are free of carbonates. This result is satisfactory from a technological point of view since the electrical properties are dependent on the quality of the raw powders used to sinter the ceramic. There was, however, a vibration band noted that is associated to the deformation of $\text{O}\text{--}\text{H}$ bonds near 1680 cm^{-1} . This is attributed to water adsorbed at the powder surface when the sample was in contact with the environment.

SEM images do not reveal a clear trend on the shape and size of the grains after niobium addition (Fig. 3). No precipitates were evident in the grain boundary indicating the formation of a continuous solid solution. A typical plate-like morphology was noted for pure and 0.02 niobium doped bismuth titanate. On the other hand, for the 0.04 composition a rounded morphology was observed indicating a change in the kinetics of the grain growth.

The niobium dependence of electrical conductivity measured in a direct current circuit containing bismuth titanate ceramics was studied at a temperature of $300\text{ }^{\circ}\text{C}$ (Fig. 4).

At lower temperatures, the conductivity was too small to be measured accurately. The conductivity of niobium doped BIT was obviously lower than that of the undoped one, which is in agreement with the fact that donor dopants decrease the conductivity of a p-type semiconductors. Actually, the conductivity was dramatically decreased with a very small content of Nb^{5+} doping ($x=0.02$). In $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, hole compensation of bismuth vacancies ($V'''_{\text{Bi}}+3h\cdot$) promotes p-type electronic conductivity. When Nb^{5+} substitutes Ti^{4+} , a positive charge center at Nb site and an electron will be created under charge neutrality restriction, which can be described as $\text{Nb}\cdot_{\text{Ti}}+e'$. These electrons neutralize the influence of the holes. According to the electronic conductivity relationship $\sigma=nq\mu$, where n is the number of the carriers, q the charge and μ the mobility, it becomes clear that the number of the hole carriers, n , was decreased, since Nb does not induce structural changes to the crystal lattice that can justify a change in the charge carrier mobility. The conductivity decreases with donor doping to a minimum value that is reached when the concentration of the electrons is equal to the hole concentration.

The dielectric constant measurements were carried out at room temperature as a function of frequency in the range of $10\text{ Hz--}10^4\text{ Hz}$. As shown in Fig. 5, the dielectric constant shows slight dispersion with frequency indicating that our ceramics possess low defect concentrations. The low dispersion of the dielectric constant and the absence of any relaxation peak indicated that both, interfacial polarization of the Maxwell Wagner type and a polarization produced by the electrode barrier can be neglected. In this way, Nb^{5+} can be considered as a kind of soft additive in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. It softens piezoelectric ceramics, i.e. increases dielectric constant and decreases electrical conductivity.

Fig. 6 shows the ferroelectric hysteresis loops for pure and niobium doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. The loops never showed saturation, instead, the ceramics behave as lossy linear dielectric materials. The narrowing of the curve when increasing the niobium concentration indicates a decrease in the system conductivity, i.e. the leakage current as dielectric loss mechanism can be discarded. These results were similar to the

investigations of other authors [14,15], where Nb^{5+} substituting for Ti^{4+} in BiTN ceramics efficiently decreased the concentration of oxygen vacancies, which weakened the influence of domain pinning on the polarization. Furthermore, as it can be seen from the SEM images, the niobium content influences the shape and size of the grains irregularly. This is also reflected in the losses determined from the hysteresis loops, which do not show a regular trend despite the obvious fact that Nb addition reduces the losses.

4. Conclusions

In summary, it was shown for the first time the successful preparation of niobium doped bismuth titanate ceramics by the polymeric precursor method. Our results support that a single phase system free of carbonate phase was obtained. The addition of niobium causes a change in the grains morphology. The conductivity of the system is strongly influenced by niobium addition. The dielectric constant was almost not influenced by the niobium content. An increase in niobium concentration leads to the narrowing of hysteresis loops due to the decrease in the conductivity.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

References

- [1] J.F. Dorrian, R.E. Newnham, K.K. Smith, *Ferroelectrics* 3 (1971) 17–27.
- [2] S.E. Cummings, L.E. Cross, *J. Appl. Phys.* 39 (1968) 2268–2274.
- [3] H.S. Shulman, M. Testorf, D. Damjanovic, N. Setter, *J. Am. Ceram. Soc.* 79 (1996) 3214–3218.
- [4] M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, *J. Am. Ceram. Soc.* 82 (1999) 2411–2416.
- [5] A.Q. Jiang, H.G. Li, L.D. Zhang, *J. Appl. Phys.* 83 (1998) 4878–4883.
- [6] S.H. Hong, J.A. Horn, S. Trolier-McKinstry, G.L. Messing, *J. Mater. Sci. Lett.* 19 (2000) 1661–1664.
- [7] J.A. Horn, S.C. Zhang, U. Selvaraj, G.L. Messing, S. Trolier-McKinstry, *J. Am. Ceram. Soc.* 82 (1999) 921–926.
- [8] G. Tomandl, A. Stiegelschmitt, R. Bohner, *Proceedings in Science of Ceramic Chemical Processing*, John Wiley & Sons, New York, 1986.
- [9] A.Z. Simões, A.H.M. Gonzalez, M.A. Zaghete, B. Stojanovic, A.A. Cavalheiro, P. Moeckli, N. Setter, J.A. Varela, *Ferroelectrics* 271 (2002) 33.
- [10] W.C. Stewart, L.S. Cosentino, *Ferroelectrics* 1 (1970) 149.
- [11] R. Lohkamper, H. Neumann, G. Arlt, *J. Appl. Phys.* 68 (1990) 4220.
- [12] B.H. Park, B.S. Kang, S.D. Bu, W. Jo, *Nature* 401 (1999) 682.
- [13] M.A. Zaghete, C.O. Paiva-Santos, J.A. Varela, E. Longo, Y.P. Mascarenhas, *J. Am. Ceram. Soc.* 75 (1992) 2088.
- [14] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, *J. Appl. Cryst.* 28 (1995) 366.
- [15] J.F. Scott, C.A. Paz de Araujo, B.M. Melnick, *J. Alloys Compd.* 211 (1994) 451.

Rietveld Analyses and Piezoelectric Properties of Niobium Doped Bismuth Titanate Systems

Éderson Carlos Aguiar¹, Alexandre Zirpoli Simões^{2,*}, Elson Longo¹, and J. A. Varela¹

¹ Laboratório Interdisciplinar em Cerâmica, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14801-907 Araraquara, São Paulo, Brazil

² Universidade Federal de Itajubá- Unifei - Campus Itabira, Rua São Paulo 377, Bairro Amazonas, P.O. Box 355, 35900-37, Itabira, Minas Gerais, Brazil

$\text{Bi}_4\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$ (BITNb) samples, with x ranging from 0 to 0.40 were obtained using a polymeric precursor solution. Rietveld analyses confirmed that the powders crystallize in an orthorhombic structure free of secondary phases with space group Fmmm. Raman analysis evidenced a sharp increase in the bands intensity located at 129 cm^{-1} and 190 cm^{-1} due the lattice distortion in BIT02Nb and BIT04Nb compositions. UV-vis spectra indicated that addition of niobium causes a reduction of defects in the BIT lattice due the suppression of oxygen vacancies located at BO_6 octahedral. Size and morphology of particles as well as electrical behavior of BIT ceramics were affected by addition of donor dopant. Polarization reversal was investigated by applying dc voltage through a conductive tip during the area scanning and was investigated by piezoresponse force microscopy (PFM). PFM measurements revealed a decrease in piezoelectric response with increasing Nb concentration originating from a reduced polarizability along the a -axis. High spontaneous polarization is noted for the less doped sample due the reduction of strain energy and pin charged defects after niobium addition.

Keywords: Ceramics, Rietveld Analysis, Electrical Conductivity, Morphology, Scanning Electron Microscopy, Piezoresponse Force Microscopy.

1. INTRODUCTION

Ferroelectric materials constitute a special electronic ceramics class that is used as: electrooptical sensors, actuators, transducers, capacitors, devices and random access memories (RAM).¹ $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (bismuth titanate, BIT) is a ferroelectric material of the Aurivillius type family having potential application in electronic devices.² It can be used as a possible substitute for the lead based-ceramics due its good properties as high dielectric permittivity and remaining polarization, low dielectric loss and high Curie temperature.^{3,4} The general formula of Aurivillius materials is $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, where A is a mono-, di- or trivalent element (or combination) with cuboctahedral coordination, B is a transition element suited to octahedral coordination, and m is the number of octahedral layers in the perovskite slab. The m value can vary from 1 to 6.⁵ It can also be fractional and compounds with $m = 1.5, 2.5$, and 3.5 are widely known.⁶ It is found that the ferroelectric properties for even ($m = 2n$) and odd layer ($m = 2n + 1$)

compounds are different.⁷ The spontaneous polarization P_s of even-layer compounds is only along the a -axis. Based on their orthorhombic space group $A2_1am$, the polarization along the c -axis is cancelled because of mirror symmetry. However, in odd-layer compound $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m = 3$, monoclinic, space group P_c) a small degree of spontaneous polarization along the c -axis can be observed besides the major polarization along the a -axis.^{8–10}

The crystal structure is characterized by three perovskite-like unit cells sandwiched between $(\text{Bi}_2\text{O}_2)^{2+}$ layers along the c -axis. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystal has two independent spontaneous polarizations with a major component of $50\text{ }\mu\text{C}/\text{cm}^2$ in the a - b plane. It undergoes a ferroelectric to paraelectric phase transition at the Curie temperature ($T_c = 675\text{ }^\circ\text{C}$). At room temperature the symmetry of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is monoclinic ($C_1h = m$)⁹, while it can be considered as orthorhombic structure with $a = 0.5448$, $b = 0.5411$ and $c = 3.283\text{ nm}$ from X-ray and neutron diffraction patterns.¹¹ This material can be used for high-temperature applications although its high electrical conductivity has been limited in the a - b plane. To overcome these problems, donor dopants can be employed

* Author to whom correspondence should be addressed.

to decrease the conductivity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ material with a *p*-type mechanism as reported by correlative investigation about modifying electrical conductivity of BIT by Nb^{5+} or Ta^{5+} substituting Ti^{4+} ion.^{12–14}

In previous work, Simoes *et al.*¹⁵ have prepared niobium doped BIT ceramics using 5 wt% of bismuth excess. The authors have observed that the donor dopant changes the grains morphology, reduction of conductivity and as a consequence narrowing of hysteresis loops. The electrical conductivity is one of the most important properties for BIT. High electrical conductivity makes it difficult to polarize the material inhibiting its use at high temperature. Shulman *et al.*¹⁶ reported that the main conducting mechanism of BIT was electronic *p*-type. The authors have also observed that the conductivity of BIT increased with acceptor addition and decreased with donor dopant. Addition of Nb in BIT with the following composition ($\text{Bi}_4\text{Ti}_{2.9}\text{Nb}_{0.04}\text{O}_{12}$) allowed a decrease in conductivity by as much as three orders of magnitude due the complete compensation of holes by electrons. Literature also reported that doping BIT with other cations (e.g., W^{6+} , Sb^{5+} , Ta^{5+})^{17–18} lead to a decrease in the conductivity by three to four orders up to 600 °C, which facilitated both the poling and high temperature application of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

It is noted that there are a lot of studies concerning the effect of doping with different ions on ferroelectric properties of BIT films as mentioned above, whereas reports on the doping effect on BIT ceramics are scarce. Thus, niobium was chosen as the doping element for BIT in the present work; the effect of niobium on the phase formation was monitored by Rietveld analysis, sintering behavior, Raman spectra, microstructure and electric properties of BIT ceramics was investigated. In the present investigation, a deep study based on structural, microstructural and electrical conductivity of Nb^{5+} -doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prepared by chemical route is shown.¹⁹

2. EXPERIMENTAL DETAILS

$\text{Bi}_4\text{Ti}_{(3-x)}\text{Nb}_x\text{O}_{12}$ samples with $x = 0, 0.1, 0.2, 0.4$ mol% Nb (all with 10 wt% of bismuth excess) were prepared by the polymeric precursor method (PPM), represented as: BIT, BITNb01, BITNb02, BITNb04 respectively. In this work, 10 wt% of bismuth excess was added to minimize bismuth loss during thermal treatment. Without this additional bismuth the pure phase could not be obtained, as it was reported in literature.¹⁷ The following reagents were employed: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (100.1%, Mallinckrodt), $\text{Ti}(\text{OC}_3\text{H}_7)_4$ (97.0%, Alfa Aesar), Nb_2O_5 (99.99%, Alfa Aesar), $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (99.5%, Merck), $\text{C}_2\text{H}_6\text{O}_2$ (99.7%, Synth), HNO_3 (99.9% Synth), $\text{C}_2\text{H}_8\text{N}_2$ (98.0%, Nuclear) and NH_4OH (99.9%, Qhemis). The precursor solutions of bismuth, titanium and niobium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. The molar ratio of metal: citric acid: ethylene glycol

was 1:4:16. Solutions were mixed and homogenized by stirring at 90 °C-2 h. Next, the temperature was increased to 130–140 °C, yielding a highly viscous polyester resin. Most of the organic material was decomposed by thermal treatment at 300 °C-2 h. The formed porous product was crushed and heated in a crucible alumina at 700 °C for 4 hours to decompose the organic material. The resulting material was milled using zirconium balls in isopropyl alcohol during 4 h. Powders were first analyzed by X-ray diffraction (XRD) for phase determination. For Rietveld analyses, X-ray diffraction data were collected with a Rigaku 20-2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, $20^\circ \leq 2\theta \leq 120^\circ$, $\Delta 2\theta = 0.02^\circ$, $\lambda\text{Cu } k_\alpha$ monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with a DBWS-941 refinement program.²⁰ The profile function used was the modified Thompson-Cox-Hasting pseudo-Voigt, in which η (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum.

A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains (Topcom SM-300). The powders were uniaxially (150 MPa) and isostatically pressed (210 MPa) into pellets and sintered inside a conventional furnace (heating and cooling rates of 10 °C/min) at 800 °C for 1 hour using an opened system in ambient atmosphere. Silver electrodes were pasted on both sides of the samples with 1 mm of thickness. The density of the pellets was determined by the water displacement method (Archimedes) and presented values above 90% of theoretical density. Raman spectroscopy was employed to determine the characteristics vibrations of BIT (RFS 100/S Bruker excited by laser Nd-YAG a 1064 nm). The band gap values were obtained from Ultraviolet spectroscopy measurements (UV-Vis-NIR Spectrophotometer—VARIAN Cary 500 X). Silver electrodes were pasted on both sides of the samples and fired at 200 °C for 30 min. Resistivity was determined by current-voltage in voltage source (KEITLEY 237-USA). Dielectric permittivity was performed in HP 4192A LF Mountain View impedance at 1 MHz, acopled in FLYEVER oven (FE50RP temperature controller). Piezoelectric measurements were carried out using a setup based on an atomic force microscope in a Multimode Scanning Probe Microscope with Nanoscope IV controller (Veeco FPP-100). In our experiments, piezoresponse images of the films were acquired in ambient air by applying a small ac voltage with an amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz while scanning the film surface. To apply the external voltage we used a standard gold coated Si_3N_4 cantilever with a spring constant of 0.09 N/m. The probing tip, with an apex radius of about 20 nm, was in mechanical contact with the uncoated film surface during the measurements. Cantilever vibration was detected using a conventional lock-in technique.

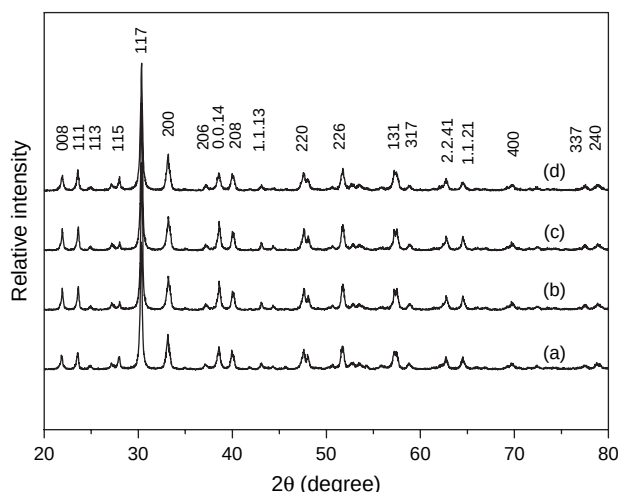


Fig. 1. X-ray diffraction of powders calcined at 700 °C for 4 h: (a) BIT, (b) BITNb01, (c) BITNb02 and (d) BITNb04.

3. RESULTS AND DISCUSSION

Phase formation of bismuth titanate powders calcined at 700 °C-4 h was evaluated by X-ray diffraction (Fig. 1). The powders are free of secondary phases and present orthorhombic structure regardless of niobium content.²¹ We can observe that the polymeric precursor method allow to obtain BIT powders at low heat treatment temperature and reduced synthesis time. Bragg reflections peaks are indicative of perovskite structure, with orientation in *c*-plane, mainly characterized by higher intense peak (*hkl*-117) and no apparent peak splitting is identified. Our XRD results are in agreement with the reported in the literature.^{22–25} The experimental lattice parameter values were calculated using Rietveld method. Table I compares the lattice parameters obtained in this work with those reported in the literature by different methods. Moreover, the lattice parameter obtained in our work presented small variations compared to those reported in the literature.^{26–31} These differences can be related to the preparation method, synthesis conditions (heat treatment temperature, time), lattice distortion, residual stresses in the lattice and/or structural defects.

The BIT system has already been investigated from a fundamental point of view, regarding the role of dopant in the crystal structure of pure bismuth titanate.³² In the

present study, we have adopted the Rietveld refinement technique to investigate the crystal structure of the BIT and BITNb systems, and have obtained adequate evidence for the preferred site for niobium substitution. Table II illustrates the *R*_w, *R*_{exp}, and *S* indexes, as well as the lattice parameters (*a*, *b* and *c*) and the unit cell volume (*V*). The phase identification was carried out in the PDF data bank, resulting in an orthorhombic structure type. The structural model (available on ICSD databank) that allows the best-fitting was the orthorhombic one (ICSD no. 24735 with space group *Fmmm*). The quantitative phase analyses for the orthorhombic phase was calculated according to the reference of Young and Wiles.²⁰ No changes occurred in the refinements when Bi³⁺ ion was substituted by Nb⁵⁺ ion in the orthorhombic BIT phase. It was observed that Nb⁵⁺ substitutes Bi³⁺ only in a perovskite-type unit cell, causing a distorted structure whereby distortion increases with raising niobium content. The covalent interaction, which originates from the strong hybridization between Ti 3d and O 2p orbitals, plays an important role in the structural distortion of BIT compound. It can be assumed that doping with Nb improves oxygen ion stability in the lattice because some of the Bi ions in the pseudo-perovskite layers containing Ti–O octahedral were substituted by Nb ions. The low *S* values (*S* = *R*_w/*R*_{exp}) reflects good refinement quality being the calculated parameters similar to literature data.³³ Niobium addition elongates *c*-axis due the differences in charge density of niobium and bismuth atoms. Also, niobium stabilizes the oxygen vacancies and consequently the structure. As a consequence, *a* and *b* parameters became closer indicating that the orthorhombic structure tends to transforms into a tetragonal one with the increase of donor dopant.

The Raman spectra of the BIT, BITNb01, BITNb02, BITNb04 powders is shown in Figure 2. The main modes located at 85, 129, 144, 190, 223, 267, 317, 536, 615, 849 cm^{−1} are characteristics of Bi₄Ti₃O₁₂ single crystal³⁴ and are in agreement with the reported in the literature.^{35–40} Usually, higher wavenumber phonon modes can be attributed to vibrations of Ti–O or Nb–O atoms inside the perovskite layer while lower wavenumber phonon modes to vibrations of Bi–O atoms within the Bi₂O₂ layer. The modes located at 267 and 223 cm^{−1} are relative to distortions in TiO₆ octahedral.^{41–42} The modes located at 536 cm^{−1} and 849 cm^{−1} are respective

Table I. Comparative results between the lattice parameter values of Bi₄Ti₃O₁₂ powders obtained by polymeric precursor (PPM) with those reported in the literature by different methods.

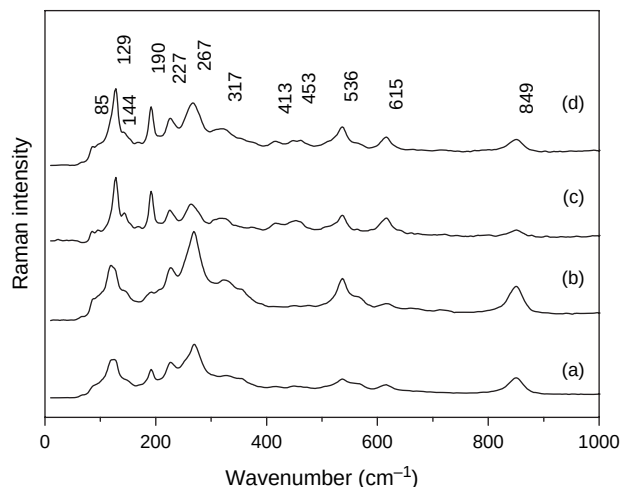
Method	Temperature (°C)	Time (h)	Lattice <i>a</i> (Å)	Lattice <i>b</i> (Å)	Lattice <i>c</i> (Å)	Ref.
SSR	850	12	5.44325	5.40995	32.8212	11
MT	900	24	5.4526	5.4076	32.793	29
SSR	1100	24	5.44758	5.40829	32.80666	31
CCP	850	1	5.44193	5.40683	32.8372	30
PPM	700	4	5.4175	5.4403	32.7862	This work

SSR = Solid-state reaction, PPM = Polymeric precursor method, MT = Mechanochemical treatment, CCP = Chemical coprecipitation and Ref. = References.

Table II. Refinements Indexes for $\text{Bi}_4\text{Ti}_{(3-x)}\text{Nb}_x\text{O}_{12}$ powders calcined at 700 °C for 4 hours with different niobium contents: (a) $x = 0$; (b) $x = 0.01$; (c) $x = 0.02$ and (d) $x = 0.04$.

Parameter	BIT	BIT01Nb	BIT02Nb	BIT04Nb
Refinement indexes				
R_{WP} (%)	11.12	12.57	10.78	10.19
R_{EXP}	7.06	9.00	6.60	7.02
S	1.57	1.39	1.62	1.44
Atomic Positions				
A1	0; 0; 0.06722	0; 0; 0.06712	0; 0; 0.06720	0; 0; 0.06733
A2	0; 0; 0.21091	0; 0; 0.21023	0; 0; 0.21132	0; 0; 0.21145
B1	0; 0; $\frac{1}{2}$	0; 0; $\frac{1}{2}$	0; 0; $\frac{1}{2}$	0; 0; $\frac{1}{2}$
B2	0; 0; 0.37099	0; 0; 0.37213	0; 0; 0.37143	0; 0; 0.37120
O1	$\frac{1}{4}$; $\frac{1}{4}$; 0	$\frac{1}{4}$; $\frac{1}{4}$; 0	$\frac{1}{4}$; $\frac{1}{4}$; 0	$\frac{1}{4}$; $\frac{1}{4}$; 0
O2	$\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$	$\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$	$\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$	$\frac{1}{4}$; $\frac{1}{4}$; $\frac{1}{4}$
O3	0; 0; 0.43786	0; 0; 0.43747	0; 0; 0.43616	0; 0; 0.43638
O4	0; 0; 0.32536	0; 0; 0.31851	0; 0; 0.31895	0; 0; 0.31989
O5	$\frac{1}{4}$; $\frac{1}{4}$; 0.11165	$\frac{1}{4}$; $\frac{1}{4}$; 0.11584	$\frac{1}{4}$; $\frac{1}{4}$; 0.11580	$\frac{1}{4}$; $\frac{1}{4}$; 0.11581
S_{Occ}				
Bi (A1)	1.00000	0.87500	0.75000	0.62500
Nb (A1)	0.00000	0.12500	0.25000	0.37500
O	0.91700	0.91000	0.91800	0.94900
Lattice				
a (Å)	5.4175	5.4141	5.4151	5.4208
b (Å)	5.4403	5.4377	5.4310	5.4213
c (Å)	32.7862	32.8409	32.8578	32.8924
V (Å ³)	966.30	966.85	966.33	966.64
d (g/cm ³)	8.02	7.89	7.78	7.67
Perovskite (mol%)	97.5 ± 0.5	97.1 ± 0.4	98.4 ± 0.4	97.7 ± 0.4
Stoichiometry	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{12}$	$\text{Bi}_4\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{11.6}$	$\text{Bi}_4\text{Ti}_{2.6}\text{Nb}_{0.4}\text{O}_{11.8}$
Refinement	$\text{Bi}_4\text{Ti}_3\text{O}_{11.6}$	$\text{Bi}_4\text{Ti}_{2.9}\text{Nb}_{0.1}\text{O}_{11.6}$	$\text{Bi}_4\text{Ti}_{2.8}\text{Nb}_{0.2}\text{O}_{11.6}$	$\text{Bi}_4\text{Ti}_{2.6}\text{Nb}_{0.4}\text{O}_{11.8}$

to stretching vibrations and c -axis symmetric stretching of TiO_6 octahedral, respectively. Niobium addition causes a sharp increase in the band intensity located at 129 cm^{-1} and the appearance of a sharp band located at 190 cm^{-1} due the lattice distortion in BIT02Nb and BIT04Nb compositions. The modes located at 413, 453 cm^{-1} correspond to vibrations of Nb–O atoms inside the perovskite layer.

**Fig. 2.** Raman spectra of powders calcined at 700 °C for 4 h: (a) BIT, (b) BIT01Nb, (c) BIT02Nb and (d) BIT04Nb.

Generally speaking, the mode at 223 cm^{-1} is Raman inactive when the symmetry of the TiO_6 octahedron is Oh, and it becomes Raman active when the TiO_6 octahedron is distorted. The mode that appeared at 223 cm^{-1} in BIT, implies the existence of the distorted TiO_6 octahedron. It is noted that the mode at 144 cm^{-1} appear in Nb doped BIT, which is absent in the BIT sample. It is also possible that the lattice vibration would be affected because of the higher electrovalence of niobium compared to titanium.

Figure 3 shows the UV-vis spectral dependence of absorbance for BIT, BITNb01, BITNb02, BITNb04 powders. The energy gap (E_g) was estimated by Kubelka model by extrapolating the linear portion of the curve or tail.⁴³ The obtained values are 2.96; 2.90; 2.97 and 3.04 eV, respectively. The optical energy band gap is related to the absorbance and to the photon energy by the following Eq. (1):

$$h\nu\alpha \propto (h\nu - E_g^{\text{opt}})^2 \quad (1)$$

where α is the absorbance, h is the Planck constant, ν is the frequency and E_g^{opt} is the optical band gap. Our BIT powders presented characteristic absorption spectra of ordered or crystalline materials. The optical band gap behavior can be associated to the changes in the local atomic structure or lattice, as observed in XRD and Raman results. Comparing the band gap values of all samples,

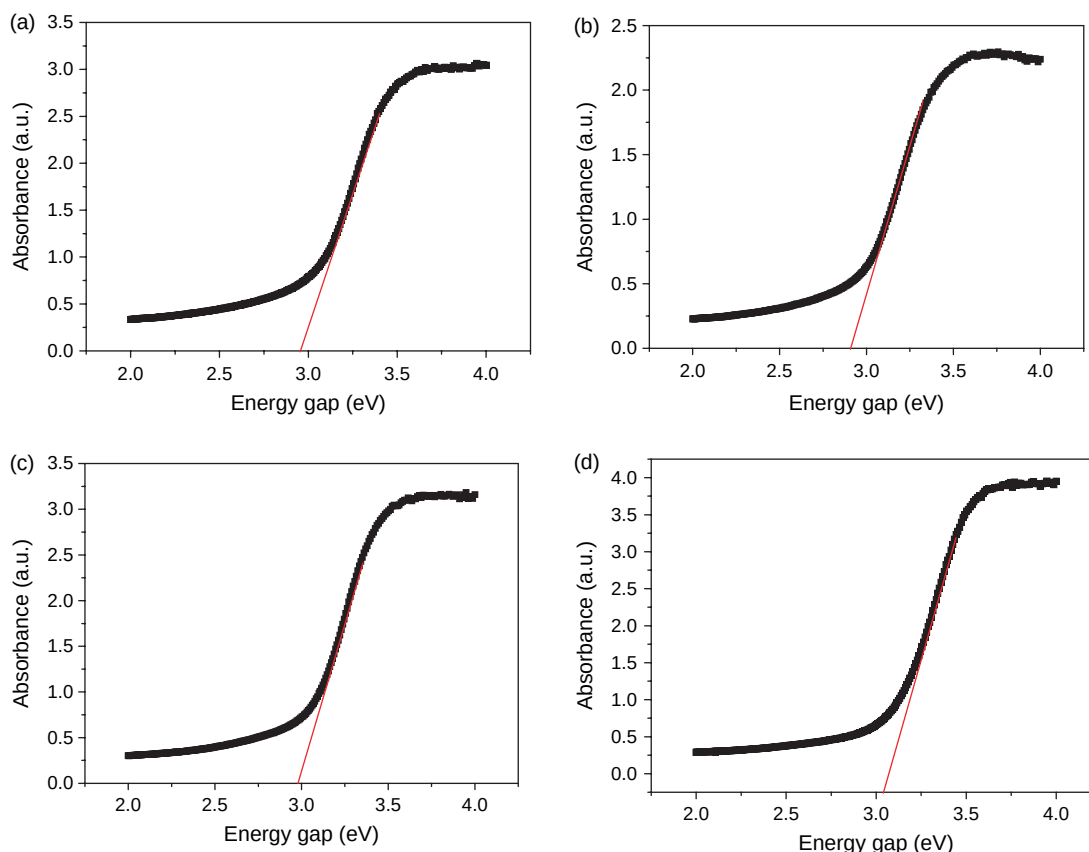


Fig. 3. UV-vis absorption spectra at room temperature for powders calcined at 700 °C for 4 h: (a) BIT, (b) BIT01Nb, (c) BIT02Nb and (d) BIT04Nb.

we observe a slight increase for the BIT04Nb composition which can be associated to reduction of intermediary energy levels within the optical band gap and reduction of oxygen vacancies located at BO_6^- octahedral. The corresponding values are in agreement with the results reported by Besland.⁴⁴ The differences in the band gap can be related to the different factors, mainly including: employed method, shape (powder, crystal or thin film), synthesis conditions and structural distortions caused by donor dopant.

The effect caused by niobium addition on the morphology and shape of the grains was evaluated by SEM analyses (Fig. 4). Niobium addition caused a pronounced effect on the grain shape leading to a plate-like morphology and a structural distortion. On the other hand, pure BIT presents a mixture of rod-like and plate-like grains. The rod-like grains might be originated from an anisotropic behavior of bismuth titanate. BIT ceramics presented porous microstructure with smaller grain sizes when compared to Nb doped BIT ceramics. There is no evidence of liquid-phase segregated at the grain boundaries indicating that the polymeric precursor method allows obtaining the phase at low sintering temperature with particles distributed in a nanometric matrix.

Leakage current density versus electric field (J - E curve) for sintered pellets is shown in Figure 5. Here, we plotted the current density behavior of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ for

comparison. We noted that the electrical behavior was obviously influenced by donor dopant. BIT presented high values of current density while for BIT-Nb compositions the current density values decreased. This result is in agreement with the idea that donor dopants decrease conductivity of a material with a p -type mechanism.¹⁶ For BITNb compositions, the ceramics presented lower electrical conductivity and therefore could be poled to develop piezoelectricity. In Nb doped BIT ceramics, hole compensation of bismuth vacancies ($V_{\text{Bi}}''' + 3h'$) promotes p -type electronic conductivity because when Nb^{5+} substitutes Ti^{4+} , a positive charge center at Nb site and an electron will be created under charge neutrality restriction, which can be described as $\text{Nb} \cdot \text{Ti} + e'$. These electrons compensates the influence of the holes according to the electronic conductivity relationship $\sigma = nq\mu$, where n is the number of the carriers, q the charge and μ the mobility. It becomes clear that the number of the hole carriers, n , was decreased, since Nb does not induce structural modifications in the crystal lattice that can justify a change in the charge carrier mobility.⁴⁵ That resulted in a low conductivity of BITNb ceramics due the reduction of current density with donor doping to a minimum value that is reached when the concentration of the electrons is equal to the hole concentration. Also, BIT has a rounded shape grains with residual porosity which might have lots of carrier traps. At

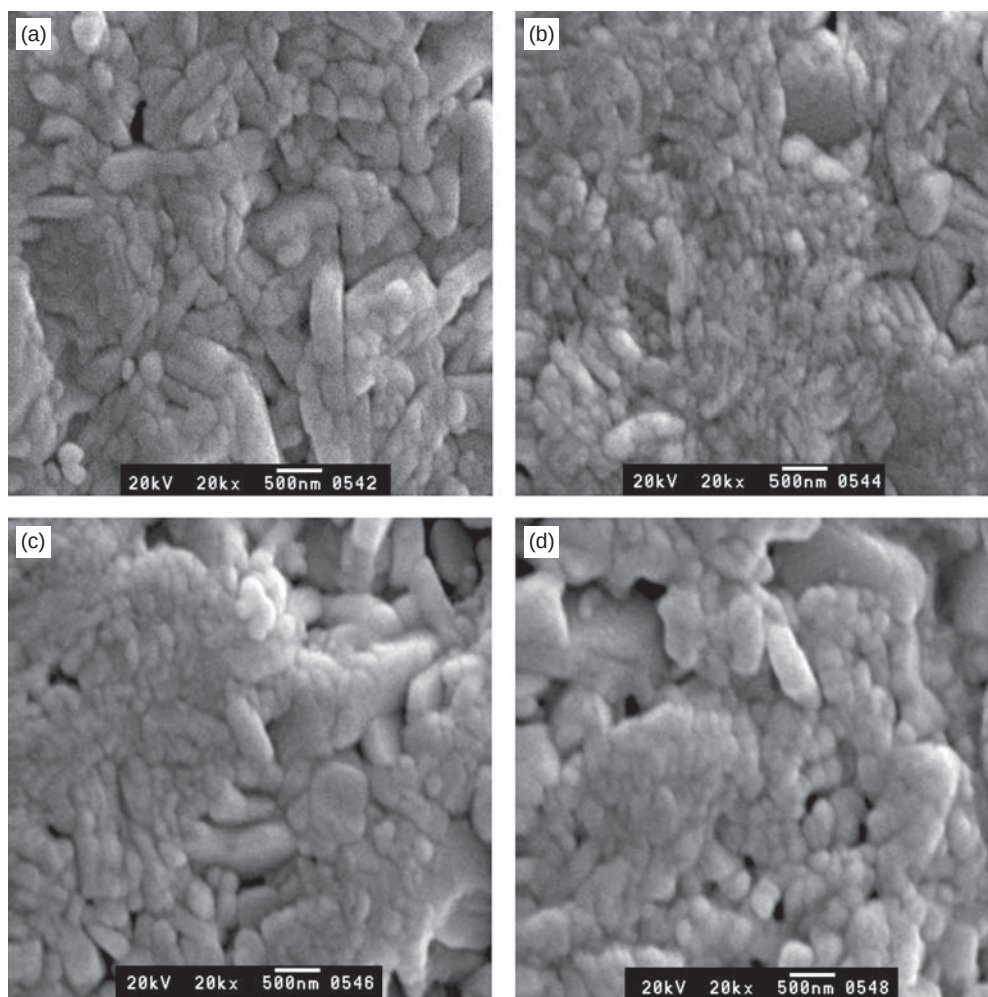


Fig. 4. Scanning electron microscopy of the pellets sintered at 800 °C for 1 h: (a) BIT, (b) BIT01Nb, (c) BIT02Nb and (d) BIT04Nb.

the high electric field region, the localized carriers begin to come out of the trap, resulting in a large increase of current density. Cho *et al.*⁴⁶ observed a large leakage current for BIT films annealed in nitrogen atmosphere. This is a consequence of a porous microstructure in which there are a lot of carrier traps inside it and at higher fields these charges are ejected. In the plate-like structure observed in the doped samples, carrier injection into the insulator looks very important, so space charge can distribute along the plate-like grain boundaries.

The temperature dependence of relative permittivity and dielectric loss measured at 1 MHz is shown in Figures 6(a–d). As expected, the dielectric permittivity and dielectric loss rapidly increased about 400 °C due to the high electrical conductivity in this region. At elevated temperatures a slightly increase in the permittivity was noted due the substitution of Nb^{5+} by Ti^{4+} in BIT lattice which efficiently decreased the V_{O} concentration. This can be explained by the reduction of electrical conductivity caused by donor substitution in the perovskite cell.⁴⁷ However, a significantly enhanced dielectric permittivity at

high temperatures is due to the increase of oxygen-vacancy concentration which affects the dielectric polarization.⁴⁸ The dielectric loss was found to be low in all compositions with a slight increase for BITNb04.

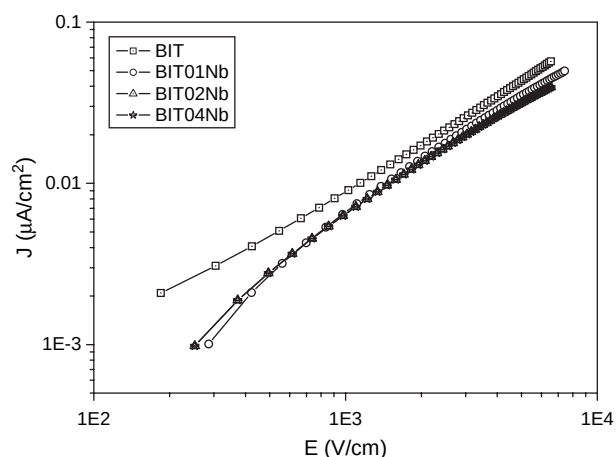


Fig. 5. Current density versus electric field for pure and niobium doped bismuth titanate ceramics sintered at 800 °C for 1 h.

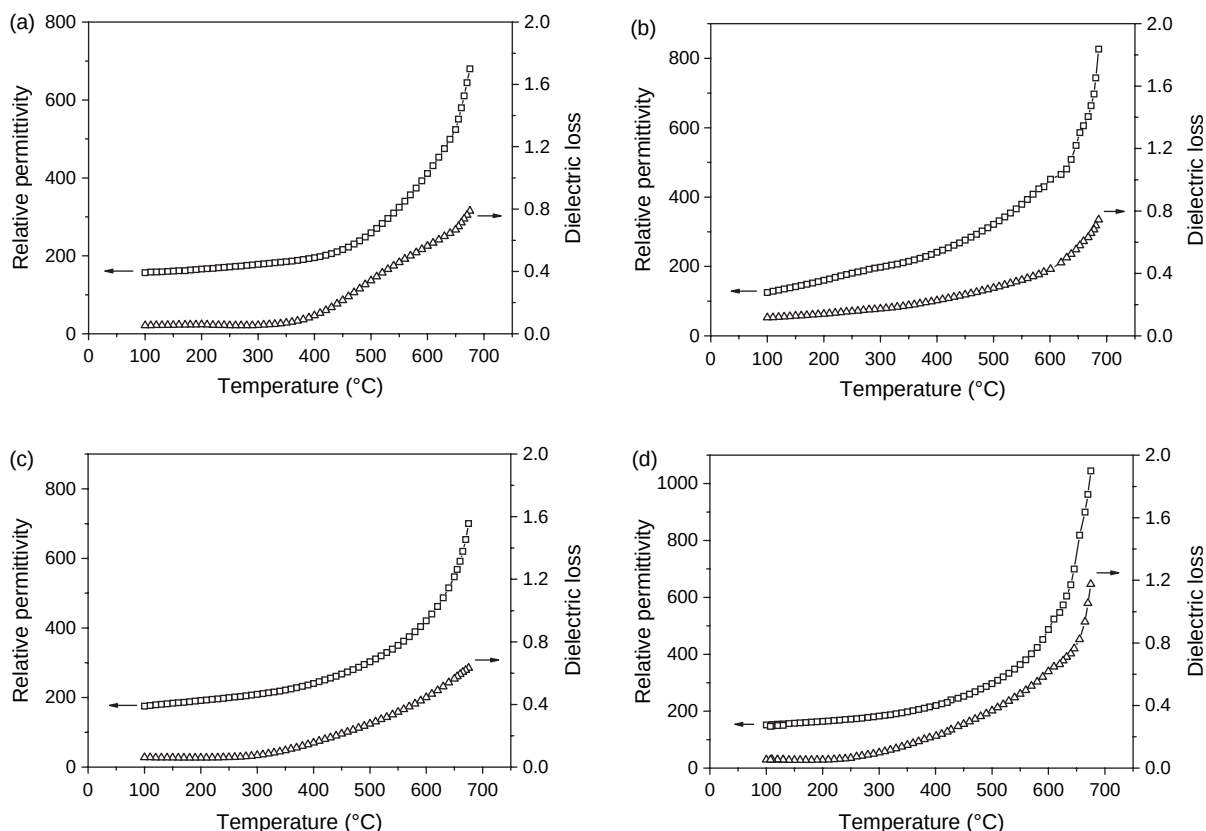


Fig. 6. Relative permittivity and dielectric loss versus temperature at 1 MHz for sintered pellets 800 °C for 1 h: (a) BIT, (b) BIT01Nb, (c) BIT02Nb and (d) BIT04Nb.

In order to characterize the local ferroelectric properties, ferroelectric domains were polarized and imaged using a commercial AFM equipped with a conducting tip and operating under ambient conditions. To polarize domains, a voltage larger than the coercive voltage of the ferroelectric was applied to the tip while scanning in contact with the sample surface. To read the resulting domain structure, the piezoelectric response was measured. In this technique, the tip is scanned in contact with the sample surface while applying an ac voltage smaller than the coercive voltage across the ferroelectric, with the resulting piezoelectric deformation being detected with a standard lock-in measurement. The out-of-plane (OP) and in-plane (IP) piezoresponse images of the as-grown sample after applying a bias of -15 V, on an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$, and then an opposite bias of $+15$ V in the central $1\ \mu\text{m} \times 1\ \mu\text{m}$ area were employed. BIT, BITNb02, BITNb04 samples were analyzed. The white regions in the out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as down polarization (Figs. 7(a), (c), (e)) while the dark regions correspond to domains oriented upward referred to as up polarization. Grains which exhibit no contrast change are associated with zero out-of-plane polarization. A similar behavior was

observed when a positive bias was applied to the ceramic. We noticed that some of the grains exhibit a white contrast associated to a component of the polarization pointing toward the bottom of the sample. On the other hand, in the in-plane PFM images (Figs. 7(b, d, and f)) the contrast changes were associated with changes of the in-plane polarization components. In this case, the white contrast indicates polarization e.g., in the positive direction of the y-axis while dark contrast are given by in-plane polarization components pointing to the negative part of the y-axis. This is a common result for bismuth-layered ferroelectrics, which exhibit a great polarization in a -axis direction, besides a smaller polarization along the c -axis and reflects the different orientation of the grains, i.e., the light regions are c -axis oriented crystallites. Since the image does not change even for high voltages, it can be concluded that it is impossible to align their polarization vector, so the total polarization in field direction is always moderate. By changing the polarity of the applied voltage it can be easily demonstrated that the light regions present a polarization vector perpendicular to the sample surface, whereas in the dark regions the polarization vector lies in the sample plane. The decrease in piezoelectric response with increasing Nb concentration originates from a reduced polarizability along the a -axis, which contributes

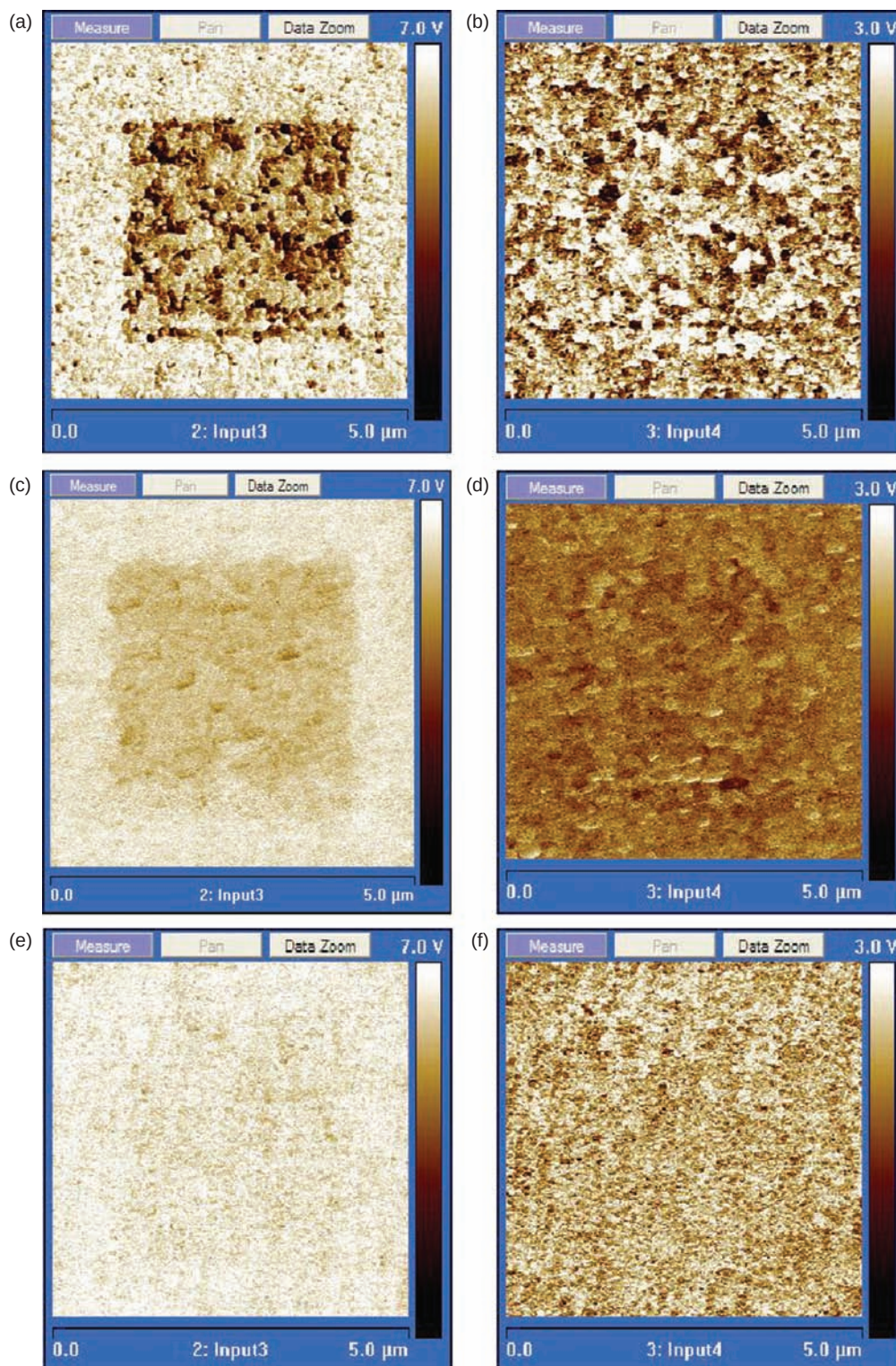


Fig. 7. Out-of-plane (OP) and in-plane (IP) PFM images of the pellets sintered at 800 °C for 1 h: (a) BIT (OP), (b) BIT (IP), (c) BIT02Nb (OP), (d) BIT02Nb (IP), (e) BIT04Nb (OP) and (f) BIT04Nb (IP).

significantly to the piezoelectric properties of bismuth titanate. The in-plane images show light-colored grains presenting a polarization vector in the positive y-axis direction and dark grains with exactly opposite polarization. Grains

with intermediate contrast do not present overall piezoelectricity, probably due to pinned domains. In this way, we supposed that Nb is changing the lattice vibration of BIT affecting the piezoelectric properties.

4. CONCLUSIONS

In summary, Rietveld analyses confirmed that the BIT and Nb doped BIT powders crystallize in an orthorhombic structure with space group Fmmm. Raman analyses confirmed that Niobium addition causes a sharp increase in the band intensity and lattice distortion due the higher electrovalence of niobium compared to titanium. UV-vis absorption spectra showed that the increase of optical band gap values is associated with the reduction of intermediary energy levels within the band gap of the BIT phase. The leakage current of BIT is strongly affected by grains morphology while Dielectric permittivity was increased by Nb^{5+} doping due to the increase of oxygen-vacancy concentration. Ferroelectric domain characteristics by PFM were also investigated to study the dependence of electrical properties on grain orientations. A simple analysis based on three types of contrast, namely, bright, dark and gray contrast was used to determine domain configuration. PFM measurements reveal a decrease in piezoelectric response with increasing Nb concentration originating from a reduced polarizability along the a -axis. High spontaneous polarization is noted for the less doped sample due the reduction of strain energy and pin charged defects after niobium addition.

Acknowledgments: The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

References and Notes

- K. H. Hellwege and A. M. Hellwege (eds.), Landolt-Bornstein, Springer, Berlin (1981), Vol. 16a.
- B. Aurivillius and P. H. Fang, *Phys. Rev.* 162, 893 (1962).
- O. Auciello and R. Ramesh, *MRS Bull.* 21, 29 (1996).
- E. C. Subbarao, *J. Phys. Chem. Solids* 23, 665 (1962).
- Y. Wu, M. J. Forbess, and S. Seraji, *J. Appl. Phys.* 90, 5296 (2001).
- T. Kikuchi, A. Watanabe, and K. Uchida, *Mater. Res. Bull.* 12, 299 (1977).
- R. E. Newnham, R. W. Wolfe, and J. F. Dorrian, *Mater. Res. Bull.* 6, 1029 (1971).
- J. V. Landuty, G. Remaut, and S. Amelinckx, *Mater. Res. Bull.* 4, 329 (1969).
- S. E. Cummins and L. Cross, *J. Appl. Phys.* 39, 2268 (1968).
- H. Yan, H. Zhang, and J. R. Michael, *Appl. Phys. Lett.* 87, 082911 (1971).
- J. F. Dorrian, R. E. Newnham, M. I. Kay, and D. K. Smith, *Ferroelectrics* 3, 17 (1971).
- L. N. Zhang and R. Q. Chu, *Mater. Sci. Eng. B* 116, 99 (2005).
- H. S. Shulman, M. Testorf, D. Damjanovic, and N. Setter, *J. Am. Ceram. Soc.* 79, 3124 (1996).
- S. H. Hong, J. A. Horn, S. Trolrier-Mckinstry, and G. L. Messing, *J. Mat. Sci. Lett.* 19, 1661 (2000).
- A. Z. Simões, E. C. Aguiar, A. Ries, J. A. Varela, and E. Longo, *Mater. Lett.* 61, 588 (2007).
- Y. M. Kan, G. J. Zhang, P. L. Wang, and Y. B. Cheng, *J. Eur. Ceram. Soc.* 28, 1641 (2008).
- H. S. Shulman, M. Testorf, D. Damjanovic, and N. Setter, *J. Am. Ceram. Soc.* 79, 3124 (1996).
- M. Villegas, A. C. Caballero, C. Moure, P. Duran, and J. F. Fernandez, *J. Am. Ceram. Soc.* 82, 2411 (1999).
- M. P. Pechini, US Patent 3,330,697, July (1967).
- R. A. Young, A. Sakthivel, T. S. Moss, and C. O. Paiva-Santos, *J. Appl. Cryst.* 28, 366 (1995).
- ICSD Number 024735, calculated from ICSD using POWD-12 (1997).
- B. D. Stojanovic, A. Z. Simões, C. O. Paiva-Santos, C. Quinelato, E. Longo, and J. A. Varela, *Ceram. Int.* 32, 707 (2006).
- Y. Kan, P. Wang, Y. Li, Y. B. Cheng, and D. Yan, *Mater. Lett.* 56, 910 (2002).
- M. E. Mendoza, F. Donado, and J. L. Carrillo, *J. Phys. Chem. Solids* 64, 2157 (2003).
- W. K. Chia, C. F. Yang, and Y. C. Chen, *Ceram. Int.* 34, 379 (2008).
- J. F. Dorrian, R. E. Newnham, and K. K. Smith, *Ferroelectrics* 3, 17 (1971).
- T. Rentschler, *Mater. Res. Bull.* 32, 351 (1997).
- A. Z. Simões, B. D. Stojanovic, M. A. Ramirez, A. A. Cavaleiro, E. Longo, and J. A. Varela, *Ceram. Int.* 34, 257 (2008).
- M. Zdujic, D. Poleti, C. Jovalekic, and L. Karanovic, *J. Non-Cryst. Solids* 352, 3058 (2006).
- K. R. Zhu, M. S. Zhang, Y. Deng, J. X. Zhou, and Z. Yin, *Solid State Commun.* 145, 456 (2008).
- M. K. Jeon, Y. I. Kim, S. H. Nahm, J. M. Sohn, C. H. Jung, and S. I. Woo, *J. Phys. D* 40, 4647 (2007).
- J. F. Scott, C. A. Paz De Araujo, and B. M. Melnick, *J. Alloys Compds.* 211, 451 (1994).
- S. Luo, Y. Noguchia, M. Miyayama, and T. Kudo, *Mater. Res. Bull.* 36, 531 (2001).
- H. Idink, V. Srikanth, W. B. White, and E. C. Subbarao, *J. Appl. Phys.* 73, 1819 (1994).
- N. Sugita, M. Osada, and E. Tokumitsu, *Jpn. J. Appl. Phys. Part 1*, 40, 6810 (2002).
- S. Kojima, R. Imaizumi, S. Hamazaki, and M. Takashige, *Jpn. J. Appl. Phys. Part 1*, 33, 5559 (1994).
- M. K. Jeon, Y. I. Kim, S. H. Nahm, and S. I. Woo, *J. Appl. Phys. D* 39, 5080 (2006).
- Z. C. Ling, H. R. Xia, W. L. Liu, H. Han, X. Q. Wang, S. Q. Sun, D. G. Ran, and L. L. Yu, *Mater. Sci. Eng. B* 128, 156 (2006).
- Q. Y. Tang, Y. M. Kan, Y. G. Li, G. J. Zhang, and P. L. Wang, *Scripta Mater.* 54, 2075 (2006).
- Z. Lazarevic, B. Stojanovic, M. Romcevic, M. Mitric, C. Jovalekic, and N. Romcevic, *J. Alloys Compds.* 453, 499 (2008).
- M. Osada, M. Tada, and M. Kakihana, *Mater. Sci. Eng. B* 120, 95 (2005).
- Q. Y. Tang, Y. M. Kan, and Y. G. Li, *Scripta Mater.* 54, 2075 (2006).
- P. Kubelka and F. Munk, *Z. Tech. Phys.* 12, 593 (1931).
- M. P. Besland and H. D. Aissa, *Thin Solid Films* 495, 86 (2006).
- L. Zhang, R. Chu, S. Zhao, G. Li, and Q. Yin, *Mater. Sci. Eng. B* 116, 99 (2005).
- H. J. Cho, W. Jo, and T. W. Noh, *Appl. Phys. Lett.* 65, 1525 (1994).
- Y. J. Qi, X. Xiao, and C. J. Lu, *J. Appl. Phys.* 98, 094101 (2005).
- Z. S. Macedo, *J. Eur. Ceram. Soc.* 24, 2567 (2004).

Received: 14 May 2010. Accepted: 2 July 2010.

ANEXO D



Piezoresponse force microscopy behaviour of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics with various excess bismuth

Ederson C. Aguiar¹, Alexandre Z. Simões^{2,*}, Francisco Moura³, Mario Cilense¹, Elson Longo¹, Jose A. Varela¹

¹São Paulo State University, UNESP, Chemistry Institute, Department of Chemistry-Physics, P.O. Box 355, 14800-900, Araraquara, São Paulo, Brazil

²São Paulo State University, UNESP, Engineering Faculty, P.O. Box 355, 12516-410, Guaratinguetá, São Paulo, Brazil

³Federal University of Itajubá- Unifei - Campus Itabira, Rua São Paulo 377, Bairro Amazonas, P.O. Box 355, 35900-37, Itabira, Minas Gerais, Brazil

Received 19 November 2010; received in revised form 21 January 2011; accepted 14 February 2011

Abstract

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$ - BIT) ceramics derived from different amounts of excess Bi_2O_3 were prepared using the polymeric precursor method. In spite of excess bismuth, single phase ceramics were obtained with a controlled microstructure. Raman analysis evidenced typical vibrational bands of the BIT phase. UV-vis spectra indicated that excess Bi_2O_3 causes a reduction in defects in the BIT lattice due to the suppression of oxygen vacancies located at the octahedral BO_6^- ion. The microstructure and electrical properties are strongly dependent on the excess Bi_2O_3 . Appropriate initial Bi_2O_3 excess reduces the leakage current and loss tangent and thereby improves the polarization of BIT ceramics. Rietveld analyses confirmed that the powders crystallize in an orthorhombic structure with a space group of Fmmm at room temperature. The polarization reversal was investigated by applying ac voltage through a conductive tip during the area scanning and was investigated by piezoresponse force microscopy (PFM).

Keywords: bismuth titanate, chemical synthesis, annealing, dielectric properties

1. Introduction

Recently, compounds with an Aurivillius structure have been investigated, such as: BBT (barium bismuth tantalate), SBN (strontium bismuth niobate), SBT (strontium bismuth titanate), BBN (barium bismuth niobate) and BIT (bismuth titanate). BIT is a promising ferroelectric material which is used in non-volatile random access memories [1,2]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has interesting properties: high Curie temperature, high remanent polarization and low coercive field. These properties are due to the Bi_2O_2 layers separated by perovskite planes of type $\text{Bi}_2\text{Ti}_3\text{O}_{10}$ in the orthorhombic structure. The crystal structures of BLSFs (bismuth-layer-structured ferroelectrics) are generally formulated as $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ where A represents

mono-, di-, or trivalent ions, B represents tetra-, penta-, or hexavalent ions with appropriate size and valence, and m is the number of BO_6 octahedra in the pseudoperovskite blocks ($m = 1, 2, 3, 4$, and 5). The perovskite blocks, $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, are sandwiched between bismuth oxide layers, $(\text{Bi}_2\text{O}_2)^{2+}$ along the c -axis [3]. The electric and dielectric properties of the blocks have been improved by the addition of excess bismuth. These studies revealed that when the value of the excess Bi content in precursor sols is 10 mol% the best polarization-electric field, capacitance-voltage and dielectric characteristics were attained. Also, the addition of a 3 mol% excess of Bi_2O_3 resulted in a drastic decrease in the leakage current [4,5]. The excess Bi_2O_3 in SBT indicated that the phase-transition and ferroelectric properties such as spontaneous polarization (P_s) showed a dependence on the Bi content. The ferroelectric Curie temperature T_c decreased with an

* Corresponding author: tel: +55 12 3123 2765
fax: +55 12 3123 2800, e-mail: alezipo@yahoo.com

increasing in the Bi content and the P_s was maximized when 2–3 mol% excess of Bi_2O_3 was added [6]. In other work, addition of 10 mol% Bi excess in $\text{BaBi}_2\text{Ta}_2\text{O}_9$ increased the dielectric permittivity with decreasing $\tan \delta$ while improve ferroelectric properties [7]. In another experiment, bismuth titanate with an excess of 5 wt.% Bi was added to the stoichiometric mixture aiming to minimize the bismuth loss during the thermal treatment. Without the addition of bismuth, pure phase could not be obtained [8].

Due to this high transition temperature, BIT ceramics are good candidates for high temperature piezoelectric applications. The main problem concerning their practical application as piezoelectrics is the relatively low electrical resistivity. The electrical conductivity in BIT is highly anisotropic, with the maximum value in the same plane of the vector polarization. As a consequence, BIT ceramics are very difficult to pole. Thus the reduction of electrical conductivity is one of the main goals the worldwide investigations of BIT [9].

The BIT-based ceramics microstructure reflects the structural anisotropy showing larger platelets-like grains growing preferentially in the a – b plane. The electrical response of these materials is strongly dependent on the microstructure [10,11]. The conventional ceramic route synthesis leads to undesirable phases due to volatilization of Bi_2O_3 at elevated temperatures [12]. The formation of secondary phases can be avoided by decreasing the calcination temperature or using wet-chemistry based methods. By using chemical methods, (e.g. coprecipitation, sol-gel, hydrothermal and the Pechini method [13]), it is possible to control the morphology and chemical composition of the powders. Due to the easy volatilization of Bi_2O_3 in the fabrication process, initial excess bismuth can strongly affect the structure and physical properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based materials. Kim and Kim [14] studied the effect of excess bismuth on the crystallization of BLT thin film prepared by MOD. Lin *et al.* [15] studied the role of excess bismuth on the orientation and ferroelectricity of BLT film by CSD. However, limited research has been conducted related to the microscopic effect that excess bismuth can cause in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ -based ceramics. The aim of this paper is to examine the effects of initial Bi_2O_3 excess content on microstructural and electrical properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) ceramics. To vary the Bi_2O_3 content, the ceramics derived from varying amount of initially excess of Bi_2O_3 (3–10 mol%) on the precursor solution were prepared by the polymeric precursor method. Measurements by piezoresponse force microscopy (PFM) reveal that addition of excess bismuth can reduce the strain energy and pin-charged defects and that the perpendicular component of polarization can be switched between two stable states: bright and dark contrast inside and outside of the square region.

II. Experimental

Titanium isopropoxide (97% - Alfa Aesar); bismuth nitrate pentahydrate (100.1% - Mallinckrodt); citric acid (99.5% - Merck); ethyleneglycol (99.7% - Synth), nitric acid (99.9% - Synth); ethylenediamine (98% - Nuclear) and ammonium hydroxide (99.9% - Qhemis) were used as raw materials. Bismuth and titanium precursor solutions were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. The molar ratio of metal : citric acid : ethylene glycol was 1 : 4 : 16. Appropriate quantities of Ti and Bi solutions were mixed and homogenized by stirring at 90°C for 2 hours. Then the temperature was increased to 130–140°C, yielding a highly viscous polyester resin. Most of the organic material was decomposed by thermal treatment at 300°C for 2 hours. The formed porous product was crushed and heated in an aluminium crucible at 700°C for 4 hours to eliminate residues of organic material. The powders were milled for 4 hours with zirconia balls and isopropyl alcohol with and without excess Bi. The bismuth titanate compositions were designed as BIT, BIT3, BIT5 and BIT10 which corresponds to 0, 3, 5 and 10 mol% of excess Bi_2O_3 . The powders were uniaxially (150 MPa) and isostatically pressed (210 MPa) into pellets. The sintering was performed on pellets packed into covered alumina crucibles, carried out in air at a temperature of 800°C for 1 hour (heating and cooling rate of 10 °C/min).

Raman scattering of powders was performed at room temperature (Fourier transform - RFS 100/S Bruker, excited by a Nd-YAG laser in 1064 nm). The band gap values were obtained using ultraviolet spectroscopy in the visible region curve (UV-vis-NIR Spectrophotometer - Varian Cary 500 X). For Rietveld analyses, X-ray diffraction data were collected with a Rigaku 20-2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, 2θ from 20° to 120°, step size of 0.02°, $\lambda\text{Cu K}\alpha$ monochromatized by a graphite crystal, divergence slit of 2 mm, reception slit of 0.6 mm and step time of 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [16]. The profile function used was the modified Thompson-Cox-Hasting pseudo-Voigt, in which η (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum.

Bulk densities and weight loss of the sintered pellets were measured by the Archimedes method. The phase formation and crystallinity were studied by X-ray diffractometry (XRD) with $\text{Cu K}\alpha$ radiation using a normal θ - 2θ scanning method (Rigaku RINT2000 diffractometer). A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains (Topcom SM-300).

Dielectric permittivity measurements were performed in HP 4192A LF Mountain View impedancemeter attached to a Flyever oven (FE50RP temperature controller). Silver electrodes for electrical measurements were deposited on the polished surface of sintered pellets by evaporation through a sputtering system. Resistivity was determined by current-voltage in a voltage source (Keithley 237 - USA).

Piezoelectric measurements were carried out using a setup based on an atomic force microscope in a Multimode Scanning Probe Microscope with Nanoscope IV controller (Veeco FPP-100). In our experiments, piezo-response images were acquired in ambient air by applying a small *ac* voltage with amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz. To apply the external voltage a standard-gold coated Si_3N_4 cantilever with a spring constant of 0.09 N/m was used. The probing tip, with an apex radius of about 20 nm, was in mechanical contact with the uncoated film surface during the measurements. Cantilever vibration was detected using a conventional lock-in technique.

III. Results and discussion

Figure 1 shows the XRD patterns of BIT powders with various amounts of excess Bi_2O_3 . All the peaks are indexed by a JCPDS card of BIT (ICSD no. 24735 with a space group of *Fmmm*). Increasing amounts of initial excess Bi_2O_3 leads to a single BIT phase crystallized in the orthorhombic structure [17]. The excess of bismuth forms a solid solution in the BIT lattice having no influence on long distance ordering. The peaks are indicative of a polycrystalline phase with orientation in the *c*-plane and mainly characterized by a higher intense peak (*hkl* - 117). Our XRD results are in agreement with the results reported in the literature [18–21]. The experimental lattice parameter values were calculated using the Rietveld method [16]. We can observe that the polymeric precursor method permits the attainment of BIT powders at a low heat treatment temperature and re-

duced synthesis time. Moreover, the lattice parameter values obtained by this method presented small variations as compared to the values reported in the literature [22–27]. These differences are related to the preparation method, synthesis conditions (heat treatment temperature, time), lattice distortion and residual stresses in the lattice and/or structural defects. To get more details about crystal structure of BIT system when more bismuth was added, Rietveld analyses of other compositions were performed and the results will be published in a near future.

The BIT system has already been investigated from a fundamental point of view [28]. In the present study, we have adopted the Rietveld refinement technique to investigate the crystal structure of the BIT10 system. Table 1 illustrates the R_{wp} , R_{exp} , and *S* indexes, as well as the lattice parameters (*a*, *b* and *c*) and the unit cell volume (*V*). The phase identification was carried out in the PDF data bank, resulting in an orthorhombic structure type. The structural model (available on the ICSD da-

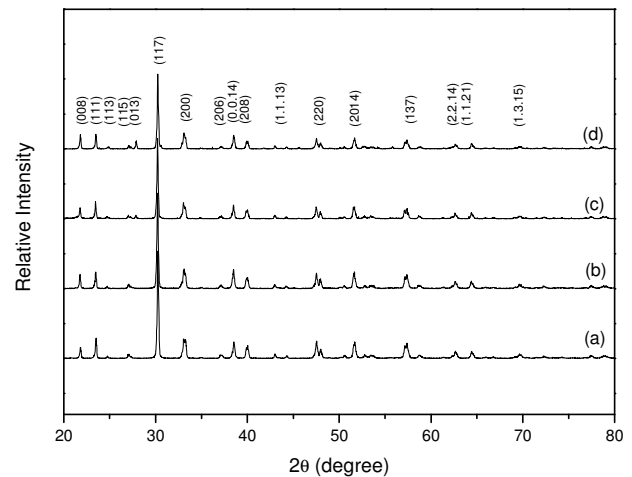


Figure 1. X-ray diffraction at room temperature for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 powders calcined at 700°C for 4 h

Table 1. Refinement Indexes for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcined at 700°C for 4 hours with 10 mol% of excess bismuth

Refinement Indexes		Atomic Positions		S _{Occ}		Lattice	
R_{WP} [%]	11.12	A1	0; 0; 0.06722	Bi (A1)	1.00000	a [Å]	5.4175
R_{EXP}	7.06	A2	0; 0; 0.21091	Nb (A1)	0.00000	b [Å]	5.4403
S	1.57	B1	0; 0; ½	O	0.91700	c [Å]	32.7862
		B2	0; 0; 0.37099			V [Å ³]	966.30
		O1	¼; ¼; 0			d [g/cm ³]	8.02
		O2	¼; ¼; ¼				
		O3	0; 0; 0.43786				
		O4	0; 0; 0.32536				
		O5	¼; ¼; 0.11165				
Perovskite [mol%]		Stoichiometry				Refinement	
97.5 ± 0.5		$\text{Bi}_4\text{Ti}_3\text{O}_{12}$				$\text{Bi}_4\text{Ti}_3\text{O}_{11.6}$	

tabank) that allows the best fit was the orthorhombic model (ICSD no. 24735 with a space group of $Fmmm$). Quantitative phase analyses for the orthorhombic phase were calculated according to the reference of Young and Wiles [16]. The covalent interaction originating from the strong hybridization between Ti 3d and O 2p orbitals, plays an important role in the structural distortion of the BIT compound. It can be assumed that addition of excess of bismuth improves oxygen ion stability in the lattice because some of the Bi ions in the pseudoperovskite layers containing Ti–O octahedral were not volatilized. The low S values ($S = R_{wp}/R_{exp}$) indicates the good quality of the refinement; the calculated parameters are closer to literature data [29]. Therefore, we can assume that the addition of excess bismuth stabilizes the oxygen vacancies and consequently the structure.

The weight loss and relative density as a function of excess Bi_2O_3 are shown in Fig. 2. It can be seen that the weight loss increases with increasing excess Bi_2O_3 because the low temperature sintering inhibits bismuth oxide volatilization. The relative density measured by the Archimedes method increases with excess Bi_2O_3 reaching around 90% of the theoretical density of BIT, corresponding to 8.038 g/cm^3 . This result is not satisfactory from an electrical point of view, since the polarization and dielectric permittivity are dependent on the level of porosity and grains morphology, but it is still a very interesting effect.

UV-vis spectroscopy measurements were evaluated in the BIT powders (see Fig. 3). The maximum absorption was located at around 400 nm with respective band gap values determined from the Kubelka Model [30]. The optical energy band gap is related to the absorbance and to the photon energy by the following equation:

$$h\nu\alpha \propto (h\nu - E_g^{\text{opt}})^2 \quad (1)$$

where α is the absorbance, h is the Planck constant, ν is the frequency and E_g^{opt} is the optical band gap [31]. The obtained values are 3.13, 3.02, 3.03, 3.03 eV, which are similar to the values reported by Wei *et al.* [32] (around

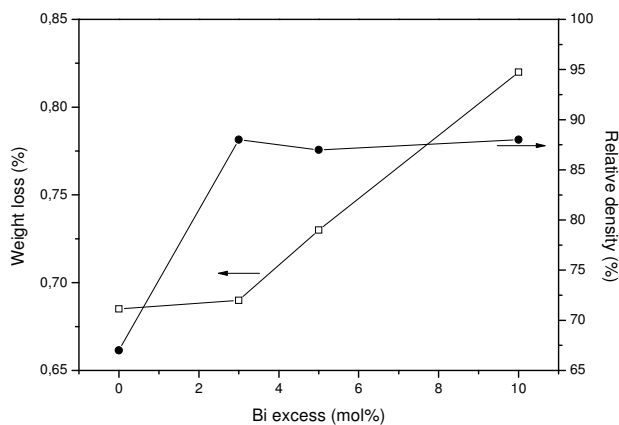


Figure 2. Relative density and weight loss of the sintered pellets versus excess bismuth

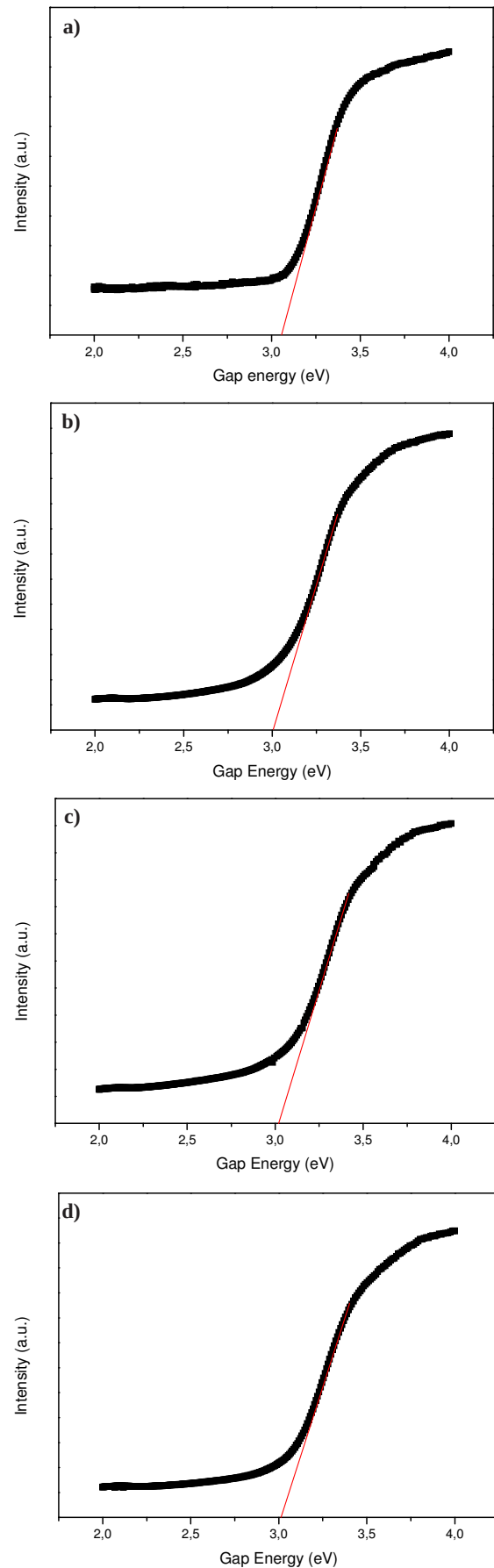


Figure 3. UV-vis absorption spectra at room temperature for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 powders calcined at 700°C for 4 h

3.08 eV). Our BIT powders presented characteristic absorption spectra of ordered or crystalline materials. These results indicate that the exponential optical absorption edge and the optical band gap are controlled by the degree of structural disorder in the BIT lattice. This decrease in the band gap can be ascribed to a reduction of defects in the lattice which decreases the intermediary energy levels due to the reduction of oxygen vacancies located at BO_6 octahedra. The main differences in optical band gaps can be related to the different factors, mainly including: synthesis method, shape (powder, crystal or thin film) and synthesis conditions.

Raman scattering has proven to be a valuable technique to obtain information about local structures within materials. Figure 4 shows the Raman spectra of BIT powders derived from different excess Bi_2O_3 at room temperature. To better denote the peak position, Raman modes are presented in Table 2. The order-disorder degree in the crystal lattice of BIT powders at short and medium distances was investigated. Raman modes located at 96, 119, 189, 223, 266, 315, 450, 536, 615 and 848 cm^{-1} are characteristics of the BIT phase [33]. The modes located under 200 cm^{-1} can be related to vibrations between Bi and O atoms [34]. For BIT10, it is evidently a characteristic mode around 100 cm^{-1} and is probably due to a distortion in the A site caused by the bismuth ion. This distortion into the A site of the perovskite enhances the Jahn-Teller distortion of TiO_6 octahedra. On the other hand, Raman modes located above 200 cm^{-1} are responsible for distortions and vibrations of TiO_6 octahedra. As the content of excess bismuth increases, there is a reduction in the Raman band intensities, (mainly the mode located at 266 cm^{-1}). This is due to the vibrations of Ti-O atoms inside the perovskite layer and to vibrations of Bi-O atoms within the Bi_2O_2 layer [35]. The main bands at 266, 536 and 848 cm^{-1} , originated from TiO_6 octahedra, share a similar excess bismuth behaviour (they reduce its intensity and become broaden with increasing Bi excess). The modes at 230, 268, 328, 530, 563 and 850 cm^{-1} are assigned to stretching and bending vibrations of TiO_6 octahedra because the addition of excess Bi_2O_3 implies a distortion of Bi_2O_2 layers. Raman results are in agreement with XRD data. The appearance of a Raman mode at low-frequency (96 cm^{-1}) is due to the atomic mass of Bi ions which causes Bi displacements in the Bi_2O_2 layer [36]. Raman modes located at 450 and 96 cm^{-1} were evident in BIT10 composition, indicating that 10 mol% of ex-

cess bismuth may cause lattice distortions and stoichiometric changes. Raman results are in agreement with XRD data, indicating an ordered structure at short and long distances.

The microstructures of the sintered pellets were examined by SEM analyses and are illustrated in Fig. 5. The influence of excess bismuth on the shape and size of the grains was evaluated. The grain size is heterogeneously distributed and presents rod-like form morphology which is different from literature data [37]. BIT presents a porous microstructure with compact region with a very small grain size when compared to ceramics with excess bismuth. The BIT3, BIT5 and BIT10 compositions are dense but pure BIT is prone to form a porous structure with a quite a number of voids which can affect the ferroelectric and dielectric properties of ceramics. All ceramics are stoichiometric, evidencing no losses of Bi_2O_3 during the calcination and sintering process indicating that the initial Bi_2O_3 excess is sufficient to compensate for the bismuth oxide volatilization and fill the Bi vacancy in the lattice. Literature data revealed that some excess of bismuth in the BIT ceramic cannot enter into the lattice. The Bi_2O_3 excess may exist as an impurity phase such as bismuth oxide, which would affect the microstructural and ferroelectric properties of ferroelectric material [38]. The densities of BIT ceramics increase with content of excess bismuth due to the formation of oxygen vacancies originate during the calcinated process of the ceramics and substitution of excess of bismuth. That leads to nega-

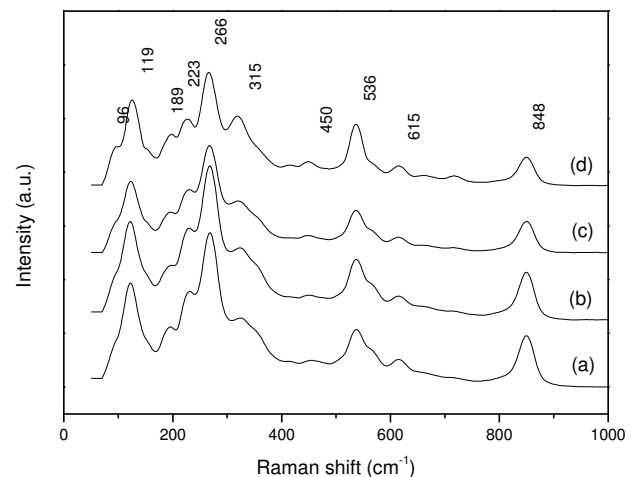
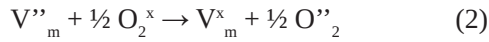


Figure 4. Raman spectra at room temperature for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 powders calcined at 700°C for 4 h

Table 2. Raman modes of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders calcinated at 700°C for 4 hours with several excess bismuth

Compositions	Raman modes [cm^{-1}]
BIT	119, 189, 223, 266, 315, 536, 615, 848
BIT3	119, 189, 223, 266, 315, 536, 615, 848
BIT5	119, 189, 223, 266, 315, 536, 615, 848
BIT10	96, 119, 189, 223, 266, 315, 450, 536, 615, 848

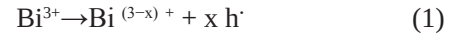
tive charges associated with the presence of negatively charged oxygen trapped at the grain boundary. The negative charge of the oxygen may be caused by charge transference between the metal vacancy and the oxygen, as shown in:



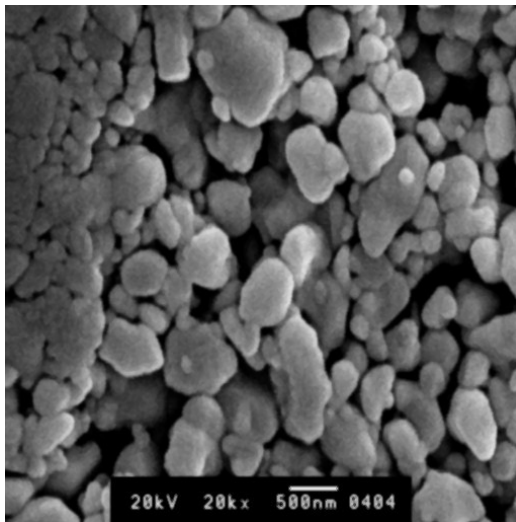
where O^x , V''_m , V_m^x and O''_2 represent the neutral oxygen ions in their normal position, metal site vacancies doubly negatively charged, neutral metal site vacancies, and oxygen ions doubly negatively charged, respectively.

The leakage current as a function of the electric field reveals a direct relationship to electrical conductivity (Fig. 6). Leakage current is one of the most important properties of BIT because high electrical conductivity makes it difficult to polarize the material and minimize the ferroelectric properties [39]. Considering bismuth oxide volatilization during sintering, it is reasonable to assume that electrical conduction associated with vacancies should occur in BIT, aside from the

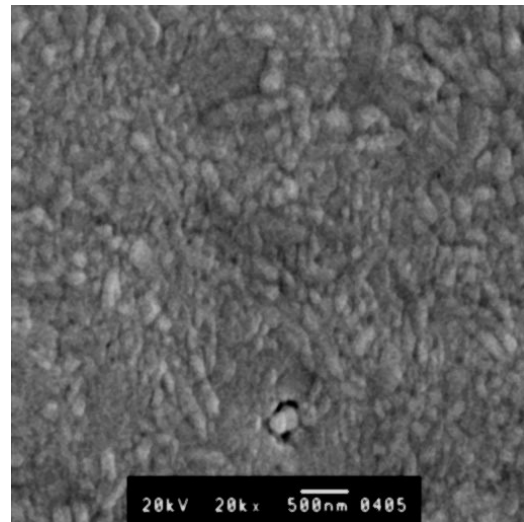
intrinsic hole conduction. The main conduction mechanism of pure BIT is an electronic *p*-type. The leakage current of samples with excess bismuth was significantly decreased in comparison with BIT. The increase in excess bismuth results in a reduction of conductivity due the improvement of BIT matrix holes. The generation of holes can be represented by the following defect reaction [40]:



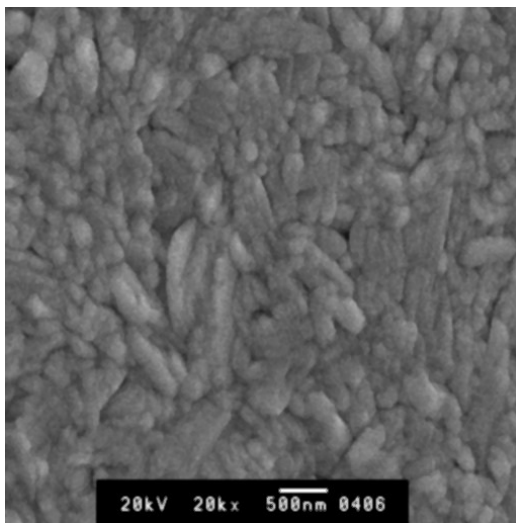
This reaction indicates that holes defects present in BIT are responsible for the leakage current behaviour and consequently the conductivity. Due to the suppression of bismuth oxide volatilization by the addition of excess bismuth the number of carriers associated with vacancy should be remarkably reduced in BIT with excess compositions, indicating a decrease in the leakage current. The addition of excess Bi_2O_3 resulted in a considerable decrease in the leakage current, due to the presence of Bi vacancies (V'''_{Bi}) accompanied by oxy-



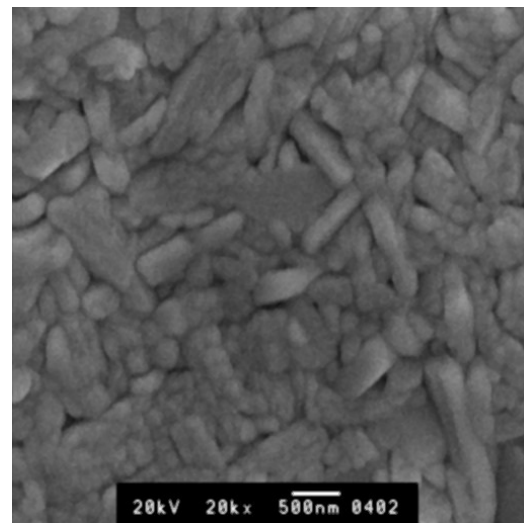
a)



b)



c)



d)

Figure 5. Scanning electronic microscopy for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 ceramics sintered at 800°C for 1 h

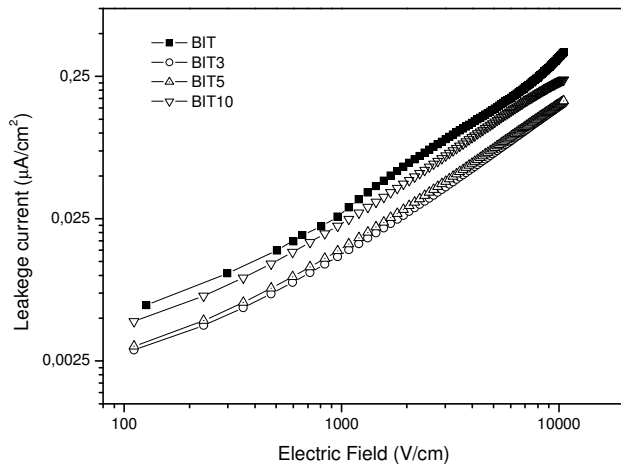


Figure 6. Leakage current behavior as a function of electric field for BIT, BIT3, BIT5 and BIT10 ceramics sintered at 800°C for 1 h

gen vacancies (V_O). Although the leakage-current properties were improved by excess bismuth, there is a decrease in the V_{Bi}''' and V_O density [41]. Also, BIT has rod-like-shaped grains with residual porosity which

could have many carrier traps. In the high electric field region, the localized carriers begin to come out of the trap, resulting in a large increase in the current density. A large leakage current was also observed by Cho *et al.* [42], who observed that for BIT films, annealed in a nitrogen atmosphere with a porous microstructure, there are many carrier traps inside it and for higher fields these charges are ejected.

Figure 7 shows the temperature-dependent dielectric permittivity measured at 100 KHz. There are several factors that affect the dielectric permittivity of ferroelectric ceramic samples, including grain size, impurity and concentration of the space charge. As expected, the dielectric permittivity rapidly increases at temperatures above 400°C due to the low electrical conductivity in this region. Below 450°C the dielectric permittivity increases with the addition of excess bismuth. Furthermore, the significantly enhanced dielectric permittivity can be understood as follows: oxygen-vacancy-induced dielectric polarization becomes predominant due to an increased vacancy concentration and inertia of oxygen ions [43]. As the grain becomes larger, an increase in the

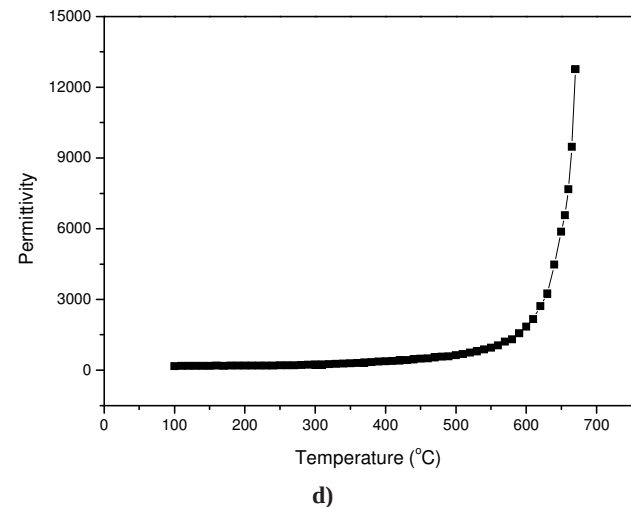
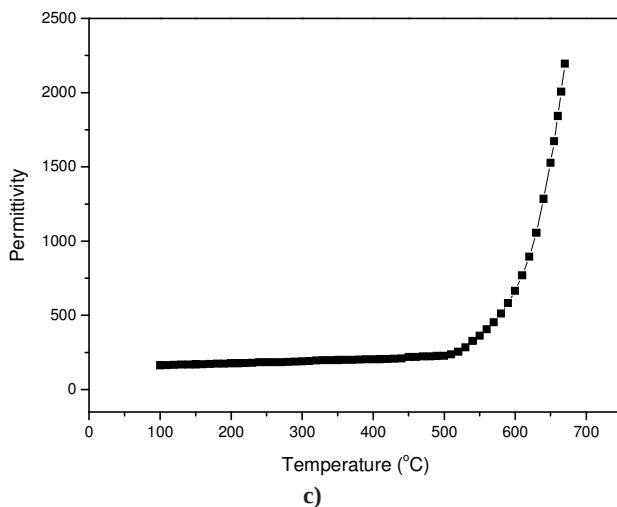
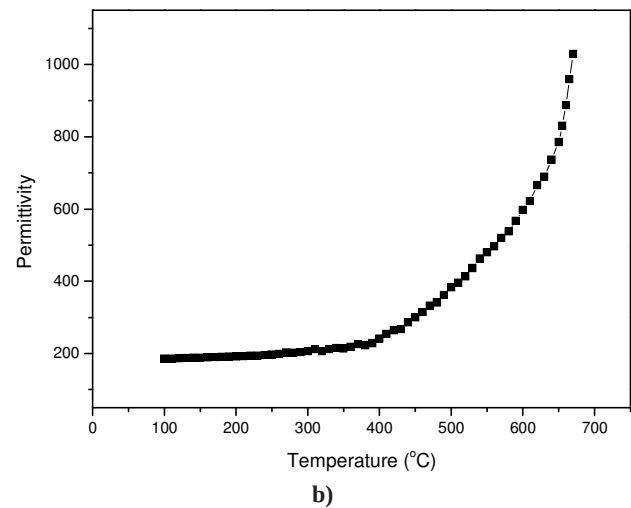
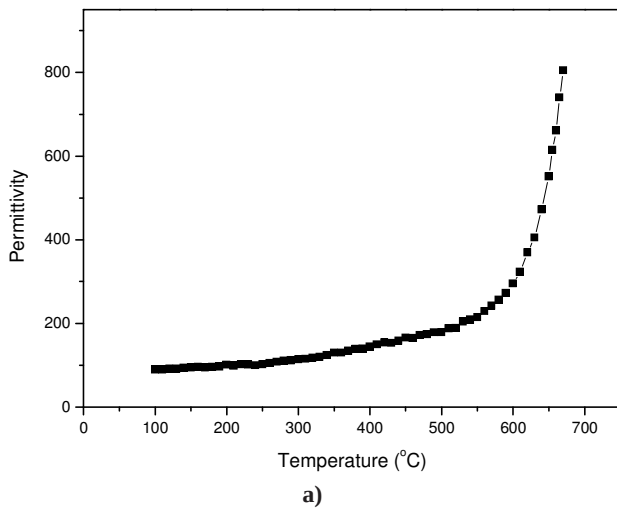


Figure 7. Dielectric permittivity as a function of temperature for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 ceramics sintered at 800°C for 1 h

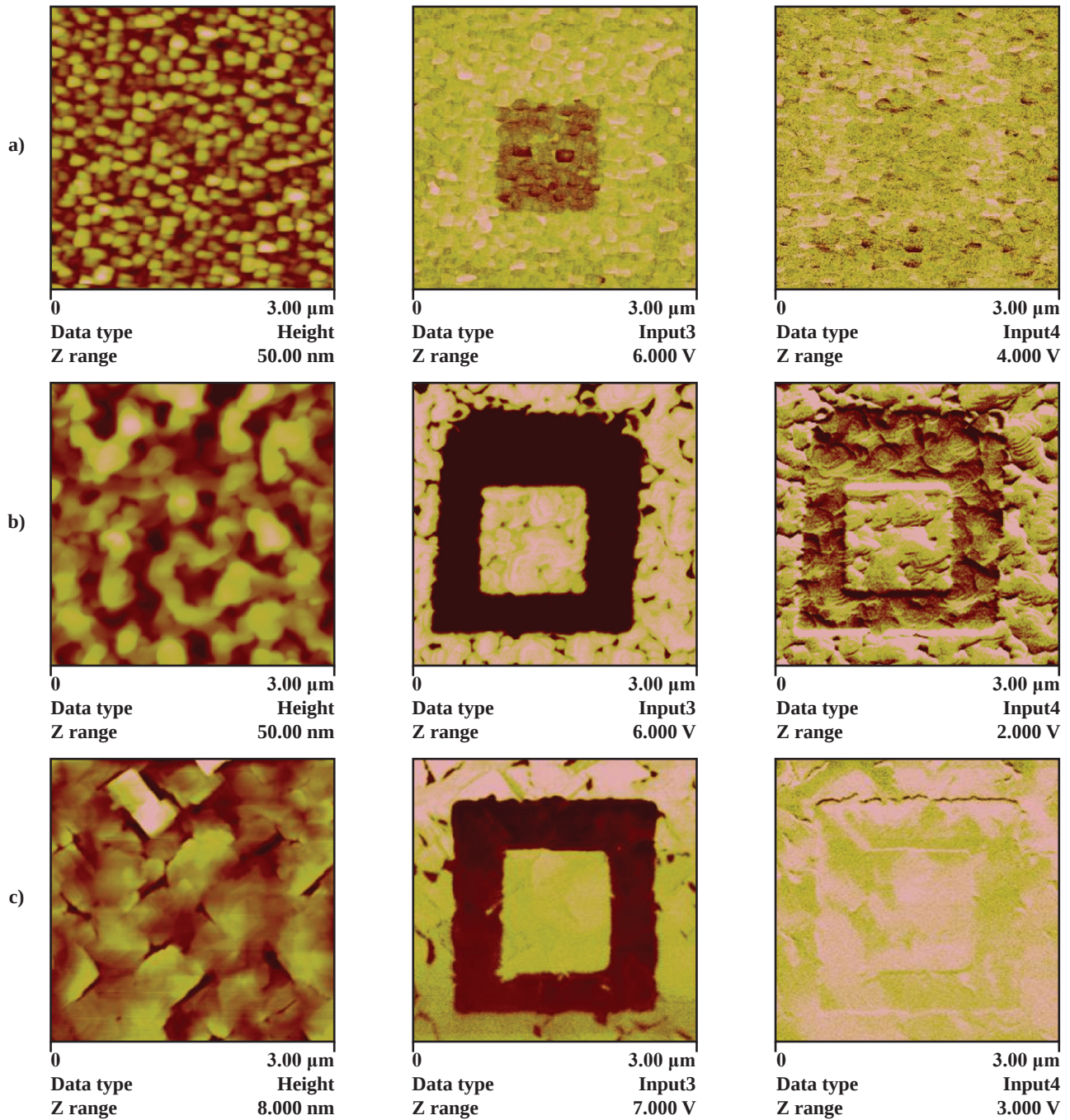


Figure 8. AFM-topography (left), out-of-plane PFM (central) and in-plane PFM (right) images of the pellets sintered at 800°C for 1 h: a) BIT, b) BIT5 and c) BIT10

dielectric permittivity was verified. The incorporation of excess bismuth suppressed the volatilization of bismuth during sintering and reduced the bismuth and oxygen vacancy concentrations in the sintered sample. As a result, the electrical conductivity was significantly reduced, and the polarization was greatly improved. In our study, the main reasons for changes in the dielectric behaviour can be associated with decreased grain size and increased concentration of the space charge. Among all investigated BIT ceramics, the highest dielectric permittivity is shown for the BIT10 sample, where a dielectric permittivity of 12600 was measured at 100 kHz.

To characterize the local ferroelectric properties, ferroelectric domains were polarized and imaged using a commercial AFM equipped with a conducting tip and operating under ambient conditions. To polarize domains, a voltage larger than the coercive voltage of the ferroelectric was applied to the tip while scanning in contact with the sample surface. To read the resulting domain structure, the piezoelectric response was measured. In this technique, the tip is scanned in contact with the sample surface while applying an *ac* voltage smaller than the coercive voltage across the ferroelectric, with the resulting piezoelectric deformation

being detected with a standard lock-in measurement. The out-of-plane (OP) and in-plane (IP) piezoresponse images of the as-grown sample (after applying a bias of -15 V), on an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$, and then an opposite bias of $+15$ V in the central $1\ \mu\text{m} \times 1\ \mu\text{m}$ area were measured. BIT, BIT3, BIT5 and BIT10 samples were analyzed. For comparison the topography of the sample was also presented (Fig. 8). The clear regions in the out-of-plane PFM images (Fig. 8) correspond to domains within the polarization vector oriented toward the bottom electrode (hereafter referred to as down polarization, while the dark regions correspond to domains oriented upward (referred to as up polarization). Grains which exhibit no contrast change are associated with zero out-of-plane polarization. A similar behaviour was observed when a positive bias was applied to the ceramic. We noticed that some of the grains exhibit a clear contrast associated with a component of the polarization pointing toward the bottom of the sample. On the other hand, in the in-plane PFM images (Fig. 8) the contrast changes were associated with changes in the in-plane polarization components. In this case, a clear contrast indicates polarization (e.g. in the positive direction of the y-axis) while a dark contrast is the result of in-plane polarization

components pointing to the negative part of the y-axis. This result is common for bismuth-layered ferroelectrics, which exhibit a great polarization in the a -axis direction, along with a smaller polarization along the c -axis and reflects the different orientation of the grains, i.e. the light regions are c -axis oriented crystallites. Since the image does not change even for high voltages, it can be concluded that it is impossible to align their polarization vector, so the total polarization in the field direction is always moderate. By changing the polarity of the applied voltage it can easily be demonstrated that the light regions present a polarization vector perpendicular to the sample surface, whereas in dark regions the polarization vector lies in the sample plane. The improvement of piezoelectric response with excess Bi_2O_3 originates from a better polarizability along the a -axis, which contributes significantly to the piezoelectric properties of bismuth titanate resulting in a reduction of strain energy and the pinning effect of charged defects. The in-plane images show light-colored grains presenting a polarization vector in the positive y-axis direction and dark grains with exactly opposite polarization. Grains with intermediate contrast do not present overall piezoelectricity, probably due to pinned domains. Therefore, we supposed

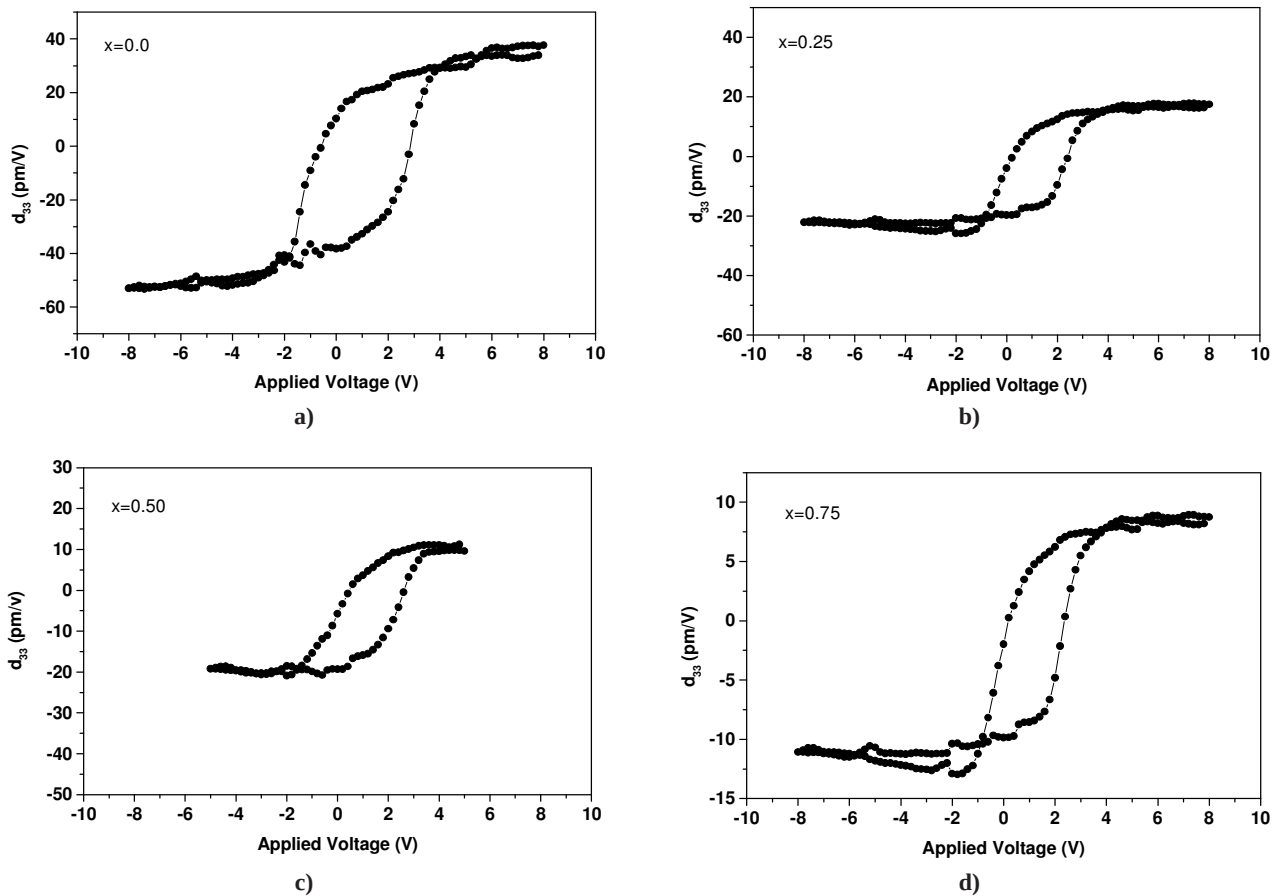


Figure 9. Piezoelectric coefficient as function of voltage for: a) BIT, b) BIT3, c) BIT5 and d) BIT10 ceramics sintered at 800°C for 1 h

that excess Bi_2O_3 is changing the lattice vibration of BIT affecting the piezoelectric properties.

Figure 9 shows the piezoelectric hysteresis loop obtained for the BIT free of excess and with various amounts of excess Bi_2O_3 . The hysteresis in the piezoresponse signal is directly associated with the polarization switching and ferroelectric properties of the sample. The maximum d_{33} value of ~ 45 pm/V is higher for the BIT10 system and approaches the reported value for a BIT single crystal [44]. Here, we point out that it is difficult to compare these values to the piezoelectric coefficients of bulk material since the measurement was performed on a local area that has a relatively intricate field distribution and vibrational modes. Considering the polycrystalline nature of our sample the effective piezoelectric coefficient depends on grain orientation. Therefore, as expected the piezoelectric response changes with increase of bismuth excess due the reduction in the strain energy and the pinning effect of charged defects after doping.

IV. Conclusions

In summary, bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BIT) ceramics derived from different amounts of initial excess Bi_2O_3 were prepared by the polymeric precursor method. An XRD analysis shows that increasing excess Bi_2O_3 single phase BIT powders with an orthorhombic structure were obtained. SEM analyses show grains in the rod-like morphology form; the size decreases with excess bismuth. Due to the suppression of bismuth oxide volatilization by the addition of excess bismuth, there is a reduction in the leakage current and an enhancement of BIT phase dielectric properties. The effective piezoelectric coefficient depends on grain orientation, and excess bismuth was found to effectively induce spontaneous polarization in BIT exhibiting good piezoelectric properties. Due to better electrical properties, BIT with 10 mol% of excess Bi_2O_3 can be considered as a promising composition for application in dynamic random access memories and piezoelectric devices.

Acknowledgements: The authors gratefully acknowledge the financial support agencies in Brazil: FAPESP, CNPq, CAPES.

References

1. B. Aurivillius, "Mixed bismuth oxides with layer lattices: II. Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ", *Ark. Kemi* **1** (1949) 499–512.
2. A.V. Murugan, S.C. Navale, V. Ravi, "Preparation of nanocrystalline ferroelectric $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ by Pechini method", *Mater. Lett.*, **60** [8] (2006) 1023–1025.
3. E.C. Subbarao, "A family of ferroelectric bismuth compounds", *J. Phys. Chem. Solids*, **23** [6] (1962) 665–676.
4. Y. Noguchi, M. Miyayama, "Large remanent polarization of vanadium-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ", *Appl. Phys. Lett.*, **78** [13] (2001) 1903–1905.
5. X.L. Zhong, J.B. Wang, S.X. Yang, Y.C. Zhou, "Dependence of excess bismuth content in precursor sols on ferroelectric and dielectric properties of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films fabricated by chemical solution deposition", *Appl. Surf. Sci.*, **253** [2] (2006) 417–420.
6. J.K. Lee, B. Park, K.S. Hong, "Effect of excess Bi_2O_3 on the ferroelectric properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ceramics", *J. Appl. Phys.*, **88** [5] (2000) 2825–2829.
7. A.Z. Simões, G.C.C. da Costa, M.A. Ramirez, J.A. Varela, E. Longo, "Effect of the excess of bismuth on the morphology and properties of the $\text{BaBi}_2\text{Ta}_2\text{O}_9$ ceramics", *Mater. Lett.*, **59** [6] (2005) 656–661.
8. A.Z. Simões, E.C. Aguiar, A. Ries, E. Longo, J.A. Varela, "Niobium doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics obtained by the polymeric precursor method", *Mater. Lett.*, **61** [2] (2007) 588–591.
9. M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, "Low-temperature sintering and electrical properties of chemically W-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics", *J. Eur. Ceram. Soc.*, **19** [6–7] (1999) 1183–1186.
10. M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, "Factors affecting the electrical conductivity of donor-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ piezoelectric ceramics", *J. Am. Ceram. Soc.*, **82** [9] (1999) 2411–2419.
11. M. Villegas, T. Jardiel, A.C. Caballero, J.F. Fernández, "Electrical properties of bismuth titanate based ceramics with secondary phases", *J. Electroceram.*, **13** [1–3] (2004) 543–548.
12. C. Jovalekic, M. Pavlovic, P. Osmokrovic, L. Atanasoska, "X-ray photoelectron spectroscopy study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric ceramics", *Appl. Phys. Lett.*, **72** [9] (1998) 1051–1054.
13. M.P. Pechini, "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor", *US Patent 3330697*, 11 July, 1967.
14. K.T. Kim, C.I. Kim, "Effect of bismuth excess on the crystallization of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films on Pt/Ti/SiO₂/Si substrates", *Microelectron. Eng.*, **71** [3–4] (2004) 266–271.
15. J.L. Lin, T.L. Chang, W.T. Lin, "Effects of excess Bi concentration, buffered Bi_2O_3 layer, and Ta doping on the orientation and ferroelectricity of chemical-solution-deposited $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ films", *J. Electron. Mater.*, **33** [10] (2004) 1248–1252.
16. R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, "DBWS-9411 - an upgrade of the DBWS*.* programs for Rietveld refinement with PC and mainframe computers", *J. Appl. Cryst.*, **28** [3] (1995) 366–367.
17. JCPDS - ICSD 024735, (1997).
18. B.D. Stojanovic, A.Z. Simões, C.O. Paiva-Santos, C. Quinelato, E. Longo, J.A. Varela, "Effect of processing route on the phase formation and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics", *Ceram. Int.*, **32** [6] (2006) 707–712.
19. Y. Kan, P. Wang, Y. Li, Y.B. Cheng, D. Yan, "Low-temperature sintering of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ derived from a co-precipitation method", *Mater. Lett.*, **56** [6] (2002) 910–914.

20. M.E. Mendoza, F. Donado, J.L. Carrillo, "Synthesis and characterization of micrometric ceramic powders for electro-rheological fluids", *J. Phys. Chem. Solids*, **64** [11] (2003) 2157–2161.
21. W.K. Chia, C.F. Yang, Y.C. Chen, "The effect of Bi_2O_3 compensation during thermal treatment on the crystalline and electrical characteristics of bismuth titanate thin films", *Ceram. Int.*, **34** [2] (2008) 379–384.
22. J.F. Dorrian, R.E. Newnham, K.K. Smith, "Crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ", *Ferroelectrics*, **3** [1] (1971) 17–27.
23. T. Rentschler, "Substitution of lead into the bismuth oxide layers of the $N = 2$ - and $N = 3$ -aurivillius phases", *Mater. Res. Bull.*, **32** [3] (1997) 351–369.
24. A.Z. Simões, B.D. Stojanovic, M.A. Ramirez, A.A. Cavaleiro, E. Longo, J.A. Varela, "Lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prepared by the soft chemical method: Rietveld analysis and piezoelectric properties", *Ceram. Int.*, **34** [2] (2008) 257–261.
25. M. Zdujic, D. Poleti, C. Jovalekic, L. Karanovic, "The evolution of structure induced by intensive milling in the system $2\text{Bi}_2\text{O}_3 \cdot 3\text{TiO}_2$ ", *J. Non-Cryst. Solids*, **352** [28–29] (2006) 3058–3068.
26. K.R. Zhu, M.S. Zhang, Y. Deng, J.X. Zhou, Z. Yin, "Finite-size effects of lattice structure and soft mode in bismuth titanate nanocrystals", *Solid State Commun.*, **145** [9–10] (2008) 456–460.
27. M.K. Jeon, Y.I. Kim, S.H. Nahm, J.M. Sohn, C.H. Jung, S.I. Woo, "Crystal structure and spontaneous polarization of $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ studied by using neutron powder diffraction data", *J. Phys. D*, **40** [15] (2007) 4647–4652.
28. J.F. Scott, C.A. Paz De Araujo, B.M. Melnick, "Loss mechanisms in fine-grained ferroelectric ceramic thin films for ULSI memories (DRAMs)", *J. Alloys Compd.*, **211–212** (1994) 451–454.
29. S. Luo, Y. Noguchia, M. Miyayama, T. Kudo, "Rietveld analysis and dielectric properties of Bi_2WO_6 - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric system", *Mater. Res. Bull.*, **36** [3–4] (2001) 531–540.
30. P. Kubelka, F. Munk, "Ein beitrag zur optik des farbanstriche", *Zeitschrift für Technische Physik*, **12** (1931) 593–601.
31. D.L. Wood, J. Tauc, "Weak absorption tails in amorphous semiconductors", *Phys. Rev. B*, **5** (1972) 3144–3151.
32. W.F. Yao, X.H. Xu, H.W., J.T. Zhou, X.N. Yang, Y. Zhang, S.X. Shang, B.B. Huang, "Photocatalytic property of perovskite bismuth titanate", *Appl. Catal. B-Environ.*, **52** [2] (2004) 109–116.
33. H. Idink, V. Srikanth, W.B. White, E.C. Subbarao, "Raman study of low temperature phase transitions in bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ", *J. Appl. Phys.*, **76** [3] (1994) 1819–1824.
34. Z.C. Ling, H.R. Xia, W.L. Liu, H. Han, X.Q. Wang, S.Q. Sun, D.G. Ran, L.L. Yu, "Lattice vibration of bismuth titanate nanocrystals prepared by metalorganic decomposition", *Mater. Sci. Eng. B*, **128** [1–3] (2006) 156–160.
35. P. Durán, F. Capel, C. Moure, M. Villegas, J.F. Fernandez, J. Tartaj, A.C. Caballero, "Processing and dielectric properties of the mixed-layer bismuth titanate niobate $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ by the metal-organic precursor synthesis method", *J. Eur. Ceram. Soc.*, **21** [1] (2001) 1–8.
36. P.R. Graves, G. Hua, S. Myhra, J.G. Thompson, "The Raman modes of the Aurivillius phases: Temperature and polarization dependence", *J. Solid State Chem.*, **114** [1] (1995) 112–122.
37. Z.S. Macedo, C.R. Ferrari, A.C. Hernandez, "Impedance spectroscopy of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic produced by self-propagating high-temperature synthesis technique", *J. Eur. Ceram. Soc.*, **24** [9] (2004) 2567–2574.
38. H. Watanabe, T. Mihara, H. Yoshimori, C.A. Paz de Araujo, "Preparation of ferroelectric thin films of bismuth layer structured compounds", *Jpn. J. Appl. Phys.*, **34** (1995) 5240–5244.
39. Y.N. Kan, G.P. Zhang, P.L. Wang, Y.B. Cheng, "Preparation and properties of neodymium-modified bismuth titanate ceramics", *J. Eur. Ceram. Soc.*, **28** [8] (2008) 1641–1647.
40. Z.Y. Zhou, X.L. Dong, H.X. Yan, H. Chen, C. Mao, "Doping effects on the electrical conductivity of bismuth layered $\text{Bi}_3\text{TiNbO}_9$ -based ceramics", *J. Appl. Phys.*, **100** [4] (2006) 044112(1–5).
41. H. Yan, C. Li, J. Zhou, W. Zhu, L. He, Y. Song, Y. Yu, "Influence of sintering temperature on the properties of high T_c bismuth layer structure ceramics", *Mater. Sci. Eng. B*, **88** [1] (2002) 62–67.
42. H.J. Cho, W. Jo, T.W. Noh, "Leakage current behaviors in rapid thermal annealed $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films", *Appl. Phys. Lett.*, **65** [12] (1994) 1525–1527.
43. Y.J. Qi, X. Xiao, C.J. Lu, X.Y. Mao, X.B. Chen, "Microstructural, ferroelectric, and dielectric properties of $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$ ceramics", *J. Appl. Phys.*, **98** [9] (2005) 094101(1–5).
44. U. Robels, J.H. Calderwood, G. Arlt, "Coercive and switching fields in ferroelectric ceramics", *Appl. Phys. Lett.*, **81** [14] (1995) 2605–2607.

Electrical Properties of Textured Niobium-Doped Bismuth Titanate Ceramics

Ederson C. Aguiar,[‡] Alexandre Z. Simões,[§] Cesar R. Foschini,[‡] Leinig A. Perazolli,[‡]
Richard E. Mistler,[¶] Elson Longo,[‡] and Jose A. Varela[‡]

[‡]UNESP – Chemistry Institute, São Paulo State University, 14800-900 Araraquara, São Paulo, Brazil

[§]UNESP – Engineering Faculty, São Paulo State University, 12516-410 Guaratinguetá, São Paulo, Brazil

[¶]Richard E. Mistler, Inc., 1038 Lafayette Drive, Yardley, Pennsylvania 19067, USA

Crystallographically textured Nb-doped bismuth titanate ceramics $\text{Bi}_4\text{Ti}_{(3-x)}\text{Nb}_x\text{O}_{12}$, were fabricated by tape casting using plate-like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ particles prepared by a molten-salt method as the templates. The templates were aligned in the fine-grained matrix by aqueous tape casting with their major surface parallel to the casting plane. Effect of niobium on the grain orientation in the material was investigated. It was found that the use of a fine precursor powder led to enhanced densification of the ceramic, while Nb doping reduced electrical conduction and dielectric loss, which enabled poling at high temperatures and high electric fields. The textured $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic showed a high anisotropy in its dielectric properties in the directions parallel and perpendicular to the casting plane. Highly textured BiT was obtained with the use of only 5 wt% of template particles by sintering at 800°C for 1 h.

I. Introduction

BISMUTH Titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a well-known member of the bismuth oxide layer structure ferroelectrics. It is a candidate for high-temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature of 675°C^{1–3} and electrooptic switching behavior.^{4–10} However, because of its platelike crystal habit and the limited number of permissible orientations for the spontaneous polarization, it is difficult to achieve high density and high piezoelectric activity in randomly oriented polycrystalline ceramics.¹¹ To solve these problems, many processing techniques have been employed to develop grain-oriented ferroelectric ceramics, such as hot forging,^{11–13} hot pressing,^{14–17} tape casting,^{18,19} and templated grain growth.^{20–25} Recently, it has been shown that donor-doping bismuth titanate with group V (Nb, Ta, Sb) and group VI (W) elements reduces the electrical conductivity by 3–4 orders of magnitude up to 600°C and facilitates both poling and the use of bismuth titanate at elevated temperatures.^{26,27} These high permittivity ceramics have proved to be excellent materials in monolithic multilayer capacitors, resonators, and delay lines in communication applications, in noiseless printing heads for bubble jet printers, ultrasonic imaging, accelerometers, hydrophones, and high resolution tomography. Reduction in dimension of all passive components without compromising on performance and improved reliability is the trend in electronics technology.²⁸ One of the means of achieving this goal, especially in electronic ceramics, is to use multiple layer ceramics. Compared to bulk electroceramics, multiple layer ceramics offer several advantages in terms of

performance reliability, cost, and space savings. The first and most critical step involved in the fabrication of multiple layer devices is tape casting.²⁹ The preparation of a stable, well-dispersed slip is a critical step in tape casting technology. As the miniaturization stresses the use of nano size powders and less and less thickness of tape to increase the effective surface area in the same volume of material with improved properties, the optimization of suitable parameters to achieve the defect free tape with specified properties is a difficult task. In $m = 4$ Aurivillius oxide bismuth titanates, the unit cell is orthorhombic allowing both 180° domain switching (switching in sign of the a -axis) and 90° domain switching (interchanging of the a and b axes). In typical bismuth titanate textures arising from hot pressing or tape casting, the possible polarization directions and ferroelastic distortions are aligned in a plane normal to the axis of fiber symmetry. The main objective of the orientation engineering is to obtain a – b plane oriented BiT ceramics. Highly c -plane orientated BiT-type ceramics are reported by mechanical force, but the texture degree of a – b plane is not mentioned.^{28–31} It is also reported that the high electrical conductivity in the a – b plane makes poling difficult.³² However, Nb-doped BiT was found to reduce the electrical conductivity obviously and facilitates both poling and the use of BiT at elevated temperature.³³ The main focus on this study is to prepare high-purity and anisotropic BiT crystal as growth templates and by using these crystals evaluate the role of niobium on the phase formation, densification, grain orientation, textured microstructure and the electrical properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ produced by tape casting.

II. Experimental Procedure

(1) Preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Powders and Templates

The $\text{Bi}_4\text{Ti}_{(3-x)}\text{Nb}_x\text{O}_{12}$ samples with $x = 0, 0.1, 0.2, 0.4$ mol% Nb (all with 10 wt% of bismuth excess) were prepared by the polymeric precursor method, represented as: BiT, BiTNb01, BiTNb02, BiTNb04, respectively. In this study, 10 wt% of bismuth excess was added to minimize bismuth loss during thermal treatment. Without this additional bismuth the pure phase could not be obtained, as was reported in the literature.¹⁷ The following reagents were employed: Bi (NO_3)₃·5H₂O (100.1%, Mallinckrodt do Brasil Ltda, São Paulo, Brazil), Ti(OC_3H_7)₄ (97.0%, Alfa Aesar), Nb₂O₅ (99.99%, Alfa Aesar, Ward Hill, MA), C₆H₈O₇·H₂O (99.5%, Merck KgaA, Darmstadt, Germany), C₂H₆O₂ (99.7%, Synth, Diadema, Brazil), HNO₃ (99.9%, Synth), C₂H₈N₂ (98.0%, Nuclear, Produtos para Laboratórios Importação e Exportação LTDA, São Paulo, Brazil) and NH₄OH (99.9%, Qhemis, São Paulo, Brazil). The precursor solutions of bismuth, titanium, and niobium were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. Solutions were mixed and homogenized by stirring at 90°C–2 h. Next, the

D. Damjanovic—contributing editor

temperature was increased to 130°C–140°C, yielding a highly viscous polyester resin. Most of the organic material was decomposed by thermal treatment at 300°C–2 h. The formed porous product was crushed and heated in an alumina crucible at 700°C for 4 h to decompose the organic material. The resulting material was milled using zirconia balls in isopropyl alcohol for 4 h. This powder showed a BET surface area of 6.7 m²/g and an average particle size of 0.2 μm. The Bi₄Ti₃O₁₂ template particles were prepared by a molten-salt method. Equal weight of Bi₄Ti₃O₁₂ powder and Na₂SO₄/K₂SO₄ eutectic mixture were mixed in a sealed alumina crucible and heated at 1000°C for 0.5 h. After slowly cooling to the room temperature, the reaction product was separated by centrifugation and washed several times with hot de-ionized water to remove the sulfate salts, and then dried at 100°C. FT-IR spectrometry analyses were employed to evaluate the sulfate group (not shown in the text). The Bi₄Ti₃O₁₂ particles obtained were plate-like with a diameter of 3–4 μm and a thickness of 0.3 μm.

(2) Slurry Preparation and Tape Casting

For slurry preparation, 10 vol% Bi₄Ti₃O₁₂ powder was dispersed in de-ionized water using 1 wt% (on the dry weight basis) acrylic acid as a dispersant (99%, Sigma-Aldrich, St. Louis, MO), and the pH value was adjusted to pH 9 with analytical grade ammonia (99.9%, Qhemis). In the middle of the ball milling, 5 wt% (on the dry weight basis) polyvinyl alcohol (99.6%, Vetec Química Fina Ltda, Duque de Caxias, Brazil) and 2.5 wt% (on the dry weight basis) glycerin (99.5%, Cromoline Química Fina Ltda, Diadema, Brazil) were added as a binder and a plasticizer, respectively. The slurry was ball milled for 24 h. The Bi₄Ti₃O₁₂ platelets (5 wt% of the fine powder) were added and mixed with the Bi₄Ti₃O₁₂ slurry under electromagnetic stirring for 4 h. Finally, the slurry was degassed under vacuum and tape cast on a glass surface at a speed of 0.5 cm/s and a single doctor blade opening of 120 μm.^{34–37} The tapes obtained were dried at room temperature, cut into pieces of 5 mm², stacked, and laminated at a pressure of 80 MPa for 10 min at 150°C. The binder and plasticizer were burned out at a temperature of 500°C for 3 h with a heating rate of 1°C/min. The laminates were then sintered in air in a sealed alumina crucible at 800°C.

(3) Characterization

Powders were first analyzed by X-ray diffraction (XRD) for phase determination. For Rietveld analyses, XRD data were collected with a Rigaku 20-2000 diffractometer (Rigaku Americas, The Woodlands, TX) under the following experimental conditions: 40 kV, 30 mA, 20° ≤ 2θ ≤ 60, Δ2θ = 0.02°, λCu K_α monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with a DBWS-941 refinement program.³⁸ The profile function used was the modified Thompson–Cox–Hasting pseudo-Voigt, in which η (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum. A scanning electron microscope (SEM) was used to analyze the morphology and shape of the grains from as sintered surfaces and templates (Topcom SM-300; Topcon America Incorporation, Paramus, NJ). Resistivity was determined by current–voltage in voltage source (KEITLEY 237; Keithley Instruments, Inc., Cleveland, OH). Dielectric permittivity was performed in HP 4192A LF Mountain View impedance at 1 MHz (HP Mountain View, Southfield, MI), coupled in FLYEVER oven (FE50RP temperature controller; Flyever, São Carlos, Brazil). Ferroelectric properties of the capacitor were measured at room temperature using a Radiant Technology RT6000A (Radiant Technology, Albuquerque, NM) in a virtual ground mode, respectively, at 1 MHz.

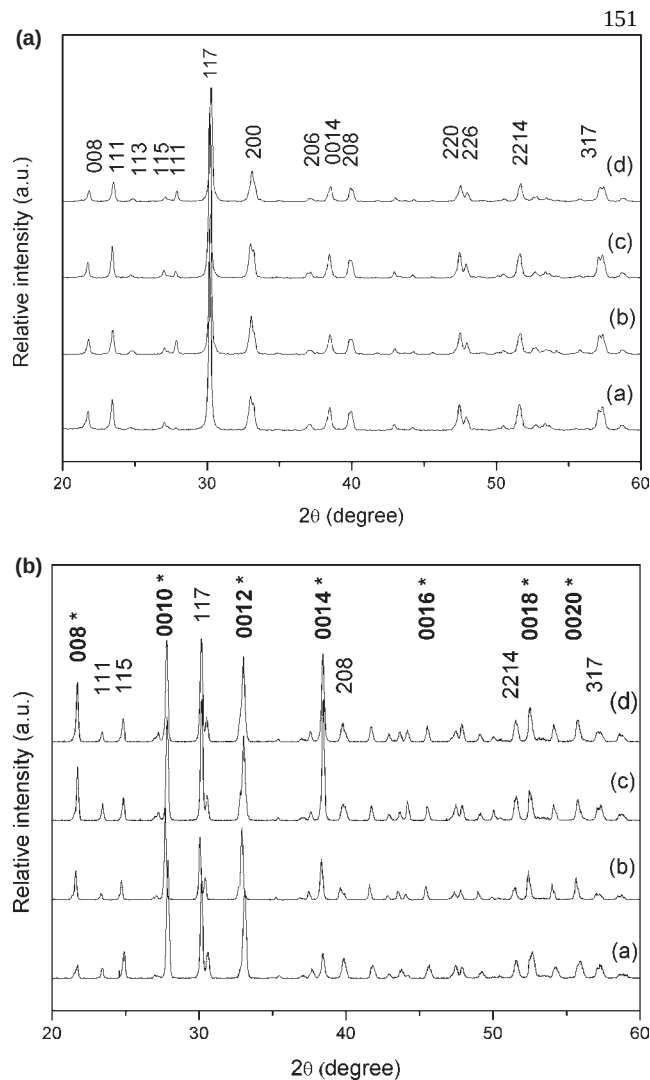


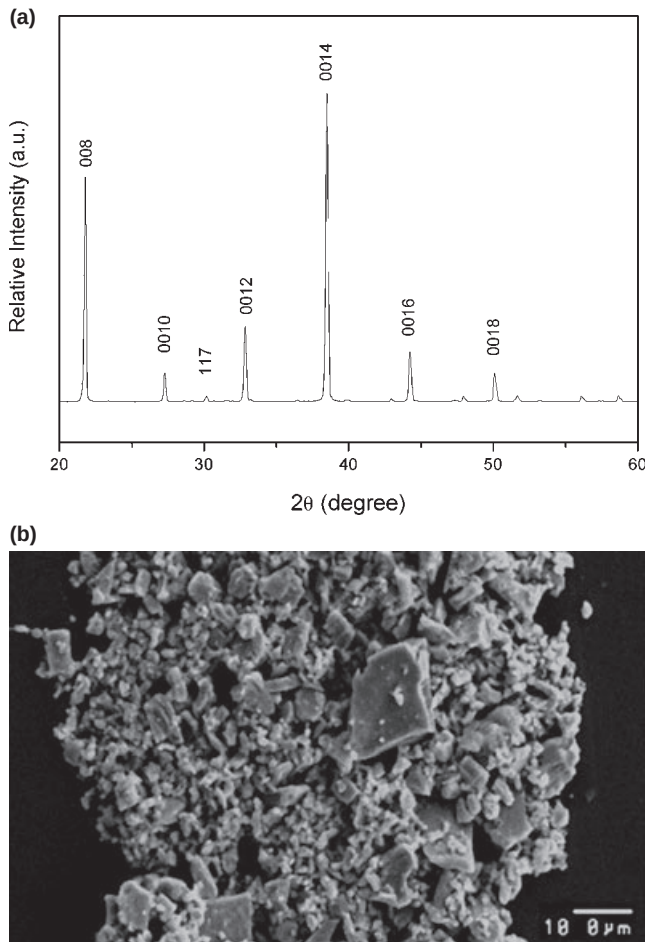
Fig. 1. X-ray diffraction at room temperature for bismuth titanate sintered at 800°C–1 h: (a) BiT, (b) BiT-0.1Nb, (c) BiT-0.2Nb, (d) BiT-0.4Nb showing [a] polycrystalline ceramic and [b] textured ceramic.

III. Results and Discussion

Phase formation of bismuth titanate powders was evaluated by XRD (Fig. 1). The powders are almost free of secondary phases and present orthorhombic structure regardless of niobium content.³⁹ We can observe that the thick films of BiT phase can be obtained at low heat treatment temperature and reduced synthesis time. Bragg reflection peaks are indicative of perovskite structure, with orientation in c-plane, mainly characterized by higher intense peak (*hkl*-117) and no apparent peak splitting is identified. Our XRD results are in agreement with those reported in the literature.^{40–43} The experimental lattice parameter values were calculated using Rietveld method. Table I compares the lattice parameters obtained in this study with those reported in the literature by different methods. Moreover, the lattice parameter obtained in our study presented small variations compared with those reported in the literature.^{44–49} These differences can be related to the preparation method, synthesis conditions (heat treatment temperature, time), lattice distortion, residual stresses in the lattice, and/or structural defects. Compared with the seed-free sample, the intensity of {0 0 *l*} peaks in the samples with seeds is enhanced in the direction perpendicular to tape casting while the intensity of other peaks weakens. In contrast, the {*h k* 0} peaks enhance and the {*h k l*} peaks weaken in the direction parallel to tape casting, while the {0 0 *l*} peaks disappear basically. The results indicate that the

Table I. Refinement Indexes for Bi₄Ti₃O₁₂ Ceramics Sintered at 800°C-1 h with 10 mol% of Excess Bismuth

BiTi10%	BiT01	BiT02	BiT04
Rwp = 12.37%	Rwp = 11.85%	Rwp = 13.26%	Rwp = 12.40%
Gof = 1.57	Gof = 1.65	Gof = 1.68	Gof = 1.46
Rbragg = 3.87%	Rbragg = 3.06%	Rbragg = 4.86%	Rbragg = 3.86%
<i>a</i> = 5.4065(3)	<i>a</i> = 5.4093(1)	<i>a</i> = 5.4065(3)	<i>a</i> = 5.4074(5)
<i>b</i> = 5.4401(3)	<i>b</i> = 5.4454(1)	<i>b</i> = 5.4416(3)	<i>b</i> = 5.4530(4)
<i>c</i> = 32.874(1)	<i>c</i> = 32.8385(7)	<i>c</i> = 32.879(1)	<i>c</i> = 32.818(2)
Bi ₁₂ TiO ₂₀	Bi ₁₂ TiO ₂₀	Bi ₁₂ TiO ₂₀	Bi ₁₂ TiO ₂₀
<i>a</i> = 10.172(1)	<i>a</i> = 10.1725(2)	<i>a</i> = 10.1731(5)	<i>a</i> = 10.1770(4)
Bi ₄ Ti ₃ O ₁₂ - 99.38%	Bi ₄ Ti ₃ O ₁₂ - 92.01%	Bi ₄ Ti ₃ O ₁₂ - 97.24%	Bi ₄ Ti ₃ O ₁₂ - 93.57%
Bi ₁₂ TiO ₂₀ - 0.62%	Bi ₁₂ TiO ₂₀ - 7.09%	Bi ₁₂ TiO ₂₀ - 2.76%	Bi ₁₂ TiO ₂₀ - 6.43%

**Fig. 2.** (a) X-ray diffraction at room temperature for bismuth titanate templates obtained by the molten-salt method and (b) scanning electronic microscopy for bismuth titanate templates obtained by the molten-salt method.

ceramics with seeds have obvious textured characteristics. It is well known that the seeds grow at the expense of fine-grained matrix particles during tape-casting. But once the fine-grained matrix particles are used up, the seeds will grow slowly despite the niobium concentration, and thus there is a slight increase in the degree of grain orientation. The origin of the texture development was partly attributed to the growth of template grains at the expense of small grains. Therefore, the growth of matrix grains and that of template grains is important to prepare highly textured ceramics by the tape-casting method. To ensure high sinterability, BiT templates were selected as matrix powders for the preparation of ceramics. As shown in Fig. 2(a), the template crystallized to form pure BiT phase. The main peaks are *c*-axis oriented (008), (0010), (0012), (0014), (0016), and (0018) which differ

from the orthorhombic matrix. The structural model that allows the best-fitting was orthorhombic (ICSD n° 50-300 with space group *F*). The powders synthesized by molten-salt method [Fig. 2(b)] show platelike rather than equiaxed morphology. The powders are 2 to 5 μm of diameter and ~0.2 μm thick. The high aspect ratio (~25–50) makes plate-like particles easily aligned in slurry/paste.

The BiT system has already been investigated from a fundamental point of view, regarding the role of dopant in the crystal structure of pure bismuth titanate. In the present study, we have adopted the Rietveld refinement technique to investigate the crystal structure of the BiT and BiTNb systems, and have obtained adequate evidence for the preferred site for niobium substitution. Table I illustrates the Rwp, Rexp, and S indexes, and the lattice parameters (*a*, *b* and *c*) and the unit cell volume (*V*). The phase identification was carried out in the PDF data bank, resulting in an orthorhombic structure type. The structural model (available on ICSD databank) that allows the best-fitting was the orthorhombic one (ICSD no. 24735 with space group *Fmmm*). The quantitative phase analyses for the orthorhombic phase were calculated according to the reference of Young and Wiles.³⁸ No changes occurred in the refinements when Bi³⁺ ion was substituted by Nb⁵⁺ ion in the orthorhombic BiT phase. It was observed that Nb⁵⁺ substitutes Bi³⁺ only in a perovskite-type unit cell, causing a distorted structure whereby distortion increases with raising niobium content. The covalent interaction, which originates from the strong hybridization between Ti 3*d* and O 2*p* orbitals, plays an important role in the structural distortion of BiT compound. It can be assumed that doping with Nb improves oxygen ion stability in the lattice because some of the Bi ions in the pseudoperovskite layers containing Ti–O octahedral were substituted by Nb ions. The low S values (*S* = Rwp/Rexp) reflect good refinement quality with the calculated parameters similar to literature data.⁵⁰ Niobium addition elongates *c*-axis due to the differences in charge density of niobium and bismuth atoms. Also, niobium stabilizes the oxygen vacancies and consequently the structure. As a consequence, *a* and *b* parameters became closer indicating that the orthorhombic structure tends to transform into a tetragonal one with the increase in donor dopant. The presence of a minor cubic Bi₁₂TiO₂₀ phase relative to the main Bi₄Ti₃O₁₂ should also be noted. Such intermediate phase, which has been identified as a complex bismuth-titanium oxides binary compound of the type Bi₁₂TiO₂₀ with cubic structure is presented in all samples and has much lower enthalpy for its formation than that required for the formation of a Bi₄Ti₃O₁₂ phase. The formation of Bi₁₂TiO₂₀ particles might be consistent with an Avrami-type nucleation and growth mechanism, in which the particles continuously nucleated three-dimensionally within the amorphous polymeric precursor matrix. After the nucleus of crystal appears, the primary particle size gradually increases from the randomly distributed nuclei with the increasing temperature. The amount of the intermediate Bi₁₂TiO₂₀ phase is evident in samples thermal treated at dif-

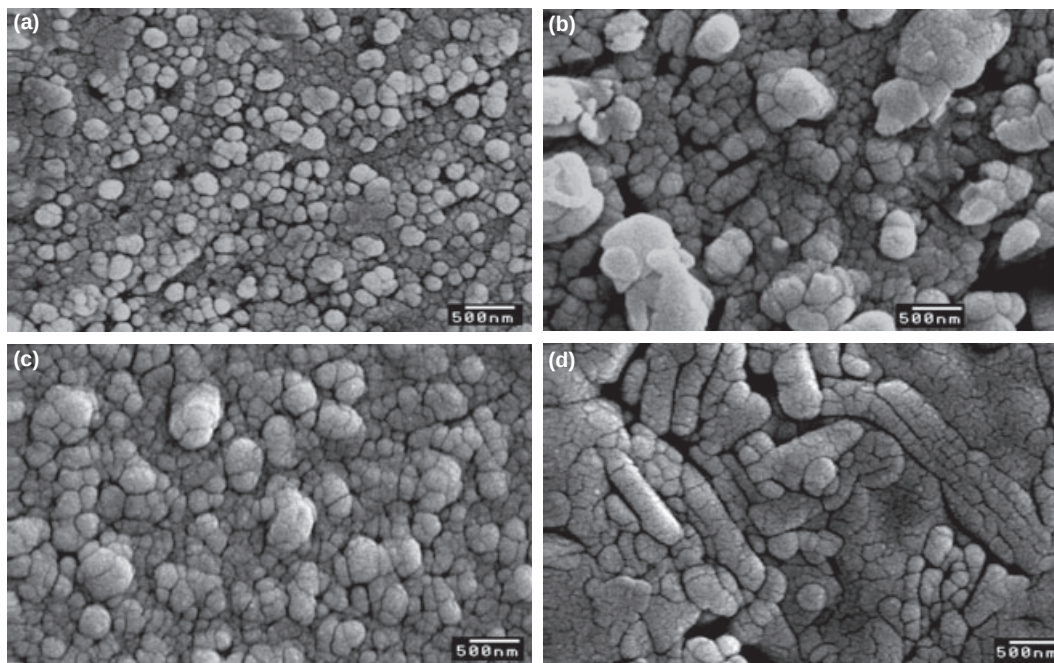


Fig. 3. Scanning electronic microscopy for bismuth titanate ceramics sintered at 800°C-1 h: (a) BiT, (b) BiT01, (c) BiT02, and (d) BiT04.

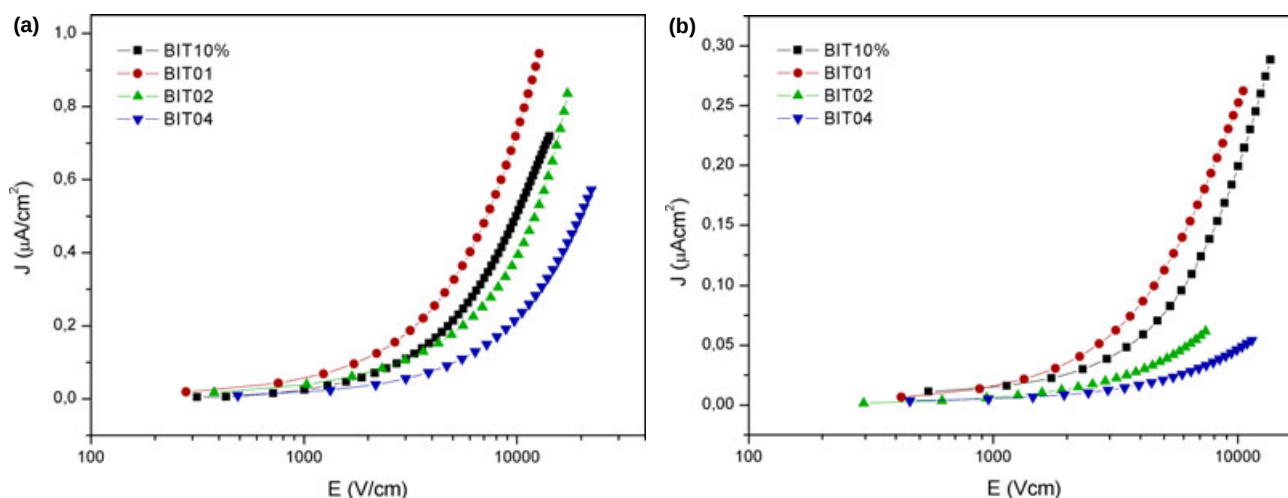


Fig. 4. Leakage current behavior as a function of electric field for pure bismuth titanate ceramics and doped with several Nb concentration sintered at 800°C-1 h: (a) parallel (//) and (b) perpendicular (⊥) to the tape-casting plane.

ferent temperatures with various excess of bismuth and niobium content.⁵¹ The same behavior was presented by Tang *et al.* in vanadium doped BiT ceramics.⁵²

The effect caused by niobium addition on the morphology and shape of the grains was evaluated by SEM analyses of sintered surfaces (Fig. 3). Niobium addition caused a pronounced effect on the grain shape leading to a plate-like morphology and a structural distortion. On the other hand, pure BiT presents a mixture of rod-like and plate-like grains. The rod-like grains might originate from an anisotropic behavior of bismuth titanate. The BiT ceramics presented a porous microstructure with smaller grain sizes when compared with Nb-doped BiT ceramics. There is no evidence of liquid-phase segregated at the grain-boundaries indicating that this methodology allows obtaining the phase at low sintering temperature with particles distributed in a nanometric matrix. The SEM micrographs of the randomly oriented samples exhibit mixed grain microstructures of equiaxed and platelike grains for both undoped [Fig. 3(a)] and Nb-doped [Figs. 3(b)–(d)] samples. The bismuth titanate template particles were plate-like with diameters ranging from 30 to 50 μm and a thick-

ness of 10 μm . Microstructures of textured Nb-doped BiT which contained 5 wt% template particles demonstrate that the bismuth titanate platelet grains are aligned in the casting direction and that the original platelets grew at the expense of fine matrix grains.

Leakage current density versus electric field (J – E curve) for sintered pellets parallel and perpendicular to the casting plane are shown in Fig. 4. Here, we plotted the current density behavior of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ for comparison. Independently of casting plane direction, we noted that the electrical behavior was obviously influenced by donor dopant, for Nb concentration above 1%. The BiT presented high values of current density while for BiT-Nb compositions the current density values decreased. This result is in agreement with the idea that donor dopants decrease conductivity of a material with a p -type mechanism.⁵³ For BiT-Nb compositions, the ceramics presented lower electrical conductivity and therefore could be poled to develop piezoelectricity. In Nb-doped BiT ceramics, hole compensation of bismuth vacancies ($V'''_{\text{Bi}} + 3h^\bullet$) promotes p -type electronic conductivity because when Nb^{5+} substitutes for Ti^{4+} , a positive charge center at the Nb site

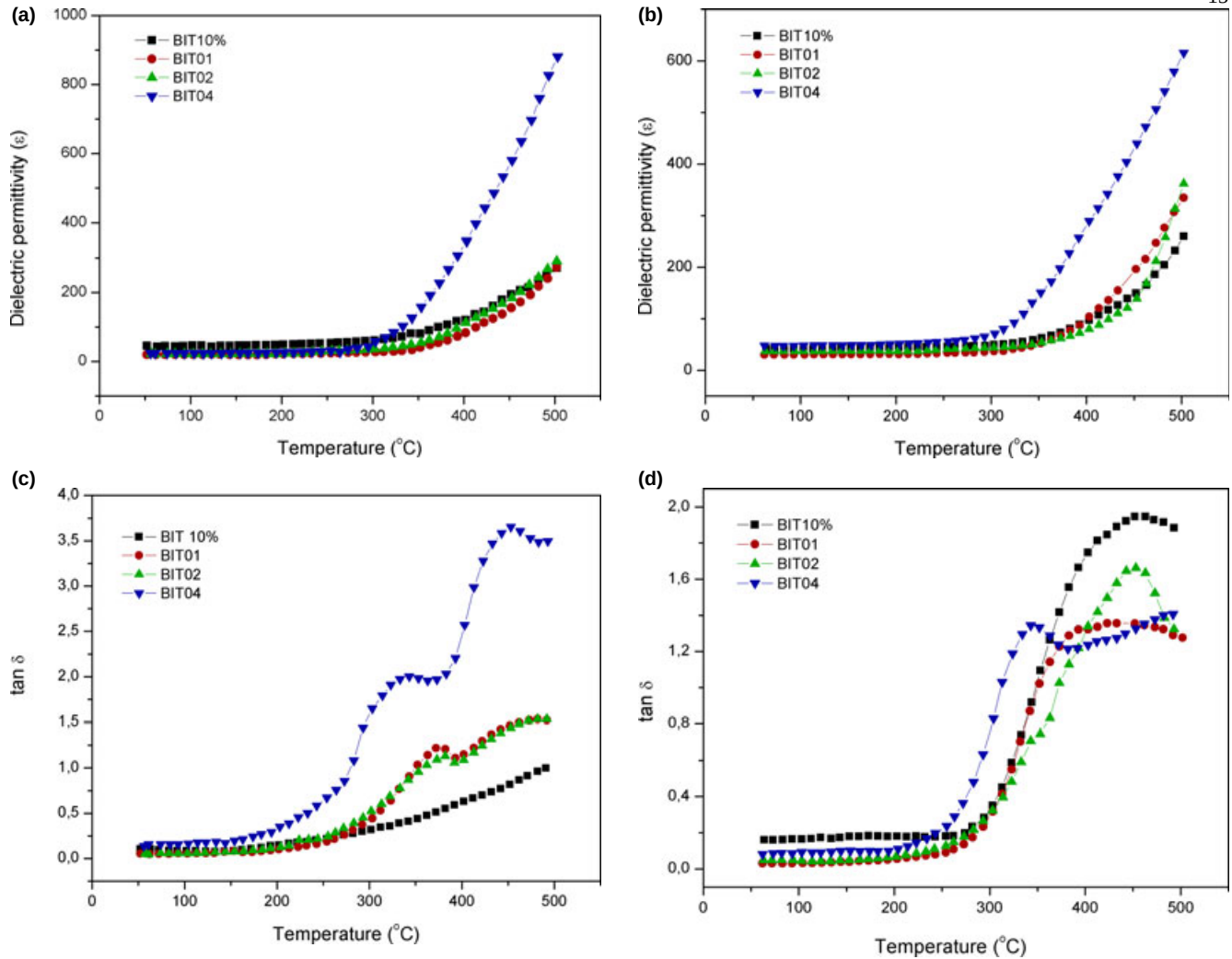


Fig. 5. Dielectric permittivity and dielectric loss as a function of temperature for bismuth titanate textured ceramics sintered at 800°C-1 h: (a) and (c) parallel ($\parallel$); (b) and (d) perpendicular ($\perp$) to the tape-casting plane.

and an electron will be created under charge neutrality restriction, which can be described as $\text{Nb}_{\text{Ti}} + e'$. These electrons compensate for the influence of the holes according to the electronic conductivity relationship $\sigma = nq\mu$, where n is the number of the carriers, q the charge, and μ the mobility. It becomes clear that the number of the hole carriers, n , was decreased, as Nb does not induce structural modifications in the crystal lattice that can justify a change in the charge carrier mobility.⁵⁴ That resulted in a low conductivity of BiT-Nb ceramics due to the reduction in current density with donor doping to a minimum value that is reached when the concentration of the electrons is equal to the hole concentration. Also, BiT has rounded shape grains with residual porosity which might have many carrier traps. At the high electric field region, the localized carriers begin to come out of the trap, resulting in a large increase in current density. H. J. Cho *et al.*⁵⁵ observed a large leakage current for BiT films annealed in nitrogen atmosphere. This is a consequence of a porous microstructure in which there are many carrier traps inside it and at higher fields these charges are ejected. In the plate-like structure observed in the doped samples, carrier injection into the insulator looks very important, so space charge can distribute along the plate-like grain-boundaries.

Figures 5(a) and 5(b) show the temperature dependence of the dielectric permittivity of doped random and textured Nb doped BiT parallel and perpendicular to the casting plane at 1 MHz. This frequency was selected due the considerable dispersion observed at low frequencies caused by space charges at the interfaces which affects the domains

switching characteristics. According to Wu *et al.*⁵⁶ the dielectric permittivity consists of contributions of ionic and atomic polarization only. Since the ionic radius of Nb^{5+} is smaller than that of Ti^{4+} , Nb^{5+} would lead to a reduced contribution of overall atomic polarization. Therefore, the increase in dielectric permittivity may be attributable to increased ionic polarization. Sun *et al.*⁵⁷ proposed that the phase transition is caused by instability of the BO_6 octahedra. The relatively larger ionic radius of the B ion enhances the thermal stability of the BO_6 octahedra resulting in an increase in BO_6 volume octahedron and consequently decreasing its stability which results in a reduction in T_c .⁵⁸ Another factor can be the instability of the oxygen octahedral that involve the B cation leading to a T_c reduction. This involves structural inhomogeneity and existence of polar nanoregions. The textured ceramics show anisotropic dielectric permittivity of 880 parallel to and 600 perpendicular to the casting plane in 4 %mol Nb.

Figures 5(c) and 5(d) show the temperature dependence of dielectric loss determined for doped random and textured Nb doped BiT parallel and perpendicular to the casting plane. The dielectric loss is almost temperature independent, although it also presents a very small peak just below T_c . At lower temperatures, a small temperature dependence of dissipation factor was observed while at elevated temperatures, niobium doping stabilizes the temperature dependence of dissipation factor. The possible formation of metal vacancies may result in a reduced dielectric loss at elevated temperatures. This reflects that good insulation resistance was main-

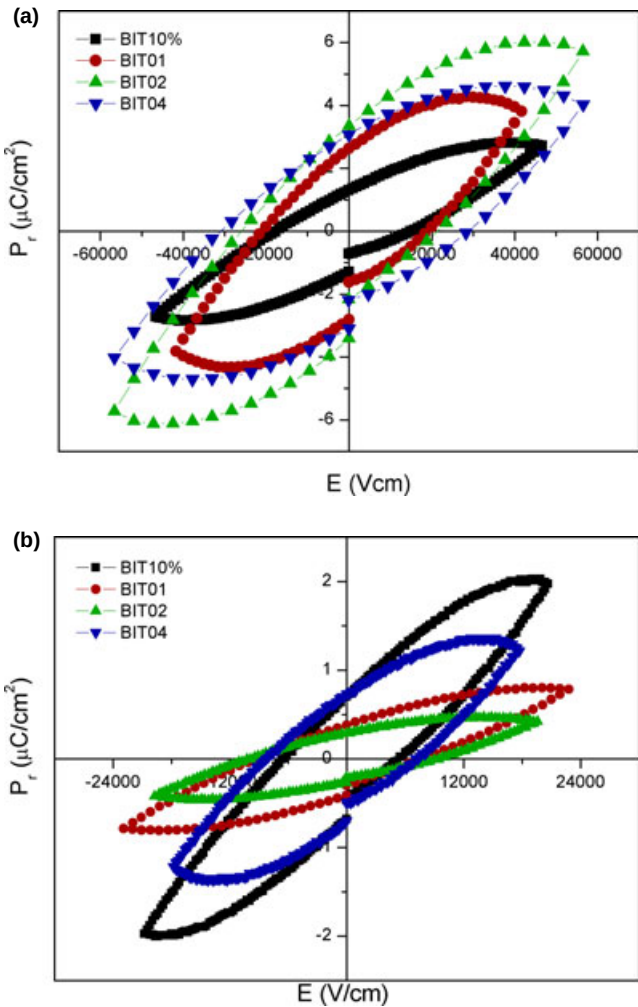


Fig. 6. P-E hysteresis loops for bismuth titanate textured ceramics sintered at 800°C-1 h: (a) parallel (//) and (b) perpendicular (⊥) to the tape-casting plane.

Table II. P_r and E_c Values of Doped Random and Textured Nb-doped BiT Parallel and Perpendicular to the Casting Plane

Composition	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)
BiT10% (⊥)	0.7	5.5
BiT01 (⊥)	0.4	7.3
BiT02 (⊥)	0.3	9.4
BiT04 (⊥)	0.7	7.1
BiT (//)	1.3	14.8
BiT01 (//)	2.7	18.3
BiT02 (//)	3.4	21.1
BiT04 (//)	3.1	28.2

tained at high temperatures, which is important for high temperature piezoelectric applications. In addition, the dielectric loss was much lower than that of pure BiT reported in our previous work,⁵⁸ which is attributed to the decrease in space charge density as niobium incorporates in the BiT lattice. This may be due to the defects (vacancy, movable ion, leaky grain-boundary, etc.) that developed in the structure of the bulk material with donor dopant.^{59–67} Two main mechanisms can be considered for substituting Nb for Ti in the BiT lattice. The compensation mechanism for substituting a 5+ ion for a 4+ ion should reduce the oxygen vacancy concentration, leading to formation of Bi³⁺ vacancies. Another possibility is that the extra electrons become somewhat delocalized leading to some conductivity. This could be the reason why the leakage current increases. Nb doping clearly

reduced the dielectric loss; the loss tangent is below 0.1 up to 450°C, which enables poling at higher electric fields and higher temperatures.^{11,15,18} The higher dielectric loss in the tapes parallel to the casting direction is due to the lower conductivity in the *a*–*b* plane of bismuth titanate.⁶⁸

The room-temperature polarization-electric field hysteresis loops of random and textured samples that have been sintered at 800°C for 1 h are shown in Fig. 6. The remanent polarization for the Nb-doped random BiT is 3.1 $\mu\text{C}/\text{cm}^2$. The loops for the doped samples are better saturated and have a smaller coercive field than those for undoped random BiT. The reduction in coercive field is probably a result of the larger grain size in the doped samples. Anisotropic remanent polarizations (P_r) and coercive fields (E_c) are observed in the sintered tapes parallel and perpendicular to the casting plane (Table II). These values are close to those previously reported for hot-forged bismuth titanate.¹³ In bismuth titanate, the spontaneous polarization P_s lies in the monoclinic *a*–*c* plane at a small angle (4.5°) to the *a*-axis and exhibits two independently reversible components: 50 $\mu\text{C}/\text{cm}^2$ along the *a*-axis and 4 $\mu\text{C}/\text{cm}^2$ along the *c*-axis.⁵

IV. Conclusions

C-axis oriented Nb-doped Bi₄Ti₃O₁₂ induced by Bi₄Ti₃O₁₂ templates were successfully prepared by tape-casting. The SEM micrographs of the randomly oriented samples exhibit mixed grain microstructures of equiaxed and platelike grains for both undoped and Nb-doped samples. The Rietveld analyses confirmed that the BiT and Nb-doped BiT powders crystallize in an orthorhombic structure with space group *Fmmm*. The leakage current of BiT is strongly affected by grain morphology while dielectric permittivity was increased by Nb⁵⁺ doping due to the increase in oxygen-vacancy concentration. The BiT and Nb-doped BiT samples showed anisotropic dielectric and ferroelectric properties in the directions parallel and perpendicular to the casting plane, due to the formation of highly textured microstructure in it. This anisotropy became more significant at temperatures close to the material's Curie temperature improving electrical properties. Additional study is needed to investigate the piezoelectric properties of oriented thick films to make them compatible with silicon micromachining and thus more useful in practical applications.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, and CAPES.

References

¹E. C. Subbarao, "Ferroelectricity in Bi₄Ti₃O₁₂ and its Solid Solutions," *Phys. Rev.*, **122** [3] 804–7 (1961).
²E. C. Subbarao, "A Family of Ferroelectric Bismuth Compounds," *J. Phys. Chem. Solids*, **23**, 665–76 (1962).
³A. Fouskova and L. E. Cross, "Dielectric Properties of Bismuth Titanate," *J. Appl. Phys.*, **41** [7] 2834–8 (1970).
⁴S. E. Cummins and L. E. Cross, "Crystal Symmetry, Optical Properties, and Ferroelectric Polarization of Bi₄Ti₃O₁₂ Single Crystals," *Appl. Phys. Lett.*, **10** [1] 14–6 (1967).
⁵S. E. Cummins and L. E. Cross, "Electrical and Optical Properties of Ferroelectric Bi₄Ti₃O₁₂ Single Crystals," *J. Appl. Phys.*, **39** [5] 2268–74 (1968).
⁶L. E. Cross and R. C. Pohanka, "A Thermodynamic Analysis of Ferroelectricity in Bismuth Titanate," *J. Appl. Phys.*, **39** [8] 3992–5 (1968).
⁷Y. Masuda, H. Masumoto, A. Baba, T. Goto, and T. Hirai, "Crystal Growth, Dielectric and Polarization Reversal Properties of Bi₄Ti₃O₁₂ Single Crystal," *Jpn. J. Appl. Phys.*, **31**, 3108–12 (1992).
⁸Y. Xu, *Ferroelectric Materials and Their Applications*. pp. 301–7. North-Holland, New York, 1991.
⁹W. J. Takei, N. P. Formigoni, and M. H. Francombe, "Preparation and Epitaxy of Sputtered Films of Ferroelectric Bi₄Ti₃O₁₂," *J. Vac. Sci. Technol.*, **7** [3] 442–8 (1970).
¹⁰S.-Y. Wu, "Polarization Reversal and Film Structure in Ferroelectric Bi₄Ti₃O₁₂ Films Deposited on Silicon," *J. Appl. Phys.*, **50** [6] 4314–8 (1979).
¹¹T. Takenaka, K. Shoji, H. Takai, and K. Sakata, "Ferroelectric and Dielectric Properties of Press Forged Bi₄Ti₃O₁₂ Ceramics," *Proc. Jpn. Congr. Mater. Res.*, **19**, 230–3 (1976).

- ¹²T. Takenaka, K. Shoji, and K. Sakada, "Grain Orientation and Microstructure of Hot-Forged Bi₄Ti₃O₁₂ Ceramics," *Proc. Jpn. Congr. Mater. Res.*, **20**, 212-4 (1977).
- ¹³T. Takenaka and K. Sakada, "Grain Orientation and Electrical Properties of Hot-Forged Bi₄Ti₃O₁₂ Ceramics," *Jpn. J. Appl. Phys.*, **19** [1] 31-9 (1980).
- ¹⁴T. Takenaka and K. Sakada, "Grain Orientation Effects on Electrical Properties of Bismuth Layer-Structured Ferroelectric Pb(12x)(NaCe)x/2Bi₄Ti₄O₁₅ Solid Solution," *J. Appl. Phys.*, **55** [4] 1092-9 (1984).
- ¹⁵V. K. Seth and W. A. Schulze, "Grain-Oriented Fabrication of Bismuth Titanate Ceramics and its Electrical Properties," *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, **36** [1] 41-9 (1989).
- ¹⁶T. Kimura, T. Yoshimoto, N. Iida, Y. Fujita, and T. Yamaguchi, "Mechanism of Grain Orientation During Hot-Pressing of Bismuth Titanate," *J. Am. Ceram. Soc.*, **72** [1] 85-9 (1989).
- ¹⁷Y. Inoue, T. Kimura, T. Yamaguchi, K. Nagata, and K. Okazaki, "Grain Orientation and Electrical Properties of Hot-Pressed Bismuth Titanate Ceramics," *Yogyo Kyokaishi*, **92** [7] 416-9 (1984).
- ¹⁸S. Swartz, W. A. Schulze, and J. V. Biggers, "Fabrication and Electrical Properties of Grain Oriented Bi₄Ti₃O₁₂ Ceramics," *Ferroelectrics*, **38**, 765-8 (1981).
- ¹⁹H. Chazono, T. Kimura, and T. Yamaguchi, "Fabrication of Grain-Oriented Bi₄Ti₃O₁₂ Ceramics by Normal Sintering: I. Tape Casting and Sintering," *Yogyo Kyokaishi*, **93** [9] 485-90 (1985).
- ²⁰M. M. Seabaugh, I. H. Kersch, and G. L. Messing, "Texture Development by Templated Grain Growth in Liquid Phase Sintered α -Alumina," *J. Am. Ceram. Soc.*, **80** [5] 1181-8 (1997).
- ²¹B. Brahmaroutu, G. L. Messing, S. Trolrier-McKinstry, and U. Selvaraj, "Templated Grain Growth of Textured Sr₂Nb₂O₇," pp. 883-6 in *Proceedings of the 10th IEEE International Symposium on Applications of Ferroelectrics*, Vol. II, Edited by B. M. Kulwicki, A. Amin, and A. Safari. Institute of Electrical and Electronics Engineers, Piscataway, NJ, 1996.
- ²²J. Horn, S. C. Zhang, U. Selvaraj, G. L. Messing, S. Trolrier-McKinstry, and M. Yokoyama, "Fabrication of Textured Bi₄Ti₃O₁₂ by Templated Grain Growth," pp. 943-6 in *Proceedings of the 10th IEEE International Symposium on Applications of Ferroelectrics*, Vol. II, Edited by B. M. Kulwicki, A. Amin, and A. Safari. Institute of Electrical and Electronics Engineers, Piscataway, NJ, 1996.
- ²³J. A. Horn, S. C. Zhang, U. Selvaraj, G. L. Messing, and S. Trolrier-McKinstry, "Templated Grain Growth of Textured Bismuth Titanate," *J. Am. Ceram. Soc.*, **82** [4] 921-6 (1999).
- ²⁴S.-H. Hong and G. L. Messing, "Development of Textured Mullite by Templated Grain Growth," *J. Am. Ceram. Soc.*, **82** [4] 867-72 (1999).
- ²⁵C. Duran, S. Trolrier-McKinstry, and G. L. Messing, "Fabrication and Electrical Properties of Textured Sr_xBa_{12-x}Nb₂O₆ Fabricated by Templated Grain Growth," *J. Am. Ceram. Soc.*, **83** [9] 2203-5 (2000).
- ²⁶S. S. Lopatin, T. G. Lupeiko, T. L. Vasiltsova, N. I. Basenko, and I. M. Berlizev, "Properties of Bismuth Titanate Ceramics Modified with Group V and VI Elements," *Inorg. Mater.*, **24**, 1328-31 (1988).
- ²⁷H. S. Shulman, M. Testorf, D. Damjanovic, and N. Setter, "Microstructure, Electrical Conductivity, and Piezoelectrical Properties of Bismuth Titanate," *J. Am. Ceram. Soc.*, **79** [12] 3124-8 (1996).
- ²⁸T. Takenaka and K. Sakata, "Grain Orientation and Electrical Properties of Hot-Forged Bismuth Titanium Oxide (Bi₄Ti₃O₁₂) Ceramics," *Jpn. J. Appl. Phys.*, **19**, 31-9 (1980).
- ²⁹J. Hao, X. Wang, R. Chen, Z. Gui, and L. Li, "Preparation of Textured Bismuth Titanate Ceramics Using Spark Plasma Sintering," *J. Am. Ceram. Soc.*, **87** [7] 1404-6 (2004).
- ³⁰Z. Shen, J. Liu, J. Grins, M. Nygren, P. Wang, Y. Kan, H. Yan, and U. Sutter, "Effective Grain Alignment in Bi₄Ti₃O₁₂ Ceramics by Superplastic-Deformation-Induced Directional Dynamic Ripening," *Adv. Mater.*, **17** [6] 676-80 (2005).
- ³¹J. A. Horn, S. C. Zhang, U. Selvaraj, G. L. Messing, and S. Trolrier-McKinstry, "Templated Grain Growth of Textured Bismuth Titanate," *J. Am. Ceram. Soc.*, **82** [4] 921-6 (1999).
- ³²S. Swartz, W. A. Schulze, and J. V. Biggers, "Fabrication and Electrical Properties of Grain-Oriented Bismuth Titanate (Bi₄Ti₃O₁₂) Ceramics," *Ferroelectrics*, **38** [1-4] 765-8 (1981).
- ³³S. Hong, S. Trolrier-McKinstry, and G. L. Messing, "Dielectric and Electromechanical Properties of Textured Niobium-Doped Bismuth Titanate Ceramics," *J. Am. Ceram. Soc.*, **83** [1] 113-8 (2000).
- ³⁴R. W. Cahn, P. Haasen, and E. J. Kramer, *Materials Science and Technology: A Comprehensive Treatment*, pp. 405 VCH, Weinheim, Germany, 1996.
- ³⁵R. E. Mistler and E. R. Twiname, *Tape Casting: Theory and Practice*. The American Ceramic Society, Westerville, OH, 2000.
- ³⁶T. F. McNulty, V. F. Janas, and A. Safari, "Multilayered Multifunctional Ceramic Materials by Tape Casting, ISAF'96," pp. 755-8 in *Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics*, Vol. 2, 1996.
- ³⁷T. Ayguavives, A. Tombak, J. P. Maria, G. T. Stauff, C. Ragaglia, J. Roeder, A. Mortazawi, and A. I. Kingon, "Physical Properties of (Ba,Sr)TiO₃ Thin Films Used for Integrated Capacitors in Microwave Applications," pp. 365-8 in *Proceedings of the 2000 IEEE International Symposium on Applications of Ferroelectrics*, 12th, Vol. 1, July 21-August 2, Honolulu, HI, United States, 2001.
- ³⁸R. A. Young, A. Sakthivel, T. S. Moss, and C. O. Paiva-Santos, "DBWS-9411 - an Upgrade of the DBWS* Programs for Rietveld Refinement with PC and Mainframe Computers," *J. Appl. Cryst.*, **28** [3] 366-7 (1995).
- ³⁹ICSD Number 024735, B. Aurivillius, "Mixed Bismuth Oxides with Layer Lattices. II. Structure of Bi₄Ti₃O₁₂," *Arkiv for Kemi*, **1**, 499-512 (1949).
- ⁴⁰B. D. Stojanovic, A. Z. Simões, C. O. Paiva-Santos, C. Quinelato, E. Longo, and J. A. Varela, "Effect of Processing Route on the Phase Formation and Properties of Bi₄Ti₃O₁₂ Ceramics," *Ceram. Int.*, **32** [6] 707-12 (2006).
- ⁴¹Y. Kan, P. Wang, Y. Li, Y. B. Cheng, and D. Yan, "Low-Temperature Sintering of Bi₄Ti₃O₁₂ Derived from a Co-Precipitation Method," *Mater. Lett.*, **56** [6] 910-4 (2002).
- ⁴²M. E. Mendoza, F. Donado, and J. L. Carrillo, "Synthesis and Characterization of Micrometric Ceramic Powders for Electrorheological Fluids," *J. Phys. Chem. Solids*, **64** [11] 2157-61 (2003).
- ⁴³W. K. Chia, C. F. Yang, and Y. C. Chen, "The Effect of Bi₂O₃ Compensation during Thermal Treatment on the Crystalline and Electrical Characteristics of Bismuth Titanate Thin Films," *Ceram. Int.*, **34**, 379-84 (2008).
- ⁴⁴J. F. Dorrian, R. E. Newnham, and K. K. Smith, "Crystal Structure of Bismuth Titanate," *Ferroelectrics*, **3** [1] 17-27 (1971).
- ⁴⁵T. Rentschler, "Substitution of Lead into the Bismuth Oxide Layers of the $n = 2$ - and $n = 3$ - Aurivillius Phases," *Mater. Res. Bull.*, **32** [3] 351-69 (1997).
- ⁴⁶A. Z. Simões, B. D. Stojanovic, M. A. Ramirez, A. A. Cavalheiro, E. Longo, and J. A. Varela, "Lanthanum-Doped Bi₄Ti₃O₁₂ Prepared by the Soft Chemical Method: Rietveld Analysis and Piezoelectric Properties," *Ceram. Int.*, **34** [2] 257-61 (2008).
- ⁴⁷M. Zdujic, D. Poletti, C. Jovalekic, and L. Karanovic, "The Evolution of Structure Induced by Intensive Milling in the System 2 Bi₂O₃·3 TiO₂," *J. Non-Cryst. Solids*, **352** [28-29] 3058-68 (2006).
- ⁴⁸K. R. Zhu, M. S. Zhang, Y. Deng, J. X. Zhou, and Z. Yin, "Finite-Size Effects of Lattice Structure and Soft Mode in Bismuth Titanate Nanocrystals," *Solid State Commun.*, **145** [9-10] 456-60 (2008).
- ⁴⁹M. K. Jeon, Y. I. Kim, S. H. Nahm, J. M. Sohn, C. H. Jung, and S. I. Woo, "Crystal Structure and Spontaneous Polarization of Bi_{4-x}Nd_xTi₃O₁₂ Studied by using Neutron Powder Diffraction Data," *J. Phys. D.*, **40** [15] 4647-52 (2007).
- ⁵⁰S. Luo, Y. Noguchia, M. Miyayama, and T. Kudo, "Rietveld Analysis and Dielectric Properties of Bi₂WO₆ - Bi₄Ti₃O₁₂ Ferroelectric System," *Mater. Res. Bull.*, **36** [3-4] 531-40 (2001).
- ⁵¹E. C. Aguiar, A. Z. Simões, F. Moura, M. Cilense, E. Longo, and J. A. Varela, "Piezoresponse Force Microscopy Behaviour of Bi₄Ti₃O₁₂ Ceramics with Various Excess Bismuth," *Process. Appl. Ceram.*, **5**, 1-11 (2011).
- ⁵²T. Qing-Yuan, Y. M. Kan, Y. G. Li, G. J. Zhang, and P. L. Wang, "Effect of Vanadium Doping on Fabrication and Property of Bi₄Ti₃O₁₂ Ceramics," *Scripta Mater.*, **54** [12] 2075-80 (2006).
- ⁵³Y. M. Kan, G. J. Zhang, P. L. Wang, and Y. B. Cheng, "Preparation and Properties of Neodymium-Modified Bismuth Titanate Ceramics," *J. Eur. Ceram. Soc.*, **28** [8] 1641-7 (2008).
- ⁵⁴L. Zhang, R. Chu, S. Zhao, G. Li, and Q. Yin, "Piezoresponse Force Microscopy Studies of Nanoscale Domain Structures in Ferroelectric Thin Film," *Mater. Sci. Eng. B*, **116** [1-3] 104-8 99 (2005).
- ⁵⁵H. J. Cho, W. Jo, and T. W. Noh, "Leakage Current Behavior in Rapid Thermal Annealed Bi₄Ti₃O₁₂ Thin Films," *Appl. Phys. Lett.*, **65** [12] 1525-7 (1994).
- ⁵⁶L. Wu, C. Wei, T. Wu, and H. Liu, "Piezoelectric Properties of Modified PZT Ceramics," *J. Phys. C: Solid State Phys.*, **16** [14] 2803-21 (1983).
- ⁵⁷C. Q. Sun, D. Jin, J. Zhou, S. Li, B. K. Tay, S. P. Lau, X. W. Sun, H. T. Huang, and P. Hing, "Intense and Stable Blue-Light Emission of Pb(Zr_xTi_{1-x})O₃," *Appl. Phys. Lett.*, **79** [8] 1082-4 (2001).
- ⁵⁸E. C. Aguiar, A. Z. Simões, E. Longo, and J. A. Varela, "Rietveld Analyses and Piezoelectric Properties of Niobium Doped Bismuth Titanate Systems," *J. Adv. Microsc. Res.*, **5** [2] 149-57 (2010).
- ⁵⁹A. Z. Simões, E. C. Aguiar, A. Ries, E. Longo, and J. A. Varela, "Niobium Doped Bi₄Ti₃O₁₂ Ceramics Obtained by the Polymeric Precursor Method," *Mat. Lett.*, **61** [2] 588-91 (2007).
- ⁶⁰L. S. Cavalcante, A. Z. Simões, L. P. S. Santos, M. R. M. C. Santos, E. Longo, and J. A. Varela, "Dielectric Properties of Ca(Zr_{0.05}Ti_{0.95})O₃ Thin Films Prepared by Chemical Solution Deposition," *J. Solid State Chem.*, **179** [12] 3739-43 (2006).
- ⁶¹A. Z. Simões, M. A. Ramirez, B. D. Stojanovic, E. Longo, and J. A. Varela, "The Effect of Microwave Annealing on the Electrical Characteristics of Lanthanum Doped Bismuth Titanate Films Obtained by the Polymeric Precursor Method," *Appl. Surf. Sci.*, **252** [24] 8471-5 (2006).
- ⁶²A. Z. Simões, S. Cava, L. S. Cavalcante, M. Cilense, E. Longo, and J. A. Varela, "Ferroelectric and Dielectric Properties of Ba_{0.5}Sr_{0.5}(Ti_{0.80}Sn_{0.20})O₃ Thin Films Grown by the Soft Chemical Method," *J. Solid State Chem.*, **179** [10] 2972-6 (2006).
- ⁶³A. Z. Simões, M. A. Ramirez, E. Longo, and J. A. Varela, "Leakage Current Behavior of Bi_{3.25}La_{0.75}Ti₃O₁₂ Ferroelectric Thin Films Deposited on Different Bottom Electrodes," *Mat. Chem. Phys.*, **107** [1] 72-6 (2008).
- ⁶⁴L. S. Cavalcante, A. Z. Simões, M. O. Orlandi, M. R. M. C. Santos, J. A. Varela, and E. Longo, "Dependence of Annealing Time on Structural and Morphological Properties of Ca(Zr_{0.05}Ti_{0.95})O₃ Thin Films," *J. Alloys Compd.*, **453** [1-2] 386-91 (2008).
- ⁶⁵D. P. Volanti, D. Keyson, L. S. Cavalcante, A. Z. Simões, M. R. Joya, E. Longo, J. A. Varela, P. S. Pizani, and A. G. Souza, "Synthesis and Characterization of CuO Flower-Nanostructure Processing by a Domestic Hydrothermal Microwave," *J. Alloys Compd.*, **459** [1-2] 537-42 (2008).
- ⁶⁶A. Z. Simões, M. A. Ramirez, C. S. Riccardi, E. Longo, and J. A. Varela, "Effect of the Microwave Oven on Structural, Morphological and Electrical Properties of SrBi₄Ti₄O₁₅ Thin Films Grown on Pt/Ti/SiO₂/Si Substrates by a Soft Chemical Method," *Mat. Characterization*, **59** [6] 675-80 (2008).
- ⁶⁷D. Keyson, D. P. Volanti, L. S. Cavalcante, A. Z. Simões, J. A. Varela, and E. Longo, "CuO Urchin-Nanostructures Synthesized from a Domestic Hydrothermal Microwave Method," *Mat. Res. Bull.*, **43** [3] 771-5 (2008).
- ⁶⁸S. K. Kim, M. Miyayama, and H. Yanagida, "Electrical Anisotropy and a Plausible Explanation for Dielectric Anomaly Bi₄Ti₃O₁₂ Single Crystals," *Mater. Res. Bull.*, **31** [1] 121-31 (1996).

Mechanically activating formation of layered structured bismuth titanate

Biljana D. Stojanovic^{a,b,*}, C.O. Paiva-Santos^a, C. Jovalekic^b, A.Z. Simoes^a,
F.M. Filho^a, Z. Lazarevic^a, J.A. Varela^a

^a Instituto de Química-UNESP, Rua Prof. Francisco Degni s/n, Bairro Quitandinha, 14801 970 Araraquara, S.P., Brazil

^b Center for Multidisciplinary Studies University of Belgrade, Belgrade, Serbia and Montenegro

Received 11 January 2005; received in revised form 7 June 2005; accepted 19 July 2005

Abstract

Bismuth titanate— $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) with wide application in the electronic industry as capacitors, memory devices and sensors is the simplest compound in the Aurivillius family, which consists of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets alternating with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-like layers. The synthesis of more resistive BIT ceramics would be preferable advance in obtaining of well-densified ceramic with small grains randomly oriented to limit the conductivity along the $(\text{Bi}_2\text{O}_2)^{2+}$ layers. Having in mind that the conventional ceramic route for the synthesis can lead to non-stoichiometry in composition, in consequence of the undesirable loss in bismuth content through volatilization of Bi_2O_3 at elevated temperature, our efforts were addressed to preparation of BIT by mechanical activation the constituent oxides. The nucleation and phase formation of BIT, crystal structure, microstructure, powder particle size and specific surface area were followed by XRD, Rietveld refinement analysis, thermal analysis, scanning electron microscopy (SEM) and the BET specific surface area measurements.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Milling; X-ray diffraction; Crystal structure; Microstructure

1. Introduction

Bismuth titanate— $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a ferroelectric material with wide application in the electronic industry, as capacitors, memory devices and sensors [1–3]. Its ferroelectric-to-paraelectric phase transition temperature is near 675 °C [3], which gives it a potential applicability as a suitable candidate for high-temperature piezoelectric device. In addition, BIT is an interesting material that is lead-free and environmental friendly.

Bismuth titanate is the simplest compound in the Aurivillius family that can be presented by the general formula $(\text{Bi}_2\text{O}_2)[\text{A}_{m-1}(\text{B})_m\text{O}_{3m+1}]$, which consists of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets alternating with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-like layers [4]. In general formula m represents the number of octahedral stacked along the direction perpendicular to the sheets, and A and B are the 12- and 6-fold coordination sites of perovskite

slab, respectively [4]. This kind of structure promotes plate-like morphology. The platelets are apparently single crystals with c -axis perpendicular to the major face [5] and with the higher component of its spontaneous polarization parallel to this face [6].

More recently, the Aurivillius phases have been the subject of the renewed interest due to their attractive anion properties. Hence, BIT poses an electrical conductivity that is highly anisotropic, with the maximum value in the same plane as the polarization [7]. As this conductivity is relatively high, it is very difficult to pole [8]. Having this in mind, the synthesis of more resistive BIT ceramics would be preferable advance in obtaining of well-densified ceramic with small grains randomly oriented to limit the conductivity along the $(\text{Bi}_2\text{O}_2)^{2+}$ layers [8].

The conventional ceramic route for the synthesis leads to non-stoichiometry in composition of the resultant BIT powder, in consequence of the undesirable loss in bismuth content through volatilization of Bi_2O_3 at elevated temperature [9]. In addition, crystallite coarsening and particle aggregation are unavoidable because of the interfacial diffu-

* Corresponding author. Tel.: +55 16 33 01 6701; fax: +55 16 33 22 7932.

E-mail addresses: smstobi@yahoo.com, biljana@ibiss.bg.ac.yu
(B.D. Stojanovic).

sions and reactions that occur at the rather high calcination temperature. Accordingly, the sintering and microstructure are adversely affected by the presence of hard agglomerates, where sintering among aggregates of different green density can occur resulting in the minor ferroelectric property [10].

Many efforts have been made to avoid this problem by lowering the calcination temperature or using wet-chemistry-based methods. One of main objectives in the wet-chemistry processing techniques is that the intimate mixing in solution form can improve phase and compositional homogeneity and, therefore, the properties of BIT-based ceramics. Powder characteristics, such as particle morphology, particle size and particle size distribution, can be more controlled. Hence, many chemistry-based preparations, such as precipitation [11–13], sol–gel [14], hydrothermal [15] and molten salt route [16], have been investigated as alternatives.

However, the wet-chemistry involve chemicals that are sensitive to moisture or light, which makes them difficult to deal with, especially for bismuth salts. In addition, those processes are expensive and also rather time consuming [17,18]. Besides, most of the chemistry-based processing routes require post-precursor calcination at elevated temperature to realize the precursor-to-ceramic conversion. Additionally, the sintering reactive behavior, such as refined particle and crystallite sizes of chemical-derived precursors, is often ruined by calcination at the elevated temperature [18,19]. Differential sintering between regions of different green densities, as a result of particle coarsening and strong agglomeration, like in conventional mixed-oxides procedure, has been commonly observed.

Benjamin and Gilman [20], along with co-workers, made the important discovery of mechanical alloying, which was devised for synthesizing alloys and intermetallics. Latter, the mechanochemical process has since been modified for magnetic materials. Mechanically activated processes have been recently employed by Benjamin and Gilman to prepare nanosized oxides and compounds. Thus, mechanically activated processes are among the earliest phenomena created by humankind and the use of flint to trigger the fires is best-known example [21]. The mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powder preparation for the several reasons. It uses low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, leading to simplified process [21,22]. Furthermore, the mechanically derived powders possess a much higher sinterability than those powders synthesized by conventional solid-state reaction and most of wet-chemical processes.

There are a number of unique phenomena associated with mechanical activation, including refinement in crystallite size, amorphization of crystallite phases, creation of point, surface and lattice defects, phase transformations and crystallization from an amorphous state and chemical reaction [23]. In addition, the nucleation and subsequent growth of

perovskite crystallites were triggered by mechanical activation at room temperature [24].

Although mechanical activation has been successful with Pb-based electroceramics [22,23] of perovskite structure, it has not been much studied for the layered structured compounds, such as $\text{Bi}_3\text{Ti}_4\text{O}_{12}$ ceramics. A few articles were published related to the preparation of BIT using milling technique for the mechanical activation processes [25–28]. Taking this in account, the objective of this work is to study the feasibility of formation $\text{Bi}_3\text{Ti}_4\text{O}_{12}$ by mechanically activating the constituent oxides. By XRD, SEM microscopy and the specific surface area followed the nucleation, phase formation and characteristic of BIT powders.

2. Experimental procedure

The bismuth titanate was prepared starting from bismuth oxide (Bi_2O_3 , Fluka, p.a. 99.8%) and titanium oxide (TiO_2), in an anatase crystal form, TiO_2 anatase, Carlo Erba p.a. 99%) commercially available. These oxide powders exhibited a particle size distribution in the range 2–4 μm for TiO_2 and 1–5 μm for Bi_2O_3 . To make a batch required for stoichiometric BIT composition, and BIT with 3 wt% excess of Bi_2O_3 , corresponding amount of Bi_2O_3 and TiO_2 were weighed and loaded into zirconium jars together with zirconium milling balls ~10 mm in diameter. Mechanical activation and mechanochemical synthesis were performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5). Milling conditions were the following: zirconium oxide jars and zirconium oxide balls ($d = 10 \text{ mm}$), ball-to-powder weight ration was 20:1, air atmosphere, basic disc rotation speed was 317 min^{-1} , rotation speed of disc with jars was 396 min^{-1} , milling time was from 0, 60, 120 and 360 min.

The X-ray diffraction data for milled powders were collected using a Rigaku® RINT2000 diffractometer ($42 \text{ kV} \times 120 \text{ mA}$) with Cu K α radiation ($\lambda_{\text{K}\alpha 1} = 1.5405 \text{ \AA}$, $\lambda_{\text{K}\alpha 2} = 1.5443 \text{ \AA}$, $I_{\text{K}\alpha 1}/I_{\text{K}\alpha 2} = 0.5$), 2θ range between 15° and 110° , step size of 0.02° (2θ), divergence slit = 0.5 mm, receiving slit = 0.3 mm. Scanning electron microscopy (SEM; Model JOEL-5300) were used to study particle size and powder morphology of activated powders and microstructure of sintered pellets. The pellets were prepared by pressing at 210 MPa and sintered in closed system at 875 and 1000 $^\circ\text{C}$ for 4 h. The average grain size of the milled powders was estimated using the Sherrer formula. Specific sample surface areas were determined based on isotherms of nitrogen adsorption using the BET method (Sorpomatic 1990).

The Rietveld analysis was performed with the Rietveld refinement program [29] and the data was calculated using the program package General Structure Analysis System (GSAS) of Larson and von Dreele [30]. The peak profile function was modeled using a convolution of the pseudo-Voigt [30] with the asymmetry function described by Finger et al. [31,32], which accounts for the asymmetry due to axial divergence.

To account for the anisotropy in the half width of the reflections, it was used the bidimensional model for crystallite size described by Larson and von Dreele [30].

3. Results and discussion

Formation mechanisms of nanosized compound powders via mechanochemical process are complicated and not yet clear. It is recognized that during the targeting ferroelectric materials formation, the process passes through few steps, unless three. Generally, it starts with the refinement in particle and grain size of starting materials following after that by the nucleation and crystallization of target compound. As the result, nanocrystalline powders can be obtained directly from their oxide mixtures after milling for certain time.

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase evolution was monitored by X-ray analysis. Fig. 1 contains the XRD patterns of TiO_2 and Bi_2O_3 powders. Figs. 2 and 3 are referred to the mixture of Bi_2O_3 and TiO_2 , milled for various times. It was evident that before

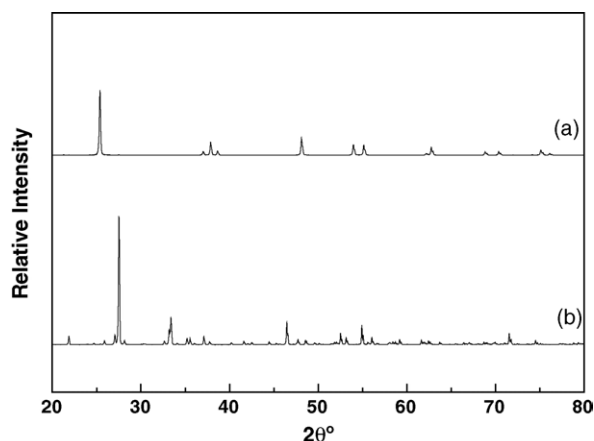


Fig. 1. XRD traces of: (a) Bi_2O_3 and (b) TiO_2 (anatase).

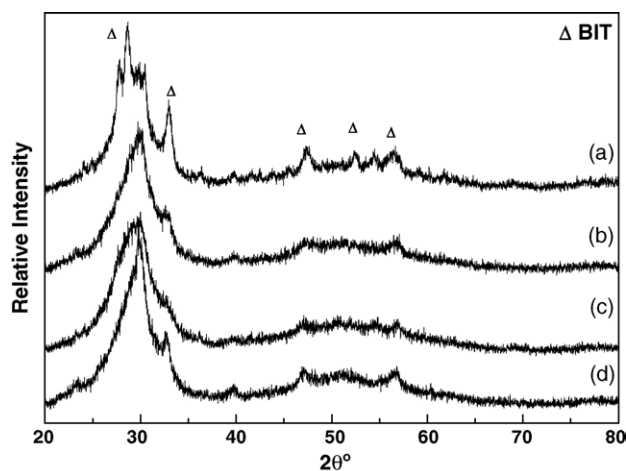


Fig. 2. XRD traces of mixed oxides of Bi_2O_3 and TiO_2 equivalent to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ in composition subjected to: (a) 120 min, (b) 180 min, (c) 240 min and (d) 360 min of mechanical activation, respectively.

mechanical activation, sharp peaks of crystalline Bi_2O_3 and TiO_2 were observed in the XRPD, since the conventional ball milling used for homogenization did not triggered any reaction among mixed oxides, either stoichiometric composition or with excess of Bi_2O_3 .

Upon 60 min of mechanical activation, the XRD pattern of milled powders prepared without and with excess of Bi_2O_3 show the different progression. Fig. 2 shows the XRD traces of mixed oxides equivalent to stoichiometric composition of bismuth titanate subjected to 120, 180, 240 and 360 min of mechanical activation, respectively. Upon 120 min, the material was started to be amorphized and the majority of sharp peaks of started oxides were diminishing. Longer time of milling respecting to 180 and 240 min triggered rather little reaction among amorphized species. Upon 360 min of mechanical activation, the broadened peaks at 2θ angle at around 30° , 32° and 39° and triple peaks at 2θ angle between 47° and 58° can be attributed to the formation of bismuth titanate. This shows that initial 180 min of mechanical activation had led to the formation of small amount of bismuth titanate besides presence of majority of starting oxides. The formed phase is rather amorphous and that is much more expressed then in the case of powders prepared with excess of Bi_2O_3 .

In the XRD pattern of milled powders prepared with excess of Bi_2O_3 (Fig. 3), the majority of these sharp peaks have dissappeared and a broadened peaks at 2θ angle at around 32° and 39° were observed. It indicates that initial oxide phases, upon grinding through mechanical activation have been initiated to transform, resulted in the nucleation and formation of a new phase in the course of milling. The peaks affected to Bi_2O_3 and TiO_2 were partly diminishing pointed to solid-state reaction between starting oxides resulting through mechanochemical synthesis reaction. After 120 min of mechanical activation, the broadened peaks can be resolved in few peaks which are centered at 2θ of 30° , 32.8° , 33.2° , 39.7° , 39.95° , 47.8° , 56.9° and 57.3° , respec-

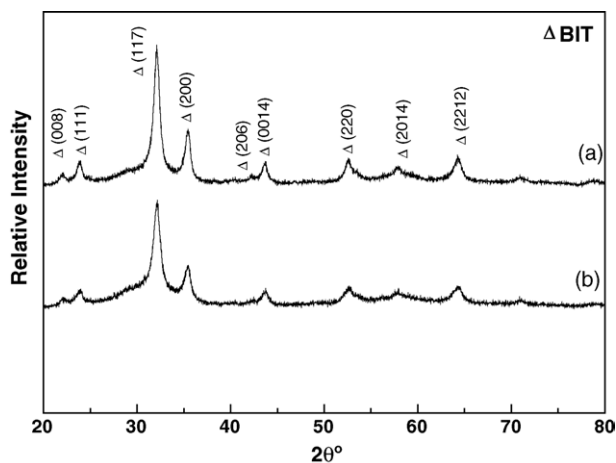


Fig. 3. XRD traces of BIT prepared with excess of 3wt% Bi_2O_3 upon mechanical activation of: (a) 120 min and (b) 360 min.

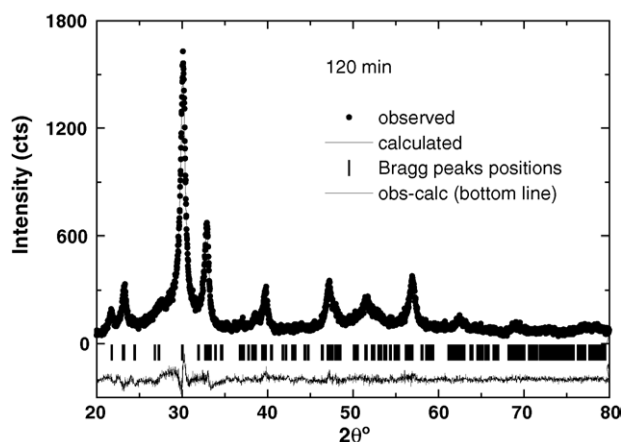


Fig. 4. Rietveld refinement analysis for BIT powders prepared with excess of 3 wt% Bi_2O_3 upon mechanical activation of 120 min.

tively, indicating the formation of the orthorhombic perovskite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. The peaks centered at 2θ of 30° , 32.8° and 39.7° , which are the strongest, can correspondent to tetragonal (hkl) planes (201) and (hkl) planes (208) or to orthorhombic structure (hkl) planes (117), (200) and (hkl) planes (208) of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The doubt about crystal structure is resolved using Rietveld analysis confirming the presence of only orthorhombic phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ formed after 120 min shows the presence of rather small amount of amorphous phase. Upon 360 min of milling, the amount of amorphous phase was increasing. This indicated that the milling time was too long and that the crystalline grains started to be destroyed resulting in bismuth titanate phase amorphization. Having this in mind, it is evident that bismuth oxide has the dominant role in the formation of bismuth titanate phase during mechanical activation of starting oxides and during mechanochemical synthesis.

Although the relation between crystal structures and chemical compositions is not thoroughly elucidated and detailed crystal and electronic structures have not been fully clarified [32], in the present study we adopted the Rietveld refinement technique to investigate the crystal structure of the BIT sample powders obtained after 120 and 360 min of milling and prepared with excess of Bi_2O_3 . Large structural distortions are revealed [33], and electronic-structure calculations revealed that covalent interaction, which originates from the strong hybridization between Ti 3d and O 2p orbital, plays an important role in the structural distortion of the materials [28–30]. The results of Rietveld refinements are presented in Figs. 4 and 5 denoted the well agreement with experimental data. It is shown that synthesized BIT has the orthorhombic structure of an Aurivillius phase Bi-layered oxide, denoted by the formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$, in which perovskite units of Ti–O octahedra are sandwiched between Bi_2O_2 layers. The Rietveld agreement indexes are presented in Table 1. The crystal lattice parameters are shown in Table 2. It is notable that the crystal lattice parameters are close to one done in literature for orthorhombic structured bismuth

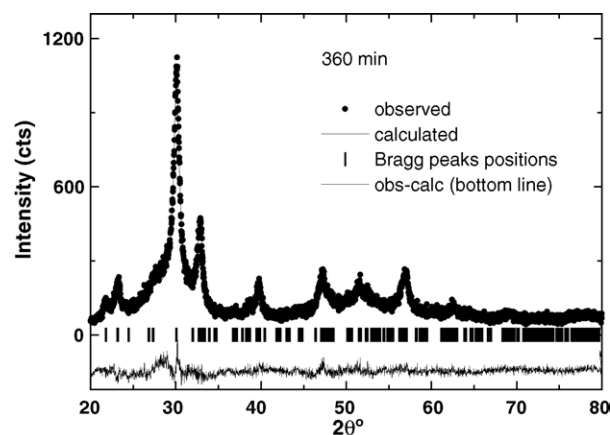


Fig. 5. Rietveld refinement analysis for BIT powders prepared with excess of 3 wt% Bi_2O_3 upon mechanical activation of 360 min.

Table 1

Rietveld agreement indexes at the end of the refinements for the BIT powder samples mechanically activated 120 and 360 min

Samples	R_{wp} (%)	R_F (%)	χ^2
120 min	10.52	5.70	1.689
360 min	10.49	16.73	1.90

titanate obtained by chemical precipitation method [19]. The calculated crystallite size was 22 nm for BIT obtained after 120 min, and 20 nm after 360 min of milling that is in agreement with step of powders amorphization.

The specific surface area powder mixtures of BIT, prepared with excess of Bi_2O_3 , changes during milling depending on whether the breaking process of particles or the secondary agglomeration process dominates or mechanically assisted synthesis occurred. At the beginning of milling, the value of specific surface area is lowering in compared to specific surface area value obtained with prolongation of milling time. When BIT becomes the dominant phase in the milling sample form, mechanically assisted synthesis process is dominant to the secondary agglomeration process. This corresponds to the increase of the value of specific surface area, from $5.6 \text{ m}^2 \text{ g}^{-1}$ at the beginning of milling to $13.1 \text{ m}^2 \text{ g}^{-1}$ after 120 min. On the contrary, the decrease trend of specific surface area from 13.1 to $9.6 \text{ m}^2 \text{ g}^{-1}$ can be seen after

Table 2

Rietveld calculation of lattice parameters (Å) for the BIT powder samples mechanically activated (a) 120 and (b) 360 min

	120 min	360 min
Lattice parameter		
a (Å)	5.465(1)	5.478(2)
b (Å)	5.445(2)	5.445(2)
c (Å)	32.578(12)	32.578(12)
V (Å ³)	971.8(6)	973.8(3)
D (g cm ^{−3})	8.02	8.00
Perovskite (mol%)	98.5 ± 0.5	97.1 ± 0.4
Stoichiometry	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$
Refinement	$\text{Bi}_4\text{Ti}_3\text{O}_{11.8}$	$\text{Bi}_4\text{Ti}_3\text{O}_{11.6}$

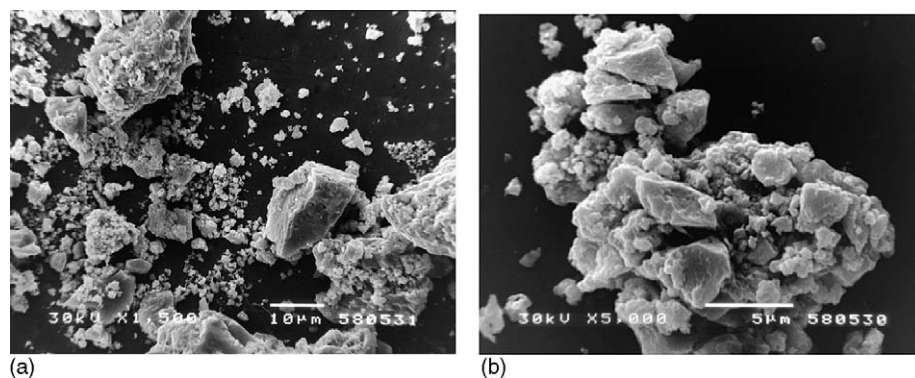


Fig. 6. SEM micrographs showing BIT powders derived from: (a) 120 min and (b) 360 min of mechanical activation.

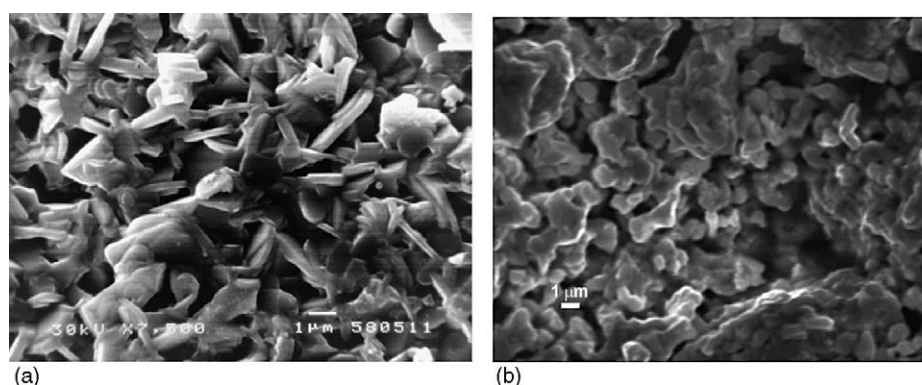


Fig. 7. Plate-like microstructure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ sintered at: (a) 875 °C and (b) 1000 °C.

360 min of milling as a result of secondary agglomeration processes. It is possible to assume that after 120 min the process of mechanochemical reaction and crystallization of formed BIT is almost finished and that the breaking process of formed particles are dominant comparing to the secondary agglomeration. This is in agreement with XRD results.

The existence of powder agglomerates and change in their size are confirmed with SEM analysis (Fig. 6a and b). Results of SEM analysis are in accordance to the conclusion based on BET analysis. The strong agglomeration of powders was noticeable. In order to determine the individual particle size, the smallest agglomerate was chosen. Meanwhile, it was rather difficult to evaluate the correct value. By rough estimation and using the Sherrer formula, it was found that the individual particle size was approximately 30 nm.

In order to determine the sintering temperature condition for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders prepared by mechanically assisted synthesis during milling 120 min, the TG analysis was performed (from room temperature up to 1000 °C using a heating rate of 10 °C min⁻¹). In temperature interval from 25 to 980 °C, no change in weight of BIT was observed.

Fig. 7 shows the microstructure of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics prepared from BIT powders obtained by mechanical activation after 120 min and with 3 wt% excess of Bi_2O_3 and sintered at 875 and 1000 °C for 4 h. It was used closed system and protective atmosphere of Bi_2O_3 powders. Both samples

exhibit plate-like grain structure. For the samples obtained on lower temperature the density was 7.65 g cm⁻³ (theoretical density is 8.04 g cm⁻³) with an average grain size about 3.5 μm along *c*-axis. On higher temperature the density showed slight decrease and it was 7.58 g cm⁻³. The average grain size was rather difficult to calculate because of low amount of liquid phase presence resulted from volatilization of bismuth oxide.

The obtained result indicated that nanosized powder synthesized by high-energy ball milling process better sinterability than those prepared by other methods, showing the advantage of the mechanochemical process over conventional solid-state reaction and chemical processes.

4. Conclusions

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics have been prepared from nanosized powders obtained by mechanochemical synthesis via a high-energy ball milling process starting from oxides. The BIT prepared with excess of Bi_2O_3 and milled 2 h shows the orthorhombic crystalline structure with small amount of amorphous phase. The crystallite size was around 20 nm, and the powder particle size was about 30 nm. It is shown that bismuth oxide has the dominant role in the formation of bismuth titanate phase during mechanical activation of starting oxides

and during mechanochemical synthesis. After sintering the plate-like structure typical for layered structure materials was obtained. The noted result indicates that nanosized bismuth titanate powder synthesized by high-energy ball milling process possesses well sinterability, showing the advantage of the mechanochemical process over conventional solid-state reaction.

Acknowledgements

The authors gratefully acknowledge the financial support of the Brazilian financing agency CAPES and to the Ministry of Science and Environmental Protection of the Republic of Serbia.

References

- [1] S. Ikegami, I. Ueda, Piezoelectricity in ceramics of ferroelectric bismuth compound with layer structure, *Jpn. J. Appl. Phys.* 13 (1974) 1572–1577.
- [2] T. Takenaka, K. Sakata, Grain orientation effects on electrical properties of bismuth layer-structured ferroelectric solid solution, ceramics of ferroelectric bismuth compound with layer structure, *Jpn. J. Appl. Phys.* 5513 (1984) 1092–1099.
- [3] J.F. Dorrian, R.E. Newnham, D.K. Smith, M.I. Kay, Crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, *Ferroelectrics* 3 (1971) 17–27.
- [4] B. Aurivillius, Mixed oxides with layer lattice, *Arkiv. Kemi.* 1 (1949) 499–512.
- [5] Q. Zhou, B.J. Kennedy, Structural studies of the ferroelectric phase transition in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, *Chem. Mater.* 15 (26) (2003) 5025–5028.
- [6] Y. Osamu, M. Noboru, H. Ken, The formation and characterization of alkoxy-derived $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, *Br. Ceram. Trans. J.* 90 (1991) 111–113.
- [7] S.E. Cummings, L.E. Cross, Electrical and optical properties of ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystal, *J. Appl. Phys.* 39 (5) (1968) 2268–2274.
- [8] S. Kojima, A. Hushur, F. Jiang, S. Hamazaki, T. Takashige, M.S. Jang, S. Shimada, Crystallization of amorphous bismuth titanate, *J. Non-Cryst. Solid* 293–295 (2001) 250–254.
- [9] C. Jovalekic, M. Pavlovic, O. Osmokriovic, Lj. Atanasoska, X-ray photoelectron spectroscopy study of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ferroelectric ceramics, *Appl. Phys. Lett.* 72 (9) (1998) 1051–1053.
- [10] M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, Factors affecting the electrical conductivity of donor-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ piezoelectric ceramics, *J. Am. Ceram. Soc.* 82 (9) (1999) 2411–2416.
- [11] H. Shulman, M. Testdorf, D. Damjanovic, N. Setter, Microstructure, electrical conductivity and piezoelectric properties of bismuth titanate, *J. Am. Ceram. Soc.* 79 (12) (1996) 3214–3218.
- [12] P. Pookmanee, P. Boonphayak, S. Phanichphant, Chemical synthesis of bismuth titanate microparticles, *Ceram. Int.* 30 (2004) 1917–1919.
- [13] A.V.P. Rao, A.I. Robin, S. Kommarneni, Bismuth titanate from nanocomposite by sol–gel technique, *J. Cryst. Growth* 237–239 (2002) 469–473.
- [14] Y.L. Du, M.S. Zvarg, Q. Chen, Z.R. Yuan, Z. Yin, Q.A. Zhang, Size effect and evidence of a size-driven phase transition in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanocrystals, *Solid State Commun.* 124 (2002) 113–118.
- [15] C. Jovalekic, S. Stevic, A study of ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics prepared from chemically derived powders, *Ferroelectrics* 132 (1992) 185–196.
- [16] H. Xu, K.J. Bowman, E.B. Slamovich, Hydrothermal synthesis of bismuth titanate powders, *J. Am. Ceram. Soc.* 86 (10) (2003) 1815–1817.
- [17] T. Thongtem, S. Thongtem, Characterization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder prepared by the citrate and oxalate coprecipitation processes, *Ceram. Int.*, in press.
- [18] S. Gopalan, K. Mehta, A.V. Virkar, Synthesis of oxide perovskite solid using the molten salt method, *J. Mater. Res.* 11 (8) (1996) 1863–1865.
- [19] Z.Y. Xu, X.M. Chen, Dielectric ceramics with TiO_2 rich compositions in Bi_2O_3 – TiO_2 system, *Mater. Lett.* 39 (1999) 18–21.
- [20] J.S. Benjamin, Mechanical alloying, *Sci. Am.* 234 (1976) 40–48.
- [21] R.M. German, *Sintering Theory and Practice*, Wiley, New York, 1996.
- [22] J. Wang, J.M. Xue, D.M. Wan, B.K. Gan, Mechanically activating nucleation and growth of complex perovskites, *J. Solid State Chem.* 154 (2000) 321–328.
- [23] K. Tkacova, *Mechanical Activation of Minerals*, Elsevier, Amsterdam, 1989.
- [24] D. Makovec, I. Pribosic, Z. Samardzija, M. Drofenik, Incorporation of aliovalent dopants into the bismuth-layered perovskite-like structure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$, *J. Am. Ceram. Soc.* 84 (11) (2001) 2702–2704.
- [25] S.H. Ng, J. Xue, J. Wang, Bismuth titanate activation of a chemically coprecipitated precursor, *J. Am. Ceram. Soc.* 85 (11) (2002) 2660–2665.
- [26] M.H. Sim, J.M. Xue, J. Wang, Layer structured calcium bismuth titanate by mechanical activation, *Mater. Lett.* 58 (2004) 2032–2036.
- [27] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, Preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ via a high-energy ball milling process, *Mater. Lett.* 51 (2001) 108–114.
- [28] J. Ricote, L. Pardo, A. Castro, P. Millan, Study of the process of mechanochemical activation to obtain Aurivillius oxides with $n=1$, *J. Solid State Chem.* 160 (2001) 1054–1061.
- [29] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Cryst.* 2 (1969) 65–71.
- [30] A.C. Larson, R.B. von Dreele, *General Structure Analysis System*, LAUR 86-748, LANSCE, MS-H805, NM 87545, Los Alamos National Laboratory, Los Alamos, Copyright 1985–2004, The Regents of the University of California.
- [31] R.A. Young, P. Desai, Crystallite size and microstrain indicators in rietveld refinement, *Archiwum Nauki o Materialach (Arch. Mater. Sci.) Moskva* 10 (1989) 71–90.
- [32] L.W. Finger, L.W. Cox, D.E. Jephcoat, A correction for powder diffraction peak asymmetry due to axial divergence, *J. Appl. Crystal.* 27 (1994) 892–900.
- [33] P.W. Stephens, Phenomenological model of anisotropic peak broadening in powder diffraction, *J. Appl. Cryst.* 32 (1999) 281–289.

Effect of processing route on the phase formation and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics

B.D. Stojanovic^{a,b,*}, A.Z. Simoes^a, C.O. Paiva-Santos^a,
C. Quinelato^a, E. Longo^c, J.A. Varela^a

^a Department for Technology and Biotechnology, Instituto de Química, UNESP-Universidade Estadual Paulista, Rua Prof., Francisco Degni, s/n, C.P. 355, Araraquara CEP 14801-970, São Paulo, Brazil

^b Center for Multidisciplinary Studies, University of Belgrade, Belgrade, Kneza Visislava 1a, Serbia and Montenegro

^c Chemistry Department, UFSCar – Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil

Received 9 March 2005; received in revised form 5 April 2005; accepted 25 May 2005

Available online 8 September 2005

Abstract

Our efforts were directed to the preparation of bismuth titanate— $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) by two procedures: mechanically assisted synthesis and polymeric precursor method to display a variety of their advantages. To follow the nucleation and phase formation of BIT, XRD and Rietveld refinement analysis were used and it was shown that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramic can be successfully prepared from nano-sized powders obtained by both methods. The ferroelectric properties were determined and the loops from BIT obtained by polymeric precursor method were not fully saturated with a remnant polarization of $20 \mu\text{C}/\text{cm}^2$ and coercitive field of $1500 \text{ kV}/\text{cm}$. BIT obtained from powders prepared by mechanically assisted synthesis shows a remnant polarization of $0.65 \mu\text{C}/\text{cm}^2$ and coercitive field of $1050 \text{ kV}/\text{cm}$. The grain morphology may be the factor causing the observed differences.

© 2005 Published by Elsevier Ltd and Techna Group S.r.l.

Keywords: A. Milling; A. Powders: chemical preparation; B. X-ray methods; B. Electron microscopy; C. Ferroelectric properties; D. Titanates

1. Introduction

Bismuth titanate— $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a ferroelectric material with wide applications in the electronic industry, as capacitors, memory devices and sensors [1–3]. Its ferroelectric-to-paraelectric phase transition temperature is near 675°C [3], which gives it a potential applicability as a suitable candidate for high temperature piezoelectric device. In addition, BIT is an interesting material that is lead-free and environmental friendly.

Bismuth titanate is the simplest compound in the Aurivillius family that can be presented by the general formula $(\text{Bi}_2\text{O}_2)[\text{A}_{m-1}(\text{B})_m\text{O}_{3m+1}]$, which consists of $(\text{Bi}_2\text{O}_2)^{2+}$ sheets alternating with $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ perovskite-like-layers [4]. BIT

possesses an electrical conductivity that is highly anisotropic with the maximum value in the same plane as the polarization that makes BIT very difficult to pole [5].

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were conventionally prepared by solid-state reaction process, where oxide mixture of Bi_2O_3 and TiO_2 was ball milled, calcined at an intermediate temperature and finally sintered at high temperature [6,7]. The conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The presence of hard particle agglomerates will also result in poor microstructure and properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics. Many efforts have been made to avoid this problem by lowering the calcination temperature [8]. The methods reported in the literature to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics include chemistry-based preparations [10], such as precipitation [11], sol–gel [12], hydrothermal [13], and molten salt route [14] and recently mechanically assisted synthesis.

* Corresponding author. Tel.: +55 16 201 6707.

E-mail addresses: biljana@iq.unesp.br, biljana@ibiss.bg.ac.yu (B.D. Stojanovic).

The wet-chemistry involve chemicals that are sensitive to moisture or light, which makes them difficult to deal with, especially for bismuth salts. In addition, those processes are time consuming and most of the chemistry-based processing routes require post-precursor calcination at elevated temperature to obtain the precursor-to-ceramic conversion. It is known that sol–gel process utilizes expensive precursors and that the drying process is a critical operation. The coprecipitation process is limited to cation solutions with similar solubility constants. However, polymeric precursor method, which employs complexing of cations in an organic media, makes use of low cost precursors resulting in a homogeneous ion distribution at molecular level [15]. Because of the formation of a polyester resin during the synthesis, there is no segregation of cations during the thermal decomposition of organic matter.

Mechanically activated processes have been recently employed by Benjamin and Gilman to prepare nano-sized oxides and compounds [16]. In many cases, the mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for the ceramic powder preparation for several reasons. It uses low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, conducting to simplified process [17]. Although mechanical activation has been successful with Pb-based electroceramics of perovskite structure, it has not been much studied for the layered structured compounds, such as $\text{Bi}_3\text{Ti}_4\text{O}_{12}$ ceramics.

The objective of this work is to study the feasibility of $\text{Bi}_3\text{Ti}_4\text{O}_{12}$ formation and ceramics properties obtained from powders prepared by polymeric precursor method and by mechanically activating the constituent oxides.

2. Experimental procedure

The procedure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesis, based on polymeric precursor method, starts from the fact that certain α -hydroxycarboxylic organic acids can form the polybasic acid chelates with several cations. After adding of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneously distribution of cations. Titanium isopropoxide (Hulls AG) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth and titanium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Bi and Ti were mixed and homogenized by stirring at 90 °C for 3 h. Next, the temperature was increased to 130–140 °C, yielding a high viscous polyester resin. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. In this work, an excess of 3 wt.% bismuth oxide was added to the solution aiming to minimize the bismuth loss during the thermal treatment. The organic part is subsequently eliminated at temperatures as low as 300 °C, forming

reactive oxides with well-controlled stoichiometry. The calcination step was performed at 700 °C for 4 h.

The bismuth titanate prepared by mechanically assisted synthesis started from bismuth oxide (Bi_2O_3 , Fluka, p.a. 99.8%) and titanium oxide (TiO_2 anatase, Carlo Erba p.a. 99%), commercially available. These oxide powders exhibited a particle size distribution in the range 2–4 μm for TiO_2 and 1–5 μm for Bi_2O_3 . To make a batch required for BIT composition, corresponding amount of Bi_2O_3 and TiO_2 were weighed and loaded into zirconia jars together with zirconia milling balls ~ 10 mm in diameter. Mechanical activation (mechanochemical synthesis) was performed in air atmosphere in a planetary ball mill (Fritsch Pulverisette 5). Milling conditions were the following: ball-to-powder weight ratio was 20:1, basic disc rotation speed was 317 min^{-1} , rotation speed of disc with jars was 396 min^{-1} , milling time was from 0, 60, 120 to 360 min.

The X-ray diffraction data for BIT powders were collected using a Rigaku[®] RINT2000 diffractometer. For Rietveld analyses X-ray diffraction data were collected under the following experimental conditions: 40 kV, 30 mA, $20^\circ \leq 2\theta \leq 120^\circ$, $\Delta 2\theta = 0.02^\circ$, $\lambda\text{Cu K}\alpha$ monochromatized by a graphite crystal, divergence slit = 2 mm, reception slit = 0.6 mm, step time = 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [18,19]. The profile function used was the modified Thompson–Cox–Hasting pseudo-Voigt, in which η (the lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum.

Specific surface areas were determined based on isotherms of nitrogen adsorption using the BET method (Micrometrics ASAP 2010). The samples were prepared by pressing at 210 MPa and sintered inside a box furnace with heating rate of 5 °C/min from room temperature up to 1000 °C for 4 h using a closed system containing 3 wt.% of B_2O_3 , relative to the pellets' mass, to generate a bismuth atmosphere. The density of the pellets was determined by the water displacement method (Archimedes). A scanning electron microscope (SEM, Topcom SM-300) was used to analyze the microstructure.

The gold electrode for electrical measurements was applied to polished surface of sintered discs by evaporation through a sputtering system. Ferroelectric properties of the BIT sample were measured on a Radiant Technology RT6600A tester equipped with a micrometer probe station in a virtual ground mode.

3. Results and discussion

The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase evolution was monitored by X-ray analysis. The best condition to obtain a single bismuth titanate prepared by polymeric precursor method was evaluated on the BIT powders calcinated on several temperatures (Fig. 1a–d). The BIT powders calcinated at 700 °C for 4 h showed the main peaks related to the pure BIT

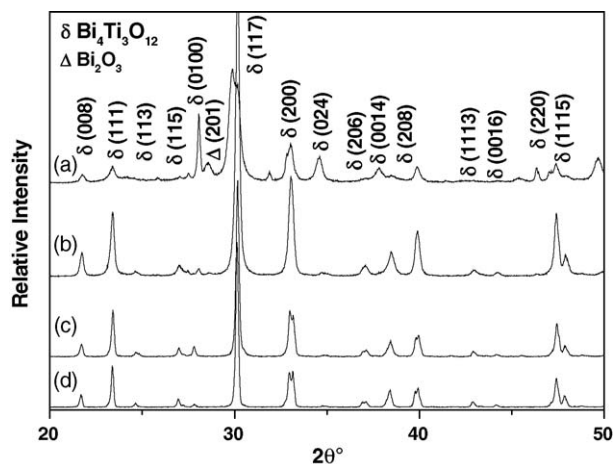


Fig. 1. X-ray data for BIT powders calculated for 4 h at: (a) 500 °C; (b) 600 °C; (c) 700 °C; and (d) 800 °C.

system indicating that the polymeric precursor method allowed obtaining a single BIT crystalline phase. The mechanically activated powders (Fig. 2) observed by XRD are referred to the mixture of Bi_2O_3 and TiO_2 , milled for various times. It was evident that before mechanical activation, sharp peaks of crystalline Bi_2O_3 and TiO_2 were observed (inset in Fig. 2), since the conventional ball milling used for homogenization did not trigger any reaction among mixed oxides. In the XRD patterns of milled powders the majority of these sharp peaks disappeared and after 60 min of milling broadened peaks at 2θ angles at around 32 and 39° were observed, which was reported previously [23,24]. It indicates that upon grinding the solid-state reaction between initial oxides starts resulting in the mechanochemical synthesis reaction. After 120 min of milling, the broadened peaks were separated in few main peaks indicating the formation orthorhombic perovskite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. The crystalline phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, formed after 120 min of milling time, possesses rather small amount of amorphous phase, which shows a small increase upon 360 min of milling.

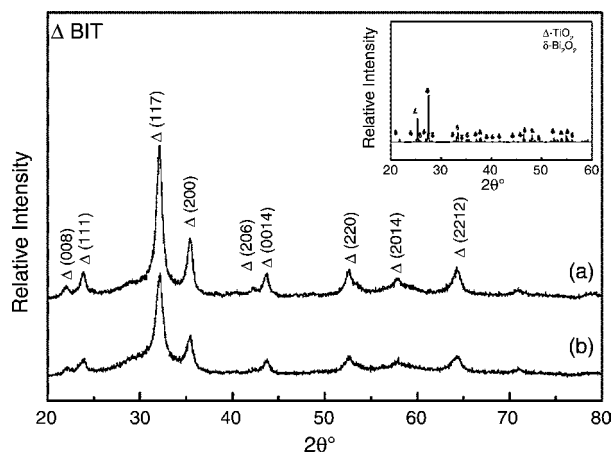


Fig. 2. X-ray data for BIT powders prepared by mechanically assisted synthesis: (a) 120 min of milling and (b) 360 min of milling; and on onset: mixture of Bi_2O_3 and TiO_2 homogenized powders.

Table 1

Rietveld calculation of lattice parameters (Å) for the BIT powder samples prepared by polymeric precursor method and mechanically assisted synthesis (milled 120 and 360 min)

Parameter	BIT	BT120	BT360
Refinement index			
R_{WP} (%)	11.12	12.57	11.78
R_{EXP}	7.06	8.00	6.60
S	1.57	1.39	1.62
Lattice parameter			
a (Å)	5.4175	5.4651	5.4782
b (Å)	5.4403	5.4452	5.4432
c (Å)	32.7862	32.5781	32.5671
V (Å ³)	966.30	971.86	973.83
D (g/cm ³)	8.02	8.01	8.00
Perovskite (mol%)	97.5 ± 0.5	98.1 ± 0.4	98.1 ± 0.3
Stoichiometry	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$	$\text{Bi}_4\text{Ti}_3\text{O}_{12}$
Refinement	$\text{Bi}_4\text{Ti}_3\text{O}_{11.6}$	$\text{Bi}_4\text{Ti}_3\text{O}_{11.8}$	$\text{Bi}_4\text{Ti}_3\text{O}_{11.7}$

The BIT system has been investigated from a fundamental point of view, regarding the crystal structures of BIT [20]. We adopted the Rietveld refinement technique to investigate the BIT crystal structure. The data collected from BIT calcinated powders (700 °C for 4 h) and that from BIT obtained by mechanical activation (2 and 6 h) were used. Table 1 illustrates the lattice parameters (a , b and c), unit cell volume (V) and refinement data. The space group obtained from the Rietveld analyses was FMM with the atomic positions belonging to the ICSD card (number 24735). The quantitative phase analysis of powders was calculated according to the reference of Young and Desai [20]. It was shown that synthesized BIT has orthorhombic structure of an Aurivillius phase Bi-layered oxide, denoted by the formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$, in which perovskite units of Ti–O octahedra are sandwiched between Bi_2O_2 layers. The difference in the crystal lattice parameters for chemically and mechanochemically prepared BIT samples is notable. Comparing to the literature data, BIT prepared by polymeric precursor method shows closer values to literature data concerning to orthorhombic structured bismuth titanate obtained by chemical precipitation method [9]. The fact that the values for crystal parameters of BIT prepared by mechanically assisted synthesis are larger than those for polymeric precursor method can be explained by closer packages of atoms in crystal lattice of BIT obtained by chemical method. Less volume of crystal lattice indicates that. Due to strains induced during milling, the distances of atoms in BIT crystal lattice are bigger resulting in a larger volume of crystal lattice [21,22].

The specific surface area of BIT powders prepared by milling process has been changing depending on whether the breaking process of particles or the secondary agglomeration process dominates or mechanically assisted synthesis occurred. When BIT becomes the dominant phase in the milling sample form, mechanically assisted process is dominant to the secondary agglomeration process. This corresponds to the increase of the value of specific surface

area, from 5.2 m²/g at the beginning of milling to 7.2 m²/g after 120 min. On the contrary, the decrease trend of specific surface area to 6.6 m²/g can be seen after milling for 360 min as a result of secondary agglomeration processes. The strong powder agglomeration of BIT prepared by mechanically assisted synthesis was confirmed by SEM analysis [24]. The individual crystallite size of approximately 30 nm of BIT powders was observed. Those results were reported previously [24]. The specific surface area of calcinated BIT powders prepared by polymeric precursor method was 7.5 m²/g. Evidently, this value is higher comparing to BIT powders prepared by high energy ball-milling process.

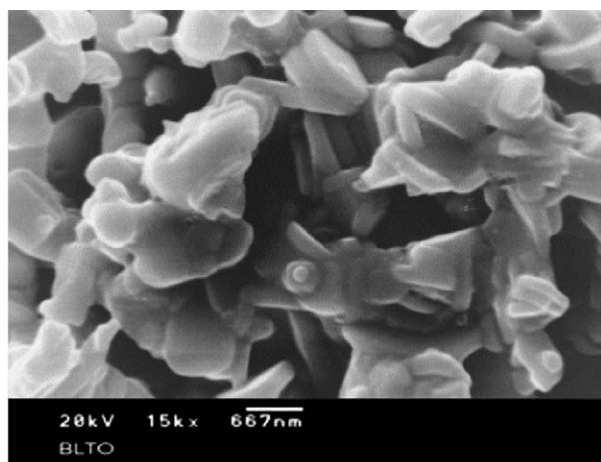
A rather significant difference in sintered densities of samples obtained by both methods was noted. The density of BIT samples obtained by polymeric precursor method was higher, at least 95% of theoretical density (TD = 8.04 g/cm³) comparing to ~90% for BIT obtained by mechanochemical process. Compared to green densities values (~60% TD for mechanically assisted synthesis and ~72% TD for polymeric precursor method), the noted difference is

assumed to be caused by strong agglomeration of milled powders [24].

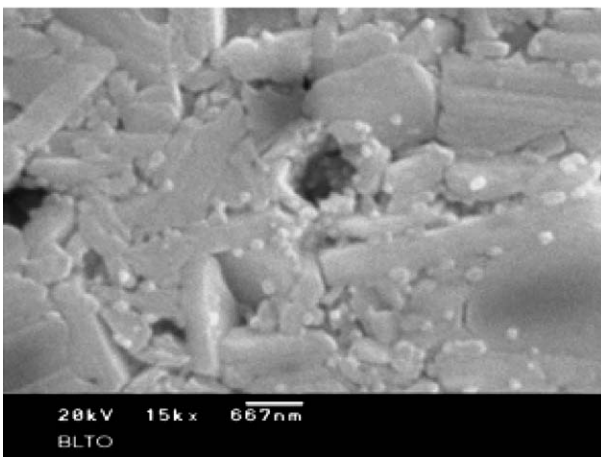
The microstructure of the Bi₄Ti₃O₁₂ ceramics prepared from BIT powders obtained by mechanical activation (120 min milling time) and by polymeric precursor method and sintered at 1000 °C for 4 h was presented in Fig. 3a–b. There is a tendency for the plate-like morphology to be more evident in the samples prepared by mechanochemically assisted synthesis. The lower density of BIT samples prepared by this method is believed to be a result of the formation of the plate-like grains as it was reported in literature [23]. BIT obtained from powders prepared by polymeric precursor method presents a mixture of plate-like grains and rod-like grains. This suggests that the powder processing has a significant influence on the structural distortion resulting in different morphology of grains.

Due to the special structure of Bi₄Ti₃O₁₂, single crystal is strongly anisotropic in all its ferroelectric properties, including saturated polarization (P_s), remnant polarization (P_r) and coercive field (E_c). The polarization direction of Bi₄Ti₃O₁₂ is 4.5° off the base plane of its cell structure, thus giving rise to a much larger in-plane polarization ($P_s = 50 \mu\text{C}/\text{cm}^2$) and E_c value for in-plane polarization is 50 kV/cm and E_c value for c -orientation is less than 5 kV/cm [23]. For randomly oriented Bi₄Ti₃O₁₂ ceramics or thin films, both remnant polarization and coercive field have values different than those as above presented. Ferroelectricity in the BIT ceramics was performed with a standardized ferroelectric tester and the results are presented in Fig. 4a and b. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 3000 kV/cm. The loops from BIT obtained by polymeric precursor method are not fully saturated with a remnant polarization of 20 $\mu\text{C}/\text{cm}^2$ and coercive field of 1500 kV/cm. The lack of saturation of the loops at these low frequencies indicates that the losses are high, suggesting the system is highly conductive. The smaller grain size of the BIT prepared by polymeric precursor method can be the reason for the difficulty in switching the domains, and therefore, the hysteresis is not saturate even at higher applied electric field. One possible explanation for high conductivity can be the presence of oxygen vacancies and dipoles complexes in the system. In order to reduce these defects a co-substitution in both A and B should be employed. Representative P – E hysteresis loop of Bi₄Ti₃O₁₂ ceramics prepared from powders obtained by mechanochemical synthesis are almost fully saturated with a remnant polarization of 0.65 $\mu\text{C}/\text{cm}^2$ and coercive field of 1050 kV/cm. The grain morphology may be the factor causing rather large coercive field. It can be assumed that the difference in the space charge density in comparison to Bi₄Ti₃O₁₂ ceramics prepared by polymeric precursor method led to less remnant polarization indicating the decrease in the system conductivity [25].

The difference in the properties of Bi₄Ti₃O₁₂ ceramics obtained by both processes can be attributed to the variation



(a)



(b)

Fig. 3. SEM micrographies for sintered BIT samples: (a) BIT obtained from mechanochemically synthesized powders milled 120 min and (b) BIT obtained from powders synthesized by polymeric precursor method.

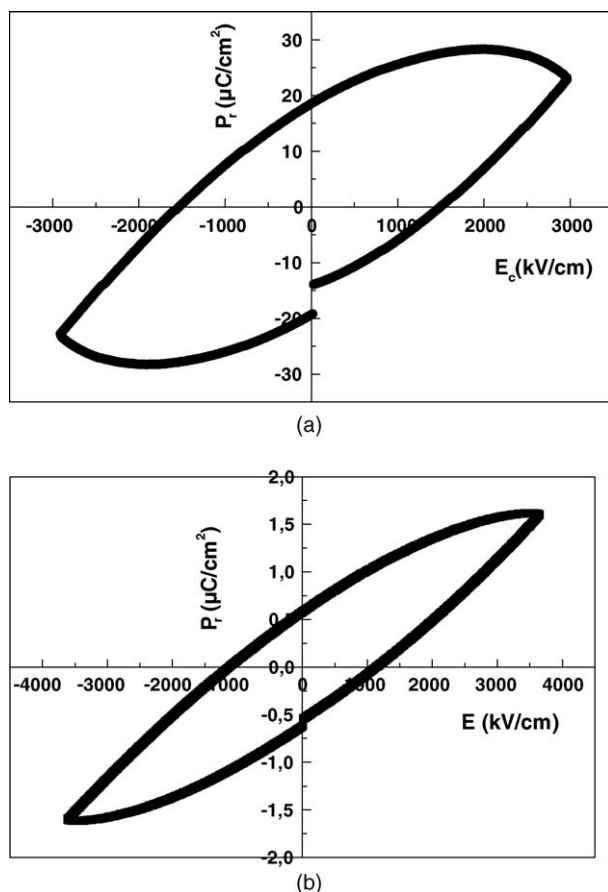


Fig. 4. Hysteresis loop for BIT: (a) obtained from powders synthesized by polymeric precursor method and (b) BIT obtained from mechanochemically synthesized powders milled 120 min.

in microstructure and grain size. The increase of grain size reduces the coupling between grain boundaries and the decrease of domain wall can be appeared as a result of more difficult reorientation and the domain wall motion. This then translates to an increase in the domain alignment, corresponding to an increase in the values of remnant polarization and in domain wall mobility [23].

4. Conclusions

Bi₄Ti₃O₁₂ ceramic has been successfully prepared from nano-sized powders obtained by both methods used: mechanochemical synthesis via a high-energy ball milling process and by chemical synthesis via polymeric precursor method. The differences in the crystal lattice parameters, specific surface area and density data for BIT prepared by both methods are caused by several reasons. The most important ones are the closer packages of atoms in Bi₄Ti₃O₁₂ crystal lattice and less powders agglomeration of powders prepared by chemical method than by mechanically assisted synthesis. BIT ceramics obtained from powders prepared by polymeric precursor method

presents a mixture of plate-like and rod-like grains comparing to plate-like structure of BIT prepared by milling process. Bi₄Ti₃O₁₂ ceramics obtained by both processes possess ferroelectric properties. The mechanochemical process has an advantage over polymeric precursor method because of using low-cost and widely available oxides as starting materials and skips the calcination step at an intermediate temperature, leading to simplified process.

Acknowledgement

The authors gratefully acknowledge to the financial support of the Brazilian financing agencies CAPES, FAPESP and CnPq and to the Ministry of Science and Environmental Protection of the Republic of Serbia.

References

- [1] S. Ikegami, I. Ueda, Piezoelectricity in ceramics of ferroelectric bismuth compound with layer structure, *Jpn. J. Appl. Phys.* 13 (1974) 1572–1577.
- [2] T. Takenaka, K. Sakata, Grain orientation effects on electrical properties of bismuth layer-structured ferroelectric solid solution, ceramics of ferroelectric bismuth compound with layer structure, *Jpn. J. Appl. Phys.* 5513 (1984) 1092–1099.
- [3] J.F. Dorrian, R.E. Newnham, D.K. Smith, M.I. Kay, Crystal structure of Bi₄Ti₃O₁₂, *Ferroelectrics* 3 (1971) 17–27.
- [4] B. Aurivillius, Mixed oxides with layer lattice, *Arkiv. Kemi.* 1 (1949) 499–512.
- [5] Q. Zhou, B.J. Kennedy, Structural studies of the ferroelectric phase transition in Bi₄Ti₃O₁₂, *Chem. Mater.* (2003) 5025–5028.
- [6] S.E. Cummings, L.E. Cross, Electrical and optical properties of ferroelectric Bi₄Ti₃O₁₂ single crystal, *J. Appl. Phys.* 39 (5) (1968) 2268–2274.
- [7] S. Kojima, A. Hushur, F. Jiang, S. Hamazaki, T. Takashige, M.S. Jang, S. Shimada, Crystallization of amorphous bismuth titanate, *J. Non-Cryst. Solids* 293–295 (2001) 250–254.
- [8] M. Villegas, A.C. Caballero, C. Moure, P. Duran, J.F. Fernandez, Factors affecting the electrical conductivity of donor-doped Bi₄Ti₃O₁₂ piezoelectric ceramics, *J. Am. Ceram. Soc.* 82 (9) (1999) 2411–2416.
- [9] P. Pookmanee, P. Boonphayak, S. Phanichphant, Chemical synthesis of bismuth titanate microparticles, *Ceram. Int.* (2004) 123–129.
- [10] A.V.P. Rao, A.I. Robin, S. Kommarneni, Bismuth titanate from nanocomposite by sol–gel technique, *J. Crystal Growth* 237–239 (2002) 469–473.
- [11] S.H. Ng, J. Xue, J. Wang, Bismuth titanate activation of a chemically coprecipitated precursor, *J. Am. Ceram. Soc.* 85 (11) (2002) 2660–2665.
- [12] Y. Osamu, M. Noboru, H. Ken, The formation and characterization of alkoxy-derived Bi₄Ti₃O₁₂, *Br. Ceram. Trans. J.* 90 (1991) 111–113.
- [13] H. Xu, K.J. Bowman, E.B. Slamovich, Hydrothermal Synthesis of bismuth titanate powders, *J. Am. Ceram. Soc.* 86 (10) (2003) 1815–1817.
- [14] S. Goplan, K. Mehta, V. Virkar, Synthesis of oxide perovskite solid using the molten salt method, *J. Mater. Res.* 11 (8) (1996) 1863–1865.
- [15] T. Thongtem, S. Thongtem, Characterization of Bi₄Ti₃O₁₂ powder prepared by the citrate and oxalate coprecipitation processes, *Ceram. Int.*, in press.
- [16] J.S. Benjamin, Mechanical alloying, *Sci. Am.* 234 (1976) 40–48.

- [17] J. Wang, J.M. Xue, D.M. Wan, B.K. Gan, Mechanically activating nucleation and growth of complex perovskites, *J. Solid-State Chem.* 154 (2000) 321–328.
- [18] J. Ricote, L. Pardo, A. Castro, P. Millan, Study of the process of mechanochemical activation to obtain Aurivillius oxides with $n = 1$, *J. Solid-State Chem.* 160 (2001) 1054–1061.
- [19] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, *J. Appl. Crystallogr.* 2 (1969) 65–71.
- [20] R.A. Young, P. Desai, Crystallite size and microstrain indicators in Rietveld refinement, *Archiwum Nauki o Materialach (Archives of Materials Science) Moskva*, 10 (1989) 71–90.
- [21] L.W. Finger, L.W. Cox, D.E. Jephcoat, A Correction for powder diffraction peak asymmetry due to axial divergence, *J. Appl. Crystallogr.* 27 (1994) 892–900.
- [22] P.W. Stephens, *J. Appl. Crystallogr.* 32 (1999) 281–289.
- [23] L.B. Kong, J. Ma, W. Zhu, O.K. Tan, Preparation of $\text{Bi}_4\text{T}_3\text{O}_{12}$ via a high-energy ball milling process, *Mater. Lett.* 51 (2001) 108–114.
- [24] B.D. Stojanovic, C.O. Paiva Santos, C. Jovalekic, A.Z. Simoes, Z. Lazarevic, M.H. Filho, J. Varela, Mechanically activating formation of layered structured bismuth titanate, *Chem. Phys. Mater.*, in press.
- [25] S. Luo, Y. Noguchia, M. Miyayama, T. Kudo, *Mater. Res. Bull.* 36 (2001) 531.

Synthesis and electrical characterization of tungsten doped $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ ceramics obtained from a hybrid process

D.M. Santos^a, A.Z. Simões^{b,*}, M.A. Zaghete^b,
C.O. Paiva-Santos^b, J.A. Varela^b, E. Longo^b

^a Universidade Federal do Maranhão (UFMA), São Luís, MA, Brazil

^b Instituto de Química, UNESP, Rua Prof. Francisco Degni s/n, Araraquara, SP, Brazil

Received 30 November 2005; received in revised form 28 August 2006; accepted 18 February 2007

Abstract

Pure and W-doped PZT ceramics (PZT and PZTW) were prepared by a hybrid process consisting in the association of polymeric precursor and partial oxalate methods. The phase formation was investigated by simultaneous thermal analysis (TG/DSC) and X-ray diffraction (XRD). The effect of W doping PZT and their electrical properties was evaluated. Substitution of W by Ti leads to an increase of Curie temperature and broadening of dielectric constant. A typical hysteresis loop was observed at room temperature and the remnant polarization was increased with the content of W.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Sintering; Dielectric properties; Ferroelectricity

1. Introduction

Lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) has the perovskite type structure (general formula ABO_3) with great interest owing to their ferroelectric, piezoelectric and other electrical properties [1,2]. A special attention is given to a compound with $x \sim 0.52$, which corresponds to the morphotropic phase boundary composition (MPB) between Ti-rich tetragonal and Zr-rich rhombohedral phases. The effect of doping on various physical and chemical properties of this material is known, and this effect has been extensively exploited in piezoelectrics and ferroelectrics to improve their performance. Many aliovalent compositional alterations to PZT have been studied either with higher valence substitutions (donors), or with lower valence ions (acceptors). In the case of niobium doping PZT materials, some recent works deal with several improvements: an increase in the electrical resistivity and an enhancement of hysteresis squareness and fatigue behavior [3]. Nielsen et al. [4] using $\text{PbO}-\text{WO}_3$ as additive showed that the excess of PbO may suppress the lead oxide vaporization from the PZT matrix resulting in fewer vacancies. Replacing Zr^{4+} and Ti^{4+} by W^{6+} is so-called donor

doping, which normally results in cation vacancies leading to soft properties.

Usually, the PZT phase is processed by the solid-state reaction among the constituent oxides PbO , ZrO_2 and TiO_2 [5–8]. However, due to intermediate reactions that lead to formation of PbTiO_3 (PT) and PbZrO_3 (PZ) the PZT formed by this method is heterogeneous in composition, containing compositional fluctuations, which modify several electrical properties [6,9].

The effect of doping on piezoelectric properties has been extensively exploited. Donor dopant such as W^{6+} induces cationic defects while occupying the B site [10,11] of the perovskite lattice. Such behavior may cause several effects on the polarization behavior through interaction with domain walls [12,13].

Alternatively, chemical routes to prepare PZT have attracted much attentions; these include the metal alkoxides hydrolysis, the polymeric precursor method derived from the Pechini Method [14,15], and the co-precipitation of metal hydroxides and oxalates [16]. The chemical route allows the preparation of fine and homogeneous oxide powders with better reactivity and sinterability.

In this work, pure and doped PZT ceramics were prepared by the association of partial oxalate and polymeric precursor methods as proposed by Yamamoto [17]. The

* Corresponding author.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

influence of tungsten on ferroelectric and dielectric properties of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47-y}\text{W}_y)\text{O}_3$ ceramics was evaluated.

2. Experimental procedure

The $\text{Zr}_{0.53}\text{Ti}_{0.47-y}\text{W}_y\text{O}_4$ (ZTW) ($y = 0, 2$ and $8 \text{ mol\%}$) was obtained by the polymeric precursor method [15]. After that, ZTW powders were diluted in oxalic acid aqueous solution. A stoichiometry amount of lead nitrate was dissolved in this solution followed by NH_4OH addition until the pH reached the value of 12. The precipitate was washed, filtered and dried at 90°C in oven. The resulting powder ($\text{ZT2W} + \text{PbC}_2\text{O}_4$) was desagglomerated by grinding and used as precursor to obtain $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47-y}\text{W}_y)\text{O}_3$ PZTW ($y = 0, 2$ and $8 \text{ mol\%}$) by the partial oxalate method. Here, the desired effect of desagglomeration is to avoid particle coarsening. After that, the material was calcined at 800°C for 3 h and characterized by X-ray diffraction using a rotate anode powder diffractometer (Rigaku Rint 2000) with $\text{Cu K}\alpha$ radiation over the 20 – 70° (2θ) range. The diffraction patterns have been analyzed by Rietveld method using GSAS program [18].

Lead oxalate and ZT2W reaction was followed by simultaneous thermal analysis, TG/DSC (Netsch-Termische Analyze-controller TASC 414/2). A heating rate of 5°C min^{-1} was used with air atmosphere from room temperature to 800°C .

The powders were pressed into a disk shape under 200 MPa and the size of the compacts was 10 mm in diameter and 2 mm in thickness. The disks were sintered isothermally with a heating rate of 5°C min^{-1} at 1130°C for 3 h. A PbO rich atmosphere was maintained to minimize lead loss during sintering. After sintering the disks were polished to 1 mm in thickness and characterized by means of electrical measurements. Silver contacts were deposited on the samples parallel surfaces and heated at 500°C for 15 min to burn out the solvent.

The dielectric permittivity and tangent loss as a function of temperature and frequency were measured by a HP 4194 A LCR Meter. The P – E hysteresis loop was determined with equipment Radiant Technology RT 6000A-ferroelectrics test system by applying a maximum field of 4 kV mm^{-1} at 50 Hz.

3. Results and discussion

Fig. 1 shows the TG/DSC curves of the oxalate precipitate on the ZT2W particles ($\text{ZT2W} + \text{PbC}_2\text{O}_4$). A continuous weight loss at 300 – 360°C was illustrated in TG curve and can be ascribed to the decomposition of the oxalate. In the DSC curve, three peaks were evident. A small endothermic one at 120°C associated with the dehydration of the sample. An exothermic peak at 340°C associated with the oxalate decomposition and

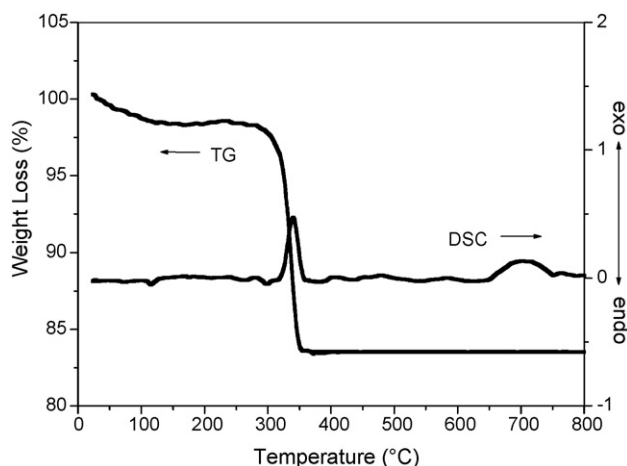


Fig. 1. TG/DSC curves of ZT2W + PbC_2O_4 with a heating rate of 5°C min^{-1} .

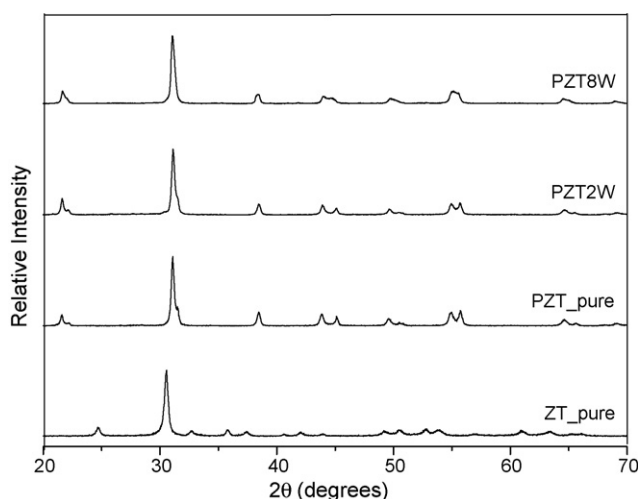


Fig. 2. X-ray diffraction for ZT, PZT, PZT2W and PZT8W powders calcined at 800°C for 3 h.

release of CO and CO_2 . Finally, a larger exothermic peak at 700°C can be attributed to the crystallization of PZT phase. No correspondent weight loss associated with the crystallization of the main phase was observed in the TG curve.

X ray diffraction of ZT, PZT and W-doped PZT were observed in Fig. 2. No secondary phases were evident indicating that our method allows to obtain powders with a good stoichiometry control [19]. All diffraction peaks of pure PZT were indexed to the tetragonal system while for the W-doped PZT were indexed to the tetragonal and rhombohedral systems.

Rietveld refinements [23] were performed for pure and doped PZT samples. The refinement was done assuming that the space groups are $P4mm$ (tetragonal) and $R3c$ (rhombohedral), respectively. Table 1 summarizes the refinement results, including unit cell parameters, tetragonality factor (c/a), angle α , reliability refinement indexes R (defined by Young [20]). The tetragonality factor (c/a) was found to decrease with W content due to the decrease of dipole momentum and, consequently, to the reduction of T_c . Also, the increase of the tetragonal unit cell volume suggests an increase in the BO_6 octahedron volume. The reduction of the packing density causes an instability in the octahedron. This explains the reduction of Curie temperature with the increase of donor dopant.

The temperature dependence of dielectric permittivity was investigated for several compositions. Plots of dielectric constant measured at 1 MHz are shown in Fig. 3. The dielectric permittivity gradually increases with an increase in temperature up to the transition temperature (T_c), Curie point, and then decreases. The maximum permittivity increases and T_c decreases with the tungsten content. The broaden around the dielectric peak is due to a disorder in the cations arrangement in one or more crystallographic sites of the structure [11,21]. Large differences in the B valence creates a disorder in the material in one or more crystallographic sites of the structure leading to a microscopic heterogeneity in the compounds with different Curie points [21]. According to Wu et al. [22], the dielectric permittivity consists of contributions of ionic and atomic polarization only. Since the ionic radius of W^{6+} is smaller

Table 1

Lattice parameters (a , b and c), unit cell volume (V) and refinement indexes for the PZT, PZT2W and PZT8W powders calcined at 800 °C for 3 h

Sample	$\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$	$\text{PbZr}_{0.53}\text{Ti}_{0.45}\text{W}_{0.02}\text{O}_3$	$\text{PbZr}_{0.53}\text{Ti}_{0.39}\text{W}_{0.08}\text{O}_3$
Space group	$P4mm$	$P4mm$	$R3c$
Unit cell parameters (Å)	$a = 4.0353$ $c = 4.1429$	$a = 4.0366$ $c = 4.1373$	$a = 5.7626$ $c = 14.201$
c/a (tetr.)	1.0267	1.0249	–
α (Romb.)	–	–	89.76
Cell volume (Å ³)	67.462	67.416	408.416
R_{wp} (%)	14.45	10.91	10.55
R_F^2 (%)	4.36	4.18	5.58
Goodness of fit	1.50	1.48	1.67

than that of Ti^{4+} , increasing the W^{6+} amount would lead to a reduced contribution of overall atomic polarization. Therefore, the increase of dielectric permittivity may be attributed to an increase of ionic polarization. The incorporation of tungsten ions into PZT structure would introduce some cationic vacancies to maintain the electroneutrality. These cationic vacancies also influence the dielectric permittivity. Further, increasing the tungsten content also resulted in a reduced Curie point, which implied decreased stability of perovskite structure. Jin et al. [23], proposed that the phase transition of PBO_3 materials is caused by instability of the BO_6 octahedra. The relatively larger ionic radius of the B ion enhances the thermal stability of the BO_6 octahedra, when compared to Ti or Zr. The packing density of the BO_6 octahedra will be determined by the B ion size. Larger B ions give more closely packed octahedral, which are, therefore, more stable. This probably explains why the Curie temperature decreased in the following order $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$; $\text{PbZr}_{0.53}\text{Ti}_{0.45}\text{W}_{0.02}\text{O}_3$ and $\text{PbZr}_{0.53}\text{Ti}_{0.39}\text{W}_{0.08}\text{O}_3$. Therefore, the addition of W can influence in two ways: (1) acting by repulsion with their next nearest neighbors [24]. This results in an increase of a and reduction of c parameters of tetragonal phase. As a consequence, the BO_6 volume octahedron increases and consequently decreasing its stability resulting in a reduction of T_c . (2) Due to a smaller ionic radius than Ti causes an

increase of the rhombohedral phase (26–60 wt%) and reduction in the rhombohedral unit cell, promoting the instability of the oxygen octahedral that involve the B cation, leading to a T_c reduction.

Fig. 4 shows the temperature dependence of tangent loss determined at 1 MHz for several compositions. For pure PZT a high tangent loss is observed at elevated temperatures. For PZT8W, a small peak just below the Curie temperature was observed while for the PZT2W the tangent loss is almost temperature independent, although it also presents a very small peak just below T_c . At lower temperatures, a small temperature dependence of tangent loss was observed while at elevated temperatures, tungsten doping stabilizes the temperature dependence of tangent loss. The possible Pb^{2+} vacancies formation may result in a reduced tangent loss at elevated temperatures, similar to La^{3+} doped PZT ceramics [25]. This reflects that good insulation resistance was maintained at high temperatures, which is important for high temperature piezoelectric applications.

Typical hysteresis loops of pure and doped PZT are shown in Fig. 5. All loops present squarer shapes which are characteristic for materials employed in ferroelectric memories [25]. With increasing W content, the remnant polarization increased from 13, 28 and 47 $\mu\text{C cm}^{-2}$, respectively. Tungsten addition favors the formation of lead vacancies (V_{Pb}) which decreases the stress within the domains [26]. The coercive field (E_c) increases slightly from 9, 11.2 and 11.8 kV cm^{-1} , respectively. W-doped

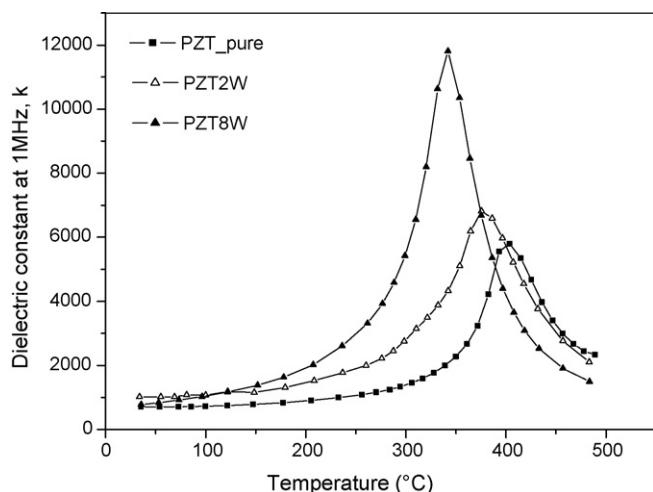


Fig. 3. Temperature dependence of dielectric permittivity at 1 MHz for PZT, PZT2W and PZT8W ceramics sintered at 1130 °C for 3 h.

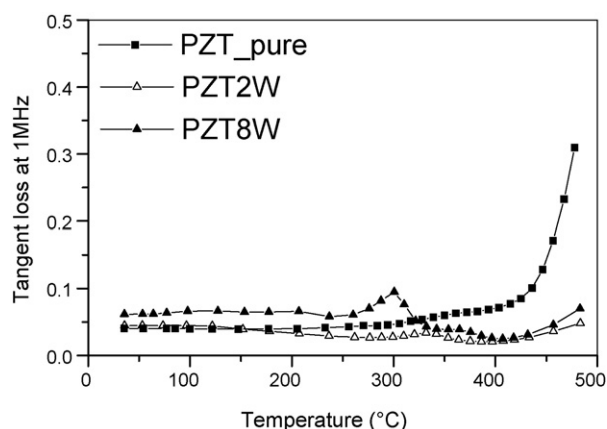


Fig. 4. Temperature dependence of tangent loss at 1 MHz for PZT, PZT2W and PZT8W ceramics sintered at 1130 °C for 3 h.

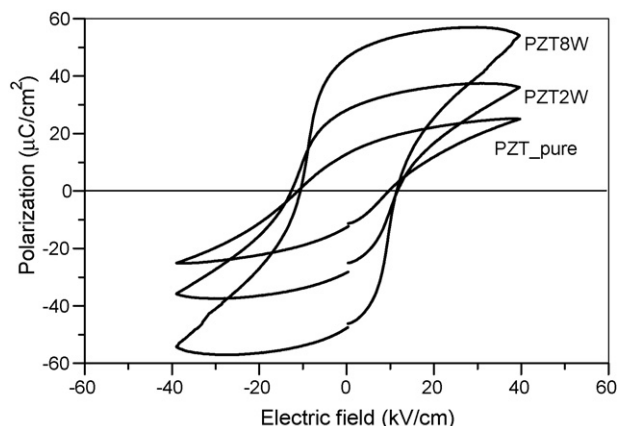


Fig. 5. P - E hysteresis loops for PZT, PZT2W and PZT8W ceramics sintered at 1130 °C for 3 h.

PZT ceramics have a high remnant polarization and therefore can be reported as “soft materials” [11,27]. No “imprint” phenomenon was evident in the present hysteresis loops indicating that our capacitors are free of defects as oxygen vacancies which pinning the domain walls and makes the saturation of the hystereses difficult to accomplish. Consequently, there is no increase in the coercive voltage in one direction.

4. Conclusions

Pure and tungsten doped PZT were prepared by a hybrid process with properties comparable to that obtained through other methods. Rietveld refinement reveals the existence of only one tetragonal phase for pure PZT and the coexistence of both tetragonal and rhombohedral phases for the tungsten doped PZT samples. The addition of tungsten increases the maximum dielectric permittivity and decreases the Curie temperature. The remnant polarization was increased with the W content due the formation of lead vacancies which compensates the charges in the net. Because the PZTW systems have a high remnant polarization and square shape, they can be reported as “soft materials”. Thus, the W-doped PZT compositions can be used for device applications around the room temperature range.

References

- [1] B. Jaffe, W. Cook, H. Jaffe, *Piezoelectric Ceramics*, Academic Press, London, 1971.
- [2] K. Okazaki, *Ferroelectrics* 41 (1982) 77.
- [3] M. Pereira, A.G. Peixoto, M.J.M. Gomes, *J. Eur. Ceram. Soc.* 21 (2001) 1353.
- [4] E.R. Nielsen, E. Ringgaard, M. Kosec, *J. Eur. Ceram. Soc.* 22 (2002) 1847.
- [5] D.L. Hankey, J.V. Biggers, *J. Am. Ceram. Soc.* 64 (1981) C-172.
- [6] K. Kakegawa, J. Mohri, S. Shirasaki, K. Takahashi, *J. Am. Ceram. Soc.* 65 (1982) 515.
- [7] R.R. Krishnan, P.B. Ramakrishnan, *Ceram. Trans. J.* 87 (1988) 99.
- [8] T.R. Shrout, P. Papet, S. Kim, G.S. Lee, *J. Am. Ceram. Soc.* 73 (1990) 1862.
- [9] S.S. Chandatreyia, R.M. Fulrath, J.A. Pask, *J. Am. Ceram. Soc.* 64 (1981) 422.
- [10] A. Carg, T.C. Goel, *Mater. Sci. Eng. B60* (1999) 128.
- [11] R. Shannigrahi, R.N.P. Choudhary, N. Acharya, *Mater. Sci. Eng. B56* (1999) 31.
- [12] D. Bolten, U. Bouger, T. Schneller, M. Grossnam, O. Lose, R. Waser, *Appl. Phys. Lett.* 77 (2000) 3830.
- [13] S. Takahashi, *Ferroelectrics* 41 (1982) 143.
- [14] M.A. Zaghet, C.O. Paiva-Santos, J.A. Varela, E. Longo, Y.P. Mascarenhas, *J. Am. Ceram. Soc.* 75 (1992) 2088.
- [15] M.P. Pechini, U.S. Patent 3,330,667, July 11, 1967.
- [16] J. Choy, Y. Han, S. Kim, *J. Mater. Chem.* 7 (1997) 1807.
- [17] T. Yamamoto, *Am. Ceram. Soc. Bull.* 71 (1992) 978.
- [18] A.C. Larson, R.B. Von Dreele, *GSAS—General Structure Analysis System*, Los Alamos National Laboratory, EUA, 2001, p. 233.
- [19] M. Cerqueira, R.S. Nasar, E.R. Leite, E. Longo, J.A. Varela, *Mater. Lett.* 22 (1995) 181.
- [20] M.E. Lines, A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials*, Oxford University Press, Oxford, 1977.
- [21] Y. Wu, S.J. Limmer, T.P. Chou, C. Nguyen, C. Guozhong, *J. Mater. Sci. Lett.* 21 (2002) 947.
- [22] D. Jin, P. Hing, C.Q. Sun, *J. Phys. D: Appl. Phys.* 33 (2000) 744.
- [23] R.A. Young, in: R.A. Young (Ed.), *IUCr Monographs on Crystallography* 5, Oxford University Press, Oxford, 1993.
- [24] J. Frantti, S. Ivanov, S. Eriksson, H. Rundlof, V. Lantto, J. Lappalainen, M. Kakihana, *Phys. Rev. B* 66 (2002) 1.
- [25] Y.H. Xu, *Ferroelectric Materials and Their Applications*, Elsevier Science Publishers, Amsterdam, 1991.
- [26] A.J. Moulson, J.M. Herbet, *Electroceramics: Materials Properties Applications*, Chapman & Hall, London, 1990.
- [27] L. Wu, C. Wei, T. Wu, H. Liu, *J. Phys. C: Solid State Phys.* 16 (1983) 2803.



Review

Lanthanum doped BiFeO₃ powders: Syntheses and characterizationF. Gonzalez Garcia^a, C.S. Riccardi^{b,1}, A.Z. Simões^{a,*}^a Universidade Federal de Itajubá - Unifei - Campus Itabira, Rua São Paulo, 377, Bairro Amazonas - Itabira-MG, CEP 35900-373, Brazil^b Laboratório Interdisciplinar em Cerâmica, Departamento de Físico-Química, Instituto de Química Universidade Estadual Paulista, Bairro: Quitandinha, CEP: 14800-900, Araraquara, SP, Brazil

ARTICLE INFO

Article history:

Received 17 February 2009

Received in revised form 6 April 2010

Accepted 10 April 2010

Available online 18 April 2010

Keywords:

Ferroelectrics

Chemical syntheses

Powder metallurgy

X-ray diffraction

ABSTRACT

A soft chemistry route was employed to fabricate single-phase lanthanum modified BiFeO₃ (BFO) powders. Effects of lanthanum concentration on the phase formation, grain size and morphologies of BFO powders were systematically investigated. X-ray diffraction results indicated that perovskite phase have been synthesized at the temperature of 850 °C/2 h while infrared data indicates no traces of carbonate. Raman analysis reveals that lanthanum atom substitutes bismuth into the BFO site. A homogeneous size distribution of BFO powders was evidenced by scanning electron microscopy.

© 2010 Elsevier B.V. All rights reserved.

Contents

1. Introduction	25
2. Experimental procedure	26
3. Results and discussion	26
4. Conclusions	28
Acknowledgments	28
References	28

1. Introduction

Perovskite and related compounds are widely investigated because of their multiferroic, photocatalytic, and magnetic properties which are useful for applications in thin-film capacitor, nonvolatile memory, nonlinear optics, and photoelectrochemical cell [1–4]. Most perovskite phases are prepared by solid-state reactions between the corresponding oxides at temperature above 1000 °C. Recently, solution based methods have been widely developed for various perovskite nanomaterials synthesis [5]. Bismuth ferrite, one of the very few multiferroics with a simultaneous coexistence of ferroelectric and antiferromagnetic order parameters in perovskite structure, has attracted much attention for many decades since 1960. BiFeO₃ (BFO) has a ferroelectric Curie temperature T_c of 850 °C and an antiferromagnetic Neel temperature

of 370 °C [6,7]. However, potential applications of BFO in the memory devices, sensors, satellite communications, optical filters and smart devices were greatly limited due to its low insulation resistance caused by the reduction of Fe³⁺ species to Fe²⁺ and oxygen vacancies for charge compensation [8,9]. Although great achievements have been made for BFO thin films prepared by the pulsed-laser deposition (PLD) method [10,11], it was hard to avoid generating impurity phases by the conventional solid-state reaction in bulk materials. BFO perovskites could only stabilize within a narrow ranged temperature. Up to date, the synthesis of single-phase BFO ceramics is still a challenging issue. In the solid-state route, nitric acid leaching was required to eliminate the impurity phases, such as Bi₂Fe₄O₉ and Bi₂₅FeO₄₀, after calcination of mixed bismuth and iron oxides [12], which resulted in coarser powders and the poor reproducibility. Most recently, Wang et al. [8] and Pradhan et al. [13] prepared pure BFO phase ceramics by a rapid liquid-phase sintering technique. The crystallization temperature of BFO in these methods was required above the ferroelectric Curie temperature T_c , which implied that the volatilization

* Corresponding author. Tel.: +55 31 3834 6472/6136.

E-mail address: alezipo@yahoo.com (A.Z. Simões).¹ Tel.: +55 16 3301 6643; fax: +55 16 3301 6692.

of bismuth was hard to avoid. Moreover, Ghosh et al. [14] made pure phase bismuth ferrite nanopowders by the tartaric acid based sol-gel method coupled with the additional calcination process. Accordingly, it is interesting to synthesize and investigate single-phase BFO-based solid solution with no other ferroelectric end member. Up to now, two main methods are reported to prepare single-phase BFO ceramics; one involves rapid liquid-phase sintering and the other leaching of the impurity phase with dilute nitric acid. These methods lead to ceramics with high leakage current, which is the main obstacle for its practical applications. So, an alternative method for preparing high quality BFO ceramics is desired. Few works have been done to prepare BFO powders by using the soft chemistry method. The advantage of soft chemical routes was that microcrystallines could be synthesized at a much lower temperature, and also energy saving and cost effective. Previous work demonstrated that lanthanum substitution reduces the strain behavior of BFO films. From leakage current density values we noted that La^{3+} substitution for Bi^{3+} is an effective way to reduce bismuth vacancies that are accompanied by oxygen vacancies decreasing the film conductivity [15]. Cheng et al. [16] have obtained $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ceramics with $x=0, 0.1, 0.2$, and 0.3 by solid-state reaction, starting from metal oxides. Below 10% La doping, $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ maintains the rhombohedral structure of BiFeO_3 . However, for $\text{Bi}_{0.8}\text{La}_{0.2}\text{FeO}_3$ and $\text{Bi}_{0.7}\text{La}_{0.3}\text{FeO}_3$, the structures change to the orthorhombic and tetragonal, respectively. The authors have observed that La doping significantly reduces electric leakage, enhances the ferromagnetic moment due to the broken cycloid spin structure caused by the changes in the crystalline structure. In other work, [17] Augustin et al. have obtained single-phase perovskite structure of La^{3+} substituted nanocrystalline strontium ferrite prepared by citrate combustion method using metal nitrate salts as cation precursors and citric acid as a fuel. A phase transition from cubic to orthorhombic has been observed with increasing La^{3+} substitution. In view of the fact that recently, more and more efforts have been undertaken to develop nontoxic lead-free piezoelectric materials, we report in this work the syntheses and characterization of La-doped bismuth ferrite powders prepared from chemical method. The main advance of this paper is to report the efficiency of chemical solution to obtain single-phase lanthanum modified bismuth ferrite powders. Comments were addressed to changes on crystal structure and morphology of the grains.

2. Experimental procedure

The procedure of $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ (BFO) synthesis, based on the polymeric precursor method, also called Pechini method [18], starts from the fact that certain α -hydroxycarboxylic organic acids can form polybasic, acid chelates with a wide range of cations. After addition of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneous cation distribution. Iron (III) nitrate nonahydrate, 99.5% purity (Merck) and bismuth nitrate, 99.5% purity (Aldrich) were used as raw materials. The bismuth and iron precursor solutions were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of Fe and Bi solutions were mixed and homogenized by stirring at 90°C . $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ powders with $x=0, 0.08, 0.15$ and 0.30 were prepared from the metal citrate complex polyesterified with ethylene glycol. The molar ratio of metal/citric acid/ethylene glycol was $1/4/16$. In this work, an excess of 5 wt% Bi was added to the solution aiming at compensating some unavoidable bismuth oxide loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Most of the organic matter is subsequently eliminated at temperatures as low as 300°C , forming a dark residue containing reactive oxides with well-controlled stoichiometry. The formed porous product was crushed and heated in an alumina crucible at 850°C for 2 h to eliminate residues of organic material. The resulting powder was milled in attritor with zirconia balls in an acetone medium for 40 min using a procedure according to the literature [19].

Phase analysis was monitored using an X-ray diffractometer (XRD, Model D500, Siemens). Infrared spectroscopy (Model 400-IR/FT, IMPACT) was used to indicate the presence of carbonates in bismuth ferrite powders. The FT-Raman analyses were done in a FRS/100/S Bruker spectrometer, using a Nd:YAG laser. XANES spectra were collected at the Bi and Fe K-edges being measured with a Si (2 2 0) monochromator

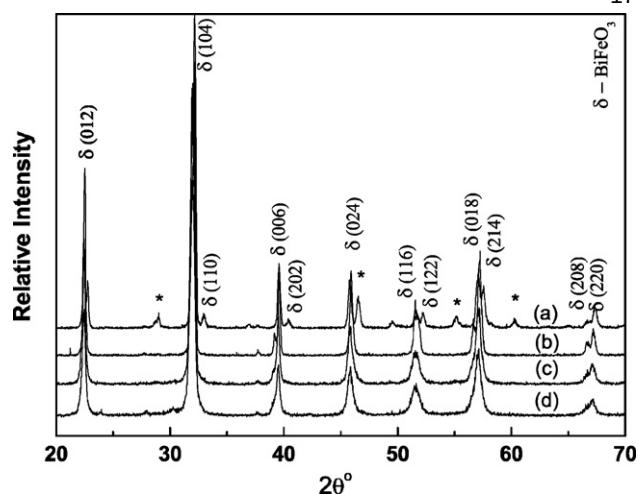


Fig. 1. X-ray data for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ powders calcinated at 850°C for 2 h as a function of lanthanum content: (a) $x=0$; (b) $x=0.08$; (c) $x=0.15$ and (d) $x=0.30$.

in the D04B-XAFS1 beam line at the Brazilian Synchrotron Light Laboratory (LNLS). Data were collected at room temperature using energy steps of 2 eV and an integration time of 3 s. A scanning electron microscopy (SEM, Model SM-300, Topcon) was used to study their particle size and powder morphology.

3. Results and discussion

Crystallinity of lanthanum modified BFO powders calcinated at 850°C for 2 h was studied by XRD analyses (Fig. 1). Upon La substitution at the Bi site, powders free of secondary phases were noted indicating the formation of solid solution. Also, as the lanthanum content increases, fewer peaks are observed in the pattern. This behavior can be ascribed to change of crystal structure as already discussed in Ref. [20]. XRD data reveal that BiFeO_3 was obtained by the soft chemistry method with rhombohedral distorted perovskite structure. The La-modified BiFeO_3 powders were also fitted. One feature that should be noted is that with increasing La composition, the intensity of some diffraction peaks, becomes weak and tends to disappear, whereas some others tend to appear near $x=0.30$. The XRD pattern is becoming close to those of orthorhombic structure. This result obviously indicates a structural phase transition near $x=0.30$, which is consistent with other reports [21,22] but different from those on epitaxial films [23]. This is reasonable since in the thin-film form, not only La substitution but also the in-plane stress has effects on structure [24,25]. The presence of $\text{Bi}_{24}\text{Fe}_{20}\text{O}_{29}$ as minor phases (marked with *) is presented in the BFO compound as a low-level impurity phase.

Infrared spectra of powders were recorded (Fig. 2). Typical band characteristics of oxygen-metal bonds were observed in the $450\text{--}640\text{ cm}^{-1}$ region. Independently of lanthanum content the samples are free of carbonates. This result is satisfactory from a technological point of view since many properties are dependent on the purity of the raw powders, especially carbonate traces. That can results in porous ceramics due to CO_2 elimination. The O-H bond stretching near 3400 cm^{-1} could be attributed to adsorbed water due to the contact of the sample with the environment.

Raman spectra are illustrated in Fig. 3. The presence of Raman-active modes can be used to evaluate the structural order degree at short-range. The modes located at 212, 316, 377, 445, 537 and 635 cm^{-1} are caused by internal vibration of FeO_6 octahedra, whereas below 200 cm^{-1} must be addressed to different sites occupied by bismuth within the perovskite units. The bands located at 97, 120 and 145 cm^{-1} are related to Bi atoms of perovskite layer and corresponds to a rigid layer. The Raman spectrum of the BLFO sam-

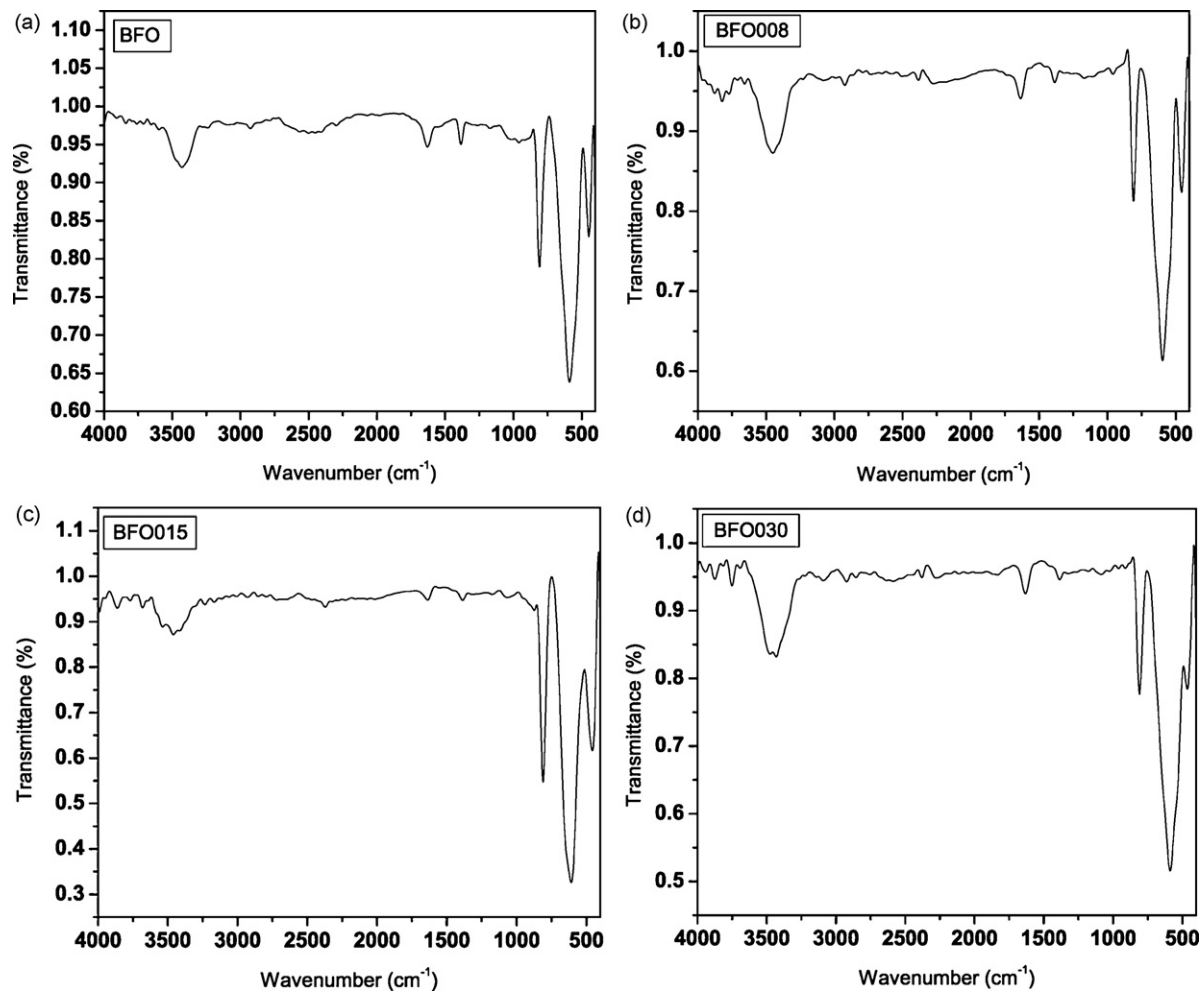


Fig. 2. Infrared data for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ powders calcinated at 850°C for 2 h as a function of lanthanum content: (a) $x=0$; (b) $x=0.08$; (c) $x=0.15$ and (d) $x=0.30$.

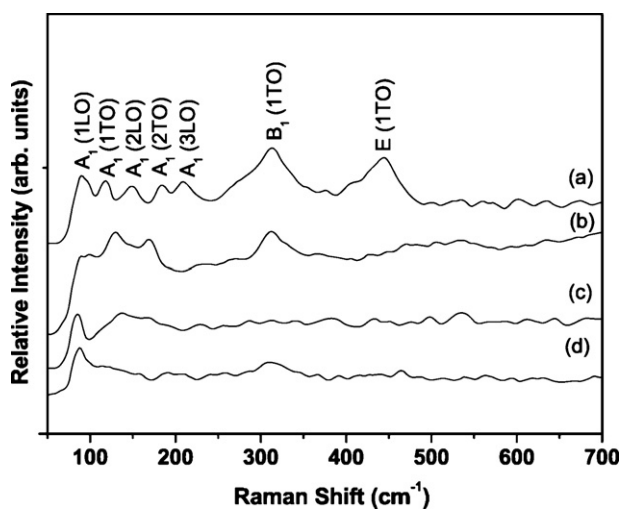


Fig. 3. Raman spectra for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ powders calcinated at 850°C for 2 h as a function of lanthanum content: (a) $x=0$; (b) $x=0.08$; (c) $x=0.15$ and (d) $x=0.30$.

ples (Fig. 3(b and c)) showed the same BFO bands, but its intensity showed a decrease accompanied by a slight shift to a higher range of energy frequencies. These bands are located at 118 and 147 cm^{-1} for the BFO and 127 and 168 cm^{-1} for the BLFO. These displacements indicate that the lanthanum atom substitutes bismuth into the BFO site. Small changes observed in all spectra can be associated

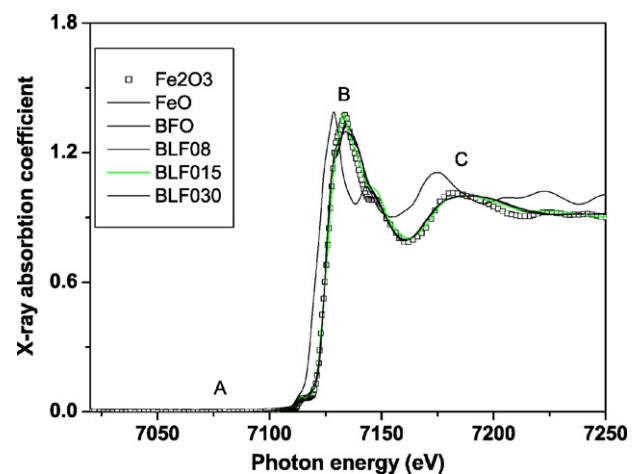


Fig. 4. XANES spectra for bismuth ferrite powders calcinated at 850°C for 2 h as a function of lanthanum content.

with the preparation method, average crystal size and structural order degree. In this way, it was noted that changes which occur above 200 cm^{-1} in the BLFO powders are caused by structural distortion and reduction of vibrations in the FeO_6 octahedra caused by substitution with lanthanum.

Fig. 4 shows the Fe K-edge XANES spectra of the lanthanum modified BFO powders. For the purpose of comparison, the XANES

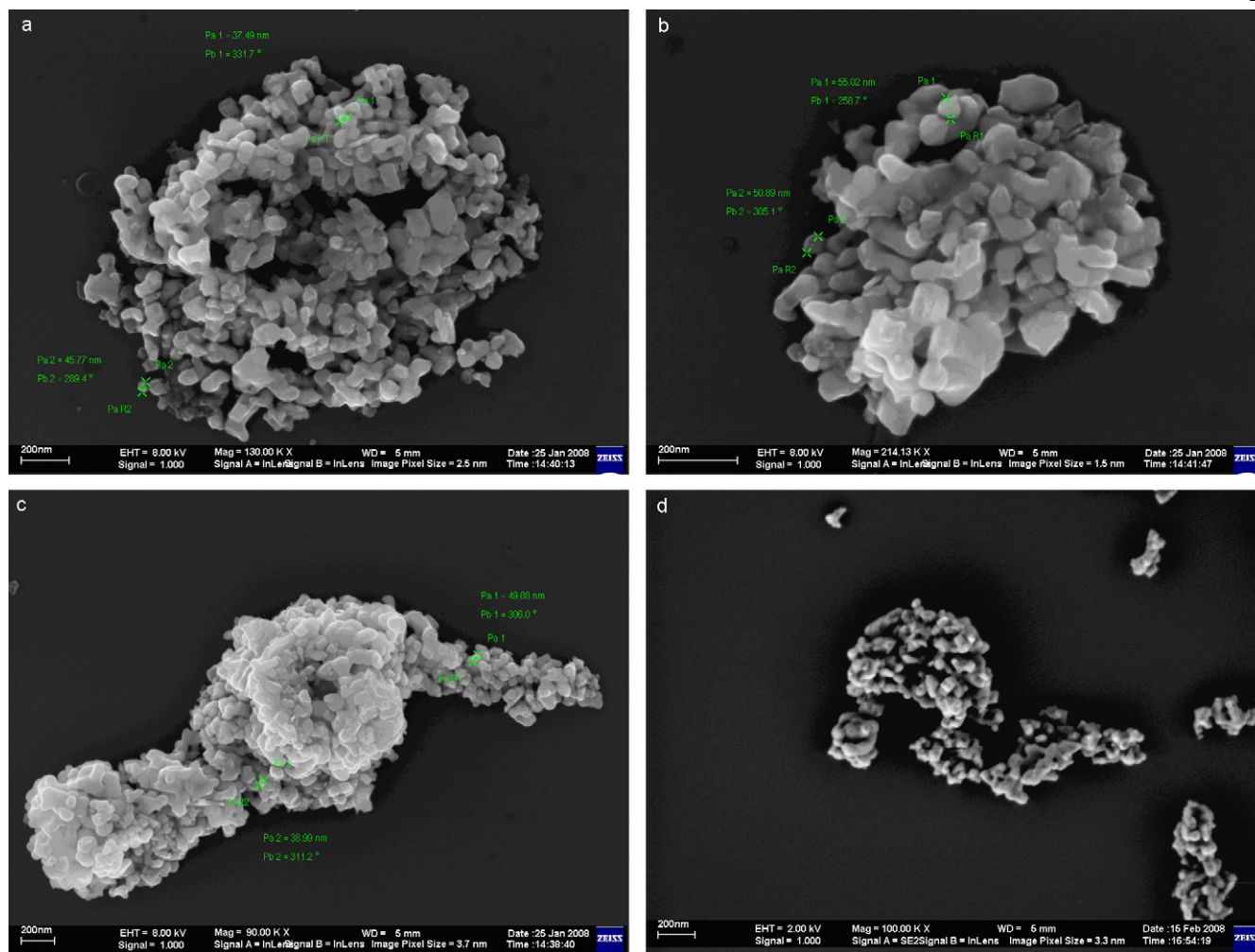


Fig. 5. SEM micrographs for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ powders calcinated at 850°C for 2 h as a function of lanthanum content: (a) $x=0$; (b) $x=0.08$; (c) $x=0.15$ and (d) $x=0.30$.

spectrum of BFO, FeO and Fe_2O_3 powders are also shown. The iron atoms present a $3+$ valence state in the BFO system once its curve is quite similar to Fe_2O_3 phase. Peak A corresponds to the $1s$ – $3d$ electric dipole–forbidden transition, whereas Peak C signifies the dipole–allowed transition (empty orbital $4p$). Peak B known as a shoulder peak is caused by the shakedown process in which $2p$ electron in the oxygen $2p$ band partially transfers to the $\text{Fe}3d$ orbital, so called ligand-to-metal charge transfer process. In this way, we observe changes in the symmetry of BFO and BFO08 compositions when compared to the BLF015 and BLF030 samples. That indicates that iron atoms have different symmetries. In this direction, a structural change is occurring from BFO to BLF030 composition.

The effect caused by lanthanum addition on the morphology and shape of the grains was evaluated by SEM analysis (Fig. 5). A large number of elongated and circular agglomerates which is typical of chemical methods were evident for all compositions. As it can be seen, addition of lanthanum caused a structural distortion leading to grains in a plate-like morphology. No precipitates were evident in the grain boundary indicating the formation of a continuous solid solution. On the other hand, BFO system consists of a mixture of rod-like and plate-like grains. The rod-like grains might be originated from an anisotropic behavior of bismuth ferrite. That indicates change in the kinetics of the grain growth. By roughly estimation and using the Scherrer formula, it was found that the individual particle size was approximately 30 nm.

4. Conclusions

In summary, we have developed and optimized a simple way to prepare single-phase bismuth ferrite samples. The powders prepared under the optimized conditions show lanthanum composition dependent structure and microstructure properties. A structure phase transition from rhombohedral to orthorhombic is observed near $x=0.30$. XANES spectra evidenced iron atoms in a $3+$ valence state while SEM analysis reveal structural distortion leading to a different grain shape after lanthanum addition. Finally, we fabricated single-phase lanthanum modified bismuth ferrite powders from the soft chemistry route.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

References

- [1] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, Y. Tokura, *Nature (Lond.)* 426 (2003) 55.
- [2] M. Zaleski, *J. Appl. Phys.* 87 (2000) 4279.
- [3] E. Nippolainen, A.A. Kamshilin, V.V. Prokofiev, T. Jaskelainen, *Appl. Phys. Lett.* 78 (2001) 859.
- [4] P.H. Borse, U.A. Joshi, S.M. Ji, J.S. Jang, E.D. Jeong, H.G. Kim, J.S. Lee, *Appl. Phys. Lett.* 90 (2007) 034103.
- [5] Y. Mao, T.J. Park, S.S. Wong, *Chem. Commun. (Camb.)* 46 (2005) 5721.
- [6] J.G. Ismailzade, *Phys. Stat. Sol. (b)* 46 (1971) K39.

- [7] G.A. Smolenskii, V.M. Yudin, *Sov. Phys. JETP* 16 (1963) 622.
- [8] Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, *Appl. Phys. Lett.* 84 (2004) 1731.
- [9] V.R. Palkar, R. Pinto, *Pramana J. Phys.* 58 (2002) 1003.
- [10] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, *Science* 299 (2003) 1719.
- [11] K.Y. Yun, M. Noda, M. Okuyama, H. Saeki, H. Tabata, K. Saito, *J. Appl. Phys.* 96 (2004) 3399.
- [12] M. Mahesh Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, *Appl. Phys. Lett.* 76 (2000) 2764.
- [13] A.K. Pradhan, K. Zhang, D. Hunter, J.B. Dadson, G.B. Loutts, *J. Appl. Phys.* 97 (2005) 093903.
- [14] S. Ghosh, S. Dasgupta, A. Sen, H. Sekhar, *J. Am. Ceram. Soc.* 88 (2005) 1349.
- [15] A.Z. Simões, E.C. Aguiar, A.H.M. Gonzalez, J. Andrés, E. Longo, J.A. Varela, *J. Appl. Phys.* 104 (2008) 104115.
- [16] Z.X. Cheng, A.H. Li, X.L. Wang, S.X. Dou, K. Ozawa, H. Kimura, S.J. Zhang, T.R. Shrout, *J. Appl. Phys.* 103 (2008), 07E507.
- [17] C.O. Augustin, R. Kalai Selvan, R. Nagaraj, L. John Berchmans, *Mater. Chem. Phys.* 89 (2005) 406.
- [18] A.Z. Simões, A.H. Gonzalez, M.A. Zaghet, B.D. Stojanovic, A.A. Cavaleiro, P. Moeckli, N. Setter, J.A. Varela, *Ferroelectrics* 271 (2002) 1623.
- [19] L.S. Cavalcante, A.Z. Simões, J.W.M. Espinosa, L.P.S. Santos, E. Longo, J.A. Varela, P.S. Pizani, *J. Alloys Compd.* 464 (2008) 340.
- [20] A.Z. Simões, B.D. Stojanovic, M.A. Ramirez, A.A. Cavaleiro, E. Longo, J.A. Varela, *Ceram. Int.* 34 (2008) 257.
- [21] Z.V. Gabbasova, M.D. Kuz'min, A.K. Zvezdin, I.S. Dubenko, V.A. Murashov, D.N. Rakov, I.B. Krynetsky, *Phys. Lett. A* 158 (1991) 491.
- [22] A.V. Zaleskii, A.A. Frolov, T.A. Khimich, A.A. Bush, *Phys. Solid State* 45 (2003), 141.
- [23] D. Lee, M.G. Kim, S. Ryu, H.M. Jang, S.G. Lee, *Appl. Phys. Lett.* 86 (2005) 222903.
- [24] J. Wang, et al., *Science* 299 (2003) 1719.
- [25] J. Li, et al., *Appl. Phys. Lett.* 84 (2004) 5261.

Review paper

Low-temperature synthesis of nanosized bismuth ferrite by the soft chemical method

E.C. Aguiar^{a,1}, M.A. Ramirez^b, F. Moura^{c,2}, J.A. Varela^{a,1}, E. Longo^{a,1}, A.Z. Simões^{b,*}^aUniversidade Estadual Paulista, UNESP, Instituto de Química, Rua Professor Francisco Degni s/n, CEP 14800-900, Araraquara, SP-Brazil^bUniversidade Estadual Paulista, Unesp, Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Pedregulho, CEP 12516-410, Guaratinguetá-SP, Brazil^cUniversidade Federal de Itajubá, Unifai, Campus Itabira, Rua São Paulo, 377, Bairro: Amazonas, CEP 35900-37, Itabira, MG, Brazil

Received 15 March 2012; received in revised form 25 May 2012; accepted 4 June 2012

Available online 12 June 2012

Abstract

This paper describes research on a simple low-temperature synthesis route to prepare bismuth ferrite nanopowders by the polymeric precursor method using bismuth and iron nitrates. BiFeO₃ (BFO) nanopowders were characterized by means of X-ray diffraction analyses, (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy (Raman), thermogravimetric analyses (TG-DTA), ultra-violet/vis (UV/Vis) and field emission scanning electron microscopy (FE-SEM). XRD patterns confirmed that a pure perovskite BiFeO₃ structure with a rhombohedral distorted perovskite structure was obtained by heating at 850 °C for 4 hours. Typical FT-IR spectra for BFO powders revealed the formation of a perovskite structure at high temperatures due to a metal–oxygen bond while Raman modes indicated oxygen octahedral tilts induced by structural distortion. A homogeneous size distribution of BFO powders obtained at 850 °C for 4 hours was verified by FE-SEM analyses.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Ceramics; B. Chemical syntheses; B. Powder metallurgy; C. X-Ray diffraction

Contents

1. Introduction	13
2. Experimental details	14
3. Results and discussion	15
3.1. X-ray diffraction analyses	15
3.2. Thermal analyses	16
3.3. FT-IR, Raman and UV–vis analyses	16
3.4. FE-SEM analyses	17
4. Conclusions	18
Acknowledgments	19
References	19

1. Introduction

As a promising candidate for a high Curie temperature ($T_C=850\text{ °C}$) and high-ferroelectric performance. BFO nanopowder was the focus of attention in the 1960s–1970s [1–6].

*Corresponding author. Tel.: 55 12 3123 2765.

E-mail address: alezipo@yahoo.com (A.Z. Simões).¹Tel.: +55 16 33019828.²Tel.: +55 31 3834 6472/6136; fax: +55 31 3834 6472/6136.

Its ferroelectric phase structure [7] shows huge shifts of Bi^{3+} and Fe^{3+} ions, as well as counter rotations of oxygen octahedrons along the (111) direction from the non-ferroelectric centro-symmetric cubic structure which produces the $R3c$ space group and a very high spontaneous electric polarization (P_s) as calculated from the structural data. BFO is also a multiferroic material with an antiferromagnetic ordering which occurs below the Néel temperature (T_N 310–370 °C) (there are discrepancies regarding T_N , measured by different authors with different methods) [8,9]. The magnetic structure of BFO is a G -type [10] with a cycloidal spiral arrangement of the magnetic moments of Fe^{3+} ions [11], and the canted spins arising from the Dzyaloshinskii–Moriya (D–M) interaction [12] result in weak ferromagnetism in BFO. Although great achievements have been made in the preparation of BFO thin films by the pulsed-laser deposition (PLD) method [13], it is difficult to avoid the formation of impurity phases by the conventional solid-state reaction in bulk materials. BFO perovskites can stabilize only within a narrow temperature range. To date, the synthesis of single-phase BFO crystallites or ceramics is still a challenging issue. In the solid-state route, nitric acid leaching was required to eliminate impurity phases such as $\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{25}\text{FeO}_{40}$, after the calcination of mixed bismuth and iron oxides [14], which resulted in coarser powders and the poor reproducibility. Most recently, Wang [15] and Pradhan et al. [16] prepared the pure phase of BFO ceramics by a rapid liquid-phase sintering technique. The required BFO crystallization temperature was above the ferroelectric Curie temperature T_c , which implies that the volatilization of bismuth was hard to avoid. Moreover, Ghosh et al. [17] produced phase pure BFO nanopowders by the tartaric acid based sol–gel method coupled with an additional calcination process. The preparation of a polycrystalline pure phase BFO is reported to be difficult because of its narrow temperature range of phase stabilization. Various impurity phases have been reported to occur which are mainly comprised of $\text{Bi}_2\text{Fe}_4\text{O}_9$, $\text{Bi}_{12}(\text{Bi}_{0.5}\text{Fe}_{0.5})\text{O}_{19.5}$ and $\text{Bi}_{25}\text{FeO}_{40}$ [18]. These impurities cause a high leakage current which leads to poor ferroelectric behavior. The most common techniques developed for the formation of pure phase polycrystalline BFO powders are (a) formation of a BFO solid solution with other ABO_3 perovskites types such as BaTiO_3 [19]; (b) calcination followed by leaching with nitric acid [20], (c) microwave assisted hydrothermal [21]; (d) rapid liquid phase sintering of BFO [22]; and (e) use of rather expensive but ultrapure starting powders of Bi_2O_3 and Fe_2O_3 or with a slight deficiency of Bi_2O_3 [23].

Although several attempts have been made to prepare BFO crystallites, few researchers have studied the formation of perovskite BFO by the polymeric precursor method at several annealing temperatures. Our group has expended significant effort to develop synthetic routes to fabricate single-phase lanthanum modified BiFeO_3 (BFO) powders by the polymeric precursor method [24,25]. Our data confirmed that a perovskite phase was synthesized at a temperature of 850 °C for 2 h while infrared data indicates no trace of carbonate. A structural phase

transition from rhombohedral to orthorhombic is observed near $x=0.30$. X-ray absorption near-edge structure (XANES) spectra revealed iron atoms in a 3+ valence state while SEM analysis confirmed structural distortion leading to a different grain shape after the lanthanum addition. Lower leakage current density and superior ferroelectric hysteresis loops at room temperature were noted with an increase in the lanthanum content. The advantage of the soft chemical route is that nanocrystallites can be synthesized at a much lower temperature with energy saving and cost effectiveness. The overall process consists of preparing a solution based on metallic citrate polymerization and eliminating the organic material to synthesize the desired phase. In this study, the effect of the annealing temperature on the phase formation, crystal structure and the morphology of BFO ceramics prepared by polymeric precursor method was investigated.

2. Experimental details

Based on the polymeric precursor method (the Pechini method) [26], the BFO synthesis procedure is associated with the fact that certain α -hydroxycarboxylic organic acids can form polybasic acid chelates with a wide range of cations. After the addition of a polyethylene glycol and heating, the chelate transforms into a polymer with a homogeneous cation distribution. Iron (III) nitrate non-hydrate (Merck) and bismuth nitrate (Aldrich) were used as raw materials. Precursor solutions of bismuth and iron were prepared by adding the raw materials to ethylene glycol and an aqueous citric acid concentrate under heating and stirring. Appropriate quantities of Fe and Bi solutions were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. In this study, an excess of 5 wt% Bi_2O_3 was added to the solution to compensate for unavoidable bismuth oxide loss during thermal treatment. Without the addition of excess bismuth oxide, a pure phase could not be obtained [27]. Pure BFO was prepared from the metal citrate complex which was polyesterified in ethylene glycol. Most of the organic matter was subsequently eliminated at temperatures as low as 300 °C, and a dark residue containing reactive oxides with well-controlled stoichiometry was formed. The formed porous product was crushed and heated in an alumina crucible from 600 to 850 °C for 4 hours (BFO600, BFO700, BFO800, BFO850) to eliminate organic material residues.

Powders were analyzed by XRD for phase determination. For Rietveld analyses, XRD data were collected with a Rigaku 20-2000 diffractometer under the following experimental conditions: 40 kV, 30 mA, $20^\circ \leq 2\theta \leq 100^\circ$, $\Delta 2\theta = 0.02^\circ$, $\lambda_{\text{Cu } K_\alpha}$ monochromatized by a graphite crystal with a divergence slit of 2 mm, a reception slit of 0.6 mm and a step time of 10 s. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [28]. A modified Thompson–Cox–Hasting pseudo-Voigt profile function was used where η (the lorentzian

fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum. TG-DTA analyses were carried out using a Netzsch-409 STA apparatus with a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under flowing air from room temperature to $1000\text{ }^{\circ}\text{C}$. FT-IR spectra were recorded with a Bruker Equinox-55 instrument. Raman spectra were collected using a Bruker RFS-100/S Raman spectrometer with Fourier transform. A 1064 nm YAG laser was used as the excitation source, and its power was maintained at 150 mW . Band gap values were obtained using ultraviolet spectroscopy in the visible region curve (UV-vis-NIR Spectrophotometer-VARIAN Cary 500 X). Microstructural characterization was performed by FE-SEM (Supra 35-VP, Carl Zeiss, Germany).

3. Results and discussion

3.1. X-ray diffraction analyses

Fig. 1 shows the diffraction patterns of thermally treated powders at temperatures between 600 and $850\text{ }^{\circ}\text{C}$. The formed perovskite must have a composition close to BiFeO_3 . At the lowest tested temperature ($600\text{ }^{\circ}\text{C}$), a mixture of initial precursors and a perovskite-structured material was obtained. At $800\text{ }^{\circ}\text{C}$, the material is practically formed by the perovskite phase without any traces of a secondary phase identified as $\text{Bi}_2\text{Fe}_4\text{O}_9$ (JCPDS 20-0836-marked with * in Fig. 1a), which is commonly observed in this system [29]. The formation of $\text{Bi}_2\text{Fe}_4\text{O}_9$ by Bi evaporation can be ruled out. Chen et al. [30] detected this phase after heating at $160\text{--}180\text{ }^{\circ}\text{C}$ where Bi evaporation is not possible. Other authors state that this phase is a consequence of the decomposition of BiFeO_3 . Recently, Selbach et al. [31] described how this secondary phase is formed at $600\text{--}800\text{ }^{\circ}\text{C}$ by the decomposition of BFO and disappears at higher temperatures because Bi and Fe are incorporated into the structure. They rule out any effect of Bi

evaporation as traces would exist at increased temperatures or even in higher amounts which was not the case. Thus, a decrease in the synthesis temperature with respect to the temperature required by the classical solid state reaction method ($850\text{--}900\text{ }^{\circ}\text{C}$) [32] is obtained. The lowering of the synthesis temperature is equivalent to sol-gel method values [33]. Patterns show that initially a bismuth rich phase of $\text{Bi}_x\text{Fe}_y\text{O}_{1.5x+1.5y}$ ($x > y$) composition forms at a temperature of $600\text{ }^{\circ}\text{C}$ followed by the evolution of a BiFeO_3 phase at $700\text{ }^{\circ}\text{C}$. Calcination between temperatures of $700\text{--}850\text{ }^{\circ}\text{C}$ suggest that the impurity phase is completely eliminated at any of these temperatures. What is more remarkable is that the amount of the secondary phase is considerably reduced in samples synthesized by the polymeric precursor method (even at low temperatures) which appears to stem from the complexation process which induced effects in the samples and enhanced the perovskite-structured BiFeO_3 formation. Fig. 1(d) shows that BFO thermally treated at $850\text{ }^{\circ}\text{C}$ for 4 hours exhibits a pure R3c structure without any impurity. The lattice parameters calculated from XRD patterns are $a = 5.6206\text{ \AA}$ and $c = 13.6924\text{ \AA}$.

XRD data reveal that BiFeO_3 was obtained with a rhombohedral distorted perovskite structure by the polymeric precursor method (see Fig. 2). In this study, we have adopted the Rietveld refinement technique to investigate the crystal structure of BFO nanopowders. Data were collected from powders calcinated at $850\text{ }^{\circ}\text{C}$ for 4 hours. Table 1 illustrates the R_{wp} , R_{exp} and S indices as well as lattice parameters (a and c) and the unit cell volume (V). Atomic positions obtained by Rietveld analyses belong to the ICSD card (86-1518). Quantitative phase analyses of powders for the rhombohedral distorted phase were calculated according to Young [28]. Obtained results confirm that the covalent interaction which originates from the strong hybridization between Fe 3d and O 2p orbitals plays an important role in the structural distortion of the BFO lattice at high temperatures. From the low S values ($S = R_{\text{wp}}/R_{\text{exp}}$), it can be assumed that the refinement

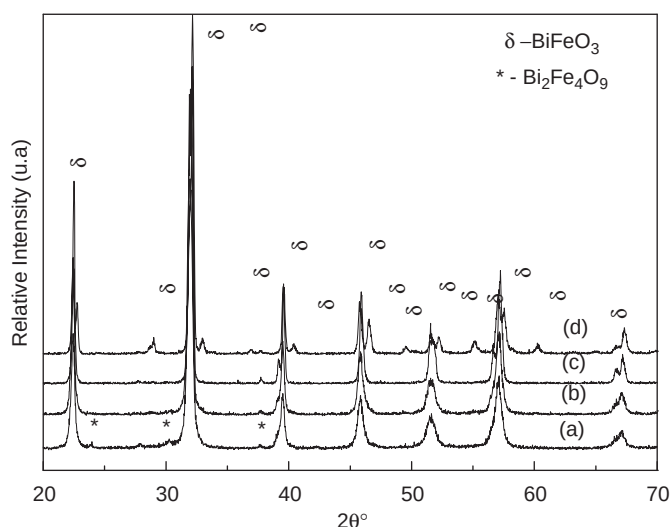


Fig. 1. XRD pattern of a BFO nanopowders thermally treated at (a) $600\text{ }^{\circ}\text{C}$ (b) $700\text{ }^{\circ}\text{C}$ (c) $800\text{ }^{\circ}\text{C}$ and (d) $850\text{ }^{\circ}\text{C}$ for 4 hours by the polymeric precursor method.

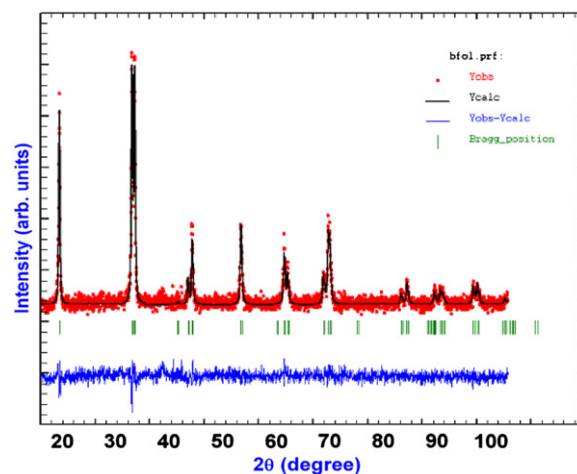


Fig. 2. Rietveld refinement of a BFO nanopowders thermally treated at $850\text{ }^{\circ}\text{C}$ for 4 hours.

Table 1

E.C. Aguiar, M.A. Ramirez, F. Moura, J.A. Varela, E. Longo, A.Z. Simões.

	Parameter	BFO
Refinement index	R_{wp} (%)	11.12
	R_{exp}	7.06
	S	1.57
Atomic positions	A1	0; 0; 0.06722
	A2	0; 0; 0.21091
	B1	0; 0; ½
	B2	0; 0; 0.37099
	O1	¼; ¼; 0
	O2	¼; ¼; ¼
	O3	0; 0; 0.43786
	O4	0; 0; 0.32536
	O5	¼; ¼; 0.11165
S_{Occ}	Bi (A1)	1.00000
	La (A1)	0.00000
	O	0.91700
Lattice parameter	a (Å)	5.6206
	c (Å)	13.6924
	V (Å ³)	374.57
	t	0.915
Perovskite (mol%)		97.5 ± 0.5
Stoichiometry		BiFeO ₃
Refinement		BiFeO _{2.6}

was successfully performed with all the investigated parameters close to literature data [34].

3.2. Thermal analyses

To determine the best annealing conditions and to evaluate the crystallization temperature necessary to obtain a single BFO phase, thermal analyses were performed. Two stages corresponding to the weight and energy change are visible (see Fig. 3). The first characterized stage (25–200 °C) with a small weight loss is related to the elimination of excess ethylene glycol and water formed during the esterification process. The second stage (380–650 °C) corresponds to the decomposition of polymeric metal–carboxylate complexes and to the formation of a metal oxide phase. The DTA curve shows two strong exothermic peaks at around 400–420 °C and 600–650 °C which corresponds to a weight loss that must be considered as the crystallization of the residual amorphous phase and the decomposition of the polymeric metal–carboxylate complexes. Preceded by the impurity phase, the formation of BFO occurs at 580–600 °C as suggested by weight loss as well as a weak endothermic peak in the DTA curve which is also confirmed by XRD patterns (see Fig. 1(a)).

3.3. FT-IR, Raman and UV–vis analyses

FT-IR spectra of crystalline BFO nanopowders derived from the polymeric precursor method are shown in Fig. 4. The broad band at 3000–3600 cm^{−1} is due to the

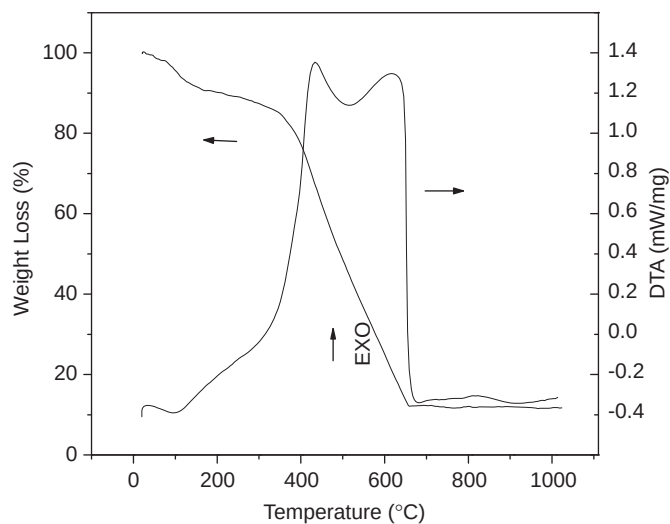


Fig. 3. TG/DTA curves of a BFO resin thermally treated at 300 °C for 4 hours by the polymeric precursor method.

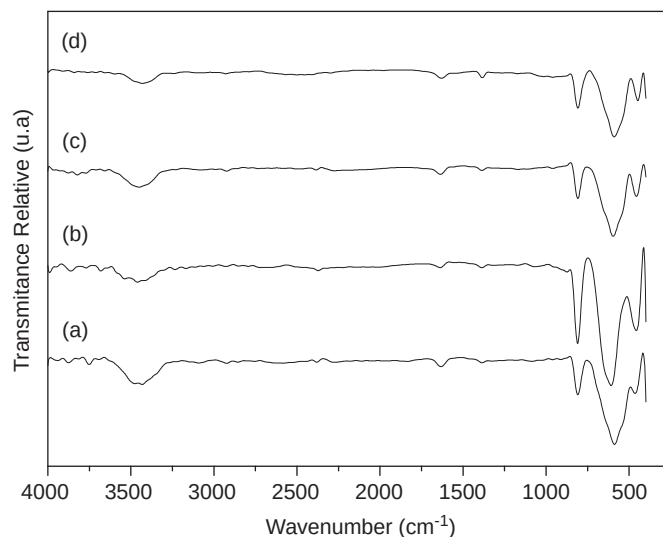


Fig. 4. (a) FT-IR spectra of a BFO nanopowders thermally treated at (a) 600 °C (b) 700 °C (c) 800 °C and (d) 850 °C for 4 hours by the polymeric precursor method.

antisymmetric and symmetric bond stretching of H₂O and OH[−] groups while a band at 1630 cm^{−1} corresponds to bending vibrations of H₂O [35]. Specifically, strong absorptive peaks at 400–600 cm^{−1} are attributed to the Fe–O stretching and bending vibration which are characteristics of octahedral FeO₆ groups in perovskite compounds. The formation of a perovskite structure can be confirmed by the presence of a metal–oxygen bond [36]. Residual water and a hydroxy group are usually detected in the as-grown samples; further heat treatment is required for their elimination. The hydroxylation of metal ions and deprotonation can be accelerated by raising the solution temperature or pressure [37]. However, there was a vibration band associated with the deformation of O–H bonds near 1680 cm^{−1} which is attributed to water adsorbed at

the powder surface when the sample was in contact with the environment. Crystallized powders were found to have OH^- ions under the present sample preparation conditions. Furthermore, the hydroxyl content was found to decrease with increased annealing temperatures which could be due to the vigorous action of annealing conditions to remove these groups at elevated temperatures. The band at around 830 cm^{-1} was due to traces of trapped NO_3^- ions in BFO nanopowders [38]. BFO nanopowders contain a few traces of carbonates ($\text{C}=\text{O}$ vibration around 1450 cm^{-1}) independent of the annealing temperature which suggests that the nanopowder surface was in contact with the CO_2 environment. This problem should be minimized during the sample preparation since many properties are dependent on the purity of the raw powders (especially carbonate traces) which can result in porous ceramics due to CO_2 elimination.

Raman scattering has proven to be a valuable technique to obtain information about local structures within materials. Fig. 5a–d shows Raman spectra for BFO nanopowders derived at different annealing temperatures. The degree of order–disorder in the crystal lattice of BFO nanopowders at short and medium distances was investigated. Modes located at 212, 316, 377, 445, 537 and 635 cm^{-1} are caused by the internal vibration of FeO_6 octahedra whereas modes below 200 cm^{-1} must be attributed to different sites occupied by bismuth within perovskite units. Bands located at 97, 120 and 145 cm^{-1} are related to Bi atoms of the perovskite layer which corresponds to a rigid layer. These modes are probably due to a distortion in the A site caused by the bismuth ion. This distortion into the A site of perovskite enhances the Jahn–Teller distortion of FeO_6 octahedra. On the other hand, Raman modes located above 200 cm^{-1} are responsible for distortions and vibrations of FeO_6 octahedra. As the temperature decreases, there is a reduction in the Raman

band intensities (mainly the mode located at 209 cm^{-1}) which is due to Fe–O atom vibrations inside the perovskite layer and to vibrations of Bi–O atoms within the Bi_2O_2 layer. The appearance of a Raman mode at low frequency (97 cm^{-1}) is due to the Bi ion atomic mass which causes Bi displacements in the Bi_2O_2 layer. All Raman modes can be indexed to the modes of a BFO molecule with a R3c structure [39]. BFO850 and BFO800 show almost identical curves except that the intensity of A_1 and E_3 modes for BFO850 is significantly stronger than the intensity of BFO800. As indicated by Simões et al. [40], the shift of Raman peaks higher than 200 cm^{-1} results from the FeO_6 octahedron. The stronger intensity of A_1 and E_3 modes for BFO850 can be attributed to the oxygen octahedral tilt-induced structural distortion. Raman results are in agreement with XRD data which indicates an ordered structure at short and long distances.

Fig. 6 shows the UV–vis optical diffuse absorbance spectra of BFO nanopowders thermally treated at different temperatures. The respective band gap values determined from the Kubelka model [41]. The optical energy band gap is related to the absorbance and to the photon energy by the following Eq. (1):

$$h\nu\alpha\mu(h\nu - E_g^{\text{opt}})^2 \quad (1)$$

where α is the absorbance, h is the Planck constant, ν is the frequency and E_g^{opt} is the optical band gap [42]. Values obtained are 3.04, 2.97, 2.95, 2.89, respectively. Our BFO nanopowders exhibited characteristic absorption spectra of ordered or crystalline materials. These results indicate that the exponential optical absorption edge and the optical band gap are controlled by the degree of structural disorder in the BFO lattice. This decrease in the band gap value as the temperature increases can be ascribed to a reduction of defects in the lattice which decreases intermediary energy levels due to the reduction of oxygen vacancies located at BO_6^- octahedra. The main differences in optical band gaps can be related to different factors which mainly include: the synthesis method, shape (powder, crystal or thin film) and synthesis conditions. The reflectance significantly decreases near the excitonic absorption edge as the temperature changes which is related to the optical band gap. The decrease in the band gap with increased temperature might be explained by the suppressed tilt angle of the oxygen octahedra which increases the $\text{Fe}^{2+}\text{--O--Fe}^{3+}$ angle. Forced higher symmetry is expected to increase the band width of occupied and unoccupied bands which reduces the band gap [43]. The band gap obtained in our study is higher than the reported value of about 2.67 eV for bulk BiFeO_3 [44] which might be due to the size effect [45].

3.4. FE-SEM analyses

The effect caused by the annealing temperature on the morphology and shape of nanopowders was evaluated by

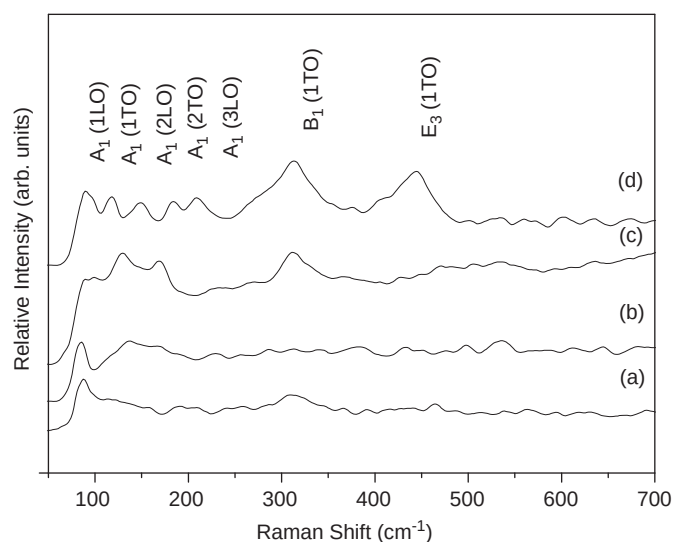


Fig. 5. (a) Raman spectra of a BFO nanopowders thermally treated at (a) 600 °C (b) 700 °C (c) 800 °C and (d) 850 °C for 4 hours by the polymeric precursor method.

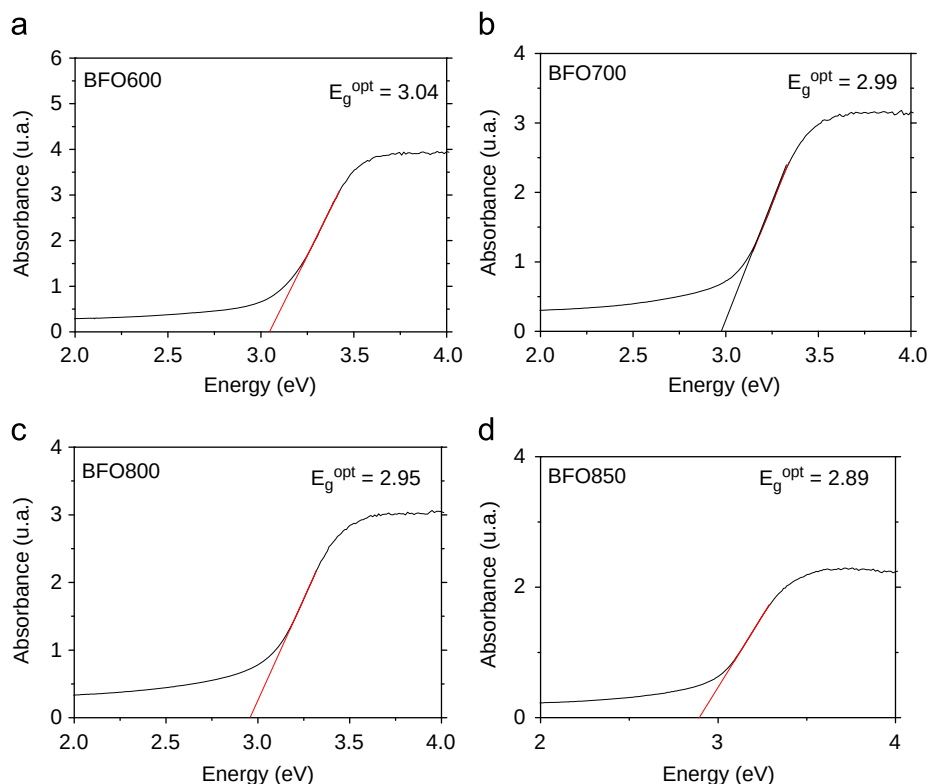


Fig. 6. UV-vis of a BFO nanopowders thermally treated at (a) 600 °C (b) 700 °C (c) 800 °C and (d) 850 °C for 4 hours by the polymeric precursor method.

FE-SEM analyses (see Fig. 6). Fig. 7 Increasing the temperature had a pronounced effect on the nanopowder shape which leads to a plate-like morphology and a structural distortion (see inset of Fig. 6d). The change in the particle size varies from 35 to 60 nm as the temperature increases. BFO nanopowders thermally treated at 600 °C present a rod-like morphology with particles of around 35 nm. Rod-like grains might originate from the anisotropic behavior of bismuth ferrite. The nanopowder size is heterogeneously distributed with a rod-like morphology form which is different from literature data [46]. According to the image, most BFO nanopowders thermally treated at low temperatures reveal a few large particles with an irregular shape. The nanopowder morphology variation may indicate the formation of impurity phases. Submicron and isotropy BFO crystallites obtained in our study are quite different from the previous research where BFO nanopowders agglomerated into a cube with a side size of 45 using the microwave assisted hydrothermal (MAH) method [47]. In our case, a critical annealing temperature existed where the formation of impurity phases was favored, and the formation of pure BFO was highly dependent upon it. Increasing the annealing temperature, causes Bi^{3+} and Fe^{3+} to react at high temperatures. If temperature conditions are carefully maintained during the experiment, neither etching of BFO crystals nor the formation of a second phase will occur. Therefore, the crystallization process continued in such a way that the system was self-stabilizing. We conjecture that the dissociation of

bismuth and iron during annealing and the formation of ionic complexes might prevent the growth of BFO crystallites and limit the size of BFO particles to the nanometric range. The agglomeration process was attributed to van der Waals forces. To reduce the surface energy, primary particles have a tendency to form nearly spherical agglomerates in a minimum surface-to-volume ratio and hence reduce surface free energy. This type of grain structure is common in oxide, ferrite and titanate ceramics [48].

4. Conclusions

A simple method was used to prepare pure BFO nanopowders which are free of impurities at a temperature of 850 °C for 4 hours. A better homogeneity of nanopowders is obtained at this temperature. The stability of the perovskite phase increases at high temperatures. A longer annealing temperature was beneficial to inhibit the formation of any impurity phases and promote the growth of BFO crystallites into single-phase perovskites. Rietveld refinement reveals a rhombohedral distorted structure with a space group of $R3c$. The polymeric precursor method is important not only for the low temperature crystallization of BFO nanopowders, but also for controlling morphological and structural properties. Therefore, this method is undeniably a genuine technique for low temperatures in comparison with solid state reactions.

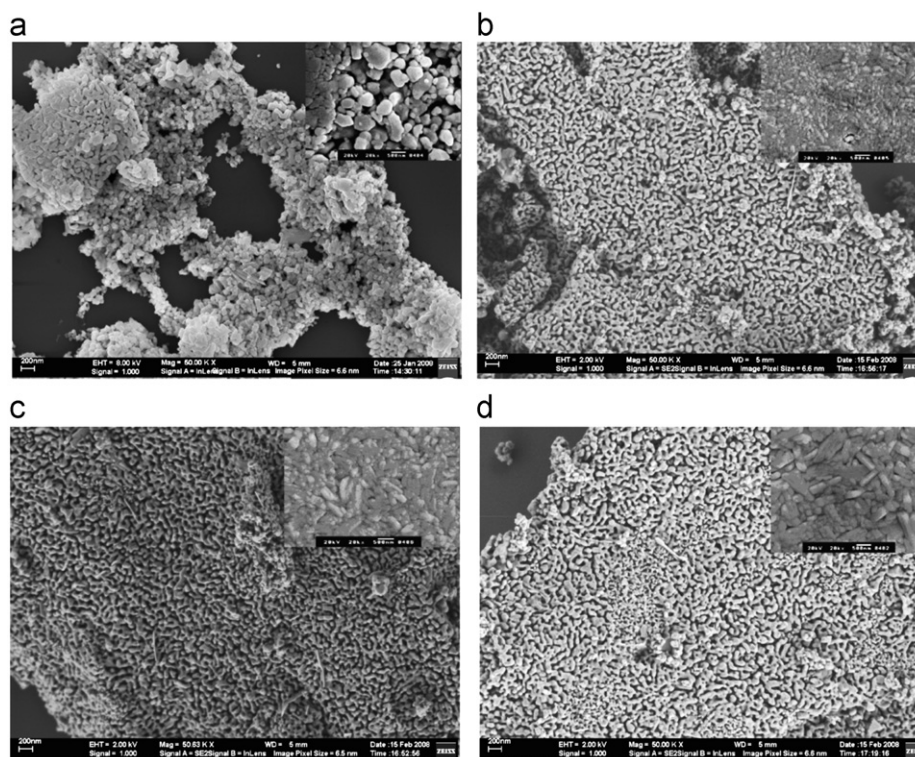


Fig. 7. FE-SEM images and inset of a BFO nanopowders thermally treated at (a) 600 °C (b) 700 °C (c) 800 °C and (d) 850 °C for 4 hours by the polymeric precursor method.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

References

- [1] E.K.H. Salje, Phase Transitions in Ferroelectrics Ferroelastic and Coelastic Crystals, Cambridge University Press, Cambridge. <http://dx.doi.org/10.1063/1.2168038>.
- [2] V.E. Wood, A.E. Austin, Possible applications for magnetoelectric materials, *International Journal of Magnetism* 5 (1974) 303–315.
- [3] N.A. Hill, Why are there so few magnetic ferroelectrics? *The Journal of Physical Chemistry B* 104 (2000) 6694–6697.
- [4] G.A. Smolenskii, V.M. Yudin, Antiferromagnetic properties of some perovskite, *Soviet Physics—JETP* 16 (1963) 622–624.
- [5] C. Michel, J.M. Moreau, G.D. Achenbach, R. Gerson, W.J. James, The atomic structure of BiFeO₃, *Solid State Communications* 7 (1969) 701–704.
- [6] J.R. Teague, R. Gerson, W.J. James, Dielectric hysteresis in single crystal BiFeO₃, *Solid State Communications* 8 (1970) 1073–1074.
- [7] F. Kubel, H. Schmid, Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite BiFeO₃, *Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry* 46 (1963) 610–616.
- [8] G. Smolenskii, New ferroelectrics of complex composition, *Soviet Physics—Solid State* 2 (1961) 2651–2654.
- [9] S.V. Kiselev, R.P. Ozerov, G.S. Zhdanov, Detection of magnetic order in ferroelectric BiFeO₃ by neutron diffraction, *Soviet Physics—Doklady* 7 (1963) 742–744.
- [10] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, Spiral magnetic ordering in bismuth ferrite, *Journal of Physics C: Solid State Physics* 15 (1982) 4835–4846.
- [11] I.E. Dzialoshinskii, Thermodynamic theory of Weak'' ferromagnetism in antiferromagnetic substances, *Soviet Physics—JETP* 5 (1957) 1259–1262.
- [12] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, Epitaxial BiFeO₃ multiferroic thin film heterostructures, *Science (New York, NY)* 299 (2003) 1719–1722.
- [13] K.Y. Yun, M. Noda, M. Okuyama, H. Saeki, H. Tabata, K. Saito, Structural and multiferroic properties of BiFeO₃ thin films at room temperature, *Journal of Applied Physics* 96 (2004) 3399–3404.
- [14] M. Mahesh Kumar, V.R. Palkar, K. Srinivas, S.V. Suryanarayana, Ferroelectricity in a pure BiFeO₃ ceramic, *Applied Physics Letters* 76 (2000) 2764–2766.
- [15] Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, Synthesis of bismuth ferrite nanoparticles via a wet chemical route at low temperature, *Applied Physics Letters* 84 (2004) 1731–1733.
- [16] A.K. Pradhan, K. Zhang, D. Hunter, J.B. Dadson, G.B. Loutts, Magnetic and electrical properties of single-phase multiferroic BiFeO₃, *Journal of Applied Physics* 97 (2005) 093903–093908.
- [17] S. Ghosh, S. Dasgupta, A. Sen, H. Sekhar, Low-temperature synthesis of nanosized bismuth ferrite by soft chemical route, *Journal of the American Ceramic Society* 88 (2005) 1349–1352.
- [18] V.R. Palkar, R. Pinto, Colossal magnetoresistance and other materials, *Pramana Journal of Physics* 58 (2002) 1003–1008.
- [19] R.T. Smith, G.D. Achenbach, R. Gerson, W.J. James, Dielectric properties of solid solutions of BiFeO₃ with Pb(Ti,Zr)O₃ at high temperature and high frequency, *Journal of Applied Physics* 39 (1968) 70–74.
- [20] V.V. Shvartsman, W. Kleemann, R. Haumont, J. Kreisel, Large bulk polarization and regular domain structure in ceramic BiFeO₃, *Applied Physics Letters* 90 (2007) 172115–172123.
- [21] Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, Room-temperature saturated ferroelectric polarization in BiFeO₃ ceramics synthesized by rapid liquid phase sintering, *Applied Physics Letters* 84 (2004) 1731–1733.

- [22] M. Kumar, K.L. Yadav, Large magnetization in Mn doped BiFeO₃ ceramics with enhanced polarization and weak magnetization, *Applied Physics Letters* 91 (2007) 112911–112913.
- [23] M. Valant, A.-K. Axelsson, N. Alford, Peculiarities of a solid-state synthesis of multiferroic polycrystalline BiFeO₃, *Chemistry of Materials: A Publication of the American Chemical Society* 19 (2007) 5431–5436.
- [24] F. Gonzalez Garcia, C.S. Riccardi, A.Z. Simões, Lanthanum doped BiFeO₃ powders: syntheses and characterization, *Journal of Alloys and Compounds* 501 (2010) 25–29.
- [25] A.Z. Simões, F. Gonzalez Garcia, C.S. Riccardi, Rietveld analysis and electrical properties of lanthanum doped BiFeO₃ ceramics, *Materials Chemistry and Physics* 116 (2009) 305–309.
- [26] M. Pechini, Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coating Method Using the Same to Form a Capacitor, U.S. Patent no. Mat3.330.697, 1967.
- [27] M.A. Zaghete, C.O. Paiva-Santos, J.A. Varela, E. Longo, Y.P. Mascarenhas, Chemical synthesis of PZT powder by auto-combustion of citrate-nitrate gel, *Journal of the American Ceramic Society* 75 (1992) 2089–2093.
- [28] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, An upgrade of the DBWS* Programms for Rietveld refinement with PC and mainframe computers, *Journal of Applied Crystallography* 28 (1995) 366–367.
- [29] L.Y. Wang, D.H. Wang, H.B. Huang, Z.D. Han, Q.Q. Cao, B.X. Gu, Y.W. Du, The magnetic properties of polycrystalline Bi_{1-x}Sr_xFeO₃ ceramics, *Journal of Alloys and Compounds* 469 (2009) 1–3.
- [30] C. Chen, J. Cheng, S. Yu, L. Che, Z. Meng, Development of new NLO Crystals for UV and IR applications, *Journal of Crystal Growth* 291 (2006) 135–139.
- [31] S.M. Selbach, M.A. Einarsrud, T. Grande, On the thermodynamic stability of BiFeO₃, *Chemistry of Materials: A Publication of the American Chemical Society* 21 (2009) 169–173.
- [32] V.A. Khomchenko, V.V. Shvartsman, P. Borisov, W. Kleemann, D.A. Kiselev, I.K. Bdikin, J.M. Vieira, A.L. Kholkin, Effect of Gd-substitution on the crystal structure and multiferroic properties of BiFeO₃, *Acta Materialia* 57 (2009) 5137–5145.
- [33] J. Wei, D. Xue, Enhanced ferromagnetic properties of multiferroic Bi_{1-x}Sr_xMn_{0.2}Fe_{0.8}O₃ synthesized by sol-gel process, *Electrochemical and Solid State Letters* 10 (2007) G85–G88.
- [34] S. Luo, Y. Noguchia, M. Miyayama, T. Kudo, Rietveld analysis and dielectric properties of Bi₂WO₆-Bi₄Ti₃O₁₂ ferroelectric system, *Materials Research Bulletin* 36 (2001) 531–540.
- [35] A.Z. Simões, B.D. Stojanovic, M.A. Ramirez, A.A. Cavalheiro, E. Longo, J.A. Varela, Lanthanum-doped Bi₄Ti₃O₁₂ prepared by the soft chemical method: Rietveld analysis and piezoelectric properties, *Ceramics International* 34 (2008) 257–261.
- [36] D. Lee, M.G. Kim, S. Ryu, H.M. Jang, S.G. Lee, Epitaxially grown La modified BiFeO₃ magnetoferroelectric thin films, *Applied Physics Letters* 86 (2005) 222903–222905.
- [37] H. Wang, J.J. Zhu, J.M. Zhu, X.H. Liao, S. Xu, T. Ding, Preparation of nanocrystalline ceria particles by sonochemical and microwave assisted heating methods, *Physical Chemistry* 4 (2002) 3794–3799.
- [38] H. Zhang, X. Fu, S. Niu, Q. Xin, Synthesis and luminescent properties of nanosized YVO₄:Ln (Ln=Sm, Dy), *Journal of Alloys and Compounds* 457 (2008) 61–65.
- [39] Y. Yang, J.Y. Sun, K. Zhu, Y.L. Liu, L. Wan, Increased efficiency of low band gap polymer solar cells at elevated temperature and its origins, *Journal of Applied Physics* 103 (2008) 093532–093537.
- [40] A.Z. Simões, E.C. Aguiar, A.H.M. Gonzalez, J. Andrés, E. Longo, J.A. Varela, Strain behavior of lanthanum modified BiFeO₃ thin films prepared via soft chemical method, *Journal of Applied Physics* 104 (2008) 104115–104120.
- [41] P. Kubelka, F. Munk, Ein Beitrag Zur Optik der Farbanstriche, *Zeitschrift für Technische Physik* 12 (1931) 593–601.
- [42] D.L. Wood, J. Tauc, Weak absorption tails in amorphous semiconductors, *Physical Review B* 5 (1972) 3144–3151.
- [43] A.Y. Borisevich, H.J. Chang, M. Huijben, M.P. Oxley, S. Okamoto, M.K. Niranjani, J.D. Burton, E.Y. Tsybal, Y.H. Chu, P. Yu, R. Ramesh, S.V. Kalinin, S.J. Pennycook, Suppression of octahedral tilts and associated changes in electronic properties at epitaxial oxide heterostructure interfaces, *Physical Review Letters* 105 (2010) 087204–087207.
- [44] P. Chen, N.J. Podraza, X.S. Xu, A. Melville, E. Vlahos, V. Gopalan, R. Ramesh, D.G. Schlom, J.L. Musfeldt, Optical properties of quasi-tetragonal BiFeO₃ thin films, *Applied Physics Letters* 96 (2010) 131907–131909.
- [45] S. Li, Y. Lin, B. Zhang, Y. Wang, C. Nan, Controlled fabrication of BiFeO₃ uniform microcrystals and their magnetic and photocatalytic behaviors, *The Journal of Physical Chemistry C* 114 (2010) 2903–2908.
- [46] Z.S. Macedo, C.R. Ferrari, A.C. Hernandez, Impedance spectroscopy of Bi₄Ti₃O₁₂ ceramic produced by self-propagating high-temperature synthesis technique, *Journal of The European Ceramic Society* 24 (9) (2004) 2567–2574.
- [47] J.-T. Han, Y.-H. Huang, X.-J. Wu, C.-L. Wu, W. Wei, B. Peng, W. Huang, J.B. Goodenough, Tunable synthesis of bismuth ferrites with various morphologies, *Advanced Materials (Weinheim, Germany)* 18 (2006) 2145–2148.
- [48] A.Z. Simões, M.A. Ramirez, C.S. Riccardi, A.H.M. Gonzalez, E. Longo, J.A. Varela, Synthesis and electrical characterization of CaBi₂Nb₂O₉ thin films deposited on Pt/Ti/SiO₂/Si substrates by polymeric precursor method, *Materials Chemistry and Physics* 98 (2006) 203–206.

Influence of temperature on the dielectric and ferroelectric properties of bismuth titanate thin films obtained by the polymeric precursor method

A.Z. Simões^{a,*}, M.A. Ramirez^a, C.S. Riccardi^a, A. Ries^a,
E. Longo^b, J.A. Varela^a

^a Chemistry Institute, Universidade Estadual Paulista (UNESP), Araraquara, SP, CEP 14801-970, Brazil

^b Chemistry Department, Universidade Federal de São Carlos (UFSCar), São Carlos, SP, CEP 13565-905, Brazil

Received 27 January 2004; received in revised form 28 December 2004; accepted 9 January 2005

Abstract

The (1 1 7) and (0 0 1 0)-oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films were fabricated on Pt/Ti/SiO₂/Si substrates by using a polymeric precursor solution under appropriate crystallization conditions. Atomic force microscopy and scanning electron microscopy showed relatively large grains, which is typical for this system. The capacitance dependence on voltage is strongly non-linear, confirming the ferroelectric properties of the films resulting from the domain switching. The (1 1 7)-oriented films exhibited a higher remanent polarization ($23.7 \mu\text{C cm}^{-2}$) than the (0 0 1 0)-oriented films ($11.8 \mu\text{C cm}^{-2}$). Fatigue tests revealed that the temperature of thermal treatment and degree of orientation affect the performance of the device.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Bismuth titanate; Thin film; Dielectric properties; Ferroelectric properties

1. Introduction

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in non-volatile random access memories [1]. Among the related materials of interest, lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) is probably the most extensively studied. Such films have favorable characteristics, including high polarization, low processing temperature, and remaining apparently fatigue-free when used conducting oxide electrodes [2,3]. Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer-structured perovskite-like strontium bismuth tantalate ($\text{SrBi}_2\text{Ta}_2\text{O}_9$) has also been studied [4]. Although it is a fatigue-free material, its practical application is limited, primarily due to its small polarization

($2P_r = 4\text{--}16 \mu\text{C cm}^{-2}$) and high processing temperature ($>750^\circ\text{C}$).

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a member of the layered Aurivillius phase perovskite ferroelectrics and has a Curie temperature of 675°C . In its ferroelectric state, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is monoclinic. Its spontaneous polarization vector lies in the a - c plane, with a component of $49 \mu\text{C cm}^{-2}$ along the a -axis and $4 \mu\text{C cm}^{-2}$ along the c -axis [5]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is an attractive material for use in non-volatile memories, since it and other Aurivillius phases exhibit an excellent fatigue resistance during repeated polarization reversals in an electrical field [6]. Furthermore, its layered perovskite structure makes it feasible to grow lattice-matched heterostructures on various substrates by different thin film growth methods [7]. X-ray diffraction is the main technique, which has been applied to characterize epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films structurally. Usually, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films grown on Pt-coated silicon substrates were reported to be oriented with their c -axis normal to the substrate surface [8].

* Corresponding author. Tel.: +55 16 3301 6600; fax: +55 16 3322 7932.
E-mail address: alezipo@yahoo.com (A.Z. Simões).

However, little work has been done to study the microstructure and ferroelectric domain configurations of randomly oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films [9]. The components of spontaneous polarization along the *a*- and *c*-directions of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ can be independently reversed with an electrical field, resulting in several different domains and domain wall configurations [10]. All these configurations, which will influence the ferroelectric properties of thin films, have not been distinguished by X-ray diffraction in thin films. The highly asymmetric crystal structure normally promotes the crystallization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films with preferential growth of (001)-oriented grains. The polarization of the resulting (001)-oriented polycrystalline films has been known to be small, because a negligible remanent polarization has been observed from their epitaxial counterparts [11]. Since nucleation with (001) facets is the energy-favorable process, preferential growth of (001)-oriented grains will persist as long as nucleation at the electrode interface is the dominant process.

Several attempts to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films have been reported in the literature. Due to the high temperatures required for the formation of the ferroelectric perovskite phase, the production of such films has not proved easy and, at present, there is a wide range of thin film synthesis techniques, such as metal-organic chemical vapor deposition (MOCVD), sol-gel, radio frequency magnetron, ion beam sputtering and laser ablation [12–16]. Nakamura et al. [17] deposited by the MOCVD technique highly *c*-oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films with a $\text{Bi}_2\text{Ti}_2\text{O}_7$ buffer layer on $\text{Pt}/\text{SiO}_2/\text{Si}(100)$. The film had a coercive field of 13 kV cm^{-1} and also a very low remanent polarization ($0.6 \mu\text{C cm}^{-2}$). Wang et al. [18] developed an atmospheric pressure MOCVD technique to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films. These films exhibited (100) orientation with a high remanent polarization ($38 \mu\text{C cm}^{-2}$) and high coercive field (45 kV cm^{-1}). Si and Desu [19] fabricated randomly oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films at low temperature (550°C) by hot-wall MOCVD. A remanent polarization of $19 \mu\text{C cm}^{-2}$ and a high coercive field of 244 kV cm^{-1} were obtained.

In previous works, our group had reported the preparation of thin films by the polymeric precursor method [20]. The overall process consists of preparing a coating solution based on metallic citrate polymerization. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. In this article, we report the growth and ferroelectric properties of (117) and (0010)-oriented, and mixed-oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ polycrystalline films prepared by chemical solution deposition under various crystallization conditions.

2. Experimental procedure

Titanium isopropoxide (Hulls AG) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth and titanium were prepared by adding the

raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti and Bi were mixed and homogenized by stirring at 90°C . The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The films were spin-coated from a deposition solution onto a $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films were completely crystallized after annealing for 2 h at temperatures ranging from 600 to 700°C . Multilayered films were obtained by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm.

In this work, an excess of 5 wt.% Bi was added to the solution, aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku, 2000) and $\text{Cu K}\alpha$ radiation. The thickness of the annealed films was studied using scanning electron microscopy (SEM; Topcom SM-300) by looking at the transversal section. In this case, back-scattered electrons were utilized. Three measurements were done to obtain an average value of thickness. The surface roughness was examined by atomic force microscopy using the tapping mode technique. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace under oxygen atmosphere at 300°C for 1 h. Here, the desired effect was to decrease eventually present oxygen vacancies.

The relative dielectric constant, ϵ_r was measured versus frequency using an impedance analyser (model 4192 A, Hewlett-Packard). The capacitance–voltage characteristics was measured in the metal–ferroelectric–metal configuration using a small alternating current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. The ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). For the fatigue measurements, internally generated $8.6 \mu\text{s}$ wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films was measured over a range of frequencies.

3. Results and discussion

Fig. 1 shows the XRD results for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films prepared under various conditions. Although diffraction peaks corresponding to the perovskite structure were detected at a quite low temperature (600°C), they were generally low and broad, indicating a poor crystallinity of the films. Above 650°C , sharp diffraction peaks appeared, and their intensity

Table 1
Electrical properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films after annealing for 2 h at various temperatures

T ($^{\circ}\text{C}$)	P_r ($\mu\text{C cm}^{-2}$)	V_c (V)	ε (1 MHz)	Roughness (nm)	Thickness (nm)	Grain size (nm)
600	11.8	2.4	87	16.4	370	80
650	9.7	2.5	112	19.0	380	140
700	23.7	3.1	160	17.3	407	179

P_r = remanent polarization; V_c = coercive voltage; ε = dielectric constant.

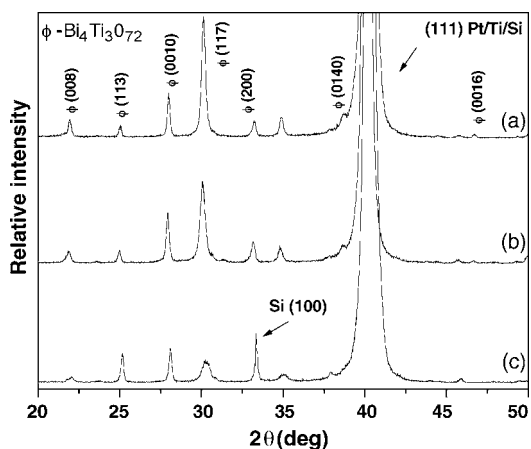


Fig. 1. X-ray diffraction diagram of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 $^{\circ}\text{C}$, (b) 650 $^{\circ}\text{C}$ and (c) 600 $^{\circ}\text{C}$. θ = diffraction angle.

was found to be sensitive to the crystallization temperature. The XRD results clearly show this trend in the crystallization pattern; that means, a low temperature favors the growth of (0 0 1 0)-oriented grains, while a high crystallization temperature favors the growth of (1 1 7)-oriented grains. The effect of crystallization temperature may have been related to the

different growth rates of (1 1 7) and (0 0 1 0)-oriented grains. Some orientation-sensitive physical properties, such as dielectric constant, remanent polarization and coercive field, should vary with the extent of mixing of orientations that is different from one film to the other. To show the effect, the proportion of (1 1 7)-oriented grains of each film was roughly estimated with $\alpha = I(1\ 1\ 7)/[(0\ 0\ 1\ 0) + (1\ 1\ 7)]$, where $I(1\ 1\ 7)$ and $(0\ 0\ 1\ 0)$ are the peak intensities of the (1 1 7) and (0 0 1 0) diffractions. For the films considered in Fig. 1, the corresponding values are 0.58, 0.53 and 0.38 at 700, 650 and 600 $^{\circ}\text{C}$, respectively.

SEM images of the film surface are shown in Fig. 2a–c. The images reveal that the surfaces appear to be dense, smooth and crack-free. The grains are homogeneously distributed with an average grain size from 80 to 179 nm, which is comparable with the results obtained by AFM (Table 1). The average grain size and surface roughness of the thin films were estimated using contact mode (AFM). Fig. 3a–c shows typical AFM images of films annealed at 600, 650 and 700 $^{\circ}\text{C}$ for 2 h. The obtained microstructures are crack-free and of small porosity. The grain size increased with temperature indicating a high mobility of the ions within the unit cell. Besides, the film porosity was also reduced with increasing temperature, which leads to better electric

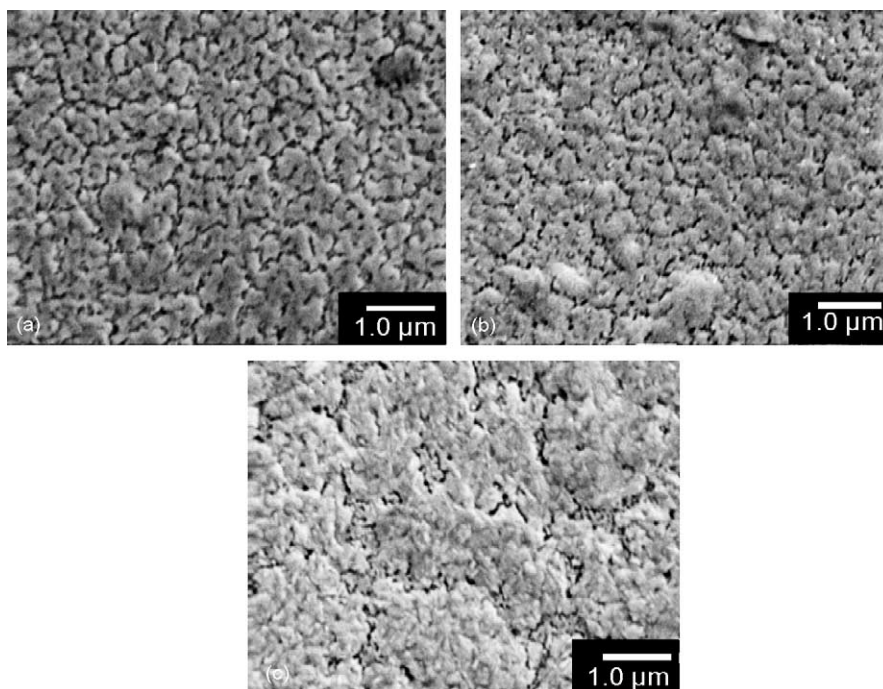


Fig. 2. SEM images of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 $^{\circ}\text{C}$, (b) 650 $^{\circ}\text{C}$ and (c) 600 $^{\circ}\text{C}$.

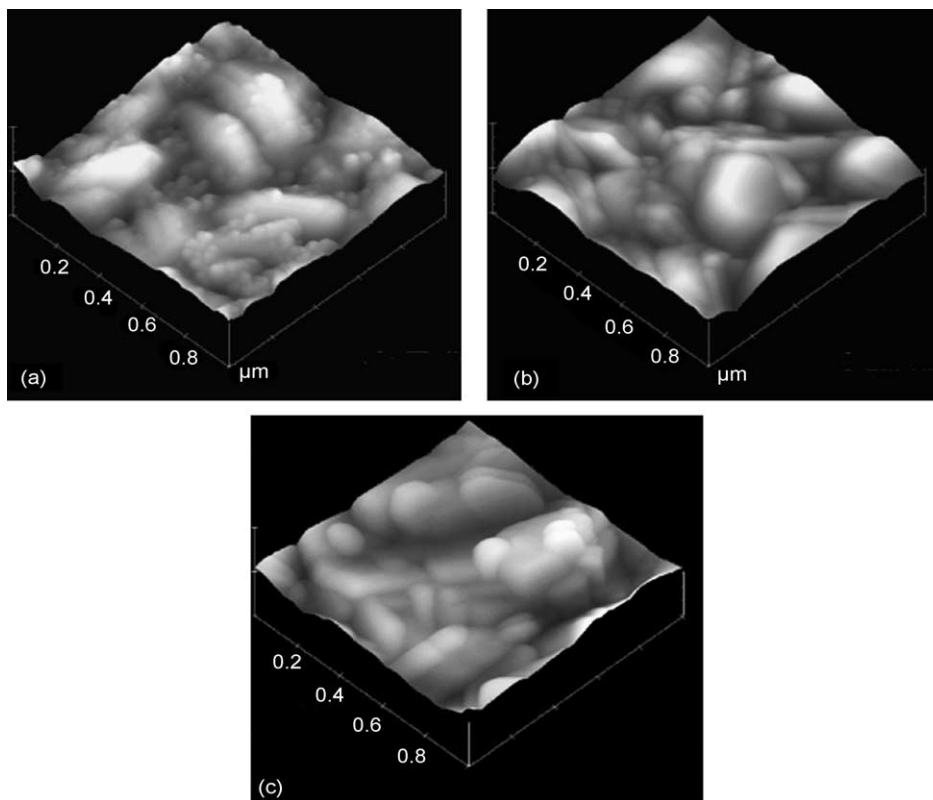


Fig. 3. AFM images of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 °C, (b) 650 °C and (c) 600 °C.

properties as low coercive field and higher remanent polarization. Another important parameter to be controlled is the roughness since the dielectric properties depend not only on the microstructure but also on the interaction between the electrode/film interface. The thickness and roughness were only significantly dependent not only on the treatment temperature.

Fig. 4 shows the dielectric constant as a function of frequency for the films studied. As shown, the dielectric constant is positively correlated with α in the measured frequency range. This observation suggests that the polar axis is closer

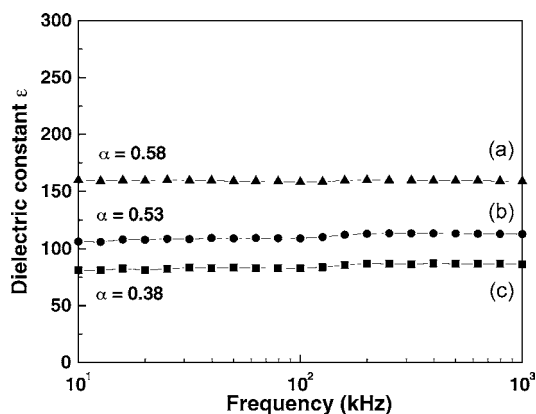


Fig. 4. Dielectric constant in dependence of frequency of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 °C, (b) 650 °C and (c) 600 °C.

to (1 1 7) than to (0 0 1 0), which is consistent with the results observed for epitaxial films. A similar observation has also been reported for bismuth titanate single crystals, for which the dielectric constant measured along the a -axis is approximately double to that along the c -axis, and the polar axis for bismuth titanate has been shown to lie at 4.5° from the a -axis [21]. A similar correlation between remanent polarization and α has also been observed.

Fig. 5 illustrates the capacitance–voltage curves for films obtained at 100 kHz and dc sweep voltage from +10 to –10 V. The capacitance dependence on voltage is strongly non-linear, confirming the ferroelectric properties of the film resulting from the domain switching. The curve for the film annealed at 700 °C for 2 h also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The curve is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film/electrode interface. For the films annealed at lower temperatures (600 and 650 °C) a slight change in capacitance values is observed, indicating the existence of charge carriers trapped near the electrode/film interface.

Fig. 6 shows the hysteresis loops measured from the thin films considered above. The measured remanent polarization and coercive field for the (1 1 7)-oriented film ($\alpha = 0.58$) are $23.7 \mu\text{C cm}^{-2}$ and 3.1 V, respectively, under a 14 V maximum applied field. As shown in the figure, both remanent polarization and coercive field decreases as α de-

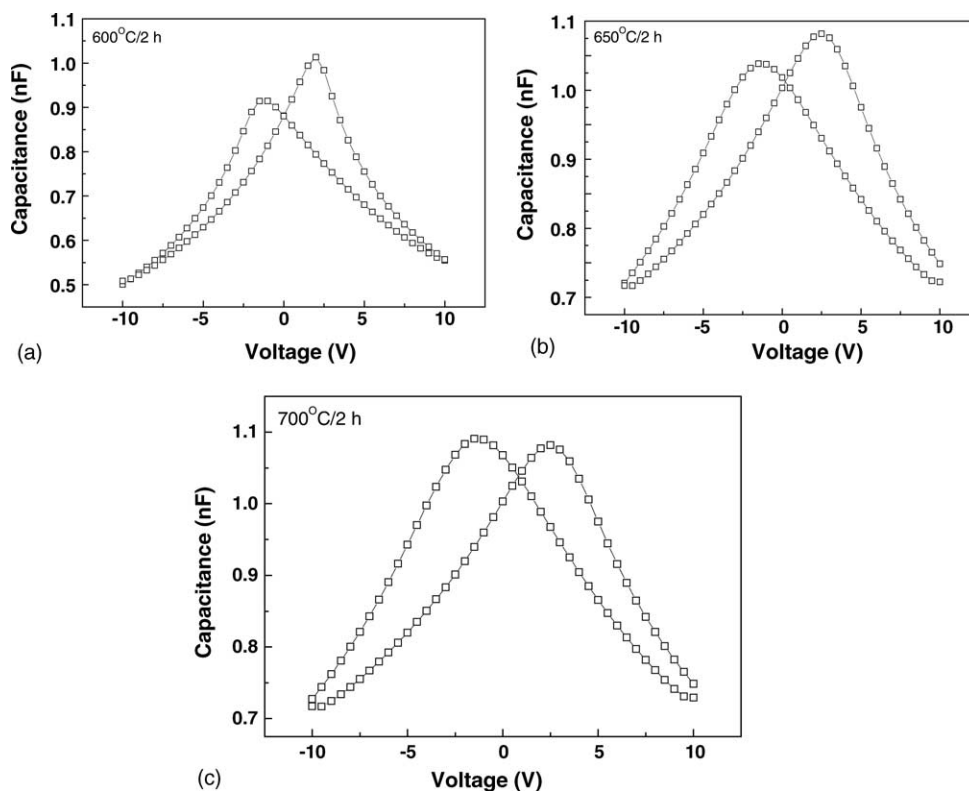


Fig. 5. Capacitance–voltage curves of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 °C, (b) 650 °C and (c) 600 °C.

creases. For the (0010)-oriented film ($\alpha = 0.38$), remanent polarization and coercive field is reduced to $12.8 \mu\text{C cm}^{-2}$ and 2.4 V. The higher remanent polarization and coercive field of (117)-oriented films are consistent to that reported for epitaxial $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films [22]. Nevertheless, the remanent polarization and coercive field for (0010)-oriented films highly exceed those for their epitaxial counterparts ($P_r = 1.1 \mu\text{C cm}^{-2}$). A plausible explanation for the difference is that the (0010)-oriented film obtained in this work still contains some (117)-oriented grains, as indicated by the non-zero value of α , which is, however, small 0.38.

The fatigue endurance of thin films as a function of switching cycles was examined by applying $8.6 \mu\text{s}$ wide bipolar pulses with a 10 mV amplitude (Fig. 7). In the figure, the switched polarization was calculated from the difference between switching and non-switching polarizations. For the films annealed at higher temperatures the switched polarization maintains without appreciable degradation to 10^{10} switching cycles. Only a small fatigue resistance was observed for films annealed at 600 °C for 2 h ($\alpha = 0.38$) due to the increase in local current caused by worst crystallinity, which eventually destroy the film/electrode

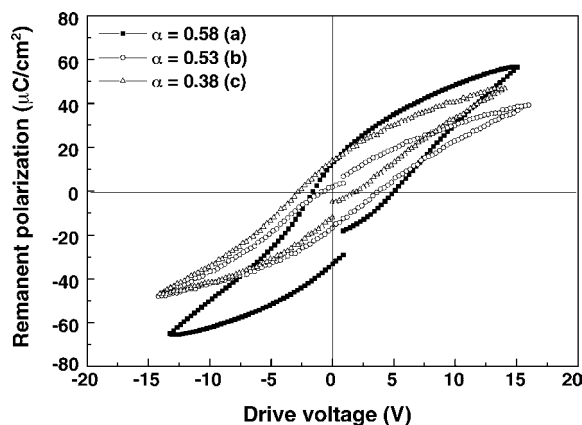


Fig. 6. Remanent polarization – drive voltage hysteresis loops of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 °C, (b) 650 °C and (c) 600 °C.

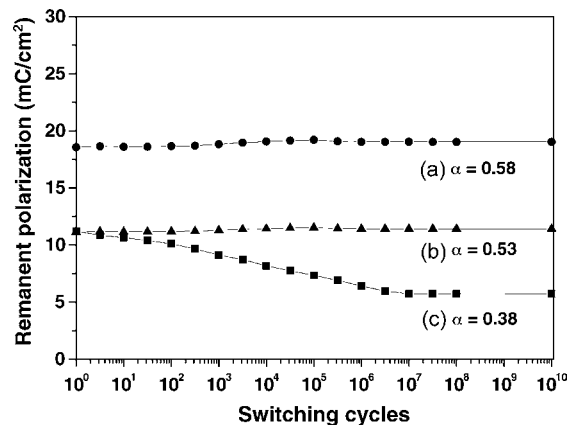


Fig. 7. Fatigue as a function of polarization cycles for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films annealed for 2 h at (a) 700 °C, (b) 650 °C and (c) 600 °C.

interface leading to a decrease in remanent polarization [23].

4. Conclusions

Dense bismuth titanate films on (1 1 1) Pt-coated silicon substrate were obtained through a polymeric precursor solution by the spin-coating technique. An increase in temperature of annealing has influence on the orientation degree of the bismuth titanate phase. The temperature and degree of orientation has a strong influence on the dielectric properties of the thin films. A more regularly shaped hysteresis loop is observed for films annealed at higher temperatures. A high fatigue resistance was observed for films annealed at 650 and 700 °C for 2 h.

Acknowledgements

The authors gratefully acknowledge the financial support from the Brazilian financing agencies FAPESP, CNPq and CAPES, and from the German Academic Exchange Service.

References

- [1] J.F. Scott, C.A. Paz de Araujo, *Science* 246 (1989) 1400.
- [2] R. Ramesh, J. Lee, T. Sands, V.G. Keramidas, O. Auciello, *Appl. Phys. Lett.* 64 (1995) 2511.
- [3] H.N. Al-Shareef, K.R. Bellur, A.I. Kingon, O. Auciello, *Appl. Phys. Lett.* 66 (1995) 239.
- [4] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. Mcmillan, M.C. Scott, J.F. Scott, *Nature (London)* 374 (1995) 627.
- [5] P.C. Joshi, S.B. Krupanidhi, A. Mansingh, *J. Appl. Phys.* 72 (1992) 5517.
- [6] S.E. Cummins, L.E. Cross, *J. Appl. Phys.* 39 (1968) 2268.
- [7] X. Du, I.-W. Chen, *J. Am. Ceram. Soc.* 81 (1998) 3253.
- [8] T. Kijima, M. Ushikubo, H. Matsunaga, *Jpn. J. Appl. Phys., Part 1* 38 (1999) 127.
- [9] A.D. Rae, J.G. Thompson, R.L. Withers, *Acta Crystallogr.* 48 (1992) 418.
- [10] A.D. Rae, J.G. Thompson, R.L. Withers, A.C. Willis, *Acta Crystallogr.* 46 (1990) 474.
- [11] H.N. Lee, D. Hesse, *Appl. Phys. Lett.* 80 (2002) 1040.
- [12] J. Zhang, R.A. Gardiner, P.S. Kirlin, R.W. Boerstler, J. Steinbeck, *Appl. Phys. Lett.* 61 (1992) 2884.
- [13] P.C. Joshi, A. Mansingh, *Appl. Phys. Lett.* 59 (1991) 2389.
- [14] M. Yamaguchi, K. Kawanabe, T. Nagamoto, O. Omoto, *Mater. Sci. Eng. B* 41 (1996) 138.
- [15] W.J. Takei, N.P. Formigoni, M.H. Framcobe, *Appl. Phys. Lett.* 15 (1969) 256.
- [16] N. Maffei, S.B. Krupanidhi, *Appl. Phys. Lett.* 60 (1992) 781.
- [17] T. Nakamura, R. Muhammet, M. Shimizu, T. Shiosaki, *Jpn. J. Appl. Phys.* 32 (1993) 4086.
- [18] H. Wang, L.W. Fu, S.X. Shang, *J. Appl. Phys.* 73 (1993) 7963.
- [19] J. Si, S.B. Desu, *J. Appl. Phys.* 73 (1993) 7910.
- [20] A.Z. Simões, A.H.M. Gonzalez, M. Cilense, M.A. Zaghet, B. Stojanovic, J.A. Varela, *Ceram. Int.* 28 (2002) 271.
- [21] S.K. Kim, M. Miyayama, H. Yanagida, *Mater. Res. Bull.* 31 (1996) 121.
- [22] J.J. Lee, C.L. Thio, S.B. Desu, *Phys. Status Solidi (a)* 151 (1995) 171.
- [23] D. Damjanovic, *Rep. Prog. Phys.* 61 (1998) 1267.

Characterization of lanthanum-doped bismuth titanate thin films prepared by polymeric precursor method

A.Z. Simões^{a,*}, C.S. Riccardi^a, F. Moura^a, A. Ries^a, N.L.A. Junior^a, M.A. Zaghete^a,
 B. Stojanovic^b, E. Longo^c, J.A. Varela^a

^aDepartment of Chemistry-Physics, Chemistry Institute, Universidade Estadual Paulista (UNESP) C.P. 355, Araraquara, SP, CEP 14801-970, Brazil

^bCenter for Multidisciplinary Studies, University of Belgrade, Belgrade, Yugoslavia

^cChemistry Department, Universidade Federal de São Carlos (UFSCAR), São Carlos, SP, CEP 13565-905, Brazil

Received 11 November 2003; received in revised form 19 April 2004; accepted 30 April 2004

Available online 20 June 2004

Abstract

Lanthanum-modified bismuth titanate, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT), with x ranging from 0 to 0.75 was grown on Pt/Ti/SiO₂/Si substrates using a polymeric precursor solution and spin-coating method. The dielectric constant of highly doped bismuth titanate was equal to 148 while dielectric losses remained low ($\tan \delta = 0.0018$), and the films showed well-saturated polarization-electric field curves ($2P_r = 40.6 \mu\text{C}/\text{cm}^2$ and $V_c = 0.99 \text{ V}$). The leakage current densities improve for the lanthanum-doped system. For five-layered BLT films with $x = 0.75$, a charge storage density of $35 \text{ fC}/\mu\text{m}^2$ and a thickness of 320 nm were found.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Dielectrics; Ferroelectrics; Thin films

1. Introduction

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) is a member of the ferroelectric, bismuth-layered perovskite structure family with a general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m-1})^{2-}$, where m represents an integer value, A is a relatively large divalent or trivalent cation, and B is a small, highly charged cation such as Ti^{+4} , Nb^{+5} , or Ta^{+5} . For BIT, the following values apply: $\text{A} = \text{Bi}$, $\text{B} = \text{Ti}$, and $m = 3$ [1]. This structure is composed of alternating stacked layers of bismuth oxide and bismuth titanate. The structure of bismuth titanate, first described by Aurivillius about 40 years ago and later by others [1], has a layered perovskite structure with the lattice constants $a = 5.4489 \text{ Å}$, $b = 5.4100 \text{ Å}$, and $c = 32.815 \text{ Å}$ when indexed to orthorhombic symmetry. Below the ferroelectric Curie temperature (675°C), there exists a spontaneous polarization vector in the b – c plane at an angle of 4.53° to the b -axis. As a result, strong anisotropic properties are observed. In bulk, BIT shows coercive field strengths of 3.5 and 50 kV/cm, spontaneous polarizations of 4 and $50 \mu\text{C}/\text{cm}^2$, and dielectric constant values of 130 and 160, along the c - and b -axis,

respectively [2]. For nonvolatile memories, ferroelectric thin films with a low coercive field are desirable. A low coercive field translates to a lower operating voltage, faster switching speed, and better fatigue resistance. Due to their anisotropic structure, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ epitaxial thin films can easily be grown with the [001] axis parallel to the film normal (perpendicular to the film plane), i.e., in the so-called c -axis orientation. However, c -axis-oriented bismuth-layered perovskite films have a small polarization component along the film normal because the vector of the principal spontaneous polarization in these layered perovskite materials is directed along the a -axis [3]. If the bismuth-layered perovskite material is to be used in a ferroelectric thin-film capacitor with electrodes on the top and bottom surfaces, as in the geometry used for dynamic random access memories, a normally oriented polarization component is essential. However, to grow a -axis-oriented films on silicon substrates required for memories is rather complicated. Therefore, the use of lattice-matched electrode materials that allow the retention of good film quality is required. For this purpose, MgO and Si substrates precoated with an electrode material such as Pt or Al have been attempted [4].

Several attempts to prepare BIT thin films are reported in the literature. Due to the high temperatures required for the

* Corresponding author. Tel.: +55-16-2016712; fax: +55-16-2227932.
 E-mail address: alezipo@yahoo.com (A.Z. Simões).

formation of the ferroelectric perovskite phase, the production of BIT thin films has not proven easy and, at present, a wide range of thin films synthesis techniques, such as MOCVD, sol-gel, RF magnetron, ion beam sputtering, and laser ablation, is subject to intensive research [5]. Nakamura et al. [6] deposited highly *c*-axis-oriented BIT thin films with a $\text{Bi}_2\text{Ti}_2\text{O}_7$ buffer layer on Pt/SiO₂/Si (100) by a MOCVD technique. Those films had a coercive field of 13 kV/cm and also a very low remnant polarization (0.6 $\mu\text{C}/\text{cm}^2$). Wang et al. [7] developed an atmospheric pressure MOCVD technique to prepare BIT thin films. These films exhibited high (100) orientation with high remnant polarization (38 $\mu\text{C}/\text{cm}^2$) and high coercive field (45 kV/cm). Si and Desu [8] fabricated randomly oriented BIT thin films at low temperature (550 °C) by hot-wall MOCVD. A remnant polarization of 19 $\mu\text{C}/\text{cm}^2$ and a high coercive field of 244 kV/cm were obtained. In previous works, our group had reported the preparation of thin films by the polymeric precursor method [9]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [10]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase.

Obviously, the substitution of bismuth by lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [11] prepared thin films of bismuth titanate doped with lanthanum (BLT) by pulsed laser deposition. The authors found that these films were appropriate for nonvolatile random access memory devices. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies (V_{Bi}''') accompanied by oxygen vacancies (V_{O}°). In order to minimize these defects, the substitution of Bi by La on A-site is required [12]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen vacancies acting as space charges. Recently, it has been reported that ferroelectric properties were improved by ion doping on A- or B- site [13]. Effects of ion doping on ferroelectric properties and electric conduction have been widely studied [14]. For practical FRAM applications, it is necessary to obtain BLT thin films with high remnant polarization and low leakage current. In this work, pure and lanthanum-doped bismuth titanate thin films were prepared by the polymeric precursor method. The effects of La doping on the ferroelectric and dielectric properties of BIT thin films were investigated.

2. Experimental procedure

Titanium isopropoxide (Hulls), hydrated lanthanum carbonate (Aldrich), and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium, and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under

heating and stirring. Appropriate quantities of solutions of Ti, Bi, and La were mixed and homogenized by stirring at 90 °C. The molar ratio of metal/citric acid/ethylene glycol was 1:4:16.

The viscosity of the resulting solution was adjusted to 20 cP controlling the water content using a Brookfield viscosimeter. From this solution, the films were deposited by the spin-coating technique on (111) Si/Ti/Pt substrates. A platinum layer (140 nm) was used as bottom electrode. The BLT films were then calcinated at 700 °C for 2 h in air resulting in a film thickness of approximately 300 nm. Next, a 0.5-mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C, in oxygen atmosphere for 1 h. Here, the desired effect is to diminish remaining oxygen vacancies.

In this work, an excess of 5 wt.% Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth, the pure phase could not be obtained. Phase analysis of the films were performed at room temperature by X-ray powder diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and $\text{CuK}\alpha$ radiation.

The thickness of the annealed films was examined using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. The thickness results obtained from SEM represent an average value of three measurements. The relative dielectric constant ϵ_r and the dissipation factor $\tan \delta$ were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). The capacitance–voltage characteristic was measured in the MFM configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). The leakage current–voltage (I – V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the collected XRD data of the BLT films with *x* ranging from 0 to 0.75. Only peaks of the main phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. The split of the (0100) and (200) peaks into two duplets indicates the change of crystal structure from the orthorhombic to the tetragonal system. Besides the BLT peaks, the characteristic peak for (111) platinum-coated silicon substrates at $2\theta = 40^\circ$ was identified. Comparing the peak intensities of the BLT pattern to some BLT literature [11], the highly doped sample

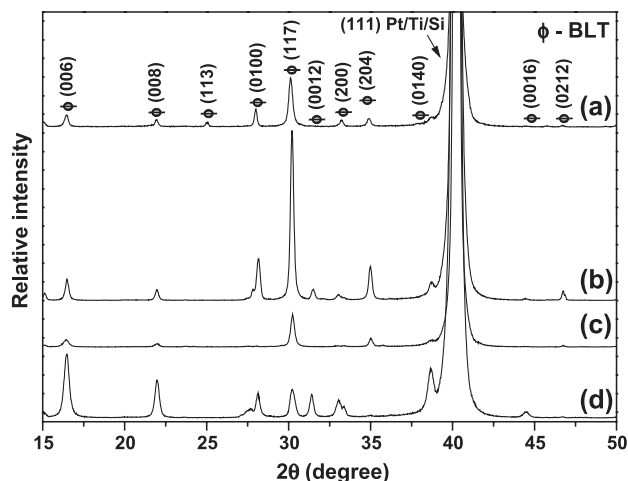


Fig. 1. X-ray diffraction data for BLT films deposited by the polymeric precursor method with different La contents: (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$; (d) $x=0.75$.

($x=0.75$) results in a preferred orientation at $2\theta=16^\circ$. This fact could be probably due to the change of the crystal system orthorhombic to tetragonal.

Fig. 2 shows a typical cross-section SEM micrograph of multilayer BLT ($x=0.75$) thin film deposited on Pt/Ti/SiO₂/Si substrates at 700 °C, in which the interface between the BLT layer and substrate can be very clearly seen. This figure shows a thin film with a 320-nm-thick multilayer structure.

The dielectric constant and the dissipation factor of the films are presented in Fig. 3. The dielectric measurements were carried out at room temperature as a function of frequency in the range from 10 kHz to 1 MHz. The annealed films exhibited good dielectric properties, a relative dielectric constant of 148, and a loss tangent ($\tan \delta$) of 1.8×10^{-3} , at 1 MHz. As it can be seen from Fig. 3, the dielectric constant shows very little dispersion with frequency indicating that the films possess low defect concentra-

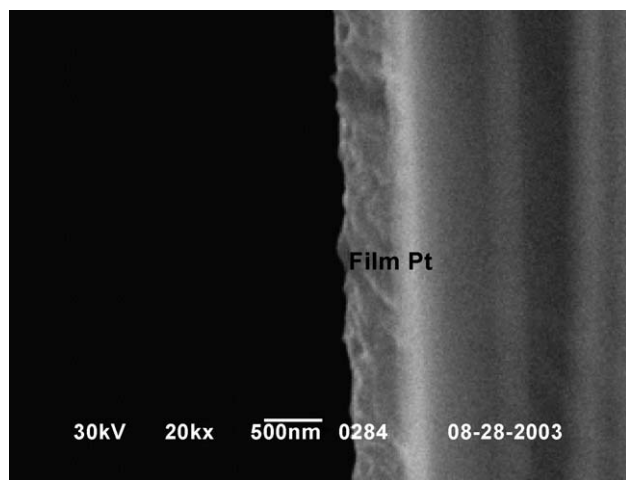


Fig. 2. SEM photograph of cross section for BLT film ($x=0.75$) deposited by the polymeric precursor method and annealed at 700 °C for 2 h.

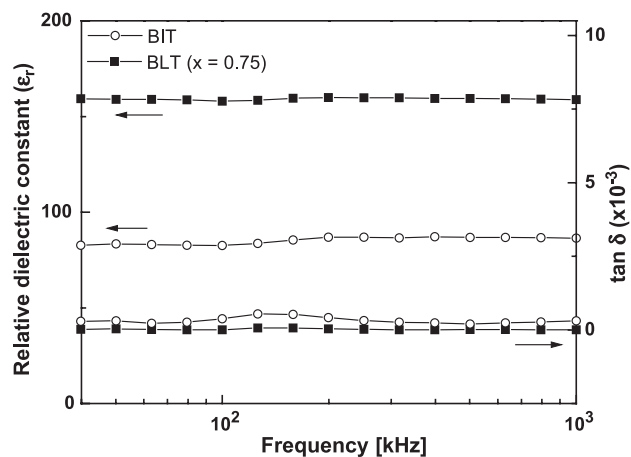


Fig. 3. Dielectric constant and loss tangent in dependence on frequency for BLT films deposited by the polymeric precursor method with the La contents: (a) $x=0$ and (b) $x=0.75$.

tions at the interface film substrate. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan \delta$ indicate that an interfacial polarization of the Maxwell Wagner type and an interfacial polarization arisen from the electrode barrier are negligible in the film. It was also observed that BLT films compared with BIT ($x=0$) possess a higher dielectric constant and a lower loss tangent indicating that lanthanum plays an important role in the electrical properties of the thin BIT layers [15]. Doping BIT with lanthanum has a strong influence on the dielectric constant of the material, even at low contents ($x=0.25$). When BLT films with $x=0.75$ were processed by polymeric precursor method, a large increase in dielectric constant was observed compared to the undoped sample. Ferroelectricity of the BIT and BLT thin films was investigated with a standardized ferroelectric tester and the results are presented in Fig. 4. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 10 V. The loops are fully saturated with a remnant polarization ranging from 15 to 22 $\mu\text{C}/\text{cm}^2$ and drive voltages from 0.66 to 1.45 V. The saturation of the loops at these low frequencies indicates that the losses are minimal, suggesting that the films are highly resistive. A more regularly shaped hysteresis loop is observed for films doped with lanthanum. It is observed that the addition of lanthanum until $x=0.75$ leads to films with preferred orientation which results in lower drive voltages to attain saturation in the hysteresis loops. It may also be seen from Fig. 4d that the remnant polarization was much higher than normally expected for a perfect c -axis-oriented single crystal and may be ascribed to the presence of a -axis polarization components, as also seen from the XRD data. However, such highly saturated loops have been reported for the first time for bismuth titanate thin films obtained by the polymeric precursor method. Further studies are in progress to gain an understanding of the relationship between process–structure–properties of the bismuth titanate thin films.

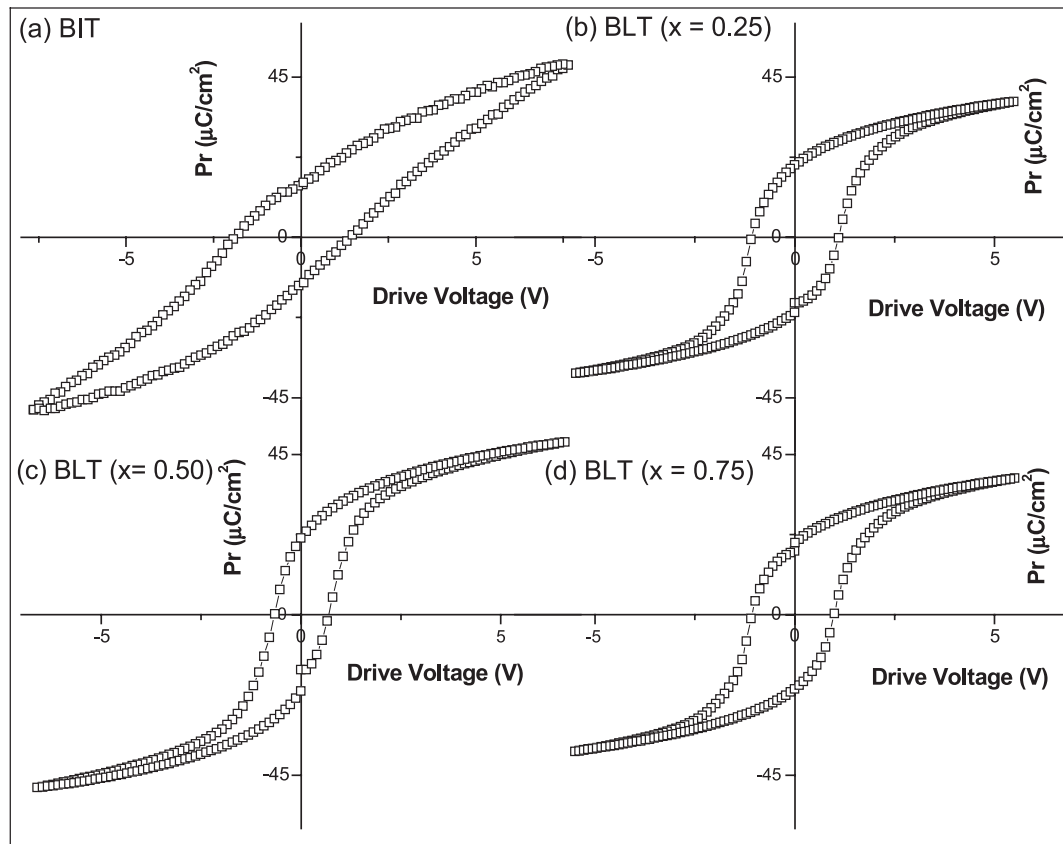


Fig. 4. P–E hysteresis loops for BLT films deposited by the polymeric precursor method with different La contents: (a) $x=0$; (b) $x=0.25$; (c) $x=0.50$; (d) $x=0.75$.

Fig. 5 illustrates the C–V curve for a highly doped BLT film ($x=0.75$) obtained at 100 kHz and DC sweep voltage from +10 to –10 V. The capacitance–voltage dependence is strongly nonlinear, confirming the ferroelectric properties of the film resulting from domain switching. The C–V curve is symmetric around the zero bias axis, indicating that the films contain only few movable ions or charge accumu-

lation at the film-electrode interface. Although the P–E hysteresis is saturated at ≥ 3 V, the C–V curve shows hystereses up to ± 10 V because both measurements were performed at different frequencies where the domain alignment is a time-dependent process and plays an important role in the switching behaviour of the domains. Therefore,

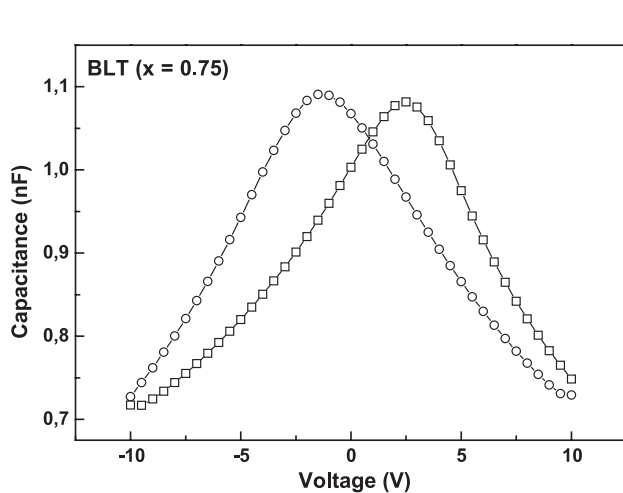


Fig. 5. C–V characteristics of BLT film deposited by the polymeric precursor method with the La content equal to 0.75.

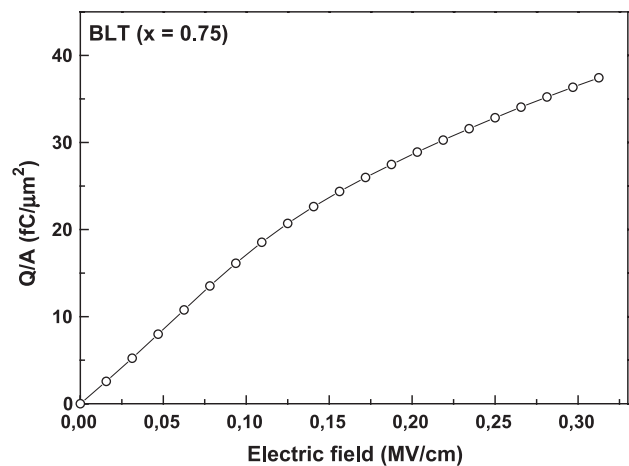


Fig. 6. Charge storage density versus applied electric field for BLT film deposited by the polymeric precursor method with the La content equal to 0.75.

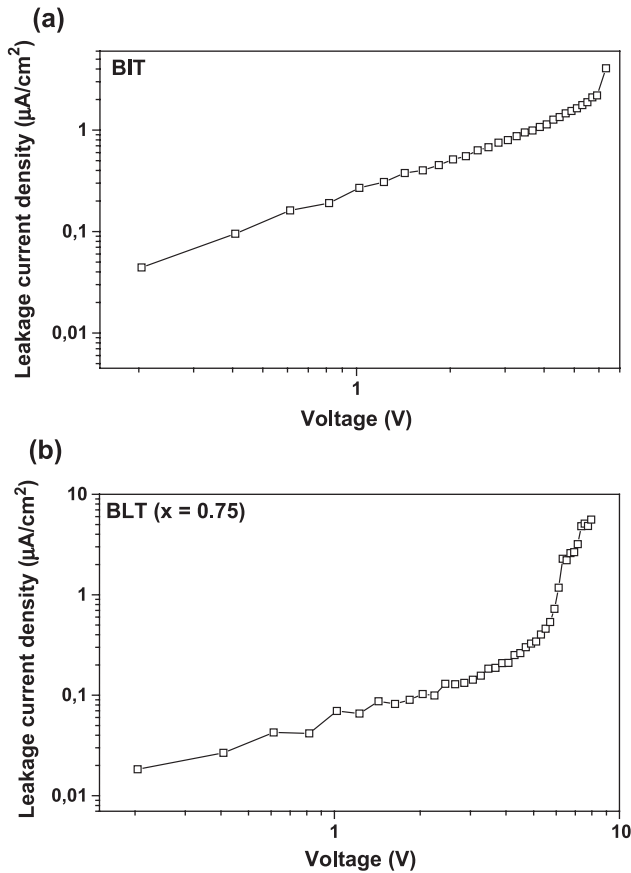


Fig. 7. Leakage current density versus applied electric field for BLT films deposited by the polymeric precursor method with the La contents: (a) $x=0$ and (b) $x=0.75$.

the sweep voltage ranges differ greatly (7 V) and consequently also the (dV/dt) voltage sweep per time unit leading to different domain alignment kinetics.

The charge storage densities were estimated from the C–V characteristics using the relationship $Q_c = \epsilon_0 \epsilon_r E$, where ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity, and E is the applied field. A practical DRAM capacitor requires a leakage current density (LCD) of 3 $\mu\text{A}/\text{cm}^2$ and a charge storage density of about 35 fC/ μm^2 [16]. From Fig. 6, it may be seen that this would be satisfied already at $E=0.27$ MV/cm.

A typical leakage current characteristic for BIT and highly doped BLT thin films is given in Fig. 7. The curves were recorded with a voltage step width of 0.1 V and

elapsed time of 1.0 s for each voltage; here, the measured logarithmic current density ($\log J$) versus the logarithmic electric field (E) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field strengths, the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V decreases from 0.27 to 0.069 $\mu\text{A}/\text{cm}^2$ when lanthanum is introduced to the system. There are some reasons for the improvement of leakage current with increasing lanthanum concentration. The first one is the reduction of the surface roughness with the increase of lanthanum concentration as shown in Table 1. Since the conductivity is strongly affected by the characteristics of the film-electrode interface, the surface morphology of BLT thin films is one of the major factors determining the leakage current in capacitors. Another explanation could be the reduction of microcracks caused by residual stress. Since the orthorhombic structure and phase transition temperature decrease with the increase in La concentration, the lattice volume change during cooling decreases and so residual stress decreases [17]. Madeswaran et al. [18] observed similar behaviour of pure BIT films prepared by sol-gel method with a leakage current density of 10^{-7} A/ cm^2 at an applied voltage of 1.0 V. In addition, Sedlar and Sayer [5] reported a leakage current density of 10 nA/ cm^2 at an electric field of 60 kV/cm for pure BIT thin films prepared by sol-gel method.

4. Conclusions

Dense lanthanum-doped bismuth titanate films were obtained on (111) platinum-coated silicon substrates through polymeric precursor solutions by a spin-coating technique. The films present good ferroelectric properties, e.g. a regularly shaped hysteresis loop ($2P_r=40.6$ $\mu\text{C}/\text{cm}^2$), a low coercive voltage ($V_c=1.0$ V), and low conductivity. Because of their high remnant polarization, BLT films with ($x=0.75$) are good candidates for FeRAM applications. The leakage current density is 0.27 $\mu\text{A}/\text{cm}^2$ for the BIT thin film and 0.069 $\mu\text{A}/\text{cm}^2$ for the highly doped BLT at 1.0 V. The leakage current density of BLT thin films suddenly increases when higher electric fields are applied. The La^{+3} substitu-

Table 1
Electric properties of BLT thin films obtained by the polymeric precursor method

BLT	P_r ($\mu\text{C}/\text{cm}^2$)	V_c (V)	ϵ (1 MHz)	$\tan \delta$ (1 MHz)	Roughness (nm)	Grain size (nm) $\pm 1\%$
$x=0$	15.1	1.45	86	0.008	17.3	179
$x=0.25$	20.2	1.09	104	0.0011	13.7	188
$x=0.50$	20.2	0.66	112	0.0068	11.4	208
$x=0.75$	20.3	0.99	148	0.0018	7.8	141

tion for Bi^{+3} is an effective way to reduce Bi vacancies which are accompanied by oxygen vacancies. From the electric field dependence of the leakage current, space charge limited currents can be dominant on BIT/Pt junction.

Acknowledgements

Financial support from the Brazilian agencies FAPESP, CNPq, CAPES, and from the German Academic Exchange Service (DAAD) is gratefully acknowledged.

References

- [1] R.E. Newnham, R.W. Wolf, J.F. Dorrian, *Mater. Res. Bull.* 6 (1971) 1029.
- [2] S.E. Cummins, L.E. Cross, *J. Appl. Phys.* 39 (1968) 2268.
- [3] H.N. Lee, D. Hesse, N. Zakharov, S.K. Lee, U. Gosele, *J. Appl. Phys.* 93 (2003) 5592.
- [4] R.C. Buchanan, *Proceedings of the International Conference on Electronic Ceramics and Applications*, Kluwer, Aveiro, Portugal, 1996, p. 309.
- [5] M. Sedlar, M. Sayer, *Ceram. Int.* 22 (1996) 241.
- [6] T. Nakamura, R. Muhammet, M. Shimizu, T. Shiosaki, *Jpn. J. Appl. Phys.* 32 (1993) 4086.
- [7] H. Wang, L.W. Fu, S.X. Shang, *J. Appl. Phys.* 73 (1993) 7693.
- [8] J. Si, S.B. Desu, *J. Appl. Phys.* 73 (1993) 7910.
- [9] A.Z. Simões, A.H.M. Gonzalez, M.A. Zaghete, B. Stojanovic, A.A. Cavaleiro, P. Moeckli, N. Setter, J.A. Varela, *Ferroelectrics* 271 (2002) 33.
- [10] S.M. Zanetti, E.B. Araújo, E.R. Leite, E. Longo, J.A. Varela, *Mater. Lett.* 40 (1999) 33.
- [11] S.D. Bu, B.S. Kang, B.H. Park, *J. Korean Phys. Soc.* 36 (2000) L9–L12.
- [12] B.H. Park, B.S. Kang, S.D. Bu, W. Jo, *Nature* 401 (1999) 682.
- [13] A.Q. Jiang, Z.X. Hu, L.D. Zhang, *Appl. Phys. Lett.* 74 (1999) 114.
- [14] Y.P. Wang, W.I. Lee, T.Y. Tseng, *Appl. Phys. Lett.* 69 (1996) 1807.
- [15] J.P. Kim, Y.S. Yang, S.H. Lee, H.J. Joo, M.S. Jang, *J. Korean Phys. Soc.* 35 (1999) 202.
- [16] D. Roy, C.J. Peng, S.B. Krupanidhi, *Appl. Phys. Lett.* 60 (1992) 2478.
- [17] T. Takenaka, K. Sakata, *Ferroelectrics* 38 (1981) 769.
- [18] S. Madeswaran, N.V. Giridharan, R. Jayavel, *Mater. Chem. Phys.* 80 (2003) 23.

The influence of crystallization route on the properties of lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films prepared from polymeric precursors

A.Z. Simões^{a,*}, C.S. Riccardi^a, C. Quinelato^a, A. Ries^a, E. Longo^b, J.A. Varela^a

^a Chemistry Institute, Universidade Estadual Paulista, UNESP—Araraquara, Brazil CEP—14801-970 SP, Brazil

^b Department of Chemistry, Universidade Federal de São Carlos, UFSCar—São Carlos, Brazil CEP—13565-905 SP, Brazil

Received 25 December 2003; accepted 3 August 2004

Abstract

Pure and lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films were deposited on Pt/Ti/SiO₂/Si substrate using a polymeric precursor solution. The spin-coated films were specular and crack-free and crystalline after annealing at 700 °C for 2 h. Crystallinity and morphological evaluation were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Multilayered films obtained using the intermediate-crystalline layer route present a dense microstructure with spherical grains. Films obtained using the intermediate-amorphous layer, present elongated grains around 250 nm in size. The dielectric and ferroelectric properties of the lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films are strongly affected by the crystallization route. The hysteresis loops are fully saturated with a remnant polarization and drive voltage of the films, heat-treated by the intermediate-crystalline ($P_r = 20.2 \mu\text{C}/\text{cm}^2$ and $V = 1.35 \text{ V}$) and for the film heat-treated by amorphous route ($P_r = 22.4 \mu\text{C}/\text{cm}^2$ and $V = 2.99 \text{ V}$).

© 2004 Elsevier B.V. All rights reserved.

Keywords: Ceramics; Electrical measurements; Film deposition; Thin films

1. Introduction

Ferroelectric switching fatigue, which is the loss of switchable polarization by repeated polarization reversals, is one of the most common and important degradation processes in ferroelectric materials [1]. Because of the fatigue-free behavior of lanthanum-substituted bismuth titanate [$\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT)], a bi-layered perovskite oxide with a platinum electrode has received increasing attention in ferroelectric applications, such as in nonvolatile memory [2,3]. Compared with another well known fatigue-free ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) which is also a bi-layered perovskite oxide, BLT has many attractive properties: low processing temperature and large values of remnant polarization. But pure bismuth titanate [$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT)] is prone to fatigue. Two reasons for the fatigue-free behavior

of BLT have been found. One is the charge-compensating role of the (Bi_2O_2) layers. Another is the chemical stability of the perovskite layers against oxygen vacancies after substituting some La atoms for Bi atoms, since the oxygen ions near Bi ions in BIT are likely to be less stable than those near Sr ions in SBT due to the high bismuth oxide volatility [3–5].

Obviously, the substitution of bismuth by lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [6] prepared thin films of BIT doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for non-volatile random access memory devices. It is known that BIT compounds have a high leakage current and domain pinning due to defects such as Bi vacancies (V_{Bi}) accompanied by oxygen vacancies (V_{O}). In order to minimize these defects, the substitution of Bi by La ion on A-site is required [7]. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress the A-site vacancies which are accompanied by oxygen

* Corresponding author. Fax: +55 16 22 7932.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

vacancies that act as space charges. It has been reported that ferroelectric properties were improved by ion doping on A- or B-site [8]. Recently, effects of ion doping on ferroelectric properties and electrical conduction have been widely studied [9]. For practical FRAM application, it is necessary to obtain BLT thin film with high remnant polarization and low leakage current.

Several thermal treatments can be used to crystallize thin films obtained by chemical methods such as: rapid thermal annealing, microwave furnace and conventional furnace. In a conventional furnace, two types of thermal treatment can be performed. The first one consists of decomposing the organic material at low temperatures (usually 400 °C) and crystallizing the film at high temperatures. Those steps are repeated until the desired thickness is obtained (this route is called “intermediate-crystalline layer”). In the second route, all organic materials are decomposed (usually 400 °C) until the desired thickness is obtained and then all layers are crystallized in a single high-temperature process (called “intermediate-amorphous layer”).

The crystallization route was found to affect the microstructure of the films [10]. It is well known that films treated by the intermediate-crystalline layer route consists of relatively small number of grains and a microstructure with isolated perovskite grains of uniform size [11,12]. This route favours a higher nucleation rate leading to a higher number of crystalline nuclei. As a consequence, the grain growth decreases leading to a fine grain microstructure. In the case of the film heat-treated by intermediate-amorphous layer route, the nucleation rate may be lower, promoting a lower number of crystallization sites (nuclei) leading to increased grain growth. One possible explanation for the increase in the grain size for the different crystallization routes can be the thermal history of the first layer. A nucleus formed on the thermal treatment of the first layer can grow during the treatment of the next layers. So, the crystallization of the film changes, leading to an increase in the grain size. Basically in this case, the nucleation starts from the film surface [13].

Several attempts to prepare BIT thin films are reported in the literature. Due to the high temperatures required for the formation of the ferroelectric perovskite phase, the production of BIT thin film has not proved easy and, at present, a wide range of thin film synthesis techniques, such as MOCVD, sol–gel, rf magnetron, ion beam sputtering, and laser ablation are subjected to intensive research [14–18]. Nakamura [19] deposited highly *c*-axis oriented BTO thin films with a $\text{Bi}_2\text{Ti}_2\text{O}_7$ buffer layer on Pt/SiO₂/Si (100) by MOCVD technique. The film had a coercive field of 13 kV/cm and also very low remnant polarization (0.6 $\mu\text{C}/\text{cm}^2$). Wang [20] developed an atmospheric pressure MOCVD technique to prepare BTO thin films. These films exhibited high (100) orientation with high remnant polarization (38 $\mu\text{C}/\text{cm}^2$) and high coercive field (45 kV/cm). Si and Desu [21] fabricated randomly oriented BIT thin films at low temperature (550 °C) by hot-wall MOCVD. A remnant polar-

ization of 19 $\mu\text{C}/\text{cm}^2$ and a high coercive field of 244 kV/cm were obtained. In previous works, our group had reported the preparation of thin films by the polymeric precursor method [22]. The overall process consists of preparing a coating solution based on metal citrate polymerization. The precursor film is deposited by dip or spin coating and then thermally treated to eliminate the organic material and synthesize the desired phase.

In this work, pure and La-doped BIT thin films were prepared by the polymeric precursor method. The effects of crystallization route on the ferroelectric and dielectric properties of BIT thin films were investigated.

2. Experimental procedure

2.1. BIT and BLT deposition solutions

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter.

2.2. Preparation of BIT and BLT films

Films were spin-coated from $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0$ —BIT) and $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0.25, 0.50$ and 0.75 —BLT) deposition solution onto Pt/Ti/SiO₂/Si substrate. From a previous paper, BLT films were completely crystallized at 700 °C for 2 h, so this was the temperature at which films were heat-treated [23]. Multilayered films were obtained by spinning five times the deposition solution on the surface of the platinum-coated silicon substrate previously cleaned in Extran solution and ethanol. Two sets of multilayered films were heat-treated by two different routes. Route A, films were heat-treated at 400 °C for 2 h with heating rate of 3 °C/min in a conventional furnace and spun again, until the desired number of layers was reached. Each layer was amorphous and all layers were crystallized at 700 °C for 2 h at the same time. Route B, each layer was heat-treated at 400 °C for 2 h with heating rate of 3 °C/min in a conventional furnace and immediately crystallized at 700 °C for 2 h, before the next one. Hereafter, this procedure will be called the intermediate-crystalline layer route. All films were heat-treated in static air. Fig. 1 illustrates the procedure. In this work, an excess of 5 wt.% Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth, the pure phase could not be obtained as

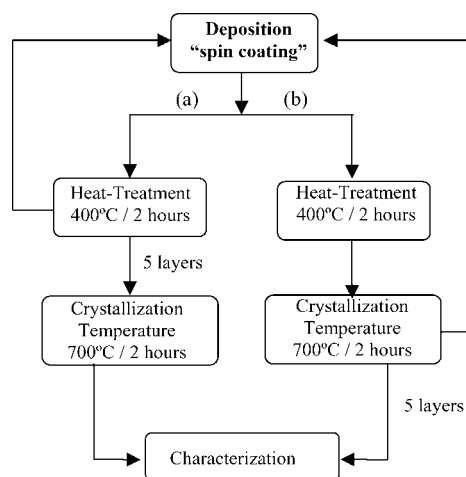


Fig. 1. Flow chart of the thin film preparation process by the polymeric precursor method.

reported in literature [24]. Phase analysis of the films was performed at room temperature by X-ray diffraction, using a Bragg–Brentano diffractometer (Rigaku, 2000) and Cu K α radiation. The morphology of the annealed films was studied using scanning electron microscopy (Topcon SM-300). The BLT film surfaces were analyzed without any cover or special preparation and with incidence of secondary electrons detection while the thickness were measured from the transversal section. In this case back-scattering electrons were utilized. The thickness results obtained from SEM represent an average value of three measurements. Surface roughness (rms) was examined by AFM, using tapping mode technique. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C with constant heating rate of 1 °C/min, in oxygen atmosphere for 1 h. Here, the desired effect is to decrease eventually present oxygen vacancies.

The relative dielectric constant ϵ_r and dissipation factor $\tan \delta$ were measured versus frequency using an impedance analyser (model 4192 A, Hewlett-Packard). The capacitance–voltage characteristic was measured in the MFM configuration using a small ac signal of 10 mV at 100 KHz. The ac signal was applied across the sample, while the dc was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). The leakage current–voltage (I – V) characteristic was determined with a voltage source-measuring unit (Radiant Technology 6000 A). All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6- μ s-wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

Fig. 2a and b show the collected XRD data of the BLT films heat-treated for both routes. Independent of the used route, only peaks of the BLT phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. Besides the BLT peaks, the characteristic peak for (1 1 1) platinum-coated silicon substrates at $2\theta = 40^\circ$ was identified. Independently of lanthanum content, films obtained by the route A (Fig. 2a) are polycrystalline. In contrast, for the route B, the increase in lanthanum content leads to preferential orientation in the (0 0 6) direction (Fig. 2b–d). Considering that the thickness of the film obtained by the intermediate-crystalline layer route is lower when compared with the film obtained by the intermediate-amorphous layer, the appearance of preferential orientation due to interface nucleation was observed [12]. In the interface nucleation the crystallization process starts from the surface of substrate which possess oriented planes with lower energy for the crystallization of BLT phase. In contrast, for route A, the higher thickness may give rise to other phenomena, like surface nucleation originating a polycrystalline film.

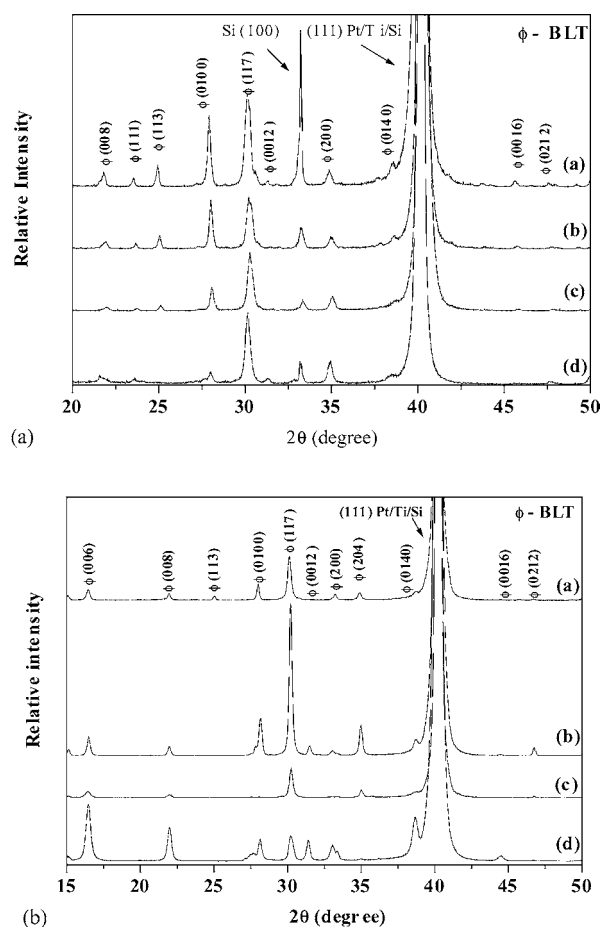


Fig. 2. X-ray diffraction for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films heat-treated by route A [a] and route B [b], respectively: (a) $x = 0$; (b) $x = 0.25$; (c) $x = 0.5$; and (d) $x = 0.75$.

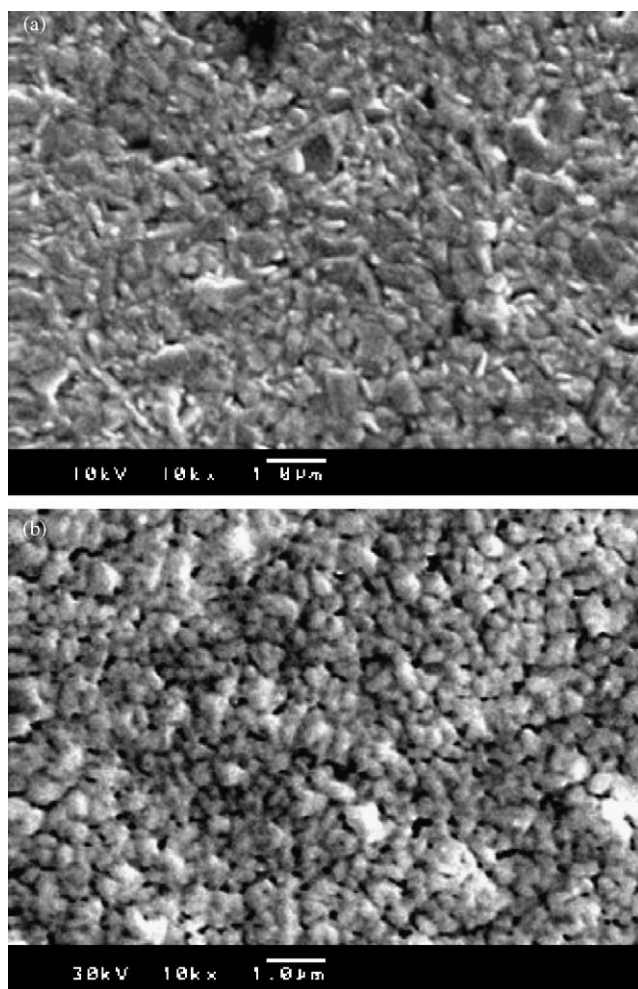


Fig. 3. SEM photographs for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) and heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

Fig. 3 presents the SEM micrographs of the $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) heat-treated by different routes. Here, the lanthanum content ($x = 0.5$) was random chosen in order to verify the effect of the crystalline route on the structural, morphological and electrical properties of the BLT thin films. The average grain sizes obtained from SEM represent an average value of several measurements performed in the length and width of each single grain. A strongly marked difference in the film microstructure can be observed for the different crystallization routes used for heat-treating the films. The film heat-treated by route B presents a dense and granular microstructure, with spherical grains around 200 nm in size. The absence of cracks and fissures indicates that the film presents a uniform microstructure. For the route A (Fig. 3a) a dense and granular microstructure is maintained, although the grains become elongated (250 nm in size). The difference in the shape of the grains is related to the amount of material deposited on the substrate surface to crystallize the films. Considering that the films treated by the intermediate-crystalline layer route, possess less material to be crystal-

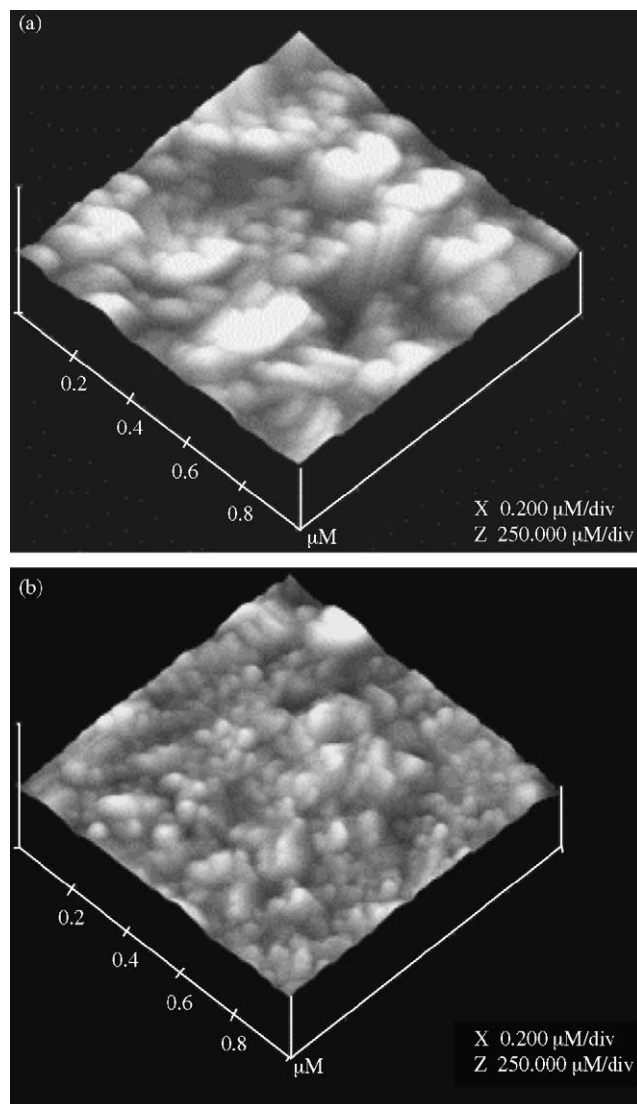


Fig. 4. AFM images for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

lized layer by layer, the grains tend to assume the more energetic favourable form (rounded). Meanwhile, the films treated by the intermediate-amorphous layer route possess a large amount of material to be crystallized in a single -step process leading to a less energetic favourable form (elongated grains).

Fig. 4 shows a typical surface morphology of the film heat-treated by both routes. The roughness measured is about 11 nm. These results are better compared to polycrystalline films obtained by chemical methods (about 17 nm) and similar to that obtained by physical method (nearly 9 nm) [25,26]. Table 1 presents the average grain size and roughness values for films heat-treated by both routes. The results presented show that different crystallization routes lead to films with different microstructures. The films crystallized using the route A presents a typical bismuth layer perovskite structure. As reported, for films with good ferroelectric properties

Table 1

Data obtained for BLT films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer

$\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0.5$)	P_r ($\mu\text{C}/\text{cm}^2$)	V_c (V)	ε (1 MHz)	$\tan \delta$ (1 MHz)	Roughness (nm)	Thickness (nm)	Average grain size (nm) $\pm 1\%$
Amorphous	22.4	2.99	112	0.024	11.6	453	250
Crystalline	20.2	1.35	112	0.024	11.4	418	208

the grain size was around 250 nm with elongated shape [27]. On the other hand, the films crystallized using the route B presented spherical grains around 200 nm in size. Considering both crystallization routes, the route B seems to favour a higher nucleation rate, leading to a higher number of crystalline nuclei. Each intermediate-crystalline BIT layer acts like a nucleation seed to the next layer to be crystallized. In the case of route A, the nucleation rate may be lower, promoting a lower number of crystallization nuclei, leading to an increase in the grain growth and resulting in a bigger grain microstructure. Basically, the nucleation occurs in the film surface and in the film–substrate interface.

The dielectric constant and dissipation factor of the films are presented in Fig. 5. The dielectric measurements were carried out at room temperature as a function of frequency

in the range of 10 kHz–1 MHz. As shown in Fig. 5, the dielectric constant shows very little dispersion with frequency indicating that our films possess low defect concentrations at the film–substrate interface. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan \delta$ indicate that both, interfacial polarization of the Maxwell–Wagner type and a polarization produced by the electrode barrier can be neglected in the film. It was also observed that the films treated by different routes lead to the identical dielectric properties. This result is not surprising because although the film heat-treated by the intermediate-crystalline layer route present a rounded grains morphology, the magnitude of the grain is comparable with the films heat-treated by the intermediate-amorphous layer route leading to identical dielectric constants. Therefore, to obtain higher dielectric properties a-oriented films are desired. Our results of ε are consistent with the crystallographic and microstructural data.

The I – V measurements were taken using the radiant technology tester in the current–voltage mode, with the voltage changing from 0 to +10 V, from +10 to –10 V, and back to 0 V. Fig. 6 shows the I – V curves for the BIT films heat-treated by different routes. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanisms. The leakage current density at 1.0 V decreases from 5.6×10^{-7} to 2.7×10^{-7} A/cm² when the intermediate-amorphous layer route is used to heat-treat the films. The lower leakage current observed for the film heat-treated by intermediate-amorphous layer might be attributed to probable differences in grain size, density, and surface structure due to differences in crystallization procedures. The characteristics of the film–electrode interface and the surface morphology of BLT thin films are the major factors determining the leakage current of capacitors in metal–ferroelectric–metal configuration. Giridharan et al. [28] observed similar behaviour to BIT films prepared by sol–gel method with leakage current density of 10^{-7} A/cm² at an applied voltage of 1.0 V. In addition, M. Sedlar [29] reported leakage current density of 10 nA/cm² at an electric field of 60 kV/cm for BIT thin films prepared by sol–gel method.

Fig. 7 illustrates the C – V curves for BLT films obtained at 100 KHz and dc sweep voltage from +10 to –10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting

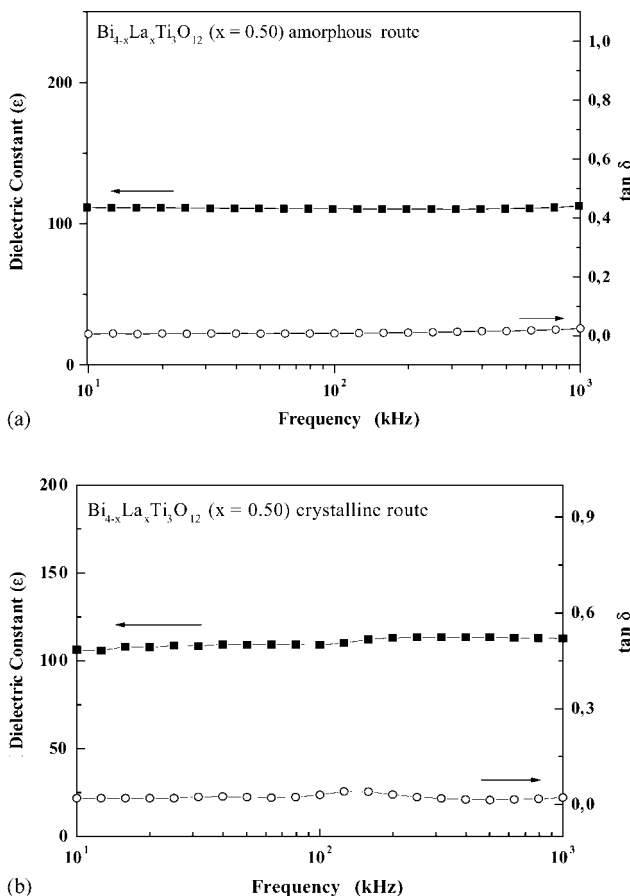


Fig. 5. Dielectric constant and loss tangent in dependence of frequency for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

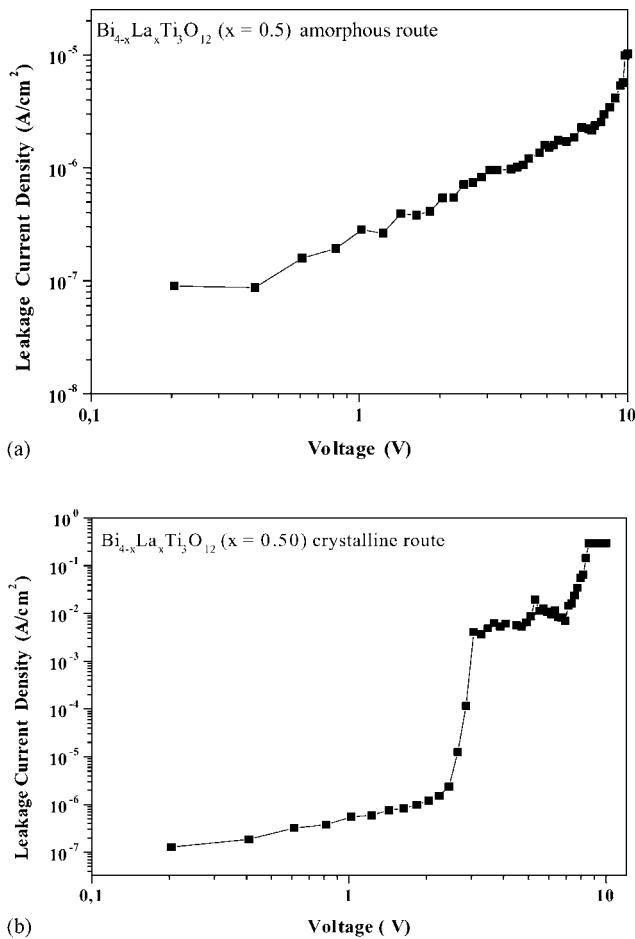


Fig. 6. Leakage current density in dependence of voltage for Bi_{4-x}La_xTi₃O₁₂ films (x = 0.5) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

from the domain switching. The *C*–*V* curve for the film heat-treated by the intermediate-crystalline layer also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The *C*–*V* curve is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film–electrode interface. For the film heat-treated by the intermediate-amorphous layer a slight change in capacitance values is observed indicating that charge carriers exist, trapped near the electrode–film interface.

Ferroelectricity in the BLT thin films was performed with a standardized ferroelectric tester and the results are presented in Fig. 8. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 10 V. The loops are fully saturated with a remnant polarization of the films ranging from 20 to 22 μC/cm² and drive voltages from 1.35 to 3.0 V. The saturation of the loops at these low frequencies indicates that the losses are minimal, suggesting that the films are highly resistive. A more regularly shaped hysteresis loop is observed for films heat-treated by the intermediate-crystalline layer. It is observed that the

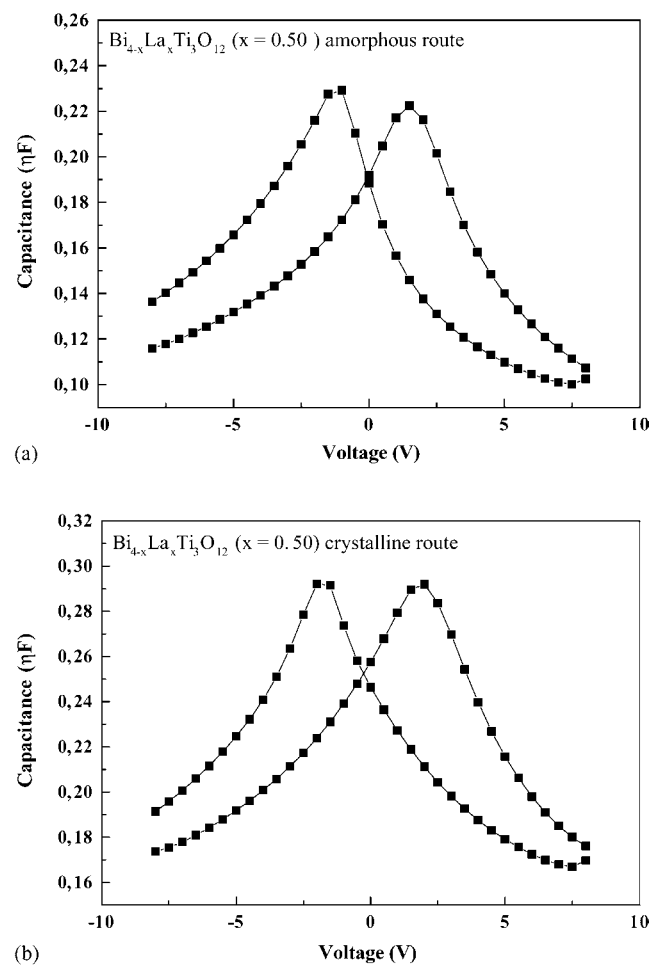


Fig. 7. *C*–*V* curves for Bi_{4-x}La_xTi₃O₁₂ films (x = 0.5) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

intermediate-crystalline layer leads to films with preferred orientation which results in lower drive voltages to attain saturation in polarization hysteresis. It may also be seen from Fig. 7a, that the remnant polarization was much higher than normally expected for a perfect *c*-axis oriented single crystal and may be ascribed to the presence of *a*-axis polarization components, as also seen from the XRD data. Compared to literature data, our results are similar to those published by Lee et al. [30]. The authors showed the fabrication of high-quality films of bismuth lanthanum titanate prepared by chemical synthesis method and their applications in handsets, smart phones and smart cards. It should also be noted that the hysteresis loop of the film heat-treated by amorphous route shows an appreciable shift along the electric field axis towards the positive side, which is defined as imprint. The voltage shifts may lead to a failure of the capacitor due to the apparent loss of polarization in one of the remnant states. Consequently, an increase in the coercive voltage in one direction occurs. These two effects may cause a memory failure. These results are consistent with the *C*–*V* measurements.

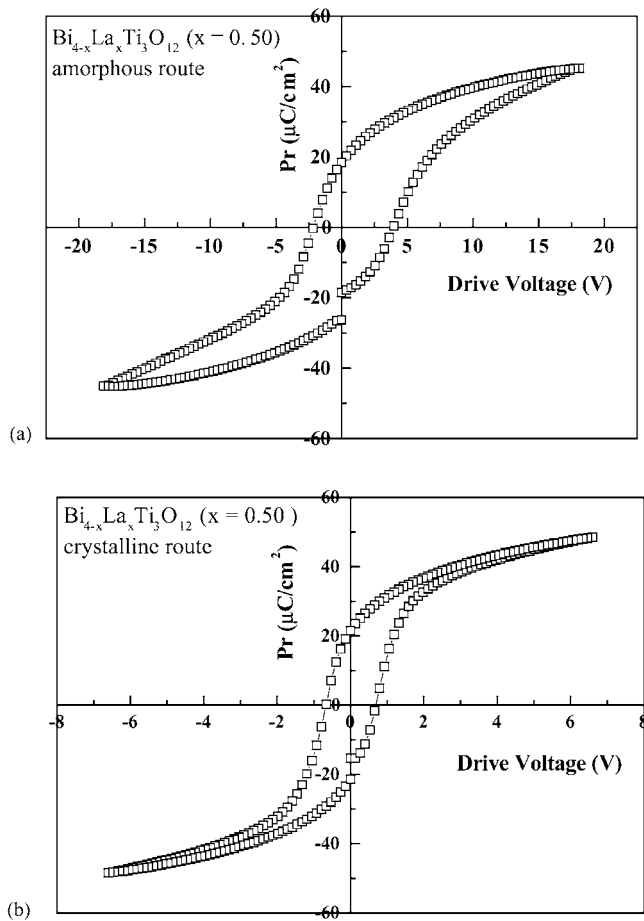


Fig. 8. P–E hysteresis loop for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

The fatigue endurance of BLT thin films, as a function of switching cycles was examined by applying 8.6- μs -wide bipolar pulses with a 10 mV amplitude (Fig. 9). Fatigue resistance was observed up to 10^{10} cycles, independent of the route used. B.H. Park et al. also verified the fatigue characteristics of BLT films deposited on platinum-coated silicon substrates. They observed that the values of $(P_{\text{sw}} - P_{\text{ns}})$ do not change significantly during the fatigue test indicating that the BLT films have good fatigue resistance [7]. Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion, which has a lone pair of 6s electrons, less hybridization with O 2p should lead to less structural distortion favouring the improvement in its properties [31]. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BIT thin films. However, it is not yet clear whether La changes the chemical environment of the perovskite layers. It is quite possible that the La substitution will enter the $(\text{Bi}_2\text{O}_2)^{2+}$ layers, since the sizes of Bi^{3+} and La^{3+} ions are quite similar. In order to understand all the phenomena involved on the fatigue behaviour of BLT thin films, new tests should be accomplished in future.

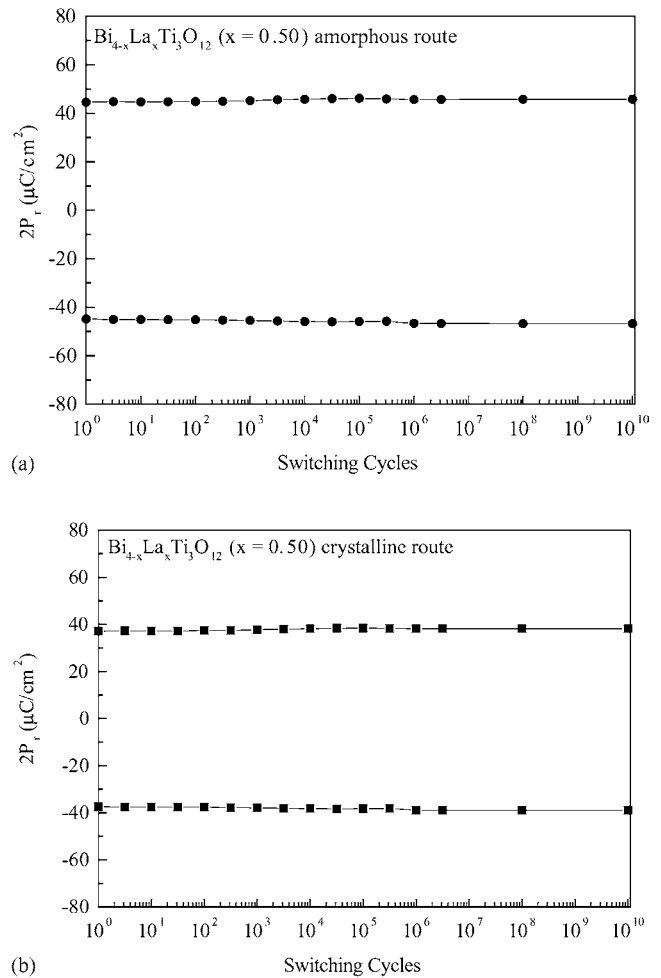


Fig. 9. Fatigue as a function of polarization cycles for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x = 0.5$) heat-treated by: (a) intermediate-amorphous layer and (b) intermediate-crystalline layer.

4. Conclusion

Independent of the route used to obtain the films, dense lanthanum-doped bismuth titanate films on (1 1 1) platinum-coated silicon substrate were obtained through polymeric precursors solution by a spin-coating technique. An evident difference in the shape of the grains was noted when the films were prepared by the intermediate-amorphous layer route. The dielectric properties of the films were independent of the crystallization route. The C – V measurements of the BLT films in metal–ferroelectric–metal configuration presented two peaks ascribed to ferroelectric domain switching. From the electric field dependence of the leakage current, space charge limited currents can be dominant on BLT/Pt junction. Because of their high remnant polarization and low drive voltage, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x = 0.5$) are good candidates for FeRAMs applications. No fatigue behaviour was verified in both cases, which proves that our films possess enough quality to be used in non-volatile random access memories. However, due to the imprint phenomenon, the films obtained by the intermediate-amorphous layer are unsuitable for memory

applications as a consequence of the substantial difference between $+V_c$ and $-V_c$.

Acknowledgments

The authors gratefully acknowledge the financial support from the Brazilian financing agencies FAPESP, CNPq, CAPES and from the German Academic Exchange Service.

References

- [1] W.L. Warren, B.A. Tuttle, D. Dimos, Appl. Phys. Lett. 67 (1995) 1426–1428.
- [2] J.F. Scott, C.A. Paz de Araujo, Science 246 (1989) 1400–1405.
- [3] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Nature 401 (1999) 682–684.
- [4] B.H. Park, S.J. Hyun, S.D. Bu, T.W. Noh, J. Lee, H.-D. Kim, T.H. Kim, W. Jo, Appl. Phys. Lett. (1999) 74.
- [5] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, Nature 374 (1995) 627–629.
- [6] S.D. Bu, B.S. Kang, B.H. Park, T.W. Noh, J. Korean Phys. Soc. 36 (2000) L9–L12.
- [7] B.H. Park, B.S. Kang, S.D. Bu, W. Jo, Nature 401 (1999) 682–684.
- [8] A.Q. Jiang, Z.X. Hu, L.D. Zhang, Appl. Phys. Lett. 74 (1999) 114–116.
- [9] Y.P. Wang, W.I. Lee, T.Y. Tseng, Appl. Phys. Lett. 69 (1996) 1807–1809.
- [10] Z.B. Xiao, X.M. Wu, H. Wang, Z. Wang, S.X. Shan, M.W. Mater. Lett. 51 (2001) 240–244.
- [11] S.M. Zanetti, E.R. Leite, E. Longo, J.A. Varela, J. Mater. Res. 14 (1999) 1026–1031.
- [12] C.K. Kwok, S.D. Desu, J. Mater. Res. 8 (1993) 339–344.
- [13] S.M. Zanetti, E.R. Leite, E.B. Araújo, A.J. Chiquito, J.A. Eiras, E. Longo, J.A. Varela, J. Mater. Res. 15 (2000) 2091–2095.
- [14] J. Zhang, R.A. Gardiner, P.S. Kirlin, R.W. Boerstler, J. Steinbeck, Appl. Phys. Lett. 61 (1992) 2884–2886.
- [15] P.C. Joshi, A. Mansing, Appl. Phys. Lett. 59 (1991) 2389–2391.
- [16] M. Yamaguchi, K. Kawanabe, T. Nagamoto, O. Omoto, Mater. Sci. Eng. B 41 (1996) 138–142.
- [17] W.J. Takei, N.P. Formigoni, M.H. Framcobe, Appl. Phys. Lett. 15 (1969) 256–258.
- [18] N. Maffei, S.B. Krupanidhi, Appl. Phys. Lett. 60 (1992) 781–783.
- [19] T. Nakamura, R. Muhammet, M. Shimizu, T. Shiosaki, Jpn. J. Appl. Phys. 32 (1993) 4086–4088.
- [20] H. Wang, L.W. Fu, S.X. Shang, J. Appl. Phys. 73 (1993) 7963–7965.
- [21] J. Si, S.B. Desu, J. Appl. Phys. 73 (1993) 7910–7913.
- [22] A.Z. Simões, A.H.M. Gonzalez, M. Cilense, M.A. Zaghet, B. Stojanovic, J.A. Varela, Ceram. Int. 28 (2002) 271–277.
- [23] A.Z. Simões, C.S. Riccardi, F. Moura, A. Ries, N.L.A. Junior, M.A. Zaghet, B. Stojanovic, E. Longo, J.A. Varela, Mater. Lett. 58 (2004) 2842–2847.
- [24] B.S. Kang, B.H. Park, S.D. Bu, S.H. Kang, T.W. Noh, Appl. Phys. Lett. 75 (1999) 2644–2646.
- [25] Y. Ito, M. Ushikubo, S. Yyokoyama, H. Matsunaga, T. Yonezawa, K. Ogi, Jpn. J. Appl. Phys. 35 (1996) 4925–4929.
- [26] J.-K. Lee, H.-J. Jung, O. Auciello, I. Kington, J. Vac. Sci. Technol. A 14 (3) (1996) 900–904.
- [27] R. Pascual, M. Sayer, A. Lo, S. Herbert, L.C. Rolim, N. Townley, J. Appl. Phys. 79 (1996) 493–499.
- [28] S. Madeswaran, N.V. Giridharan, R. Jayavel, Mater. Chem. Phys. 80 (2003) 23–28.
- [29] M. Sedlar, M. Sayer, Ceram. Int. 22 (1996) 241–247.
- [30] S.-H. Lee, Y.-J. Kang, J.-G. Park, S.-I. Lee, W.-J. Lee, Proceedings of the 15th International Symposium on Integrated Ferroelectrics, Hynix Semiconductor Inc., Colorado Springs, Colorado, 2003.
- [31] Y. Shimakawa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, F. Izumi, Appl. Phys. Lett. 79 (2001) 2791–2793.

Ferroelectric and Dielectric Properties of Lanthanum-Modified Bismuth Titanate Thin Films Obtained by the Polymeric Precursor Method

A.Z. SIMÕES,¹ A.H.M. GONZALEZ,¹ C.S. RICCARDI,¹ E.C. SOUZA,¹ F. MOURA,¹ M.A. ZAGHETE,¹
E. LONGO² & J.A. VARELA^{1,*}

¹Chemistry Institute, Universidade Estadual Paulista, UNESP - Araraquara, SP, Brazil CEP - 14801-970

²Chemistry Department, Universidade Federal de São Carlos, UFSCar - São Carlos, SP, Brazil CEP - 13565-905

Submitted February 5, 2003; Revised February 6, 2004; Accepted February 9, 2004

Abstract. Lanthanum-modified bismuth titanate, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT), thin films with a La concentration of 0.75 was grown on Pt/Ti/SiO₂/Si substrates by using the polymeric precursor solution and spin-coating method. The scanning electron microscopy (SEM) showed rounded grains, which is not typical for these system. The BLT films showed well-saturated polarization-electric field curve which $2P_r = 41.4 \mu\text{C}/\text{cm}^2$ and $V_c = 0.99 \text{ V}$. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domains switching. These properties make BLT a promising material for FERAM applications.

Keywords: bismuth lanthanum titanate, FERAM, thin film

1. Introduction

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) is a member of the ferroelectric, bismuth-layered perovskite structure family with a general formula $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m-1})^{2-}$ where m takes on integer values, A is a relatively large divalent or trivalent cation, and B a small, highly charged cation such as Ti^{+4} , Nb^{+5} , or Ta^{+5} . For BTO, the following values apply: $A = \text{Bi}$, $B = \text{Ti}$, and $m = 3$ [1]. This structure is composed of alternating stacked layers of bismuth oxide and bismuth titanate. The structure of bismuth titanate, first described by Aurivillius some 40 years ago and later by others [1], has the layered perovskite structure with lattice constants $a = 5.4489 \text{ \AA}$, $b = 5.4100 \text{ \AA}$ and $c = 32.815 \text{ \AA}$, when indexed to orthorhombic symmetry. Below the ferroelectric Curie temperature (675°C), there exists a spontaneous polarization vector which lies in the b - c plane at an angle of 4.53° to the b -axis. As a result, strong anisotropic properties are observed. In bulk, BTO shows coercive

field values of 3.5 and 50 kV/cm, spontaneous polarization values of 4 and 50 $\mu\text{C}/\text{cm}^2$, and dielectric constant of 130 and 160, along the c - and b -axis, respectively [2]. For nonvolatile memories, ferroelectric thin films with low coercive field are required. Low coercive field translates to lower operating voltage, faster switching speed, and better fatigue resistance. Since the c -component of polarization involves only 180° switching, there is no associated transverse strain. The small coercive field and 180° switching of the c -component make the c -axis-oriented BIT thin films an attractive capacitor material in destructive readout (DRO) ferroelectric random access memory (FERAM) or a gate dielectric in nondestructive readout (NDRO) ferroelectric memory or field-effect transistor (FEMFET) designs [3]. To optimize the properties of BTO thin films, it is obvious that c -axis [001]-oriented films are preferred. Another advantage of BTO is its high Curie temperature. This should minimize thermal depolarization problems.

Several attempts to prepare BTO thin films are reported in the literature. Due to the high temperatures required for the formation of the ferroelectric perovskite

*To whom all correspondence should be addressed. E-mail: varela@iq.unesp.br

phase, the production of BTO thin film has not proved easy and, at present, a wide range of thin films synthesis techniques, such as MOCVD, sol-gel, RF magnetron, ion beam sputtering, and laser ablation are subject to intensive research [4]. Nakamura [5] deposited by MOCVD technique highly *c*-axis-oriented BTO thin films with a $\text{Bi}_2\text{Ti}_2\text{O}_7$ buffer layer on Pt/SiO₂/Si (100). The film had a relatively low coercive field (13 kV/cm), but the remanent polarization was very low ($0.6 \mu\text{C}/\text{cm}^2$). Wang [6] developed an atmospheric pressure MOCVD technique to prepare BTO thin films. These films exhibited high (100) orientation with high remanent polarization ($38 \mu\text{C}/\text{cm}^2$) and high coercive field (45 kV/cm). Si and Desu [7] fabricated randomly oriented BIT thin films at low temperature (550°C) by hot-wall MOCVD. A remanent polarization of $19 \mu\text{C}/\text{cm}^2$ and a high coercive field of 244 kV/cm was obtained.

Obviously, the substitution of bismuth for lanthanum influences the ferroelectric properties of this material dramatically. Bu et al. [8] prepared thin films of BTO doped with lanthanum by pulsed laser deposition. The authors found that these films were appropriate for non-volatile random access memory devices.

In previous works, our group have reported the preparation of thin films by the polymeric precursor method [9]. The overall process consists of preparing a coating solution by the type process, based on metallic citrate polymerization [10]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase.

Considering that the literature reports no data about the preparation of lanthanum doped BTO films through a polymeric precursor method, in this work, we describe our preliminary results on the deposition of thin films and their electrical properties relating to random access memory applications.

2. Experimental Procedure

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti,

Bi and La were mixed and homogenized by stirring at 90°C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16.

The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. From this solution the films were deposited by the spin-coating technique on (111) Si/Ti/Pt substrates. A platinum layer (140 nm) was used as bottom electrode. The BLT films were then calcinated at 700°C for 2 h in air resulting in a film thickness of approximately 220 nm. Next, a 0.3 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300°C, in oxygen atmosphere for 1 hour. Here, the desired effect is to decrease eventually present oxygen vacancies.

In this work, an excess of 5% wt of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis of the films were performed at room temperature by X-ray powder diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 20-2000) and Cu K α radiation.

Microstructural characterization of the films was carried out using scanning electron microscopy SEM (Topcon SM-300). The thickness of the annealed films was studied using scanning electron microscopy (Topcon SM-300) by looking the transversal section. The thickness results obtained from SEM represent an average value of three measurements. The relative dielectric constant ϵ_r and dissipation factor $\tan \delta$ were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard).

The capacitance-voltage characteristic was measured by the MFM configuration using a small AC signal of 10 mV at 100 kHz. The signal was measured across the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000 A). All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and Discussion

Figure 1 shows the collected XRD data of the BLT film. Only peaks of the BTO phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. The split of the (0100) and (200) peaks into two duplets indicates the change of crystal structure from the orthorhombic to the tetragonal system. Besides the BLT peaks, the characteristic peak for (111) platinum coated silicon substrates at $2\theta = 40^\circ$ was identified. Comparing the peak intensities of the BLT pattern to some BTO literature [8], the addition of 0.75 La results in a preferred orientation at $2\theta = 16^\circ$. This fact could be probably due to the change of the crystal system orthorhombic to tetragonal.

SEM photograph of the surface of BLT film is shown in Fig. 2. For pure BTO obtained by several methods a plate-like morphology of the grains was observed [11]. Our results show that lanthanum changes this typical morphology because the grains are rounded. The image also reveals that the surface appears to be dense, smooth and cracks free. The grains are evenly distributed with an average grain size of 140 nm.

The dielectric constant and dissipation factor of the films are presented in the Fig. 3. The dielectric measurements were carried out at room temperature as a

function of frequency in the range of 10 kHz – 1 MHz. The annealed films exhibited good dielectric properties, a dielectric constant, ϵ , of 158 and loss tangent, $\tan \delta$, of 3.6×10^{-3} , at 1 MHz. As shown in Fig. 3, the dielectric constant shows very little dispersion with frequency indicating that our films possess low defects concentration at the interface film-substrate. Otherwise, with an increase of frequency, the dissipation factor rises, indicating that the conductivity of the films increases with the measuring frequency. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan \delta$ indicate that interfacial polarization of the Maxwell Wagner type and that produced by the electrode barrier is negligible in the film. It was also observed that La doped films comparing with pure BTO possess higher dielectric constant and lower loss tangent indicating that the lanthanum plays an important role on the electrical properties of the thin BTO layers [11].

Figure 4 illustrates the C-V curve for BLT film obtained at 100 kHz by imposing a dc voltage of +10 to -10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domains switching. The C-V curve also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization

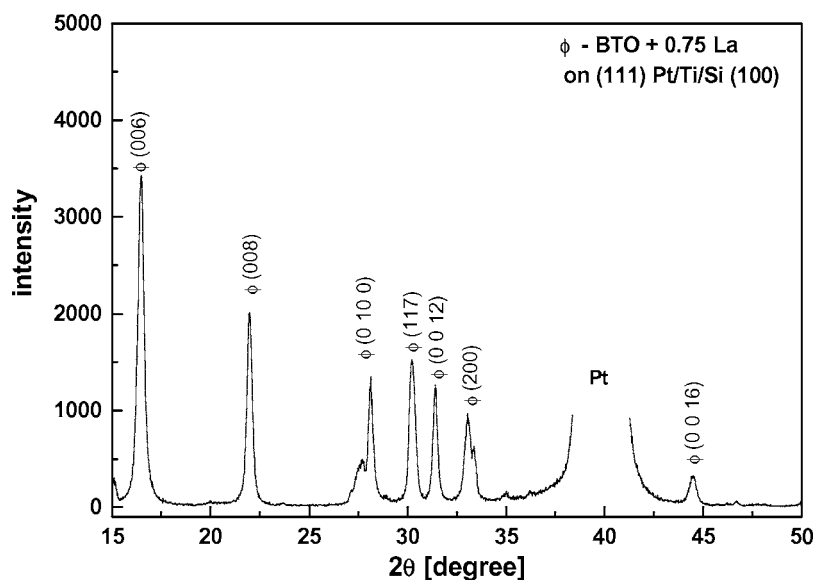


Fig. 1. X-ray diffraction for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

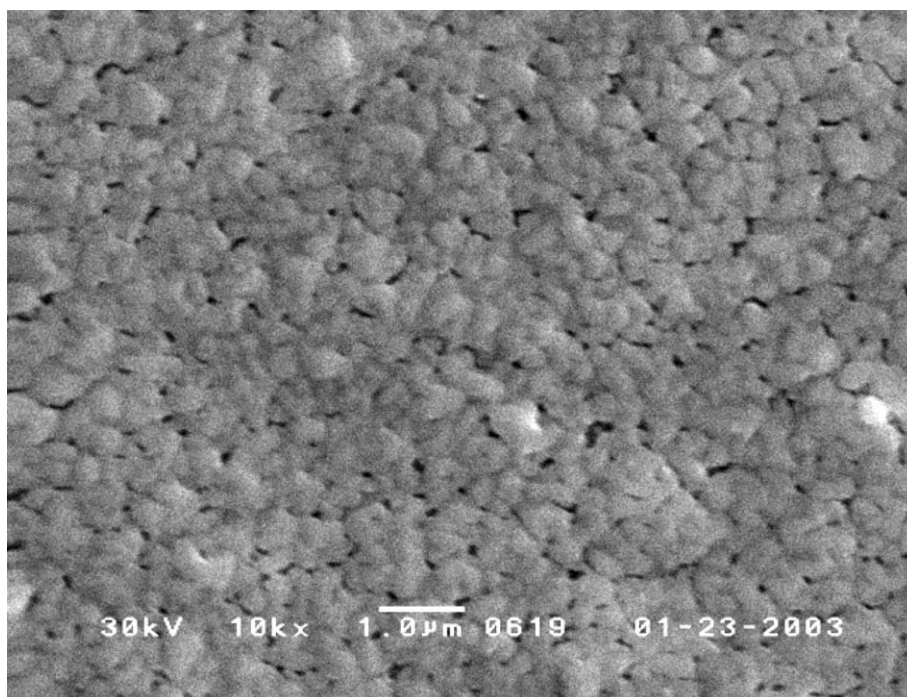


Fig. 2. SEM photograph for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

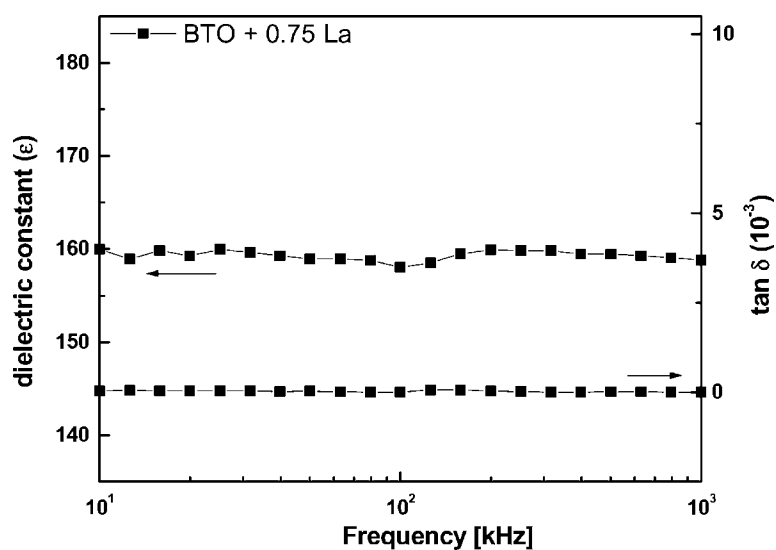


Fig. 3. Dielectric constant and loss tangent in dependence of frequency for BLT films obtained by the polymeric precursor method and annealed at 700°C for 2 hours.

switching. The C-V curve is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface.

Ferroelectricity in the BLT thin films was performed in a standardized ferroelectric tester and the resulting hysteresis curve is presented in Fig. 5. The hysteresis loop was measured at a frequency of 100 Hz and an

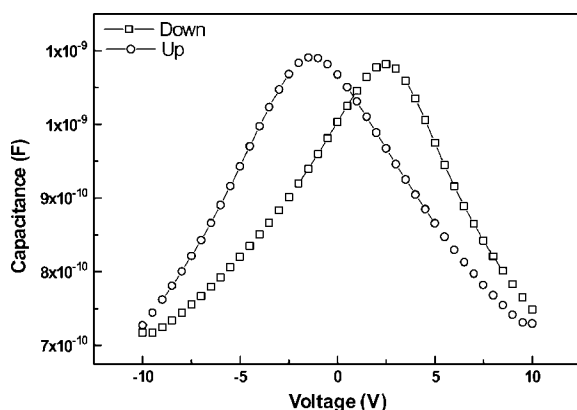


Fig. 4. C-V curve for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

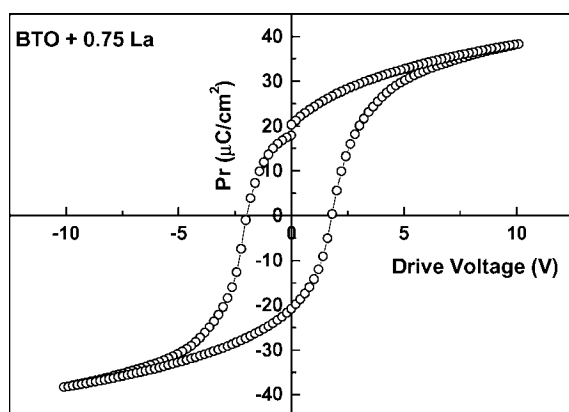


Fig. 5. P-E hysteresis loop for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

applied voltage in the order of 10 V. The loop is fully saturated with a remanent polarization $2P_r$ of $41.4 \mu\text{C}/\text{cm}^2$ and drive voltage of 1.0 V. The saturation of the loop at this low frequency indicates that the losses are minimal, suggesting the films are highly resistive. It may also be seen from Fig. 4 that the remanent polarization was much higher than that normally expected for a perfect *c*-axis oriented single crystal and may be ascribed to the presence of *a*-axis polarization components, as also seen from the XRD data. However, to the best of our knowledge, such highly saturated loops are being reported for the first time from the polymeric precursors method of bismuth titanate thin films.

The fatigue endurance of BLT thin films as a function of switching cycles was examined by applying 8.6 μs wide bipolar pulses with a 10 mV amplitude (Fig. 6).

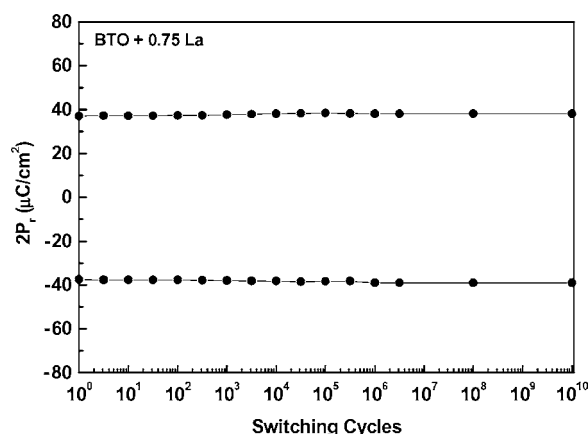


Fig. 6. Fatigue as a function of polarization cycles for BLT film deposited by the polymeric precursor method and annealed at 700°C for 2 hours.

Fatigue resistance was observed up to 10^{10} cycles indicating that the substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BTO thin films. However, it is not yet clear whether La changes the chemical environment of the perovskite layers. It is quite possible that the La substitution will enter the $(\text{Bi}_2\text{O}_2)^{2+}$ layers since the sizes of Bi^{3+} and La^{3+} ions are quite similar. In order to understand all the phenomena involved on the fatigue behaviour of BLT thin films new tests should be accomplished in future.

4. Conclusions

Dense lanthanum doped bismuth titanate films on (111) platinum coated silicon substrate were obtained through polymeric precursors solution by a spin-coating technique. The films show a homogeneous structure with low porosity combined with good ferroelectric properties, e.g. a regularly shaped hysteresis loop and low conductivity ($2P_r = 41.4 \mu\text{C}/\text{cm}^2$ and low drive voltage $V_c = 1.0\text{V}$). Because of their high remanent polarization and fatigue free behaviour, the 0.75 lanthanum doped BTO films are good candidate for FeRAMS applications.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, and CAPES.

References

1. R.E. Newnham, R.W. Wolf, and J.F. Dorrian, *Materials Research Bulletin*, **6**, 1029 (1971).
2. S.E. Cummins and L.E. Cross, *Journal of Applied Physics*, **39**, 2268 (1968).
3. S. Sinharoy, H. Buhay, D.R. Lampe, and M.H. Francombe, *Journal of Vacuum Science Technology, A*, **10**, 1554 (1992).
4. M. Sedlar and M. Sayer, *Ceramics International*, **22**, 241 (1996).
5. T. Nakamura, R. Muhammet, M. Shimizu, and T. Shiosaki, *Japanese Journal of Applied Physics*, **32**, 4086 (1993).
6. H. Wang, L.W. Fu, and S.X. Shang, *Journal of Applied Physics*, **73**, 7693 (1993).
7. J. Si and S.B. Desu, *Journal of Applied Physics*, **73**, 7910 (1993).
8. S.D. Bu, B.S. Kang, B.H. Park, and T.W. Noh, *Journal of the Korean Physical Society*, **36**, L9 (2000).
9. A.Z. Simões, A.H.M. Gonzalez, M.A. Zaghete, B. Stojanovic, A.A. Cavalheiro, P. Moeckli, N. Setter, and J. A. Varela, *Ferroelectrics*, **271**, 33 (2002).
10. S.M. Zanetti, E.B. Araújo, E.R. Leite, E. Longo, and J.A. Varela, *Materials Letters*, **40**, 33 (1999).
11. J.P. Kim, Y.S. Yang, S.H. Lee, H.J. Joo, and M.S. Jang, *Journal of the Korean Physical Society*, **35**, 202 (1999).

Influence of the solution pH on the morphological, structural and electrical properties of $\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{12}$ thin films obtained by the polymeric precursor method

A.Z. Simões^{a,*}, A. Ries^a, F. Moura^a, C.S. Riccardi^a, E. Longo^b, J.A. Varela^a

^aChemistry Institute, Universidade Estadual Paulista (UNESP), Araraquara-SP, CEP, 14801-970, Brazil

^bChemistry Department, Universidade Federal de São Carlos (UFSCAR), São Carlos-SP, CEP, 13565-905, Brazil

Received 19 January 2005; accepted 31 March 2005

Available online 31 May 2005

Abstract

Lanthanum-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films (BLT) were deposited on Pt/Ti/SiO₂/Si substrates using a polymeric precursor solution. The spin-coated films were specular, crack-free and crystalline after annealing at 700 °C for 2 h. Crystallinity and morphological evaluation were examined by X ray diffraction (XRD) and atomic force microscopy (AFM). The stability of the formed complex is of extreme importance for the formation of the perovskite phase. Films obtained from acid pH solution present elongated grains around 200 nm in size, whereas films obtained from basic solution present a dense microstructure with spherical grains (100 nm). The dielectric and ferroelectric properties of the BLT films are strongly affected by the solution pH. The hysteresis loops are fully saturated with a remnant polarization and coercive voltage of $P_r=20.2 \mu\text{C}/\text{cm}^2$ and $V_c=1.35 \text{ V}$ and $P_r=15 \mu\text{C}/\text{cm}^2$ and $V_c=1.69 \text{ V}$ for the films obtained from basic and acid solutions, respectively. © 2005 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Dielectrics; Ferroelectrics; Thin films

1. Introduction

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in nonvolatile random access memories [1]. Among related materials of interest, lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, PZT) is probably the most extensively studied. PZT films have favourable characteristics, including high polarization, a low processing temperature, and remaining apparently fatigue-free when used as conducting oxide electrodes [2,3]. Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer-structured perovskite like strontium bismuth tantalate ($\text{SrBi}_2\text{Ta}_2\text{O}_9$, SBT) has also been studied [4]. Although

SBT is a fatigue-free material, the practical application of SBT is limited, primarily due to its small polarization ($2P_r=4\text{--}16 \mu\text{C}/\text{cm}^2$) and high processing temperature of over 750 °C.

Recently, polycrystalline La-substituted bismuth titanate ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, BLT) films have attracted attention because of their possible application to ferroelectric random access memories due to their high fatigue endurance as well as low deposition temperature [5]. Compared with another well-known fatigue-free ferroelectric material $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) which is also a Bi-layered perovskite oxide, BLT has many attractive properties, such as low processing temperature and large values of remnant polarization. However, pure bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$, BIT) is prone to fatigue. Two reasons for the fatigue-free behaviour of BLT have been found. One is the charge-compensating role of the (Bi_2O_2) layers. Another is the suppression of oxygen vacancies after substituting some La atoms for Bi atoms, since the oxygen ions near Bi ions in BIT are likely to be

* Corresponding author. Tel.: +55 16 2016712; fax: +55 16 2227932.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

less stable than those near Sr ions in SBT due to the high volatility of bismuth oxide [6–8].

It is well known that the phase formation is directly related with the purity of the precursor, processing method, as well as of the time and temperature of the reaction. Any change in these parameters can induce the formation of the undesired phases [9], as it was already observed in the process of preparation of PZT [10] by the polymeric precursor method. This chemical method involves the formation of a chelate through the reaction of the citric acid with the metallic cation, followed by polyesterification with ethylene glycol. Even so, this reaction presents a chemical memory, in which the metallic cations responsible to form the net can be separated. The key for the obtaining of perovskite phase is intimately related with the structure originating from the chemical memory.

Ferroelectric films have been fabricated by rf sputtering [11], pulsed laser deposition [12], electron cyclotron resonance plasma sputtering [13] and metalorganic chemical vapor deposition [14]. In this work, we report the preparation of BLT thin films on platinum-coated silicon substrates by the polymeric precursor method. Compared with other techniques, the polymeric precursor method has the advantages of easier composition control, better homogeneity, low processing temperature (compatible with Si processing), easier fabrication of large areas and low cost [15]. In this work, BLT thin films were prepared by the polymeric precursor method. The effects of solution pH on the structural, morphological and electrical properties of BLT thin films were investigated.

2. Experimental procedure

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogenized by stirring at 90 °C. The solution pHs were adjusted at values of 3 and 9. To obtain the basic pH, ethylenediamine was added to the solution until a complete complexation of the cations was present in the system. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. Films were spin-coated from $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x=0.50$) deposition solution onto Pt/Ti/SiO₂/Si substrate. It was observed from a previous work that BLT films were completely crystallized at 700 °C for 2 h; so this was the temperature at which films were heat-treated [16]. Multilayered films were obtained by spinning 5 times (pH=3, [M]=0.1 mol L⁻¹) and 10 times (pH=9, [M]=0.05 mol L⁻¹) the deposition solution on the surface of the platinum-

coated silicon substrate previously cleaned with Extran solution and ethanol. The films were heat-treated at 400 °C for 2 h with a heating rate of 3 °C/min in a conventional furnace and immediately crystallized at 700 °C for 2 h, before the next deposition. All films were heat-treated in static air. In this work, an excess of 5.0 wt.% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as it has been reported in the literature [17]. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and CuK α radiation. The morphology of the annealed films was studied using scanning electron microscopy. The thicknesses were measured from the transversal section by using back-scattering electrons (Topcom SM-300). The thickness results obtained from SEM represent an average value of three measurements. Surface roughness (RMS) was examined by AFM, using tapping mode technique. Next, a 0.5-mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C with a constant heating rate of 1 °C/min, in oxygen atmosphere for 1 h. Here, the desired effect is to decrease eventually present oxygen vacancies.

The relative dielectric constant ϵ_r and dissipation factor ($\tan \delta$) were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). The capacitance–voltage characteristic was recorded in the MFM configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). The leakage current–voltage (I – V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

It is well known that the thickness of the layer is a function of viscosity, ionic concentration of the solution and spinning speed. It is important to control the thickness of the layer due to its strong influence on the grain size, dielectric and ferroelectric properties. It was observed that for thinner films interfacial “dead layers” could appear at the interface between films and substrate. These layers possess poor dielectric properties influencing the performance of the device [18]. These dead layers are originated from oxygen interdiffusion, chemical reaction, or structural defects at the

interfaces and could be suppressed with thickness of films higher than 200 nm. Considering that the ionic concentration differs greatly from one solution to another it was necessary to increase the number of layers for the basic solution in order to reach the minimum thickness value to get desired electrical properties.

Fig. 1 shows the collected XRD data of the BLT films deposited from solution with different pHs. Independent of the solution pH only peaks of the BLT phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. Besides the BLT peaks, the characteristic peak for (111) platinum-coated silicon substrates at $2\theta=40^\circ$ was identified. It is confirmed from XRD results that the BLT films are polycrystalline in nature with a single perovskite phase independent from the pH of the solution.

Fig. 2 shows a typical surface morphology of the film obtained from different pHs solution. The roughness measured is about 11 nm. These results are better compared to polycrystalline films obtained by chemical methods (about 17 nm) and similar to that obtained by physical method (nearly 9 nm) [19,20]. Table 1 presents the average grain size and roughness values for films obtained at different pHs. The average grain sizes obtained from AFM represent an average value of several measurements performed in the length and width of each single grain. An increase in the grain size was observed for acid solution and can be caused by the higher ionic concentration of this solution which retains more material deposited on the surface of the substrate leading to bigger grains. A strongly marked difference in the film microstructure can be observed for the different solution pHs used to obtain the films. The films obtained from solution with pH=3 present a typical bismuth layer perovskite structure. As reported for films with good ferroelectric properties the grain size was around 200 nm with an elongated shape [21]. On the other hand, the films obtained from solution with pH=9 presented spherical grains around 100 nm in size. The difference in the shape of the grains could be of the fact that the complexation of the metals by the carboxyl groups is dependent of the solution pH. The complexation of bismuth by citric acid leads to a linear polymer and a typical plate-like morphology. Meanwhile, the addition of ethylenediamine competes with the citric acid for the complexation of the bismuth site making the volumetric effect more pronounced and

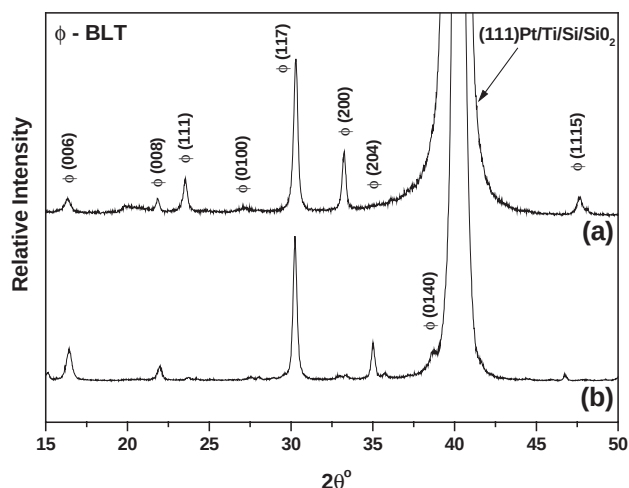


Fig. 1. X ray diffraction data for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x=0.5$) thin films deposited from (a) acid solution and (b) basic solution.

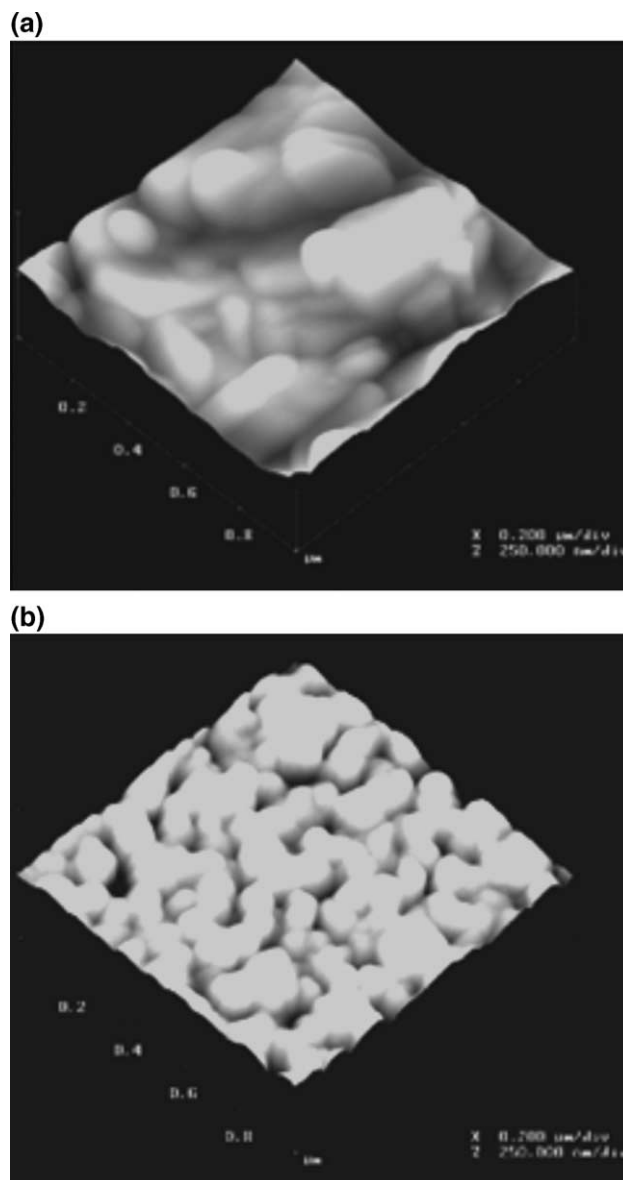


Fig. 2. AFM images for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.

leading to a rounded grain morphology. Another reason is that in acid pH the molecule is more symmetrical because of the largest number of tied up hydrogen, which increases the possibility of a homogeneous interaction between any of the carboxyl groups. However, in the basic pH citric acid is partly deprotonated, decreasing the symmetry of the molecule and the possibilities of a homogeneous interaction. A similar behaviour was observed for (PMN) thin films obtained by the polymeric precursor method where it was noticed that basic pH of niobium solution lead to pyrochlore phase and neutral pH to the perovskite [22].

The dielectric constant and dissipation factor of the films are presented in Table 1. The obtained results indicate that the films obtained from acid solution possess a dielectric constant higher than films obtained from basic solution. Considering that the dielectric constant depends on several factors such as annealing temperature, grain size, type of electrodes and phase composition it

Table 1
Overview of BLT film properties depending on the solution pH

pH	P_r ($\mu\text{C}/\text{cm}^2$)	J (1V) ($\mu\text{A}/\text{cm}^2$)	V_c (V)	ε (1 MHz)	$\tan \delta$ (1 MHz)	Roughness (nm)	Thickness (nm)	Average grain size (nm)
3	20.2	0.55	1.35	112	0.024	11.4	418	208
9	15.1	4.29	1.69	80	0.048	13.9	275	103

could be observed that the dielectric constant increases with the increase in grain size. Taking into account that the magnitude of the grain size is mainly dependent on the ionic concentration and solution pH one can say that both parameters deeply influence the dielectric properties of lanthanum-doped bismuth titanate thin films. The increase in losses for the basic solution can also be attributed to the small grain size present in these films favouring the pinning of domain walls by defects segregated in the wall regions. Our dielectric properties are consistent with the crystallographic and microstructural data.

The I – V measurements were taken using the radiant technology tester in the current–voltage mode, with the voltage changing from 0 to +10 V, from +10 to –10 V and back to 0 V. Table 1 shows the leakage data for the BLT films obtained from different pH solutions. The leakage current density at 1.0 V increases from 0.55 to 4.29 $\mu\text{A}/\text{cm}^2$ when the pH is increased from 3 to 9. The lower leakage current observed for the film obtained from the acid solution may be attributed to probable differences in grain size, density, and surface structure. The characteristics of the film–

electrode interface and the surface morphology of BLT thin films are the major factors determining the leakage current of capacitors in metal–ferroelectric–metal configuration.

Ferroelectricity in the BLT thin films was performed with a standardized ferroelectric tester and the results are presented in Fig. 3. The hysteresis loops were measured at a frequency of 100 Hz and an applied voltage in the order of 10 V. The loops are fully saturated with a remnant polarization of the films ranging from 15 to 20 $\mu\text{C}/\text{cm}^2$ and coercive voltages from 1.35 to 1.7 V. The saturation of the loops at these low frequencies indicates that the losses are minimal, suggesting the films are highly resistive. A more regularly shaped hysteresis loop is observed for films obtained from solution with acid pH. It may also be seen in Fig. 3 that the remnant polarization was much higher than normally expected for a perfect c -axis-oriented single crystal and may be

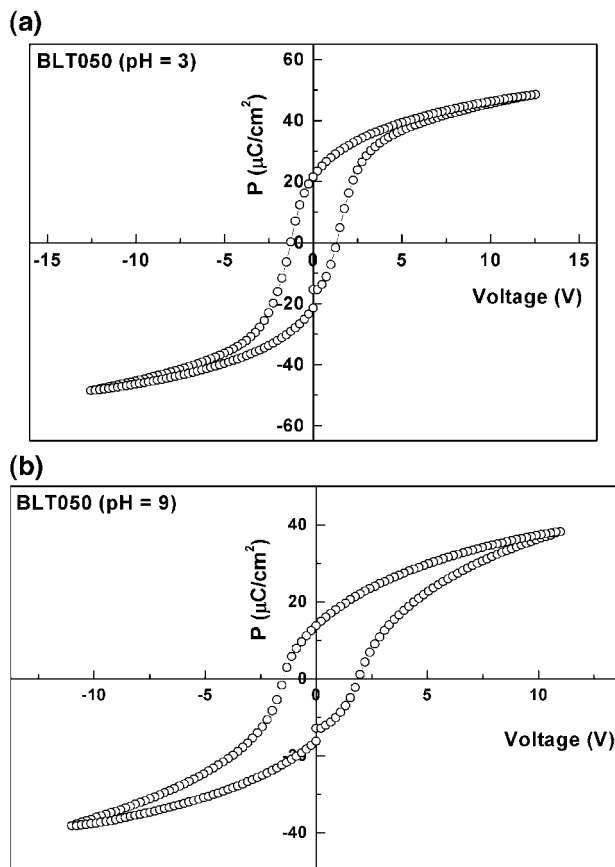


Fig. 3. P – E hysteresis loop for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.

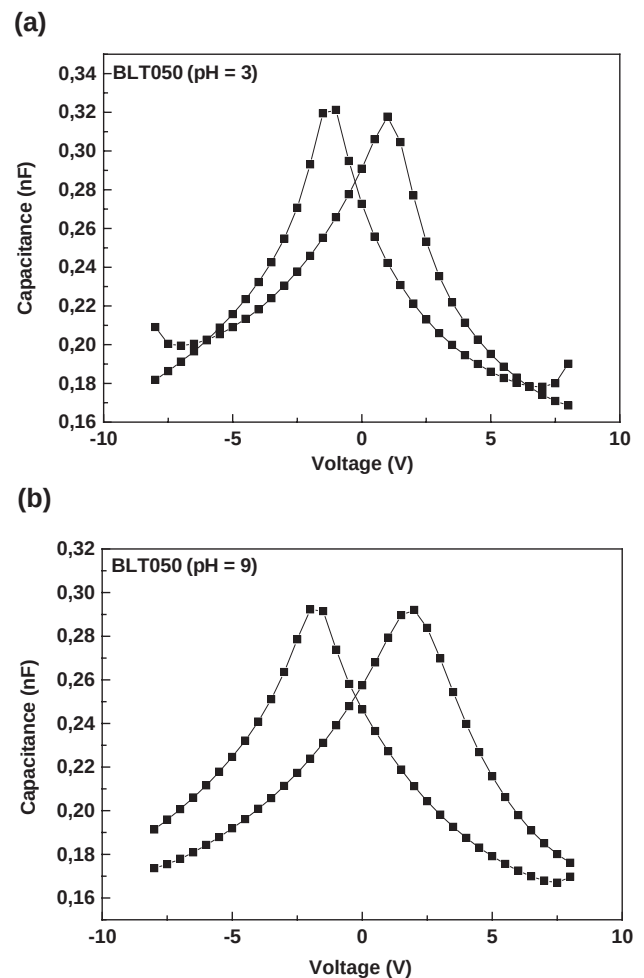


Fig. 4. C – V curves for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.

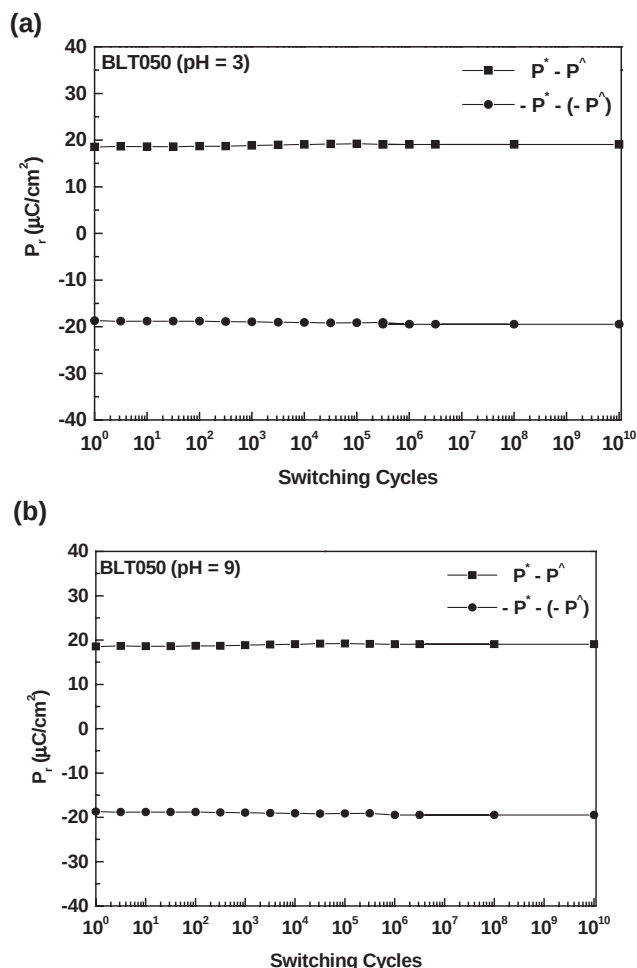


Fig. 5. Fatigue as a function of polarization cycles for BLT films ($x=0.5$) deposited from (a) acid solution and (b) basic solution.

ascribed to the presence of a -axis polarization components [23]. Compared to literature data, our results are similar to those published by Lee et al. [24]. The authors showed the fabrication of high-quality films of bismuth lanthanum titanate prepared by chemical synthesis method and their applications in handsets, smart phones and smart cards.

Fig. 4 illustrates the C – V curves for BLT films obtained at 100 kHz and DC sweep voltage from +10 to –10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The C – V curves for the films obtained from both solutions indicate symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. Symmetry of C – V curves around the zero bias axis indicates that the films contain few movable ions or charge accumulation at the film–electrode interface. Although the P – E hysteresis is saturated at ≥ 7 V the C – V curve shows hystereses up to ± 10 V because both measurements were performed at different frequencies where the domain alignment is a time-dependent process and plays an important role in the switching behaviour of the domains. Therefore, the sweep voltage ranges differ (3 V) and consequently also the (dV/dt) voltage sweep per time unit leading to different domain alignment kinetics.

The fatigue endurance of BLT thin films as a function of switching cycles was examined by applying 8.6 μ s wide bipolar

pulses with a 10-mV amplitude (Fig. 5). P^* is the switched polarization between two opposite polarity pulses and $P^\wedge$ is the nonswitched polarization between the same two polarity pulses. The $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denote the switchable remnant polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 10^{10} cycles independently of the pH solution used. B. H. Park et al. also verified the fatigue characteristics of BLT films deposited on platinum-coated silicon substrates. They observed that the values of $(P_{sw} - P_{ns})$ do not change significantly during the fatigue test indicating that the BLT films have good fatigue resistance [6]. Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion which has a lone pair of 6 s electrons, less hybridization with O 2p should lead to less structural distortion favouring the improvement of its properties [25]. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BIT thin films.

4. Conclusions

Independently of the solution pH used to obtain the films, dense lanthanum-doped bismuth titanate films on (111) platinum-coated silicon substrate were obtained through polymeric precursors solution by a spin-coating technique. An evident difference in the shape of the grains was noted when the films were obtained from different solution pHs. The C – V measurements of the BLT films in metal–ferroelectric–metal configuration presented two peaks ascribed to ferroelectric domain switching. Because of their high remnant polarization and low coercive voltage, $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ($x=0.50$) films are good candidates for FeRAM applications. No fatigue behaviour was verified in both cases which proves that these films possess enough quality to be used in non-volatile random access memories.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq, and CAPES and of the German Academic Exchange Service.

References

- [1] W.L. Warren, B.A. Tuttle, D. Dimos, Appl. Phys. Lett. 67 (1995) 1426.
- [2] B.G. Chae, S.J. Lee, S.H. Kim, Y.S. Yang, J.P. Kimand, M.S. Jang, J. Korean Phys. Soc. 32 (1998) S1438.
- [3] B.G. Chae, S.J. Lee, Y.S. Yang, S.H. Kim, M.S. Jang, J. Korean Phys. Soc. 31 (1997) 874.
- [4] K. Ishikawa, H. Funakubo, Appl. Phys. Lett. 75 (1999) 1970.
- [5] S.D. Bu, B.S. Kang, B.H. Park, T.W. Noh, J. Korean Phys. Soc. 36 (2000) L9.
- [6] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Nature 401 (1999) 682.
- [7] B.H. Park, S.J. Hyun, S.D. Bu, T.W. Noh, J. Lee, H.-D. Kim, T.H. Kim, W. Jo, Appl. Phys. Lett. 74 (1999) 1907.

- [8] C.A. Paz de Araujo, J.D. Cuchiaro, L.D. McMillan, M.C. Scott, J.F. Scott, *Nature* 374 (1995) 627.
- [9] D.H. Kang, K.H. Yoon, *J. Mater. Sci.* 26 (1991) 56.
- [10] V.V. Grigoeva, I.V. Golubeva, *Russ. J. Inorg. Chem.* 9 (1997) 580.
- [11] W.J. Takei, N.P. Formigoni, M.H. Framcobe, *Appl. Phys. Lett.* 15 (1969) 256.
- [12] N. Maffei, S.B. Krupanidhi, *Appl. Phys. Lett.* 60 (1992) 781.
- [13] P.C. Joshi, A. Mansing, *Appl. Phys. Lett.* 59 (1991) 2389.
- [14] J. Zhang, R.A. Gardiner, P.S. Kirlin, R.W. Boerstler, J. Steinbeck, *Appl. Phys. Lett.* 61 (1992) 2884.
- [15] A.Z. Simões, M.A. Zaghet, B.D. Stojanovic, C.S. Riccardi, A. Ries, A.H. Gonzalez, J.A. Varela, *Mater. Lett.* 57 (2003) 2333.
- [16] A.Z. Simões, M.A. Ramirez, C.S. Riccardi, A. Ries, E. Longo, J.A. Varela, *Mater. Chem. Phys.* 92 (2005) 373.
- [17] B.S. Kang, B.H. Park, S.D. Bu, S.H. Kang, T.W. Noh, *Appl. Phys. Lett.* 75 (1999) 2644.
- [18] M.V. Raymond, D.M. Smyth, *J. Phys. Chem. Solids* 57 (1996) 1507.
- [19] Y. Ito, M. Ushikubo, S. Yyokoyama, H. Matsunaga, T. Yonezawa, K. Ogi, *Jpn. J. Appl. Phys.* 35 (1996) 4925.
- [20] J.-K. Lee, H.-J. Jung, O. Auciello, I. Kingon, *J. Vac. Sci. Technol., A, Vac. Surf. Films* 14 (1996) 900.
- [21] R. Pascual, M. Sayer, A. Lo, S. Herbert, L.C. Rolim, N. Townley, *J. Appl. Phys.* 79 (1996) 493.
- [22] V.V. Grigoeva, I.V. Golubeva, *Sov. Prog. Chem.* 45 (1979) 39.
- [23] M. Toyoda, Y. Hamage, U. Tomono, D.A. Payne, *Jpn. J. Appl. Phys.* 32 (1993) 4158.
- [24] S.-H. Lee, Y.-J. Kang, J.-G. Park, S.-I. Lee, and W.-J. Lee, (Hynix semiconductor incorporation), Lecture Given at 15th International Symposium on Integrated Ferroelectrics, Colorado Springs, Colorado, 2003.
- [25] Y. Shimakawaa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, Z. Hiroi, *Appl. Phys. Lett.* 79 (2001) 2791.

ANEXO P

Fatigue-free behavior of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films grown on several bottom electrodes by the polymeric precursor method

218

A. Z. Simões,^{a)} A. Ries, F. M. Filho, C. S. Riccardi, and J. A. Varela
Chemistry Institute, UNESP—Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

E. Longo
Chemistry Department, UFSCar - Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil

(Received 1 June 2004; accepted 26 October 2004)

Fatigue-free $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films were grown on LaNiO_3 , RuO_2 , and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ bottom electrodes in a microwave furnace at 700 °C for 10 min. The remanent polarization (P_r) and the drive voltage (V_c) were in the range of 11–23 $\mu\text{C}/\text{cm}^2$ and 0.86–1.56 V, respectively, and are better than the values found in the literature. The BLT capacitors did not show any significant fatigue up to 10^{10} read/write switching cycles. © 2004 American Institute of Physics. [DOI: 10.1063/1.1834999]

As a fatigue-free material, $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) is of particular interest because it can be crystallized at relatively low processing temperatures close to 650 °C. Fatigue-free BLT films have been grown on Pt/Ti/SiO₂/Si substrates. However, a possible interfacial reaction between platinum and bismuth can lead to undesired electrical properties. Therefore, the substitution of metallic electrodes based on noble metals, such as platinum by conductive oxides is an alternative to reach better electrical properties caused by the high oxygen affinity of these electrodes.¹ For this purpose, it is interesting to evaluate the properties of BLT films deposited on electrodes based on metallic oxides, such as LaNiO_3 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, and RuO_2 .

Several attempts have been made to enhance the crystallization ability of ferroelectric thin films and metallic oxide electrodes.^{2,3} Recently, the use of a domestic microwave furnace has been developed as a way to process materials and has opened an opportunity to enhance crystallization with a lower annealing processing time since it decreases the interfacial reactions between ferroelectric thin films and electrodes and also improves the control over the crystallographic orientation of the thin films.⁴

Among various methods, such as metalorganic chemical vapor deposition, pulse laser deposition, and sol gel, the polymeric precursor method has a better potential for technological applications, because of their precise control of composition and homogeneity and good conformality.⁵ In the present work, we present the preparation of BLT films on the metallic oxides with excellent structural, microstructural, and electrical properties by the polymeric precursor method.

The LaNiO_3 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, RuO_2 , and BLT thin films were prepared the polymeric precursor method, as described elsewhere.⁵ The bottom electrodes thin films were spin coated on (100) Si/SiO₂ substrates by a commercial spinner operating at 5,000 revolutions/min for 30 s (spin coater KW-4B, Chemat Technology). Each annealing layer was pre-fired at 400 °C for 2 h in a conventional oven. After the pre-firing, each layer was crystallized in a microwave oven at 700 °C for 10 min. Using the same procedure, the BLT thin films were deposited by spinning the precursor solution on the

desired substrates. Through this process, we have obtained thickness values of about 150 nm for the bottom electrodes and around 300 nm for BLT, reached by repeating the spin-coating and heating treatment cycles. Phase analysis of the films were performed at room temperature by x-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu K α radiation. The morphology and the thickness of the films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) and scanning electron microscopy (Topcom SM-300), respectively. The electric properties were measured by an Au/BLT/ LaNiO_3 / $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ / RuO_2 /SiO₂/Si (100) capacitor structure. Dielectric and ferroelectric properties of the capacitor were measured by an HP4192A impedance/gain phase analyzer and a Radiant Technology RT6000 A.

Figure 1 shows the XRD results for BLT films deposited on different bottom electrodes. All films consisted of a single phase of bismuth layered structure showing preferred (001) and (117) orientations. The XRD results clearly show that films deposited on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode favor the growth of (117)-oriented grains, whereas in films deposited on LaNiO_3 and RuO_2 the growth of (001)-oriented grains dominated. According to Takenaka *et al.*,⁶ for lanthanum contents higher than 0.50 the orthorhombicity of the struc-

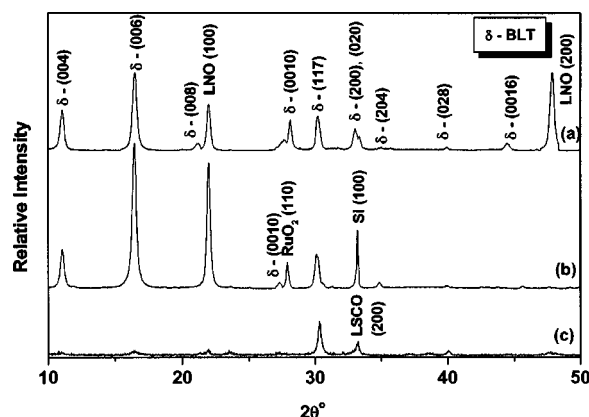


FIG. 1. XRD for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on different bottom electrodes at 700 °C for 10 min (a) LaNiO_3 , (b) RuO_2 , and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

^{a)}Electronic mail: alezipo@yahoo.com

TABLE I. Data obtained for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on different bottom electrodes at 700 °C for 10 min (a) LaNiO_3 , (b) RuO_2 and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

Electrodes	P_r ($\mu\text{C}/\text{cm}^2$)	V_c (V)	ϵ (1 MHz)	$\tan \delta$ (1 MHz)	Roughness (nm)	Average grain size (nm) $\pm 1\%$	$J(1\text{V})$ ($\mu\text{A}/\text{cm}^2$)	Thickness (nm)
LaNiO_3^a	11.4	1.26	176	0.047	4.4	81	4.3	283
RuO_2^a	16.7	1.56	160	0.019	4.3	58	2.2	270
$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3^a$	23.1	0.84	182	0.012	7.5	65	0.4	305
SrRuO_3^b	10.2	3.60	...	...	...	...	...	300
$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}^c$	10.0	...	220	0.01	...	...	...	...
LaNiO_3^d	8.0	1.92	128	0.024	...	...	0.1	240
$\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}^e$	11.4	2.22	260	0.028	...	...	...	...

^aThis work.^cRef. 10.^eRef. 11.^bRef. 15.^dRef. 13.

ture decreases. This structural distortion might be responsible for the unusual electrical properties of the BLT system. The here discussed preferred orientations can be caused by differences in lattice parameters and thermal expansion coefficients for different oxide electrodes and indicate that the polar axis is closer to (117) than (001). AFM studies (not shown) revealed that, independent of the electrode used, a homogeneous surface was observed indicating that the microwave furnace allows the preparation of films with controlled morphology. The average surface roughness value is in the range from 4.3 to 7.5 nm while the average grain size is in the range from 58 to 85 nm (Table I).

Ferroelectricity of the lanthanum-doped bismuth titanate thin films was observed independently of the bottom electrode used (Fig. 2). However, for the films deposited on the LaNiO_3 and RuO_2 electrodes the trapped charge (O_2') associated with other defects (V_0'') or even defect dipole complexes, such as oxygen vacancies associated with bismuth vacancies ($\text{V}'''_{\text{Bi}}-\text{V}_0''$) located in the grain boundary and in film-electrode interface can promote a local stoichiometry deviation influencing the shape of the hysteresis loops. As a consequence of these space charges, a significant shift along the electric-field axis toward the positive side, which is defined as an imprint, may lead to a failure of the capacitor. A more symmetric hysteresis loop is observed for the film deposited on $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode indicating that the high oxygen affinity of this material avoids the migration of charge species to the electrode-film interface. This behavior can be ascribed to the platelike grains of the BLT films (not shown as a figure). The domain walls in platelike grains are easier to be switched under an external field. Similar phenomena have been found in SBT and PT thin films.^{7,8} Therefore, the growth of the film in one direction not coincident to *c*-axis preferred orientation will favor the platelike morphology, such as the ones grown on $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ oxide electrode leading to a lower E_c when compared to those grown on LaNiO_3 and RuO_2 electrodes. Comparing the BLT thin films deposited on several bottom electrodes and obtained from different methods, the polymeric precursor method combined with the microwave processing allows the preparation of films with high dielectric and ferroelectric properties, as can be seen in Table I. The inset in Fig. 2 illustrates the Capacitance—voltage (*C*–*V*) curves for BLT films obtained at 100 kHz and dc sweep voltage from +10 to –10 V. The capacitance dependence on the voltage is strongly non-linear, confirming the ferroelectric properties of the film resulting from the domain switching. The *C*–*V* curve for the

film deposited on a $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode is symmetric around the zero-bias axis, indicating that the films contain few movable ions or charge accumulation at the film–

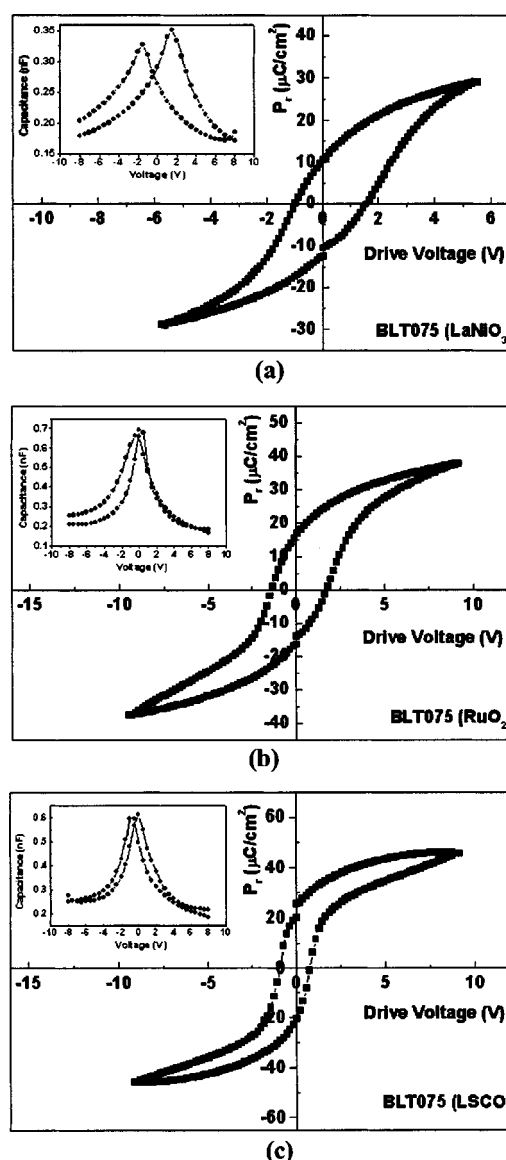


FIG. 2. P–E hysteresis loops for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on different bottom electrodes at 700 °C for 10 min (a) LaNiO_3 , (b) RuO_2 , and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. Inset of *C*–*V* curves for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on different bottom electrodes at 700 °C for 10 min (a) LaNiO_3 , (b) RuO_2 , and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

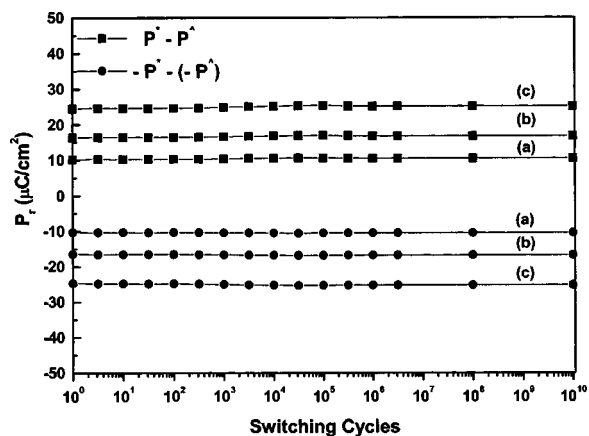


FIG. 3. Fatigue as a function of polarization cycles for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on different bottom electrodes at 700°C for 10 min (a) LaNiO_3 , (b) RuO_2 , and (c) $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$.

electrode interface. For films deposited on LaNiO_3 and RuO_2 , a slight change in capacitance values is observed indicating the existence of charge carriers (oxygen vacancies) trapped near the film–electrode interface. These charges may originate during the heat treatment process due to the decomposition of the polymeric precursor.⁹ The narrowing of the C – V curves obtained for the films deposited on RuO_2 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrodes indicates that the process to switch the domains is faster in these electrodes and the saturation occurs with low energy for the ferroelectric domain alignment.

The insulating properties of the films were found to be dependent on the bottom electrode (Table I). The leakage current density decreased for the films deposited on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode. Such a reduction in leakage current density may be attributed to a high oxygen affinity of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode avoiding that oxygen in the electrode material will be depleted by the ferroelectric material, thus leaving an oxygen deficient layer of the electrode at the interface and increasing the contact resistance. From this study, it can be demonstrated that the microstructures of ferroelectric films play an important role in their conductivity properties.¹² Comparing with literature data, our films present a higher leakage current than the films obtained on highly oriented LaNiO_3 -buffered $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates by sol–gel process.¹³ Since the conductivity is strongly affected by the characteristics of the film–electrode interface, the lower leakage current observed in the literature may be attributed probably to differences in grain size, density, and preferred orientation due to differences in the metal–ferroelectric–metal configuration. Besides that, normally thin films on oxide electrodes exhibit higher leakage current in comparison to metal electrodes.¹⁴

Figure 3 presents the fatigue endurance of BLT thin films as a function of switching cycles. Fatigue resistance was observed up to 10^{10} cycles for all electrode oxides utilized in this study. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BLT thin films. Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion, which has a lone pair of 6s electrons, less hybridization with O $2p$ should lead to less structural distortion.^{15,16} As a consequence, the in-plane lattice constant, a , decreases while b increases as La is substituted, resulting in a decrease in the orthorhombicity

suggesting that the relaxation of the structural distortion arises from the substitution. However, the addition of La reduces the polarization along the a axis leading to a significant decrease in the ferroelectric polarization when compared to pure BLT films. Since all oxide electrodes, such as RuO_2 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, and LaNiO_3 , result in fatigue-free films [Figs. 3(a)–3(c)], it is consequently, one may believe that if an oxygen vacancy accumulation near the film–electrode interface occurs during fatigue, the conductive oxide can consume the oxygen vacancies by changing their oxygen nonstoichiometry and thus, the accumulation of oxygen vacancies near the interface is prevented or reduced. In conclusion, BLT thin films were obtained on LaNiO_3 , RuO_2 , and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrodes from a polymeric solution and annealed by a microwave oven process through the spin-coating technique. A regularly shaped hysteresis loop is observed for the films deposited on the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrode due to the high oxygen affinity which avoids the migration of charge species for the electrode–film interface. High fatigue resistance was observed for films deposited on LaNiO_3 , RuO_2 , and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ electrodes which proves that our films possess enough quality to be used in nonvolatile random access memories. However, due to the imprint phenomenon, the films deposited on LaNiO_3 and RuO_2 electrodes are unsuitable for memory applications as a consequence of the substantial difference between $+V_c$ and $-V_c$. Moreover, the polymeric precursor method combined with annealing in a microwave oven is an alternative approach to obtaining excellent BLT thin films and bottom electrodes. A remarkable improvement in the remanent polarization and drive voltage suggests that BLT thin films deposited on a LSCO oxide electrode are suitable for integrated device applications and can be used for ferroelectric random access memories.

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq, CAPES, and of the German Academic Exchange Service (DAAD).

¹C. S. Liang, J. M. Wu, and M. C. Chang, Appl. Phys. Lett. **81**, 3624 (2002).

²H. N. Lee, D. Hesse, N. Zakharov, and U. Gösele, Science **296**, 2006 (2002).

³R. Ramesh and D. G. Schlom, Science **296**, 1975 (2002).

⁴N. S. L. S. Vasconcelos, J. S. Vasconcelos, V. Bouquet, M. Guilloux-Viry, M. I. Bernardi, and J. A. Varela, Thin Solid Films **436**, 213 (2003).

⁵A. Z. Simões, B. D. Stojanovic, A. Tangstev, N. Setter, and J. A. Varela, Integr. Ferroelectr. **43**, 123 (2002).

⁶T. Takenaka and K. Sakata, Ferroelectrics **38**, 769 (1981).

⁷S. B. Ren, C. J. Lu, J. S. Liu, H. M. Shen, and Y. N. Wang, Phys. Rev. B **54**, R14337 (1996).

⁸M. Nagata, D. P. Vijay, X. B. Zhang, and S. B. Desu, Phys. Status Solidi A **157**, 75 (1996).

⁹J. G. Simmons, Handbook of Thin-Film Technology, edited by L. I. Maise and R. Glang (McGraw-Hill, New York, 1970), pp. 14–35.

¹⁰M. Sedlar and M. Sayer, Ceram. Int. **22**, 241 (1996).

¹¹N. Maffei and S. B. Krupanidhi, Appl. Phys. Lett. **60**, 781 (1992).

¹²J. F. Scott, C. A. Araujo, B. M. Melnick, L. D. McMillan, and R. Zuleeg, J. Appl. Phys. **70**, 382 (1991).

¹³J. Zhai and H. Chen, Appl. Phys. Lett. **82**, 442 (2003).

¹⁴C. S. Hwang, B. T. Lee, C. S. Kang, J. W. Kim, K. H. Lee, H.-J. Cho, H. Horii, W. D. Kim, S. I. Lee, Y. B. Roh, and M. Y. Lee, J. Appl. Phys. **83**, 3703 (1998).

¹⁵Y. Shimakawa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, F. Izumi, and Z. Hiroi, Appl. Phys. Lett. **79**, 2791 (2001).

¹⁶H. N. Lee and D. Hesse, Appl. Phys. Lett. **80**, 1040 (2002).

Retention characteristics in $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin films prepared by the polymeric precursor method

A. Z. Simões, M. A. Ramirez, N. A. Perruci, and C. S. Riccardi
Chemistry Institute, UNESP, Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

E. Longo
Department of Chemistry, UFSCar, Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil

J. A. Varela
Chemistry Institute, UNESP, Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

(Received 27 July 2004; accepted 1 February 2005; published online 9 March 2005)

Ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films were deposited on Pt/Ti/SiO₂/Si substrates by the polymeric precursor method. The films present *c*-axis preferred orientation after annealing at 700 °C for 2 h in conventional furnace. All the capacitors showed good polarization fatigue characteristics at least up to 1×10^{10} bipolar pulse cycles and excellent retention properties up to 1×10^4 s. We found that the polarization loss is insignificant with five write/read voltages at a waiting time of 10 000 S. Independently of the applied electric field the retained switchable polarization approached a nearly steady-state value after a retention time of 10 s. © 2005 American Institute of Physics. [DOI: 10.1063/1.1886893]

Ferroelectric materials have attracted much attention due to their potential use for nonvolatile memory devices, such as ferroelectric random access memory (FRAM). There have been many reports on the electrical properties of candidate materials, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT).¹ One property required for ferroelectric memories is long term stability. The application of ferroelectric thin films to the microelectronic industry is currently limited by the degradation of the polarization state. Device reliability, including factors such as fatigue, imprint and retention, have constituted the main obstacle to commercialization of FRAM devices. Recently, ferroelectric $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) was found to be a new candidate material for FRAM applications due to its high resistance to fatigue and low processing temperature.² However, the retention characteristics of BLT films have so far not been reported by the polymeric precursor method. In a memory element, a data bit (1 or 0) should be stored and made available for query at some later time. Retention is the ability of a memory element to maintain a given data state as time elapses. In most retention studies, ferroelectric capacitors exhibited a significant loss in retained polarization within the first 1 s after writing and then a relatively slight decay thereafter.^{3–7} Retention loss causes a reduction in the difference between switched (P^*) and non-switched (P^-) polarizations, i.e., $\Delta P = (P^*) - (P^-)$ and leads to an inability to distinguish between the two logic states. Therefore, it is quite important to have good retention properties for any ferroelectric material to be utilized for FRAM applications. In this letter, we report systematic studies on the retention characteristics of BLT thin films obtained by the polymeric precursor method. We have also investigated the influence of the applied electric field on the retention properties of the BLT thin films. The BLT thin films were prepared by the polymeric precursor method, as described elsewhere.^{8,9} The BLT thin films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Che-

mat Technology). In this work, an excess of 5% wt of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature.¹⁰ The thin films were annealed at 700 °C for 2 h in the conventional furnace. Through this process, we have obtained thickness values of about 400 nm for BLT, reached by repeating the spin coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case back scattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. The morphology of the thin films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa). A 0.5 mm diameter top Au electrode for the electrical measurements were prepared by evaporation through a shadow mask at room temperature. The electric properties were measured by an Au/BLT/Pt/Ti/SiO₂/Si (100) capacitor structure. Ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000 A tester equipped with a micrometer probe station in a virtual ground mode. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. The retention characteristics of the films were measured by observing the time-dependent changes of P^* and P^- independently. For P^* , the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time *t*. For P^- , positive pulses were used for both writing and reading.

Figure 1 presents the XRD of $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films deposited on Pt/Ti/SiO₂/Si substrates by a chemical-soft method. Only peaks of the main phase were detected suggesting that substitution of Bi by La does not lead to formation of secondary phases. The split of the (0010) and (200) peaks into two duplets indicates the change of crystal structure from the orthorhombic to the tetragonal

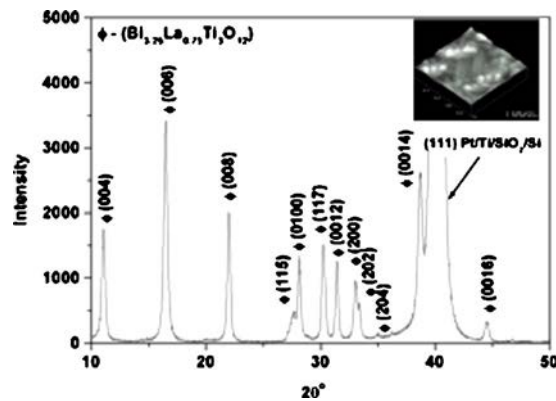


FIG. 1. X-ray diffraction of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method. Inset of AFM image obtained in the contact mode for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method.

system. Besides the BLT peaks, the characteristic peak for (111) platinum coated silicon substrates at $2\theta=40^\circ$ was identified. It can be observed that the addition of lanthanum ($x=0.75$) results in a c -axis preferred orientation. Such a well-developed c orientation in the La-doped films was also reported by other methods.^{11,12} The inset in Fig. 1 shows the AFM surface morphology obtained in the contact mode of the film deposited on Pt/Ti/SiO₂/Si substrate. A homogeneous surface, smooth and crack free was observed indicating that the chemical soft method allows the preparation of films with controlled morphology. The surface morphology of the BLT films shows grains in the form of platelets, as expected from the preference for the c orientation observed in XRD. The grains are evenly distributed with an average grain size of 140 nm and surface roughness equal to 8.0 nm.

Figure 2 shows the hysteresis loops acquired before and after waiting time of 10 000 s with 5 V write/read voltages, respectively. The switchable polarization exhibits almost no loss with 5 V write/read voltage after 10 000 s retention time. This suggests that there no pinning of domain walls in BLT thin film at 5 V write/read voltage. Similar results were observed for SBT thin films deposited on platinum coated silicon substrates where the switchable polarization present no loss with 9 V write/read voltage, while it exhibited polarization loss with 3 V write/read voltage after a waiting period of 30 000 s.¹³ Ferroelectricity of the lanthanum doped bismuth titanate thin films was observed with remanent po-

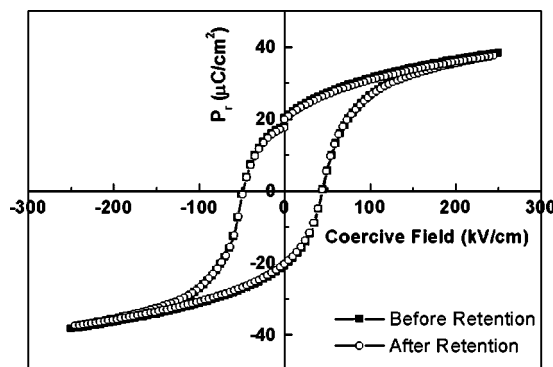


FIG. 2. P - E hysteresis loops before and after 10 000 S waiting time for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h by the soft chemical method.

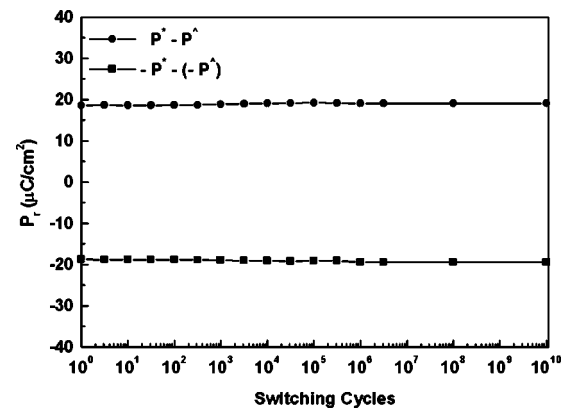


FIG. 3. Fatigue as a function of polarization cycles for $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films ($x=0.75$) deposited on Pt/Ti/SiO₂/Si substrates at 700 °C for 2 h.

larization of 21 $\mu\text{C}/\text{cm}^2$ and coercive field 44 kV/cm. The remanent polarization of the BLT film obtained by the soft chemical method is larger than those of other reported in the literature.^{2,14}

When a ferroelectric material is repeatedly cycled from one polarization state to another, its dielectric and ferroelectric properties are observed to change. This phenomenon, known as ferroelectric fatigue, is a limiting factor for the performance of the ferroelectric random access memory (FRAM) devices. The fatigue endurance of BLT thin films were tested at 1 MHz as a function of switching cycles by applying 8.6 μs wide bipolar pulses with maximum amplitudes of ± 5 V. (Fig. 3). P^* is the switched polarization between two opposite polarity pulses and $P^\wedge$ is the non-switched polarization between the same two polarity pulses. The $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 1×10^{10} cycles suggesting that BLT has good potential for applications in memories. The substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of pure BIT thin films. Since a La^{3+} ion has no outer electron, in contrast to a Bi^{3+} ion, which has a lone pair of 6s electrons, less hybridization with O 2p should lead to less structural distortion favoring the improvement of its ferroelectric properties.¹⁵

Retention, which is the time dependent change of the polarization state of the ferroelectric film, is another factor which limits the life of a ferroelectric memory device. Ferroelectric retention properties were measured at room temperature using a Radiant Technology RT6000 A test system (Fig. 4). The test pulse sequence used for retention measurement is as follows: At first, a triangular pulse of -5 V was applied to write a known logic state, then, after a predetermined time, the logic state was sequentially read by applying two triangular pulses of $+5$ V and -5 V. The pulse width for all triangular pulses is 1.0 ms. Time delay between the right pulse and the first read pulse is called the retention time. The capacitor poled with a negative voltage pulse corresponds to the binary digit "1." Similarly the state "0" was written by poling the capacitor by applying a positive pulse and read after a predetermined time interval t with a positive pulse. Figure 4(a) shows the retention characteristics of the BLT films, where the retained switchable polarization $\Delta P = (P^*) - (P^\wedge)$ was plotted as a function of retention time from 1 to 1×10^4 s at various applied electric fields from

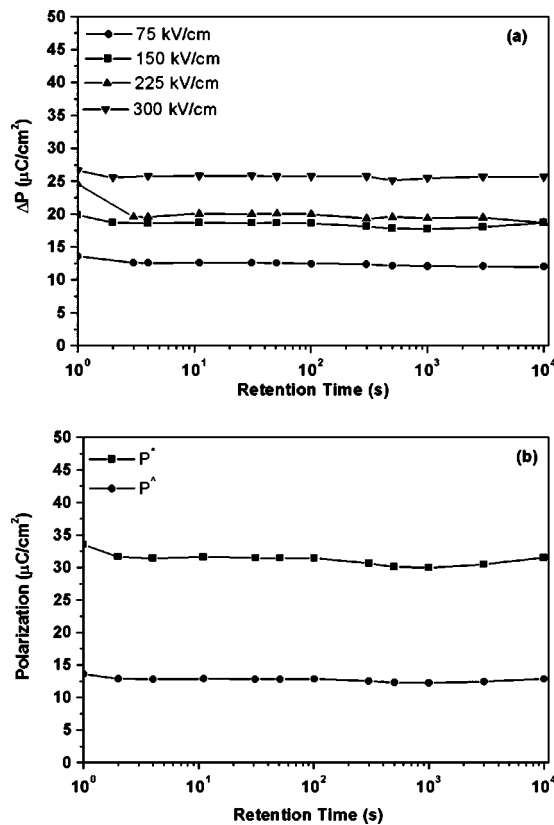


FIG. 4. (a) Retention time dependence of the retained polarization of the BLT film with various applied electric fields (75–300 kV/cm) and (b) P^* and P^+ of the BLT film for retention time up to 1×10^4 s and applied electric field of 150 kV/cm.

75 to 300 kV/cm. The value of initial polarization decayed and approached a nearly steady-state value after a retention time of 10 s. The corresponding hysteresis loops obtained after the retention test was also essentially identical to that observed before the retention test, indicating that the switchable polarization has almost no loss and the structures have little or no tendency to imprint after 1×10^4 s. The small decay of the retained charge in BLT thin films even after about 1×10^4 s is a favorable indication for memory applications. The long-time retention characteristics of the BLT films are shown in Fig. 4(b). The overall retention time dependence of polarization retention for the BLT film is quite good. After a retention time of 1×10^4 s, the polarization loss was only about 6% of the value measured at $t=1$ s for an applied electric field of 150 kV/cm. Depolarization fields generated by the redistribution of space charge, defects and dipole charges could be the mechanisms for the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss. The depolarization field increases with increasing the retained polarization and is time dependent. The long-time retention loss is attributed to the effects of redistribution of defect charges. This effect leads to a small decrease in the polarization by compensating the polarization charges when the redistribution of defect charges is driven by polarization.¹⁶ Due to the dielectric relaxation, the retained charge is generally less than the switched charge measured from the P - E hysteresis loop and the difference between them should be small as possible to maintain enough margin

between the digits “1” and “0.” Retention, like fatigue, is also dependent on the thickness of the film, nature of the electrodes, microstructure of the film, temperature, and the details of the test conditions. The understanding and improvement of the degradation behavior of ferroelectric thin films will have an essential impact on the future success of these films for device applications. Detailed fatigue and retention measurements in close correlation with process conditions are being done to evaluate the merits of lanthanum bismuth titanate thin films for memory applications. In conclusion, c -axis preferred orientation BLT thin films were obtained on Pt/TiO₂/SiO₂/Si substrates by using the soft chemical method through the spin coating technique. High fatigue resistance was observed which proves that our films possess enough quality to be used in nonvolatile random access memories. The polarization retention characteristics of ferroelectric BLT thin films deposited on Pt/TiO₂/SiO₂/Si substrates by the soft chemical method have been investigated. The retention failure tests showed that the BLT films have quite good long-time retention characteristics, retaining 94% of the values measured at $t=1 \times 10^4$ s for an applied electric field of 150 kV/cm. Polarization charge compensation by the redistribution of defect charges should be considered to explain the retention loss in lanthanum doped bismuth titanate thin films for memory applications. The results of these studies are very promising and suggest that BLT thin films are attractive for use as storage element in nonvolatile ferroelectric random access memories.

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq, and CAPES.

- ¹J. F. Scott, *Ferroelectric Memories* (Springer, New York, 2000), and references therein.
- ²B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, *Nature (London)* **401**, 682 (1999).
- ³Z. G. Zhang, Y. N. Wang, J. S. Zhu, F. Yan, X. M. Lu, H. M. Shen, and J. S. Liu, *Appl. Phys. Lett.* **73**, 3674 (1998).
- ⁴R. R. Mehta, B. D. Silverman, and J. T. Jacobs, *J. Appl. Phys.* **44**, 3379 (1973).
- ⁵I. G. Jenkins, T. K. Song, S. Madhukar, A. S. Prakash, S. Aggarwal, and R. Ramesh, *Appl. Phys. Lett.* **72**, 3300 (1998).
- ⁶J. M. Benedetto, R. A. Moore, and F. B. McLean, *J. Appl. Phys.* **75**, 460 (1994).
- ⁷Y. Shimada, M. Azuma, K. Nakao, S. Chaya, N. Moriwaki, and T. Otsuki, *Jpn. J. Appl. Phys., Part 2* **36**, 5912 (1997).
- ⁸A. Z. Simões, A. H. Gonzalez, C. S. Riccardi, M. Cilense, M. A. Zaghe, B. D. Stojanovic, A. Tangstev, N. Setter, and J. A. Varela, *Integr. Ferroelectr.* **43**, 123 (2002).
- ⁹A. Z. Simões, M. A. Zaghe, B. D. Stojanovic, C. S. Riccardi, A. Ries, A. H. Gonzalez, and J. A. Varela, *Mater. Lett.* **57**, 2333 (2003).
- ¹⁰B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, *Appl. Phys. Lett.* **75**, 2644 (1999).
- ¹¹S. D. Bu, B. S. Kang, and B. H. Park, *J. Korean Phys. Soc.* **36**, L9 (2000).
- ¹²D. Wu, A. Li, T. Zhu, Z. Liu, and N. Ming, *J. Appl. Phys.* **88**, 5491 (2000).
- ¹³Z. G. Zhang, Y. N. Wang, J. S. Zhu, F. Yan, X. M. Lu, H. M. Shen, and J. S. Liu, *Appl. Phys. Lett.* **73**, 3674 (2001).
- ¹⁴S. H. Hong, S. Trolle-McKinstry, and G. L. Messing, *J. Am. Ceram. Soc.* **83**, 113 (2000).
- ¹⁵Y. Shimakawa, Y. Kubo, Y. Tauchi, H. Asano, T. Kamiyama, F. Izum, and Z. Hiroi, *Appl. Phys. Lett.* **79**, 2791 (2001).
- ¹⁶B. S. Kang, J.-G. Yoon, T. K. Song, S. Seo, Y. W. So, and T. W. Noh, *Jpn. J. Appl. Phys., Part 1* **41**, 5281 (2002).

ANEXO R

Electromechanical properties of calcium bismuth titanate films: A potential candidate for lead-free thin-film piezoelectrics

A. Z. Simões,^{a)} M. A. Ramírez, A. Ries, J. A. Varela, and E. Longo
 Departamento de Química, Universidade Estadual Paulista, UNESP, P. O. Box 355, 14801-970,
 Araraquara, SP, Brazil

R. Ramesh
 Department of Materials Science and Engineering and Department of Physics, University of California,
 Berkeley, California 94720

(Received 13 September 2005; accepted 11 January 2006; published online 17 February 2006)

$\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBTi144) thin films were evaluated for use as lead-free thin-film piezoelectrics in microelectromechanical systems. The films were grown by the polymeric precursor method on (100) Pt/Ti/SiO₂/Si substrates. The *a/b*-axis orientation of the ferroelectric film is considered to be associated with the preferred orientation of the Pt bottom electrode. The P_r and E_c were 14 $\mu\text{C}/\text{cm}^2$ and 64 kV/cm, respectively, for a maximum applied field of 400 kV/cm. The domain structure was investigated by piezoresponse force microscopy. The film has a piezoelectric coefficient, d_{33} , equal to 60 pm/V and a current density of 0.7 mA/cm². © 2006 American Institute of Physics. [DOI: 10.1063/1.2172071]

Recently, more and more efforts are being made to develop nontoxic lead-free piezoelectric materials. Bismuth-layered ferroelectrics are considered to be candidate materials.¹ $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ (CBTi144) is a member of the Aurivillius family, $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$, in which A represents mono-, di-, tri-valent ions and B represents tetra-, penta- or hexa-valent ions. The *n* value is the number of stacking oxygen octahedrons along the *c* axis in one crystal unit cell, and is equal to 4. For practical applications, a large piezoelectric coefficient is desired.^{2,3} CBTi144 is characterized by its high Curie point of about 790 °C and is therefore expected to be useful for special applications at relatively high temperatures.⁴ Compounds in this family have anisotropic ferroelectricity, which is strongly associated with the crystal structure, especially the compounds with *n* equal to an even number which have no polarization along the *c* axis because there is a mirror plane perpendicular to the axis.⁵ The polarization of the compounds is along the *a* axis. Therefore, thin films with *a*-axis orientation are preferred for use in many kind of devices, such as ferroelectric random access memories, piezoelectric microactuators, and resonators.

Among various methods such as metalorganic chemical vapor deposition, pulsed laser deposition and sol gel, the polymeric precursor method has advantages such as the possibility of working in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method due to inexpensive precursors and equipments.⁶

In the present work, we describe the fabrication and characterization of polar-axis-oriented CBTi144 films without any nucleation layer by the polymeric precursor method. Calcium citrate (Synth), titanium isopropoxide (Hulls AG) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth and titanium were prepared by adding the raw materials to a mixture of

ethylene glycol and concentrate aqueous citric acid under heating and stirring. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The CBTi144 thin films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 310 nm for CBTi144, reached by repeating the spin-coating and heat treatment cycles. Phase analysis was performed at room temperature by x-ray diffraction (XRD) in Bragg-Brentano geometry (Rigaku 2000) at CuK_α radiation. Furthermore, topography and thickness were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IV) and scanning electron microscopy (Topcom SM-300), respectively. The top Pt electrodes were prepared by photolithography with 8×10^{-4} mm² dot area. The AFM module is also capable of providing piezoresponse force microscopy (PFM) characterization of polarized region ferroelectric films. When an external ac voltage is applied across a ferroelectric film through the tip, the region under the tip will vibrate with the applied voltage due to the converse piezoelectric effect, $\Delta Z(t) = \pm d_{33} V \sin(\omega t)$, where ΔZ is the longitudinal displacement, d_{33} the piezoelectric coefficient and V amplitude of the ac voltage, respectively. This small displacement can be detected by AFM with a standard lock-in technique. A silicon cantilever with a tip radius less than 40 nm, a force constant of 0.15 N/m, and a resonance frequency around 12 kHz, was coated with Ti and Pt for electrical conductivity. A function generator (Hewlett-Packard, model 33120A) produced an ac field of 1.5 V to induce the converse piezoelectric response and also served as the reference signal for the lock-in amplifier. We selected a dc field of 12 V to ensure a high fraction of local domain switching.⁷ Such a poling process should improve the piezoelectric properties. To reduce the interference of surface roughness, an ac field with a frequency far from the resonant frequency of the cantilever was selected

^{a)} Author to whom correspondence should be addressed; electronic mail: alezipo@yahoo.com

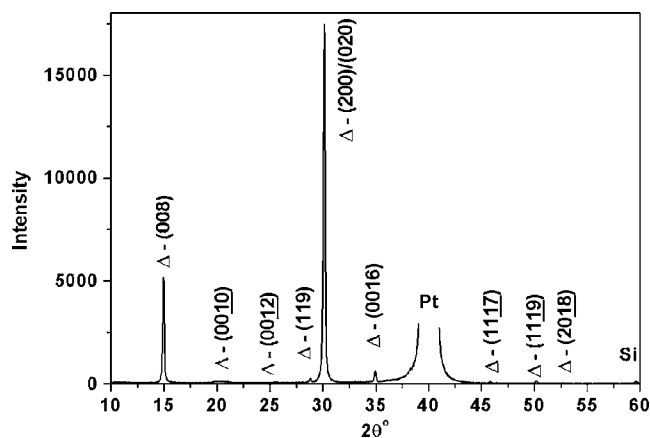


FIG. 1. X-ray diffraction for CBTi144 thin film.

for domain visualization. Artifacts could be obtained by the clamping effect due to the substrate, which leads to the significant decrease in the effective longitudinal piezoelectric coefficient. Also if the force constant of the cantilever is too low, for some instants an air gap between the tip and the sample may arise that lowers the actual voltage drop in the sample. The ferroelectric properties of the capacitors were examined by a Radiant Technology Tester RT6000 A in a virtual ground mode.

Figure 1 shows the XRD pattern of a CBTi144 thin film annealed at 700 °C for 2 h. CBTi144 films on the platinum coated silicon substrates showed a high intensity of the (200)/(020) diffraction line compared to the other lines, although the (200) and (020) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to good matching of atomic arrangements in CBTi144 (100)/(010) and underlying Pt planes. The characteristic peak for platinum coated silicon (100) substrates was observed in the range of $38^\circ < 2\theta < 41^\circ$ and no preferred orientation of CBTi144 films was noticed. Since the lattice constants of (a) [or (b)] and (c) of the CBTi144 film is close to 0.5417 and 4.086 nm, the lattice mismatches between the ferroelectric phase and Pt lattice were given as remarkably small as 1.1% and 4.9%, respectively. The characteristic (100)/(010) orientation of the CBTi144 film is based on the good lattice matching of CBTi144 (001) with Pt (100) planes. Ferroelectricity of the calcium bismuth titanate thin films was observed with remanent polarization equal to $14 \mu\text{C}/\text{cm}^2$ and coercive field equal to $64 \text{ kV}/\text{cm}$ (Fig. 2).

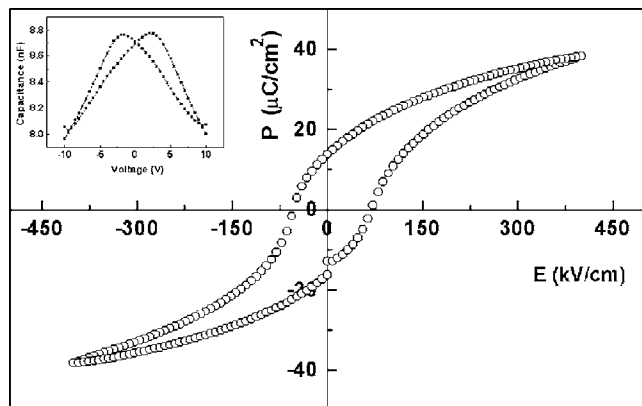


FIG. 2. P-E hysteresis loop for CBTi144 thin film. Inset shows the corresponding C-V curve.

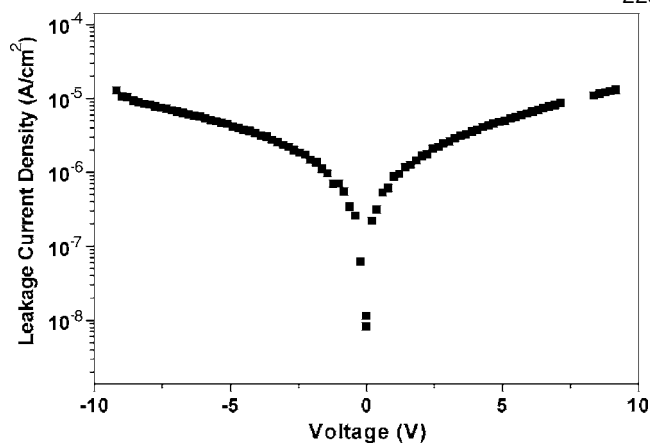


FIG. 3. Leakage current density as a function of applied voltage for CBTi144 thin film.

Almost absent is the imprint effect which causes a significant shift along the electric field axis towards the positive side. This indicates that our films present only a very small concentration of space charges at the electrode-film interface. The P_r and E_c values were improved compared with the values obtained for CBTi144 thin films with random orientation.⁸ The higher P_r value suggests that the (100) orientation is preferred rather than the (010) orientation with respect to the present CBTi144 film. However, our P_r values are much lower than those found by Kato *et al.*^{2,3} ($25 \mu\text{C}/\text{cm}^2$). This can be explained by the lower grain size of 100 nm of our films. Kato *et al.* prepared their films by sol-gel method and reported grain sizes of 200 nm. The inset of Fig. 2 illustrates the C-V curve for CBTi144 films obtained at 100 kHz and dc sweep voltage from +10 to -10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The C-V curve also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. This confirms that the films contain few movable ions or charge accumulation at the film-electrode interface. A typical leakage current characteristic for a ferroelectric thin film is given in Fig. 3. Here, the measured logarithmic current density ($\log J$) versus the voltage (V) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. This ohmic behavior occurs in insulating films as long as the films are quasi neutral, that means, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominate the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole-Frenkel emission mechanisms. The leakage current density at 1.0 V is equal to $10^{-7} \text{ A}/\text{cm}^2$. The low current density is caused by a low defect concentration, particularly by a small derivation from ideal oxygen stoichiometry due to the oriented growth in the a/b -axis direction. Figure 4 shows the out-of-plane [inset (a)] and in-plane [inset (b)] piezoresponse images of the as-grown films

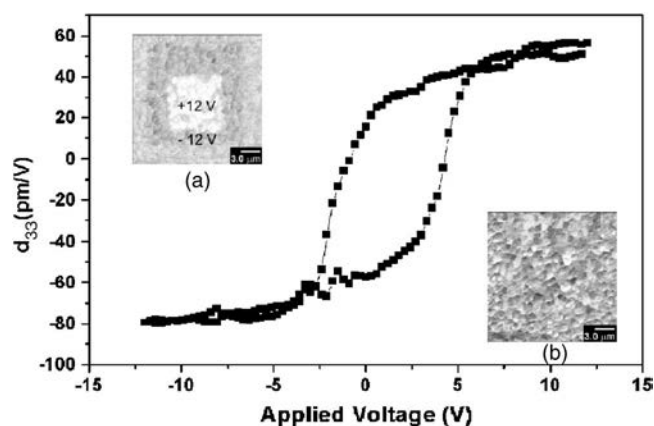


FIG. 4. Piezoresponse loop of CBTi144 thin film. Inset shows the out-of-plane (a) and in-plane (b) PFM images.

after applying a bias of -12 V, on an area of $2\text{ mm} \times 2\text{ mm}$, and then an opposite bias of $+12$ V in the central $1\text{ mm} \times 1\text{ mm}$ area. To obtain the domain images of the CBTi144 films, a high voltage in order to exceed the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.⁷ The white regions in the out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as down polarization [Fig. 4, inset (a)] while the dark regions correspond to domains oriented upward referred to as up polarization.

The $d_{33}(V)$ hysteresis loop is also given in Fig. 4. The maximum d_{33} value, $\approx 65\text{ pm/V}$, approaches the reported value for a CBTi144 single crystal.⁹ The enhancement of polarization could be caused by the a/b -axis orientation of the ferroelectric films due to the preferred orientation of the Pt substrates. As can be seen, the hysteresis loop shows an offset in the vertical direction which can be caused by non-switchable domains pinned near the electrode-film interface.¹⁰ A vertical shift in the d_{33} hysteresis loop can also be associated with different materials of the bottom electrode and the PFM tip. However, in our measurements, both materials were the same. The presented values reported for our

CBTi144 films suggest that this material can be considered as a viable alternative for lead-free piezo-ferroelectric devices. In comparison with other lead-free ferroelectrics, 65 pm/V is higher than the d_{33} value of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ films¹¹ (17 pm/V) and Nd-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ¹¹ (38 pm/V). On the other hand, this value is much lower than that obtained for sol-gel-derived films deposited onto Pt foil which present an extremely high piezoelectric coefficient of d_{33} , equal to 180 pm/V .¹²

In conclusion, polar-axis-oriented CBTi144 films were fabricated on Pt substrate using a polymeric precursor method. The 700°C annealed CBTi144 thin films showed polar-orientation and exhibited P-E hysteresis loops. The a/b -axis orientation of the ferroelectric films is considered to associate with the preferred orientation of the Pt substrate. The films showed improved ferro- and piezoelectric properties. The P_r , E_c , and d_{33} values were enhanced compared to those of the CBTi144 thin film with random orientation. The polar-axis-oriented CBTi144 films would open possibilities for devices as Pb-free piezoelectric materials.

The authors gratefully acknowledge the financial support of the Brazilian agencies FAPESP, CNPq and CAPES.

¹K. Kato, K. Suzuki, D. Fu, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **81**, 3227 (2002).

²K. Kato, D. Fu, K. Suzuki, K. Tanaka, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **84**, 3771 (2004).

³K. Kato, K. Tanaka, K. Suzuki, T. Kimura, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **86**, 112901 (2005).

⁴L. Korzanova, Ferroelectrics **134**, 175 (1992).

⁵W. Xu, W. I. Lee, T. Ko, and J. K. Lee, Appl. Phys. Lett. **82**, 3496 (2003).

⁶A. Z. Simoes, A. Ries, F. M. Filho, J. A. Varela, and E. Longo, Appl. Phys. Lett. **85**, 5962 (2004).

⁷A. Gruverman, O. Auciello, and H. Tokumoto, Annu. Rev. Mater. Sci. **28**, 101 (1998).

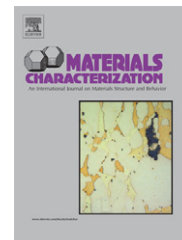
⁸K. Kato, K. Suzuki, K. Nishizawa, and T. Miki, Appl. Phys. Lett. **78**, 1119 (2001).

⁹D. Fu, K. Suzuki, and K. Kato, Jpn. J. Appl. Phys., Part 1 **42**, 5994 (2003).

¹⁰A. L. Kholkin, E. L. Colla, A. K. Tagantsev, D. V. Taylor, and N. Setter, Appl. Phys. Lett. **96**, 2577 (1996).

¹¹H. Maiwa, N. Iizawa, D. Togawa, T. Hoyashi, W. Sakamoto, M. Yamada, and S. Hirano, Appl. Phys. Lett. **82**, 1760 (2003).

¹²D. Fu, K. Suzuki, and K. Kato, Jpn. J. Appl. Phys., Part 1 **43**, 3519 (2004).



Effect of the microwave oven on structural, morphological and electrical properties of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ thin films grown on $\text{Pt/Ti/SiO}_2/\text{Si}$ substrates by a soft chemical method

A.Z. Simões, M.A. Ramirez*, C.S. Riccardi, E. Longo, J.A. Varela

Chemistry Institute, Department of Chemistry–Physics, UNESP C.P. 355, CEP 14801-970 Araraquara-SP, Brazil

ARTICLE DATA

Article history:

Received 28 May 2006

Received in revised form

24 March 2007

Accepted 25 May 2007

Keywords:

Thin films

Atomic force microscopy

Dielectric properties

Fatigue

ABSTRACT

Thin films of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBTi), a prototype of the Bi-layered-ferroelectric oxide family, were obtained by a soft chemical method and crystallized in a domestic microwave oven. For comparison, films were also crystallized in a conventional method at 700 °C for 2 h. Structural and morphological characterization of the SBTi thin films were investigated by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. Using platinum coated silicon substrates, the ferroelectric properties of the films were determined. Remanent polarization P_r and a coercive field E_c values of 5.1 $\mu\text{C}/\text{cm}^2$ and 135 kV/cm for the film thermally treated in the microwave oven and 5.4 $\mu\text{C}/\text{cm}^2$ and 85 kV/cm for the film thermally treated in conventional furnace were found. The films thermally treated in the conventional furnace exhibited excellent fatigue-free characteristics up to 10^{10} switching cycles indicating that SBTi thin films are a promising material for use in non-volatile memories.

© 2007 Elsevier Inc. All rights reserved.

1. Introduction

Related to their reversible spontaneous polarization, ferroelectric materials have several properties. For example, pyro- and piezo-electricity and linear and nonlinear optical effects, which are used for various sensors, actuators and photo-electronic devices. In recent years, ferroelectric thin films have attracted much attention because the progress of sophisticated thin film processing methods and materials allows integration of ferroelectric thin films in a complementary metal oxide semiconductor circuits (CMOS) as high-speed non-volatile ferroelectric random access memories (NVFRAM) [1–3].

Bismuth layered perovskites belonging to the Aurivillius family, denoted $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n-1})^{2-}$, where $n=2, 3, 4$ and 5, have received attention as ferroelectric materials with excellent fatigue-resistant properties [4]. These materials are constructed by stacking n perovskite units between $(\text{Bi}_2\text{O}_2)^{2+}$ layers. Among them $\text{SrBi}_2\text{Ta}_2\text{O}_9$ or $\text{SrBi}_2\text{Nb}_2\text{O}_9$ and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ or

$\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$, which have two and three perovskite units, respectively, have been extensively studied so far [5–14]. But $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ (SBTi) thin films have some drawbacks. For example, a low Curie temperature (310 °C) [15], which may induce a drift in temperature of ferroelectric properties, [16] and a high processing temperature (800 °C) [4]. So, it is of great interest to investigate ferroelectric properties of SBTi.

Higher order structures may have larger remanent polarization, with the increased number of perovskite units generating ferroelectric properties. So far, high order structures, such as $n=4$ or 5, were often studied in bulk form, but they have seldom been studied in thin film form [17–19]. Watanabe et al. [20] reported the ferroelectric property of SBTi. Several other investigators have also reported the deposition of SBTi thin films, but they did not measure the ferroelectric properties [21,22].

Solution deposition is a process that improves the stoichiometric control of complex mixed oxides and is compatible

* Corresponding author. Tel.: +55 201 6600; fax: +55 16 222 7932.

E-mail address: alezipo@yahoo.com (M.A. Ramirez).

with many semiconductor manufacturing technologies. In previous works, our group has reported the preparation of thin films by the polymeric precursor method [23]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [24]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. This method presents many advantages, such as the possibility to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method with inexpensive precursors and equipments.

The electric furnace has been mostly used for the thermal treatment of these ferroelectric materials. Rapid thermal annealing (RTA) has been used in processing of materials, in order to reach the desirable heating temperature in a shorter time. The RTA has advantages such as reduction in surface damage and minimization of the film-substrate interaction [25–27]. Recently the energy in the frequency of the microwave spectrum has been used for the processing of materials at high temperatures. This technology is comparable to RTA and provides the advantages: low investment, rapid and uniform heating, low sintering temperatures, improved product quality and the achievement of unique material properties, which cannot be reached using conventional processes [28,29].

In this work, SBTi thin films were prepared by the soft chemical method, deposited by spin coating on Pt/Ti/SiO₂/Si substrate and heat treated in a domestic microwave oven, using a SiC susceptor to absorb the microwave energy and transfer the heat to the film. The crystallization temperature is reached with the main advantage of reducing the time of the thermal treatment. The susceptor was placed below the films which were crystallized for 10 min. For comparison, a film treated in a conventional furnace was prepared in order to evaluate the influence of type of furnace on the crystallization, morphology and electrical properties of the films.

2. Experimental

The coating solution was prepared by the soft chemical method, which is based on the chelation of cations with citric acid in an aqueous solution. Ethylene glycol was added to the

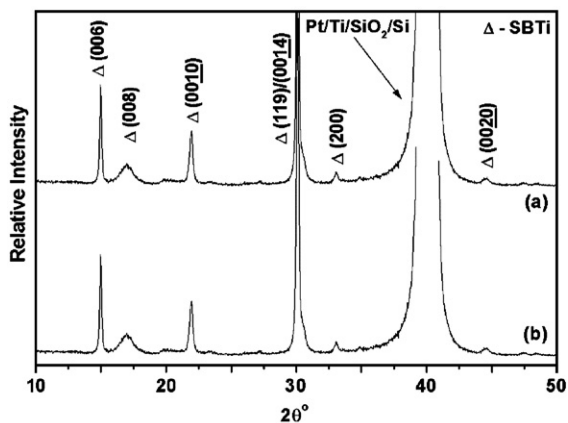


Fig. 1 – X ray diffraction for SrBi₄Ti₄O₁₅ thin film thermally treated in: (a) Microwave oven and (b) Conventional furnace.

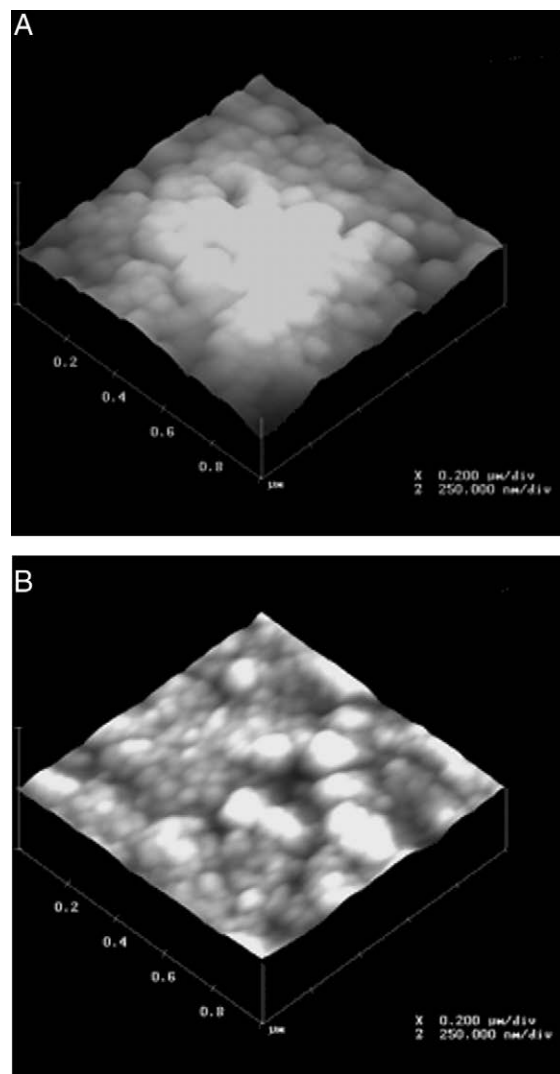


Fig. 2 – AFM images for SrBi₄Ti₄O₁₅ thin film thermally treated in: (A) Microwave oven and (B) Conventional furnace.

metallic citrate formed and the heating of this mixture led to polymerization and resulted in a homogeneous resin. The viscosity of the coating solution was adjusted to 20 cP (centipoise) by the controlled evaporation of water. The SBTi precursor resin was deposited by spin-coating on Pt/Ti/SiO₂/Si substrates at a rotation speed of 5000 rpm for 30 s and heat treated at 400 °C for 2 h in a conventional tubular furnace to eliminate organic materials. The desired thickness was obtained by successive depositions followed by pre-treatment. The crystallization of the films was also performed in a microwave oven after all layers had been deposited and thermally treated at 400 °C for 2 h. A SiC susceptor of 40 mm diameter and 10 mm thickness was used to absorb the microwave energy and transfer the heat to the film, once the volume of the film and substrate are insufficient to couple with the microwave. The temperature of the susceptor was measured using a thermocouple placed 4 mm above the film. To achieve homogeneous temperatures, the susceptor and the film were placed inside an alumina sample holder. Due to its low volume, the temperature gradient was found to be

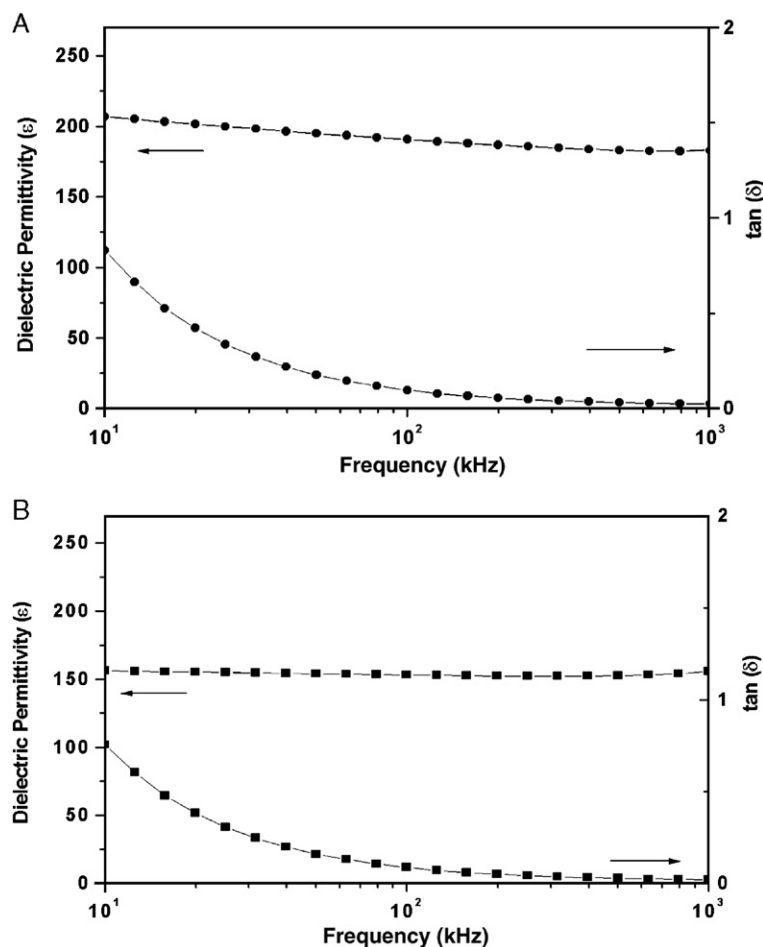


Fig. 3 – Dependence of dielectric properties of frequency for $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ thin film thermally treated: (A) Microwave oven and (B) Conventional furnace.

minimal inside the sample holder. The SBTi films were crystallized at 700 °C for 10 min with the susceptor placed below the substrate. A simple domestic microwave oven model¹ was used. A 3.83 °C/s heating rate was applied, using an automatic temperature controller. The films were characterized by X-ray diffraction (XRD) using Cu K α radiation (RIGAKU, 20–2000), 40 kV and 150 mA from 10 to 50°. Microstructural characterization was performed by atomic force microscopy (AFM) using a DIGITAL, Nanoscope 3A. The average grain size was determined in several regions of the film by measuring each individually one in length, height and width. A 0.5 mm diameter top Au electrode for the electrical measurements was prepared by evaporation through a shadow mask at room temperature. The electric properties were measured on Au/SBTi/(111)Pt/Ti/SiO₂/Si capacitor structure. The relative dielectric permittivity ϵ_r was measured versus frequency using an impedance analyser.² The capacitance-voltage characteristic was measured in the metal-ferroelectric-metal (MFM) configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across

the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000A). For fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristic of the films was measured at a constant frequency (1 MHz).

3. Results and Discussion

Fig. 1a illustrates the XRD pattern for the SBTi films heat treated in a microwave oven at 700 °C for 10 min with the susceptor placed below the substrate. For comparison, XRD pattern of the films annealed at 700 °C for 2 h in a conventional furnace is shown in Fig. 1b. The films were grown with both (100)- and (001)- orientated polycrystalline grains because no other diffraction planes were observed. Platinum coated silicon (111) substrate peak was observed in the range of $38^\circ < 2\theta < 41^\circ$ and no impurity phase was identified, indicating that the polymeric precursor method allows a single perovskite phase to be obtained.

¹ M-301, CCE, 2.45 GHz frequency, 900 W power.

² Model 4192 A, Hewlett Packard.

The changes in the surface morphology of the films submitted to different methods of crystallization were followed by AFM measurements. Fig. 2A and B present the micrographs for the films treated at 700 °C in microwave oven for 10 min with the susceptor placed below the substrate and in conventional furnace for 700 °C for 2 h, respectively. The film thermally treated in the microwave furnace presents bigger grains surrounded by a heterogeneous region (center of the film with strong white contrast) which can be caused by the damage suffered by the electrode-film interface. Because the susceptor was placed under the substrate, the film was crystallized by an upward heat flux coming from the film-substrate interface, so these regions may have originated from the stress caused by the dissimilar thermal expansion rates of the substrate and the film. The microwave energy probably plays an important role in addition to simply heating the susceptor, but that role is not yet clear. The morphology of the films treated at 700 °C in a conventional furnace consists of small spheroidal grains. The morphology is crack free with small porosity (Fig. 2B). The average surface roughness value is 27.0 nm with an average grain size of 100 nm for the film thermal treated in the microwave oven and 6.4 nm and 85 nm for the film thermally treated in the conventional furnace. It worth emphasizing that the microwave treatment leads to films with higher superficial roughness. This is not surprising because the films crystallized in a microwave oven present some bigger grains while those obtained in a conventional furnace, normally generate small rounded grains.

Fig. 3 illustrates the room temperature dielectric permittivity (ϵ) and the dissipation factor ($\tan \delta$) as a function for the film thermally treated in the microwave oven and in conventional furnace, respectively. The dielectric permittivity and the dissipation factor ($\tan \delta$) at a frequency of 1 MHz were 185 and 0.025 for the film thermally treated in the microwave oven and 157 and 0.023 for the film thermal treated in the conventional furnace, respectively. This enhancement may be due to the larger grain size of the SBTi thin films obtained in the microwave oven. This supports our hypothesis that the microwave oven suppresses the formation of a very low dielectric permittivity layer at the bottom thin film/electrode interface. However, it may damage the electrode-film interface probably due to the electrical discharge between the SiC susceptor and the thermocouple caused by the high electric field in the microwave environment [30,31]. Considerable dispersion can be observed at low frequencies for the dissipation factor, which may attribute to space charges at the film-electrode interface.

The capacitance versus voltage (C–V) dependence is shown in Fig. 4. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. The two peaks, which characterize spontaneous polarization switching, are clearly shown in Fig. 4. Also, the curve displays asymmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The curve for the film thermally treated in the microwave oven present a slight change in capacitance values (Fig. 4A). This can be originated from the thermal shock caused by the rapid heating of the SiC susceptor, which favors the accumulation of the static charges on the interface film-substrate. For films

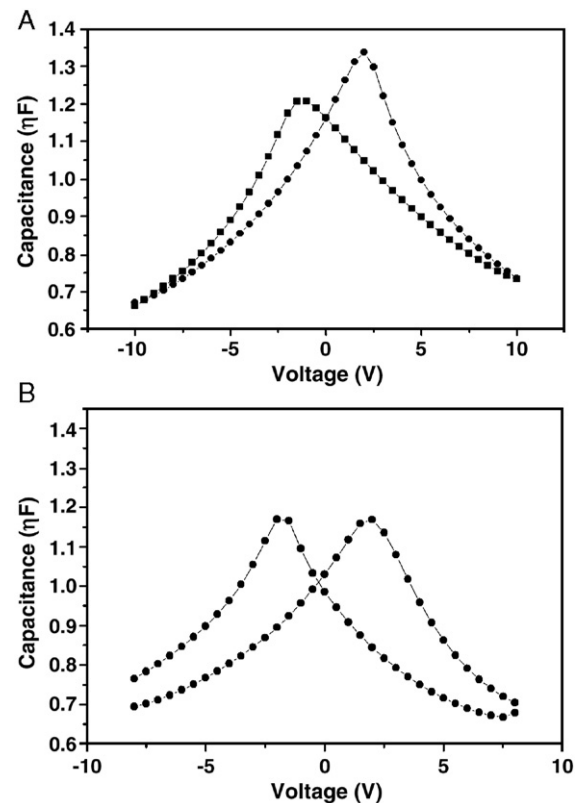


Fig. 4—C–V curve for SrBi₄Ti₄O₁₅ thin film thermally treated in: (A) Microwave oven and (B) Conventional furnace.

thermally treated in the conventional furnace the C–V curve is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface (Fig. 4B).

Fig. 5 shows hysteresis loops of SBTi films thermally treated in different type of furnaces. For both films, the hysteresis loops were not saturated indicating poor ferroelectric properties along c-axis growth (Fig. 5A and B). These results were similar to those reported by Watanabe et al. [20]. Recently, Irie and Miyayama reported on ferroelectric properties of SBTi single crystals [19]. *a*- and *b*-axes orientations were obtained with a typical ferroelectric behavior ($P_r = 29 \mu\text{C}/\text{cm}^2$), whereas dielectric behavior was observed for *c*-axis orientation. This indicates the remanent polarization of polycrystalline film is strongly dependent on the orientation of grains. A high coercive field is mainly observed in the films crystallized in the microwave oven due to the generation of defect sites at the film-substrate interface, which affects the domains switching characteristics. The actual temperature in the susceptor may be some degrees higher, which, allied to the effect of the microwave energy, may cause degradation of the film-electrode interface and hence to a loss of ferroelectric properties.

When a ferroelectric material is repeatedly cycled from one polarization state to another, its dielectric and ferroelectric properties change. This phenomenon, known as ferroelectric fatigue, is a limiting factor for the performance of the ferroelectric random access memory (FRAM) devices. The fatigue endurance of SBTi thin films were tested at 1 MHz as a

function of switching cycles by applying 8.6 μs wide bipolar pulses with maximum amplitudes of ± 9 V (Fig. 6). P^* is the switched polarization between two opposite polarity pulses and $P^\wedge$ is the nonswitched polarization between the same two polarity pulses. The legend $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denotes the switchable polarization, which is an important variable for nonvolatile memory application. No fatigue resistance was observed for films thermally treated in the microwave oven. This was due to the increase of local current which eventually destroys the film-electrode interface leading to a decrease of remnant polarization (Fig. 6A) [32]. Fatigue resistance was observed up to 10^{10} cycles for the films thermally treated in the conventional furnace suggesting that SBTi has good potential for applications in memories (Fig. 6B).

Ferroelectric fatigue can be explained by considering the oxygen vacancy in ferroelectric films. The vacancy has a detrimental role in the fatigue properties. It can stabilize the charges trapped at domain walls, and make the unpinning difficult [33]. At the same time, its accumulation near electrodes can increase the electron injection, which in turn increases the pinning rate [34]. Because strontium in the Sr-Ti-O blocks is very stable, it leads to a lower concentration of oxygen vacancies and thus prompt the unpinning of domain walls. For practical applications, the high coercive field of SBTi is not favorable for ordinary ferroelectric random access memory (FRAM). However, because it has a large P_r and there is a small difference between P_r (remnant polarization) and P_s (saturation polarization), it may have several possible applications in new memory devices. For instance, it may be used as a virtual read only memory (ROM). That is, if both

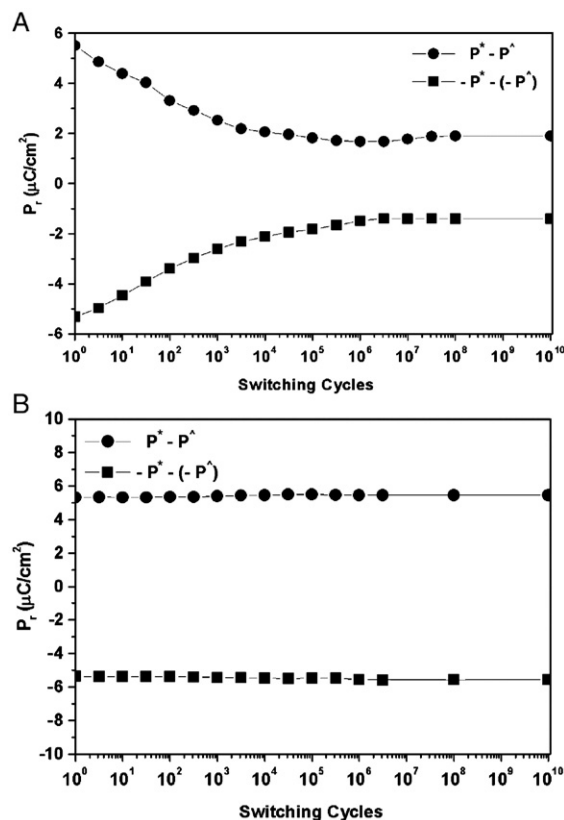


Fig. 6 – Fatigue as a function of polarization cycles for $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ thin film thermally treated in: (A) Microwave oven and (B) Conventional furnace.

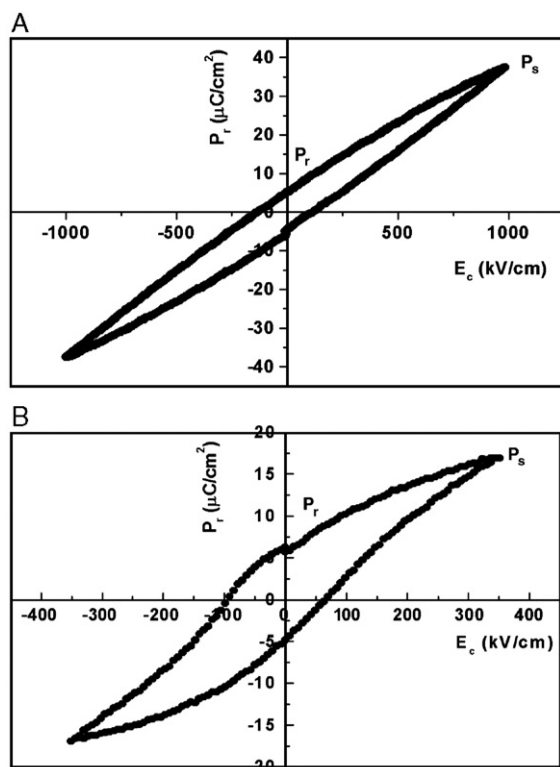


Fig. 5 – P–E hysteresis loop for $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ thin film thermally treated in: (A) Microwave oven and (B) Conventional furnace.

ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ capacitors were fabricated on the same FRAM memory chip, only $\text{SrBi}_2\text{Ta}_2\text{O}_9$ capacitors could be switched by the application of 2–3 V. About 5 V would be necessary to switch SBTi capacitors.

These findings strongly encourage investigations into the crystallization of thin films using microwave energy. Studies are ongoing to optimize the temperature and time required for good crystallization of SBT films using a microwave oven, without degradation of the electrical properties. An alternative to minimize the effect of several thermal shock, when the film is placed directly on the susceptor, is to put the susceptor above the film. Another possibility is to place ceramic wool between the susceptor and the substrate to prevent electric sparks. In this case, the platinum substrate will receive less influence of microwave energy and as consequence will inhibit the formation of a good interface layer, leading to an increase of dielectric permittivity.

4. Conclusions

We have grown polycrystalline, homogeneous and crack-free SBTi thin films on Pt(111)/Ti/SiO₂/Si(100) substrate by the polymeric precursor method using a microwave oven and a conventional furnace. The microwave oven reduces significantly the time required to crystallize the SBTi phase when compared to a conventional furnace. The films thermally

treated in the microwave oven present a slight change in capacitance values, high coercive field and exhibit no fatigue resistance due to the generation of defect sites at the film-substrate interface. The time required to obtain the film is reduced and the use of ceramic wool placed between the susceptor and the substrate seems to be ideal to prevent thermal shock from electric sparks. This technique is aimed at obtaining fatigue free SBTi films produced in the microwave furnace.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

REFERENCES

- [1] Scott JF, Paz Araujo CA. Ferroelectric memories. *Science* 1989;246:1400–5.
- [2] Auciello O, Scott JF, Ramesh R. NVFRAMs story spurs volatile debate about physics applications. *Phys Today* 1998;51(11):84–6.
- [3] Paz de Araujo CA, Cuchiaro JD, McMillan LD, Scott MC, Scott JF. Fatigue-free ferroelectric capacitor with platinum electrodes. *Nature* 1995;374:627–9.
- [4] Subbarao EC. Family of ferroelectric bismuth compounds. *J Phys Chem Solids* 1962;23:665–74.
- [5] Kim J, Chae HK, Lee KS, Lee WI. Preparation of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films with a single alkoxide sol–gel precursor. *J Mater Chem* 1998;8:2317–9.
- [6] Amanuma K, Hase T, Miyasaka Y. Preparation and ferroelectric properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin-films. *Appl Phys* 1995;66(2):221–3.
- [7] Boyle TJ, Buchheit CD, Rodriguez MA, Al-Shareef HN, Hernandez BA, Scott B, et al. Formation of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ synthesis and characterization of a novel sol–gel solution for production of ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films. *J Mater Res* 1996;11(9):2274–81.
- [8] Bu SD, Park BH, Kang BS, Kang SH, Noh TW, Jo W. Influence of the laser fluency on the electrical properties of pulsed-laser-deposited $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films. *Appl Phys Lett* 1999;75(8):1155–7.
- [9] Al-Shareef HN, Dimos D, Boyle TJ, Warren WL, Tuttle BA. Qualitative model for the fatigue-free behavior of $\text{SrBi}_2\text{Ta}_2\text{O}_9$. *Appl Phys Lett* 1996;68(5):690–2.
- [10] Kang BS, Park BH, Bu SD, Kang SH, Noh TW. Different fatigue behaviors of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Bi}_3\text{TiTaO}_9$ films: role of perovskite layers. *Appl Phys Lett* 1999;75(17):2644–6.
- [11] Park BH, Kang BS, Bu SD, Noh TW, Lee J, Jo W. Lanthanum-substituted bismuth titanate for use in on-volatile memories. *Nature* 1999;401:682–4.
- [12] Joshi PC, Krupanidhi SB. Structural and electrical studies on thermally processed ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films by metallo-organic solution deposition. *J Appl Phys* 1992;72(12):5827–33.
- [13] Tani K, Yamanobe T, Matsushashi H, Nishikawa S. Formation of c-axis oriented $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films with extremely flat surface by spin-coating. *Jpn J Appl Phys Part 1* 1997;36:1460–4.
- [14] Kijima T, Satoh S, Matsunaga H, Koba M. Ultrathin fatigue-free $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films for nonvolatile ferroelectric memories. *Jpn J Appl Phys Part 1* 1996;35:1246–50.
- [15] Landolt-Bornstein, Group 3, edited by K.-H. Hellwege and A. M. Hellwege Springer, Berlin, 1969, Vol. 3.
- [16] Furuya A, Cuchiaro JD. Compositional dependence of electrical characteristics of $\text{SrBi}_2(\text{Ta}_{1-x}\text{Nb}_x)_2\text{O}_9$ thin-film capacitors. *J Appl Phys* 1998;84(12):6788–94.
- [17] Smolenskii GA, Isupov VA, Agranovskaya AI. Ferroelectrics of the oxygen-octahedral type with layered structure. *Sov Phys Solid State* 1961;3(3):651–5.
- [18] Gelfuso MV, Thomazini D, Eiras JA. Synthesis and structural, ferroelectric and piezoelectric properties of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ ceramics. *J Am Ceram Soc* 1999;82(9):2368–73.
- [19] Irie H, Miyayama M. Dielectric and ferroelectric properties of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ single crystals. *Appl Phys Lett* 2001;79(2):251–2.
- [20] Watanabe H, Mi hara T, Yoshimori H, Paz de Araujo CA. Preparation of ferroelectric thin films of bismuth layer structured compounds. *Jpn J Appl Phys Part 1* 1995;34:5240–4.
- [21] Oka H, Hirose M, Tsukada T, Watanabe Y, Nomura T. Thickness-shear vibration mode characteristics of $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ -based ceramics. *Jpn J Appl Phys Part 1* 2000;39:5613–5.
- [22] Tachiki M, Yamamuro K, Kobayashi T. Optical characterization of $\text{Sr}_{m-3}\text{Bi}_4\text{Ti}_m\text{O}_{3m+3}$ ($m=4,5,6$) thin films grown by pulsed laser deposition method. *Jpn J Appl Phys Part 2* 1996;35:L719–21.
- [23] Simões AZ, Gonzalez AHM, Zaghete MA, Stojanovic B, Cavalheiro AA, Moekli P, et al. Influence of oxygen flow on crystallization and morphology of LiNbO_3 thin films. *Ferroelectrics* 2002;271:1623–8.
- [24] Simões AZ, Gonzalez AH, Riccardi CS, Cantoni M, Zaghete MA, Stojanovic BD, et al. Influence of oxygen atmosphere on crystallization and properties of LiNbO_3 thin films. *J Eur Ceram Soc* 2004;24(6):1607–13.
- [25] Kato K, Zheng C, Fi nder JM, Dey SK, Tory Y. Sol–gel route to ferroelectric layer-structured perovskite $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{SrBi}_2\text{Nb}_2\text{O}_9$ thin films. *Am Ceram Soc* 1998;81(7):1869–75.
- [26] Chung CW, Chung I. Effect of pre-annealing on physical and electrical properties of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films prepared by chemical solution deposition. *Thin Solid Films* 1999;354:111–7.
- [27] Araujo EB, Eiras JA. PZT thin films produced by oxide precursors and crystallized by conventional and RTA process. *J Eur Ceram Soc* 2001;21:1513–6.
- [28] Metaxas AC. Foundations of electroheat: a unified approach. New York: Wiley; 1995.
- [29] Clark DE, Folz DC, West JK. Processing materials with microwave energy. *Mater Sci Eng A* 2000;287:153–8.
- [30] Bao D, Wakiya N, Shinozaki K, Mizutani N, Yao X. Improved electrical properties of $(\text{Pb},\text{La})\text{TiO}_3$ thin films using compositionally and structurally compatible LaNiO_3 thin films as bottom electrodes. *Appl Phys Lett* 2001;78(21):3286–8.
- [31] Tagantsev AK, Landivar M, Colla E, Setter N. Identification of passive layer in ferroelectric thin films from their switching parameters. *J Appl Phys* 1995;78(4):2623–30.
- [32] Damjanovic D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. *Rep Prog Phys* 1998;61(9):1267–324.
- [33] Warren WL, Tuttle BA, Di mos D. Ferroelectric fatigue in perovskite oxides. *Appl Phys Lett* 1995;67(10):1426–8.
- [34] Scott JF, Paz de Araujo CA, Melnick BM, Mcmillan LD, Zuleeg RZ. Quantitative measurement of space-charge effects in lead zirconate–titanate memories. *J Appl Phys* 1991;70(1):382–8.

Synthesis and electrical characterization of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films deposited on Pt/Ti/SiO₂/Si substrates by polymeric precursor method

A.Z. Simões^a, M.A. Ramírez^{a,c,*}, C.S. Riccardi^a, A.H.M. Gonzalez^a, E. Longo^b, J.A. Varela^a

^a Chemistry Institute, UNESP—Paulista State University, C.P. 355, 14801-970 Araraquara, SP, Brazil

^b Chemistry Department, UFSCar—Federal University of São Carlos, C.P. 676, 13560-905 São Carlos, SP, Brazil

^c Materials Science and Technology, UNESP—Paulista State University, C.P. 473, 17033-36, Bauru, SP, Brazil

Received 25 May 2005; accepted 5 September 2005

Abstract

We report the successful deposition of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBN) thin films on platinum coated silicon substrates by polymeric precursor method. The CBN thin films exhibited good structural, dielectric and CBN/Pt interface characteristics. The leakage current of the capacitor structure was around 0.15 A cm^{-2} at an applied electric field of 30 kV cm^{-1} . The capacitance–voltage measurements indicated good ferroelectric polarization switching characteristics. The typical measured small signal dielectric constant and the dissipation factor at a frequency of 100 kHz were 90 and 0.053, respectively. The remanent polarization and the drive voltage values were 4.2 C cm^{-2} and 1.7 V at an applied voltage of 10 V. No significant fatigue was observed at least up to 10^8 switching cycles.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Thin films; Annealing; Electrical properties

1. Introduction

Ferroelectric thin films have been widely investigated for their use in a variety of devices exploiting their unique piezoelectric, pyroelectric, polarization switching and electro-optic properties [1]. Recently, there has been a surge in research activity on ferroelectric thin films for nonvolatile random access memory (NVRAM) applications. Ferroelectric thin films with large remanent polarization, low coercive field and low fatigue rate characteristics have the potential for use as memory elements in high density 1T-1C nonvolatile memories [2].

$\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBN) is a member of Bi-based layer-structured perovskite compounds [3] such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{TaNb}_2\text{O}_9$ (SBTN) for which there has been a huge amount of research on nonvolatile random access memory applications [4]. Compared with SBT and SBNT thin films, there has been little reported on electrical properties of CBN thin films. Since the *c*-axis oriented CBN thin film had a low dielectric constant, it was considered to be a good candidate for application to nonvolatile ferroelectric memories. So far, the ferroelectric

properties of CBN thin films have not been reported. CBN is a layered perovskite ferroelectric oxide, whose lattice constants are: $a = 50.5435 \text{ nm}$, $b = 50.54658 \text{ nm}$ and $c = 52.4970 \text{ nm}$ [5]. For device applications, a single crystalline film has an edge over a polycrystalline film in obtaining stable and desirable properties. To obtain a good ferroelectric memory device exploiting ferroelectric film, it is required that the ferroelectric films have good ferroelectric properties, low interface state density, high breakdown strength and low leakage current. Usually, metal–ferroelectric–semiconductor is the desired configuration for a one transistor high density memory array for applications to nonvolatile memories. In this configuration, it is required the direct deposition of ferroelectric thin film on Si wafer. However, it is difficult to preserve ferroelectricity on Si due to existence of interfacial traps and/or interdiffusion of the constituent elements. Therefore, it is interesting to evaluate the ferroelectric properties of these films on metal electrodes such as platinum.

In previous works, our group has reported the preparation of thin films by the polymeric precursor method [6]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [7]. The precursor film is deposited by dip or spin-coating and then treated to eliminate the organic material and synthesize the desired phase. The polymeric precursor method presents many advantages, such as the possibility

* Corresponding author.

E-mail address: miganr@kenter.com (M.A. Ramírez).

to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments).

Considering that the literature reports no data about the preparation of $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBN) films through a polymeric precursor method, in this work, we describe our preliminary results on the deposition of thin films and their electrical properties relating to ferroelectric random access memory applications.

2. Experimental procedures

Calcium citrate (Synth), niobium oxide (Aldrich) and bismuth oxide (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth and niobium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of Ca, Bi and Nb solutions were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 12 cP by controlling the water content using a Brookfield viscosimeter. The CBN thin films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 revolutions per minute for 30 s (spin coater KW-4B, Chemat Technology). In this work, an excess of 5 wt% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature [8]. The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness values of about 320 nm for CBN, reached by repeating the spin-coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case, back scattering electrons were used. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu K α radiation. The morphology of the thin films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) by using a silicon nitride tip in the contact mode. AFM was used to obtain a three-dimensional image reconstruction of the sample's surface. These images allow for an accurate analysis of the sample's surface and the quantification of very important parameters such as roughness and grain size. The scan area was 1 m $\times$ 1 m in the *x*–*y* plane. For electrical measurements, a 0.5 mm diameter top Au electrode were deposited by evaporation through a shadow mask at room temperature. The electric properties were measured by an Au/CBN/Pt/Ti/SiO₂/Si (1 0 0) capacitor structure. The capacitance–voltage (*C*–*V*) characteristic was measured in the metal–ferroelectric–metal (MFM) configuration using a small alternate current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. The relative dielectric constant ϵ_r were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). *J*–*E* characteristics of the films were measured using a Radiant Technology RT6000 A in a virtual ground mode at room temperature. A contact with probe electrodes was made with a wire-bonding method. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology RT6000 A). For the fatigue measurements, internally generated 8.6 s wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

Fig. 1 shows the XRD pattern of the 700 °C crystallized CBN thin film on platinum coated silicon substrate. The annealed thin film was a single phase of a layer-structured perovskite with orthorhombic crystallographic structure. The peaks were indexed according to following ref. [9]. The thin film showed random orientation with the highest intensity peak at $2\theta = 29^\circ$. The main peak is very sharp, suggesting the presence of large

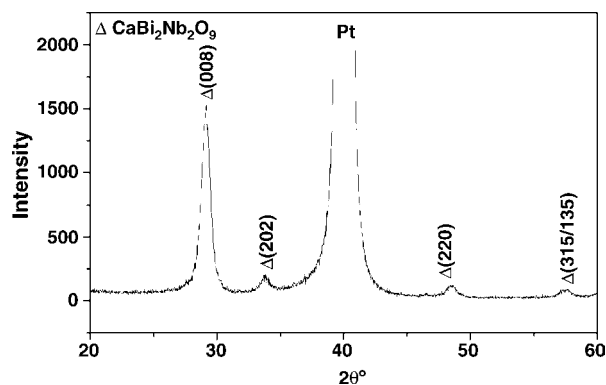


Fig. 1. X ray diffraction for CBN thin film annealed at 700 °C for 2 h.

crystalline grains in the film. Characteristic peak for platinum coated silicon (1 1 1) substrates was observed in the range of $38^\circ < 2\theta < 41^\circ$.

Fig. 2 shows the typical AFM micrograph of the CBN thin film annealed at 700 °C for 2 h. Average grain size and surface roughness were estimated using a contact mode. The obtained morphology is crack free and of small porosity. The average surface roughness value is 16 nm while the average grain size consisting of isotropic round shape is 120 nm. This parameter roughness is extremely important since the dielectric properties depend not only on a well-defined microstructure but also of the relationship between the electrode interface–film. The morphology consists of large and small grains distributed along the films surface. The large grains was flat and their sizes was slightly smaller than the film thickness, implying that the growth behavior of each large grain was not similar to an epitaxial growth.

Low leakage current density is another important parameter for memory device applications. Here, the measured logarithmic current density ($\log J$) versus the voltage (*V*) is shown (Fig. 3). The CBN thin films exhibited good leakage current characteristics. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. This ohmic behaviour occurs in insulat-

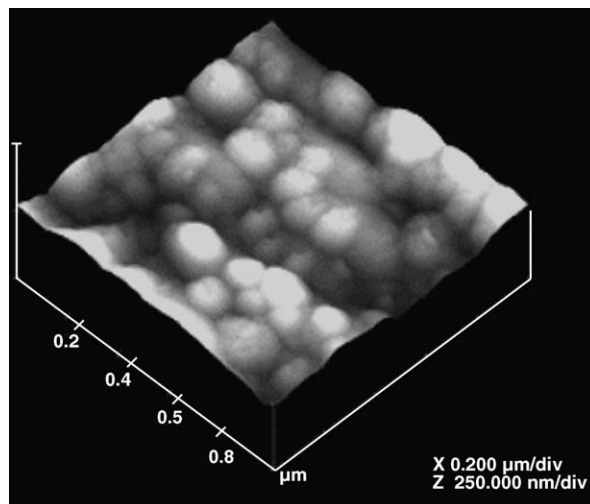


Fig. 2. AFM image for CBN thin film annealed at 700 °C for 2 h.

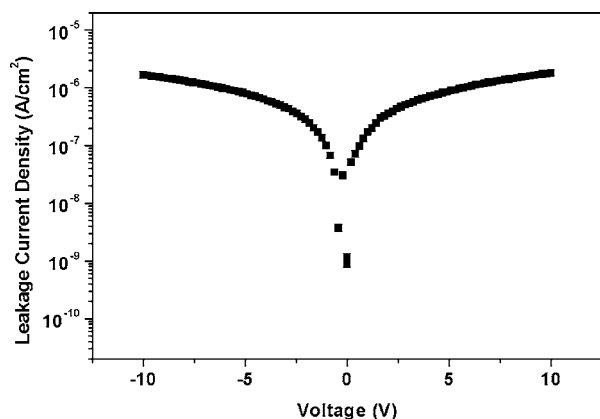


Fig. 3. Leakage current density in dependence of voltage for CBN thin film annealed at 700 °C for 2 h.

ing film as long as the film is quase neutral, that is, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominates the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V is equal to $1.5 \times 10^{-7} \text{ A cm}^{-2}$ up to an applied electric field of 30 kV cm^{-1} establishing good insulating characteristics. It was noted a symmetric J – V characteristic for both voltage polarity indicating that the bulk controls the properties once we have used different top and bottom electrodes and having different processing conditions. Since the conductivity is strongly affected by the characteristics of the film–electrode interface, the surface morphology of CBN thin films is one of the major factors determining the leakage current in capacitors. The low leakage current value can be attributed to the small surface roughness as was observed in Fig. 2.

Fig. 4 illustrates the C – V curve for CBN films obtained at 100 kHz and dc sweep voltage from +10 to –10 V. The capacitance dependence on the voltage is strongly nonlinear, confirming the ferroelectric properties of the film resulting from the domain switching. The C – V curve for the film annealed at

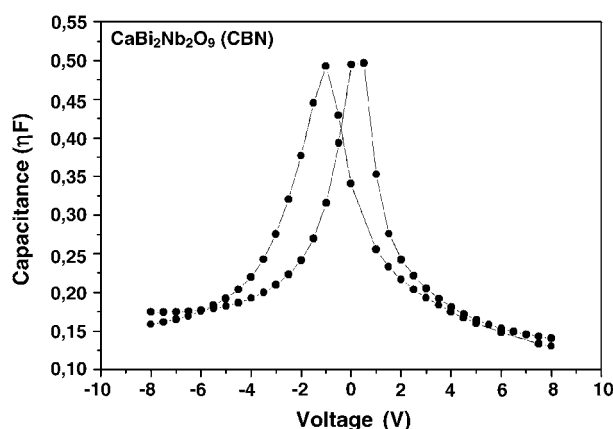


Fig. 4. C – V curve for CBN thin film annealed at 700 °C for 2 h.

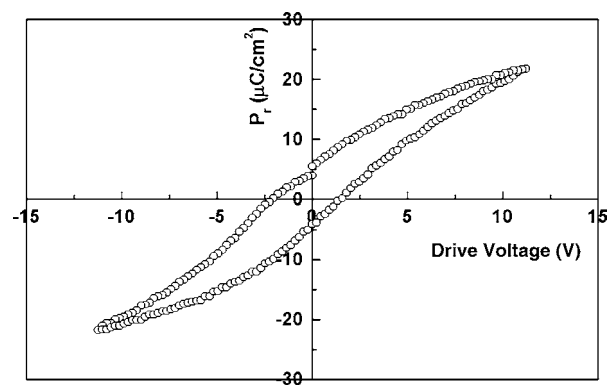


Fig. 5. P – V hysteresis loop for CBN thin film annealed at 700 °C for 2 h.

700 °C for 2 h also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The symmetry around the zero bias axis indicates that the films contain few movable ions or charge accumulation at the film–electrode interface. The dielectric constant of the CBN thin films calculated from C_{max} was 90. The dissipation factor was 0.053 at 100 kHz. Similar results were obtained by CBN films deposited on $n(+)$ –Si(100) substrates by pulsed laser deposition [10]. Because the CBN thin film shown ferroelectric nature, hysteresis curve were examined at room temperature in MFM configuration (Fig. 5). Ferroelectricity of the calcium bismuth niobate was observed with remanent polarization (P_r) and a drive voltage V_c of 4.2 C cm^{-2} and 1.7 V, though the hysteresis loop was not fully saturated at the applied voltage. The low remanent polarization value can be related to the growth in c -axis direction, which is evident for bismuth-based layer-structured perovskite compounds [11]. New studies should be performed in order to understand the contribution of c -axis direction on the ferroelectric properties of this system. It can be also noted the absence of imprint which causes a significant shift along the electric field axis towards the positive side. This indicates that our films presents a small concentration of space charges in the electrode–film interface. These results are consistent with the C – V measurements where was observed symmetry around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film–electrode interface (Fig. 4).

Among the degradation processes in ferroelectric thin films, polarization fatigue has received the most attention especially in thin films deposited on platinum electrodes. The fatigue endurance of CBN thin films were tested at 1 MHz as a function of switching cycles by applying 8.6 s wide bipolar pulses with maximum amplitudes of $\pm 10 \text{ V}$ (Fig. 6). P^* is the switched polarization between two opposite polarity pulses and $\hat{P}$ is the nonswitched polarization between the same two polarity pulses. The $P^* - \hat{P}$ or $-P^* - (-\hat{P})$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 1×10^8 cycles suggesting that CBN has good potential for applications in memories. However, new studies should be performed aiming to understand its source and improve the fatigue resistance to higher cycles.

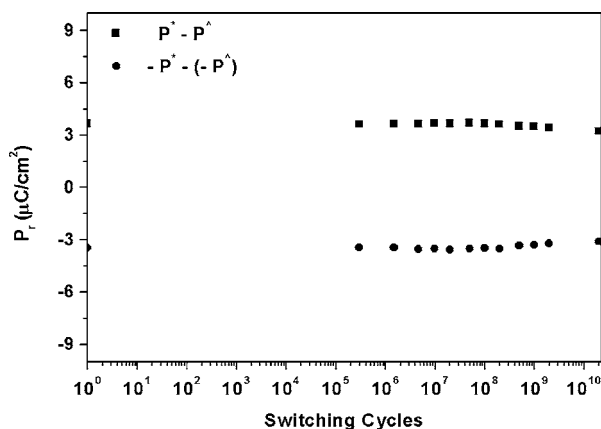


Fig. 6. Fatigue as a function of polarization cycles for CBN thin film annealed at 700 °C for 2 h.

4. Conclusions

Highly *c*-axis oriented $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBN) thin films were successfully deposited directly on platinum coated silicon substrates by the polymeric precursor method. The CBN thin films exhibited good structural and a dense microstructure. The typical measured small signal dielectric constant and dissipation factor at 100 kHz were 90 and 0.053, respectively. The leakage current density was around $10^{-7} \text{ A cm}^{-2}$ at an applied electric field of 30 kV cm^{-1} . The remanent polarization and the drive voltage values were 4.2 C cm^{-2} and 1.7 V, respectively. No significant fatigue was observed at least up to 10^8 switching cycles. The results of these studies are very promising and suggest that

CBN thin films can be used as storage element in nonvolatile ferroelectric random access memories.

Acknowledgments

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq and CAPES.

References

- [1] S.B. Desu, R. Ramesh, B.A. Tuttle, R.E. Jones, I.K. Yoo (Eds.), *Ferroelectric Thin Films V*, vol. 433, 1996.
- [2] S. Sinharoy, H. Buhay, D.R. Lampe, M.H. Francombe, J. Vac. Sci. Technol. A 10 (1992) 1554.
- [3] G.A. Smolenskii, V.A. Bokov, V.A. Isupov, N.N. Krainik, R.E. Pasynkov, A.I. Sokolov, in: G.A. Smolenskii (Ed.), *Ferroelectrics and Related Materials*, Gordon and Breach Science Publishers, New York, 1984 (Chapter 15).
- [4] C.A.P. Araujo, J.D. Cuchiaro, L.D. McMillian, M.C. Scott, J.F. Scott, *Nature (London)* 374 (1995) 627.
- [5] G.V. Gibbs, M.B. Boisen Jr., R.T. Downs, K.L. Bartelmehs, XPOW-PLOT Version 2.0, 1993.
- [6] A.Z. Simões, A. Ries, F.M. Filho, C.S. Riccardi, E. Longo, J.A. Varela, *Appl. Phys. Lett.* 85 (2004) 5962.
- [7] A.Z. Simões, A.H. Gonzalez, C.S. Riccardi, M. Cantoni, M.A. Zaghet, B.D. Stojanovic, J.A. Varela, *J. Eur. Ceram. Soc.* 24 (2004) 1607.
- [8] B.S. Kang, B.H. Park, S.D. Bu, S.H. Kang, T.W. Noh, *Appl. Phys. Lett.* 75 (1999) 2644.
- [9] S.B. Desu, H.S. Cho, P.C. Joshi, *Appl. Phys. Lett.* 70 (1997) 1393.
- [10] H.S. Cho, S.B. Desu, *Phys. Status Solidi A, Appl. Res.* 161 (1997) 371.
- [11] M.-W. Chu, M. Ganne, M.T. Caldes, L. Brohan, *J. Appl. Phys.* 91 (2002) 3178.

ANEXO U

High Curie point $\text{CaBi}_2\text{Nb}_2\text{O}_9$ thin films: A potential candidate for lead-free thin-film piezoelectrics

A. Z. Simões,^{a)} A. Ries, C. S. Riccardi, A. H. M. Gonzalez, E. Longo, and J. A. Varela
 Chemistry Institute, Universidade Estadual Paulista (UNESP), P.O. Box 355,
 14801-970 Araraquara, Sao Paulo, Brazil

(Received 29 March 2006; accepted 23 July 2006; published online 12 October 2006)

$\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) thin films deposited on platinum coated silicon substrates by the polymeric precursor method exhibited good structural, dielectric, and piezoelectric characteristics. Capacitance-voltage measurements indicated good ferroelectric polarization switching characteristics. Remanent polarization and drive voltage values were $4.2 \mu\text{C}/\text{cm}^2$ and 1.7 V for a maximum applied voltage of 10 V. The film has a piezoelectric coefficient d_{33} equal to 60 pm/V, current density of $0.7 \mu\text{A}/\text{cm}^2$, and Curie temperature of 940 °C. The polar-axis-oriented CBNO is a promising candidate for use in lead-free high Curie point in ferroelectric and piezoelectric devices. © 2006 American Institute of Physics. [DOI: 10.1063/1.2357419]

I. INTRODUCTION

High-temperature sensing technology is of major importance for chemical and material processing, as well as automotive, aerospace, and power generating industries. Electro-mechanical transducer materials are required to sense strains, vibrations, and noise under several thermal conditions. Among the different types of acoustic and strain sensors, piezoelectric ones are the best candidates considering sensitivity, cost, and design.¹

When an operating temperature of 400 °C or greater is required, the choice of materials for high-temperature piezoelectric transducers is limited. Modified bismuth titanate compositions are interesting for sensor applications up to 500 °C.² When an operating temperature of up to 750 °C is required, there is no suitable commercial ceramic available. $\text{CaBi}_2\text{Nb}_2\text{O}_9$ (CBNO) is a member of Bi-based layer-structured perovskite compounds³ such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{SrBi}_2\text{TaNb}_2\text{O}_9$ (SBTN) for which there has been a huge amount of research on nonvolatile random access memory applications.⁴ Compared with SBT and SBNT thin films, there has been little reported on electrical properties of CBNO thin films. CBNO is a layered perovskite ferroelectric oxide, whose lattice constants are $a=50.5435 \text{ nm}$, $b=50.54658 \text{ nm}$, and $c=52.4970 \text{ nm}$.⁵ The spontaneous polarization P_s for CBNO is along the a -axis direction. Therefore, thin films with a -axis orientation are preferred for use in many kinds of devices, such as ferroelectric random access memories, piezoelectric microactuators, and resonators. The crystallinity and orientation of the Pt bottom electrodes were found to affect the phase transition of paraelectric to ferroelectric in bismuth layered compounds.⁶

Among various methods such as metal-organic chemical vapor deposition, pulsed laser deposition, and sol gel, the polymeric precursor method has its advantages over the other production techniques including its low cost, good compositional homogeneity, relatively low processing temperatures, and the ability to coat large substrate areas.^{7,8}

However, there is no publication on CBNO thin films deposited on (100) Pt/Ti/SiO₂/Si bottom electrodes by the polymeric precursor method. In this article, we report the oriented lead-free high Curie point (T_C) ferroelectric thin film through a polymeric precursor method, CBNO, which has the highest known T_C (943 °C) of the Aurivillius-phase structure materials.

II. EXPERIMENTAL PROCEDURE

Calcium citrate (Synth), niobium oxide (Aldrich), and bismuth oxide (Aldrich) were used as raw materials. The precursor solutions of calcium, bismuth, and niobium were prepared by adding the raw materials to ethylene glycol and concentrate aqueous citric acid under heating and stirring. Appropriate quantities of Ca, Bi, and Nb solutions were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 12 cP by controlling the water content using a Brookfield viscosimeter. The CBNO thin films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). In this work, an excess of 5% by weight of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as was reported in literature.⁹ The thin films were annealed at 700 °C for 2 h in a conventional furnace. Through this process, we have obtained thickness value of about 320 nm for CBNO, reached by repeating the spin coating and heating treatment cycles. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case backscattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. The morphology of the thin films was examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) by using a silicon nitride tip in the contact

^{a)}FAX: 55-16-3322-7932; electronic mail: alezipo@yahoo.com

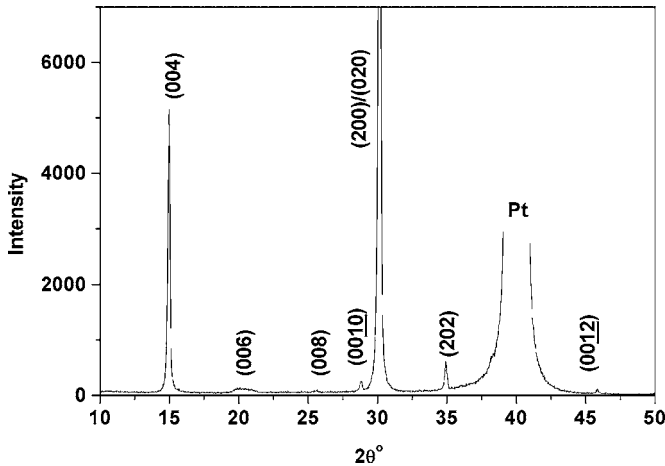


FIG. 1. X-ray diffraction for CBNO thin film annealed at 700 °C for 2 h.

mode. AFM was used to obtain a three-dimensional image reconstruction of the sample's surface. These images allow for an accurate analysis of the sample's surface and the quantification of very important parameters such as roughness and grain size. The scan area was $1 \times 1 \mu\text{m}^2$ in the x - y plane. For electrical measurements, a 0.5 mm diameter top Au electrode was deposited by evaporation through a shadow mask at room temperature. The electric properties were measured by a Au/CBNO/Pt/Ti/SiO₂/Si (100) capacitor structure. The capacitance-voltage (C - V) characteristic was measured in the metal-ferroelectric-metal (MFM) configuration using a small alternate current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. The relative dielectric constant ϵ_r was measured versus frequency using an impedance analyzer (model 4192 A, Hewlett Packard). J - E characteristics of the films were measured using a Radiant Technology RT6000 A in a virtual ground mode at room temperature. A contact with probe electrodes was made with a wire-bonding method. Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology RT6000 A). The dielectric characterization was accomplished in an impedance analyzer, model 4192 of HP, and measurements of the capacitance as a function of the temperature for the frequency of 100 kHz were performed. The Curie temperature of the material is obtained from the capacitance dependent temperature curves.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of CBNO thin film annealed at 700 °C for 2 h. CBNO films on the platinum coated silicon substrates showed a high intensity of the (200)/(020) diffraction line compared to the other lines, although the (200) and (020) diffraction lines could not be distinguished from each other. The characteristic orientation is considered to be due to good matching of atomic arrangements in CBNO (100)/(010) and underlying Pt planes. The annealed thin film was a single phase of a layer-structured

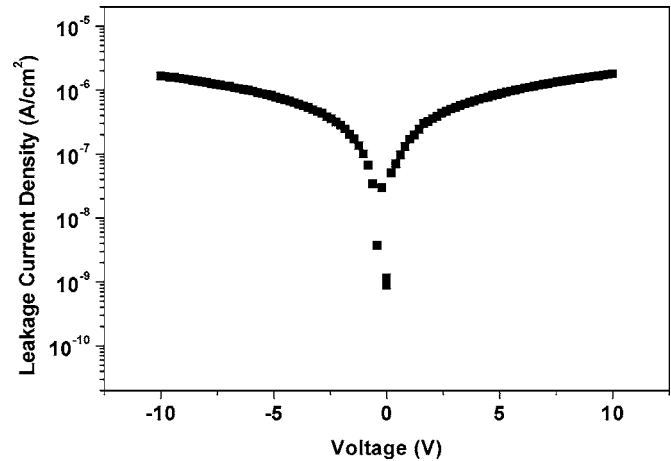


FIG. 2. Leakage current density in dependence of voltage for CBNO thin film annealed at 700 °C for 2 h.

perovskite with orthorhombic crystallographic structure. The diffraction peaks are matched and indexed based on CBNO crystal-structure parameters.¹⁰

Low leakage current density is another important parameter for memory device applications. Here the measured logarithmic current density ($\log J$) versus the voltage (V) is shown (Fig. 2). The CBNO thin films exhibited good leakage current characteristics. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an Ohmic conduction. This Ohmic behavior occurs in insulating film as long as the film is almost neutral, that is, as long as the bulk generated current in the film exceeds the current due to injected free carriers from the electrode. This current would be due to the hopping conduction mechanism in a low electric field, because thermal excitation of trapped electrons from one trap site to another dominates the transport in the films. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole-Frenkel emission mechanism. The leakage current density at 1.0 V is equal to 10^{-7} A/cm^2 up to an applied electric field of 30 kV/cm, establishing good insulating characteristics. A symmetric J - V characteristic for both voltage polarities was noted, indicating that the bulk controls the properties once we have used different top and bottom electrodes and different processing conditions. Therefore, the low leakage current can be an effect of a small grain size and roughness, which implies several grain boundaries along the current flow acting as potential barriers. Since the conductivity is strongly affected by the characteristics of the film-electrode interface, the surface morphology of CBNO thin films is one of the major factors determining the leakage current in capacitors.

Because the CBNO thin film showed ferroelectric nature, hysteresis curve was examined at room temperature (Fig. 3). Ferroelectricity of the calcium bismuth niobate was observed with remanent polarization (P_r) and a drive voltage V_c of $4.2 \mu\text{C/cm}^2$ and 1.7 V. The P_r and E_c values were improved compared with the values obtained for polycrystalline CBNO thin films.¹¹ The higher P_r value suggests that the

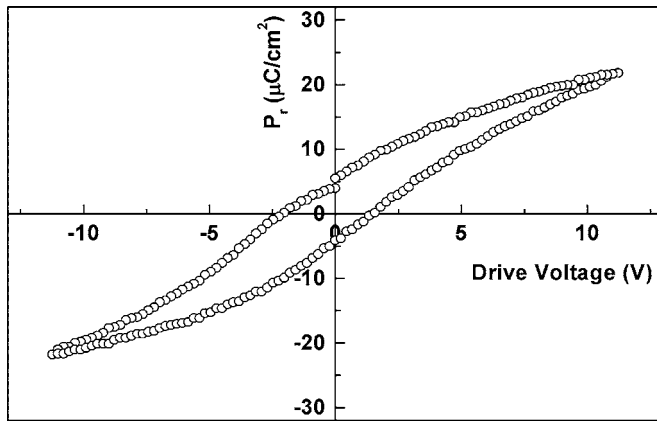


FIG. 3. C-V curve for CBNO thin film annealed at 700 °C for 2 h.

(100) orientation is preferred rather than the (010) orientation with respect to the present CBNO film. The reason for this improvement is that the ferroelectric polarization switching occurs in the *a-b* plane in CBNO.

Figure 4 illustrates the C-V curve for CBNO films obtained at 100 kHz and dc sweep voltage from +8 to −8 V. The capacitance dependence on the voltage is strongly non-linear, confirming the ferroelectric properties of the film resulting from the domain switching. The C-V curve for the film annealed at 700 °C for 2 h also indicates the symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The symmetry around the zero bias axis indicates that the films contain few movable ions or charge accumulation at the film-electrode interface. The dielectric constant of the CBNO thin films calculated from $C_{\max}$ was 1000. The dissipation factor was 0.053 at 100 kHz.

Figure 5 shows the temperature dependence of the dielectric constant of CBNO thin film at 100 kHz. The Curie point of CBNO was (944 ± 2) °C. This value of the Curie point is much higher than that reported by Ismailzade for CBNO.¹² The fact that the Curie point of our CBNO thin films is higher suggests that Ismailzade's result for T_C may be an error because it was obtained under the assumption that it coincided with a phase transformation observed by XRD.

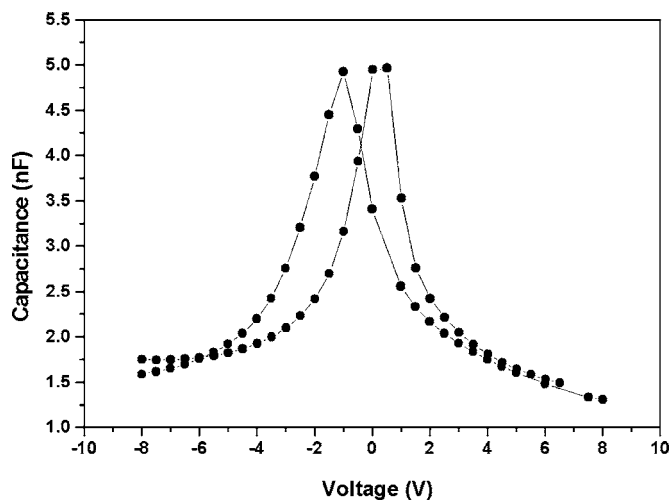


FIG. 4. P-V hysteresis loop for CBNO thin film annealed at 700 °C for 2 h.

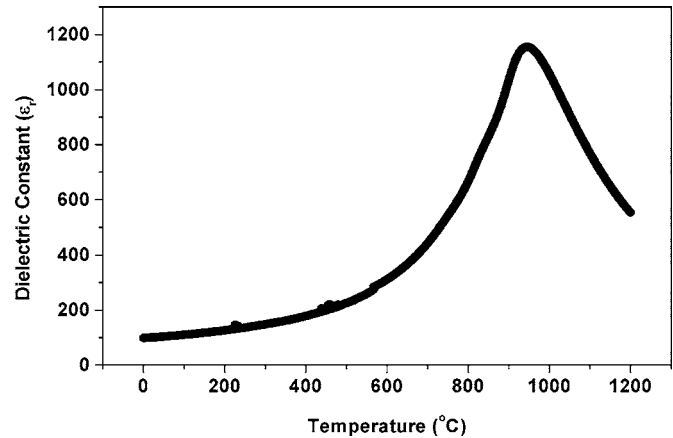


FIG. 5. Temperature dependence of dielectric constant in CBNO thin film annealed at 700 °C for 2 h.

In spite of their relatively larger P_s , the piezoelectric activity of bismuth layer-structured ferroelectrics (BLSFs) is limited because of two-dimensional orientation restriction of the rotation of their spontaneous polarization and their higher coercive field E_c . Orientation of films is an effective method to improve piezoelectric activity of BLSFs because of the anisotropy of their microstructure and properties. Figures 6 and 7 show the out-of-plane (OP) and in-plane (IP) piezoresponse images of the as-grown films after applying a bias of −12 V on an area of $2 \times 2 \mu\text{m}^2$, and then an opposite bias of +12 V in the central $1 \times 1 \mu\text{m}^2$ area. To obtain the domain images of the CBNO films, a high voltage that exceeds the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.¹³ The white regions in the out-of-plane piezoresponse force microscopy (PFM) images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as downpolarization (Fig.

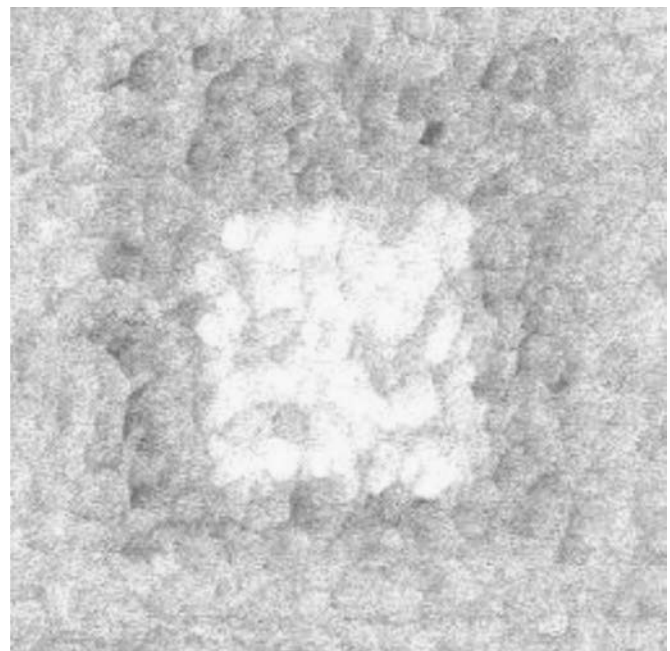


FIG. 6. Out-of-plane (OP) PFM image of CBNO thin film deposited on (100) Pt/Ti/SiO₂/Si substrate at 700 °C for 2 h.

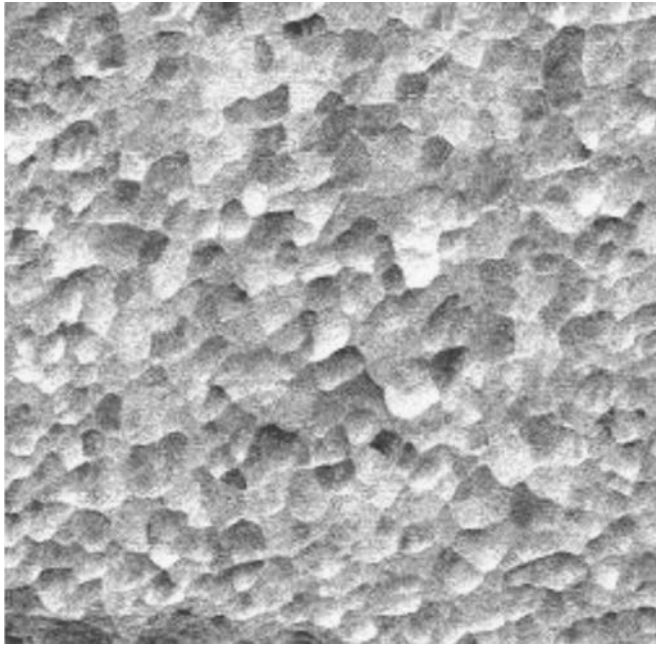


FIG. 7. In-plane (IP) PFM image of CBNO thin film deposited on (100) Pt/Ti/SiO₂/Si substrate at 700 °C for 2 h.

6), while the dark regions correspond to domains oriented upward referred to as up-polarization. Grains which exhibit no contrast change are associated with zero out-of-plane polarization. After a negative bias was applied, a polarization pointing predominantly out of plane was observed. A similar situation was observed when a positive bias was applied to the film. We noticed that some of the grains exhibit a white contrast associated with a component of the polarization pointing toward the bottom electrode. On the other hand, in the in-plane PFM images (Fig. 7) the contrast changes were associated with changes of the in-plane polarization components. In this case, the white contrast indicates polarization, e.g., in the positive direction of the y axis, while dark contrast are given by in-plane polarization components pointing to the negative part of the y axis. The $d_{33}(V)$ hysteresis loop is shown in Fig. 8. The maximum d_{33} value, ~ 58 pm/V, is higher than the textured ceramics grown by plasma spark sintering.¹⁴ The enhancement of polarization could be caused

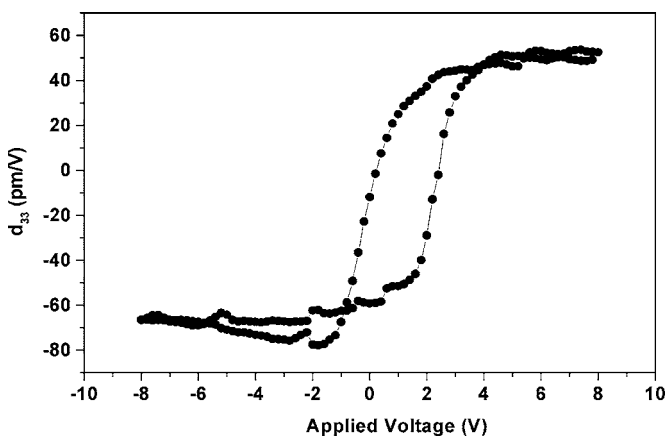


FIG. 8. Piezoresponse loop of CBNO thin film deposited on (100) Pt/Ti/SiO₂/Si substrate at 700 °C for 2 h.

by the a/b -axis orientation of the ferroelectric films due to the preferred orientation of Pt substrate. Considering the oriented growth of our films the effective piezoelectric coefficient depends on grain orientation. Therefore, as expected the piezoelectric response is rather larger due to the a/b -axis orientation of the ferroelectric films. As can be seen, the hysteresis loop shows an offset in the vertical direction which can be probably caused by clamping effect due to the substrate and the existence of an ultrathin air gap between the tip and the sample which might lower the actual voltage drop in the film.¹⁵ The presented values reported for our CBNO films suggest that this material can be considered as a viable alternative for lead-free piezoelectric devices. This value is much higher compared to that of single phase CBNO ceramics (piezoelectric coefficient d_{33} equal to 7 and 20 pm/V) derived from ordinary firing (OF) and Spark plasma sintering (SPS), respectively.¹⁴

IV. CONCLUSION

Highly polar-axis-oriented CaBi₂Nb₂O₉ (CBNO) thin films were deposited on platinum coated silicon substrates by the polymeric precursor method. The a/b -axis orientation of the ferroelectric films is considered to associate with the preferred orientation of Pt substrate. The leakage current density was around 10^{-7} A/cm² at an applied electric field of 30 kV/cm. The film showed improved ferro- and piezoelectric properties. The P_r , E_c , ϵ , and d_{33} values were enhanced compared to those of the CBNO ceramics with random orientation. The polar-axis-oriented CBNO films would open up possibilities for devices as Pb-free piezoelectric materials.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Brazilian financing agencies FAPESP, CNPq, and CAPES.

- ¹R. C. Turner, P. A. Fuierer, R. E. Newnham, and T. R. Shrout, *Appl. Acoust.* **41**, 299 (1994).
- ²D. Damjanovic, *Curr. Opin. Solid State Mater. Sci.* **3**, 469 (1998).
- ³G. A. Smolenskii, V. A. Bokov, V. A. Isupov, N. N. Krainik, R. E. Pasynkov, and A. I. Sokolov, in *Ferroelectrics and Related Materials*, edited by G. A. Smolenskii (Gordon and Breach, New York, 1984), Chap. 15.
- ⁴C. A. P. Araujo, J. D. Cuchiaro, L. D. McMillian, M. C. Scott, and J. F. Scott, *Nature (London)* **374**, 627 (1995).
- ⁵G. V. Gibbs, M. B. Boisen, Jr., R. T. Downs, and K. L. Bartelmehs, (XPOWLOT, Version 2.0, 1993).
- ⁶K. Kato, K. Suzuki, D. Fu, K. Nishizawa, and T. Miki, *Appl. Phys. Lett.* **81**, 3227 (2002).
- ⁷A. Z. Simões, B. D. Stojanovic, A. Tangastev, N. Setter, and J. A. Varela, *Integr. Ferroelectr.* **43**, 123 (2002).
- ⁸A. Z. Simões, A. Ries, F. M. Filho, J. A. Varela, and E. Longo, *Appl. Phys. Lett.* **85**, 5962 (2004).
- ⁹B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, *Appl. Phys. Lett.* **75**, 2644 (1999).
- ¹⁰S. B. Desu, H. S. Cho, and P. C. Joshi, *Appl. Phys. Lett.* **70**, 1393 (1997).
- ¹¹H. S. Cho and S. B. Desu, *Phys. Status Solidi A* **161**, 371 (1997).
- ¹²I. G. Ismailzade, *Bull. Acad. Sci. USSR, Phys. Ser. (Engl. Transl.)* **24**, 1201 (1960).
- ¹³A. Gruverman, O. Auciello, and H. Tokumoto, *Annu. Rev. Mater. Sci.* **28**, 101 (1998).
- ¹⁴V. K. Seth and W. A. Schulze, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **36**, 41 (1989).
- ¹⁵S. V. Kalinin and D. A. Bonnell, *Appl. Phys. Lett.* **78**, 1116 (2001).

Ferroelectric characteristics of BiFeO₃ thin films prepared via a simple chemical solution deposition

A. Z. Simões and A. H. M. Gonzalez

Faculdade de Ciências, Departamento de Química, Universidade Estadual Paulista, Av. Luiz Edmundo Carrijo Coube, 14-01, Vargem Limpa, 17033-360, Bauru-São Paulo, Brazil

L. S. Cavalcante^{a)}

Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Departamento de Química, Universidade Federal de São Carlos, P.O. Box 676, 13565-905, São Carlos, São Paulo, Brazil

C. S. Riccardi

School of Chemistry and Biochemistry, Georgia Institute of Technology, 770 State Street, Boggs Building, Atlanta, Georgia 30332-0400

E. Longo and J. A. Varela

Laboratório Interdisciplinar em Cerâmica, Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, P.O. Box 355, 14801-907, Araraquara, São Paulo, Brazil

(Received 6 November 2006; accepted 26 January 2007; published online 6 April 2007)

BiFeO₃ (BFO) thin films were fabricated on Pt(111)/Ti/SiO₂/Si substrates by using a polymeric precursor solution under appropriate crystallization conditions. The capacitance dependence on voltage is strongly nonlinear, confirming the ferroelectric properties of the films resulting from the domain switching. The leakage current density increases with annealing temperature. The polarization electric field curves could be obtained in BFO films annealed at 500 °C, free of secondary phases. X-ray photoelectron spectroscopy spectra of films annealed at 500 °C indicated that the oxidation state of Fe was purely 3+, demonstrating that our films possess stable chemical configurations. © 2007 American Institute of Physics. [DOI: [10.1063/1.2715513](https://doi.org/10.1063/1.2715513)]

I. INTRODUCTION

Multiferroic materials are becoming shining stars on the stage of new materials, which have attracted ever-increasing interest from perspectives of both fundamental physics and practical applications.¹ To date more than 80 single-phase multiferroic compounds have been grown either as a discrete composition or as a solid solution. Among these, BiFeO₃ is a compound most extensively studied, which is ferroelectric, ferroelastic, and weakly ferromagnetic.^{2,3} BiFeO₃ (BFO) is characterized by a rhombohedrally distorted perovskite structure having unit cell parameters $a_r=3.96$ Å and $\alpha_r=0.6^\circ$.^{4,5} The high polarization and piezoelectric response in thin BiFeO₃ films suggests a possible environmentally benign substitute for Pb-based ferroelectrics, though considerable optimization of ferroelectric properties is necessary.⁶ Interest in this compound is due to its high Curie temperature ($T_C\sim 1100$ K) and magnetic ordering temperature ($T_N\sim 650$ K)^{3,7} which are important for practical applications. However, ferroelectric characterization on bulk BiFeO₃ has been very difficult because of its low resistivity, which is likely due to defects and nonstoichiometry.

Recently, a few studies focusing on the preparation of BiFeO₃ thin films have presented a promising potential for this material. Among them, Palkar *et al.*⁸ first observed ferroelectric hysteresis loop of BiFeO₃ films prepared by pulsed laser deposition (PLD) with a saturation polarization $P_s=2.2$ μC/cm² at room temperature. Wang *et al.*⁹ reported

PLD epitaxial BiFeO₃ thin films with a greatly enhanced polarization with remanent polarization $P_r=55$ μC/cm² along (001). Yun *et al.*^{10,11} reported $P_r=35.7$ μC/cm² for PLD polycrystalline BiFeO₃ thin films, and in their subsequent work, they have obtained a giant $P_s=158$ μC/cm² at 90 K. In these works the PLD technique was employed and most BiFeO₃ films were grown on the oxide electrodes⁹ which are difficult to synthesize in comparison with the metal electrodes sputtered on Si substrates.

The major problem of BFO thin films is their low electrical resistivity, which affects the application of their ferroelectric order at room temperature. The relatively high conductivity of BFO films is known to be attributed to the variable oxidation states of Fe ions (Fe³⁺ to Fe²⁺)¹² which requires oxygen vacancies for charge compensation and produces electron hopping in films. The oxidation state of Fe is greatly dependent on the processing conditions and the type and amount of dopants.

In previous works, our group had reported the preparation of thin films by the polymeric precursor method.¹³ The overall process consists of preparing a coating solution based on metallic citrate polymerization. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. In this work, we use a simple chemical solution spin-coating technique to prepare pure-phase BiFeO₃ thin films on a common Pt(111)/Ti/SiO₂/Si substrate. We report the growth and ferroelectric properties of polycrystalline BFO thin films prepared by chemical solution deposition under various crystallization conditions.

^{a)}Electronic mail: laeciosc@bol.com.br

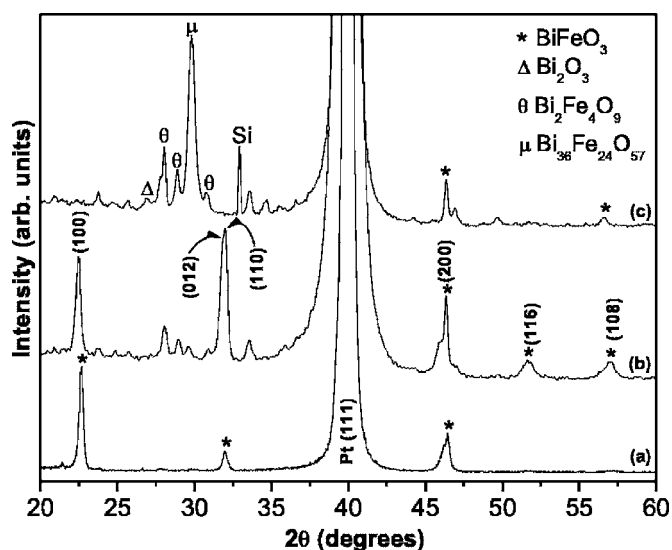


FIG. 1. X-ray diffraction diagram of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

II. EXPERIMENT

Iron (III) nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$], 99.5% purity (Merck) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth and iron were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Fe and Bi were mixed and homogenized by stirring at 90 °C. The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cp by controlling the water content using a Brookfield viscosimeter. The films were spin coated from a BFO deposition solution onto a Pt(111)/Ti/SiO₂/Si substrate. The BFO films were completely crystallized after annealing for 2 h at temperatures ranging from 500 to 700 °C. Multilayered films were obtained by spinning ten times the deposition solution on the surface of the substrate at 5000 rpm.

In this work, an excess of 5 wt % Bi was added to the solution, aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis was performed at room temperature by x-ray diffraction in the θ -2 θ mode scan, recorded on a Rigaku diffractometer (Rigaku-DMAX 2500PC) using Cu $K\alpha$ radiation. The thickness of the annealed films was studied using scanning electron microscopy (Topcom SM-300) by looking at the transversal section. In this case, backscattered electrons were utilized. Three measurements were done to obtain an average value of thickness. The surface roughness was examined by atomic force microscopy using tapping mode technique. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a postannealing treatment in a tube furnace under oxygen atmosphere at 300 °C for 1 h. Here, the desired effect was to decrease eventually present oxygen vacancies.

The capacitance-voltage characteristics were measured in the metal-ferroelectric-metal configuration using a small

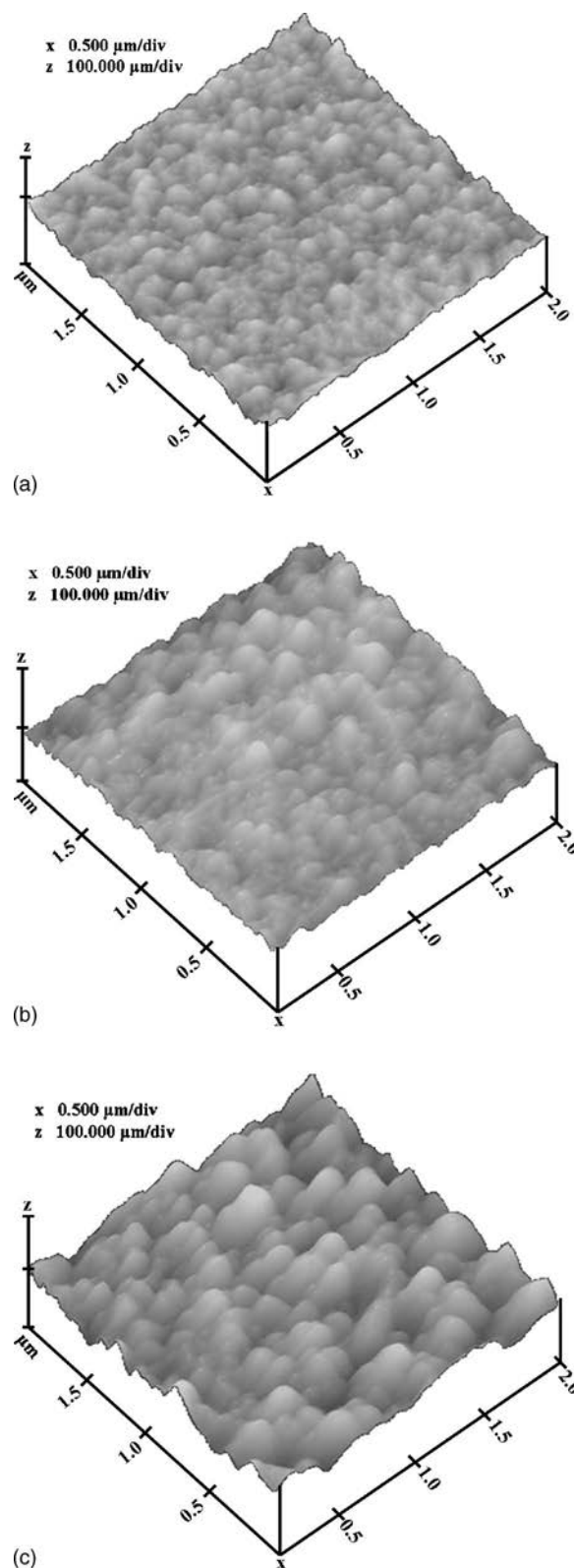


FIG. 2. AFM images of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

alternating current (ac) signal of 10 mV at 100 kHz. The ac signal was applied across the sample, while the direct current (dc) was swept from positive to negative bias. A PHI-5702 multifunction x-ray photoelectron spectrometer was used, working with an Al $K\alpha$ x-ray source of 29.35 eV passing

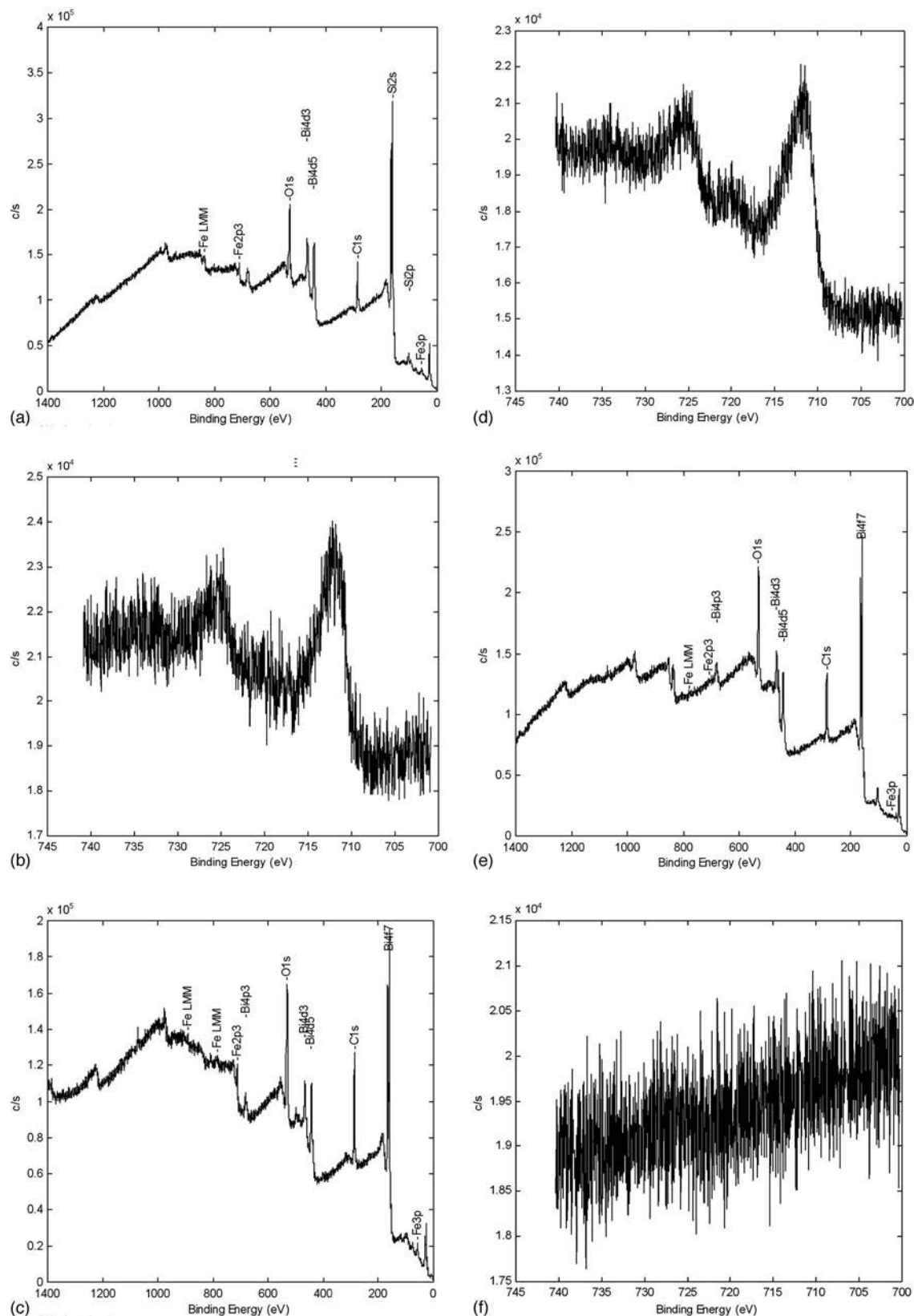


FIG. 3. XPS spectra of (a) Bi 4f, (b) Bi 5d, (c) Fe 2p, (d) O 1s peaks for BFO thin films annealed in static air for 2 h at (a) and (b) 500, (c) and (d) 600, and (e) and (f) 700 °C.

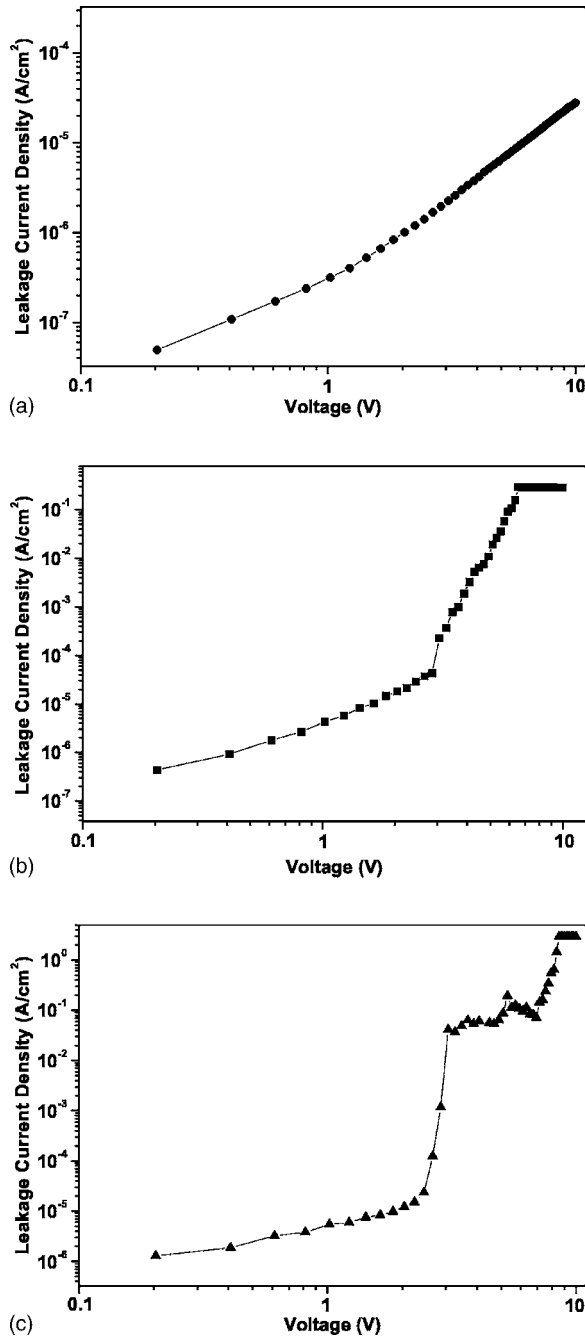


FIG. 4. Leakage current density of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

energy. The pressure in the chamber during the experiments was about 4.5×10^{-9} Torr. Calibration of binding energy scale was controlled using the O 1s line, which appears in the photoelectron spectra of the as-received samples. The ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A).

III. RESULTS AND DISCUSSION

Figure 1 displayed the x-ray diffraction (XRD) patterns of BFO films annealed at various temperatures, demonstrating that a pure perovskite phase is formed at 500 °C with no second phases detected. This means that the amount of sec-

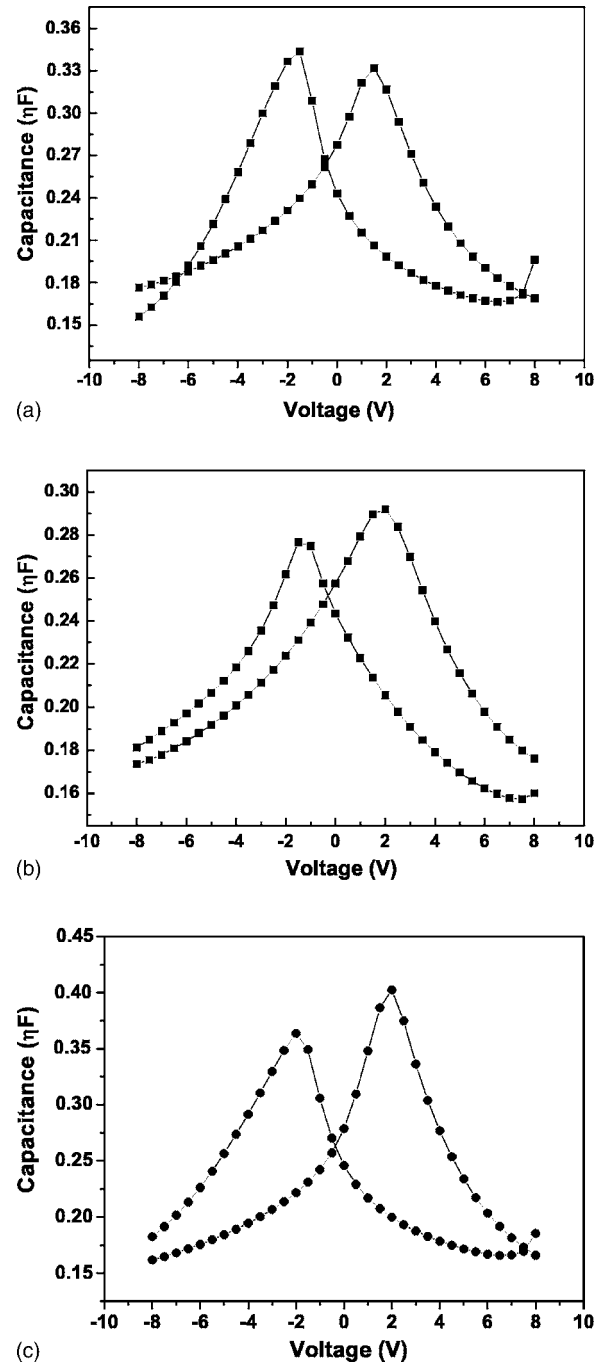


FIG. 5. Capacitance-voltage curves of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

ond phases was less than 1 vol. %, which was approximately the detection limit of the XRD system used. The diffraction peaks were identified using the pseudocubic structure. The intensity of (100) and (200) diffraction peaks were strong with respect to that of the (110) peak. As the temperature increases, secondary phases, such as Bi_2O_3 , $\text{Bi}_2\text{Fe}_4\text{O}_9$, and $\text{Bi}_{36}\text{Fe}_{42}\text{O}_{57}$ were present in the BFO films. Also, other unidentified phases were present, especially in the film annealed at 700 °C for 2 h.

Atomic force microscopy (AFM) images of BFO thin films annealed at 500, 600, and 700 °C for 2 h are illustrated in Fig. 2. The BFO films were dense with uniform grains for films annealed at 500 °C without the presence of any second

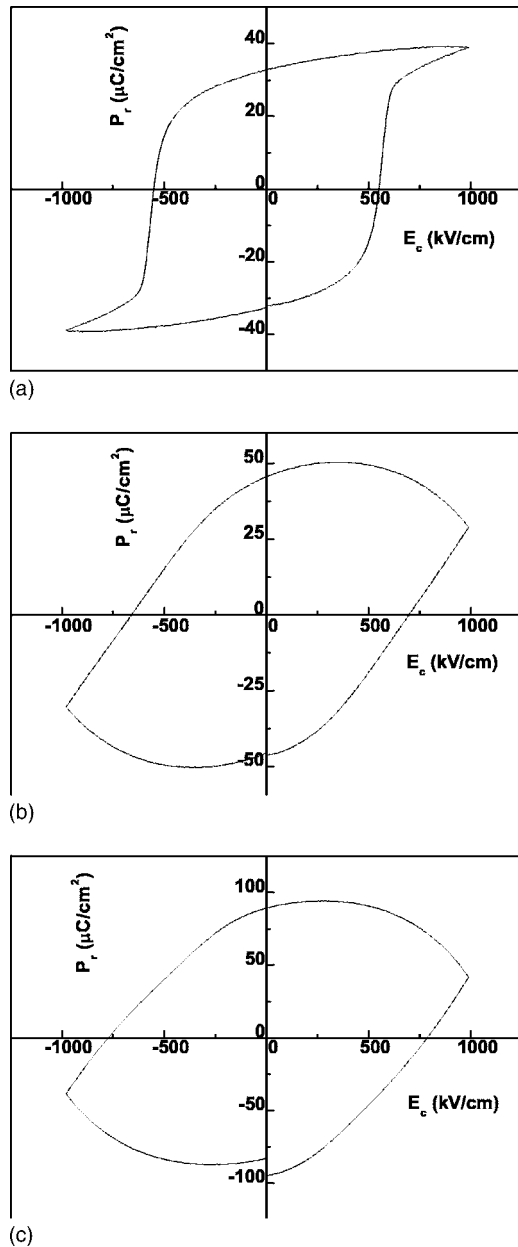


FIG. 6. Hysteresis loops of BFO films annealed in static air for 2 h at (a) 500, (b) 600, and (c) 700 °C.

phase [Fig. 2(a)]. The grains started to grow abnormally at 600 °C, when some grains grew faster than others and tended to consume surrounding small grains [Fig. 2(b)]. The size of the large grain of BFO thin film annealed at 600 °C was about 170 nm, while that of the small ones varied from 90 to 120 nm. The grain size and the uniformity of the microstructure were thought to have great influence on the leakage properties.

Generally, it was assumed that the conduction mechanism of BFO was related to the hopping of electrons from Fe^{2+} to Fe^{3+} when oxygen vacancies are present in the lattice, which act as a “bridge” between Fe^{2+} and Fe^{3+} and play an important role in the electronic conduction.¹⁴ In order to identify the chemical bonding of BFO thin films, we performed x-ray photoelectron spectroscopy (XPS) studies. The wide-range spectrum of BFO thin films deposited at several

temperatures is shown in [Figs. 3(a), 3(c), and 3(e)]. The spectrum expanded from 700 to 745 eV is also shown. The 3/2 and 1/2 spin-orbit doublet components of the Fe 2p photoemission were located at 711.1 and 724.6 eV, respectively. The XPS results show that BFO thin film annealed at 500 °C has a single phase with a Fe^{3+} valence state, consistent with XRD result shown in Fig. 1. The 3/2 and 1/2 spin-orbit doublet of the Fe 2p photoemission located at 711.1 and 724.6 eV were identified as Fe^{3+} , respectively. No Fe^{2+} and Fe were found. The oxidation state of Fe was purely 3+, which was advantageous for producing BFO films with low leakage [Fig. 3(b)]. The absence of Fe^{2+} ions suggests the reduction of oxygen vacancies in our films, which may be one of the reasons for enhanced ferroelectric property, as will be discussed in the present article. Although the film annealed at 600 °C has a small amount of secondary phases, the Fe^{2+} and Fe^{3+} ions are not seen in the spectrum because of their presence being below the XPS detection limit or their photoemission coinciding in binding energies with the other two peaks [Fig. 3(d)]. No evidence of Fe 2p photoemission is noted in the film annealed at 700 °C [Fig. 3(f)]. This is a surprising result and indicates that the penetration depth of only a few nanometers of XPS technique was not enough to exclude the possible difference between the topmost surface and inside bulk of the film. New experiments are being performed in order to probe these differences.

Figure 4 plotted the current density versus electric field curves of BFO films annealed at various temperatures. Generally, the leakage current density should be less than 10^{-7} A/cm² during operation in memory device applications. The leakage current density of the film annealed at 500 °C is around 10^{-7} A/cm² demonstrating the quality of the obtained BFO films [Fig. 4(a)]. The leakage current for the films annealed at 600 and 700 °C was only 10^{-6} A/cm² at 1 V, which is much lower than those reported in the literature [Figs. 4(b) and 4(c)]. They were 10^{-5} A/cm² chemical solution deposition (CSD)¹⁵ and 5×10^{-1} A/cm² (PLD)¹⁶ for pure BFO films. The leakage current increases with annealing temperature and its dependence is addressed to the presence of secondary phases. Increase temperature leads to bigger grains and also to raise of leakage current once the grain growth became nonuniform. The strong dependence of leakage current on grain size suggested that grain boundary related mechanisms dominated the conduction.

Figure 5 illustrates the capacitance-voltage curves for BFO films obtained at 100 kHz and dc sweep voltage from +8 to -8 V. The capacitance of the film showed a strong dependence on the applied voltage, confirming the ferroelectric properties of the film resulting from the domain switching. There is no polarization gap toward along the positive and negative direction of the applied electric field for the film annealed at 500 °C for 2 h also indicating symmetry in the vicinity of the spontaneous polarization switching [Fig. 5(a)]. On the other hand, the films annealed at higher temperatures (600 and 700 °C) present a polarization gap toward the direction of negative field, suggesting the presence of charge carriers trapped near the electrode/film interface [Figs. 5(b) and 5(c)]. Typically, this behavior is mainly at-

tributed to the difference of work function, crystallographic defect distribution, and thermal history between top electrode and bottom electrode.

The room temperature P - E hysteresis loops of BFO thin films annealed at several temperatures are shown in Fig. 6. The BFO films annealed at 600 and 700 °C for 2 h exhibit poor P - E hysteresis loops, which has been typically observed from conductive ferroelectrics [Figs. 6(b) and 6(c)]. In contrast, the BFO thin film annealed at 500 °C shows well-saturated hysteresis characteristics with a remanent polarization (P_r) of 31 $\mu\text{C}/\text{cm}^2$ and a coercive field (E_c) of 560 kV/cm at a maximum applied electric field of 1000 kV/cm [Fig. 6(a)]. We attribute the value of our P_r to the intense (100) preferred orientation. According to Wang *et al.*,¹² the ferroelectricity of BFO originates from the relative displacements of Bi ion and Fe-O octahedron along the (111) orientation in epitaxial BFO films and the projection polarization along the (110) orientation is larger than that of the (100) orientation. Since the films in our work are intense (100) we reasonably did not expect a larger polarization. A high coercive field was observed in our BFO films, which is probably originated from the small grain size of the BFO films. The polarization switching is usually more difficult in films with fine grains. Therefore, to increase the grain size and reduces the coercitive field, the use of oxygen atmosphere and substitution of bismuth site are under progress, and the results will be published in the near future.

IV. CONCLUSIONS

Single phase BFO thin films were deposited at 500 °C for 2 h on the Pt(111)/Ti/SiO₂/Si substrates by the chemical solution deposition method. The leakage-current density of the film annealed at low temperature was around 10^{-7} A/cm² with a remanent polarization P_r of 31 $\mu\text{C}/\text{cm}^2$ at room tem-

perature. These results indicate that the control of BFO film composition is effective to reach good ferroelectric properties. Furthermore, it was clearly demonstrated that the good ferroelectric BFO thin films could be fabricated by a chemical solution deposition method at low temperatures, which is advantageous for real device applications.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of the Brazilian agencies CAPES, FAPESP, and CNPq and to Dr. Hess of Georgia Institute of Technology for XPS facilities.

¹M. Fiebig, J. Phys. D **38**, R132 (2005).

²S. M. Skinner, IEEE Trans. Parts Mater. Pack. **6**, 68 (1970).

³F. Kubel and H. Schmid, Acta Crystallogr., Sect. B: Struct. Sci. **46**, 698 (1990).

⁴C. Michel, J.-M. Moreau, G. D. Achenbechi, R. Gerson, and W. J. James, Solid State Commun. **7**, 701 (1969).

⁵J. M. Moreau, C. Michel, R. Gerson, and W. J. James, J. Phys. Chem. Solids **32**, 1315 (1971).

⁶S. Y. Yang, F. Zavaliche, Y. H. Chu, Y. J. Lee, L. Mohaddes-Ardabili, T. Zhao, Q. Zhan, and R. Ramesh, APS March Meeting, 2005, p. 21.

⁷S. V. Kiselev, R. P. Ozerov, and G. S. Zhdanov, Sov. Phys. Dokl. **7**, 742 (1963).

⁸V. R. Palkar, J. John, and R. Pinto, Appl. Phys. Lett. **80**, 1628 (2002).

⁹J. Wang *et al.*, Science **299**, 1719 (2003).

¹⁰K. Y. Yun, M. Noda, and M. Okuyama, Appl. Phys. Lett. **83**, 3981 (2003).

¹¹K. Y. Yun, D. Ricinschi, T. Kanashima, M. Noda, and M. Okuyama, Jpn. J. Appl. Phys., Part 2 **43**, L647 (2004).

¹²Y. P. Wang, L. Zhou, M. F. Zhang, X. Y. Chen, J. M. Liu, and Z. G. Liu, Appl. Phys. Lett. **84**, 1731 (2004).

¹³A. Z. Simões, M. A. Ramírez, A. Ries, E. Longo, J. A. Varela, and R. Ramesh, Appl. Phys. Lett. **88**, 072916 (2006).

¹⁴W. M. Zhu and Z.-G. Ye, Ceram. Int. **30**, 1435 (2004).

¹⁵H. Uchida, R. Ueno, H. Nakaki, H. Funakubo, and S. Koda, Jpn. J. Appl. Phys., Part 2 **44**, L561 (2005).

¹⁶X. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus-Driscoll, Appl. Phys. Lett. **86**, 062903 (2005).

Improvement of fatigue resistance on La modified BiFeO₃ thin films

A.Z. Simões^a, L.S. Cavalcante^{b,*}, C.S. Riccardi^a, J.A. Varela^a, E. Longo^a

^a Laboratório Interdisciplinar em Cerâmica, Departamento de Físico-Química, Instituto de Química, Universidade Estadual Paulista, PO Box 355, 14801-907 Araraquara, SP, Brazil

^b Laboratório Interdisciplinar de Eletroquímica e Cerâmica – LIEC, Departamento de Química, Universidade Federal de São Carlos, PO Box 676, 13565-905 São Carlos, SP, Brazil

Received 26 February 2008; received in revised form 24 April 2008; accepted 1 May 2008
Available online 15 May 2008

Abstract

The effect of lanthanum (La) addition in BiFeO₃ (BFO) thin films deposited on Pt(111)/Ti/SiO₂/Si(100) substrates prepared by soft chemical method was explained. Increasing La concentration promotes changes on structure, microstructure and dielectric/ferroelectric response of films. X-ray diffraction reveals that the films are free of preferred orientations and structural distortion. La addition promotes an increase in dielectric permittivity. The polarization switching and the fatigue behavior of the BFO films were significantly enhanced by the La concentration.

© 2008 Elsevier B.V. All rights reserved.

PACS: 77.55.+f; 77.80.Fm; 68.55.Ac; 77.80.Dj; 81.15.Lm

Keywords: Fatigue resistance; BiFeO₃; Ferroelectric; Multiferroic

1. Introduction

Ferroelectric and magnetic materials have been considered one of the most important technological advances. Magnetism and ferroelectricity are involved with local spins and off-centre structural distortions, respectively [1]. Materials that presents the fusion of ferroelectric and magnetic properties are known as multiferroic materials. Sometimes called magnetoelectrics, possess two or more switchable states such as polarization, magnetization or strain [2,3]. The multiferroic materials such as BiFeO₃ (BFO) [4], BiCrO₃ [5] and BiMnO₃ [6] can be employed in a wide range of applications including the emerging field of spintronics [7], multiple-state memories and data-storage media [8].

Amongst multiferroic materials, the BFO has been extensively studied, due to their superior ferroelectric

properties in epitaxial thin film form in comparison to counterpart bulk single crystals or ceramics [9–11]. The BFO is known to be the only material that exhibits ferroelectromagnetism at room temperature. It is a rhombohedrally distorted ferroelectric perovskite ($T_C \sim 850^\circ\text{C}$) with the space group $R3c$ [12] and shows G-type antiferromagnetism up to 370°C (T_N) [13]. The specific characteristics, including a simple crystal structure, a high Curie temperature (electrical), and a high Néel temperature (magnetic), are advantageous for research and various applications [14]. In bismuth-based ferroelectrics, such as SrBi₄Ti₄O₁₅ [15] and Bi₄Ti₃O₁₂ [16], the lanthanum (La) addition was effective to enhance the insulating and ferroelectric properties because of the reduced oxygen vacancy stabilizes the oxygen octahedron [17]. Some studies reported in literature [18,19] suggest that the inhomogeneous magnetic spin structure can be effectively suppressed by La addition. Therefore, the influence of La doping on polarization switching, ferroelectric reliability, and multiferroic properties of BFO films deserves more attention.

* Corresponding author. Tel.: +55 16 3361 5215, mobile: +55 16 9176 49 43; fax: +55 16 3351 8214.

E-mail address: laeciosc@bol.com.br (L.S. Cavalcante).

In this paper, we discuss the structure, microstructure, dielectric, ferroelectric and fatigue behavior of La modified BFO thin films, which are deposited by chemical solution deposition on Pt(111)/Ti/SiO₂/Si(100) substrates.

2. Experimental details

Iron(III) nitrate nonahydrate, 99.5% purity (Merck), bismuth nitrate, 99.5% purity (Aldrich) and lanthanum acetate, 99.9% purity (Aldrich) were used as raw materials. The precursor solutions of bismuth and iron were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of Fe and Bi solutions were mixed and homogenized by stirring at 90 °C. An excess of 5 wt% Bi was added to the solution, aiming to minimize the bismuth loss during annealing. Without bismuth addition, single phase Bi_{1-x}La_xFeO₃ ($x = 0.00$, 0.08 and 0.15 or BFO, 8-BLFO and 15-BLFO) thin films could not be obtained. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. The viscosity of the resulting solution was adjusted to 20 cp by controlling the water content using a Brookfield viscosimeter. The multilayered deposited onto Pt(111)/Ti/SiO₂/Si substrates by spinning the deposition solution at 5000 rpm, performing 10 times deposition. All films were crystallized after annealing at 500 °C for 2 h. Multilayered films were prepared by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm. In these experiments, thin films were characterized by X-ray diffraction patterns recorded on a (Rigaku-DMax 2500PC, Japan) with Cu K α radiation in the 2θ range from 20° to 60° with 0.02°/min. The morphology of the films was examined by atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) and thickness was evaluated by observing the cross-section of the films using a high-resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss). Electrical properties were measured by an Au/Bi_{1-x}La_xFeO₃/Pt capacitor structure. The Au top electrode area 3×10^{-4} cm² was deposited by sputtering through a designed mask onto the film surfaces. Dielectric and ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000A tester equipped with a micrometer probe station in a virtual ground mode. For the fatigue measurements, internally or externally generated 8.6 μ s wide square pulses with maximum amplitudes of ± 9 V were used.

3. Results and discussion

Fig. 1 displays the X-ray diffraction (XRD) patterns of Bi_{1-x}La_xFeO₃ ($x = 0.00$, 0.08 and 0.15) thin films deposited at Pt(111)/Ti/SiO₂/Si(100) substrates.

All peaks of the films are indexed to a rhombohedral structure in agreement with literature [20,21]. XRD reveals that the films are free of preferred orientations and present structural distortion. La-addition at 30% in BFO films does not show any structural distortion, although presents a deleterious phase (it was not reported in this paper). It can

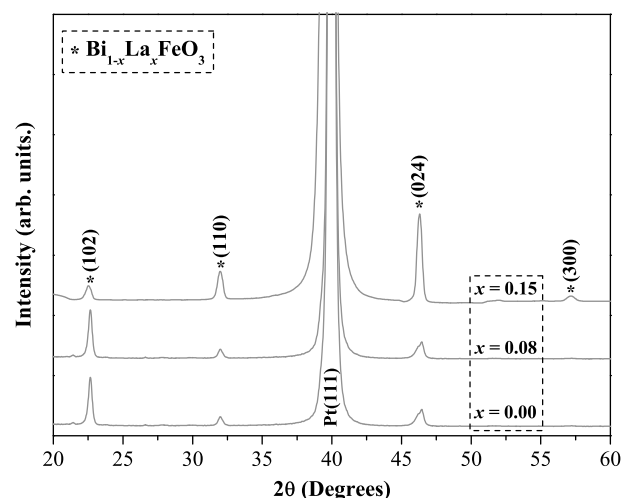


Fig. 1. XRD patterns of Bi_{1-x}La_xFeO₃ ($x = 0.00$, 0.08 and 0.15) thin films deposited on Pt substrates and annealed at 500 °C for 2 h in air atmosphere.

also be seen that all films are well crystallized at 500 °C for 2 h in air atmosphere.

The surface morphology of the Bi_{1-x}La_xFeO₃ ($x = 0.00$, 0.08 and 0.15) thin films deposited at Pt substrates and annealed at 500 °C for 2 h in air atmosphere were evaluated by AFM and shown in Fig. 2.

8-BLFO film exhibited bimodal distribution of grains, low porosity and roughness. The larger number of nucleation sites provided by Pt substrate was probably responsible for some small grain size of the 8-BLFO films. A great improvement in average grains size of 8-BLFO films was observed. That is compared to pure BFO reported by sol-gel method [22]. The increase of La-addition decreases the average grain size of the films. AFM analysis indicated that the BFO and 15-BLFO thin films present a homogeneous, smooth and crack-free surface. This indicates that the chemical-soft method allows the preparation of films with controlled morphology. The average grain size, surface roughness and thickness of the films are presented in Table 1.

Fig. 3a shows the frequency dependence of the dielectric permittivity (ϵ_r) and dielectric loss ($\tan \delta$) and Fig. 3b shows the hysteresis loops of the Bi_{1-x}La_xFeO₃ ($x = 0.00$, 0.08 and 0.15) thin films on Pt substrates annealed at 500 °C for 2 h in air atmosphere.

The ϵ_r value in BFO film is approximately 50.5 at 1 kHz and it increases the La concentration to approximately 114.2 at 1 kHz. The $\tan \delta$ value raises with a increase La (%) of 0.0173–0.0241. That is 8% and 15% of the La-substituted BFO film exhibit the ϵ_r values of 83.4 and 114.2, respectively at 1 kHz (see Fig. 3a). The different ϵ_r values in La substituted films are considered to be due to the size effect, as observed by changes on the surface morphology [22,23]. As shown, the remanent polarization (P_r) is reduced by La-substitution into BFO films. The P_r values are 32.7, 20.3 and 16.6 μ C/cm² (see Fig. 3b). The reason for the significant decrease is not well understood at their

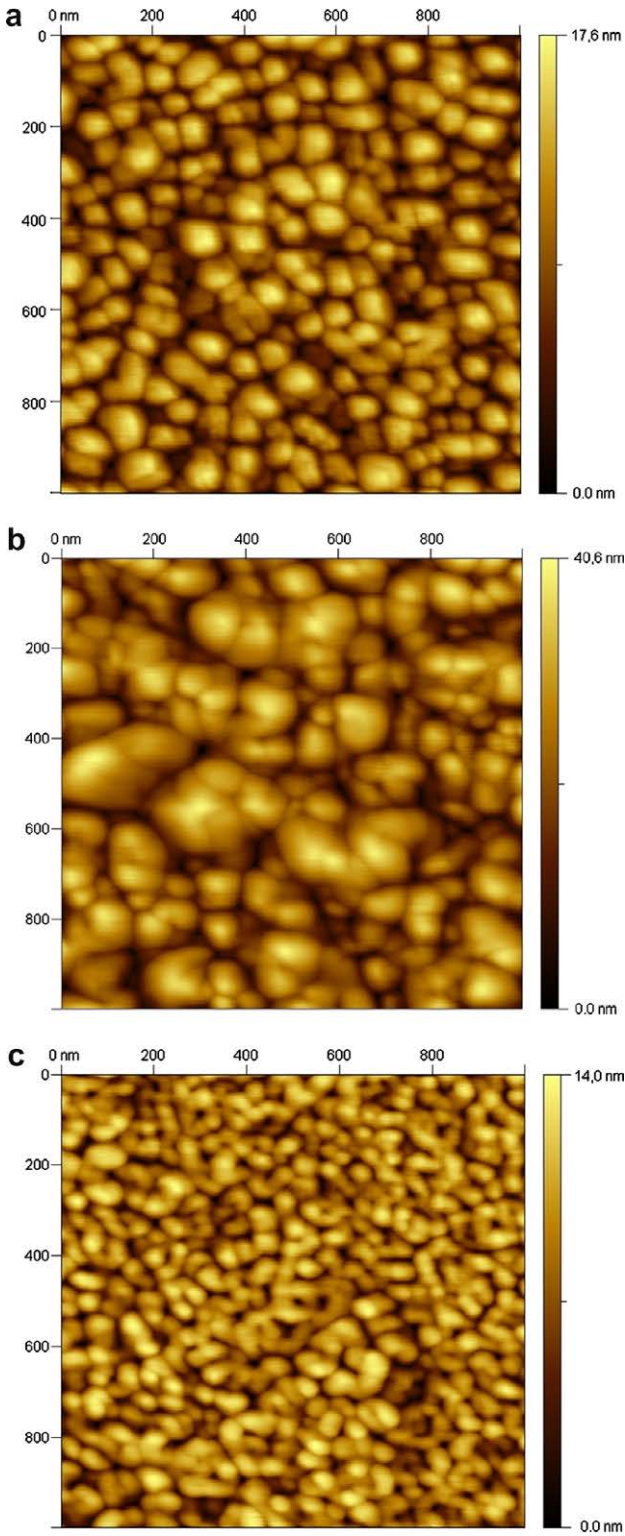


Fig. 2. AFM micrographies for: (a) BiFeO₃, (b) Bi_{0.92}La_{0.08}FeO₃ and (c) Bi_{0.85}La_{0.15}FeO₃ thin films deposited on Pt substrates and annealed at 500 °C for 2 h in air atmosphere.

moment. It might be originated from the decrease in Curie temperature, as is the case of La-substituted Bi₄Ti₃O₁₂ thin films. The electric field is 550, 54 and 51 kV/cm, respectively. We presumed that the loops are dominated by the displacement current related to polarization switching.

Table 1
Data obtained of AFM analysis for thin films deposit on Pt substrates in different compositions of La

Bi _{1-x} La _x FeO ₃ x	Roughness (nm)	Thickness (nm)	Average grain size (nm) ± 2%
0	5.0	360	53
0.08	4.0	360	60
0.15	3.8	355	30

The fatigue endurance for Bi_{1-x}La_xFeO₃ (x = 0.00, 0.08 and 0.15) thin films on Pt substrates annealed at 500 °C for 2 h in air atmosphere was evaluated (Fig. 4).

The switched polarization between two opposite polarity pulses, $P^*-\dot{P}$ or $-P^*(-\dot{P})$ denote the switchable polarization, which is an important variable for nonvolatile memory applications. Fatigue resistance was observed up to 10¹⁰ cycles with an applied pulse voltage of 9 V for 15-BLFO thin films suggesting a good potential for applications in ferroelectric memories. In the BFO and 8-BLFO films there is an increase in local current around the nucleation sites which can destroy the film-electrode interface

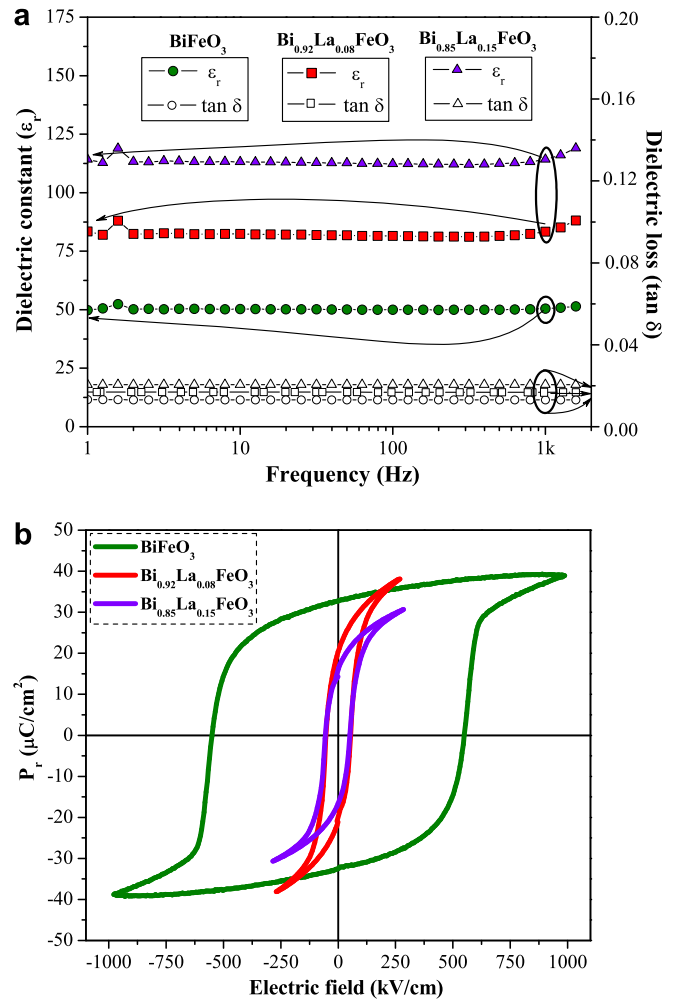


Fig. 3. (a) Frequency dependence of the dielectric permittivity and dielectric loss (b) P - E hysteresis loops for Bi_{1-x}La_xFeO₃ (x = 0.00, 0.08 and 0.15) thin films annealed at 500 °C for 2 h in air atmosphere.

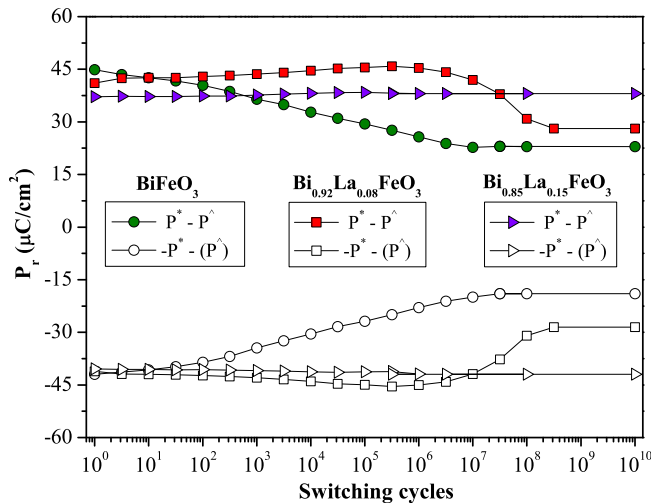


Fig. 4. Fatigue as a function of polarization cycles for $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.00, 0.08$ and 0.15) thin films annealed at 500°C for 2 h in air atmosphere.

and suppress the nucleation of oppositely oriented domains at the surface. In this film an increase in switching polarization leads to a local increase in conductivity at the film-electrode interface region [24].

4. Conclusions

In short, $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$ with $x = 0.00, 0.08$ and 0.15 thin films were obtained by the soft chemical method on Pt substrates. All films showed random crystallites orientation without any preferred orientations and structural distortion. In a 8-BLFO film, prolonged grains with average size of approach 60 nm were noted. The dielectric permittivity and dielectric loss is increased with La-addition in the vicinity of spontaneous polarization switching and fatigue resistance was observed with increasing its concentration. The films show ferroelectric behavior at room temperature.

Acknowledgements

The authors thank the financial support of the Brazilian research financing institutions: CAPES, FAPESP and CNPq.

References

- [1] N. Hur, S. Park, P.A. Sharma, J.S. Ahn, S. Guha, S.W. Cheong, *Nature* 429 (2004) 392.
- [2] H. Schmid, *Ferroelectrics* 162 (1994) 317.
- [3] G.A. Smolenski, I.E. Chupis, *Usp. Fiz. Nauk.* 137 (1982) 415.
- [4] A.H.M. Gonzalez, A.Z. Simões, L.S. Cavalcante, E. Longo, J.A. Varela, C.S. Riccardi, *Appl. Phys. Lett.* 90 (2007) 052906.
- [5] D.H. Kim, H.N. Lee, M. Varela, H.M. Christen, *Appl. Phys. Lett.* 89 (2006) 162904.
- [6] A.M. dos Santos, S. Parashar, A.R. Raju, Y.S. Zhao, A.K. Cheetham, C.N.R. Rao, *Solid State Commun.* 122 (2002) 49.
- [7] N.A. Hill, *J. Phys. Chem. B* 104 (2000) 6694.
- [8] M. Fiebig, Th. Lottermoser, D. Fröhlich, A.V. Golsev, R.V. Pisarev, *Nature* 419 (2002) 19.
- [9] C.D. Zheng, D.M. Zhang, J. Yu, B. Yang, Y.Y. Wu, L.H. Wang, Y.B. Wang, W.L. Zhou, *Integr. Ferroelectr.* 94 (2007) 23.
- [10] G.D. Hu, X. Chen, W.B. Wu, C.H. Yang, *Appl. Phys. Lett.* 91 (2007) 232909.
- [11] T. Kawae, H. Tsuda, M. Shiimoto, S. Yamada, M. Nagao, A. Morimoto, M. Kumeda, *Jpn. J. Appl. Phys.* 47 (2008) 237.
- [12] F. Kubel, H. Schmid, *Acta Crystallogr. Sect. B: Struct. Sci.* 46 (1990) 698.
- [13] P. Fischer, M. Polomska, I. Sosnowska, M. Szymanski, *J. Phys. C: Solid State Phys.* 13 (1980) 1931.
- [14] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, *Science* 229 (2003) 1719.
- [15] Y.P. Chen, Y.Y. Yao, Z.H. Bao, J.S. Zhu, Y.N. Wang, *Mater. Lett.* 57 (2003) 3623.
- [16] A.Z. Simões, C.S. Riccardi, L.S. Cavalcante, E. Longo, J.A. Varela, B. Mizaikoff, D.W. Hess, *J. Appl. Phys.* 101 (2007) 084112.
- [17] C.Y. Yau, R. Palan, K. Tran, R.C. Buchanan, *Appl. Phys. Lett.* 86 (2005) 032907.
- [18] T. Kojima, T. Sakai, T. Watanabe, H. Funakubo, *Appl. Phys. Lett.* 80 (2002) 2746.
- [19] J.K. Lee, C.H. Kim, H.S. Suh, K.S. Hong, *Appl. Phys. Lett.* 80 (2002) 3593.
- [20] V.R. Singh, A. Garg, D.C. Agrawal, *Appl. Phys. Lett.* 92 (2008) 152905.
- [21] Z.X. Cheng, X.L. Wang, S.X. Dou, H. Kimura, K. Ozawa, *Phys. Rev. B* 77 (2008) 092101.
- [22] S.K. Singh, K. Maruyama, H. Ishiura, *J. Phys. D: Appl. Phys.* 40 (2007) 2705.
- [23] Y.-H. Lee, J.-M. Wu, C.-H. Lai, *Appl. Phys. Lett.* 88 (2006) 042903.
- [24] A.Z. Simões, M.A. Ramírez, A.H.M. Gonzalez, C.S. Riccardi, A. Ries, E. Longo, J.A. Varela, *J. Solid State Chem.* 179 (2006) 2206.

Strain behavior of lanthanum modified BiFeO₃ thin films prepared via soft chemical method

A. Z. Simões, E. C. Aguiar, A. H. M. Gonzalez, J. Andrés, E. Longo et al.

Citation: *J. Appl. Phys.* **104**, 104115 (2008); doi: 10.1063/1.3029658

View online: <http://dx.doi.org/10.1063/1.3029658>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v104/i10>

Published by the AIP Publishing LLC.

Additional information on J. Appl. Phys.

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT



The advertisement banner features a green and yellow background with abstract wavy lines. In the center, the text "AIPAdvances" is displayed in a stylized font, with "AIP" in blue and "Advances" in green. To the right of the text is a circular seal that reads "Now Indexed in Thomson Reuters Databases". Below the main text, there is a blue horizontal bar containing the text "Explore AIP's open access journal:". To the right of this bar, there is a list of three bullet points: "• Rapid publication", "• Article-level metrics", and "• Post-publication rating and commenting".

AIPAdvances

Now Indexed in
Thomson Reuters
Databases

Explore AIP's open access journal:

- Rapid publication
- Article-level metrics
- Post-publication rating and commenting

Strain behavior of lanthanum modified BiFeO₃ thin films prepared via soft chemical method

A. Z. Simões,¹ E. C. Aguiar,^{1,a)} A. H. M. Gonzalez,¹ J. Andrés,² E. Longo,¹ and J. A. Varela¹

¹*Departamento de Físico-Química, Instituto de Química, Laboratório Interdisciplinar em Cerâmica—LIEC, UNESP, CEP, Araraquara, São Paulo 14800-900, Brazil*

²*Departamento de Química Física y Analítica, Universitat Jaume I, 12071 Castelló, Spain*

(Received 27 June 2008; accepted 9 October 2008; published online 24 November 2008)

Pure and lanthanum modified BFO (La_xBi_{1-x}FeO₃, $x=0.0, 0.08, 0.15, 0.30$) thin films were fabricated on Pt(111)/Ti/SiO₂/Si substrates by the soft chemical method. The effect of La substitution on the structural and electrical properties was studied. Scanning electron microscopy, x-ray diffraction, and Raman spectroscopy have been employed to characterize the thin films while the piezoelectric measurements were carried out using a setup based on an atomic force microscope. It was found that La-doped BFO thin films exhibited good ferroelectric properties, such as improved leakage current density and retention-free characteristics. The unipolar strain is strongly reduced by the amount of lanthanum added to the system. © 2008 American Institute of Physics.

[DOI: 10.1063/1.3029658]

I. INTRODUCTION

Multiferroic materials have attracted renewed interest in recent years^{1–5} due to both its potential applications for electronic device and its fascinating fundamental physics.^{6–8} In particular, special attention has been designed for multiferroic oxides such as BiFeO₃ (BFO),⁹ BiMnO₃,¹⁰ TbMnO₃,¹¹ and TbMn₂O₅ (Ref. 12) due the potential to provide a wide range of applications, including the emerging field of spintronics,¹³ data-storage media,¹⁴ and multiple-state memories.⁸ These multiferroic materials have simultaneous ferromagnetic, ferroelectric, and/or ferroelastic ordering.¹⁵

The well-known single phase multiferroics are mainly Mn- or Fe-based oxides.^{16–19} Among them, BFO is the only known material that is both ferroelectric ($T_C \sim 1083$ K) and antiferromagnetic ($T_N \sim 625$ K).^{20,21} It has a rhombohedrally distorted ferroelectric perovskite structure ($T_C=123$ K) with the space group $R3c$.^{22,23} Recent reports of a large spontaneous polarization (~ 100 $\mu\text{C}/\text{cm}^2$) in thin films,²⁴ bulk ceramic,²⁵ and single crystals²⁶ of BFO have led to an explosion of interest in its growth and properties.

The ferroelectric mechanism in BFO is controlled by the stereochemical activity of the Bi³⁺ 6s² lone pair, responsible of a charge transfer process from 6s² to formally empty 6p orbitals,^{27,28} while the weak ferromagnetic property can be associated with the residual moment from the canted Fe³⁺ spin structure.²⁹ The coupling effect between both magnetic and electric behaviors occurs through lattice distortion of BFO (Ref. 30) and Khomskii³¹ has been emphasized the different ways to combine magnetism and ferroelectricity in multiferroics materials.

The structure and properties of thin films are well known to exhibit a number of deviations from those of bulk ceram-

ics and single crystals. The origin of the size-dependent ferroelectric properties remains a challenging problem, and a better understanding as to which extent the bulk physical properties can be used for design of thin-layer devices, is actually required. Retention, which is the time-dependent change in the polarization state of the ferroelectric film, is another factor which limits the life of a ferroelectric memory device. In bismuth-based ferroelectrics, such as Bi₄Ti₃O₁₂ (Ref. 32) and SrBi₄Ti₄O₁₅,³³ the doping of lanthanum (La) was effective to enhance the insulating and ferroelectric properties because of the reduced oxygen vacancy by the stabilized oxygen octahedron.³⁴ Some studies reported in literature^{35–37} suggest that the inhomogeneous magnetic spin structure can be effectively suppressed by La doping. Therefore, the influence of La doping on polarization switching, ferroelectric reliability, and multiferroic properties of BFO films deserves more attention.³⁸ In this respect, strain engineering and functional tuning of thin films are the leading activities for the development of the next generation of electronic devices. Recently, several research groups have substituted Bi by La and Tb in order to study the effect of doping on electric and magnetic behavior of pure BFO and lanthanum doped (BLFO) thin films.^{39–42} Recently, Zheng *et al.*⁴³ presented synthesis and ferroelectric properties of BiFeO₃ thin films grown by sputtering, while Li *et al.*⁴⁴ employed a cosputtering method to obtain BiFeO₃ thin films on Pt/Ti/SiO₂/Si substrates.

Our group has expanded significant effort in developing synthetic routes of BiFeO₃ thin films^{45,46} and we have previously reported the preparation of BLFO thin films grown on Pt(111)/Ti/SiO₂/Si substrates with good structural, microstructural, and electrical properties by the soft chemical method.^{9,32,47,48} In the present investigation and as a natural extension of previous work, pure and lanthanum modified Bi_{1-x}La_xFeO₃ ($x=0.0, 0.08, 0.15, 0.30$) thin films were prepared on Pt(111)/Ti/SiO₂/Si substrates by the soft chemical

^{a)}Author to whom correspondence should be addressed. Electronic mail: ederson.carlos@yahoo.com.br.

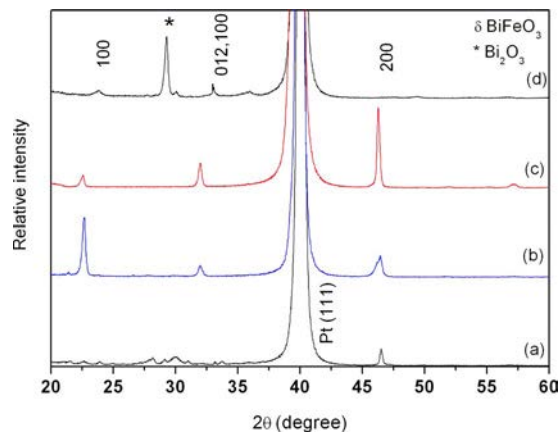


FIG. 1. (Color online) XRD data for BFO films deposited by the polymeric precursor method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

method. Structural and electrical properties of the films, mainly related to strain behavior, were investigated by using various techniques with a view to explore their technological applications.

II. EXPERIMENTAL PROCEDURE

Lanthanum modified bismuth ferrite thin films were prepared by the soft chemical method, as described elsewhere.⁴⁶ The films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 rpm for 30 s (spin coater KW-4B, Chemat Technology). An excess of 5 wt % of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. The thin films were annealed at 500 °C for 2 h in the conventional furnace under static air atmosphere. The film thickness was reached by repeating ten times the spin coating and heating treatment cycles. The thickness of the annealed films was measured using scanning electron microscopy (Topcom SM-300) at the transversal section. We have obtained films with thickness in the range of 340–360 nm. In this case backscattering electrons were used. Phase analysis of the films was performed at room temperature by x-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu $K\alpha$ radiation. Raman measurements were performed using an ISA T 64000 triple monochromator. An optical microscope with 80 $\times$ objective was used to focus the 514.5 nm radiation from a Coherent Innova 99 Ar⁺ laser on the sample. The same microscope was used to collect the backscattered radiation. The

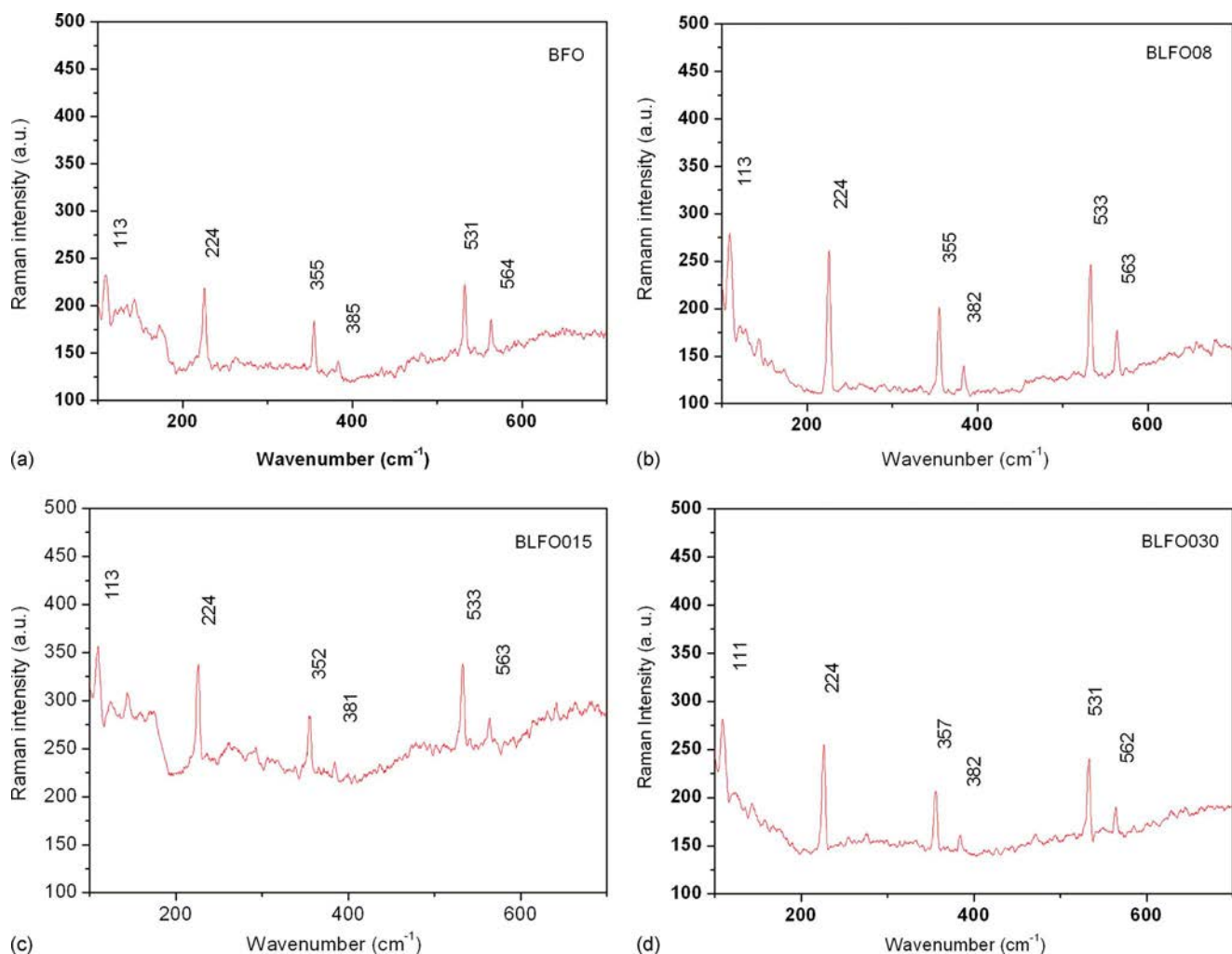


FIG. 2. (Color online) Micro-Raman spectra for BFO film deposited by the polymeric precursor method and annealed at 500 °C for 2 h, with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

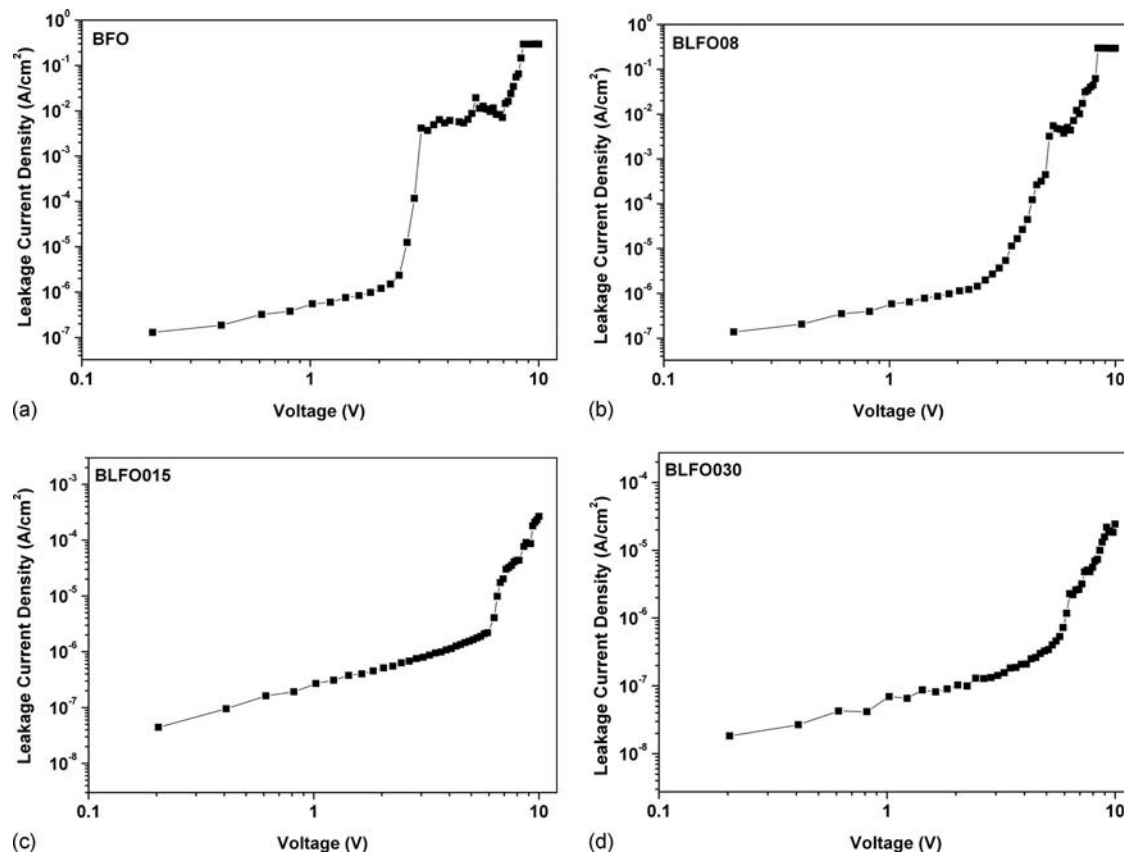


FIG. 3. Leakage current density vs applied electric field for BFO films deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

scattering light dispersed was detected by a charge-coupled device detection system ≈ 0.3 mm. The leakage current-voltage (I - V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). Piezoelectric measurements were carried out using a setup based on an atomic force microscope in a multimode scanning probe microscope with Nanoscope IV controller (Veeco FPP-100). In our experiments, piezoresponse images of the films were acquired in ambient air by applying a small ac voltage with an amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz while scanning the film surface. To apply the external voltage we used a standard gold coated Si_3N_4 cantilever with a spring constant of 0.09 N/m. The probing tip, with an apex radius of about 20 nm, was in mechanical contact with the uncoated film surface during the measurements. Cantilever vibration was detected using a conventional lock-in technique. Top Au electrodes (0.5 mm diameter) were prepared for the electrical measurements by evaporation through a shadow mask at room temperature. Retention characteristics of the films were measured by independently observing the time-dependent changes in P^* (switched polarization), and $P^\wedge$ (nonswitched polarization). For P^* , the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time t . For $P^\wedge$, positive pulses were used for both writing and reading. The pulse width for all triangular pulses was 1.0 ms. The time delay between the right pulse and the first read pulse is referred to as retention time.

III. RESULTS AND DISCUSSION

Figure 1 presents the XRD patterns of BFO and BLFO films deposited on platinum coated silicon substrates. The films were well crystallized at a processing temperature of 500 °C. The BFO film self-organized to produce (200)-preferred orientation, while the BLFO film crystallized with random orientation and better crystallinity. With partial substitution of isovalent La ions for A-site bismuth ions, the (100) diffraction peak of the BLFO film shifted toward a higher angle. Increasing lanthanum content leads to an additional peak at $2\theta=28^\circ$ that could be assigned to the diffraction peak of Bi_2O_3 , probably formed due to the substitution of lanthanum by bismuth in the crystal lattice.

An analysis of the evolution of Raman spectra in the lanthanum modified bismuth ferrite shows the order-disorder degree of the atomic structure at short range (Fig. 2). The modes further split into longitudinal and transverse components due the long electrostatic forces associated with lattice ionicity. Substitution of lanthanum in the A-site of the lattice reduces the distortion of octahedral clusters having little influence in the relative intensity of the bands. The vibrational modes located at 224, 355, 385, 531, and 564 cm^{-1} result from the FeO_6 octahedral ($\text{Fe}=5$ or $\text{Fe}=6$). The band located below 200 cm^{-1} is due to the different sites occupied by bismuth within the perovskite layer. Raman frequencies are not strongly affected by lanthanum substitution. Slight changes which occur above 200 cm^{-1} in the BFO can be associated with structural distortion and reduction in vibra-

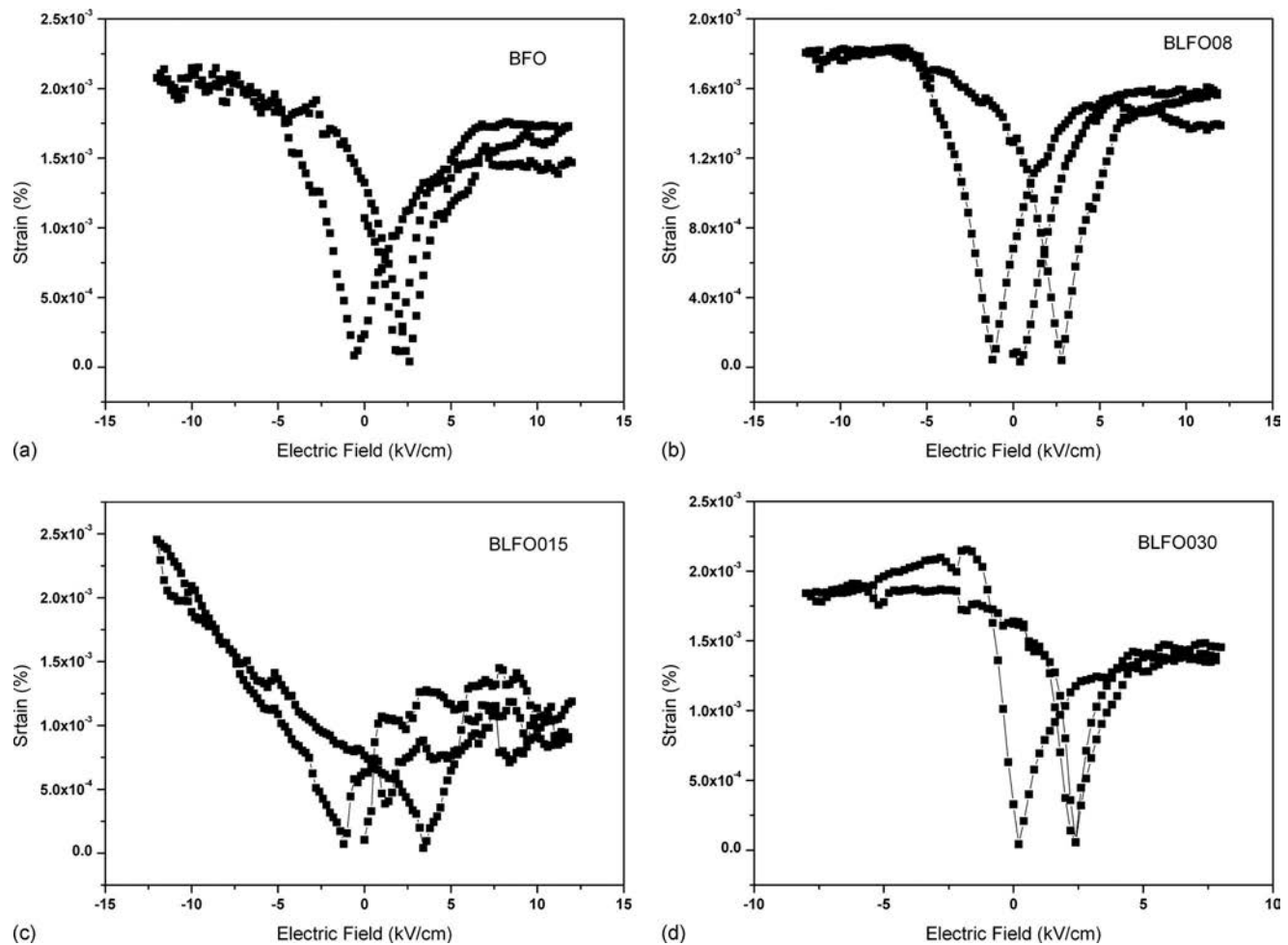


FIG. 4. Strain response for BFO films deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

tions in the FeO_5 octahedra. Lanthanum atoms substitute bismuth within the perovskite structure having marginal influence in the interactions between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite.

A typical leakage current characteristic for the films is given in Fig. 3. The curves were recorded with a voltage step width of 0.1 V and elapsed time of 1.0 s for each voltage, here the measured logarithmic current density ($\log J$) versus the logarithmic electric field (E) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an Ohmic conduction. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V decreases after substitution for lanthanum. The main reasons for such behavior can be attributed to changes in the surface roughness and reduction in microcracks due the modification in the lattice volume after lanthanum addition. In this way, lanthanum acts reducing the oxygen vacancies and as consequence improves the switching process of electrical dipoles. On the other hand, undoped BFO present defects as Bi or Ti vacancies resulting in an increase in conductivity. Therefore, this fact indicates the presence of mobile carriers which are

positively charged and that the possibility of hopping through the Bi ion can be considered. The unipolar strain behavior at room temperature is shown in Fig. 4. The unipolar strain presents a maximum at 5 kV/cm while the saturation regime is reached at 10 kV/cm. Lanthanum decreases the strain behavior, in part, due to domain reorientation. Beyond that point, it is possible that a modest bias field results in the transition from asymmetric to symmetric phase. This field-induced phase transition may be ascribed to the pinching effect, that is, the consequent decrease in free energy difference among polymorphic phases. A careful inspection of the S – E plots reveals that there are two apparent linear regions at low fields ($E < 5$ kV/cm) and high fields ($E > 10$ kV/cm) and one transition region, which corresponds to domain reorientation induced by external electric fields. The hysteretic strain could be associated with domain reorientation. The strain is hysteresis-free at electric fields higher than 5 kV/cm, indicating a stable single domain/poling state induced by the high external electric fields. In addition, from the S versus E profiles, no noticeable induced phase transition is observed at such high electric fields. It is shown that lanthanum reduces the unipolar strain when compared to BFO films, i.e., the strain was ($S=0.16\%$, 0.12% , and 0.11%) and ($S=0.17\%$) for lanthanum doped films and BFO, respectively. The decreasing of both strain response and strain en-

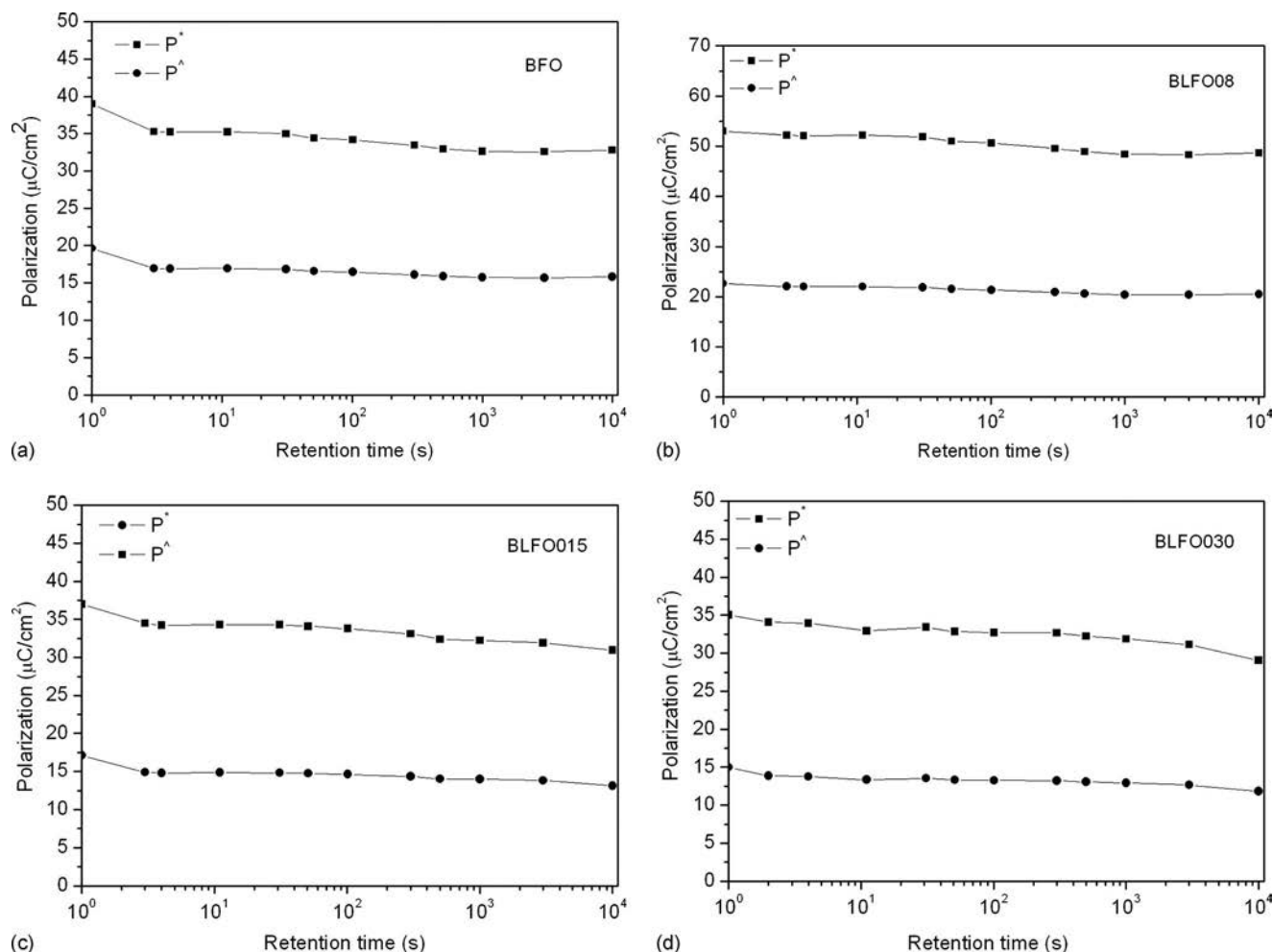


FIG. 5. Retention curve characteristics of BFO film deposited by the soft chemical method with different La contents: (a) $x=0.0$, (b) $x=0.08$, (c) $x=0.15$, and (d) $x=0.30$.

ergy after doping process can be associated with the reduced polarizability and the pinning effect. As can be seen, the small strain variations one each curve with electric field can be probably caused by clamping effect due to the stress created in the film-substrate interface and the existence of an ultrathin air gap between the tip and the sample which might lower the actual voltage drop in the film.

Figures 5(a)–5(d) show the retention characteristics of the films as a function of retention time from 1 to 1×10^4 s. The value of initial polarization decayed and approached a nearly steady-state value after a retention time of 10 s. The small decay of the retained charge in the films is a favorable indication for memory applications. After a retention time of 1×10^4 s, the polarization loss was only about 6% of the value measured at $t=1$ s for an applied electric field of 150 kV/cm. Depolarization fields generated by the redistribution of space charge, defects, and dipole charges could be the origin of the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss. The depolarization field increases with increasing the retained polarization and is time dependent. The long-time retention loss is attributed to the effect of redistribution of defect charges. This effect leads to a small decrease in the polarization by

compensating the polarization charges when the redistribution of defect charges is driven by polarization.³⁶ The retention failure tests showed that the BLFO films have quite good long-time retention characteristics, retaining 94% of the values measured at $t=1 \times 10^4$ s for an applied electric field of 150 kV/cm. Polarization charge compensation by the redistribution of defect charges should be considered to explain this small retention loss in lanthanum doped bismuth ferrite thin films. The results of these studies are very promising and suggest that BLFO thin films are attractive for use as storage element in nonvolatile ferroelectric random access memories.

IV. CONCLUSIONS

Pure and lanthanum doped bismuth titanate thin films were fabricated on Pt substrate using the soft chemical method through annealing at 500 °C for 2 h. Raman modes are not strongly affected by lanthanum substitution. It was found that lanthanum reduces the strain behavior of BFO films. From leakage current density values we noted that La^{+3} substitution for Bi^{+3} is an effective way to reduce bismuth vacancies that are accompanied by oxygen vacancies decreasing the film conductivity. The results of these studies

are very promising and suggest that BLFO thin films can be used as storage element in nonvolatile ferroelectric random access memories.

ACKNOWLEDGMENTS

The authors thank the financial support of the Brazilian research financing institutions: CAPES, FAPESP, and CNPq.

- ¹N. A. Spaldin and M. Fiebig, *Science* **309**, 391 (2005).
- ²W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature (London)* **442**, 759 (2006).
- ³S. W. Cheong and N. Mostovoy, *Nature Mater.* **6**, 13 (2007).
- ⁴R. Ramesh and N. A. Spaldin, *Nature Mater.* **6**, 21 (2007).
- ⁵W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, *Nature Mater.* **6**, 348 (2007).
- ⁶M. Fiebig, *J. Phys. D* **38**, R123 (2005).
- ⁷G. Catalan, *Appl. Phys. Lett.* **88**, 102902 (2006).
- ⁸N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ⁹A. H. M. Gonzalez, A. Z. Simões, L. S. Cavalcante, E. Longo, J. A. Varela, and C. S. Riccardi, *Appl. Phys. Lett.* **90**, 052906 (2007).
- ¹⁰A. M. dos Santos, S. Parashar, A. R. Raju, Y. S. Zhao, A. K. Cheetham, and C. N. R. Rao, *Solid State Commun.* **122**, 49 (2002).
- ¹¹T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, *Nature (London)* **426**, 55 (2003).
- ¹²N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S. W. Cheong, *Nature (London)* **429**, 392 (2004).
- ¹³H. Béa, M. Bibes, M. Sirena, G. Herranz, K. Bouzehouane, E. Jacquet, S. Fusil, P. Paruch, M. Dawber, J. P. Contour, and A. Barthelemy, *Appl. Phys. Lett.* **88**, 062502 (2006).
- ¹⁴M. Fiebig, Th. Lottermoser, D. Frhlich, A. V. Golsev, and R. V. Pisarev, *Nature (London)* **419**, 818 (2002).
- ¹⁵H. Schmid, *Ferroelectrics* **62**, 317 (1994).
- ¹⁶O. P. Vajk, M. Kenzelmann, J. W. Lynn, S. B. Kim, and S.-W. Cheong, *Phys. Rev. Lett.* **94**, 087601 (2005).
- ¹⁷B. B. Van Aken, T. T. M. Plastra, A. Filippetti, and N. A. Spaldin, *Nature Mater.* **3**, 164 (2004).
- ¹⁸J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ¹⁹M. Fiebig, M. T. Lottermoser, D. Fröhlich, A. V. Goltsev, and R. V. Pisarev, *Nature (London)* **419**, 818 (2002).
- ²⁰J. R. Teague, R. Gerson, and W. J. James, *Solid State Commun.* **8**, 1073 (1970).
- ²¹G. A. Smolenskii and I. E. Chupis, *Sov. Phys. Usp.* **25**, 475 (1982).
- ²²F. Kubel and H. Schmid, *Acta Crystallogr. B* **46**, 698 (1990).
- ²³C. Michel, J. M. Moreau, G. D. Achenbach, R. Gerson, and W. J. James, *Solid State Commun.* **7**, 701 (1969).
- ²⁴J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ²⁵V. V. Shvartsman, W. Kleemann, R. Haumont, and J. Kreisel, *Appl. Phys. Lett.* **90**, 172115 (2007).
- ²⁶D. Lebeugle, D. Colson, A. Forget, M. Viret, P. Bonville, J. F. Marucco, and S. Fusil, *Phys. Rev. B* **76**, 024116 (2007).
- ²⁷R. Seshadri and N. A. Hill, *Chem. Mater.* **13**, 2892 (2001).
- ²⁸T. Shishidou, N. Mikamo, Y. Uratani, F. Ishii, and T. Oguchi, *J. Phys.: Condens. Matter* **16**, S5677 (2004).
- ²⁹P. Fischer, M. Polomska, I. Sosnowska, and M. Szymanski, *J. Phys. C* **13**, 1931 (1980).
- ³⁰S.-W. Cheong and M. Mostovoy, *Nature Mater.* **6**, 13 (2007).
- ³¹D. I. Khomskii, *J. Magn. Magn. Mater.* **306**, 1 (2006).
- ³²A. Z. Simões, C. S. Riccardi, L. S. Cavalcante, E. Longo, J. A. Varela, B. Mizaikoff, and D. Hess, *J. Appl. Phys.* **101**, 084112 (2007).
- ³³Y. P. Chen, Y. Y. Yao, Z. H. Bao, J. S. Zhu, and Y. N. Wang, *Mater. Lett.* **57**, 3623 (2003).
- ³⁴Y. Kan, X. Jin, G. Zhang, P. Wang, Y.-B. Cheng, and D. Yan, *J. Mater. Chem.* **14**, 3566 (2004).
- ³⁵D. Lee, M. G. Kim, S. Ryu, H. M. Jang, and S. G. Lee, *Appl. Phys. Lett.* **86**, 222903 (2005).
- ³⁶C. Ederer and N. A. Spaldin, *Phys. Rev. B* **71**, 224103 (2005).
- ³⁷Y. Zhong, G. Hu, and T. A. Tang, *Jpn. J. Appl. Phys., Part 1* **42**, 7424 (2003).
- ³⁸Y.-H. Lee, J.-M. Wu, and C.-H. Lai, *Appl. Phys. Lett.* **88**, 042903 (2006).
- ³⁹Y. Wang and C.-W. Nan, *J. Appl. Phys.* **103**, 024103 (2008).
- ⁴⁰D. Lee, M. G. Kim, S. R. Ryu, and H. M. Jang, *Appl. Phys. Lett.* **86**, 222903 (2005).
- ⁴¹V. R. Palkar, K. G. Kumara, and S. K. Malik, *Appl. Phys. Lett.* **84**, 2856 (2004).
- ⁴²C. Wang, M. Takahashi, H. Fujino, X. Zhao, E. Kume, T. Horiuchi, and S. Sakai, *J. Appl. Phys.* **99**, 054104 (2006).
- ⁴³Z. Chaodan, Z. Duanming, Y. Jun, Y. Bin, W. Yunyi, W. Longhai, W. Yunbo, and Z. Wenli, *Integr. Ferroelectr.* **94**, 23 (2007).
- ⁴⁴Y. Li, T. Sritharan, S. Zhang, X. He, Y. Liu, and T. Chen, *Appl. Phys. Lett.* **92**, 132908 (2008).
- ⁴⁵A. Z. Simoes, A. H. M. Gonzalez, C. S. Riccardi, E. C. Souza, F. Moura, M. A. Zaghete, E. Longo, and J. A. Varela, *J. Electroceram.* **13**, 65 (2004).
- ⁴⁶A. Z. Simões, B. D. Stojanovic, M. A. Zaghete, C. S. Riccardi, A. Ries, F. Moura, E. Longo, and J. A. Varela, *Integr. Ferroelectr.* **60**, 21 (2004).
- ⁴⁷A. Z. Simoes, C. S. Riccardi, L. S. Cavalcante, J. A. Varela, and E. Longo, *Mater. Res. Bull.* **43**, 158 (2008).
- ⁴⁸A. Z. Simões, L. S. Cavalcante, C. S. Riccardi, J. A. Varela, and E. Longo, *J. Sol-Gel Sci. Technol.* **44**, 269 (2007).



Effect of annealing atmosphere on phase formation and electrical characteristics of bismuth ferrite thin films

A.Z. Simões^{a,*}, C.S. Riccardi^{b,1}, M.L. Dos Santos^{b,1}, F. González Garcia^{a,2}, E. Longo^{b,1}, J.A. Varela^{b,1}

^a Universidade Federal de Itajubá, UNIFEI - CAMPUS ITABIRA, Rua São Paulo, 377, Bairro Amazonas, CEP: 35900-373 Itabira, MG, Brazil

^b Laboratório Interdisciplinar em Cerâmica, Departamento de Físico-Química, Instituto de Química Universidade Estadual Paulista, Bairro: Quitandinha, CEP: 14800-900 Araraquara, SP, Brazil

ARTICLE INFO

Article history:

Received 16 October 2008

Received in revised form 4 March 2009

Accepted 16 March 2009

Available online 27 March 2009

Keywords:

A. Thin films

B. Chemical synthesis

C. Atomic force microscopy

D. Ferroelectricity

ABSTRACT

Bismuth ferrite thin films were deposited on Pt/Ti/SiO₂/Si substrates by a soft chemical method and spin-coating technique. The effect of annealing atmosphere (air, N₂ and O₂) on the structure and electrical properties of the films are reported. X-ray diffraction analysis reveals that the film annealed in air atmosphere is a single-phase perovskite structure. The films annealed in air showed better crystallinity and the presence of a single BFO phase leading to lower leakage current density and superior ferroelectric hysteresis loops at room temperature. In this way, we reveal that BFO film crystallized in air atmosphere by the soft chemical method can be useful for practical applications, including nonvolatile digital memories, spintronics and data-storage media.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

BiFeO₃ is a ferromagnetic compound with uniquely high temperatures of magnetic and electric ordering. That makes it a very prospective material for the applications in nonvolatile ferroelectric random access memory (NVFRAM), dynamic random access memory, sensors and microactuators [1]. Recently, it has been reported that pulsed laser deposited BFO thin films with reasonably high resistivity show large polarization [2,3]. For example, (0 0 1)-oriented BFO thin films display a polarization of 55 μC/cm², comparable to the very popular ferroelectric system, Pb(Zr_xTi_{1-x})O₃ (PZT), which has been studied for decades for applications in memory, transducers and micro-electro-mechanical systems (MEMS). Since then, several researchers have prepared BFO thin films by pulsed laser deposition (PLD) [4] and sol-gel method [5,6], but the thin films did not show good ferroelectric properties, especially sol-gel grown films have shown poor leakage behavior. Therefore, the challenge still remains to obtain polycrystalline BFO thin films with reasonably good ferroelectricity properties and low leakage currents and here the role of post deposition heat treatment can be crucial. Some

researchers have also reported the production of BFO films via the CSD method [7–10]. These BFO films were annealed at relatively high temperatures from 500 to 650 °C in N₂ or O₂ in order to eliminate second phases such as Bi₂O₃, Bi₂Fe₄O₉, and Bi₃₆Fe₂O₅₇, etc. Besides that, in order to be compatible with semiconductor technology in applications such as FeRAM devices, it is advantageous to fabricate BFO films at temperatures as low as possible to prevent interactions among the silicon substrate, electrode, and ferroelectric materials. Solution deposition is a process that improves the stoichiometric control of complex mixed oxides and is compatible with many semiconductor manufacturing technologies.

In previous works, our group has reported the preparation of thin films by the polymeric precursor method [11]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [12]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. This method presents many advantages, such as the possibility to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method with inexpensive precursors and equipments.

In this study, we report the preparation of pure BFO films at 500 °C and crystallized in air atmosphere from the soft chemical method with low leakage current. We have studied the effects of annealing atmospheres (oxygen, air and nitrogen) on the structure and electrical properties of these films.

* Corresponding author. Tel.: +55 31 3834 6472/6136.

E-mail address: alezipo@yahoo.com (A.Z. Simões).

¹ Tel.: +55 16 3301 6643; fax: +55 16 3301 6692.

² Tel.: +55 31 3834 6472/6136.

2. Experimental procedure

Iron(III) nitrate nonahydrate (99.5% purity, Merck) and bismuth nitrate (99.5% purity, Aldrich) were used as raw materials. The precursor solutions of bismuth and iron were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Fe and Bi were mixed and maintained under stirring at 90 °C. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The films were spin-coated from a BFO deposition solution onto Pt/Ti/SiO₂/Si substrates. A platinum layer (140 nm) was used as bottom electrode. The BFO films were annealed in convention furnace at 500 °C for 2 h in different atmospheres. The thickness of the annealed films ranging from 250 to 300 nm being examined in a scanning electron microscopy (SEM, Topcom, SM-300) by looking at the cross section. The thickness results obtained from SEM represent an average value of three measurements. After that, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was thermal treated in a tube furnace at 300 °C for 1 h in oxygen atmosphere. Here, the desired effect is to diminish eventually present oxygen vacancies. An excess of 5 wt% Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment and to obtain more purity phase. Phase analysis of the films was performed at room temperature by X-ray powder diffraction (XRD) using a Bragg-Brentano diffractometer (Rigaku 2000) and Cu K α radiation. Surface roughness

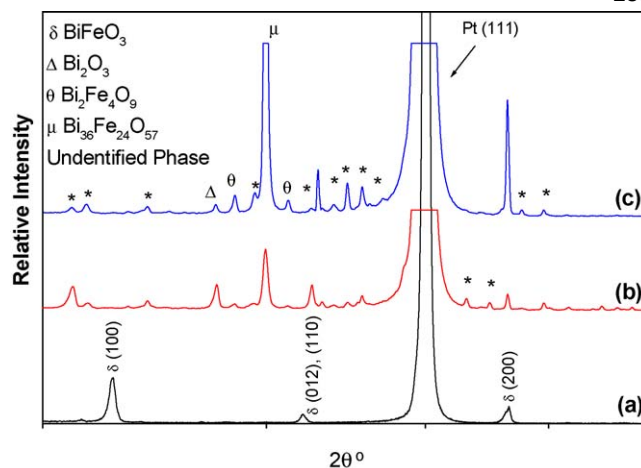


Fig. 1. X-ray diffraction data for BFO films crystallized at different atmospheres: (a) air; (b) O₂; (c) N₂.

(RMS) was examined by AFM, using tapping mode techniques. The capacitance–voltage characteristic was measured in the MFM configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. The current–voltage (*I*–*V*) characteristic was determined with a voltage source measuring unit (Radiant Technology, 6000 A). Ferroelectric property was investigated using a Sawyer–Tower circuit attached to a computer controlled standardized test system (Radiant Technology 6000 A). For the

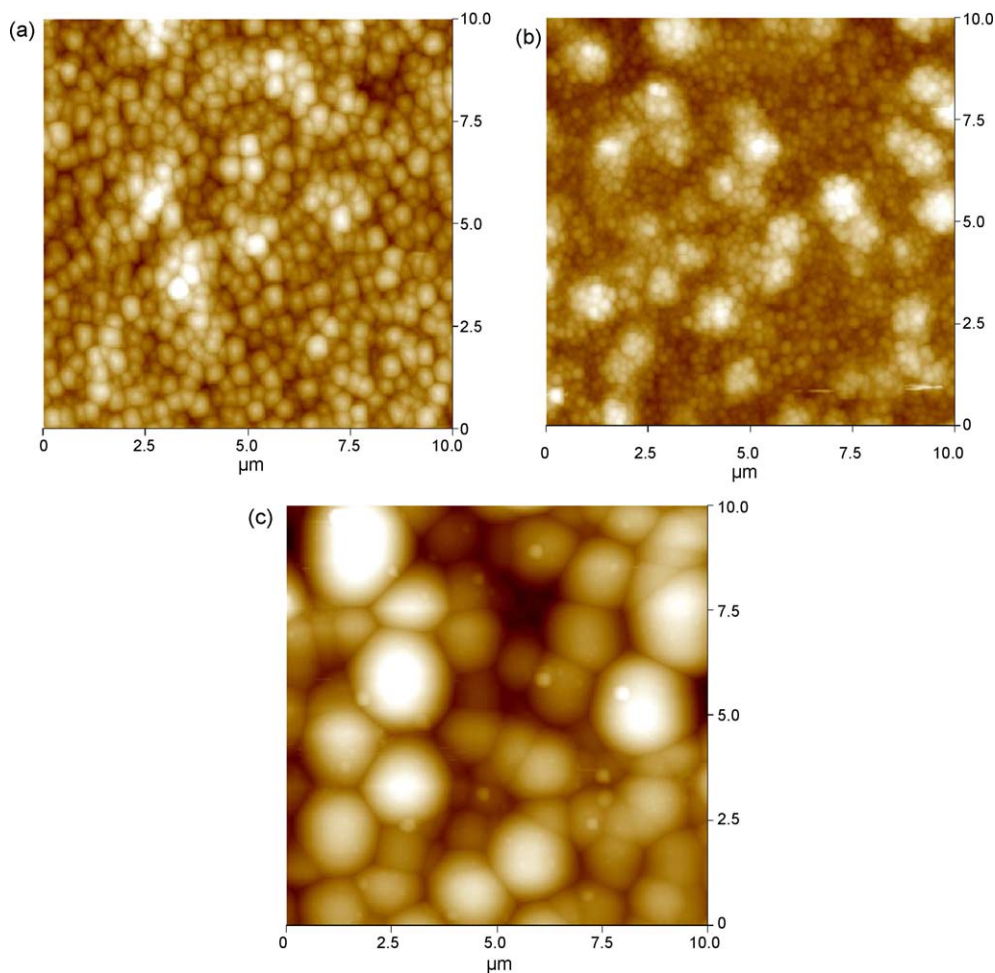


Fig. 2. AFM microographies for BFO films crystallized at different atmospheres: (a) air; (b) O₂; (c) N₂.

fatigue measurements, internally generated $8.6\ \mu\text{s}$ wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies. All measurements were performed at room temperature ($25 \pm 1^\circ\text{C}$).

3. Results and discussion

Fig. 1 shows the XRD patterns of the BFO films annealed at different atmospheres. The peaks of BiFeO_3 phase were found in all samples suggesting a polycrystalline behavior. The films annealed in air consist of a single phase. However, the films annealed in oxygen and nitrogen showed the formation of secondary phases, along with the formation of BiFeO_3 phase. This indicates that the static air atmosphere showed good crystallinity with no second phase formation. The presence of secondary phases prominent in the films heat treated in N_2 and O_2 atmosphere suggests loss of bismuth from the samples. Literature reports suggest that due to the kinetics of the phase formation, a mixture of BiFeO_3 as a major phase along with other phases ($\text{Bi}_2\text{Fe}_4\text{O}_9$ and $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$) are repeatedly obtained during synthesis of BFO, especially in bulk form, as reported by Munoz et al. [13] and Teague et al. [14], respectively. It is possible that annealing in air compensate the bismuth vacancies created due to bismuth volatilization, leading to the formation of relatively pure phase samples. Also, other unidentified peaks were observed in the XRD spectra.

Fig. 2a–c shows the AFM images of BiFeO_3 films annealed at 500°C for 2 h in different atmospheres. All the films have a continuous surface microstructure with no presence of particulates and cracks. The average grain size of the films annealed in air and oxygen atmospheres was 53 nm and 58 nm, respectively, and increased marginally for the films heat treated in nitrogen (130 nm). But, annealing in O_2 ambient promotes a rather dense

morphology material, whereas annealing in N_2 ambient leads to a slightly porous morphology. The annealing ambient was found to dramatically affect the electrical properties of the films [13]. The increase in the grain size could possibly be due to creation of oxygen vacancies in nitrogen atmosphere (as vacancy concentration exponentially raises with increase in the temperature) which may affect the kinetics of grain growth by altering the diffusion flux of oxygen vacancy species. However, average roughness of the films was in the range of 11–14 nm. AFM images suggest that only the nitrogen annealed films showed an increase in grain size, implying a reduction in the grain boundary area. Thus, if grain boundaries were insulating as compared to grains, the conductivity should have gone up at smaller grain size whereas the results suggest the opposite. It is likely that conduction takes place via conduction of electrons, through grain boundaries. In addition, higher conductivity of films annealed in oxygen and nitrogen could be due to the presence of secondary phases of the films.

Fig. 3a–c plotted the current density vs. electric field (J – E) curves of BFO films annealed at various atmospheres. The leakage behavior of the thin films depends upon factors such as phase purity, grain size as well as roughness. Usually, the leakage current density should be less than $10^{-7}\ \text{A}/\text{cm}^2$ during operation in memory device applications. The leakage current was $10^{-6}\ \text{A}/\text{cm}^2$ at 1 V for films annealed in oxygen and nitrogen atmospheres (Fig. 3b and c). The leakage current decreased for the film annealed under air atmosphere being much lower than those reported in the literature (Fig. 3a). They were $10^{-5}\ \text{A}/\text{cm}^2$ (CSD) [8] and $5.10^{-1}\ \text{A}/\text{cm}^2$ (PLD) [14] for BFO films. The variation of leakage with annealing atmosphere corresponded to the film free of secondary phase. We can see that the leakage resistance is significantly improved by annealing in static air. While air annealed films still show the lowest current densities, the nitrogen annealed films are leakier than those annealed in oxygen. In this way, we can assume that the leakage

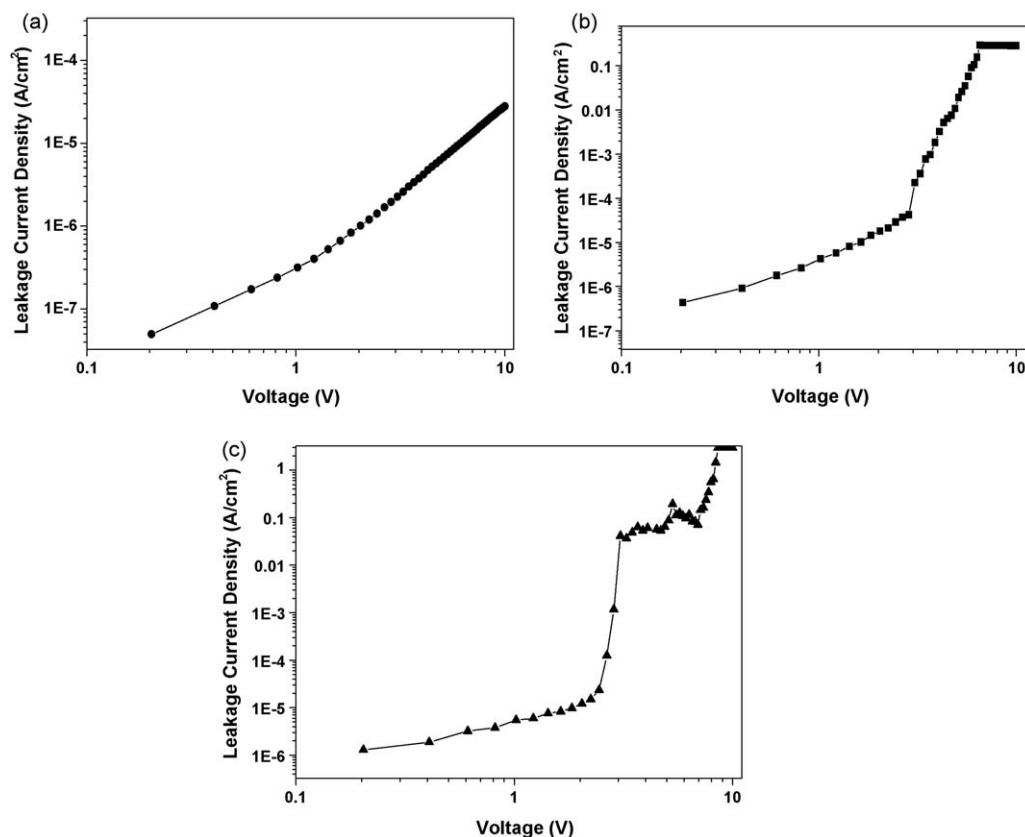


Fig. 3. Leakage current density vs. applied electric field for BFO films crystallized at different atmospheres: (a) air; (b) O_2 ; (c) N_2 .

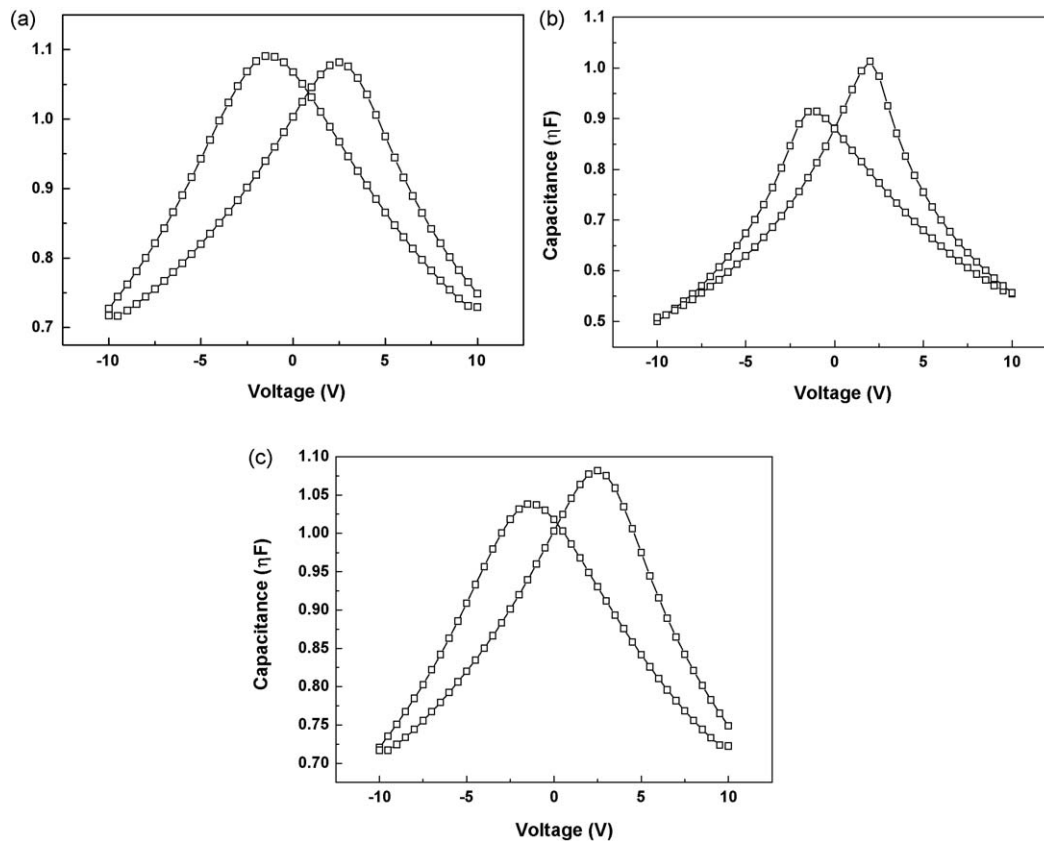


Fig. 4. C–V characteristics for BFO films crystallized at different atmospheres: (a) air; (b) O₂; (c) N₂.

current was found to be closely related to the phase purity, which suggested that the annealing atmosphere has a fundamental importance in the conduction mechanisms of the thin films.

Due to the anisotropic characteristics, the dielectric properties of bismuth ferrite films are always determined by the crystal structure and orientation, which defines the magnitude of switchable domains that contribute to the dielectric displacement. The C–V results are shown in Fig. 4. The C–V curve for BFO films was obtained at 100 kHz and DC sweep voltage from +10 to –10 V. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. The two peaks, which characterize spontaneous polarization switching, are clearly shown. Also, the curve displays symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The curve for the film crystallized in air atmosphere is symmetric around the zero bias axes, indicating that the film contains few movable ions or charge accumulation at the film–electrode interface (Fig. 4a). On the other hand, when the capacitor was treated in oxygen and nitrogen atmospheres, the V_m voltage at which the capacitance is at its maximum C_m value is not located at the zero bias field, but shifted toward the positive bias region. This suggests that the existence of additional capacitance at the interface arises from the space charge, originating from thermal treatment in N₂ and O₂ atmospheres (Fig. 4b and c) [15].

The room temperature P – E hysteresis loops of BFO films annealed at 500 °C for 2 h in air, O₂ and N₂ ambient are shown in Fig. 5. All the polarization measurements were done at 60 Hz. As can be seen, the films annealed in oxygen and nitrogen atmospheres showed poor ferroelectric properties (Fig. 5b and c). The hysteresis loop for the film annealed in static air was saturated at 1000 kV/cm, the remnant polarization (P_r) was 32 $\mu\text{C}/\text{cm}^2$ and the coercive field (E_c) was as high as 540 kV/cm (Fig. 4a). This indicates

the remnant polarization of polycrystalline BFO film is strongly dependent on the phase purity. The lower remnant polarization of the films annealed in oxygen and nitrogen atmospheres can probably be caused by trapped charge ($\text{O}_2^{\bullet\bullet}$) associated with other defects ($\text{V}_0^{\bullet\bullet}$ or even defect dipole complexes such as oxygen vacancies associated to bismuth vacancies ($\text{V}_{\text{Bi}}^{\bullet\bullet} - \text{V}_0^{\bullet\bullet}$) located in the grain boundary and in film–electrode interface. These results are consistent with the C–V measurements and are caused by the high concentration of bismuth and oxygen vacancies trapped in the interface film/electrode.

Ferroelectric reliability of BFO films was examined by monitoring the fatigue-resistance characteristics. In Fig. 6, P^* is the switched and $P^\wedge$ is the non-switched polarization between two opposite polarity pulses. The $P^* - P^\wedge$ or $-P^* - (-P^\wedge)$ denote the switchable polarization, which is an important variable for nonvolatile memory application. Fatigue resistance was observed up to 10^{10} cycles for the film annealed in static air suggesting a good potential for applications in memories device. On the other hand, the films annealed in both oxygen and nitrogen atmospheres have no fatigue resistance due to the increase in local current around the nucleation sites which can destroy the film–electrode interface and suppress the nucleation of oppositely oriented domains at the surface [16]. In these films an increase in switching polarization leads to a local increase in conductivity in the film–electrode interface region. The marked improvement in the fatigue behavior may result from the crystallinity, electrode/ferroelectric interface, and defect concentration. The absence of ferroelectric fatigue observed in the films annealed in static air can be explained as follows: considering that the oxygen vacancy in ferroelectric films plays detrimental roles in the fatigue properties, it can stabilize the charges trapped at domain wall, and make the unpinning of domain wall difficult [17]. At the same time, its accumulation near electrodes can increase the electron injection, which in turn increases the pinning rate [18–20].

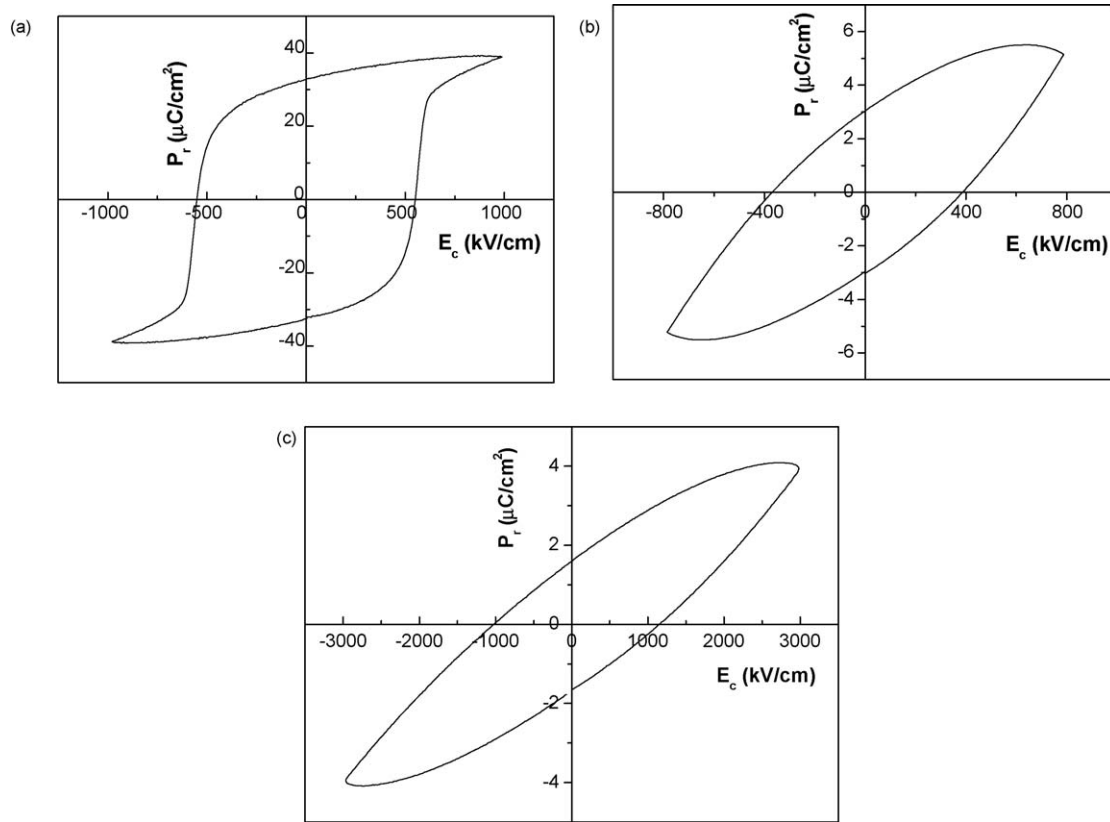


Fig. 5. P - E hysteresis loops for BFO films crystallized at different atmospheres: (a) air; (b) O_2 ; (c) N_2 .

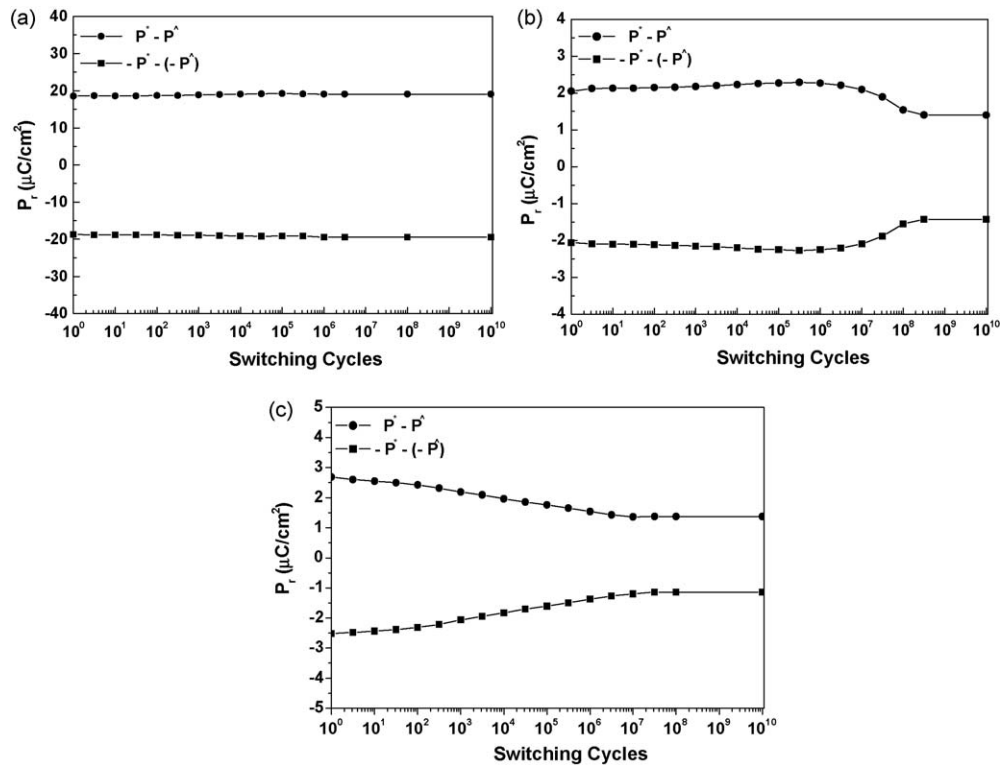


Fig. 6. Fatigue resistance for BFO films crystallized at different atmospheres: (a) air; (b) O_2 ; (c) N_2 .

4. Conclusions

BiFeO₃ films were prepared by a simple chemical solution deposition process on platinum coated silicon substrates. XRD analysis showed that the BFO films annealed in all atmospheres were polycrystalline. However, the crystallization and electrical properties of BiFeO₃ thin films were critically dependent on the choice of the annealing atmosphere. It was found that the films annealed in air showed better crystallinity and the presence of a single BFO phase leading to a leakage current density of 10^{-7} A/cm² at 1 V. This film presents a remnant polarization of 32 μ C/cm² and fatigue free properties up to 10¹⁰ cycles. The study suggests that BFO crystallized in air atmosphere could be fundamental in enhancing the structure and the properties of the films for practical applications.

Acknowledgments

Financial support from the Brazilian agencies FAPESP, CNPq, CAPES is gratefully acknowledged.

References

[1] J. Wang, Ph.D. thesis, University of Maryland, USA, 2005.

- [2] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, N.A. Spaldin, M. Wutting, *Science* 299 (2003) 1791.
- [3] K.Y. Kun, M. Noda, M. Okuyama, *Appl. Phys. Lett.* 83 (2003) 398.
- [4] V.R. Palkar, J. John, R. Pinto, *Appl. Phys. Lett.* 80 (2002) 1628.
- [5] H. Liu, Z. Liu, Q. Liu, K. Yao, *Thin Solid Films* 500 (2006) 105.
- [6] G. Teowee, K. McCarthy, T.J. Bukowski, T.P. Alexander, *Integr. Ferroelectr.* 18 (1997) 329.
- [7] K.-Y. Yun, M. Noda, M. Okuyama, *J. Korean Phys. Soc.* 42 (2003) S1153.
- [8] H. Uchida, R. Ueno, H. Nakaki, H. Funakubo, S. Koda, *Jpn. J. Appl. Phys.* 44 (2005) L561.
- [9] S. Iakovlev, C.-H. Solterbeck, M. Kuhnke, M. Es-Souni, *J. Appl. Phys.* 97 (2005) 094901.
- [10] S.K. Singh, H. Ishiwara, *Jpn. J. Appl. Phys. Part 2* 44 (2005) L734.
- [11] A.H. Gonzalez, A.Z. Simoes, L.S. Cavalcante, E. Longo, J.A. Varela, C.S. Riccardi, *Appl. Phys. Lett.* 90 (2007) 052906.
- [12] A.Z. Simões, M.A. Ramírez, A. Ries, E. Longo, J.A. Varela, R. Ramesh, *Appl. Phys. Lett.* 88 (2006) 072916.
- [13] C.T. Munoz, J.P. Rivera, A. Monnier, H. Schmid, *Jpn. J. Appl. Phys.* 24 (1985) 1051.
- [14] J.R. Teague, R. Gerson, W.J. James, *Solid State Commun.* 8 (1970) 739.
- [15] J.K. Kim, S.S. Kim, W.J. Kim, *Integr. Ferroelectr.* 76 (2005) 103.
- [16] X. Qi, J. Dho, R. Tomov, M.G. Blamire, J.L. MacManus-Driscoll, *Appl. Phys. Lett.* 86 (2005) 062903.
- [17] F.M. Pontes, E.R. Leite, E. Longo, J.A. Varela, E.B. Araújo, J.A. Eiras, *Appl. Phys. Lett.* 76 (2000) 2433.
- [18] D. Damjanovic, *Rep. Prog. Phys.* 61 (1998) 1267.
- [19] W.L. Warren, B.A. Tuttle, D. Dimos, *Appl. Phys. Lett.* 67 (1995) 1426.
- [20] J.F. Scott, C.A. Araujo, B.M. Melnick, L.D. Mcmillan, R.Z. Zuleeg, *J. Appl. Phys.* 70 (1991) 382.



Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom



Review

Effect of niobium dopant on fatigue characteristics of BiFeO₃ thin films grown on Pt electrodes

A.Z. Simões*, R.F. Pianno, E.C. Aguiar, E. Longo, J.A. Varela

Chemistry Institute, Department of Chemistry Physics, UNESP, Rua Prof. Francisco Degni, s/n, Quitandinha, CEP:14800-900, Araraquara, SP, Brazil

ARTICLE INFO

Article history:

Received 2 September 2008

Received in revised form 6 January 2009

Accepted 15 January 2009

Available online 31 January 2009

Keywords:

Ferroelectrics

Thin films

Chemical synthesis

X-ray diffraction

Transmission electron microscopy

ABSTRACT

Pure BiFeO₃ (BFO) and Nb-doped (BFN) thin films were fabricated by the soft chemical method. The films were polycrystalline when deposited on Pt/Ti/SiO₂/Si substrate and annealed at 500 °C for 2 h. X-ray diffraction analysis revealed that the film was fully crystallized. The grain size decreased in the BFN films due the suppression of oxygen vacancy concentration in the BFO lattice. The Nb dopant is effective in improving electrical properties of BFO films. With increase niobium content we obtained thin films free of fatigue up to 10⁸ cycles.

© 2009 Published by Elsevier B.V.

Contents

1. Introduction.....	274
2. Experimental procedure	275
3. Results and discussion.....	276
4. Conclusions.....	278
Acknowledgments	279
References.....	279

1. Introduction

Multiferroic BiFeO₃ (BFO) has been discovered since the 1960s [1]. However, material characteristics and physical properties of BiFeO₃ are still controversial. During the past few years, progress on thin film growth techniques, such as pulse laser deposition (PLD) [2–8], metal–organic chemical vapor deposition (MOCVD) [9], and chemical solution deposition (CSD) [10–13], provided new data to understanding the physical properties of BFO thin films. Recently, multiferroic BFO has attracted enormous attention due to its potential applications in advanced magnetoelectric devices and ferroelectric random access memories. BFO has a distorted perovskite structure with rhombohedral symmetry which belongs to the R3c space group [14,15]. The distinctive feature of BFO is the simultaneous existence of ferroelectric order ($T_C = 1123$ K)

and antiferromagnetic order ($T_N = 643$ K) at room temperature [16,17].

One of the major problems of BFO materials is their large leakage current densities which limits its application. The relatively large leakage current density is usually attributed to the variable oxidation state of iron ions (Fe³⁺ and Fe²⁺) [18] which are resulted from charge compensation of oxygen vacancies. The coexistence of Fe³⁺ and Fe²⁺ produces electron hopping which increases leakage current. According to defect chemistry theory, charge compensation via aliovalent-ion doping affects the oxidation state of iron and the concentration of oxygen vacancies, which further influences the leakage behaviors of BFO films. Qi et al. reported the effects of Ni²⁺ and Ti⁴⁺-doped BFO films on conduction mechanism using PLD technique [19]. So as to modify the magnetic property, cation doping is one of the most promising and popular approaches [20–24]. In order to solve the leakage current problem in BFO thin films, the site engineering concept has been proposed. Actually, Bi-site substitution with rare earth atoms [25] for controlling volatile Bi atoms and for suppressing generation of oxygen vacancies has been

* Corresponding author. Tel.: +55 16 33016643; fax: +55 16 33016643.
E-mail address: alezipo@yahoo.com (A.Z. Simões).

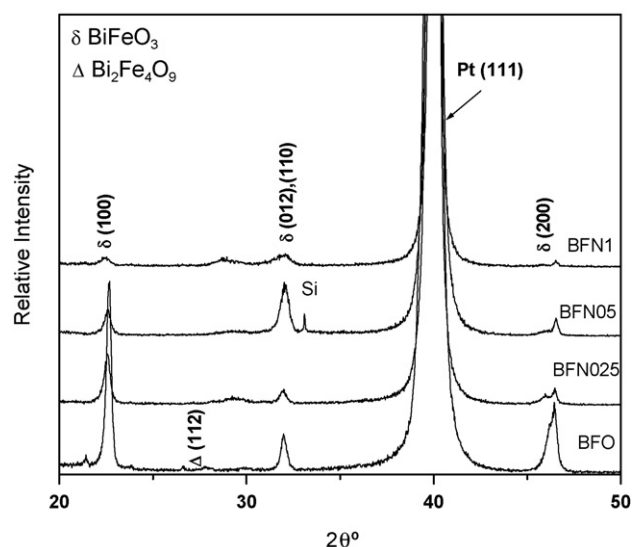


Fig. 1. X-ray diffraction data for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the polymeric precursor method with different Nb contents: (a) $x = 0.0$; (b) $x = 0.025$; (c) $x = 0.05$; (d) $x = 0.10$.

attempted. Further, Fe-site substitution with donor atoms such as Nb and Mn atoms [26,27] has been reported in bulk ceramics.

In our previous studies, we have verified the effect of lanthanum (La) addition in BiFeO_3 (BFO) thin films deposited on $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}(100)$ substrates prepared by soft chemical method. Increasing La concentration promotes changes on structure, microstructure and dielectric/ferroelectric response of films. X-ray diffraction (XRD) reveals that the films are free of preferred orientations and structural distortion. La addition promotes an

increase in dielectric permittivity. The polarization switching and the fatigue behavior of the BFO films were significantly enhanced by the La concentration [28,29].

It is quite desirable to obtain large polarization properties at low temperatures. In this regard, a viable manufacturable process (such as a chemical solution deposition) is required for deposition of the ferroelectric layer. The polymeric precursor method has a suitable potential for technological applications because of their precise control of composition and homogeneity and good conformality [30]. In this letter, we show that the leakage current density in BFO films can be suppressed in the high electric field region by Fe-site substitution with Nb atoms. The films were deposited on $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate substrates by the polymeric precursor method.

2. Experimental procedure

Iron(III) nitrate nonahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, 99.5% purity (Merck), bismuth oxide $[\text{Bi}_2\text{O}_3]$, 99.9 purity (Aldrich) and niobium oxide $[\text{Nb}_2\text{O}_5]$, 99.5 purity (Merck) were used as raw materials. The precursor solutions of bismuth, niobium and iron were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Fe, Nb and Bi were mixed and homogenized by stirring at 90°C . The molar ratio of metal: citric acid: ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cp by controlling the water content using a Brookfield viscosimeter. The films were spin-coated from the deposition solution onto a $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate. $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films with x ranging from 0.0 to 0.10 mol% (BFO, BFO025, BFO050 and BFO1) were completely crystallized after annealing for 2 h at temperature of 500°C . Multilayered films were obtained by spinning 10 times the deposition solution on the surface of the substrate at 5000 rpm. The films were annealed at 400°C for 2 h with heating rate of $3^\circ\text{C}/\text{min}$ in a conventional furnace and later crystallized at 500°C for 2 h in static air. The number of layers was fixed as a function of the desired thickness to obtain good electrical properties. An excess of 5 wt% Bi was added to the solution, aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained. Phase analysis of the films was performed at room temperature by X-ray diffraction patterns recorded on a (Rigaku-DMAX 2000PC) with $\text{Cu K}\alpha$ radi-

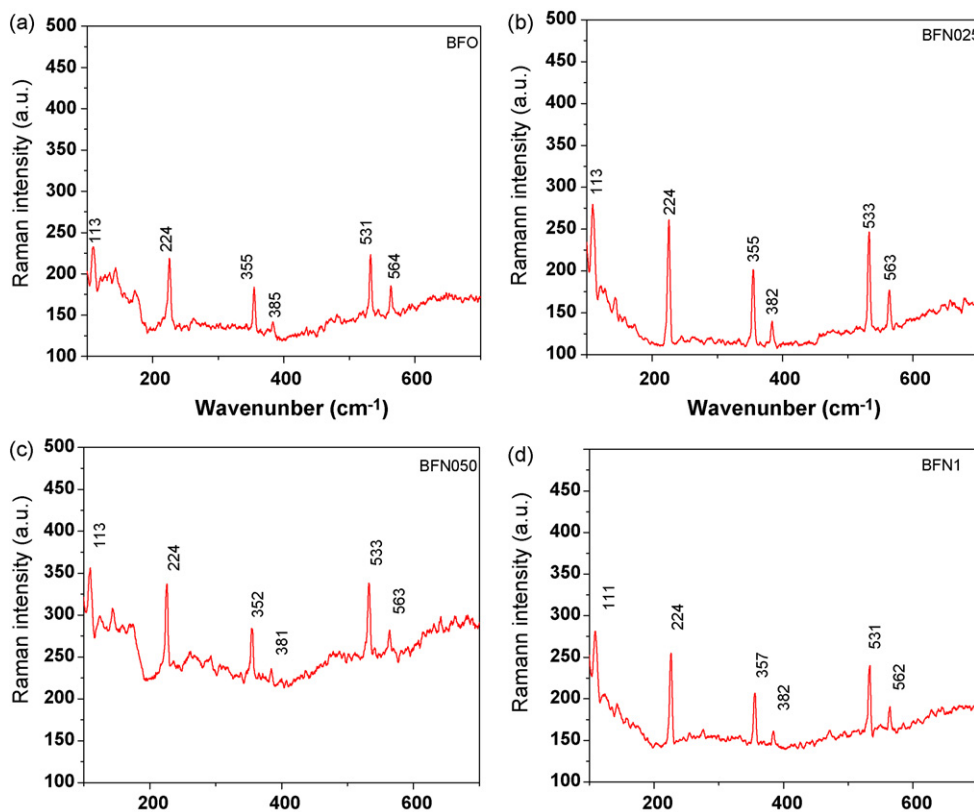


Fig. 2. Micro Raman spectra for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the polymeric precursor method and annealed at 500°C for 2 h, with different Nb contents: (a) $x = 0.0$; (b) $x = 0.025$; (c) $x = 0.05$; (d) $x = 0.10$.

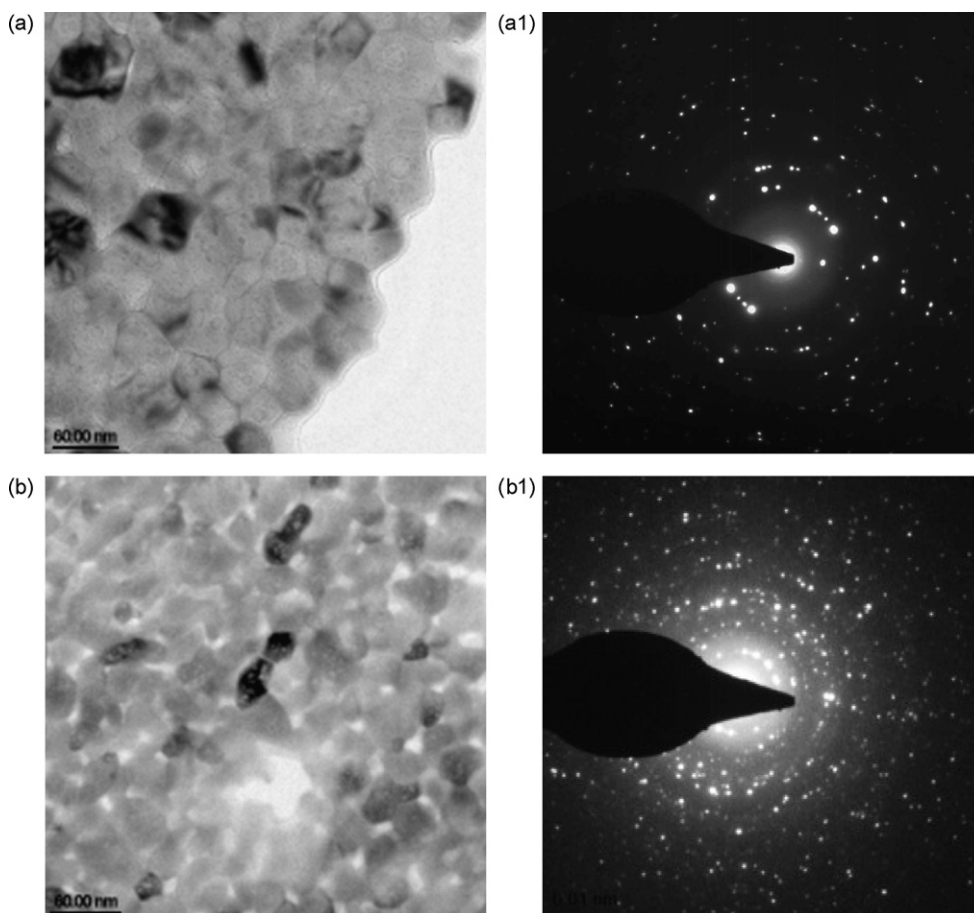


Fig. 3. TEM micrographies for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the polymeric precursor method and annealed at 500°C for 2 h, with different Nb contents: (a) $x=0.0$; (b) $x=0.10$.

tion in the 2θ range from 20° to 50° with $0.3^\circ/\text{min}$. The thickness of the annealed films was studied using scanning electron microscopy (SEM-Topcom SM-300) by looking at the transversal section. In this case, back-scattered electrons were utilized. Three measurements were done to obtain an average value of thickness close to 300 nm. Raman measurements were performed using an ISA T 64000 triple monochromator. An optical microscope with $80\times$ objective was used to focus the 514.5-nm radiation from a Coherent Innova 99 Ar^+ laser on the sample. The same microscope was used to collect the back-scattered radiation. The scattering light dispersed was detected by a charge-coupled device (CCD) detection system = 0.3 mm. Microstructural characterization of the films was carried out using transmission electron microscopy (TEM) with a Philips CM-20 unit. Next, a 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace under oxygen atmosphere at 300°C for 1 h. Here, the desired effect was to decrease eventually present oxygen vacancies. Ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000 A tester equipped with a micrometer probe station in a virtual ground mode at a frequency of 60 Hz. For the fatigue measurements, internally or externally generated $8.6\ \mu\text{s}$ wide square pulses with maximum amplitudes of $\pm 9\ \text{V}$. The J - V measurements were recorded on the Radiant technology tester in the current-voltage mode, with a voltage changing from 0 to $+10\ \text{V}$, from $+10$ to $-10\ \text{V}$ and back to 0 V. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the XRD pattern of the BFO film deposited on Pt/Ti/ SiO_2 /Si substrate annealed at 500°C for 2 h. The film is fully crystallized since intense peaks are evident. The presence of $\text{Bi}_2\text{Fe}_4\text{O}_9$ secondary phase was observed in the pattern. This peak is more prominent in the BFO film being its presence not evidenced in the Nb-doped samples. That suggests that the addition of niobium can either eliminate oxygen vacancies or avoid compositional fluctuations of Fe^{3+} to Fe^{2+} oxidation state influencing on the appearance of secondary phases. The diffraction peaks

were indexed in the pseudo-cubic structure. Besides BFO peaks, the characteristic peak for (1 1 1) platinum coated silicon substrates at $2\theta = 40^\circ$ was identified. It is easy to see that the film is randomly oriented. At this concentration range, there is no influence of niobium in the crystal structure of the BFO system.

Raman analysis shows the order-disorder degree of the atomic structure at short range (Fig. 2). The modes further split into longitudinal and transverse components due the long electrostatic forces associated with lattice ionicity. Substitution of niobium in the B-site of the lattice reduces the distortion of octahedral clusters having little influence in the relative intensity of the bands. The vibrational modes located at 224, 355, 385, 531, and $564\ \text{cm}^{-1}$ result from the FeO_6 octahedral ($\text{Fe} = 5$ or $\text{Fe} = 6$). The band located below $200\ \text{cm}^{-1}$ is due to the different sites occupied by bismuth within the perovskite layer. Raman frequencies are not strongly affected by niobium substitution. Slight changes which occur above $200\ \text{cm}^{-1}$ in the BFO can be associated to structural distortion and reduction of vibrations in the FeO_5 octahedra. Niobium atoms substitute iron in the perovskite structure having marginal influence in the interactions between the $(\text{Bi}_2\text{O}_2)^{2+}$ layers and perovskite.

In order to evaluate the role exerted by niobium dopant on the microstructure of BFO film, we present TEM images of pure and highly doped niobium compositions. A plan-view TEM image shows the microstructure and the selected area diffraction (SAD) patterns. It could be noticed the polycrystallinity of the grains in the plane of the films. The grains are regularly shaped and the estimates size obtained from dark field images is about 70 nm for BFO film and 50 nm for BFN1 film (Fig. 3a and c, respectively). Tiny pores less than 10 nm in size are present within the grains and along the grain boundaries. The role of niobium is to eliminate vacancies which act

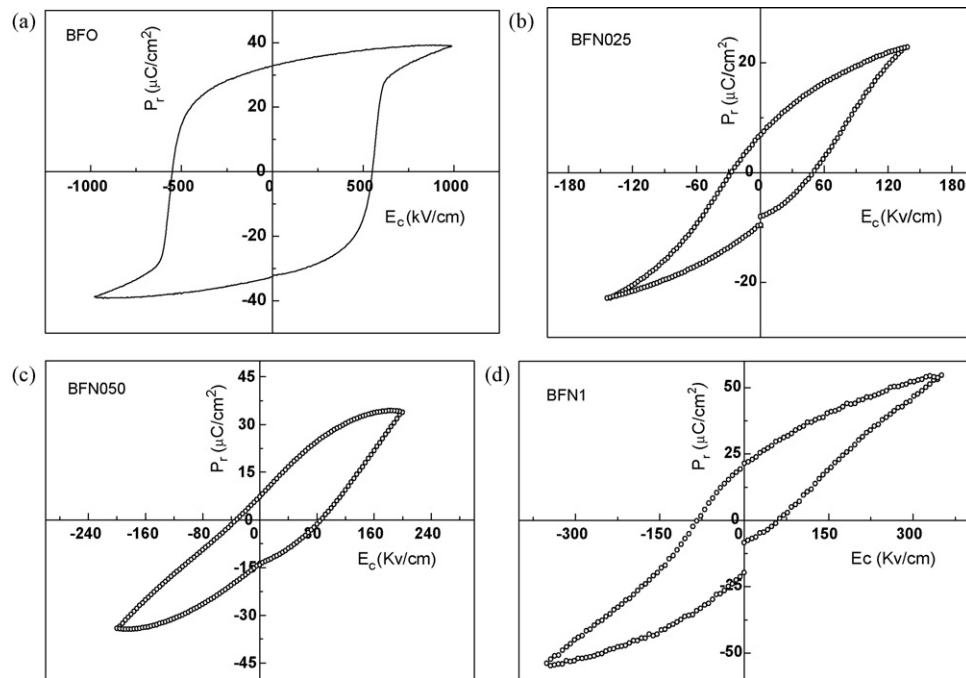


Fig. 4. Hysteresis loops for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the polymeric precursor method with different Nb contents: (a) $x=0.0$; (b) $x=0.025$; (c) $x=0.05$; (d) $x=0.10$.

as point defects and therefore decrease the surface heterogeneity in the films. Niobium ion plays a role of donor in BFO because it possesses a higher valence than Fe. One of the defect chemistry models in accordance with Ref. [19] for Nb^{5+} (0.064 nm) doping of Fe^{3+} (0.069 nm) sites is that donors suppress the formation of oxygen vacancies. The decrease of grain size for Nb-doped BFO films can be interpreted by the suppression of oxygen vacancy concentration, which results in slower oxygen ion motion and consequently lower

grain growth rate. Also, as the niobium amount increases, small nucleation cores aggregate together into bigger grains leading to a more smooth surface (not shown in the text). In this way, the lower grain size obtained in the doped samples can be a reflex of increase in crystallization temperature due to differences of chemical bond strength between Fe–O and Nb–O atoms. From TEM analyses we could observe that the crystallinity of materials is poor and the presence of non-crystalline phase is more than evident. Besides that, the

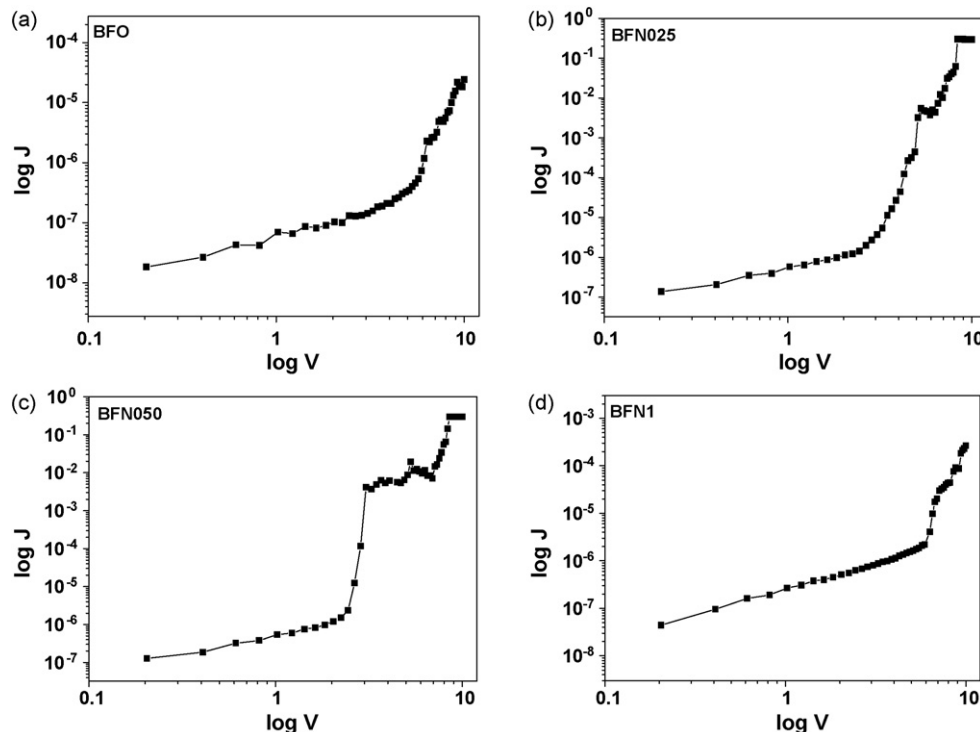


Fig. 5. Leakage current density versus applied electric field for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the polymeric precursor method with different Nb contents: (a) $x=0.0$; (b) $x=0.025$; (c) $x=0.05$; (d) $x=0.10$.

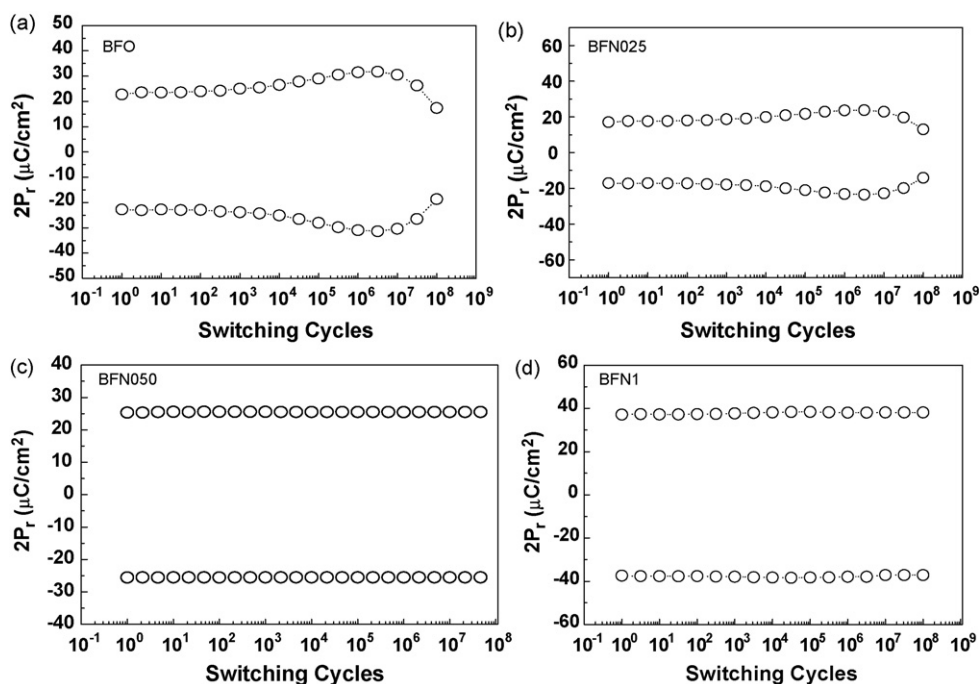


Fig. 6. Fatigue curves for $\text{BiFe}_{1-x}\text{Nb}_x\text{O}_3$ films deposited by the soft chemical method with different Nb contents: (a) $x=0.0$; (b) $x=0.025$; (c) $x=0.05$; (d) $x=0.10$.

diffraction patterns indicate strong randomness of atom position, as previous noted in the XRD data. In this way, we assume that niobium has no strong effect on crystal structure of BFO films. However, electrical properties of Nb-doped, and pure BFO films will shown remarkable difference.

The ferroelectric characteristics of pure and Nb-doped BFO films annealed at 500°C were shown in Fig. 4. Pure BFO film showed high saturated (P_s) and remnant polarizations (P_r) of 40 and $32\ \mu\text{C}/\text{cm}^2$, respectively. The P - E hysteresis loop of the BFO film clear shows a saturation and has a quite different shape from what have been reported previously, e.g., Wang et al. [2] and Yun et al. [6] which obtained a much reduced remnant polarization. This is probably due to the orientation and the lattice symmetry of the perovskite grains in the BFO films. The BFO films reported by Wang et al. were (001) epitaxial, while those reported by Yun et al. displayed more X-ray diffraction peaks than ours. The hysteresis loop of BFO film prepared at low temperature by the soft chemical method indicates a less degree of anisotropy in the BFO lattice. Compared with those reported in literature, the polarization values are very good. The P - E loop was actually not closed because the applied field was very high, up to $1000\ \text{kV}/\text{cm}$. The clear difference in the hysteresis shapes among the samples is due to the difference of the leakage current at high electric field. The Nb-doped BFO film displayed worst ferroelectricity than the pure one, although lower voltages were required to obtain saturated curves. The smaller coercitive field of Nb-doped BFO films was consistent with the decrease of the concentration of oxygen vacancies according to defect chemistry [31,32]. The leakage current density of the Nb-doped films is lowered one to two orders of magnitude in comparison with pure BFO films. In this way, the charge compensation required by addition of Nb^{5+} ions could be achieved by reducing oxygen vacancies as discussed above, which induces a reduction in the leakage current of the films.

A typical leakage current characteristic is given in Fig. 5. The curves were recorded with a voltage step width of $0.1\ \text{V}$ and elapsed time of $1.0\ \text{s}$ for each voltage, here the measured logarithmic current density ($\log J$) versus the logarithmic voltage (V) is shown. It can be seen that there are two clearly different regions. The current density increases linearly with the external electric field

in the region of low electric field strengths, suggesting an ohmic conduction. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole-Frenkel emission mechanism. The leakage current density at $1.0\ \text{V}$ decreases when niobium is introduced to the system. There are some reasons for the improvement of leakage current with increasing niobium concentration. In fact, it occurs a reduction of the surface roughness from 6.4 to $2.5\ \text{nm}$ as niobium is introduced in the BFO lattice which results in less microcracks caused by residual stress. Since the crystal structure and phase transition temperature decrease with niobium concentration, the lattice volume change during cooling decreases and so residual stress decreases.

Fig. 6 plots the degradation of normalized switchable polarization P^*/P_0 of the BFO-based films against the number of switching cycles. P^* represents the switching polarization between two pulses with opposite polarity, and P_0 represents the nonswitching polarization between two pulses with the same polarity. The switchable polarization of the BFN film is relatively unchanged up to 10^7 cycles. Although 30% decay in the switchable polarization occurs after 10^8 cycles, the improvement in the fatigue is remarkable in comparison with that of the BFO film, which shows significant lowering of polarization since 10^6 cycles. The marked improvement in the fatigue behavior may result from the crystallinity, electrode/ferroelectric interface, and defect concentration fatigue resistance was observed up to 10^8 cycles with an applied pulse voltage of $9\ \text{V}$ for BFN05 and BFN1 thin films suggesting a good potential for applications in ferroelectric memories. In the BFO and BFN025 films there is an increase in local current around the nucleation sites which can destroy the film-electrode interface and suppress the nucleation of oppositely oriented domains at the surface. In this film an increase in switching polarization leads to a local increase in conductivity at the film-electrode interface region [33].

4. Conclusions

Pure BFO and Nb-doped films were fabricated by chemical solution deposition method. The XRD analysis and TEM obser-

vation showed that the films possess a pseudo-cubic structure with dense and smooth surface. Nb-dopant decreased the grain sizes of BFO films although has no influence on Raman modes. *P–E* hysteresis loops and leakage behavior are remarkable influence by niobium dopant in the BFO lattice. Defect chemistry and chemical reaction during chemical process were able to explain the electric properties caused by niobium dopant. Niobium addition leads to fatigue resistance suggesting that BFN films can be used as storage element in nonvolatile ferroelectric random access memories.

Acknowledgments

The authors thank the financial support of the Brazilian research financing institutions: CAPES, FAPESP and CNPq.

References

- [1] Y.E. Roginskaya, Y.N. Venevtsev, S.A. Fedulov, G.S. Zhdanov, *Kristallografiya* 8 (1963) 610–616.
- [2] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, M. Wuttig, R. Ramesh, *Science* 299 (2003) 1719–1722.
- [3] J. Wang, H. Zheng, Z. Ma, S. Prasertchoung, M. Wuttig, R. Droopad, J. Yu, K. Eisenbeiser, R. Ramesh, *Appl. Phys. Lett.* 85 (2004) 2574–2576.
- [4] D. Lee, M.G. Kim, S. Ryu, H.M. Jang, S.G. Lee, *Appl. Phys. Lett.* 86 (1–3) (2005) 222903.
- [5] V.R. Palkar, J. John, R. Pinto, *Appl. Phys. Lett.* 80 (2002) 1628–1630.
- [6] K.Y. Yun, M. Noda, M. Okuyama, *Appl. Phys. Lett.* 83 (2003) 3981–3983.
- [7] J. Li, J. Wang, M. Wuttig, R. Ramesh, A.P. Pyatakov, A.K. Zvezdin, D. Viehland, *Appl. Phys. Lett.* 84 (2004) 5261–5263.
- [8] K.Y. Yun, D. Ricinschi, T. Kanashima, M. Noda, M. Okuyama, *Jpn. J. Appl. Phys.* 43 (2004) L647–L648.
- [9] S.Y. Yang, F. Zavaliche, L. Mohaddes-Ardabili, V. Vaithyanathan, D.G. Schlom, Y.J. Lee, Y.H. Chu, M.P. Cruz, Q. Zhan, T. Zhao, R. Ramesh, *Appl. Phys. Lett.* 87 (1–3) (2005) 102903.
- [10] K.-Y. Yun, M. Noda, M. Okuyama, *J. Korean, Phys. Soc.* 42 (2003) S1153–S1156.
- [11] H. Uchida, R. Ueno, H. Nakaki, H. Funakubo, S. Koda, *Jpn. J. Appl. Phys.* 44 (2005) L561–563.
- [12] S. Iakovlev, C.-H. Solterbeck, M. Kuhnke, M. Es-Souni, *J. Appl. Phys.* 97 (1–6) (2005) 094901.
- [13] S.K. Singh, H. Ishiwara, *Jpn. J. Appl. Phys.* 44 (2005) L734–L736.
- [14] F. Kubel, H. Schmid, *Acta Crystallogr., Sect. B: Struct. Sci.* 46 (1990) 698–702.
- [15] J.G. Ismilzade, *Phys. Status Solidi (b)* 46 (1971) K39–K41.
- [16] G.A. Smolenskii, I. Chupis, *Sov. Phys. Usp.* 25 (1982) 475–493.
- [17] F. Kubel, H. Schmid, *J. Cryst. Growth* 129 (1993) 515–524.
- [18] Y.P. Wang, L. Zhou, M.F. Zhang, X.Y. Chen, J.M. Liu, Z.G. Liu, *Appl. Phys. Lett.* 84 (2004) 1731–1733.
- [19] X. Qi, J. Dho, R. Tomov, M.G. Blamire, J. Manus-Driscoll, *Appl. Phys. Lett.* 86 (1–3) (2005) 062903.
- [20] K. Ueda, H. Tabata, T. Kawai, *Appl. Phys. Lett.* 75 (1999) 555–557.
- [21] J.S. Kim, C.I. Cheon, C.H. Lee, P.W. Jang, *J. Appl. Phys.* 96 (2004) 468–474.
- [22] V.R. Palkar, D.C. Kundaliya, S.K. Malik, *J. Appl. Phys.* 93 (2003) 4337–4339.
- [23] T. Kanai, S. Ohkoshi, K. Hashimoto, *J. Phys. Chem. Solids* 64 (2003) 391–397.
- [24] I. Sosnowska, W. Schäfer, W. Kockelmann, K.H. Andersen, I.O. Troyanchuk, *Appl. Phys. A: Mater. Sci. Process* 74 (2002) S1040–S1042.
- [25] J.R. Cheng, L.E. Cross, *J. Appl. Phys.* 94 (2003) 5188–5192.
- [26] S.K. Singh, H. Ishiwara, *Jpn. J. Appl. Phys.* 1 45 (2006) 3194–3197.
- [27] Y.K. Jun, W.T. Moon, C.M. Chang, H.S. Kim, H.S. Ryu, J.W. Kim, K.H. Kim, H.Y. Hong, *Solid State Commun.* 135 (2005) 133–136.
- [28] A.Z. Simões, L.S. Cavalcante, C.S. Riccardi, J.A. Varela, E. Longo, *Curr. Appl. Phys.* 9 (2009) 520–523.
- [29] A.Z. Simões, E.C. Aguiar, A.H.M. Gonzalez, J. Andrés, E. Longo, J.A. Varela, *J. Appl. Phys.* 104 (1–6) (2008) 104115.
- [30] A.Z. Simões, A.H.M. Gonzalez, L.S. Cavalcante, C.S. Riccardi, J.A. Varela, E. Longo, *Appl. Phys. Lett.* 90 (1–3) (2007) 052906.
- [31] C. Ederer, N.A. Spaldin, *Phys. Rev. B* 71 (2005) 060401–060404.
- [32] Y. Wang, Q.H. Jiang, H.C. He, C.W. Nan, *Appl. Phys. Lett.* 88 (2006) 142503–142505.
- [33] A.Z. Simões, M.A. Ramírez, C.S. Riccardi, E. Longo, J.A. Varela, *Mater. Lett.* 60 (2006) 2020–2023.



Structure, ferroelectric/magnetoelectric properties and leakage current density of $(\text{Bi}_{0.85}\text{Nd}_{0.15})\text{FeO}_3$ thin films

A.Z. Simões^a, L.S. Cavalcante^{b,*}, F. Moura^c, E. Longo^b, J.A. Varela^b

^a Universidade Estadual Paulista, Faculdade de Engenharia de Guaratinguetá, P.O. Box 333, 12516-410 SP, Brazil

^b Universidade Estadual Paulista, P.O. Box 355, 14801-907 Araraquara, SP, Brazil

^c UNIFEI–Universidade Federal de Itajubá–Campus Itabira, Rua São Paulo, P.O. Box 377, 35900-37 Itabira, MG, Brazil

ARTICLE INFO

Article history:

Received 13 October 2010

Received in revised form 2 February 2011

Accepted 4 February 2011

Available online 12 February 2011

Keywords:

Ferroelectrics

Chemical synthesis

Piezoelectricity

Magnetic measurements

ABSTRACT

In this paper, we report on the structure, ferroelectric/magnetoelectric properties and improvement of leakage current density of $(\text{Bi}_{0.85}\text{Nd}_{0.15})\text{FeO}_3$ (BNFO) thin films deposited on Pt(1 1 1)/Ti/SiO₂/Si substrates from the polymeric precursor method. X-ray patterns and Rietveld refinement indicated that BNFO thin films with a tetragonal structure can be obtained at 500 °C for 2 h in static air. Field emission scanning electron, atomic force and piezoelectric force microscopies showed the microstructure, thickness and domains with polarization-oriented vectors of BNFO thin films. Ferroelectric and magnetoelectric properties are evident by hysteresis loops. The magnetoelectric coefficient measurement was performed to show the magnetoelectric coupling behavior. The maximum magnetoelectric coefficient in the longitudinal direction was close to 12 V/cm Oe. Piezoresponse force microscopy micrographs reveal a polarization reversal with 71° and 180° domain switchings and one striped-domain pattern oriented at 45° besides the presence of some nanodomains with rhombohedral phase involved in a matrix with tetragonal structure. The cluster models illustrated the unipolar strain behavior of BNFO thin films. The leakage current density at 5.0 V is equal to 1.5×10^{-10} A/cm² and the dominant mechanism in the low-leakage current for BNFO thin films was space-charge-limited conduction.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, multiferroic materials have attracted much attention in the scientific community due to the possibility of manipulating the magnetic state by an electric field or vice versa [1]. Researchers have reported [2,3] that the composite materials (yttrium iron garnet/lead magnesium niobate-lead titanate and barium titanate/cobalt ferrite) present separate piezoelectric and magnetic phases with magnetoelectric coupling at room temperature. In addition, the preparation of these composite materials is very difficult and few magnetoelectric multiferroics materials at room temperature have been reported so far [4].

Among multiferroic materials, bismuth ferrite (BiFeO_3) has been extensively investigated in the form of ceramics, crystals, nanopowders and thin films [5–12] due to its superior magnetic, visible-light photocatalytic, photoconductive and ferroelectric properties and high ferroelectric polarization with a ferroelectric Curie temperature (T_C) of 820 °C and an antiferromagnetic Néel temperature (T_N) of 370 °C [13,14]. Both ferroelectricity

and antiferromagnetism have long been known in BiFeO_3 single crystals [15–18]. Recently, several experimental papers reported the existence of a large ferroelectric polarization as well as a small magnetization in doped BiFeO_3 [19–21]. However, one of the major drawbacks related to BiFeO_3 is its high leakage current density. Therefore, it allows current to pass through when a high voltage is applied [22–24]. Currently, great efforts have been made to improve electrical properties by doping with rare-earth elements such as: lanthanum [25–29], praseodymium [30,31], samarium [32–35], europium [36–39], gadolinium [40,41], dysprosium [42,43] and neodymium (Nd) [44–48]. Among these rare-earth elements, the employment of Nd as a dopant in BiFeO_3 thin films/ceramics has shown an improvement in ferroelectric and ferromagnetic properties [49,50].

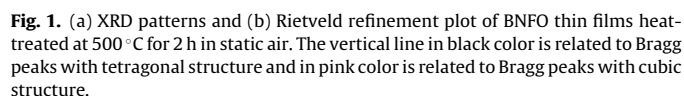
Thus, in this paper, we report on the structural refine, ferroelectric/magnetoelectric properties and leakage current density of $(\text{Bi}_{0.85}\text{Nd}_{0.15})\text{FeO}_3$ (BNFO) thin films prepared by the polymeric precursor method and grown on Pt(1 1 1)/Ti/SiO₂/Si substrates after heat treatment at 500 °C for 2 h in static air. These films were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and piezoelectric force microscopy (PFM). The electrical properties were investigated by polarization/magnetic hysteresis loops, strain response, magnetic electric coefficients and improvement of leakage current density.

* Corresponding author. Tel.: +55 16 3361 5215; fax: +55 16 3351 8214; mobile: +55 16 8149 8182.

E-mail address: laeciosc@bol.com.br (L.S. Cavalcante).

3. Results and discussion

To verify and confirm if the structure of BNFO thin films is tetragonal it was performed a structural refinement by the Rietveld method. The Rietveld method is a least squares refinement procedure where the experimental step-scanned values are adapted to calculated ones. The profiles are considered to be known, and a model for a crystal structure available [56]. This structural refinement method presents several advantages over conventional



The structural refinement was performed in Maud program [58], employing the Rietveld texture and stress analysis [59]. According to the literature [60], the quality of the data from structural refinement is generally checked by R -values (R_{wnb} , R_b , R_{exp} , R_w and σ). Since, that the numbers obtained for R -values and σ are easy to communicate and with good consistency to tetragonal structure of the BNFO thin films. However, the difference between the plot observed and calculated patterns still is the best way to judge the success of a Rietveld refinement. We have obtained and selected the R -values that are given by the following equations [60,61]:

$$R_b = \frac{\sum |I_k(\text{observed}) - I_k(\text{calculated})|}{\sum I_k(\text{observed})} \quad (2)$$

$$R_{\text{exp}} = \frac{\sum |y_i(\text{observed}) - (1/c)y_i(\text{calculated})|}{\sum y_i(\text{observed})} \quad (3)$$

$$R_w = \left[\frac{\sum w_i(y_i(\text{observed}) - (1/c)y_i(\text{calculated}))^2}{\sum w_i(y_i(\text{observed}))^2} \right]^{1/2} \quad (4)$$

$$\sigma = \frac{R_w}{R_{\text{exp}}} \quad (5)$$

where y_i is the the measured (and calculated) intensities at each step, or channel, in the energy dispersive mode. The summation index i is running over all points in the diffraction pattern, or in some routines running over the section of the pattern selected for fitting and w_i is data equal a $1/(\sqrt{I_i^{\text{exp}}})$.

Moreover, other parameters and additional functions were applied to find a structural refinement with better quality and reliability. The optimized parameters were scale factor, background with exponential shift, exponential thermal shift and polynomial coefficients, basic phase, microstructure, crystal structure, size-strain (anisotropic no rules), structure solution model (genetic algorithm SDPD), shift lattice constants, profile half-width parameters (u , v , w), texture [62–64], lattice parameters (a , b , c), factor occupancy, atomic site occupancies (Wyckoff). The Rietveld refinement for BNFO thin films was performed based on the BNFO phase with perovskite-type tetragonal structure with a better approximation and indexing with the Crystallographic Information File (CIF) (see [Supplementary data-SD1](#)) and with the CIF No. 64917 referent to platinum substrate (cubic structure) [65].

The quality of structural refinement also can be verified by the value of R_w factor, that is very important. Its absolute value does not depend on the absolute value of the intensities, but it depends on the background. With a high background is more easy to reach very low values. Increasing the number of peaks (sharp peaks) is more difficult to get a good value. The structural refinement data are acceptable, when the $R_w < 10\%$ for a medium complex phase, for

Table 1

Rietveld refinement results and atomic coordinates employed to model the BNFO supercells.

Atoms	Wyckoff	Site	x	y	z
Bismuth	1a	4 mm	0	0	0
Neodymium	1b	4 mm	0	0	0
Iron	1d	4 mm	0.5	0.5	0.51226
Oxygen 1	1b	4 mm	0.5	0.5	−0.0224
Oxygen 2	2c	2 mm	0	0.5	0.48979

$a = b = 3.9042(4) \text{ \AA}$, $c = 3.9503(0) \text{ \AA}$, $c/a = 1.0118$, $V = 60.21(1) \text{ \AA}^3$, space group = $P4mm$, No. 99.

$R_w = 9.7866\%$; $R_{\text{wnb}} = 7.8866\%$; $R_b = 6.0232\%$; $R_{\text{exp}} = 4.8884\%$ and $\sigma = 2.002$.

Weights of the phases in the thin films: $(\text{Bi}_{0.85}\text{Nd}_{0.15})\text{FeO}_3 = 25.35\%$ and $\text{Pt}(111) = 74.65\%$.

a high complex phases (monoclinic to triclinic) a value of $R_w < 15\%$ and for a highly symmetric material or compound (cubic) with few peaks a value of $R_w < 8\%$ [66]. Finally, is very important verified the σ values. A good refinement gives σ values lower than 2. However, in the experimental XRD patterns with very high intensities and low noise is difficult to reach a value of 2. As it can be observed in [Fig. 1\(b\)](#), a good agreement between the observed XRD patterns and theoretical results can be noted indicating the success of Rietveld refinement method. The obtained results from the structural refinement are displayed in [Table 1](#).

In this table, the fitting parameters (R_{wnb} , R_b , R_{exp} , R_w and σ) indicate a good agreement between the refined and observed XRD patterns for the BNFO thin films with a tetragonal structure. The small variations in the lattice parameters, unit cell volumes and displacements on Fe atoms (network formers) are indicative of distortions/strain into the lattice caused by differences in the crystal lattice parameters and the thermal expansion behavior between the BNFO film and the underlying substrate or arising from defects promoted by $[\text{BiO}_{12}]$ and $[\text{NdO}_{12}]$ clusters (network modifiers).

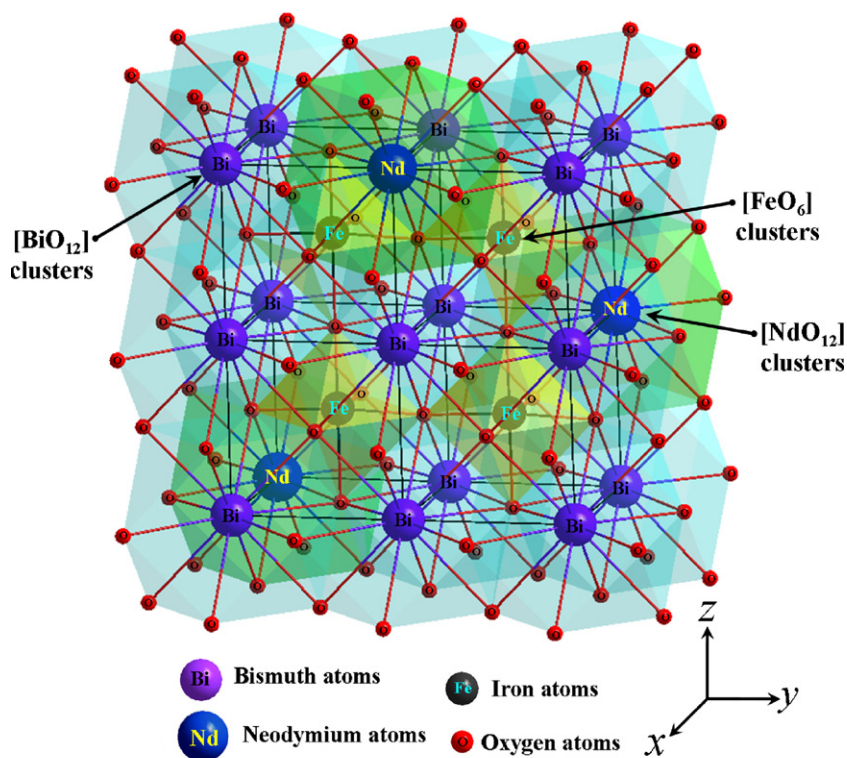


Fig. 2. Schematic representation of crystalline BNFO supercells ($1 \times 2 \times 2$) with three type of clusters: $[\text{FeO}_6]$, $[\text{BiO}_{12}]$ and $[\text{NdO}_{12}]$.

3.2. Superstructures with distorted clusters for the BNFO supercells

Fig. 2 illustrates the schematic representation for a tetragonal BNFO supercells ($1 \times 2 \times 2$) performed from the Rietveld refinement data.

This supercells were modeled through Diamond Crystal and Molecular Structure Visualization (Version 3.2f for Windows) software [67], using the atomic coordinates presented in Table 1. In this supercells, the Fe atoms (lattice formers) are coordinated to six O atoms in an octahedral configuration and symmetry (O_h) forming the distorted $[\text{FeO}_6]$ clusters (Fig. 2) [68]. In this tetragonal supercells, the Fe atoms are slightly displaced along the $[001]$ direction (z -axis). This behavior can be probably influenced by the neighboring $[\text{BiO}_{12}]$ and $[\text{NdO}_{12}]$ clusters that are interconnected as verified by the Rietveld refinement data listed in Table 1. While, the Bi and Nd atoms (lattice modifiers) are coordinated to 12 O-atoms in a cuboctahedral configuration and symmetry (O_h) forming the $[\text{BiO}_{12}]$ and $[\text{NdO}_{12}]$ clusters (Fig. 2) [68]. We believe that the good index for tetragonal structure in BNFO thin films can be a consequence of smaller difference between the ionic radii of Nd^{3+} (1.109 Å) in relation to ionic radii of Bi^{3+} (1.17 Å) [69].

3.3. FE-SEM analyses

Fig. 3(a) and (b) shows the FE-SEM micrographs of the surface microstructure and cross-section of BNFO thin films heat-treated at 500 °C for 2 h in static air, respectively.

As it can be seen in Fig. 3(a), grain growth occurs by the reduction in the total grain boundary area and favors the junction between grains, resulting in the formation of necks [70]. Moreover, the surface is compact and smooth. Also, some elongated grains associated with the high crystallization rate of BNFO thin films was noted. The grain growth process and film densification is characterized by a pore volume elimination related to a mass transport mechanism by grain diffusion with low energy in the grain boundary [71]. Fig. 3(b) shows the presence of a good film/substrate interface obtained by heat treatment at 500 °C for 2 h in static air and an average thickness (t) of about 520 nm.

3.4. AFM and PFM analyses

Fig. 4(a)–(c) illustrates the AFM topography micrographies: (a), PFM micrographs (b) out-of-plane and (c) in-plane of BNFO thin films heat-treated at 500 °C for 2 h in static air.

The piezoelectric effect is a direct manifestation of the presence of polarization. Therefore, PFM micrographs are an indispensable tool to understand the polarization distribution within domains at nanoscale [72]. Also, the PFM micrographs have been employed in this paper to investigate the ferroelectric domain structure and domain dynamics in $[001]$ oriented BNFO thin films. Fig. 4(a) shows the AFM topography micrograph illustrating the presence of grains with two stable states: bright plateaus that we interpret to arise from the tetragonal phase, and areas of dark contrast that we interpret to arise from the rhombohedral phase. Thus, the PFM micrographies indicate the existence of some nanodomains with rhombohedral phase (white contrast) involved in a matrix formed globally by tetragonal structure. These results are in agreement with recent papers reported in the literature [73,74]. Fig. 4(b) shows a PFM micrograph which corresponds to out-of-plane (OP) with the switching of the polarization upon application of an electric field. The grains which exhibit no contrast change are associated with zero out-of-plane polarization. A similar situation was observed when a positive bias was applied to the film [73,74]. We noticed that some of the grains exhibit a white contrast associated with a

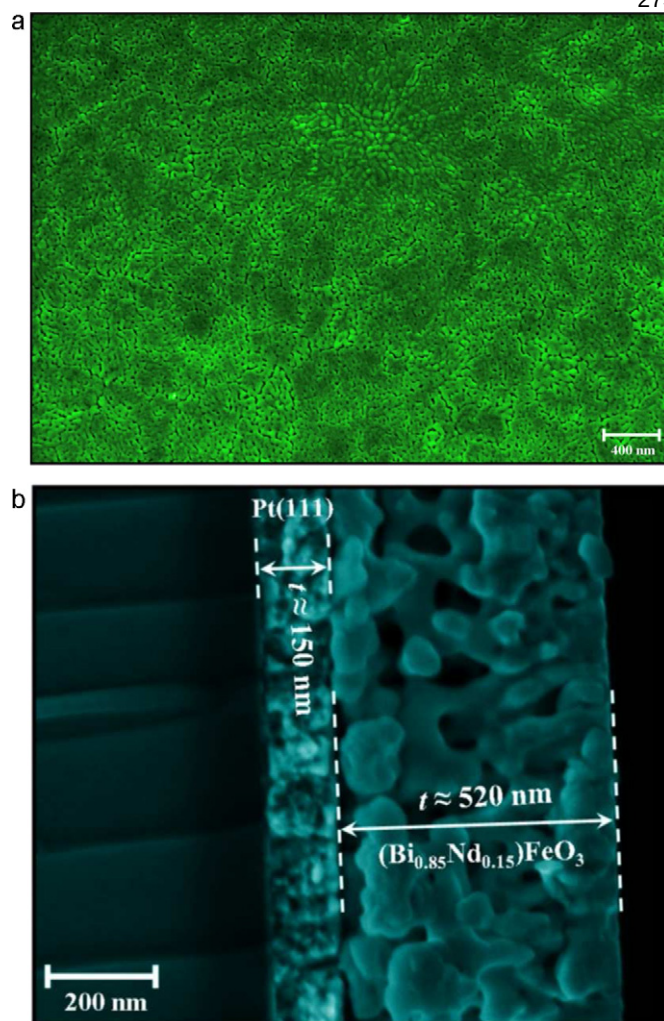


Fig. 3. FE-SEM micrographs of BNFO thin films deposited on Pt substrates heat-treated at 500 °C for 2 h in static air: (a) surface; and (b) cross section.

component of the polarization pointing toward the bottom electrode. On the other hand, in the in-plane PFM images (Fig. 4(c)), the contrast changes were associated with changes in the in-plane polarization components. In this case, the white contrast indicates polarization (for example, in the positive direction of the z -axis) while the dark contrast shows in-plane polarization components pointing to the negative part of the y -axis. In this case, two types of domain behavior in 71° and 180° domain switchings are characteristic of the rhombohedral phase, but the uniform image contrast in PFM micrographs suggests a striped-domain pattern oriented at 45° which is related to the tetragonal phase [75–77].

3.5. Strain behavior analysis

Fig. 5 illustrates electric field induced changes in surface displacement which are represented as strains of BNFO thin films heat-treated at 500 °C for 2 h in static air.

The unipolar strain exhibits a classic “butterfly” loop structure and presents a maximum at 5 kV/cm while the saturation regime is reached at 10 kV/cm. The $[\text{NdO}_{12}]$ clusters in the lattice affect the strain behavior, in part due to domain reorientation [78] (Fig. 5). Beyond that point, it is possible that a moderate bias field results in the transition from an asymmetric phase to a symmetric phase. This field-induced phase transition may be ascribed to the pinch-

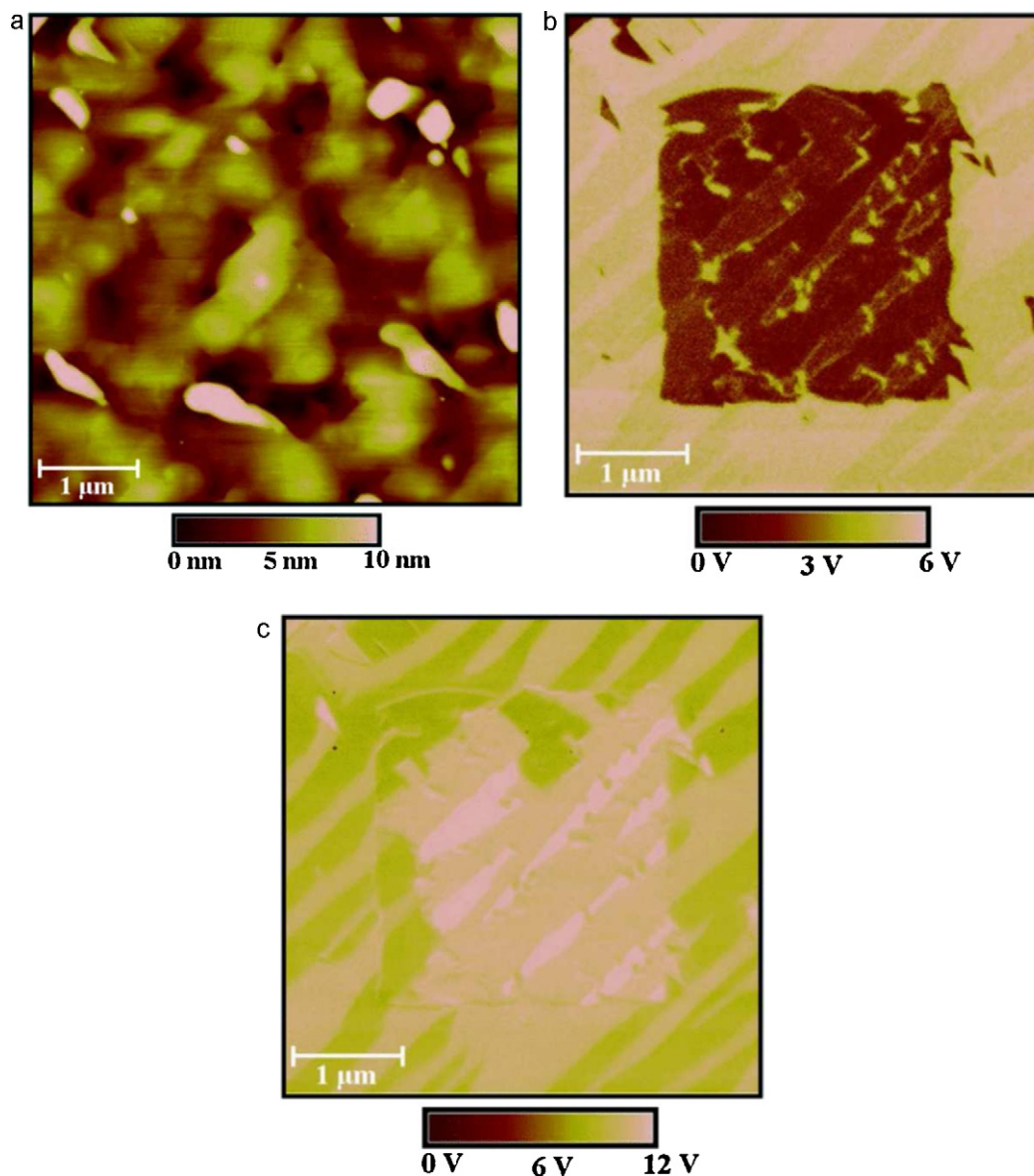


Fig. 4. AFM and PFM micrographs of BNFO thin films heat-treated at 500 °C for 2 h in static air: (a) AFM micrograph topography of surface, PFM micrographs (b) out-of-plane of surface and (c) in-plane of surface.

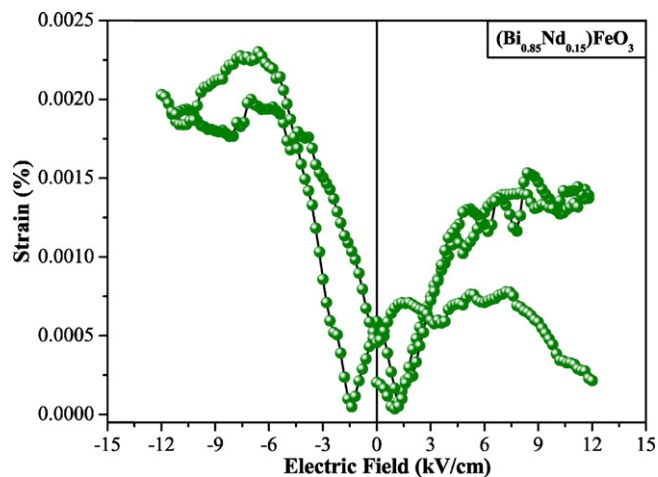


Fig. 5. Strain response of BNFO thin films heat-treated at 500 °C for 2 h in static air.

ing effect; i.e., the consequent decrease in free energy difference among polymorphic phases [78]. A careful inspection of the S – E plots reveals that there are two apparent linear regions at low fields ($E < 5$ kV/cm) and high fields ($E > 10$ kV/cm) and one transition region that corresponds to a domain reorientation induced by external electric fields. The hysteretic strain could be associated with domain reorientation. The strain is hysteresis-free at electric fields higher than 5 kV/cm, indicating a stable single domain/poling state induced by the high external electric fields [79]. In addition, from the S vs E profiles, no noticeable induced phase transition is observed at such high electric fields. It is shown that the unipolar strain was ($S = 0.17\%$). The strain response can be associated with the reduced polarizability and the pinning effect caused by the addition of neodymium [80]. As can be seen, the small strain variations on each curve with an electric field can probably be caused by a clamping effect due to the stress created in the film–substrate interface and the existence of an ultrathin air gap between the tip and the sample which might lower the actual voltage drop in the film.

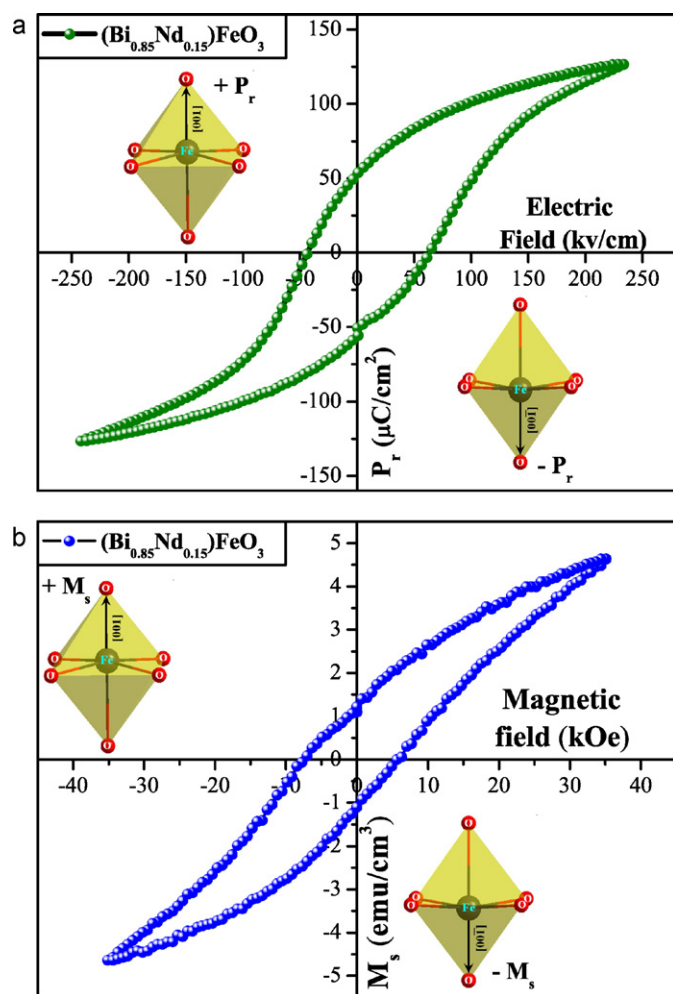


Fig. 6. Ferroelectric properties of BNFO thin films heat-treated at 500 °C for 2 h in static air: (a) P - E hysteresis loops and (b) M - H hysteresis loops.

3.6. Ferroelectric and magnetic properties analyses

Fig. 6(a) and (b) illustrates the ferroelectric (P - E) and magnetic (M - H) hysteresis loops which explain the ferroelectric and magnetic properties of BNFO thin films heat-treated at 500 °C for 2 h in static air, respectively.

The P - E hysteresis loop is well saturated and rectangular with a remnant polarization (P_r) of 54 $\mu\text{C}/\text{cm}^2$ under an applied field of 230 kV/cm (Fig. 6(a)). During the hysteresis loop measurement, no sign of leakage was observed under such a measuring frequency. Liu et al. [81] have reported a low P_r for BiFeO₃ thin films doped with Ti. This behavior may be attributed to unsaturated polarization. In research reported recently, Hu et al. [82] showed an enhancement of the multiferroic properties of BiFeO₃ thin films by Nd and high-valence Mo co-doping (BNFM film) which exhibited a well-saturated P_r of 43 $\mu\text{C}/\text{cm}^2$. Also, Singh and Ishiwara [83] related an improvement in the electrical properties of BiFeO₃ thin films doped with La and a significant P_r of 52 $\mu\text{C}/\text{cm}^2$. In the research of these authors, the P_r is lower than our results, probably due to the displacement of [FeO₆] octahedron clusters along the [1 1 1] direction (rhombohedral) and projection polarization along different orientations in the [0 0 1] direction (tetragonal) with a larger polarization (inset Fig. 6(a)). Jang et al. [84] found that (0 0 1)-oriented films exhibit a strong strain tunability of their out-of-plane remanent polarization, indicating that the strain induced rotation mechanism of the spontaneous polarization direction. M - H hys-

teresis loops were recorded at 300 K (Fig. 6(b)). The saturation magnetization (M_s) for the BNFO thin film was 1.3 emu/cm³. A weak ferromagnetic response was noted for BNFO thin films due to Nd³⁺ substitution for the volatile Bi³⁺ which causes a reduction in Fe²⁺ valence states and induces a low value for M_s as reported and investigated by X-ray photoelectron spectroscopy (see Refs. [52,82]). Therefore, the substitution of Fe³⁺ ions with higher valence requires a charge compensation for its electric neutrality. In our work, we suggested a larger distribution of iron ions with valence (+3) states in [FeO₆] clusters into the BNFO lattice, leading to weak ferromagnetism (inset Fig. 6(b)). Also, the presence of weak ferromagnetism in the BNFO thin film may be attributed to either the canting of the antiferromagnetically ordered spins by a structural distortion [85–87] or the breakdown of the balance between the antiparallel sublattice magnetization of Fe³⁺ ions due to metal ion substitution with a different electron densities [88]. As can be seen in Fig. 6(b), the magnetization of our film linearly increases with the applied magnetic field. However, further studies are required to understand the magnetic behavior of BNFO thin film. The low coercive magnetic fields of BNFO thin films are indicative of their magnetically soft nature and device application suitability.

Fig. 7(a) and (b) illustrates the magnetoelectric coefficient vs the dc bias magnetic field in the longitudinal and transversal directions. The curve presents hysteretic behavior as observed in the magnetic field cycles for BNFO thin films heat-treated at 500 °C for 2 h in static air, respectively.

As shown in Fig. 7(a), BNFO thin films have a maximum magnetoelectric coefficient (α_{ME}) longitudinal of about 12 V/cm Oe. This longitudinal direction is much larger than the results recently reported [89–91] for BiFeO₃ ceramics with doping (Sr, Ba, La, Nd) (as high as 2.3 and 6.3 V/cm Oe at zero fields). This behavior is related to the antiferromagnetic z -axis of BNFO thin films with a predominant tetragonal structure due to the splitting of magnetic diffraction maxima which can be interpreted in terms of a magnetic cycloidal spiral with a long period $620 \pm 20 \text{ \AA}$ [92]. Fig. 7(b) shows that a maximum α_{ME} transversal of about 3 V/cm Oe at zero field for our BNFO thin films which are very close to the literature value for BiFeO₃ multiferroic thin film heterostructures [79]. Moreover, other researchers reported that a necessary condition to observe a linear magnetoelectric effect and spontaneous magnetization in BiFeO₃ materials is that the spatially modulated spin structure be destroyed [93]. Significant magnetization ($\approx 0.5 \mu\text{B}/\text{unit cell}$) and a strong magnetoelectric coupling have been observed in epitaxial thin films, suggesting that the magnetic moments of iron ions, preserving a locally antiparallel orientation can be turned in a spiral-oriented direction and could be suppressed in BNFO thin films [94].

Fig. 8(a) and (b) illustrates the complex impedance and capacitive measurements for BNFO thin films heat-treated at 500 °C for 2 h in static air, respectively.

The feature at the highest measuring frequency is characteristic of the R - L resonance form as well as the measuring leads and electrode itself. On the other hand, the region of lower frequencies shows an inverse behavior as can be observed by complex impedance (Fig. 8(a)). This range accounts for grain-grain junctions and controls the global conductivity response as it is strongly related to the dielectric mechanism [95]. Moreover, the complex capacitive diagram indicates that the capacitance of the electrodes is only slightly affected by the structure of the ferroelectric material. With regard to the reduction of dielectric properties above 10^7 Hz , it can be inferred that the number of active internal domains is minimized at such high frequency, particularly the grain's internal domain. The chemistry of dielectric internal domains most likely depends on the neodymium amount to increase its effectiveness. Fig. 8(b) illustrates the effects of the interface on the capacitance

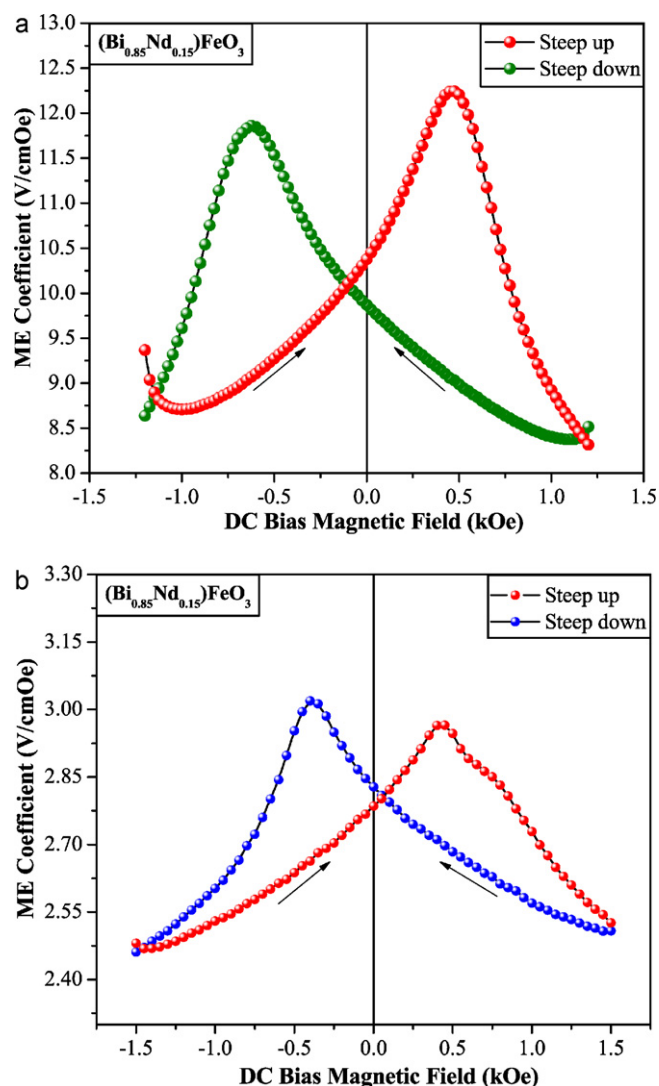


Fig. 7. M – E curve coefficient dependence on dc bias magnetic field of BNFO thin films heat-treated at 500 °C in static air for 2 h in 7 kHz ac magnetic field at room temperature: (a) longitudinal and (b) transversal.

from intermediate to low frequencies. Such a relaxation pattern can be described by an equivalent circuit consistent with three parallel contributions: (I) the high frequency limit related to grain boundary capacitances; (II) the complex incremental capacitance at intermediate frequencies related to the relaxation of the particular structure found in the space charge region; and finally (III) in the low frequency region, the term representing the dc conductance of the multi-junction device. The high frequency region of the complex capacitance diagrams shows the presence of a dipolar relaxation process possessing a near-Debye pattern. It is important to emphasize here that, in the present discussion, because the dielectric properties may be strongly related to the a multi-junction domain [96,97], it is inappropriate to use parameters such as dielectric permittivity or susceptibility since it is almost impossible to have sufficient knowledge about the geometry (i.e., the thickness of the region in question [domain boundaries existing in the grain]) to determine the complex permittivity. Thus we prefer to express the response in terms of complex capacitance (C^*) instead of complex dielectric form (ϵ^*) [98]. Responses to sample–electrode interfaces are evident and appear at the lowest measuring frequencies. These sample–electrode interfaces have very high polarization (due to the thin film geometry of the interface) and high charge density (due

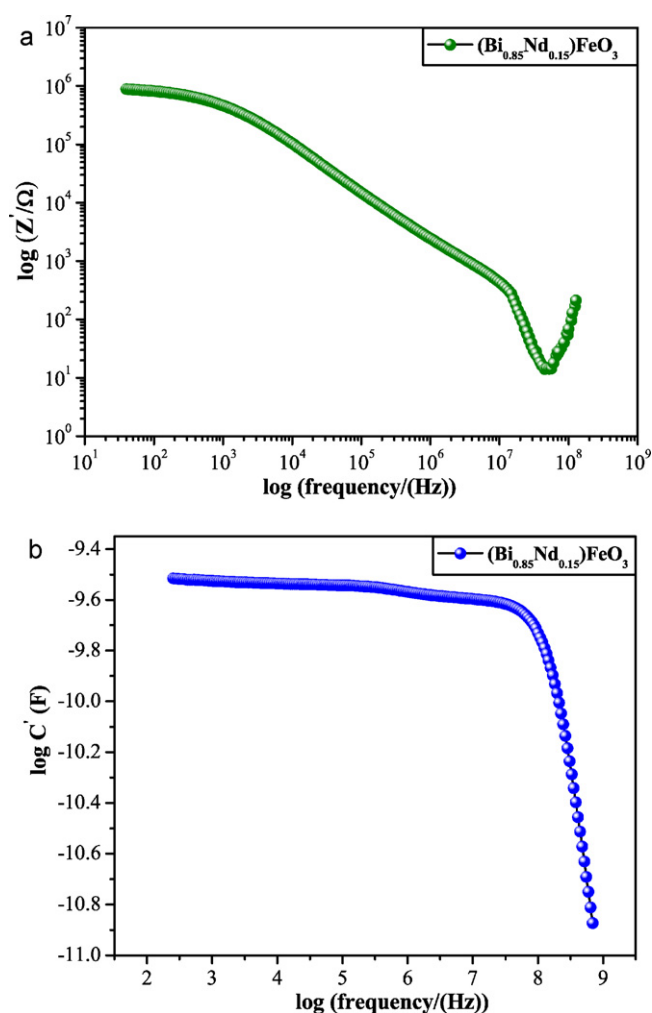


Fig. 8. (a) Bode capacitive diagrams and (b) logarithm of the real part of the complex capacitance as a function of frequency of BNFO thin films heat-treated at 500 °C for 2 h in static air.

to any space charge effects). For practical applications, the films are preferred to be less conductive. As previously verified in our early research [99], the oxygen vacancy concentration is affected by the annealing atmosphere. The thermal treatment in an oxidant atmosphere in materials with p -type conductivity increases the defects as Bi or Fe vacancies, resulting in an increase in conductivity with increasing oxygen content, indicating that the mobile carriers are positively charged and that the possibility of hopping through the Bi^{3+} ion can be considered. Taking into account that we have annealed the BNFO thin film in static air, the oxygen vacancies are ordered, avoiding polarization and therefore reducing conductivity. Thus, fewer possibilities for the electron trapping results in a highly resistance film.

3.7. Leakage current density analyses

Fig. 9(a) and (b) illustrates the bias curve of the leakage current density $\log(J)$ as a function of the applied electric field and the J – E curve leakage current density as a function of an applied electric field in a logarithmic scale for BNFO thin films heat-treated at 500 °C for 2 h in static air, respectively.

Fig. 9(a) shows the measurement bias curve of the leakage current density $\log(J)$ vs the electric field (E) plot for a BNFO thin film. The measured low leakage current densities confirmed that the BNFO thin film had high resistivity. Even at high positive and nega-

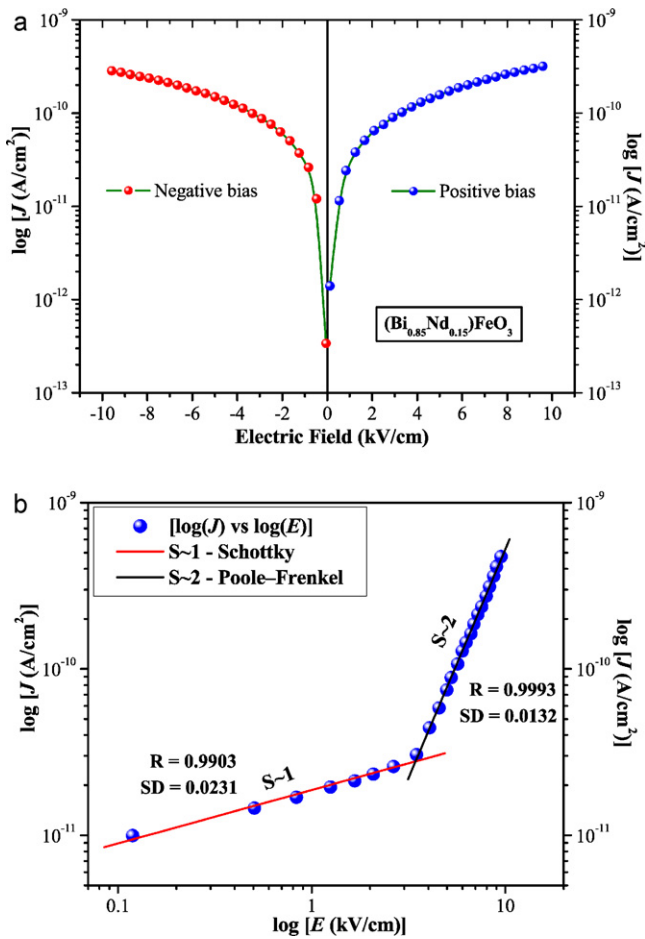


Fig. 9. (a) $\log J$ - E bias curve of the leakage current density as a function of the applied electric field and (b) $\log J$ - $\log E$ curve leakage current density as a function of an applied electric field for the BNFO thin films heat-treated at 500 °C for 2 h in static air.

tive applied electric fields of 10 kV/cm, the leakage current densities were both 1.5×10^{-10} A/cm² which were quite reasonable, considering recent publications for BNFO thin films reported in the literature [100,101]. There are many possible mechanisms to deal with the leakage current limiting mechanisms for BNFO thin films in Fig. 9(a). These mechanisms are concentrated in two categories: (I) interface-limited conduction mechanisms; and (II) bulk limited conduction mechanisms. The leakage current density increases linearly with the external electric field in the low electric field region, suggesting an ohmic conductor which characteristic of the Schottky emission as a first mechanism [102]. This first mechanism is the interface-limited Schottky emission which arises from a difference in Fermi levels between a metal (Pt-electrode) and an insulator or semiconductor (BNFO film). The energy difference creates a potential barrier between the metal and the insulator that charges must overcome [103]. The current density across a Schottky barrier is described by the equation below:

$$J_S = A^* T^2 \exp \left(\frac{\beta E^{1/2} - \phi_B}{k_B T} \right) \quad (6)$$

The term B is defined below:

$$B = \left(\frac{q^3}{4\pi\epsilon_0\epsilon_r} \right)^{1/2} \quad (7)$$

where A^* is the effective Richardson constant, k_B is the Boltzmann constant, T is the temperature, E is an applied electric field, ϕ_B is the

Schottky barrier height, ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant of the ferroelectric material, and q is the electron charge, respectively. The second mechanism considered is the bulk-limited space-charge-limited conduction (SCLC). The limitation arises from a current impeding space charge which forms as charges are injected into the film from the electrode at a rate faster than they can travel through the BNFO film. The current density for SCLC is described by the equation below:

$$J_{\text{SCLC}} = \frac{9\mu\epsilon_0\epsilon_r V^2}{8t^3} \quad (8)$$

where μ is the carrier mobility and t is the thin film thickness. The third mechanism is the bulk-limited Poole-Frenkel emission. This conduction mechanism involves the consecutive hopping of charges between defect trap centers [104]. The ionization of the trap charges can be both thermally and field activated. The conductivity for the Poole-Frenkel emission is described by the equation below:

$$\sigma_{\text{FP}} = c \exp \left[-\frac{E_1}{k_B T} - \frac{1}{k_B T} \left(\frac{q^3 V}{\pi\epsilon_0\epsilon_r t} \right)^{1/2} \right] \quad (9)$$

where c is a constant and E_1 is the trap ionization energy.

To confirm the conduction mechanism of the BNFO thin film, the leakage current density as a function of an applied electric field in a logarithmic scale [$\log(J)$ vs $\log(E)$] was plotted as shown in Fig. 9(b). The plot can be fitted well by linear segments with different slopes. At a low electric field regime, the slope is close to 1 ($S \sim 1$), indicating a linear Ohmic conduction which is dominated by thermally stimulated free electrons. The leakage current for Ohmic conduction can be expressed by the equation below:

$$J = q\mu NeE \quad (10)$$

where Ne is the density of the thermally stimulated electrons. With an increasing applied field, electrons will be injected into the insulator. At a sufficiently high applied electric field regime, the density of free electrons due to carrier injection becomes greater than the density of thermally stimulated free electrons. Then the current density follows the SCL current law [105]. The change of the slope to 2 ($S \sim 2$) indicates a transition of the conduction mechanism from Ohmic to SCLC with increasing electric field strength. Therefore, we believe that the origin of reduced leakage current in the BNFO thin film can be related to several effects, such as: no presence of deleterious phases in the lattice, reduction of oxygen vacancies, stabilization of oxidation state (Fe^{3+}) and smooth surface microstructure with dense grains due to incorporation of Nd modifier in Bi site.

4. Conclusions

In summary, we have obtained BNFO thin films on the $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates by the polymeric precursor method after heat treatment at 500 °C for 2 h in static air. XRD patterns and Rietveld refinements analysis confirmed that BNFO thin films present a tetragonal structure at long range. FE-SEM micrographs showed that BNFO thin films present a homogeneous, smooth surface without cracks and with an average thickness of about 520 nm. AFM and PFM micrographs exhibited the presence of grains with two stable states: bright plateaus to the tetragonal phase and dark contrasts to the rhombohedral phase. Moreover, these micrographs reveal the possible co-existence of the tetragonal and rhombohedral phases in nanodomains of BNFO thin films. Two types of nanodomain behavior in 71° and 180° for the main domain switchings are characteristic of the rhombohedral phase, but a uniform image contrast in the PFM micrographs suggests a striped-domain pattern oriented at 45° which is related to the tetragonal

phase. A unipolar strain response with ($S=0.17\%$) can be associated with the reduced polarizability and the pinning effect caused by the addition of neodymium into the lattice. Ferroelectric and magnetoelectric properties are evidenced by hysteresis loops. The maximum magnetoelectric coefficient in the longitudinal direction was close to 12 V/cm Oe . The leakage current density at 5.0 V is equal to $1.5 \times 10^{-10} \text{ A/cm}^2$ with two main dominant mechanisms in the low-leakage current (Schottky and Poole–Frenkel). Finally, the Nd modifier was found to effectively induce spontaneous magnetization in antiferromagnetic BiFeO_3 , thus exhibiting good ferroelectric/magnetoelectric properties and leakage current density due to reduction of oxygen vacancies, stabilization of oxidation state (Fe^{3+}) and smooth surface microstructure with dense grains.

Acknowledgements

The authors thank the financial support of the Brazilian Research Financing Institutions: FAPESP-Postdoctorate (No. 2009/50303-4), CNPq and CAPES.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2011.02.030.

References

- [1] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M.P. Cruz, Y.H. Chu, C. Ederer, N.A. Spaldin, R.R. Das, D.M. Kim, S.H. Baek, C.B. Eom, R. Ramesh, *Nat. Mater.* 5 (2006) 823–829.
- [2] S. Shastry, G. Srinivasan, M.I. Bichurin, V.M. Petrov, A.S. Tatarenko, *Phys. Rev. B* 70 (2004) 064416–064421.
- [3] H. Zheng, J. Wang, S.E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S.R. Shinde, S.B. Ogale, F. Bai, D. Viehland, Y. Jia, D.G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, *Science* 303 (2004) 661–663.
- [4] N.A. Hill, *J. Phys. Chem. B* 104 (2000) 6694–6709.
- [5] H. Yang, H. Wang, G.F. Zou, M. Jain, N.A. Suvorova, D.M. Feldmann, P.C. Dowden, R.F. DePaula, J.L. MacManus-Driscoll, A.J. Taylor, Q.X. Jia, *Appl. Phys. Lett.* 93 (2008) 142904–142906.
- [6] M. Popa, S. Preda, V. Fruth, K. Sedláčková, C. Balázsi, D. Crespo, J.M. Calderón-Moreno, *Thin Solid Films* 517 (2009) 2581–2585.
- [7] S. Mukherjee, R. Gupta, A. Garg, V. Bansal, S. Bhargava, *J. Appl. Phys.* 107 (2010) 123535–123537.
- [8] S. Das, S. Basu, S. Mitra, D. Chakravorty, B.N. Mondal, *Thin Solid Films* 518 (2010) 4071–4075.
- [9] X. Tang, J. Dai, X. Zhu, H. Lei, L. Yin, W. Song, Y. Cheng, D. Wu, Y. Sun, *J. Magn. Magn. Mater.* 322 (2010) 2647–2652.
- [10] Z. Wen, G. Hu, S. Fan, C. Yang, W. Wu, Y. Zhou, X. Chen, S. Cui, *Thin Solid Films* 517 (2010) 4497–4501.
- [11] J.H. Xu, H. Ke, D.C. Jia, W. Wang, Y. Zhou, *J. Alloys Compd.* 472 (2009) 473–477.
- [12] H. Liu, X. Wang, *J. Sol–Gel Sci. Technol.* 47 (2008) 154–157.
- [13] S.V. Kiselev, R.P. Ozerov, G.S. Zhdanov, *Sov. Phys. Dokl.* 7 (1963) 742–744.
- [14] J.R. Teague, R. Gerson, W.J. James, *Solid State Commun.* 8 (1970) 1073–1074.
- [15] F. Kubel, H. Schimid, *Acta Crystallogr. B* 46 (1990) 698–702.
- [16] P. Fischer, M. Polomska, M. Szymanski, *J. Phys. Solid State Phys.* 13 (1980) 1931–1940.
- [17] C. Michel, J.M. Moreau, G.D. Achenbach, R. Gerson, W.J. James, *Solid State Commun.* 7 (1969) 701–704.
- [18] R. Ramesh, N.A. Spaldin, *Nat. Mater.* 6 (2007) 21–29.
- [19] S.K. Pradhan, J. Das, P.P. Rout, S.K. Das, S. Samantray, D.K. Mishra, D.R. Sahu, A.K. Pradhan, K. Zhang, V.V. Srinivasu, B.K. Roul, *J. Alloys Compd.* 509 (2011) 2645–2649.
- [20] A. Huang, S.R. Shannigrahi, *J. Alloys Compd.* 509 (2011) 2054–2059.
- [21] X. Zhang, Y. Sui, X. Wang, Y. Wang, Z. Wang, *J. Alloys Compd.* 507 (2010) 157–161.
- [22] V. Shelke, V.N. Harshan, S. Kotru, A. Gupta, *J. Appl. Phys.* 106 (2009) 104114–104120.
- [23] T. Kawae, Y. Terauchi, H. Tsuda, M. Kumeda, A. Morimoto, *Appl. Phys. Lett.* 94 (2009) 112904–112906.
- [24] Z. Wen, X. Shen, J. Wu, D. Wu, A. Li, B. Yang, Z. Wang, H. Chen, J. Wang, *Appl. Phys. Lett.* 96 (2010) 202904–202906.
- [25] A.Z. Simões, L.S. Cavalcante, C.S. Riccardi, J.A. Varela, E. Longo, *Curr. Appl. Phys.* 9 (2009) 520–523.
- [26] J. Yan, G.D. Hu, X.M. Chen, W.B. Wu, C.H. Yang, *J. Appl. Phys.* 104 (2008) 076103–104120.
- [27] V.R. Singh, A. Garg, D.C. Agrawal, *Solid State Commun.* 149 (2009) 734–737.
- [28] Y. Du, Z.X. Cheng, M. Shahbazi, E.W. Collings, S.X. Dou, X.L. Wang, *J. Alloys Compd.* 490 (2010) 637–641.
- [29] F. Yan, T.J. Zhu, M.O. Lai, L. Lu, *Scripta Mater.* 63 (2010) 780–783.
- [30] B. Yu, M. Li, Z. Hu, L. Pei, D. Guo, X. Zhao, S. Dong, *J. Appl. Phys.* 93 (2008) 182909–182911.
- [31] P. Uniyal, K.L. Yadav, *J. Phys.: Condens. Matter* 21 (2009) 405901–405906.
- [32] C.J. Cheng, A.Y. Borisevich, D. Kan, I. Takeuchi, V. Nagarajan, *Chem. Mater.* 22 (2010) 2588–2596.
- [33] K.S. Nalwa, A. Garg, A. Upadhyaya, *Matter Lett.* 62 (2008) 878–881.
- [34] K.S. Nalwa, A. Garg, *J. Appl. Phys.* 103 (2008) 044101–044106.
- [35] C.J. Cheng, D. Kan, S.H. Lim, W.R. McKenzie, P.R. Munroe, L.G. Salamanca-Riba, R.L. Withers, I. Takeuchi, V. Nagarajan, *Phys. Rev. B* 80 (2009) 014109–014119.
- [36] H. Liu, T. Liu, X. Wang, *Solid State Commun.* 149 (2009) 1958–1961.
- [37] D. Kothari, V.R. Reddy, A. Gupta, C. Meneghini, G. Aquilanti, *J. Phys.: Condens. Matter* 22 (2010) 356001–435610.
- [38] J. Liu, L. Fang, F. Zheng, S. Ju, M. Shen, *Appl. Phys. Lett.* 95 (2009) 022511–022513.
- [39] V.R. Reddy, D. Kothari, A. Gupta, S.M. Gupta, *Appl. Phys. Lett.* 94 (2009) 082505–082507.
- [40] S.K. Pradhan, J. Das, P.P. Rout, S.K. Das, D.K. Mishra, D.R. Sahu, A.K. Pradhan, V.V. Srinivasu, B.B. Nayak, S. Verma, B.K. Roul, *J. Magn. Magn. Mater.* 322 (2010) 3614–3622.
- [41] C. Fanggao, S. Guilin, F. Kun, Q. Ping, Z. Qijun, *J. Rare Earths* 24 (2006) 273–276.
- [42] F.Z. Qian, J.S. Jiang, S.Z. Guo, D.M. Jiang, W.G. Zhang, *J. Appl. Phys.* 106 (2009) 084312–184312.
- [43] J. Xu, G. Wang, H. Wang, D. Ding, Y. He, *Mater. Lett.* 63 (2009) 855–857.
- [44] J. Wang, M. Li, X. Liu, L. Pei, J. Liu, B. Yu, X. Zhao, *Chin. Sci. Bull.* 55 (2010) 1594–1597.
- [45] B. Vengalis, J. Devenson, A.K. Oginskis, V. Lissauskas, F. Anisimovas, R. Butkute, L. Dapkus, *Phys. Status Solidi C* 12 (2009) 2746–2749.
- [46] F. Huang, X. Lu, Z. Wang, S. Xu, X. Wu, J. Zhu, *Integrat. Ferroelect.* 96 (2008) 1607–8489.
- [47] F. Huang, X. Lu, W. Lin, X. Wu, Y. Kan, J. Zhu, *Appl. Phys. Lett.* 89 (2006) 242914–242916.
- [48] S. Karimi, I.M. Reaney, Y. Han, J. Pokorny, I. Sterianou, *J. Mater. Sci.* 44 (2009) 5102–5112.
- [49] Z.X. Cheng, X.L. Wang, S.X. Dou, H. Kimura, K. Ozawa, *J. Appl. Phys.* 104 (2008) 116109–116111.
- [50] Y.J. Zhang, H.G. Zhang, J.H. Yin, H.W. Zhang, J.L. Chen, W.Q. Wang, G.H. Wu, *J. Magn. Magn. Mater.* 322 (2010) 2251–2255.
- [51] A.H.M. Gonzalez, A.Z. Simões, L.S. Cavalcante, E. Longo, J.A. Varela, C.S. Riccardi, *Appl. Phys. Lett.* 90 (2007) 052906–052908.
- [52] K.Y. Yun, M. Noda, M. Okuyama, H. Saeki, H. Tabata, K. Saito, *J. Appl. Phys.* 96 (2004) 3399–3403.
- [53] Z. Hu, M. Li, Y. Yu, J. Liu, L. Pei, J. Wang, X. Liu, B. Yu, X. Zhao, *Solid State Commun.* 150 (2010) 1088–1091.
- [54] K.Y. Yun, D. Ricinchi, T. Kanashima, M. Okuyama, *Appl. Phys. Lett.* 89 (2006) 192902–192904.
- [55] Z. Cheng, X. Wang, S. Dou, H. Kimura, K. Ozawa, *Phys. Rev. B* 77 (2008) 092101–092104.
- [56] H.M. Rietveld, *J. Appl. Cryst.* 2 (1969) 65–71.
- [57] D.L. Bish, J.E. Post, *Am. Mineral.* 78 (1993) 932–940.
- [58] <http://www.ing.unitn.it/maud/index.html>.
- [59] L. Lutterotti, S. Matthies, H.-R. Wenk, A.J. Schultz, J.J. Richardson, *Appl. Phys.* 81 (1997) 594–600.
- [60] G. Will, *Powder Diffraction: the Rietveld Method and the Two Stage Method to Determine and Refine Crystal Structures from Powder Diffraction Data*, Springer-Verlag, Berlin, Heidelberg, 2006, pp. 44–69.
- [61] S.R. Hall, F.H. Allen, I.D. Brown, *Acta Crystallogr. A* 47 (1991) 655–685.
- [62] M. Ferrari, L. Lutterotti, *J. Appl. Phys.* 76 (1994) 7246–72556.
- [63] L. Lutterotti, M. Bortolotti, *IUCr: Compcomm Newslett.* 1 (2003) 43–50.
- [64] L. Lutterotti, S. Matthies, H.-R. Wenk, *IUCr: Newslett. CPD* 21 (1999) 14–15.
- [65] T. Barth, G. Lundey, *Zeitsch. Phys. Chem.* 121 (1926) 78–102.
- [66] <http://ftp.ccp14.dl.ac.uk/ccp/web-mirrors/lutterotti/~luttero/laboratoriomateriali/Rietveld.pdf>.
- [67] <http://www.crystalimpact.com/diamond/Default.htm>.
- [68] K. Fukushima, M. Kobune, T. Yamaji, H. Tada, A. Mineshige, T. Yazawa, H. Fujisawa, M. Shimizu, Y. Nishihata, J. Mizuki, H. Yamaguchi, K. Honda, *Jpn. J. Appl. Phys.* 46 (2007) 6938–6943.
- [69] R.D. Shannon, *Acta Cryst. A* 32 (1976) 751–767.
- [70] L.S. Cavalcante, J.C. Sczancoski, F.S. De Vicente, M.T. Frabbro, M. Siu Li, J.A. Varela, E. Longo, *J. Sol–Gel Sci. Technol.* 49 (2009) 35–46.
- [71] D. Gouvêa, R.H.R. Castro, *Appl. Surf. Sci.* 217 (2003) 194–201.
- [72] F. Zavaliche, S.Y. Yang, T. Zhao, Y.H. Chu, M.P. Cruz, C.B. Eom, R. Ramesh, *Phase Transit.* 79 (2006) 991–1017.
- [73] A. Kumar, S. Denev, R.J. Zeches, E. Vlahos, N.J. Podraza, A. Melville, D.G. Schlom, R. Ramesh, V. Gopalan, *Appl. Phys. Lett.* 97 (2010) 112903–112905.
- [74] R.J. Zeches, M.D. Rossell, J.X. Zhang, A.J. Hatt, Q. He, C.H. Yang, A. Kumar, C.H. Wang, A. Melville, C. Adamo, G. Sheng, Y.H. Chu, J.F. Ihlefeld, R. Erni, C. Ederer, V. Gopalan, L.Q. Chen, D.G. Schlom, N.A. Spaldin, L.W. Martin, R. Ramesh, *Science* 326 (2009) 977–980.
- [75] Y.H. Chu, Q. He, C.H. Yang, P. Yu, L.W. Martin, P. Shafer, R. Ramesh, *Nano Lett.* 9 (2009) 1726–1730.
- [76] D. Mazumdar, V. Shelke, M. Iliev, S. Jesse, A. Kumar, S.V. Kalinin, A.P. Baddorf, A. Gupta, *Nano Lett.* 10 (2010) 2555–2561.

- [77] D.H. Kim, H.N. Lee, M.D. Biegalski, H.M. Christen, *Appl. Phys. Lett.* 92 (2008) 012911–012912.
- [78] A.Z. Simões, E.C. Aguiar, A.H.M. Gonzalez, J. Andrés, E. Longo, J.A. Varela, *J. Appl. Phys.* 104 (2008) 104115–104121.
- [79] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, *Science* 299 (2003) 1719–1722.
- [80] I. Apostolova, J.M. Wesselinowa, *J. Magn. Magn. Mater.* 321 (2009) 2477–2482.
- [81] H. Liu, Z. Liu, K. Yao, *J. Sol–Gel Sci. Technol.* 41 (2007) 123–128.
- [82] Z. Hu, M. Li, B. Yu, L. Pei, J. Liu, J. Wang, X. Zhao, *J. Phys. D: Appl. Phys.* 42 (2009) 185010–185015.
- [83] S.K. Singh, H. Ishiwara, *Jpn. J. Appl. Phys.* 45 (2006) 3194–3197.
- [84] H.W. Jang, S.H. Baek, D. Ortiz, C.M. Folkman, R.R. Das, Y.H. Chu, P. Shafer, J.X. Zhang, S. Choudhury, V. Vaithyanathan, Y.B. Chen, D.A. Felker, M.D. Biegalski, M.S. Rzchowski, X.Q. Pan, D.G. Schlom, L.Q. Chen, R. Ramesh, C.B. Eom, *Phys. Rev. Lett.* 101 (2008) 107602–1107602.
- [85] M. Fiebig, *J. Phys. D: Appl. Phys.* 38 (2005) R123–R152.
- [86] M.M. Kumar, S. Srinath, G.S. Kumar, S.V. Suryanarayana, *J. Magn. Magn. Mater.* 188 (1998) 203–212.
- [87] T. Kanai, S.I. Ohkoshi, A. Nakajima, T. Watanabe, K. Hashimoto, *Adv. Mater.* 13 (2001) 487–490.
- [88] K. Ueda, H. Tabata, T. Kawai, *Appl. Phys. Lett.* 75 (1999) 555–557.
- [89] V.B. Naik, R. Mahendiran, *Solid State Commun.* 149 (2009) 754–758.
- [90] E.V. Ramana, T.B. Sankaram, *Mater. Chem. Phys.* 120 (2010) 231–235.
- [91] A.A. Amirov, I.K. Kamilov, A.B. Batdalov, I.A. Verbenko, O.N. Razumovskaya, L.A. Reznichenko, L.A. Shilkina, *Tech. Phys. Lett.* 34 (2008) 760–762.
- [92] I. Sosnowskat, T. Peterlin-Neumaier, E. Steichele, *J. Phys. C: Solid State Phys.* 15 (1982) 4835–4846.
- [93] A.K. Zvezdin, A.P. Pyatakov, *Phys. Usp.* 47 (2004) 416–421.
- [94] V.M. Mukhortov, Y.I. Golovko, Y.I. Yuzyuk, *Phys. Usp.* 52 (2009) 856–860.
- [95] E. Joanni, R. Savu, P.R. Bueno, E. Longo, J.A. Varela, *Appl. Phys. Lett.* 92 (2008) 132110–132112.
- [96] T.T. Fang, C.P. Liu, *Chem. Mater.* 17 (2005) 5167–5171.
- [97] J. Li, A.W. Sleight, M.A. Subramanian, *Solid State Commun.* 135 (2005) 260–262.
- [98] A.K. Jonscher, *Solid State Electron.* 33 (1990) 737–742.
- [99] A.Z. Simões, C.S. Riccardi, M.L. Dos Santos, F. González Garcia, E. Longo, J.A. Varela, *Mater. Res. Bull.* 44 (2009) 1747–1752.
- [100] H. Uchida, R. Ueno, H. Funakubo, S. Koda, *J. Appl. Phys.* 100 (2006) 014106–014114.
- [101] T. Kawae, H. Tsuda, A. Morimoto, *Appl. Phys. Express* 1 (2008) 051601–151601.
- [102] G.W. Pabst, L.W. Martin, Y.-H. Chu, R. Ramesh, *Appl. Phys. Lett.* 90 (2007) 072902–072904.
- [103] W. Mönch, *Phys. Rev. B* 37 (1988) 7129–7132.
- [104] C. Chanelliere, J.L. Autran, R.A.B. Devine, B. Balland, *Mater. Sci. Eng. R* 22 (1996) 269–322.
- [105] S.W. Yi, S.S. Kim, J.W. Kim, H.K. Jo, D. Do, W.J. Kim, *Thin Solid Films* 517 (2009) 6737–6741.

Magnetoelectric Coefficient in Strontium Ruthenate Buffered Lanthanum Modified Bismuth Ferrite Thin Films Grown by Chemical Method

Alexandre Zirpoli Simões^{1,*}, Filiberto Gonzalez Garcia¹, and Francisco Moura²

¹Universidade Federal de Itajubá-Unifei-Campus Itabira, Rua São Paulo 377, Bairro Amazonas, P. O. Box 355, 35900-37, Itabira, Minas Gerais, Brazil

²Laboratório Interdisciplinar em Cerâmica, Instituto de Química, Universidade Estadual Paulista, P. O. Box 355, 14801-907 Araraquara, São Paulo, Brazil

This paper focuses on the magnetoelectric coupling (ME) at room temperature in lanthanum modified bismuth ferrite thin film (BLFO) deposited on SrRuO₃-buffered Pt/TiO₂/SiO₂/Si(100) substrates by the soft chemical method. BLFO film was coherently grown at a temperature of 500 °C. The magnetoelectric coefficient measurement was performed to evidence magnetoelectric coupling behavior. Room temperature magnetic coercive field indicates that the film is magnetically soft. The maximum magnetoelectric coefficient in the longitudinal direction was close to 12 V/cmOe. Dielectric permittivity and dielectric loss demonstrated only slight dispersion with frequency due the less two-dimensional stress in the plane of the film. Polarization reversal was investigated by applying dc voltage through a conductive tip during the area scanning. We observed that various types of domain behavior such as 71° and 180° domain switching, and pinned domain formation occurred.

Keywords: Piezoelectricity, Piezoelectric Force Microscopy, Ceramics, Dielectric Response, Chemical Syntheses, Multiferroics.

1. INTRODUCTION

Multiferroics materials^{1,2} exhibit several ferroic (or anti-ferroic) orders simultaneously and can be for instance ferroelectric and ferroelastic³ or ferroelectric and ferro- or ferrimagnetic.^{4,5} The concomitance of several order parameters in a given material is attractive for storage applications as it offers the possibility to store twice as much information in a given memory cell volume, thereby providing an exponential increase in storage density.⁶ Ferromagnetic and ferroelectric order parameters are widely used to store binary information in MRAMs⁷ and FeRAMs,⁸ respectively but, unfortunately, ferroelectric ferromagnets (or ferrimagnets) are very scarce and the quest for a material with both large finite polarization and magnetization at room temperature is still in progress. To reach this goal, a first goal is to obtain materials with magnetoelectric coupling. Among all known multiferroics, the only compound that satisfies these criteria is bismuth ferrite (BFO). First synthesized in the late 1950s,⁹ BFO was shown to be a G-type antiferromagnet with a Néel

temperature of 630 K by Kiselev et al.¹⁰ Later, Sosnowska et al. showed that the magnetic order of bulk BFO is not strictly collinear and that a cycloidal modulation with a period of 62 nm is present.¹¹ The magnetoelectric (ME) coefficient $ME = dE/dH = dV/(tdH)$ is the most critical indicator for the magnetoelectric coupling properties in multiferroic materials, where V is the induced magnetoelectric voltage, H is the exciting ac magnetic field, and t is the thickness of the sample used for measuring V across the laminate.¹² In previous work, we grow bismuth ferrite thin films on strontium ruthenate layer in which the conducting oxide was used as both the bottom electrode and the buffer layer.¹³ We have observed an improvement in the crystal growth and electric properties of ferroelectric oxide. Wang et al.¹⁴ reported the considerable enhancement in the leakage, ferro/piezoelectric, and magnetic properties of the epitaxial bismuth ferrite films with conductive strontium ruthenate electrodes. Of particular interest, the SRO electrode is promising in inducing the preferred orientation and improving the film/electrode interface of ferroelectric films. Previous studies suggested that the fatigue endurance can be effectively suppressed by La doping.¹⁵ To our knowledge, few reports are available

*Author to whom correspondence should be addressed.

on the magnetoelectric coefficient dependence on dc bias magnetic field of lanthanum modified bismuth ferrite thin film (BLFO) grown in oxide electrode. In this way, the magnetic and dielectric properties of BLFO thin films crystallized by the polymeric precursor method was investigated. The main focus was to evaluate the role exerted by the SRO bottom electrode on crystal structure and electrical properties of BLFO ferroic material.

2. EXPERIMENTAL PROCEDURE

The SRO and BLFO thin films were prepared using the polymeric precursor method, as described elsewhere.¹⁶ The electrical properties of Pt/BLFO/SRO/Pt/Ti/SiO₂/Si(100) capacitor structure were measured. The upper electrodes of Pt for the electrical measurements were prepared by evaporation through a shadow mask with a 0.2 mm² dot area. Dielectric properties of the capacitor were measured with an HP4192A impedance/gain phase analyzer under zero bias for a film thickness of 270 nm.

Impedance measurements were performed with a frequency response analyser (HP 4192) with amplitude of 100 mV. The magnetoelectric coefficient measurements in BLFO films were attained in a dynamic lock-in technique. The dc magnetic bias field was produced by an electromagnet (Cenco Instruments J type). The time-varying dc field was achieved by a programmable dc power supply (Phillips PM2810 60 V/5 A/60 W). To measure the dc magnetic field, a Hall probe was employed. Magnetization measurements were done by using a vibrating-sample magnetometer (VSM) from Quantum DesignTM. The magnetoelectric signal was measured by using a lock-in amplifier (EG&G model 5210) with input resistance and capacitance of 100 MΩ and 25 pF, respectively. Piezoelectric measurements were carried out using a setup based on an atomic force microscope in a Multimode Scanning Probe Microscope with Nanoscope IV controller (Veeco FPP-100). In our experiments, piezoresponse images of the films were acquired in ambient air by applying a small ac voltage with an amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz while scanning the film surface. To apply the external voltage we used a standard gold coated Si₃N₄ cantilever with a spring constant of 0.09 N/m. The probing tip, with an apex radius of about 20 nm, was in mechanical contact with the uncoated film surface during the measurements. Cantilever vibration was detected using a conventional lock-in technique.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of BLFO deposited on SRO electrode. The polycrystalline film exhibits a pure perovskite phase. Furthermore, except for the Si(100) and Pt(111) peaks, no peaks of impure phases such as Bi₂Fe₄O₉ and Bi₄₆Fe₂O₇₂ were spotted so pure phase

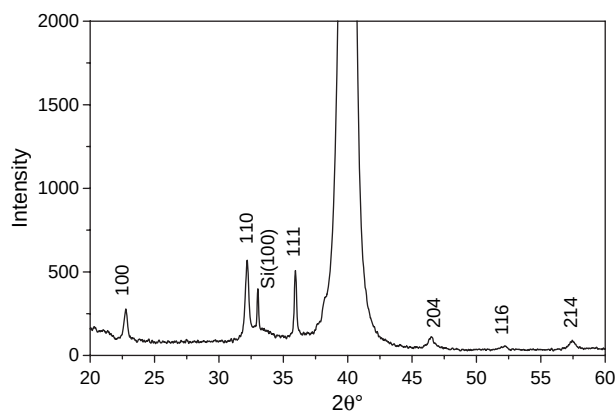


Fig. 1. X-ray diffraction of BLFO thin film deposited by the polymeric precursor method on SRO electrode and annealed at 500 °C in static air for 2 h.

BiFeO₃ films were obtained by the soft chemical method. The polycrystalline nature of the film can be attributed to the differences in nucleation energy between the ferroelectric material and the oxide electrode. The insertion of SRO can avoid a possible interfacial reaction between platinum and bismuth which can lead to undesired electrical properties. Therefore, the substitution of metallic electrodes based on noble metals like platinum by conductive oxides is an alternative to reach better electrical properties caused by the high oxygen affinity of these electrodes.¹⁷

Figure 2 displayed frequency-dependent dielectric behavior of BLFO film annealed at 500 °C. The dielectric measurements were carried out at room temperature as a function of frequency in the range of 10 kHz–1 MHz. It is easy to see that the film possess small dielectric dispersion at low frequency since at which the dielectric constants decrease slightly with the frequency. It means that the films has good interface between the BLFO film and SRO bottom electrode. As shown, the dielectric constant shows very little dispersion with frequency indicating that our films possess low defect concentrations at the

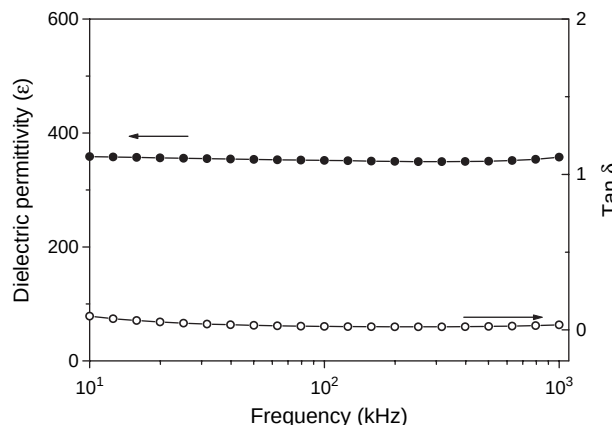


Fig. 2. Dielectric permittivity and dielectric loss spectra of BLFO thin films deposited by the polymeric precursor method and annealed at 500 °C for 2 hours as function of frequency.

interface film-substrate. The low dispersion of the dielectric constant and the absence of any relaxation peak in $\tan \delta$ indicate that both, interfacial polarization of the Maxwell Wagner type and a polarization produced by the electrode barrier can be neglected in the film. The dielectric constant and dissipation factor, at 100 kHz, were found to be 122 and 0.05, respectively. The BLFO film had higher relative dielectric permittivity when compared with those previously reported in ceramics or films.^{18–23} The observed improvement of dielectric permittivity may be associated with less structural disorder and less two-dimensional stress in the plane of the film. The $\tan \delta$ values of the BLFO films keeps unchanged with increasing frequency suggesting that the films exhibited low defect concentration.

The magnetoelectric coefficient versus dc bias magnetic field in the longitudinal and transversal directions reveals hysteretic behavior, as observed in the magnetic field cycles shown in Figures 3(a and b). The maximum magnetoelectric coefficient of 12 V/cmOe in the longitudinal direction is much larger than that previously reported

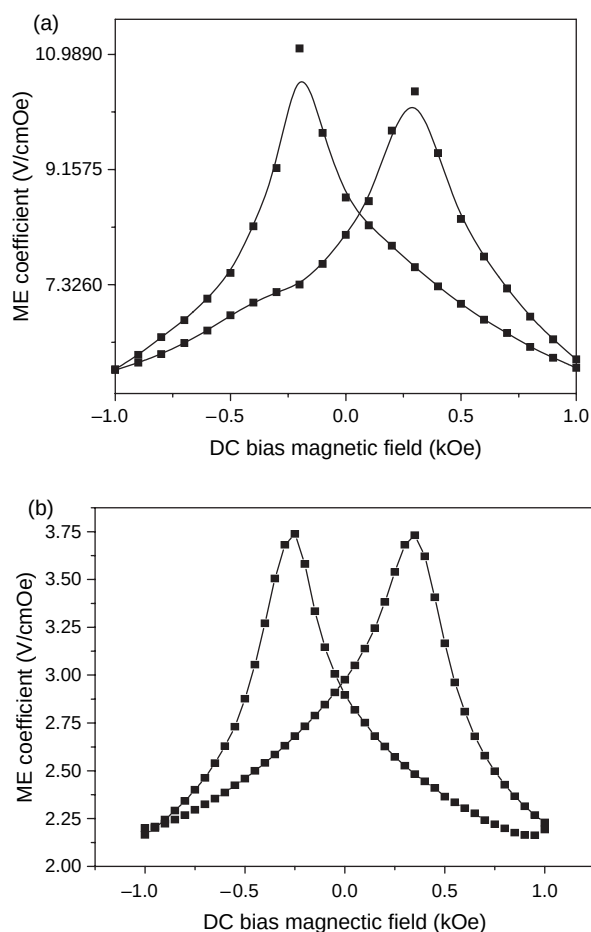


Fig. 3. The magnetoelectric coefficient dependence on dc bias magnetic field for BLFO thin films deposited by the polymeric precursor method and annealed at 500 °C for 2 hours at a 7 kHz ac magnetic field at room temperature. (a) Longitudinal and (b) Transversal.

for thin films as high as 3 V/cmOe in the same direction at zero fields.²⁴ This is a consequence of the antiferromagnetic axis of BLFO which rotates through the crystal with an incommensurate long-wavelength period of ~ 620 Å.^{25,26} Early reports showed that the spiral spin structure leads to a cancellation of any macroscopic magnetization and would inhibit the observation of the linear magnetoelectric effect.²⁷ Significant magnetization (~ 0.5 μB /unitcell) and a strong magnetoelectric coupling have been observed in epitaxial thin films, suggesting that the spiral spin structure could be suppressed.²⁸

Magnetization (M) versus field (H) loops were recorded at 300 K (Fig. 4). The magnetization for the film was observed with a magnetic field of 2.5 emu/g. A weak ferromagnetic response was noted, although enhanced magnetization was observed as compared to bulk specimens. Gehring²⁹ and Goodenough et al.³⁰ suggested that statistical distribution of Fe^{3+} and Ti^{4+} ions in the octahedra or creation of lattice defects might lead to bulk magnetization and weak ferromagnetism. The appearance of weak ferromagnetism in this compound may be attributed to either the canting of the antiferromagnetically ordered spins by a structural distortion^{31–33} or the breakdown of the balance between the antiparallel sublattice magnetization of Fe^{3+} due to metal ion substitution with a different valence.^{34,35} As can be seen, the magnetization of our film linearly increases with the applied magnetic field. This behavior is characteristic of antiferromagnets and can be changed by introducing a small fraction of rare-earth additives. That will change the magnetic structure of pure bismuth ferrite. A change in the magnetic properties in this case is explained not only by different magnetic moments and ion radii of lanthanum (the La atom does not possess any intrinsic magnetic moment), but also by the anisotropy of the magnetic moments of lanthanum ions. Further studies are required to understand the magnetic behaviour of this compound. The low coercive magnetic fields of BLFO film

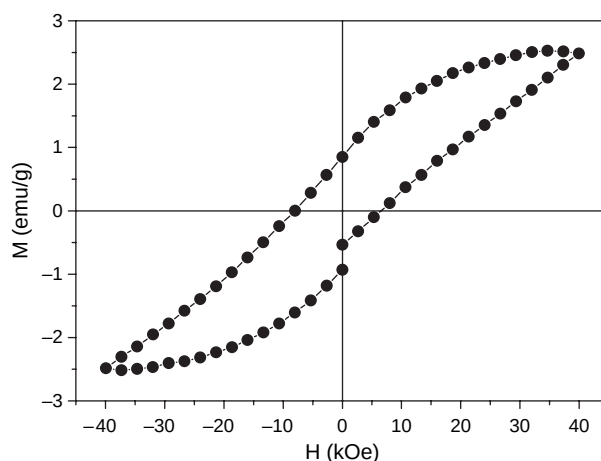
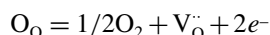


Fig. 4. Field dependencies of the magnetization obtained for BLFO films deposited by the soft chemical method and annealed at 500 °C for 2 hours.

is indicative of its magnetically soft nature and suitability for device applications.

Impedance spectroscopic analysis was employed to verify the presence of intrinsic as well as the space-charge contributions to our measured values of the dielectric permittivity (Fig. 5). The Cole–Cole plot for the complex impedance in the 10 kHz to 1 MHz frequency range clearly reveals the presence of three overlapping semicircular arcs which are attributable to contributions from electrode-grain interface (circle I), grain boundary (circle II), and grains contribution (circle III) in the decreasing order of measuring frequencies.^{36–38} The possible origin of different resistivities of grains and grain boundaries can be caused by the equilibrium concentration of oxygen vacancies in ABO_3 type perovskites and addition of lanthanum which results in loss of oxygen during sintering. This loss can be written in the Kröger-Vink notation as follows:



The electrons released in the above reaction may be captured by Fe^{3+} leading to the formation of Fe^{2+} . This leads to hopping of electrons among the two different valence states, which increases conductivity of the grains. During cooling down period after sintering, the reverse reaction occurs. However due to insufficient time available during cooling, the reoxidation occurs preferentially at grain boundaries only. Thus grain boundaries regain their insulating character, while the grains remain more or less semiconducting. The grain boundaries thus act as barriers against the hopping electrons, which pile up against them leading to space charge polarization. A similar space charge polarization occurs at the electrode-grain interface. These space charge polarization processes are responsible for the extremely large value of dielectric permittivity at very low and medium frequencies. However, at high frequencies the space charge polarizations are not able to contribute.

The domain structures observed in the film by piezoelectric force microscopy (PFM) was illustrated

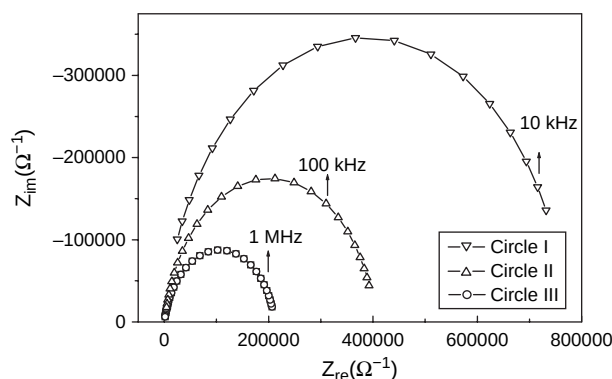


Fig. 5. Cole–Cole plot of complex-impedance diagram in the frequency range 100 Hz to 1 MHz.

in Figure 6. The out-of-plane (OP) and in-plane (IP) piezoresponse images of the as-grown films after applying a bias of -12 V, on an area of $2\ \mu\text{m} \times 2\ \mu\text{m}$, and then an opposite bias of $+12$ V in the central $1\ \mu\text{m} \times 1\ \mu\text{m}$ area

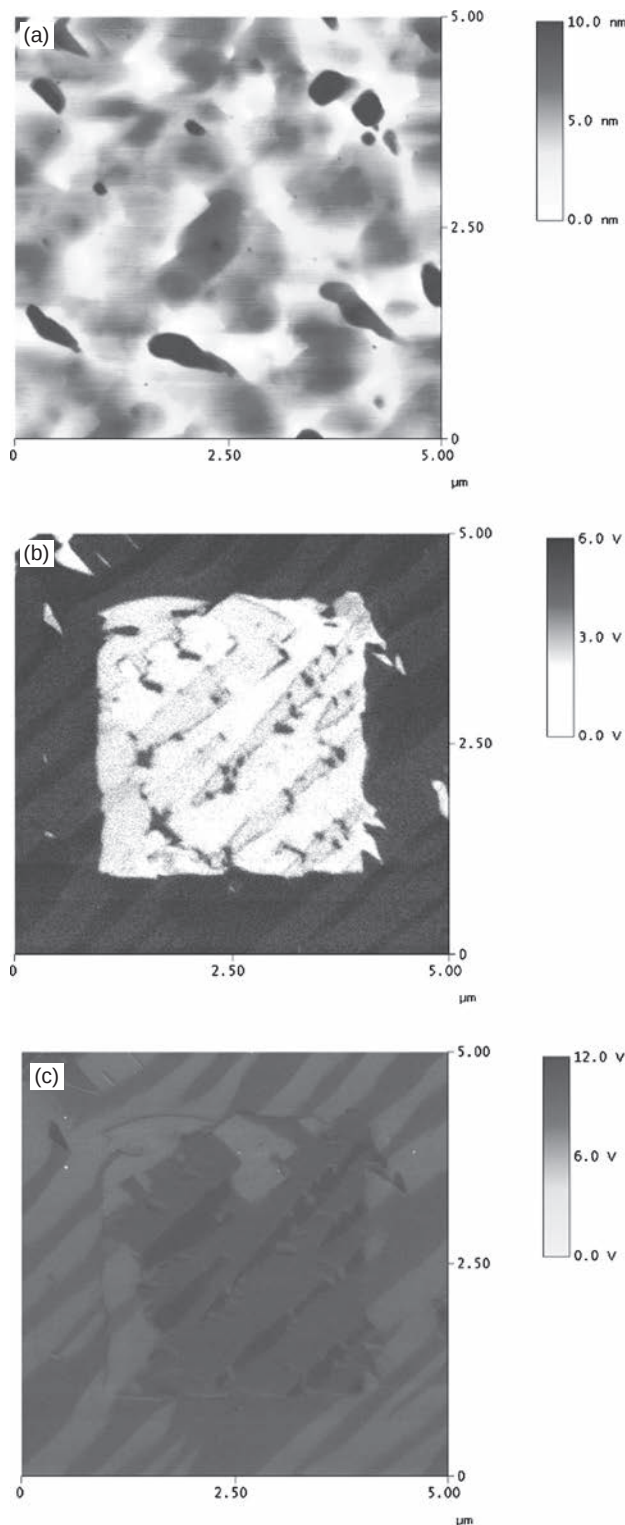


Fig. 6. Topography (TP), out-of-plane (OP) and in-plane (IP) PFM images of BLFO thin films deposited by the polymeric precursor method and annealed at $500\ ^\circ\text{C}$ for 2 hours: (a) TP, (b) OP and (c) IP.

were employed. For comparison the topography of the film was also analysed (Fig. 6(a)). To obtain the domain images of the films, a high voltage that exceeds the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization.³⁹ The PFM image indicates that the perpendicular component of polarization can be switched between two stable states: bright and dark contrast inside and outside of the square region. Higher PFM magnification images showed that the regions without piezoresponse exhibit a strong contrast in the PFM images. The white regions in the out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode hereafter referred to as down polarization (Fig. 6(b)) while the dark regions correspond to domains oriented upward referred to as up polarization. Grains which exhibit no contrast change is associated with zero out-of-plane polarization. A similar situation was observed when a positive bias was applied to the film. We noticed that some of the grains exhibit a white contrast associated to a component of the polarization pointing toward the bottom electrode. On the other hand, in the in-plane PFM images (Fig. 6(c)) the contrast changes were associated with changes of the in-plane polarization components. In this case, the white contrast indicates polarization e.g., in the positive direction of the y-axis while dark contrast are given by in-plane polarization components pointing to the negative part of the y-axis. The ferroelectric domains in the BLFO film consist of a multiple domain state in a mixture of 71° and 180° domains which grow large into blocks. The domains grow in multiple states is a consequence of films thickness being close to 300 nm. In this way, lanthanum acts reducing the strain energy and the pinning effect of charged defects. The main differences in the out-of-plane (OP) and in-plane (IP) piezoresponse images may be understood as follows: First, the piezoelectric tensor for the rhombohedral symmetry is complex, resulting in an effective piezoelectric

coefficient that is not proportional to the component of polarization along the detection direction, as explained in Ref. [40]. In this scenario, the IP response may not change its sign upon polarization switching, while the OP response does. Second, the 180° switching process may take place via two non-180° (i.e., 71° and/or 109°,⁴¹) switching steps, which also implies switching of only one component of the electrical polarization.

The d_{33} (V) hysteresis loop is shown in Figure 7. The maximum d_{33} value, ~80 pm/V is better than the reported value for a BFO deposited on Si.⁴² The enhancement of polarization could be caused by the (111) orientation of the ferroelectric film deposited on SRO oxide which reduces the initial nucleation rate when crystallizing the film. The presented value reported for our BLFO film suggests that this material can be considered as a viable alternative for lead-free piezo-ferroelectric devices.

4. CONCLUSIONS

In summary, we have observed magnetoelectric effect in BLFO films grown on the SRO buffered Pt coated silicon substrates by the soft chemical method. The maximum magnetoelectric coefficient was close to 12 V/cmOe in the longitudinal direction. The high dielectric permittivity of the BLFO films was mainly due to the less structural disorder and less two-dimensional stress in the plane of the film. Ferroelectric domain characteristics by PFM were also investigated to study the dependence of electrical properties on grain orientations. A simple analysis based on three types of contrast, namely, bright, dark and gray contrast was used to determine domain configuration. It was found that 71° and 180° domain switchings, and pinned domain formation can occur in BLFO thin films. In-plane magnetization-field curves revealed magnetization of the BLFO films. Piezoelectric force microscopy images reveals that *in-plane* response may not change its sign upon polarization switching, while the out-of-plane response does. Lanthanum substitution was found to effectively induce spontaneous magnetization in antiferromagnetic BiFeO₃ exhibiting good piezoelectric properties.

Acknowledgments: The financial support of this research project by the Brazilian research funding agencies CNPq and FAPESP is gratefully acknowledged.

References and Notes

1. G. A. Smolenskii and I. E. Chupis, *Sov. Phys. Usp.* 25, 475 (1982).
2. W. Eerenstein, F. D. Morrison, J. Dho, M. G. Blamire, and J. F. Scott, *Science* 307, 1203 (2005).
3. A. Vasudevarao et al., *Phys. Rev. Lett.* 97, 257602 (2006).
4. K. Kato and S. Iida, *J. Phys. Soc. Jpn.* 51, 1335 (1982).
5. Y. Yamasaki et al., *Phys. Rev. Lett.* 96, 207204 (2006).
6. M. Gajek et al., *Nature Mater.* 6, 296 (2007).
7. W. J. Gallagher and S. S. P. Parkin, *IBM J. Res. Develop.* 50, 5 (2006).

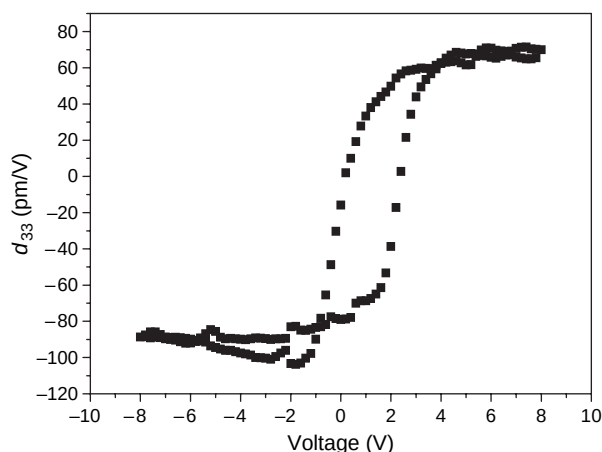


Fig. 7. Piezoelectric coefficient loop, d_{33} , of BLFO thin film deposited by the polymeric precursor method on SRO electrode and annealed at 500 °C in static air for 2 h.

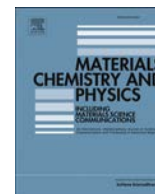
8. M. Dawber, K. M. Rabe, and J. F. Scott, *Rev. Mod. Phys.* 77, 083 (2005).
9. P. Royen and K. Swars, *Angew. Chem.* 24, 779 (1957).
10. S. V. Kiselev, R. P. Ozerov, and G. S. Zhdanov, *Sov. Phys. Dokl.* 7, 742 (1963).
11. I. Sosnowksa, T. Peterlin-Neumaier, and E. Steichele, *J. Phys. C* 15, 4835 (1982).
12. J. Lu, D.-A. Pan, and L. Qiao, e-print ar Xiv:0704/0704.2990.
13. A. Z. Simões, A. H. M. Gonzalez, E. C. Aguiar, C. S. Riccardi, E. Longo, and J. A. Varela, *Appl. Phys. Lett.* 93, 142902 (2009).
14. J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* 299, 1719 (2003).
15. A. Z. Simões, L. S. Cavalcante, C. S. Riccardi, J. A. Varela, and E. Longo, *Curr. Appl. Phys.* 9, 520 (2009).
16. A. Z. Simões, M. A. Ramirez, C. S. Riccardi, A. Ries, E. Longo, and J. A. Varela, *Mat. Chem. Phys.* 92, 373 (2005).
17. C. S. Liang, J. M. Wu, and M. C. Chang, *Appl. Phys. Lett.* 81, 3624 (2002).
18. M. Mahesh Kumar, V. R. Palkar, K. Srinivas, and S. V. Suryanarayana, *Appl. Phys. Lett.* 76, 2764 (2000).
19. J. K. Kim, S. S. Kim, and W.-J. Kim, *Mater. Lett.* 59, 4006 (2005).
20. H. Liu, Z. Liu, Q. Liu, and K. Yao, *Thin Solid Films* 500, 105 (2006).
21. V. R. Palkar, J. John, and R. Pinto, *Appl. Phys. Lett.* 80, 1628 (2002).
22. A. K. Pradhan, K. Zhang, D. Hunter, J. B. Dadson, G. B. Loutts, P. Bhattacharya, R. Katiyar, J. Zhang, Y. Sellmyer, and A. Burger, *J. Appl. Phys.* 97, 093903 (2005).
23. G. L. Yuan, S. W. Or, Y. P. Wang, Z. G. Liu, and J. M. Liu, *Solid State Commun.* 138, 76 (2006).
24. J. Li, J. Wang, M. Wuttig, R. Ramess, N. Wang, B. Ruetter, A. P. Pyatakov, A. K. Zvezdin, and D. Viehland, *Appl. Phys. Lett.* 84, 5261 (2004).
25. R. Ramesh and N. A. Spaldin, *Nat. Mater.* 6, 21 (2007).
26. I. Sosnowska, T. Peterlin-Neumaier, and E. Streichele, *J. Phys. C* 15, 4835 (1982).
27. Y. F. Popov, A. K. Zvezdin, G. P. Vorbev, A. M. Kadomtseva, V. A. Murashev, and D. N. Racov, *JETP Lett.* 57, 69 (1993).
28. F. Bai, J. Wang, M. Wuttig, J. F. Li, N. Wang, A. P. Pyatakov, A. K. Zvezdin, L. E. Cross, and D. Viehland, *Appl. Phys. Lett.* 86, 032511 (2005).
29. M. M. Kumar, A. Srinivas, and S. V. Suryanarayana, *J. Appl. Phys.* 87, 855 (2000).
30. G. A. Gehring, *Ferroelectrics* 161, 275 (1994).
31. J. B. Goodenough and J. M. Lango, *Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology*, Springer, New York (1978), Vol. III/4a.
32. M. M. Kumar, S. Srinath, G. S. Kumar, and S. V. Suryanarayana, *J. Magn. Magn. Mater.* 188, 203 (1998).
33. T. Kanai, S. I. Ohkoshi, A. Nakajima, T. Watanabe, and K. Hashimoto, *Adv. Mater.* 13, 487 (2001).
34. J. Wang, A. Scholl, H. Zheng, S. B. Ogale, L. Viehland, D. G. Schlom, N. A. Spaldin, K. M. Rabe, M. Wuttig, L. Mohaddes, J. Neaton, U. Waghmare, T. Zhao, and R. Ramesh, *Science* 307, 1203 (2005).
35. K. Ueda, H. Tabata, and T. Kawai, *Appl. Phys. Lett.* 75, 555 (1999).
36. T. Kanai, S. I. Ohkoshi, and K. Hashimoto, *J. Phys. Chem. Solids* 64, 391 (2003).
37. T. Kojima, T. Sakai, T. Watanabe, and H. Funakubo, *Appl. Phys. Lett.* 80, 2746 (2002).
38. A. K. Joncher, *Dielectric Relaxation in Solids*, Chelser Dielectric, London (1983).
39. A. Z. Simões, A. H. M. Gonzalez, L. S. Cavalcante, C. S. Riccardi, E. Longo, and J. A. Varela, *Appl. Phys. Lett.* 90, 052906 (2007).
40. C. Harnagea, A. Pignolet, M. Alexe, and D. Hesse, *Integr. Ferroelectr.* 44, 113 (2002).
41. F. Zavaliche, P. Shafer, R. Ramesh, M. P. Cruz, R. R. Das, D. M. Kim, and C. B. Eom, *Appl. Phys.* 87, 252902 (2005).
42. J. Wang, J. B. Neaton, H. Zheng, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* 299, 1719 (2003).

Received: 2 November 2009. Revised/Accepted: 10 December 2009.



Contents lists available at ScienceDirect

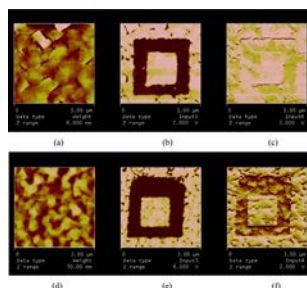
Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphysExperimental evidence of enhanced ferroelectricity in Ca doped BiFeO₃L.V. Costa^{a,1}, R.C. Deus^{a,1}, C.R. Foschini^{b,1}, E. Longo^{b,1}, M. Cilense^{c,2}, A.Z. Simões^{a,*}^a Universidade Estadual Paulista, UNESP, Faculdade de Engenharia de Guaratinguetá, Av. Dr. Ariberto Pereira da Cunha, 333, Bairro Portal das Colinas, CEP 12516-410 Guaratinguetá, SP, Brazil^b Universidade Estadual Paulista, UNESP, Faculdade de Engenharia de Bauru, Dept. de Eng. Mecânica, Av. Eng. Luiz Edmundo C. Coube 14-01, 17033-360 Bauru, SP, Brazil^c Universidade Estadual Paulista, UNESP, Instituto de Química – Laboratório Interdisciplinar em Cerâmica (LIEC), Rua Professor Francisco Degni s/n, 14800-90 Araraquara, SP, Brazil

HIGHLIGHTS

- Ca doped BiFeO₃ thin films were obtained by the polymeric precursor method.
- Co-existence of distorted rhombohedral and tetragonal phases are evident.
- Enhanced ferroelectric and piezoelectric properties are produced by the internal strain in the Ca doped BiFeO₃ film.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 14 June 2013

Received in revised form

15 October 2013

Accepted 12 January 2014

Keywords:

- A. Ceramics
- A. Thin films
- B. Coatings
- B. Chemical synthesis

ABSTRACT

Calcium (Ca)-doped bismuth ferrite (BiFeO₃) thin films prepared by using the polymeric precursor method (PPM) were characterized by X-ray diffraction (XRD), field emission gun scanning electron microscopy (FEG-SEM), transmission electron microscopy (TEM), polarization and piezoelectric measurements. Structural studies by XRD and TEM reveal the co-existence of distorted rhombohedral and tetragonal phases in the highest doped BiFeO₃ where enhanced ferroelectric and piezoelectric properties are produced by internal strain. Resistive switching is observed in BFO and Ca-doped BFO which are affected by the barrier contact and work function of multiferroic materials and Pt electrodes. A high coercive field in the hysteresis loop is observed for the BiFeO₃ film. Piezoelectric properties are improved in the highest Ca-doped sample due to changes in the crystal structure of BFO for a primitive cubic perovskite lattice with four-fold symmetry and a large tetragonal distortion within the crystal domain. This observation introduces magnetoelectronics at room temperature by combining electronic conduction with electric and magnetic degrees of freedom which are already present in the multiferroic BiFeO₃.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Multiferroic materials with ferroelectric and ferromagnetic simultaneous ordering are currently attracting significant attention due to their interesting fundamental physics as well as their potential applications [1–5]. Among the single-phase multiferroic materials studied, BiFeO₃ (BFO) with a rhombohedrally distorted

^{*} Corresponding author. Tel.: +55 12 3123 2228.E-mail address: alezipo@yahoo.com (A.Z. Simões).¹ Tel.: +55 12 3123 2228.² Tel.: +55 16 3301 9828.

perovskite structure and a space group of $R3c$ is the only material which exhibits both ferroelectricity and G-type antiferromagnetism at room temperature (with a Curie temperature T_c of 1103 K and Néel temperature T_N of 643 K) which facilitates applications at room temperature [6–8]. However, pure BFO has a serious high leakage current problem resulting from charge defects such as oxygen vacancies and the cancellation of ion magnetic moments due to its spatial periodic inhomogeneous spin structure [9] which hinders its practical applications in multiferroic devices. Considerable efforts have been expended to improve BFO properties; e.g., A-site substitution with La^{3+} , Nd^{3+} , Ce^{3+} and Tb^{3+} [10–15] and B-site substitution with Ni^{2+} , Cu^{2+} , Co^{2+} , Cr^{3+} , Mn^{3+} , Ti^{4+} , Zr^{4+} and V^{5+} [16–18] etc. These studies confirmed that ion doping is an effective method to improve BFO properties. Since BFO ferroelectricity of BFO evolves from a lone pair of A-site Bi^{3+} ion electrons [3–5], ferroelectric property effects are very important [19,20]. Ramesh et al. studied the quasi-non-volatile and reversible modulation of electric conduction accompanied by the modulation of the ferroelectric state in Ca-doped BiFeO_3 films using an electric field as the control parameter. The mechanism of this modulation in Ca-doped BiFeO_3 is based on electronic conduction as a consequence of naturally produced oxygen vacancies that act as donor impurities to compensate Ca acceptors and maintain a highly stable Fe^{3+} valence state [21]. For the low Ca doping regime ($x < 0.1$), films with a monoclinic structure undergo a first-order transition to a pseudo-tetragonal phase at higher temperatures with a thermal hysteresis. The extrapolation of the transition temperature results in the well known ferroelectric Curie temperature (T_c) of BiFeO_3 at 1100 K. With increased Ca doping, the ferroelectric T_c rapidly decreases, and a T_c of 600 K with a thermal hysteresis of 240 K is recorded. It has been reported that the T_c of some ferroelectrics such as BaTiO_3 and PbTiO_3 is very sensitive to the strain state [22,23]. However, because BiFeO_3 ferroelectricity is primarily attributed to Bi 6s lone-pair electrons, ferroelectric properties and the T_c are expected to be less sensitive to strain [24]. However, a number of studies related to this phenomenon have been reported. Therefore, for this paper, we prepared A-site Ca-doped BFO films with different compositions on Pt/Ti/SiO₂/Si substrates by using the PPM and investigated their influence on the structure, microstructure and ferro/piezoelectric properties.

2. Experimental procedure

Ca-modified BiFeO_3 thin films were prepared by the PPM as described elsewhere [25]. Films were spin coated on Pt/Ti/SiO₂/Si substrates by a commercial spinner operating at 5000 revolutions/min for 30 s (spin coater KW-4B, Chemat Technology). An excess of 5% wt of Bi was added to the solution to minimize bismuth loss during thermal treatment. Thin films were annealed at 500 °C for 2 h in a conventional furnace under static air atmosphere. The film thickness was reached by repeating spin-coating and heating treatment cycles ten times. Annealed film thicknesses were measured using SEM (Topcom SM-300) at the transversal section. We have obtained films with thicknesses in the range of 340–360 nm. A phase analysis of films was performed at room temperature by XRD using a Bragg-Brentano diffractometer (Rigaku 2000) and $\text{CuK}\alpha$ radiation; in this case, back scattering electrons were used. The Rietveld analysis was performed with the Rietveld refinement program DBWS-941 1 [26]. The profile function used was the modified Thompson-Cox-Hastings pseudo-Voigt where η (the Lorentzian fraction of the function) varies with the Gauss and Lorentz components of the full width at half maximum. The morphology of the films was observed using a high resolution FEG-SEM (Supra 35-VP, Carl Zeiss, Germany). To obtain better insight into the nature of the deposited phases and their crystallographic

relationship, cross-sectional samples from different films were further investigated by TEM and selected area diffraction (SAD) patterns onto 300 mesh Cu grids. Measurements were then taken at an accelerating voltage of 200 kV on a Philips model CM 200 instrument. Top Au electrodes (0.5 mm diameter) were prepared for electrical measurements by evaporation through a shadow mask at room temperature. The current–voltage characteristic was determined with an amperimeter (Keithley 6430) with a 10 μA current compliance (used here to prevent permanent damage on films). Piezoelectric measurements were carried out using a set-up based on an atomic force microscope in a multimode scanning probe microscope with a nanoscope IV controller (Veeco FPP-100). In our experiments, piezoresponse images of films were acquired in ambient air by applying a small ac voltage with an amplitude of 2.5 V (peak to peak) and a frequency of 10 kHz while scanning the film surface. To apply the external voltage, we used a standard gold-coated Si_3N_4 cantilever with a spring constant of 0.09 N m^{-1} . With an apex radius of about 20 nm, the probing tip was in mechanical contact with the uncoated film surface during measurements. Cantilever vibration was detected using a conventional lock-in technique. Ferroelectric properties of the capacitor were measured on a Radiant Technology RT6000 instrument and a tester equipped with a micrometer probe station in a virtual ground mode at a frequency of 60 Hz. These loops were traced using the Charge 5.0 program included in the software of the RT6000HVS in a virtual ground mode test device. All measurements were taken at room temperature.

3. Results and discussion

Fig. 1 illustrates XRD patterns of BFO and Ca-doped BFO films deposited on platinum-coated silicon substrates. The films were well crystallized at a processing temperature of 500 °C. BFO and Ca-doped BFO films self-organized to produce (110)-preferred orientation with good crystallinity. With partial substitution of Ca ions for A-site bismuth ions, the BCFO film (108) diffraction peak shifted toward a higher angle. No additional peak related to CaO could be assigned by revealing partial substitution of Ca by bismuth in the crystal lattice and solid solution of Ca substitution in BFO. The $\text{BCFO}_{0.30}$ film has a tetragonal structure with a $P4mm$ space group while BFO has a rhombohedral structure with a $R3c$ space group which can be treated as a special triclinic structure [14]. To verify and confirm the structure of BCFO thin films a structural refinement by the Rietveld method was performed. The Rietveld method is a

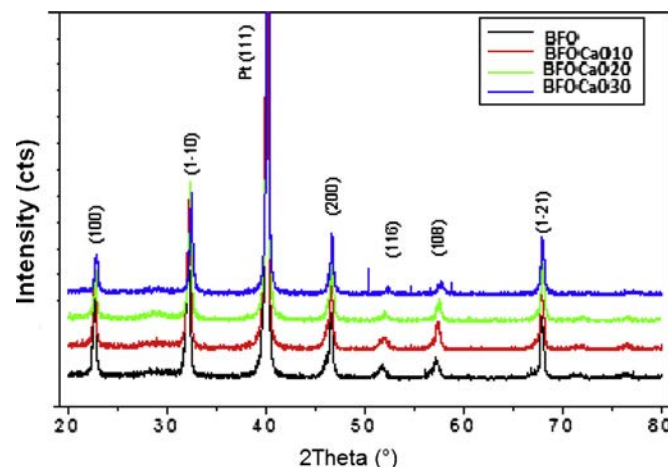
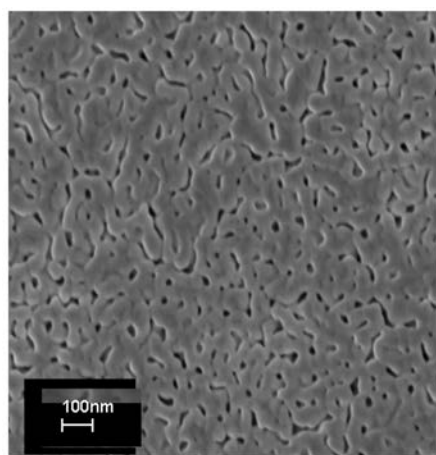


Fig. 1. X-ray diffraction of BFO, $\text{BFOCa}_{0.10}$, $\text{BFOCa}_{0.20}$, $\text{BFOCa}_{0.30}$ thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h.

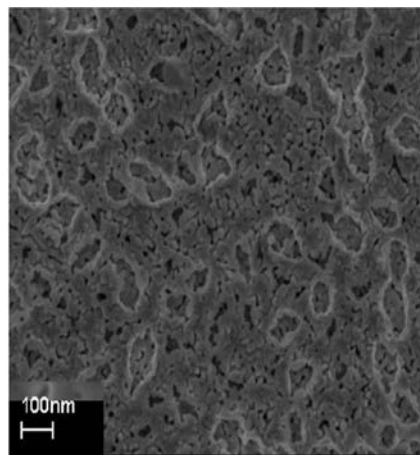
Table 1

Index refinements for BFO, BFOCa010, BFOCa020 and BFOCa030 thin films annealed at 500° for 2 h.

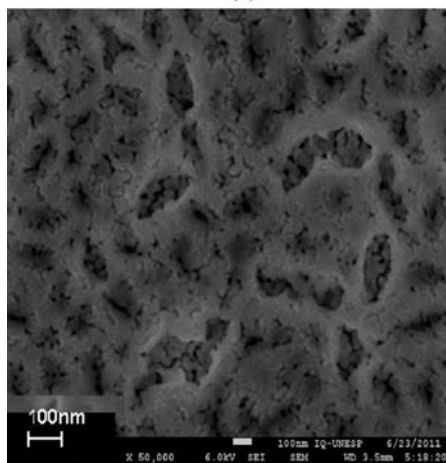
	Parameter	BFO	BFOCa010	BFOCa020	BFOCa030
Refinement index	R_{wp} (%)	8.14	5.97	5.51	4.59
	R_{exp}	4.67	3.91	3.76	3.31
	S	1.74	1.52	1.46	1.38
Atomic Positions	A1	0; 0; 0.06722	0; 0; 0.06712	0; 0; 0.06720	0; 0; 0.06733
	A2	0; 0; 0.21091	0; 0; 0.21023	0; 0; 0.21132	0; 0; 0.21145
	B1	0; 0; ½	0; 0; ½	0; 0; ½	0; 0; ½
	B2	0; 0; 0.37099	0; 0; 0.37213	0; 0; 0.37143	0; 0; 0.37120
	O1	¼; ¼; 0	¼; ¼; 0	¼; ¼; 0	¼; ¼; 0
	O2	¼; ¼; ¼	¼; ¼; ¼	¼; ¼; ¼	¼; ¼; ¼
	O3	0; 0; 0.43786	0; 0; 0.43747	0; 0; 0.43616	0; 0; 0.43638
	O4	0; 0; 0.32536	0; 0; 0.31851	0; 0; 0.31895	0; 0; 0.31989
	O5	¼; ¼; 0.11165	¼; ¼; 0.11584	¼; ¼; 0.11580	¼; ¼; 0.11581
	S_{Occ}				
	Bi (A1)	1.00000	0.87500	0.75000	0.62500
Lattice Parameter	Ca (A1)	0.00000	0.12500	0.25000	0.37500
	O	0.91700	0.91000	0.91800	0.94900
	a (Å)	5.577352	5.576058	5.577687	5.578439
	c (Å)	13.867785	13.807185	13.773235	13.764944
	V (Å ³)	373.529	371.784	371.086	370.963
Perovskite (mol%)	t	0.915	0.916	0.919	0.920
Stoichiometry		97.5 ± 0.5	97.1 ± 0.4	98.4 ± 0.4	97.7 ± 0.4
Refinement		BiFeO ₃	Bi _{0.9} Ca _{0.1} FeO ₃	Bi _{0.80} Ca _{0.2} FeO ₃	Bi _{0.70} Ca _{0.30} FeO ₃
		BiFeO _{2.6}	Bi _{0.9} Ca _{0.1} FeO _{2.6}	Bi _{0.80} Ca _{0.2} FeO _{2.6}	Bi _{0.70} Ca _{0.30} FeO _{2.8}



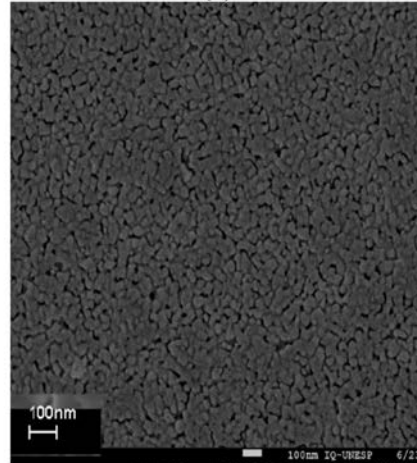
(a)



(b)



(c)



(d)

Fig. 2. FEG-SEM micrograph of thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h. (a) BFO, (b) BFOCa010, (c) BFOCa020 and (d) BFOCa030.

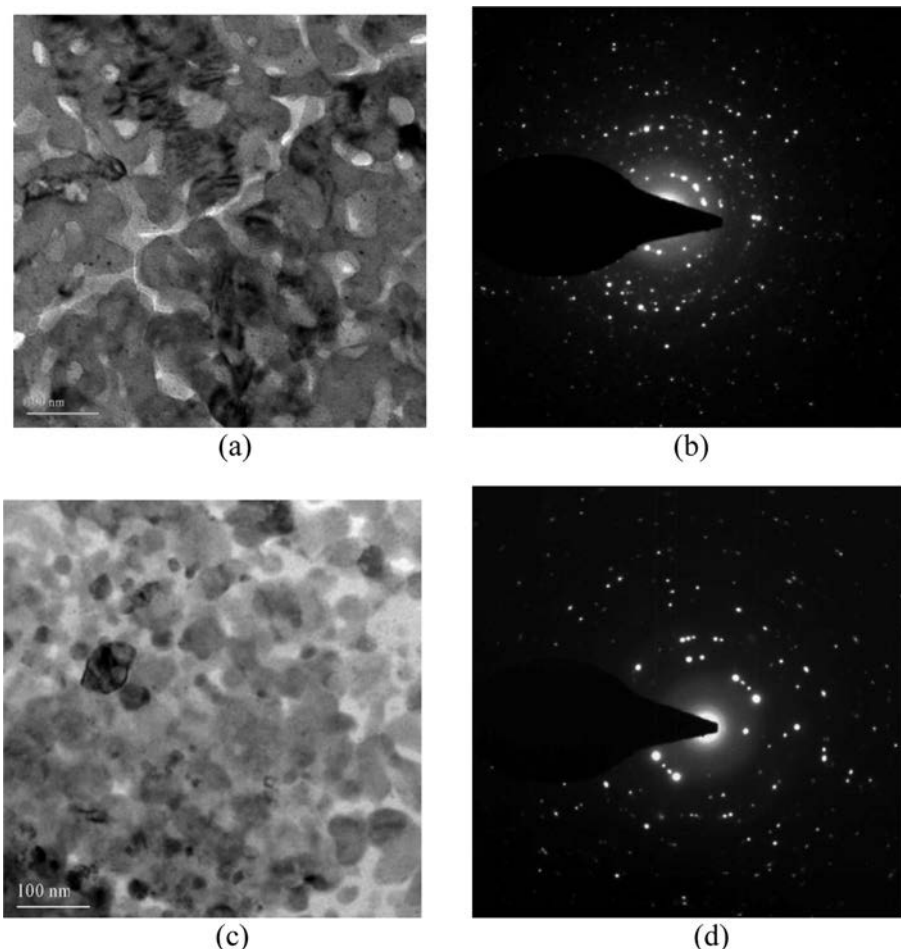


Fig. 3. TEM and SAD micrographies of thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h. (a) BFO (TEM), (b) BFO (SAD), (c) BFOCa030 (TEM) and (d) BFOCa030 (SAD).

least squares refinement procedure where the experimental step-scanned values are adapted to calculated values. The profiles are considered to be known, and a model for a crystal structure is available [27]. This structural refinement method presents several advantages over conventional quantitative analysis methods because this method uses a whole pattern fitting algorithm where all lines for each phase are explicitly considered, and even severely overlapped lines are usually not a problem. Thus, it is not necessary to decompose patterns into separate Bragg peaks as is often the case for traditional methods. The use of all reflections in a pattern rather than just the strongest reflections minimizes both uncertainty in derived weight fractions and effects of preferred orientation, primary extinction and nonlinear detection systems [28]. The structural refinement was performed by using a Maud program [29] which employs the Rietveld texture and stress analysis [30]. According to the literature [31,32], the quality of data from structural refinement is generally checked by R -values (R_{wp} , R_{exp} , and S). The quality of structural refinement also can be verified by the R_{wp} factor value. Its absolute value does not depend on the absolute value of the intensities; instead it depends on the background with a high background, it is easier to reach very low values. Increasing the number of peaks (sharp peaks) created more difficulty in obtaining a good value. Structural refinement data are acceptable when the R_{wp} is $<10\%$ for a medium complex phase, when high complex phases (monoclinic to triclinic), have a value of $R_{wp} < 15\%$ and when a highly symmetric material or compound (cubic) with few peaks has a value of $R_{wp} < 8\%$ [33].

Table 1 lists R_{wp} , R_{exp} , and S indexes as well as lattice parameters (a and c) and the unit cell volume (V). Atomic positions obtained by Rietveld analyses belong to the ICSD card (86-1518). Quantitative phase analyses of powders for the rhombohedral phase were calculated according to Young and Wiles [26]. Results obtained confirm that the Bi^{3+} ion was substituted by the Ca^{2+} ion in the rhombohedral BFO phase, and no changes occurred in refinements. Ca^{2+} substitutes for Bi^{3+} only in a perovskite-type unit cell which causes a distorted structure whereby distortion increases with a higher Ca content. The covalent interaction which originates from the strong hybridization between Fe $3d$ and O $2p$ orbitals plays an important role in the structural distortion of the BFO lattice. Doping with Ca improves oxygen ion stability in the lattice because some of the Bi ions in the pseudo-perovskite layers containing Fe–O octahedra are substituted by the rare earth ion. From low S values ($S = R_{wp}/R_{exp}$), it can be assumed that the refinement was successfully performed with all the investigated parameters close to literature data [34]. It can be inferred that the c -axis is less elongated after Ca addition which is caused by differences in charge densities of Ca and bismuth atoms. Also, the addition of Ca has a radial substitution effect higher than bismuth and stabilizes oxygen vacancies and consequently the structure. The decrease in the lattice parameter and unit cell volume is almost linear as expected due to the stoichiometric replacement of Bi^{3+} with a smaller ionic radii substituent (in this case Ca^{2+}).

The results obtained from the structural refinement are displayed in Table 1. In this table, the fitting parameters (R_{wp} , R_{exp} , and

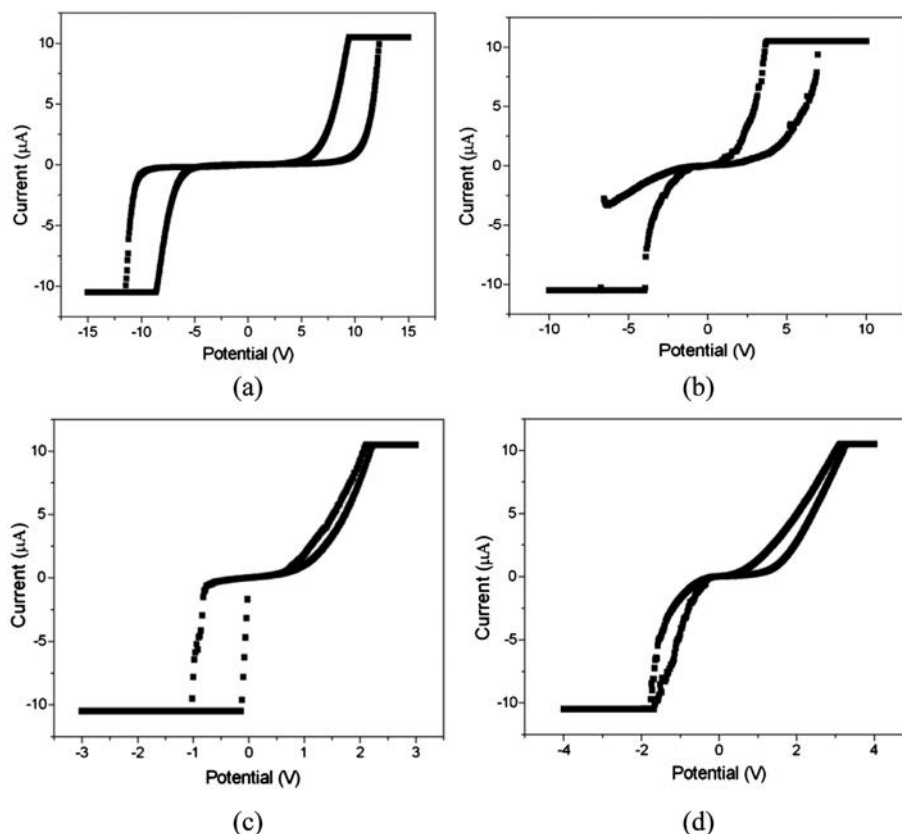


Fig. 4. Typical I – V hysteresis curve of thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h. (a) BFO, (b) BFOCa010, (c) BFOCa020 and (d) BFOCa030.

S) indicate good agreement between refined and observed XRD patterns. Small variations in lattice parameters, unit cell volumes and displacements on Fe atoms (network formers) are indicative of distortions/strain in the lattice caused by differences in crystal lattice parameters and the thermal expansion behavior between the film and the underlying substrate or arising from defects promoted by $[\text{BiO}_{12}]$ and $[\text{CaO}_{12}]$ clusters (network modifiers).

FEG-SEM was used to confirm the surface morphology (see Fig. 2). Changes in the surface of the Ca-doped BFO films were evaluated; and the results reveal that the BCF030 film consists of a homogeneous surface although BFO film has a degree of porosity. It was also found that the Ca dopant tends to suppress grain growth. BCF030 was found to be effective in improving the surface morphology of synthesized BFO-based films because the precursor film underwent the optimized nucleation and growth process to produce films with a homogeneous and dense microstructure. On the other hand, for low and middle Ca concentrations, the surface consists of irregularities which were caused by distortion and strain influenced by differences in the thermal expansion coefficient of the multiferroic material and the substrate. The average grain size is 63 nm for the BFO film and 33 nm for the highest doped film. The substitution of Ca^{2+} for Bi^{3+} in BiFeO_3 can produce oxygen vacancies which apparently induce distortions and causes structural irregularities within the crystallites. Thus the local distortion and strain caused by the rhombohedral co-existing phase is reflected in physical properties of the tetragonal phase. Also, the homogeneous microstructure of BCF030 films may affect ferroelectric properties because the voltage can be uniformly applied on them.

To evaluate the role exerted by Ca on the BFO film microstructure, TEM images of pure and highly doped Ca compositions were produced. A plane-view TEM image shows the microstructure and

SAD patterns and the grain polycrystallinity in film planes. Grains are regularly shaped, and the estimated size obtained from dark field images is about 60 nm for a BFO film and 30 nm for a BCF030 film (see Fig. 3a and c, respectively). Tiny pores less than 10 nm in size are present within grains and along grain boundaries. The role of Ca is to create vacancies which act as point defects and induce distortions within crystallites. Also, as the amount of Ca increases, small nucleation cores aggregate together into bigger grains and produce a smoother surface (not shown in the text). Thus, the lower grain size obtained in doped samples reflects an increase in the crystallization temperature due to differences in chemical bond strengths between Fe–O and Ca–O atoms. The BiFeO_3 pattern shows a rhombohedral lattice similar to the pattern previously reported for BiFeO_3 [35,36] while the BCF030 pattern is similar to patterns expected for a primitive cubic perovskite lattice possessing four-fold symmetry with a large tetragonal distortion within the crystal domain.

Much effort has been expended to understand resistive switching effects in metal semiconductor materials, but the mechanisms responsible for these effects are not completely understood. In this context, aside from enrolling BFO as a material candidate in this field, we would like to investigate the role of a Ca-doped BFO interface and barrier contact on resistive switching effects. Au is the top electrode in both samples forming ohmic contact. However, the bottom electrode (Pt) has a different work function, and contact barriers at bottom electrode/film interfaces are different because Pt forms a Schottky contact which could be causing different screen electric fields at the bottom electrode/film interface. Thus, the formation of the Schottky contact increases the difference between low and high resistance states as a consequence of an increase in the current flow in the forward voltage which

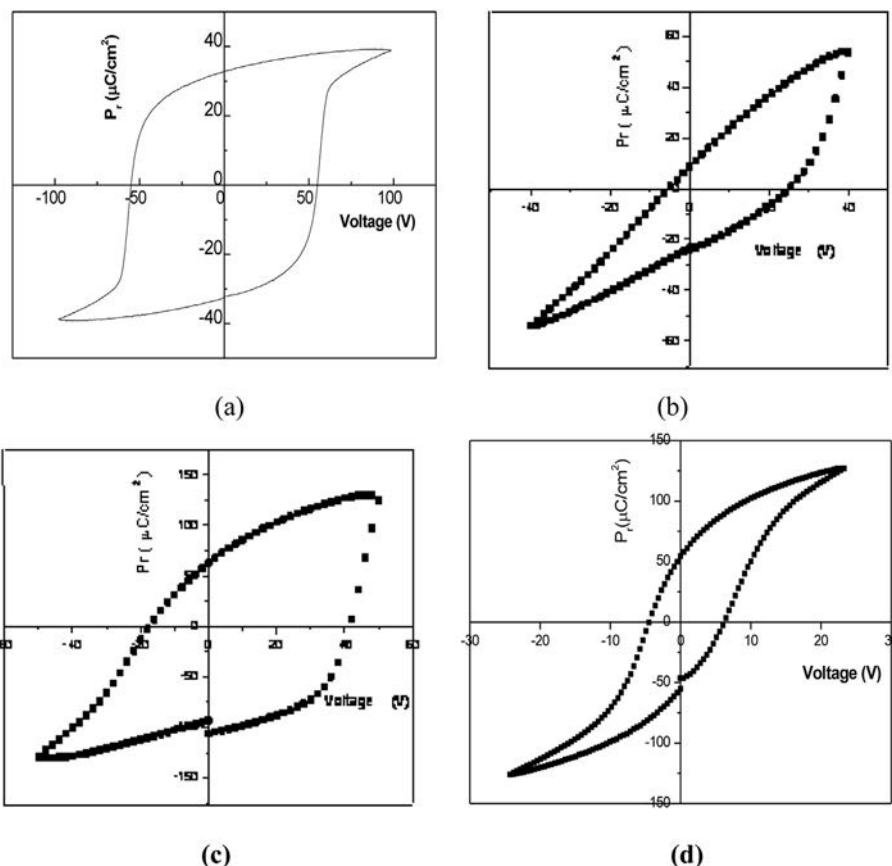


Fig. 5. Hysteresis loop of thin films deposited by the polymeric precursor method and annealed at 500 °C in static air for 2 h. (a) BFO, (b) BFOCa010, (c) BFOCa020 and (d) BFOCa030.

results in a shift in the hysteresis loop and an enhanced resistive switching effect. Our results clearly indicate that the resistive switching effect in BFO thin films is influenced by the barrier contact and the work function difference between BFO and Ca-doped BFO and electrodes where metal electrodes with high work function values forming Schottky contacts can produce increased hysteresis. In general, Schottky contacts in BFO films may be beneficial for the electronic charge transport in resistance random access memory applications. Current–voltage characteristics of the BFO and Ca-doped BFO samples were performed at room temperature with a current compliance limited to 10 μA in the measurement unit (see Fig. 4). Plots illustrate hysteresis curves usually related to resistive switching effects and commonly observed in heterostructured ferroelectric thin films [37]. This switching mechanism as a function of polarity is an intrinsic effect, and may be related to intrinsic dipole formation and/or to trap state relaxation [38]. It is observed that BFO films have a larger decrease of this effect while BCFO30 films maintain this effect because Ca inhibits grain growth. Clear I – V hysteresis is observed and is replicated reversibly. This huge difference between the measured conductivity and the estimated ionic conductivity suggests that the main carrier type which produces observed transport behavior must be electronic rather than ionic in nature. This hysteric I – V shape can potentially be used for a resistive memory device.

Room temperature P – E hysteresis loops of BFO and Ca-doped BFO films are shown in Fig. 5. The BFO loop is well saturated and rectangular with a $P_r \sim 51 \mu\text{C cm}^{-2}$ under a voltage of 50 V. No sign of leakage has been observed under this measuring frequency. Liu et al. [39] reported substantially reduced leakage of BiFeO₃ films by introducing a LaNiO₃ intermediate layer. Although a saturated hysteresis loop was observed, they obtained only a remnant

polarization of $26.9 \mu\text{C cm}^{-2}$ under 1.25 MV cm^{-1} . To our knowledge, very few reports on a large P_r and a rectangular loop of BFO film obtained from chemical methods [40,41] have been reported. However, the hysteresis loop in our study is more saturated than some BFO films on the Pt bottom electrode by the CSD method [42]. In fact, pure BFO film loops on the Pt bottom electrode are unsaturated in some cases. Gonzalez et al. [25] observed saturated hysteresis loops at room temperature in pure BFO films on a Pt bottom electrode while they observed only a small remnant polarization $\sim 36 \mu\text{C cm}^{-2}$ under 800 kV cm^{-1} . In other typical studies from Singh et al. [43], Hu et al. [44] and Uchida et al. [45], unsaturated loops were observed under 10 kHz at room temperature. Our results are comparable to results observed in epitaxial BFO films on a (1 0 0) SrTiO₃ substrate prepared by the PLD method. The film possesses well saturated hysteresis characteristics with a remnant polarization (P_r) of $31 \mu\text{C cm}^{-2}$ and a coercive field (E_c) of 560 kV cm^{-1} at a maximum applied electric field of 1000 kV cm^{-1} . According to Wang et al. [46], the BFO ferroelectricity originates from relative displacements of a Bi ion and a Fe–O octahedron along the (111) orientation in epitaxial BFO thin films, and the projection polarization along the (110) orientation is larger than the (100) orientation polarization. We claim that Ca decreases the remnant polarization and stabilizes the charged domain walls which interact with oxygen vacancies and reduce the coercive field. Imprint phenomena which cause a significant shift along the electric field axis toward the positive side is also evident in low and middle Ca-doped BFO as a consequence of oxygen vacancy accumulation near the electrode–film interface which reduces the effective applied electric field. A symmetric BCFO30 curve probably originates from the local distortion and strain caused by the rhombohedral co-existing phase and is reflected in physical

properties of the tetragonal phase. Adding Ca^{2+} ions to BFO in high concentrations requires charge compensation which can be achieved by the formation of Fe^{4+} or oxygen vacancies. If Fe^{4+} exists, the statistical distribution of Fe^{3+} and Fe^{4+} ions in the octahedron may also lead to strong polarization while high coercivity can be caused by the pinning of ferroelectric domain walls which results from the ferroelectric anisotropy.

Domain structures observed in the film by piezoelectric force microscopy (PFM) are illustrated in Fig. 6. Out-of-plane (OP) and in-plane (IP) piezoresponse images of as-grown films after applying a bias of -12 V on an area of $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$, and then an opposite bias of $+12$ V in the central $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ area were employed. For comparison, the film topography was also analyzed (see Fig. 6a and d). To obtain domain images of the films, a high voltage that exceeds the coercive field was applied during scanning. The contrast in these images is associated with the direction of the polarization [25]. The PFM image indicates that the perpendicular component of polarization can be switched between two stable states: bright and dark contrast inside and outside of the square region. Higher PFM magnification images confirm that regions without a piezoresponse exhibit a strong contrast in PFM images. White regions in out-of-plane PFM images correspond to domains with the polarization vector oriented toward the bottom electrode (down polarization) (see Fig. 6b and e) while the dark regions correspond to domains oriented upward (up polarization. Grains which exhibit no contrast change are associated with zero out-of-plane polarization). A similar situation was observed when a positive bias was

applied to the film. We noticed that some grains exhibit a white contrast associated with a component of the polarization pointing toward the bottom electrode. On the other hand, in the in-plane PFM images (see Fig. 6c and f), the contrast changes are associated with changes in the in-plane polarization components. In this case, the white contrast indicates polarization (e.g., in the positive direction of the y-axis) while the dark contrast is given by in-plane polarization components pointing to the negative part of the y-axis. Ferroelectric domains in the BFO film consist of a multiple domain state in a mixture of 71° and 180° domains which largely grow into blocks. Domains grow in multiple states as a consequence of film thicknesses close to 350 nm . The main differences in the OP and IP piezoresponse images may be understood as follows: First, the piezoelectric tensor for the rhombohedral symmetry is complex which results in an effective piezoelectric coefficient that is not proportional to the polarization component along the detection direction as explained in Ref. [47]. In this scenario, the IP response may not change its sign upon polarization switching while the OP response does change its sign. Second, the 180° switching process may take place via two non- 180° (i.e., 71° and/or 109°) [48] switching steps which also implies switching of only one component of electrical polarization. Piezoelectric properties are improved by Ca content due to the strain energy and pinning effects which can be caused by BFO crystal structure modifications for a primitive cubic perovskite lattice with four-fold symmetry and a large tetragonal distortion within the crystal domain which affects ferroelectric and piezoelectric properties. The main difference in

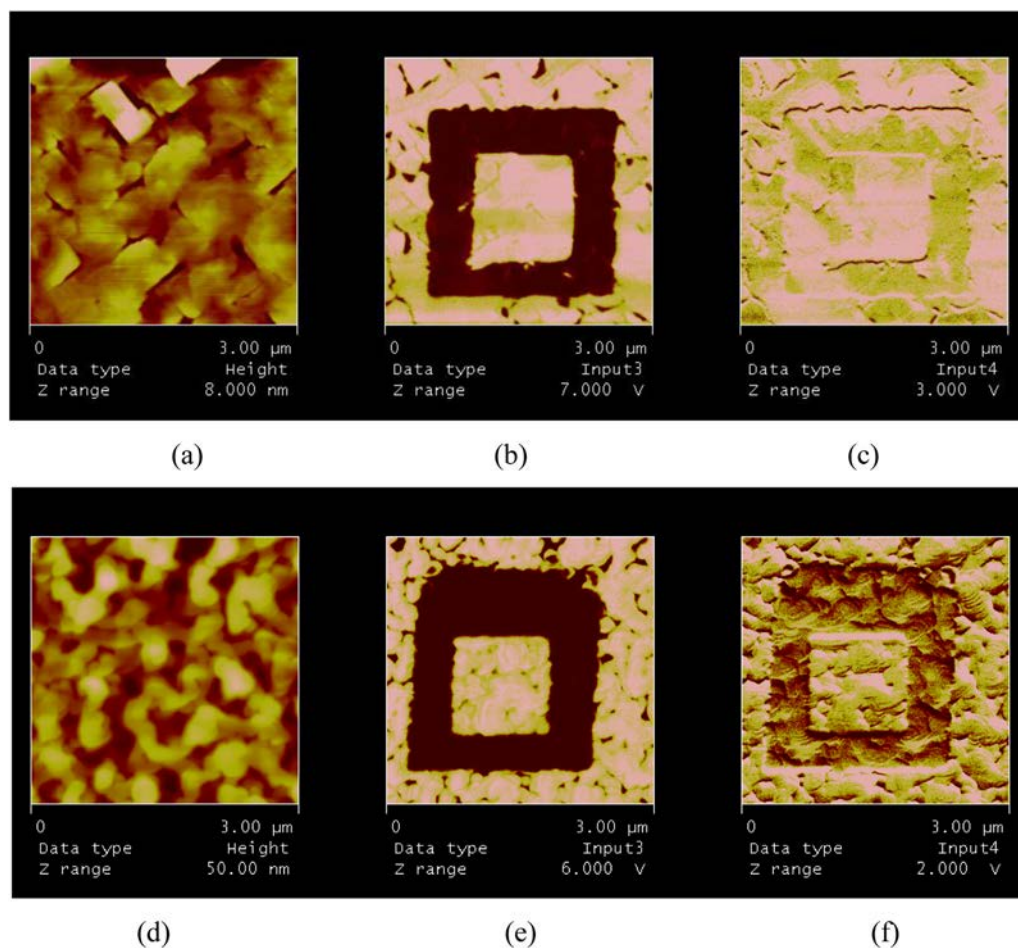


Fig. 6. Topography (TP), out-of-plane (OP) and in-plane (IP) PFM images of thin films deposited by the polymeric precursor method and annealed at 500°C for 2 h: (a) BFO (TP), (b) BFO (OP), (c) BFO (IP), (d) BFOCa030 (TP), (e) BFOCa030 (OP) and (f) BFOCa030 (IP).

ferroelectric and piezoelectric results is caused by the contribution of leakage current in hysteresis loops which is absent in the piezoresponse image mainly due to the effect of piezoelectric domains. Further studies are necessary to comprehend polarization switching in this system.

4. Conclusions

In summary, the effect of divalent-ion-Ca doping on multiferroic BiFeO₃ films was investigated on a Pt substrate using the soft chemical method through annealing at 500 °C for 2 h. The highest Ca concentration changes the local distortion and strain caused by the rhombohedral co-existing phase which is reflected in physical properties of the system. Among these films studied, the BCFO30 film exhibited a better microstructure, leakage current density behavior, a good *P*–*E* loop and strong piezoelectric characteristics. In addition, a comparative study shows that A-site Ca doping with various contents have notable influences on electrical properties, including leakage current and ferroelectric and piezoelectric properties of BFO films which may be related to modification of the structure and elimination of charge defects due to A-site Ca doping. Results of these studies are very promising and suggest that BCFO30 thin films can be used as storage elements in non-volatile ferroelectric random access memories.

Acknowledgments

The financial support of this research project by the Brazilian research funding agencies CNPq and FAPESP is gratefully acknowledged.

References

- [1] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare, N.A. Spaldin, K.M. Wuttig, R. Ramesh, *Science* 299 (2003) 1718.
- [2] W. Eerenstein, F.D. Morrison, J. Dho, M.G. Blamire, J.F. Scott, N.D. Mathur, *Science* 307 (2005) 1203.
- [3] L.W. Martin, S.P. Crane, Y.H. Chu, M.B. Holcomb, M. Gajek, M. Huijben, C.H. Yang, N. Balke, R. Ramesh, *J. Phys. C Condens. Matter* 20 (2008) 434220.
- [4] G. Catalan, J.F. Scott, *Adv. Mater.* 21 (2009) 2463.
- [5] K.F. Wang, J.M. Liu, Z.F. Ren, *Adv. Phys.* 58 (2009) 321.
- [6] G.A. Smolenskii, I.E. Chupis, *Sov. Phys. Usp.* 25 (1982) 475.
- [7] I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, *J. Phys. C Condens. Matter* 15 (1982) 4835.
- [8] C. Ederer, N.A. Spaldin, *Phys. Rev. B* 71 (2005) 060401.
- [9] X.D. Qi, J. Dho, R. Tomov, M.G. Blamire, J.L. MacManus-Driscoll, *Appl. Phys. Lett.* 86 (2005) 062903.
- [10] F.Z. Huang, X.M. Lu, W.W. Lin, X.M. Wu, Y. Kan, J.S. Zhu, *Appl. Phys. Lett.* 89 (2006) 242914.
- [11] B.F. Yu, M.Y. Li, J. Liu, D.Y. Guo, L. Pei, X.Z. Zhao, *J. Phys. D Appl. Phys.* 41 (2008) 065003.
- [12] Y. Wang, C.W. Nan, *J. Appl. Phys.* 103 (2008) 024103.
- [13] J. Liu, M.Y. Li, L. Pei, B.F. Yu, D.Y. Guo, X.Z. Zhao, *J. Phys. D Appl. Phys.* 42 (2009) 115409.
- [14] J. Liu, M.Y. Li, L. Pei, J. Wang, B.F. Yu, X. Wang, X.Z. Zhao, *J. Alloys Compd.* 493 (2010) 544.
- [15] A. Lahmar, S. Habouti, M. Dietze, C.-H. Solterbeck, M. Es-Souni, *Appl. Phys. Lett.* 94 (2009) 012903.
- [16] Y. Wang, C.W. Nan, *Ferroelectrics* 357 (2007) 172.
- [17] H. Naganuma, J. Miura, S. Okamura, *Appl. Phys. Lett.* 93 (2008) 052901.
- [18] P. Kharel, S. Talebi, B. Ramachandran, A. Dixit, V.M. Naik, M.B. Sahana, C. Sudakar, R. Naik, M.S.R. Rao, G. Lawes, *J. Phys. C Condens. Matter* 21 (2009) 036001.
- [19] J. Liu, M.Y. Li, L. Pei, J. Wang, Z.Q. Hu, X. Wang, X.Z. Zhao, *Europhys. Lett.* 89 (2010) 57004.
- [20] G.L. Yuan, S.W. Or, *J. Appl. Phys.* 100 (2006) 024109.
- [21] C.-H. Yang, J. Seidel, S.Y. Kim, P.B. Rossen, P. Yu, M. Gajek, Y.H. Chu, L.W. Martin, M.B. Holcomb, Q. He, P. Maksymovych, N. Balke, S.V. Kalinin, A.P. Baddorf, S.R. Basu, M.L. Scullin, R. Ramesh, *Nature* 8 (2009) 485.
- [22] M. Fiebig, *J. Phys. D.* 38 (2005) R123.
- [23] R. Ramesh, N.A. Spaldin, *Nat. Mater.* 6 (2007) 21.
- [24] S.W. Cheong, M. Mostovoy, *Nat. Mater.* 6 (2007) 13.
- [25] A.Z. Simões, A.H.M. Gonzalez, L.S. Cavalcante, C.S. Riccardi, E. Longo, J.A. Varela, *Appl. Phys. Lett.* 90 (2007) 052906.
- [26] R.A. Young, A. Sakthivel, T.S. Moss, C.O. Paiva-Santos, *DBWS-9411—an upgrade of the DBWS.* programs for Rietveld refinement with PC and mainframe computers*, *J. Appl. Crystallogr.* 28 (1995) 366–367.
- [27] H.M. Rietveld, *J. Appl. Cryst.* 2 (1969) 65.
- [28] D.L. Bish, J.E. Post, *Am. Mineral.* 78 (1993) 932.
- [29] <http://www.ing.unitn.it/maud/index.html>.
- [30] L. Lutterotti, S. Matthies, H.-R. Wenk, A.J. Schultz, J.J. Richardson, *Appl. Phys.* 81 (1997) 594.
- [31] G. Will, *Powder Diffraction: The Rietveld Method and the Two Stage Method to Determine and Refine Crystal Structures from Powder Diffraction Data*, Springer-Verlag, Berlin, Heidelberg, 2006, pp. 44–69.
- [32] T. Barth, G. Lunde, *Z. Physiol. Chem.* 121 (1926) 78.
- [33] C. Lepoittevin, S. Malo, N. Barrier, N. Nguyen, G. Van. Tendeloo, M. Hervieu, *J. Solid State Chem.* 181 (2008) 2601.
- [34] S.K. Singh, K. Maruyama, H. Ishiwara, *J. Phys. D Appl. Phys.* 40 (2007) 2705.
- [35] J.K. Kim, S.S. Kim, W.J. Kim, *Integr. Ferroelectr.* 76 (2005) 103.
- [36] Y. Huang, K. Zhao, H.B. Lu, K.J. Jin, M. He, Z.H. Chen, Y.L. Zhou, G.Z. Yang, *Appl. Phys. Lett.* 88 (2006) 061919.
- [37] P.R. Bueno, R. Tararan, R. Parra, E. Joanni, M.A. Ramírez, W.C. Ribeiro, E. Longo, J.A. Varela, *J. Phys. D Appl. Phys.* 42 (2009) 055404.
- [38] X.J. Luo, C.P. Yang, S.S. Chen, X.P. Song, H. Wang, K. Barner, *J. Appl. Phys.* 108 (2010) 014107.
- [39] H. Liu, Z. Liu, K. Yao, *J. Sol-Gel. Sci. Technol.* 41 (2007) 123.
- [40] X.J. Meng, J.G. Cheng, J.L. Sun, H.J. Ye, *J. Cryst. Growth* 220 (2000) 100.
- [41] W. Zhu, M.S. Tse, W. Lu, *Integr. Ferroelectr.* 12 (1996) 167.
- [42] J.K. Kim, S.S. Kim, W. Kim, *J. Appl. Phys. Lett.* 88 (2006) 132901.
- [43] S.K. Singh, H. Ishiwara, K. Maruyama, *Appl. Phys. Lett.* 88 (2006) 262908.
- [44] G.D. Hu, X. Cheng, W.B. Wu, C.H. Yang, *Appl. Phys. Lett.* 91 (2007) 232909.
- [45] H. Uchida, R. Ueno, H. Funakubo, S. Koda, *J. Appl. Phys.* 100 (2006) 014106.
- [46] Y. Wang, C.W. Nan, *Appl. Phys. Lett.* 89 (2006) 052903.
- [47] C. Harnagea, A. Pignolet, M. Alexe, D. Hesse, *Integr. Ferroelectr.* 44 (2002) 113.
- [48] F. Zavaliche, P. shafer, R. Ramesh, M.P. Cruz, R.R. Das, D.M. Kim, C.B. Eom, *Appl. Phys.* 87 (2005) 252902.