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An Approach to Analyzing Synthesis, Structure and Properties of Bismuth Titanate Ceramics

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Abstract:

The family of bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) layered-structured ferroelectrics materials is attractive from the viewpoint of their application as electronic materials such as dielectrics, piezoelectrics and pyroelectrics, because they are characterized by good stability of piezoelectric properties, a high Curie temperature and a good resistance vs temperature. Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) powders can be prepared using different methods, depending if the creation will be film coating or ceramics. The structure and properties of bismuth titanate materials show a significance dependence on the applied synthesis method. In this review paper, we made an attempt to give an approach to analyzing the structure, synthesis methods and properties of bismuth titanate ferroelectrics materials.

Keywords: $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics; Layered perovskite structure, Synthesis technique, Dielectric and Ferroelectric Properties

1. Introduction

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$, since its discovery in 1949 by Aurivillius [1], has been extensively studied for its ferroelectric and other excellent properties. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a candidate material for high temperature piezoelectric applications, memory storage, and optical displays because of its high Curie temperature and electrooptical properties [2]. Ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics are potential candidates for device applications due to their high dielectric constant and high breakdown strength [3, 4]. The properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ have been reported in a number of papers, cited among others in refs [5, 6, 7].

Ceramic materials with a perovskite structure are very significant electronic materials. Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), belongs to the group of ferroelectric materials with a perovskite structure. Bismuth titanate is most often used in the production of capacitors as it has a high temperature coefficient of resonant frequency, large dielectric constant and high dielectric losses [8]. Development of wireless telecommunication technologies in the last few years requires very stringent criteria for dielectric ceramic materials. In order to be applied as microwave filters and resonators dielectric ceramic materials must have a high

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dielectric constant, low dielectric loss and a thermally stable resonant frequency coefficient [8].

2. General Features of Ferroelectric Materials

The phenomenon of ferroelectricity was first observed by Valasek in 1921 [8], during an investigation of Rochelle salt (sodium tartarate tetrahydrate). Ferroelectric materials are a special type of dielectric materials that possess a spontaneous dipole. Ferroelectric materials are generally definite by reversible spontaneous polarization in the absence of electric field [9]. Spontaneous polarization is generated from a non-centrosymmetric arrangement of ions in a unit cell, which produces an electric dipole moment related to the unit cell. Adjacent unit cells are inclined to polarize in the same direction and form a region called a ferroelectric domain. A unit cell of a typical ferroelectric material, ABO_3 , is illustrated in Fig. 1 where A atom, B atom, and O oxygen occupy the corner site, body-centered site, and face-centered site, respectively.

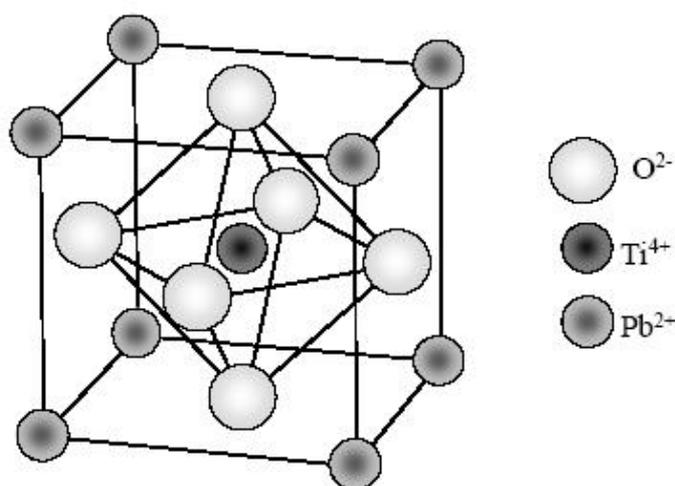


Fig. 1 The ideal perovskite structure of $PbTiO_3$.

Since the discovery of piezoelectricity $BaTiO_3$ in the 1940's, the nature and search for new perovskite ferroelectrics has been guided by traditional crystal chemistry concepts, with limited success. The perovskite structure has a general formula ABO_3 , where the Roman numerals represent the corresponding cation: anion coordination number. Based on their geometrical packing, Goldschmidt proposed the concept of a tolerance factor t ($t < 1$) [10]. Ferroelectric materials exhibit a characteristic hysteresis loop as shown in Fig. 2.

Ferroelectric materials are characterized by properties such as a high dielectrical constant, high piezoelectric constants, relatively low dielectric loss and high electrical resistivity. For ordinary dielectric materials the relationship between the applied electric field and the induced polarization is linear. When an electrical field is applied to the ferroelectric material, the B atom, which has two thermodynamically stable positions inside the oxygen octahedral, is displaced relative to the oxygen's upward or downward, depending on the polarity of the electric field. This displacement generates a dipole moment inside the oxygen octahedral, which is called saturated polarization ($\pm P_s$). When the applied electric field is removed, the B atom remains in the displaced position and generates a residual polarization in the absence of the applied electric field, or remanent polarization ($\pm P_r$). In order to reverse the direction of polarization, it is necessary to apply a coercive electric field ($\pm E_c$), which is defined as a minimum electric field for switching the polarization. Therefore, the basic characteristics of a ferroelectric material that make it suitable for non-volatile memory

applications are its ability to retain two stable remanent polarization values at zero field, thus providing nonvolatility. The state of polarization can be controlled and sensed by reversing the polarization from up (+) to down (0) or vice versa as a function of the applied voltage. For a crystal to exhibit ferroelectricity it has to belong to a non-centrosymmetric space group in a certain temperature range. The breakdown temperature where the non-centrosymmetry and ferroelectric properties are lost is called the Curie temperature (T_c) and above this temperature the material becomes paraelectric [11, 12].

The ferroelectric properties of such oxides have been known for around 50 years [13], yet the structural origins of their ferroelectricity have only recently been established [14]. The ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase has a high Curie temperature of 675 °C, possesses a high dielectric strength and a relatively high dielectric constant ~ 200 [15]. At 600 °C and below, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has a tetragonal phase and undergoes the phase transformation to orthorhombic at 750 °C [16]. It is useful for various applications such as memory storage, optical display, piezoelectric converters or pyroelectric devices over a wide range of temperatures [17, 18, 19-22].

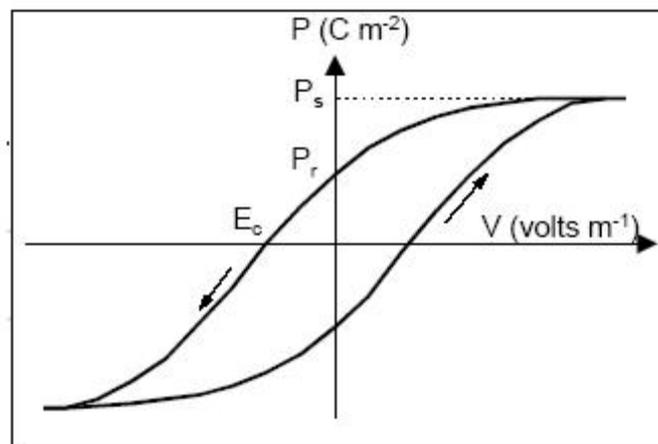


Fig. 2 A typical P-E hysteresis loop in ferroelectrics.

A large number of ferroelectric systems adopt the perovskite structure such as BaTiO_3 , $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST), PbTiO_3 , $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) and $\text{Pb}_{1-x}\text{La}_x\text{Zr}_y\text{Ti}_{1-y}\text{O}_3$ (PLZT) [11, 12]. Many of these ferroelectrics are lead-based but these are believed to be replaced in numerous applications by bismuth based-layered ferroelectrics. This is due to the fact that bismuth-based ferroelectrics consist of pseudo perovskite units sandwiched in between bismuth oxide layers, which gives them a better fatigue nature [23]. In addition there is also a desire to limit the integration of lead containing compounds into electronic products and here bismuth based layered ferroelectrics can be a more environmentally friendly alternative. Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, is one of the bismuth based layered ferroelectric materials that is a candidate for replacing lead based ferroelectric materials in for instance non-volatile ferroelectric random access memories (FRAM) [24, 25].

Ceramics of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ type of materials are also candidate materials for high temperature acoustic piezo-sensors [26]. The discovery of ferroelectricity and optical activity in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystals started a vast new area of research [17, 27].

3. Structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

Bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a bismuth based layered ferroelectric oxide and it belongs to the family of structures closely investigated by Bengt Aurivillius in the late 1940s

and early 1950s [28, 29]. The structure of the so-called Aurivillius phases can simply be described by the general formula $(\text{Bi}_2\text{O}_2)^{2+} (\text{M}_{n-1}\text{R}_n\text{O}_{3n+1})^{2-}$ where n can have the number 1 to 6. The $(\text{M}_{n-1}\text{R}_n\text{O}_{3n+1})^{2-}$ formula unit consists of n pseudo perovskite units which are sandwiched in between two $(\text{Bi}_2\text{O}_2)^{2+}$ layers. The M cation is a rather large mono-, di- or trivalent cation (e.g. Na^+ , Pb^{2+} , Bi^{3+}) and the R cation is smaller in size and either a tri-, tetra-, penta- or hexavalent cation (e.g. Fe^{3+} , Ti^{4+} , Ta^{5+} , W^{6+}) [30-32]. The R is a diamagnetic transition metal such as Ti^{4+} or Nb^{5+} and M is an alkali or alkaline earth cation [28]. The structure of Aurivillius oxides consists of arrays of Bi_2O_2 and perovskite-like $\text{M}_{n-1}\text{R}_n\text{O}_{3n+1}$ layers. Several different compounds having this general formula have been synthesized and structurally determined since the original work of Aurivillius, e.g. $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($n = 2$), $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$) and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ($n = 4$) [17, 33-35]. In Fig. 3 a simplified crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is shown. The three pseudo perovskite units and bismuth oxide layers have been marked.

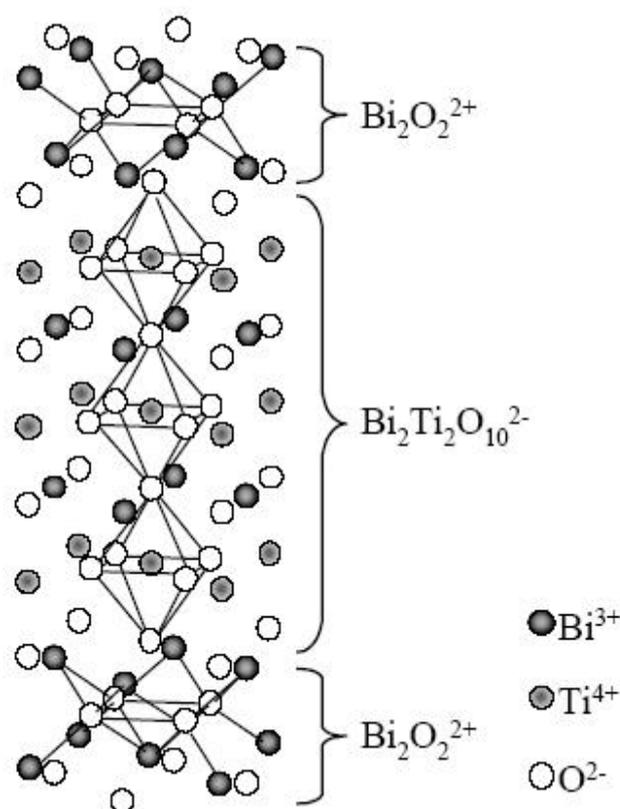


Fig. 3 Idealized structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ showing the bismuth oxide layers and pseudo perovskite units.

More recently, Aurivillius phases have been the subject of renewed interest due to their attractive anion properties. Hence, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ possesses an electrical conductivity that is highly anisotropic, with the maximum value in the same plane as the polarization [27]. As this conductivity is relatively high, it is very difficult to pole [36]. Having this in mind, synthesis of more resistive $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics would be a preferable advance in obtaining of well-densified ceramics with small grains randomly oriented to limit the conductivity along the $(\text{Bi}_2\text{O}_2)^{2+}$ layers [36].

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is monoclinic at room temperature, very-high-resolution powder diffraction data suggest that powder samples of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are actually orthorhombic at room temperature [37]. In addition to the ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase [27, 38, 39] the ternary Bi-Ti-O system contains several other bismuth titanates such as the dielectric $\text{Bi}_2\text{Ti}_2\text{O}_7$ phase

[40] and the electrooptical and photo-conducting $\text{Bi}_{12}\text{TiO}_{20}$ phase [41]. The phase diagram of the $\text{Bi}_2\text{O}_3\text{-TiO}_2$ system has been investigated by Speranskaya *et al.* [42]. They reported the existence of two additional phases: $\text{Bi}_8\text{TiO}_{14}$ and $\text{Bi}_2\text{Ti}_4\text{O}_{11}$. There are some divergent opinions about the true symmetry of the ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. It has optically been determined to be monoclinic but diffraction studies have defined it as orthorhombic [27, 28, 43, 44]. The reason for this is that the optically determined monoclinic β -angle is very close to 90° .

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ single crystals demonstrate *bi*-axial polarization. Along the *a*-axis they can be polarized up to $50 \mu\text{C}/\text{cm}^2$ while the polarization along the *c*-axis does not exceed $4 \mu\text{C}/\text{cm}^2$ [27]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ also has a unique rotation of the optical indicator upon polarization switching [45].

4. Methods for synthesis of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were conventionally prepared by a solid-state reaction process, where an oxide mixture of Bi_2O_3 and TiO_2 was ball milled, calcined at an intermediate temperature and finally sintered at a high temperature [46, 47, 48]. The conventional method requires a high calcination temperature, usually leading to inevitable particle coarsening and aggregation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. The presence of hard particle agglomerates will also result in a poor microstructure and properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics [49]. Many efforts have been made to avoid this problem by lowering the calcination temperature. The methods reported in literature for preparing $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics include co-precipitation [46, 50, 51], sol-gel [52, 53], hydrothermal [54], and molten salt synthesis [55].

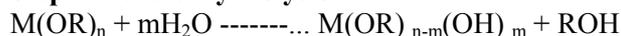
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesis techniques were mentioned in a lot of papers. All techniques and methods can produce ceramics with device-quality characteristics. Numerous different thin film deposition techniques exist, and these techniques are usually divided in two main groups, Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD) [56].

4.1. Chemical methods for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powder synthesis

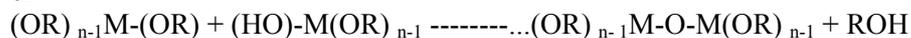
A lot of papers showed the advantages of chemical methods. Most ceramic techniques consist of control of morphology, particle size, homogeneity and possible reduction in the sintering temperature. A $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ precursor can be prepared by coprecipitating bismuth and titanium hydroxides. Most of the chemistry-based preparation routes for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ involve calcination at elevated temperatures in order to realize the precursor-to-ceramic conversion. In a completely different approach using an amorphous $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ hydroxide precursor, nanocrystalline particles of layered perovskite $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ are synthesized by mechanical activation, skipping the detrimental crystallite coarsening and particle aggregation encountered at high temperatures.

Sol-gel is a method for preparing metal oxide glasses and ceramics by hydrolyzing a chemical precursor to form a sol and then a gel, which on drying (evaporation) and pyrolysis gives an amorphous oxide. Upon further heat treatment crystallization can be induced. There are three basic steps involved: (i) partial hydrolysis of metal alkoxides to form reactive monomers; (ii) polycondensation of these monomers to form colloid-like oligomers (sol); (iii) additional hydrolysis to promote polymerization and cross-linking leading to a 3-dimensional matrix (gel) [57, 58].

As polymerization and cross-linking progress, the viscosity of the sol gradually increases until the sol-gel transition point, where viscosity abruptly increases and gelatin occurs.

Step 1- Partial hydrolysis**Step 2 -Condensation**

or

**Step 3**3D cross-linking between $(RO)_{n-m}M-O-M(OR)_{n-m}$ molecules

In the sol-gel technique, the structural and electrical properties of the final product (films) are strongly dependent on the nature of precursor solution, deposition conditions, and the substrate. Sedlar and Sayer [59] describe a modified sol-gel method. Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in concentrated nitric acid or glacial acetic acid, diluted and mixed with titanium stock solution. The latter solution consists of titanium isopropoxide, acetylacetone and methoxyethanol mixed in the molar ratio 1:1:4. Gu and others [60] prepared a Bi-Ti solution by mixing bismuth nitrate and titanium butoxide in the presence of acetic acid. Rao and others [61] prepared $Bi_4Ti_3O_{12}$ by the above two methods. Bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$, and titanium isopropoxide, $Ti(OC_3H_7)_4$ were the starting materials. Bismuth hydroxide was prepared by dissolving bismuth nitrate in water containing a sufficient amount of nitric acid to give a clear solution, which was then added slowly to an equal volume of concentrated ammonia under constant stirring. Titanium hydroxide was prepared by dissolving $Ti(OC_3H_7)_4$ in isopropanol and adding this solution slowly to a mixture containing 1:1:2 ammonium hydroxide (30%)-isopropanol and deionised water while stirring. Known amounts of bismuth and titanium hydroxides were individually heat treated at 600 °C for 1h to determine the exact amounts of Bi_2O_3 and TiO_2 contents in the required proportion so as to yield 0.02 mol stoichiometric $Bi_4Ti_3O_{12}$ and made into a slurry with 1:1 ammonium hydroxide, stirred for about 12h and dried at 60 °C. Rao and others authors [60] showed a second way of synthesis of $Bi_4Ti_3O_{12}$ from a sol-gel process. Bismuth acetate $Bi(CH_3COO)_3$ and $Ti(OC_3H_7)_4$ were the starting materials with 2-methoxy ethanol (2-MOE) and acetic acid (HAC) as a solvent for sol-gel synthesis. 0.04 mol of $Bi(CH_3COO)_3$ was added to a mixture containing 2-MOE and HAC in the ratio 2:1. The wet gel was dried in an oven at 100 °C and the gel powder was heat treated at 300 °C for several hours until all carbon was removed. From their results it is apparent that $Bi_4Ti_3O_{12}$ can be easily synthesized from corresponding hydroxide precursors at a temperature as low as 750 °C. Pellets derived from a mixture of hydroxide precursors showed a density close to 88 % of the theoretical density that was slightly higher than that of pellets derived from the sol-gel method.

Dhage and other [62] used a simple *citrate-gel* process to prepare nanocrystalline $Bi_4Ti_3O_{12}$ (Fig. 4). The citrate gel process offers a number of advantages for the preparation of fine powders of many complex oxides as quoted in literature [63-66]. Bi_2O_3 , $TiCl_4$ and citric acid were used for the preparation of $Bi_4Ti_3O_{12}$. $TiCl_4$ was diluted with ice-cold water to form $TiOCl_2$; a stoichiometric quantity of Bi_2O_3 was dissolved in hydrochloric acid and added to the mixture containing the required amount of $TiOCl_2$ and heated in a water bath. The molar ratio used for Bi:Ti: citric acid was 4:3:7. Since there was no precipitation during mixing, the pH of the solution was not varied. On heating in a water bath at 373 K, a light yellowish gel was formed after evaporation of water. Subsequently, the gel was decomposed at various temperatures ranging from 423 to 1173 K. The gel initially started to swell and filled the beaker producing a foamy precursor. This foam consisted of very light and homogeneous flakes of a very small particle size. On the basis of all experimental results it can be concluded that the values of coercive field and spontaneous polarization obtained for the citrate method are superior to those for ceramic samples.

Hydrothermal material processing is becoming a popular field of research, particularly after the successful development of the ceramic processing technology during 1970s. Further there is growing interest to enhance hydrothermal reaction kinetics using

microwave, mechanical mixing, and electrochemical reactions. The duration of the experiments is reduced by two orders of magnitude, at least, which makes the technique more economic. The *microwave hydrothermal* technique is more economic. The microwave hydrothermal technique is especially handy for synthesis of oxide ceramics. Additionally, the crystal size, morphology and level of agglomeration of different ceramic oxides can be controlled through careful selection of the ratio of starting materials, pH, time, and temperature. Submicron sized powders of TiO_2 , ZrO_2 , KNbO_3 , BaTiO_3 , and others, and their solid solutions have been prepared by this way. This has made the technique a more valuable one in the low temperature production of fine ceramic powders [67-69].

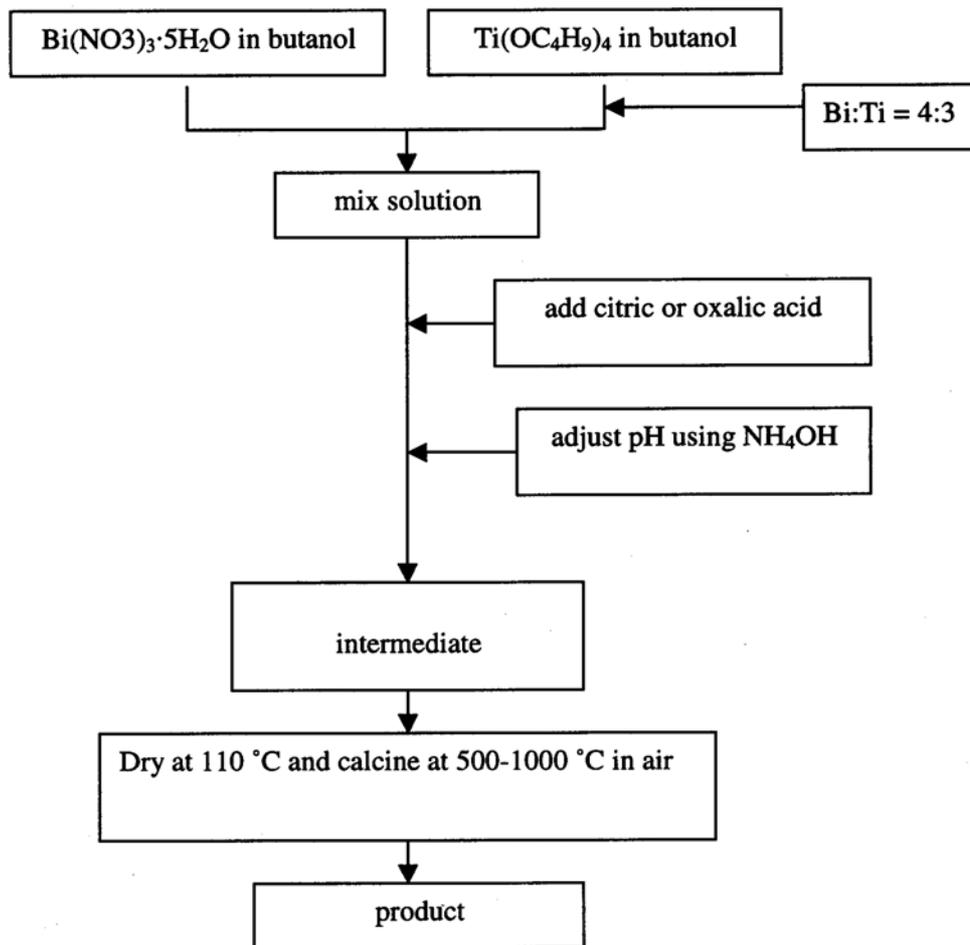


Fig. 4 Schematic diagram used for preparing citrate and oxalate intermediates and the final product.

As a method for synthesizing high quality powders that have many advantages, such as a high degree of crystallinity, well-controlled morphology, high purity and narrow particle size distribution, hydrothermal synthesis was regarded as a promising way to prepare bismuth titanate powders [70, 71]. Until now, several papers have reported on successful synthesis of bismuth titanate powders by hydrothermal processes. The starting materials for hydrothermal synthesis may be all kinds of compounds that can be dissolved in water under high-temperature and high-pressure. Yang and other [72] used titanium butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$), titanium chloride (TiCl_4) and anatase titania (TiO_2) powder as titanium salts, bismuth nitrate ($\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$) and bismuth hydroxide ($\text{Bi}(\text{OH})_3$) were used as bismuth salts in their

experiment. The hydrothermal process of bismuth titanate is shown in Fig. 5. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanocrystalline particles were hydrothermally synthesized at temperatures of 180-230°C. The crystallinity and particle sizes of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders increased with rinsing reaction temperature and time.

A simple *urea precipitation* route was adopted for the preparation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders. Urea is used as fuel, precipitating agent and as a resin former with formaldehyde [73-77]. When urea is used along with nitrate salt of a cation and heated at 673 K, an exothermic reaction between nitrate (oxidant reactant) and urea (fuel) leads to the formation of corresponding nanocrystalline oxides. The main advantage is that the necessary heat for synthesis is obtained directly from the reaction [73, 74]. Urea decomposed around 373 K to produce carbon dioxide and ammonia, thereby increasing the pH of the solution at which metal cation precipitation takes place [75]. Dhage and other used Bi_2O_3 , TiCl_4 and urea for the preparation of bismuth titanate. The molar ratio used was $\text{Bi}:\text{Ti}:\text{urea} = 4:3:35$. The precipitate was decomposed at various temperatures ranging from 423 to 1173 K. The precipitate initially started to swell and fill a beaker, producing a foamy precursor. This foam consisted of very light and homogeneous flakes of a very small particle size. The values of the coercive field and spontaneous polarization obtained for the urea method are superior to those samples prepared by the ceramic method [76].

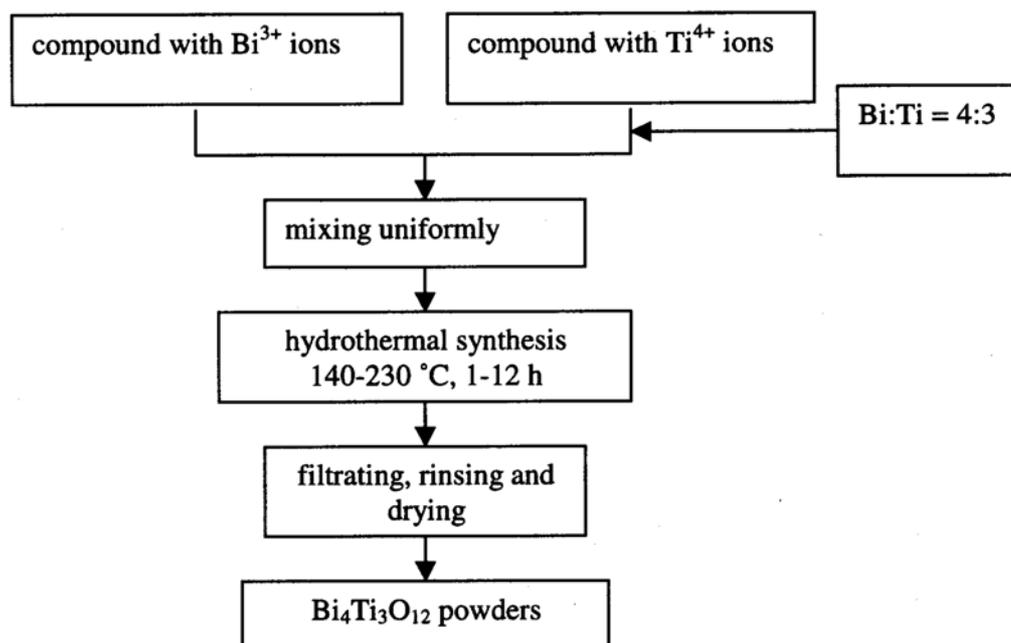


Fig. 5 Flow chart of the hydrothermal process.

Although the sol-gel process utilizes expensive precursors and depends on a critical drying process, the co-precipitation process is limited by similar solubility constants in cation solutions. On the other hand, the *polymeric precursor method* named Pechini's method [78], which employs complexing of cations in an organic media, makes use of low cost precursors and results in a homogeneous ion of a polyester resin during the synthesis. No segregation of cations was observed during thermal decomposition of the organic material. The procedure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ synthesis, based on Pechini's method (Fig. 6) [78], starts from the fact that certain

α -hydroxycarboxylic organic acid can form polybasic acid chelates with several cations. After addition of a polyhydroxylic alcohol and heating, the chelate transforms into a polymer, with homogeneously distributed cations. The organic part is subsequently eliminated at temperatures as low as 300°C, forming reactive oxides with well-controlled stoichiometry.

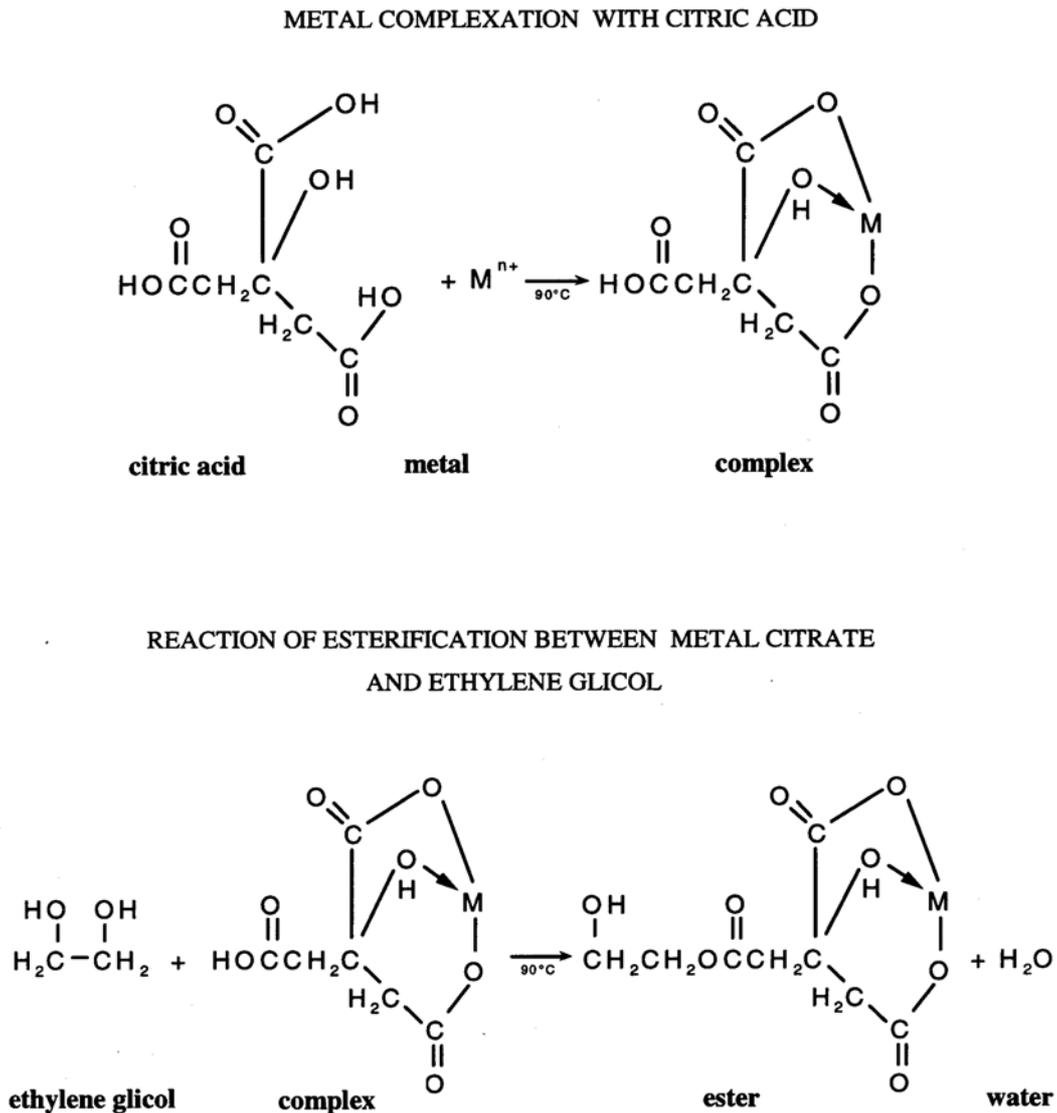


Fig. 6 The procedure of synthesis, based on Pechini's method.

4.2 Mechanically assisted synthesis

The most effective method for mechanically activated synthesis (mechanical activation and mechanochemical synthesis), especially for obtaining highly disperse systems,

is grinding bodies compared to the grains of materials being ground [79]. Mechanical activation is a process during which, from the viewpoint of changes of free energy, changes occur in the amount of accumulated energy. During the formation of a new surface, the increase of the energy in surface layers occurs. In that stage the starting material is transformed into a new material with a completely different structure and properties. Even though the mechanisms of energy exchange during these processes are not completely clear, they efficiently contribute to mechanical activation, generally leading to physical and in some cases to chemical changes in the material. Proper selection of milling parameters has an influence on the onset of the solid-state reaction. Intensive milling enables increased reactivity of the starting powders due to appropriate physicochemical changes in the material, which can lead to a reduction in the synthesis temperature. The chemical reactivity of starting materials could be improved significantly upon appropriate mechanically assisted treatment and the subsequent calcination temperature for forming the ceramic phase was lowered.

A mechanochemical process, which is also known as mechanical alloying, has been recently employed to prepare nano-sized oxides and compounds, superconductors, magnetic ferrites and ferroelectric powders [80]. This mechanical technique is superior to both the conventional solid-state reaction and the wet-chemistry-based processing routes for ceramic powders for several reasons. It uses low-cost and widely available oxides as the starting materials and skips the calcinations step at an intermediate temperature, leading to a simplified process [81]. Furthermore, the mechanically derived powders possess a much higher sinterability than those powders synthesized by conventional solid-state reaction and most of the wet-chemical processes [82].

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 [80]. In addition, the nucleation and subsequent growth of perovskite crystallites were triggered by mechanical activation at room temperature [81].

Formation of bismuth titanate during mechanical activation starting from Bi_2O_3 and TiO_2 has been the subject of research of lot of authors. Synthesis of bismuth titanate, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, was performed by mechanical activation and thermal treatment. Milling for up to several hours in a planetary ball mill mechanically activated an equimolar mixture of Bi_2O_3 and TiO_2 powders. A small amount of mechanically activated mixtures have been pressed into briquettes and calcined at high temperature. Kong and coauthors [80], prepared nano-sized $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders directly from their oxide mixture by a high-energy ball milling process. A $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase can be formed after milling for 9h. An almost single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics was obtained by sintering the synthesized powders at temperatures ranging from 750–950°C. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h exhibited a density of 7.91 g cm^{-3} .

5. Properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a material with a typical plate-like microstructure that has anisotropic properties, a low coercive field (E_c), small remnant polarization (P_s) excellent fatigue properties and retention time. The synthesis route has a strong influence on the structure and properties of BIT.

It is important to point out the influence of microstructure on the properties of bismuth titanate. A typical example of a plate-like structure can be observed in Fig. 7. Xu and Chen [83] obtained BIT with the noted microstructure after sintering at 1150°C in air for 3h, where grains with two different morphologies were determined. However, the major phase was identified as $\text{Bi}_4\text{Ti}_3\text{O}_{12}$.

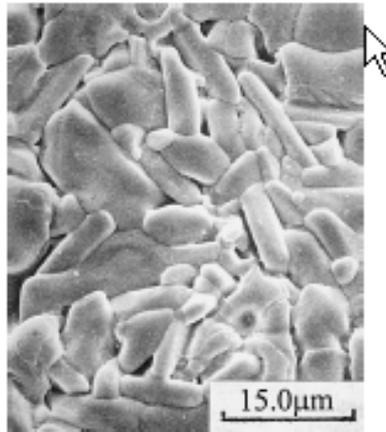


Fig. 7 Microstructure of $\text{Bi}_2\text{O}_3 \cdot 2\text{TiO}_2$ ceramics sintered at 1150°C in air for 3h.

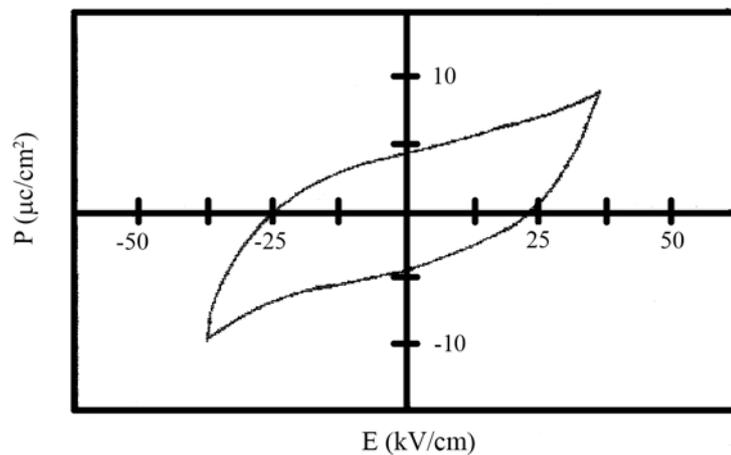


Fig. 8 Hysteresis loop of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ prepared by the citrate method.

Dhages and co-authors [62] synthesized $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ by the citrate method showing the influence of processing on ferroelectric properties (Fig. 8). The ferroelectric hysteresis loop parameters measurements of the pellet sintered at 1273 K showed the values of spontaneous polarization, $P_s = 9\ \mu\text{C cm}^{-2}$, remnant polarization, $P_r = 4\ \mu\text{C cm}^{-2}$ and coercive field, $E_c = 25\ \text{kV cm}^{-1}$ at an applied voltage of $53.6\ \text{kV cm}^{-1}$ without an electric breakdown occurring. The relative density of the pellet was 90%. The reported values of these parameters varied in the range of $E_c = 25\text{-}100\ \text{kV cm}^{-1}$ and $P_s \sim 24\text{-}40\ \mu\text{C cm}^{-2}$ depending on preparation conditions [80]. The samples prepared by the ceramic technique have $P_s = 2\ \mu\text{C cm}^{-2}$, remnant polarization $P_r = 0.5\ \mu\text{C cm}^{-2}$ and coercive field, $E_c = 23\ \text{kV cm}^{-1}$ at an applied field of $40\ \text{kV cm}^{-1}$ without an electric breakdown occurring.

$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics were conventionally prepared by a solid-state reaction process, where an oxide mixture of Bi_2O_3 and TiO_2 was ball milled [80]. Fig. 9 shows the dielectric constant and dielectric loss of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h, as a function of frequency from 100 Hz to 100 kHz at room temperature. The dielectric slightly decreases within the measured frequency range. Dielectric loss remains almost constant from 100 kHz to 10 kHz and increases thereafter. Dielectric constants of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 750°C and 950°C are 189 and 312, respectively. P - E hysteresis loops of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at different temperatures are shown in Fig. 10 [80].

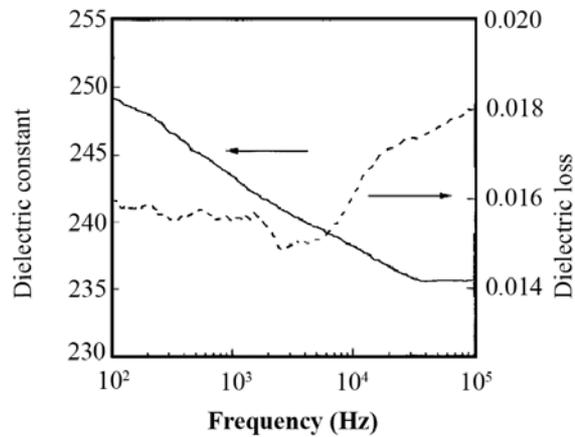


Fig. 9 Dielectric constant and dielectric loss of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C as a function of frequency

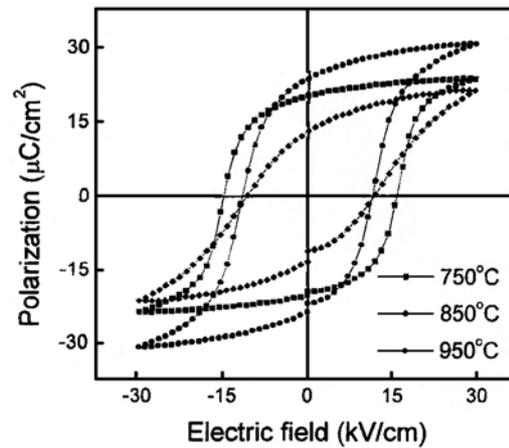


Fig. 10 Representative P - E hysteresis loops for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics.

The remnant polarization and coercive field are derived from the loops and are plotted in Fig. 11 [80].

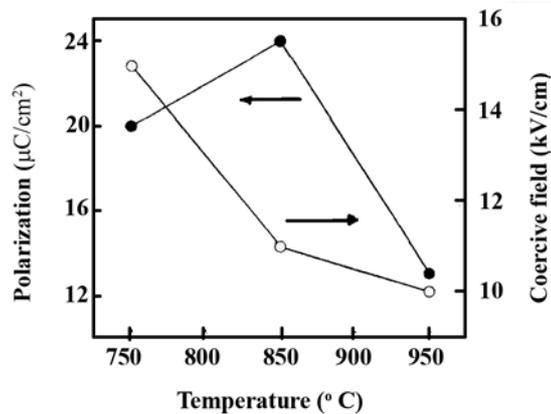


Fig. 11 Ferroelectric parameters of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics as a function of sintering temperature.

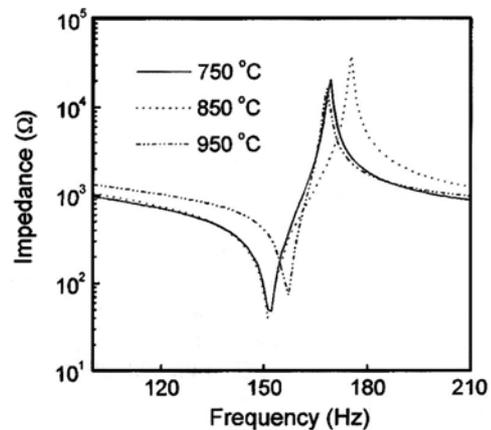


Fig. 12 Impedance characteristic curve of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at different temperatures for 1h.

Fig. 12 [80] shows the impedance characteristic curve of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h. Piezoelectric parameters calculated from the impedance-frequency curves as a function of the sintering temperature are shown in Fig. 13 [80]. The samples sintered at 850°C exhibit the best piezoelectric property.

The pyroelectric coefficient as a function of measuring temperature for the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h is presented in Fig. 14 [80]. The fresh-sintered sample shows a broadened peak at about 100°C , which disappears when measured for the second time with a great reduction in the pyroelectric coefficient. The fresh-poled sample exhibits the most distinguished pyroelectric property with a maximum value at about 175°C , which diminishes when measured for the third time, of the poled sample remains almost unchanged, especially at the end of low temperature. This indicates a rather strong influence of processing and measurement' conditions on the BIT properties.

Kong and coauthors [80], prepared nano-sized $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ powders directly from their oxide mixture by a high-energy ball milling process. A $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase can be formed after milling for 9h. An almost single phase of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics was obtained by sintering the synthesized powders at temperatures ranging from $750\text{--}950^\circ\text{C}$. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h exhibited a density of 7.91 g cm^{-3} , a dielectric constant of 243, a dielectric loss of 0.017, a remnant polarization of $24\text{ }\mu\text{C cm}^{-2}$ and a coercive field of 11 kV cm^{-1} , respectively.

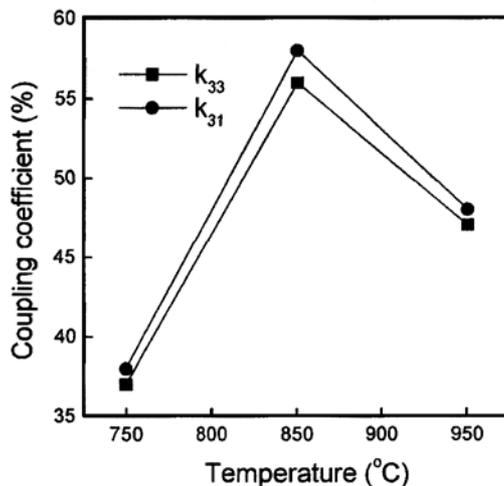


Fig. 13 Piezoelectric coupling coefficient of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics as a function of the sintering temperature.

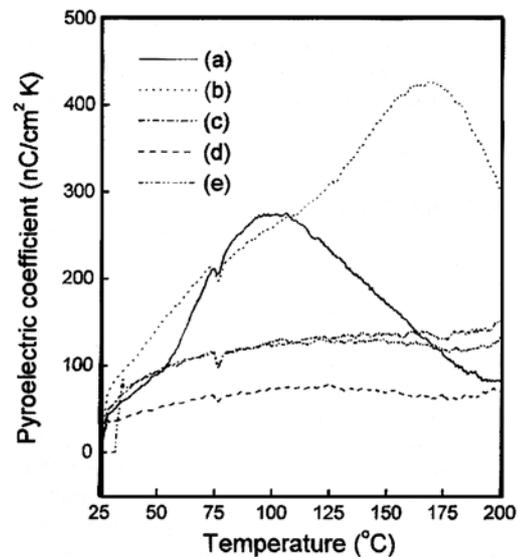


Fig. 14 Pyroelectric coefficient curves of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics sintered at 850°C for 1h: (a) fresh sintered sample, (b) second measurement of the fresh sample, (c) fresh poled sample, (d) second measurement of the poled sample and (e) third measurement of the poled sample.

Piezoelectric parameters of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics are $k_{33} = 56\%$, $k_{31} = 58\%$. The $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics also possessed good pyroelectric properties. These results indicate that the high-energy ball milling process is a promising way to prepare $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics.

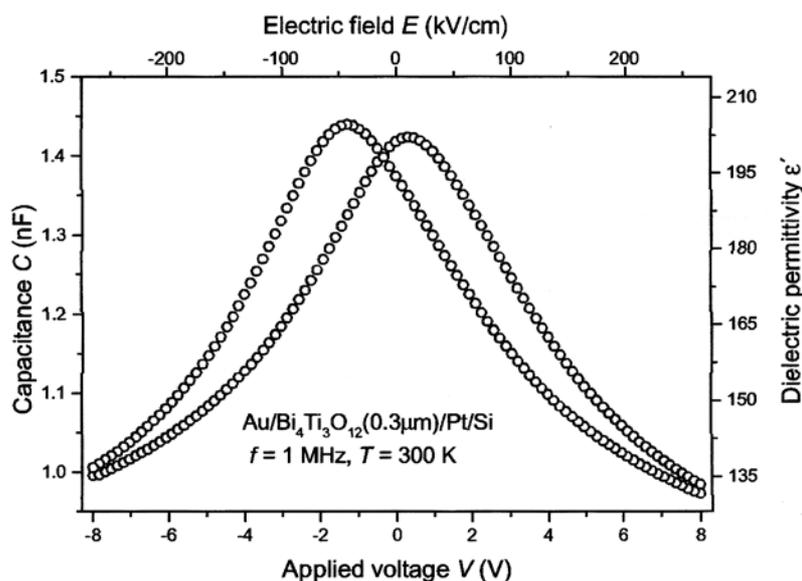


Fig. 15 Capacitance-voltage (C - V) characteristic.

Many authors investigated the properties of bismuth titanate thin films. Schuisky [84] demonstrates the electric field dependence of the dielectric permittivity ϵ for film deposited by the conventional CVD method. The measurement was carried out at a frequency of 100 kHz (Fig. 15). C - V characteristics are non-linear with a hysteresis behavior. Attainability as high as 51% was achieved since ϵ could be decreased to 51% of the maximum value by applying a bias voltage of 10.5 V (electric field strength of 350 kV cm^{-1}).

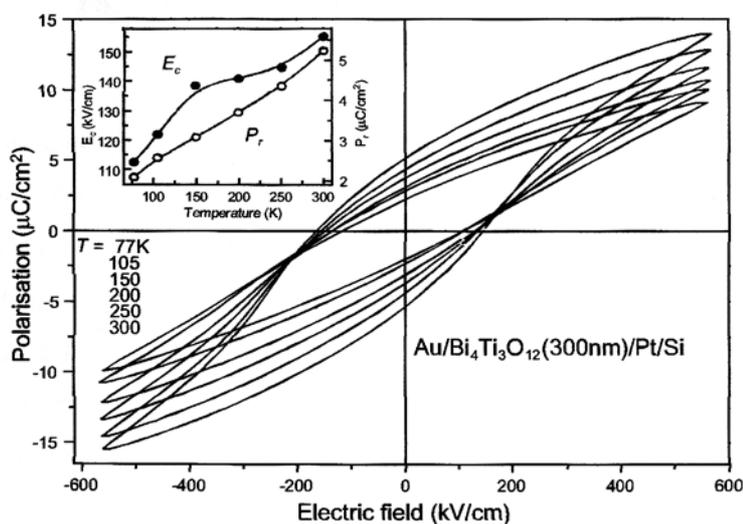


Fig. 16 Ferroelectric polarization loops measured at various temperatures. E_c and P_r vs. temperature are shown in the insert.

This performance in combination with sufficient low $\tan \delta \sim 0.018$ promises a wide variety of electrically tunable device applications. Measurements of I - V characteristics yielded at room temperature a resistivity of $2 \cdot 10^9 \Omega \text{ cm}$ and a leakage current of about $3 \cdot 10^{-5} \text{ A cm}^{-2}$ at 100 kV cm^{-1} [84]. Schuisky also presented the results obtained for thin films of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ deposited by the same method (chemical vapor deposition) starting from other

precursors such as metal iodides, BiI_3 and TiI_4 . Fig. 16 [83] shows ferroelectric hysteresis P - E polarization loops traced at various temperatures. Measurements at room temperature yield the remanent polarization $P_r = 5.3 \mu\text{C cm}^{-2}$, induced polarization of $14.9 \mu\text{C cm}^{-2}$ at 560 kV cm^{-1} , and coercive field as high as 150 kV cm^{-1} . It is important to note that the values for thin films compared to bulk are different.

6. Applications of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$

It was pointed out that bismuth titanate belongs to the Aurivillius family, having three oxygen octahedrals between two bismuth oxide layers. Its crystal symmetry in the paraelectric phase is tetragonal, and it appears that $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is one of the few compounds within the Aurivillius family that has a monoclinic ferroelectric structure, with one component of polarization in plane of the layers. The resulting domain-wall structure is complex, leading to complicated but also interesting electric and piezoelectric properties. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ is a ferroelectric material, which in thin film form can be used for ferroelectric or electrooptic devices [85]. High Curie temperature, excellent fatigue behavior and reasonable ferroelectric properties make $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ an attractive candidate for ferroelectric (FERRAM) or dynamic (DRAM) random access memories [85]. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films formed on a superconductor showed promising ferroelectric properties and the potential for integration into a semiconductor device processing technology [86]. Single crystal $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has low dielectric permittivity, which makes it useful for various applications such as memory elements, optical displays, and piezoelectric converters of pyroelectric devices in a wide temperature range from 20-600 °C. $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics have been used in capacitors, transducers, sensors, etc [87].

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Резюме: Семейство висмут-титанатовых сегнетоэлектрических материалов слоистой структуры - $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), из-за исключительных диэлектрических, пьезоэлектрических и пироэлектрических свойств очень привлекательно для применения в электронике. Характеризуется хорошей сегнетоэлектрической стабильностью, высокой температурой Кюри и хорошей устойчивостью к температурным изменениям. Методы синтеза BIT материалов зависят от конечного продукта – керамики или пленки. Структура и свойства висмут-титанатовых материалов выявляют значительную зависимость от используемого метода синтеза. В данной обзорной работе мы попытались представить более обширный анализ

структуры методов синтеза и свойств висмут-титанатовы́й сегнетоэлектрических материалов.

Ключевые слова: *Керамика $Bi_2Ti_3O_{12}$, слоистая перовскитная структура, методы синтеза, диэлектрические и сегнетоэлектрические свойства.*

Сadržaj: *Фамилија бизму́й-тита́на́йних фероелеќтричних ма́теријала слојеви́те ст́рукту́ре - $Bi_2Ti_3O_{12}$ (BIT) врло је а́трактивна за приме́ну у елеќтрониче́и збо́г изузе́йних диелеќтричних, пиезоелеќтричних и пироелеќтричних караќтерис́тика. Одлику́је се добром пиезоелеќтричном ст́абилно́шћу, високом Кири те́мпера́туром и добром о́порно́шћу на те́мпера́турне промене. Ме́тоде синте́зе BIT ма́теријала су различите, зависно од то́га да ли се жели доби́ти керамика или филм. Ст́рукту́ра и свој́ства бизму́й-тита́на́йних ма́теријала по́казују значајну зависно́ст од приме́њене ме́тоде синте́зе. Овим пре́гледним радом смо учинили по́кушај да дамо де́таљнију анализу ст́рукту́ре, ме́тода синте́зе и свој́ста бизму́й-тита́на́йних фероелеќтричних ма́теријала.*

Кључне речи: *$Bi_2Ti_3O_{12}$ керамика; слојевита перовскитна структура; методе за синтезу; диелектрична и фероелектрична својства.*
