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Citation: [Journal of Applied Physics](#) **101**, 084112 (2007); doi: 10.1063/1.2719013

View online: <http://dx.doi.org/10.1063/1.2719013>

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# Ferroelectric fatigue endurance of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ thin films explained in terms of x-ray photoelectron spectroscopy

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(Received 27 December 2006; accepted 21 February 2007; published online 26 April 2007)

The nature of defects in polycrystalline  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  (BLT) thin films with  $x=0.00, 0.25, 0.50,$  and  $0.75$  was evaluated by x-ray photoemission spectroscopy measurements. The influence of oxygen vacancies and substitution of Bi for La atoms were discussed. In the BLT thin films, it was found that the oxygen ions at the metal-oxygen octahedral were much more stable than those at the  $[\text{Bi}_2\text{O}_2]$  layers. On the other hand, for  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT) thin film, oxygen vacancies could be induced both at the titanium-oxygen octahedral and at the  $[\text{Bi}_2\text{O}_2]$  layers. The oxygen-vacancy defect pairs determined in BIT and  $\text{Bi}_{3.75}\text{La}_{0.25}\text{Ti}_3\text{O}_{12}$  (BLT025) can pin the polarization of surrounding lattices leading to fatigue of capacitors. Meanwhile, the concentration of similar defect pairs is relatively low in heavily doped BIT films and then good fatigue resistance is observed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719013]

## I. INTRODUCTION

There have been extensive investigations of ferroelectric thin films due to their potential application in nonvolatile ferroelectric random access memories (NVRAMs).<sup>1</sup> In most applications involving ferroelectric films, there are several parameters to technological adoption, such as fatigue-endurance, remnant polarization ( $2P_r$ ), coercive field ( $2E_c$ ), and processing temperature.<sup>2,3</sup> Recently, lanthanum bismuth titanate,  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  (BLT), has attracted considerable attention for the NVRAM applications, because it includes no lead, and it has large  $2P_r$ , low processing temperature and fatigue-endurance with Pt electrode.<sup>2</sup> BLT belongs to the family of bismuth layer structured ferroelectrics (BLSFs) with a general formula of  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ . In this notation  $A$  represents a mono-, bi-, or trivalent ion,  $B$  denotes a tetra-, penta-, or hexavalent ion, and  $m$  is the number of  $\text{BO}_6$  octahedral in each pseudoperovskite block ( $m=1,2,3,\dots$ ). The pseudoperovskite blocks  $[(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}]$  are interleaved with bismuth oxide layers  $[(\text{Bi}_2\text{O}_2)^{2+}]$  along the  $c$  axis.<sup>4</sup> It is widely known that the  $[\text{Bi}_2\text{O}_2]$  layers have an important influence on the properties of BLSFs: the  $[\text{Bi}_2\text{O}_2]$  layers act as the insulating layers and are self regulated to compensate for space charge due to their net electric charge.<sup>5,6</sup> The remnant polarization of  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  shows a dependence on the La content: it increases first, maximizes at  $x=0.75$  and then decreases with further doping.<sup>7</sup> The improvement of  $2P_r$  for BLT can be ascribed to the restraint of oxygen vacancies due to the substitution of more stable La ions for the volatile Bi.<sup>2</sup> The decrease of  $2P_r$  is related to the relaxation of the structural distortion induced by La substitution.<sup>8</sup> Earlier work<sup>6</sup> pro-

posed that the self-regulating  $(\text{Bi}_2\text{O}_2)^{2+}$  layers in  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) can compensate the space charge near the electrode, playing a crucial role in its fatigue-free behavior, whereas another Aurivillius compound,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BT) (Ref. 9) exhibits a severe fatigue failure. From recent x-ray photoelectron spectroscopy (XPS) studies of BT ceramics,<sup>10</sup> and (001) epitaxial thin films of SBT and BIT.<sup>11</sup> Park *et al.*<sup>11</sup> argued that the difference in oxygen stability in the perovskite layer between SBT and BT, should be related to their distinct fatigue resistance, in addition to the universally accepted role of the  $(\text{Bi}_2\text{O}_2)^{2+}$  layer. In another investigation on the different fatigue behaviors of two iso-structural Aurivillius compounds, SBT and  $\text{Bi}_3\text{TiTaO}_9$ ,<sup>12</sup> Kang *et al.* more directly suggested that a Bi-free perovskite layer enhances its oxygen stability and, hence, leads to the fatigue-free property of SBT supporting the qualitative fatigue-free model inferred from previous XPS measurements.<sup>11</sup> However, a controversy arises from applying this hypothesis to fatigue-free behavior of  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ,<sup>2,13,14</sup> which has a significant amount of Bi in its perovskite layer  $(\text{Bi}_{1.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{10})^{2-}$ , even when the author<sup>2</sup> suggested that a partial La substitution for Bi can improve its fatigue resistance. In this article, x-ray photoelectron spectroscopy (XPS) analysis were undertaken on various La-substituted bismuth titanate films in order to probe their surface characteristics and to explore the fatigue-free and the role of La in the crystal lattice.

## II. EXPERIMENTAL PROCEDURE

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich), and bismuth nitrate (Aldrich) were used as raw materials.  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  thin films with  $x=0.00, 0.25, 0.50,$  and  $0.75$  (BIT, BLT025, BLT050, and BLT075) were prepared by the polymeric precursor method<sup>15</sup> from the spin-coating process. The viscosity of the resulting solution

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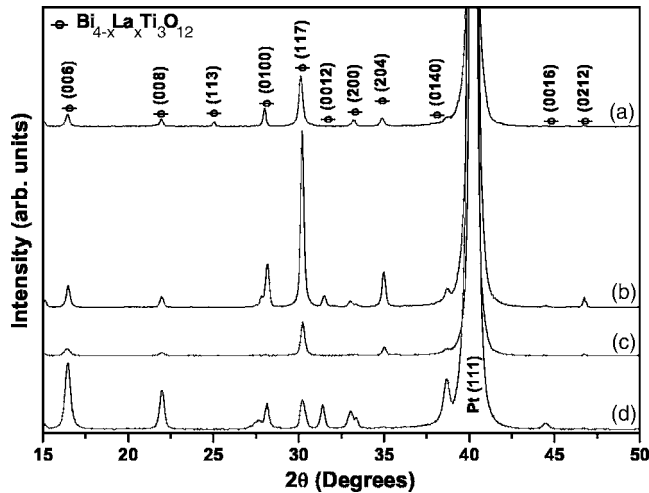


FIG. 1. X-ray diffraction for  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  films deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si and annealed at 700 °C for 2 h in static air: (a)  $x=0.00$ , (b)  $x=0.25$ , (c)  $x=0.50$ , and (d)  $x=0.75$ .

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 Pt(111)/Ti/SiO<sub>2</sub>/Si substrates. A platinum layer (140 nm) was used as the bottom electrode. The films were then annealed at 700 °C for 2 h in static atmosphere, always resulting in a thickness of approximately 410 nm. Phase analysis of the films was performed at room temperature by x-ray diffraction in the  $\theta$ - $2\theta$  mode scan, recorded on a Rigaku diffractometer (Rigaku-DMax 2500PC) using Cu  $K\alpha$  radiation. Thickness was evaluated by observing the cross section of the films using a scanning electron microscopy (Carl Zeiss, DSM940A). Since XPS is sensitive to the local electronic structure of constituent atoms, it can be used to probe the chemical nature and to investigate differences in the defect charge of the films. High-resolution photoelectron spectra were collected on a Physical Electronics PHI 1600/3057 spectrometer equipped with a monochromized Al  $K\alpha$  (1486.6 eV) X-ray beam with detection on the surface normal was used. The spectrometer was operated in fixed analyzer energy transmission mode and the pressure during analysis was about  $5.0 \times 10^{-10}$  Torr. Photoelectron spectra of Bi 4*f*, Ti 2*p*, and O 1*s* core levels were recorded using a computer controlled data collection system. The electron analyzer was set at pass energy of 10 eV.

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. 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). For the fatigue measurements, internally generated 8.6  $\mu\text{s}$  wide square pulses were used. After

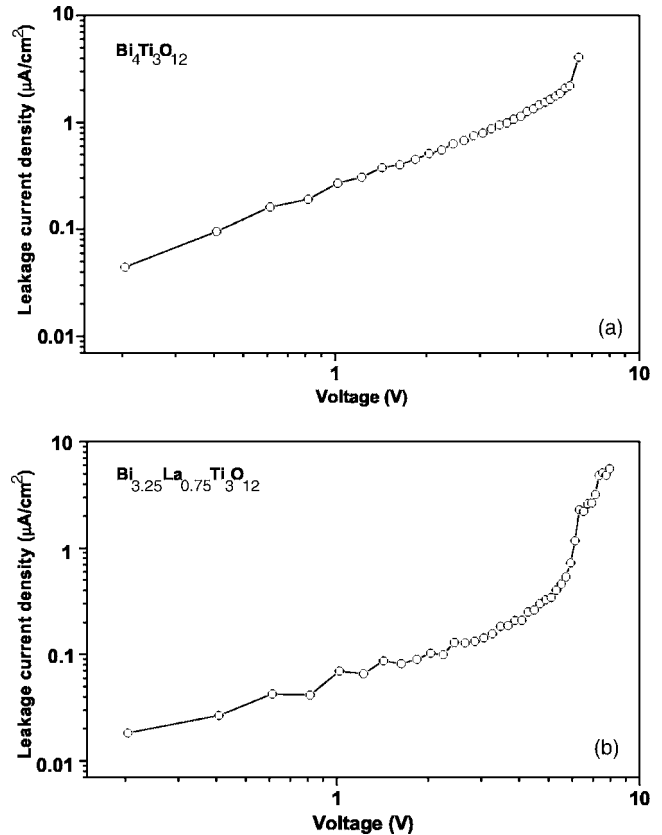


FIG. 2. Leakage current density in dependence of applied voltage for  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  thin films deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si and annealed at 700 °C for 2 h in static air: (a)  $x=0.00$ , (b)  $x=0.75$ .

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.

### III. RESULTS AND DISCUSSION

Figure 1 illustrates the x-ray diffraction data of the  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  films with  $x=0.00$ , 0.25, 0.50, and 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 orthorhombic to tetragonal being more evident in the  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$  film which possess a preferred orientation at  $2\theta=16$ . Besides the BLT peaks, the characteristic peak of Pt(111)/Ti/SiO<sub>2</sub>/Si substrates at  $2\theta=40$  was also identified.

A typical leakage current behavior for BIT and highly doped BLT thin films is given in Fig. 2. The curves were recorded with a voltage step width of 0.1 V and elapsed time of 1.0 s for each voltage. The measured logarithmic current density ( $\log J$ ) versus the logarithmic electric field ( $E$ ) is shown. Two clearly different regions were observed. In the low electric field region, the current density increases linearly with the external electric field, suggesting an ohmic conduction. At the higher field, the current density increases exponentially, which implies that at least one part of the conductivity results from the 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

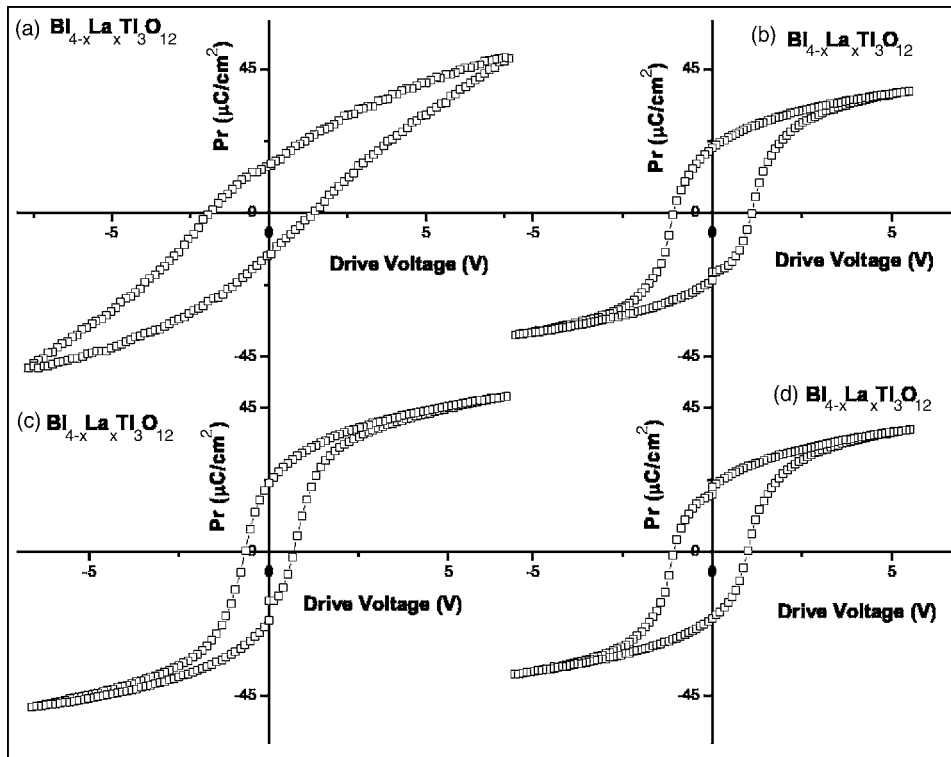


FIG. 3.  $P$ - $V$  hysteresis loops for  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  deposited on  $\text{Pt}(111)/\text{Ti}/\text{SiO}_2/\text{Si}$  and annealed at  $700^\circ\text{C}$  for 2 h in static air: (a)  $x=0.00$ , (b)  $x=0.25$ , (c)  $x=0.50$ , and (d)  $x=0.75$ .

introduced into the system. The improvement of leakage current with the lanthanum addition could be explained by a reduction of microcracks caused by residual stress. Since the orthorhombic structure and phase transition temperature reduces with increasing La concentration, the lattice volume changes and residual stress decreases during cooling.<sup>7</sup>

The hysteresis loops of the BIT and BLT thin films were measured at a frequency of 100 Hz (Fig. 3). 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 the films are highly resistive. A more regularly shaped hysteresis loop is observed for the lanthanum doped films. The preferred orientation of  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$  film leads to lower drive voltages to attain saturation in the hysteresis loops. 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  $x$ -ray diffraction data.

The fatigue endurance of pure and La substituted BIT thin films were tested at 1 MHz as a function of switching cycles by applying  $8.6\ \mu\text{s}$  wide bipolar pulses with maximum amplitudes of  $\pm 9$  V (Fig. 4).  $P^*$  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 polarization, which is an important variable for nonvolatile memory application. We claim that lanthanum decreases the ferroelectric properties and stabilizes the charged domain walls which interact with oxygen vacancies and inhibit fatigue. During fatigue there is an accumulation of oxygen vacancies near the electrode-film interface, which reduces the effective applied electric field. This fact is well-reflected

in fatigue measurements [Figs. 4(a)–4(d)], that clearly show that even after  $10^{10}$  switching cycles, no decay in the remnant polarization is observed for the heavily La substituted films ( $x=0.50$  and  $x=0.75$ ). In fact, the substitution of La for Bi can change the chemical environment of the perovskite layers and solve the fatigue problem of BIT thin films. Since a  $\text{La}^{3+}$  ion has no outer electron, in contrast to a  $\text{Bi}^{3+}$  ion, which has a lone pair of  $6s$  electrons, less hybridization with O  $2p$  should lead to less structural distortion.<sup>8,16</sup> 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 BIT films.

It is widely accepted that fatigue failure of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  thin films should be related to oxygen vacancies present at the titanium-oxygen octahedral.<sup>11</sup> Thus, to understand the fatigue failure in the layered perovskite materials is important to evaluate the nature of those defects. Photoemission of Bi  $4f$ , Ti  $2p$ , and O  $1s$  core levels are shown in [Figs. 5(a)–5(c)]. The binding energy of Bi  $4f$  slight changes for BLT025 thin film by about 0.2 eV, in contrast to those of BIT, suggesting the increase of chemical valence of Bi and Ti. That is to say, the chemical valence of Bi and Ti approaches three and four valence states, which implies that La substitution for the Bi brings about the restraint of the oxygen vacancy concentration in the vicinity of Bi and Ti. However, the binding energy is not so much affected by the increase of lanthanum concentration, indicating saturation of oxygen vacancies. This is evidence that the substitution can restrain the generation of oxygen vacancies. Our results are in agreement with the work of Lee *et al.*<sup>17</sup> Therefore, higher

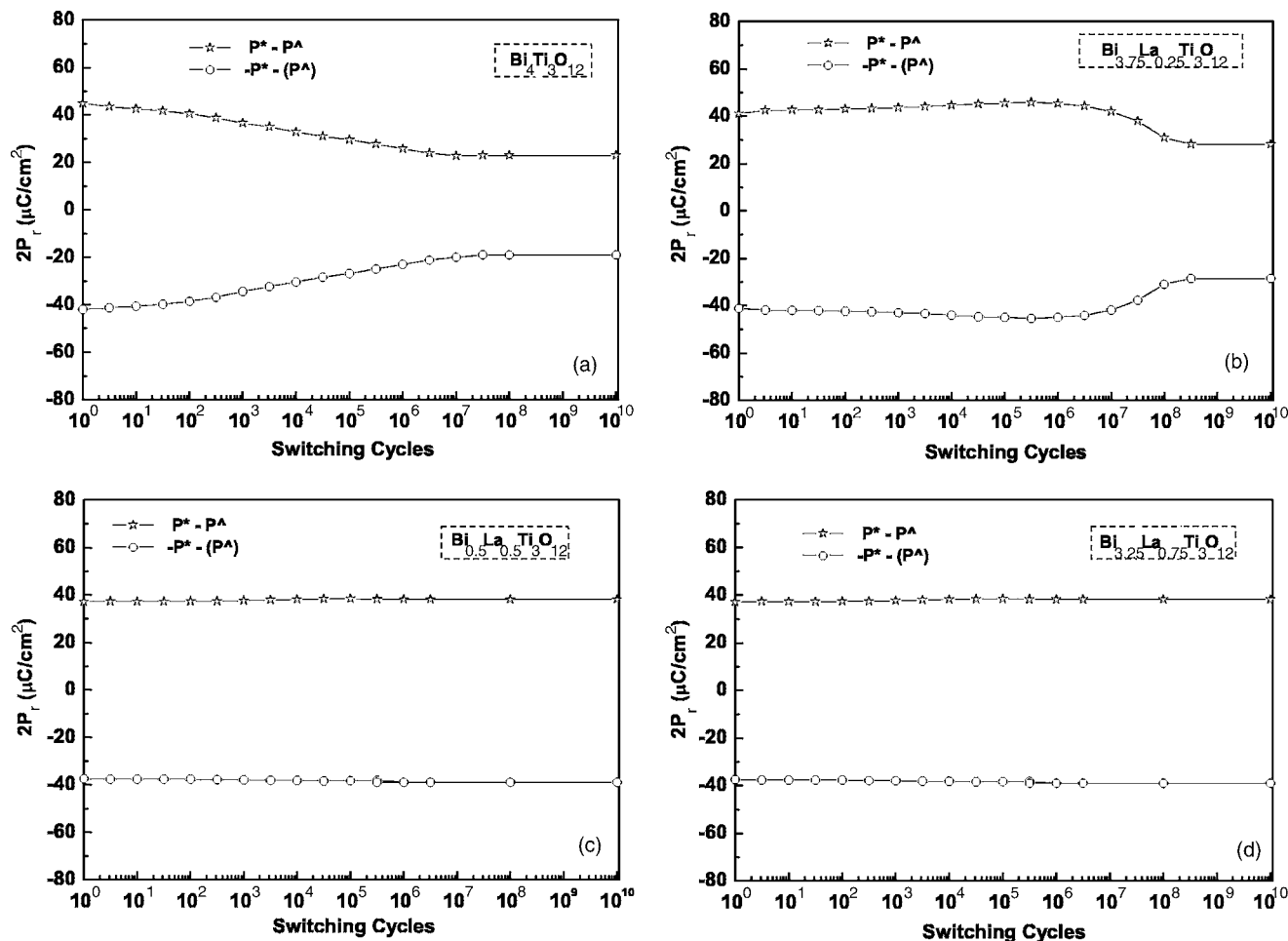


FIG. 4. Remanent polarization in dependence of switching cycles for  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  thin films deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si and annealed at 700 °C for 2 h in static air: (a)  $x=0.00$ , (b)  $x=0.25$ , (c)  $x=0.50$ , and (d)  $x=0.75$ .

lanthanum concentrations stabilize BIT film, suggesting that oxygen vacancies in BIT and BLT025 are the reason of unstable phase. Thus, when La content is lower than 0.50, the  $\text{TiO}_6$  octahedra linked to  $\text{Bi}_2\text{O}_2$  shrinks, restricting the movement of  $\text{Ti}^{4+}$  ions destroying the original functions of electrical insulation and space charge compensation. The oxygen vacancy acting as space charge will cause strong domain pinning and inhibits fatigue endurance. The photoemission spectra of Bi  $4f$  core levels for the BIT and BLT thin films indicates that the  $7/2$  and  $5/2$  spin-orbit double component are located at 159.1 and 164.4 eV, respectively. The spin-orbit splitting of Bi  $4f$  core levels is around 5.3 eV. The observed shift after lanthanum substitution suggests the existence of bismuth in the  $(+3-x)$  valence state. The Bi  $(+3-x)$  formal oxidation state can be generated due to a deficiency in oxygen and an enhanced concentration of oxygen vacancies in the vicinity of bismuth cations, either in the perovskite lattice structure or in the  $\text{Bi}_2\text{O}_3$  layer. Oxygen vacancies neighboring bismuth ions are more likely inside the  $\text{Bi}_2\text{O}_2$  layer than in the perovskite  $\text{BiTiO}_3$  structure. In the perovskite portion of the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  structure, the Bi ion is placed in the center of the unit cell built by Ti cations. The oxygen anions form octahedral ( $\text{TiO}_6$ ) enclosing the titanium ions. The Bi and Ti cations share oxygen atoms in the  $\text{BiTiO}_3$  unit cell and thus the strong Ti–O bonds in the per-

ovskite lattice are not easily broken implying a nonrandom distribution of oxygen vacancies and their confinement inside the  $\text{Bi}_2\text{O}_2$  layer.

Photoemission spectrum of Ti  $2p$  core levels for BIT and BLT thin films are shown in [Fig. 5(b)]. The Ti  $2p_{3/2}$  photoelectron peak appears at a binding energy position of 458.1 eV. The Ti  $2p_{3/2}$  peak is located at the binding energy lower than those reported for  $\text{TiO}_2$ , which range from 458.4 to 459.0 eV (Refs. 18 and 19) but it is close to the binding energy of 458.3 eV, reported by Murata *et al.*<sup>20</sup> for the  $\text{BaTiO}_3$  and  $\text{PbTiO}_3$  compounds. This indicates the  $4+$  valence state of the titanium atoms within the perovskite layer of bismuth titanate supporting our assumption about the oxygen vacancies residing inside the  $\text{Bi}_2\text{O}_2$  layer. The outstanding affinity of Ti toward oxygen could further explain the proposed BIT defect structure. Taking into account that ferroelectric responses of the Bi-layered perovskite materials are originated mainly from metal-oxygen octahedra, we argue that fatigue failures of BIT films should be related to the oxygen vacancies present at the titanium-oxygen octahedra. Therefore, the Ti  $2p$  peak for the BLT050 and BLT075 films are broader than that for the BLT025 suggesting some oxygens at the perovskite layers are taken out. Compare with BIT, the broadening of Ti  $2p$  peaks are similar and probably can be caused by the preferred orientation and other defects

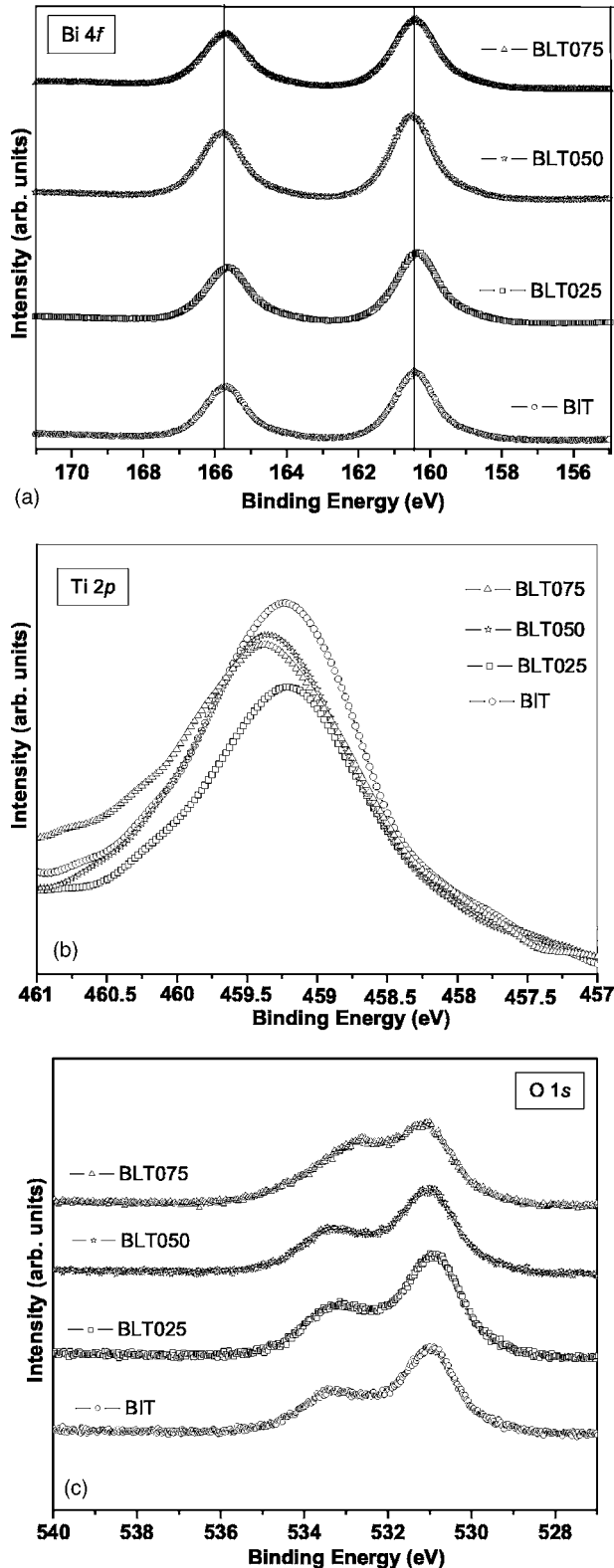
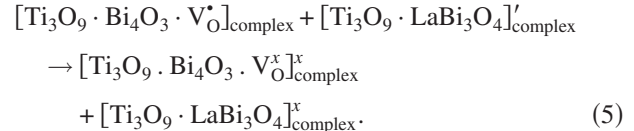
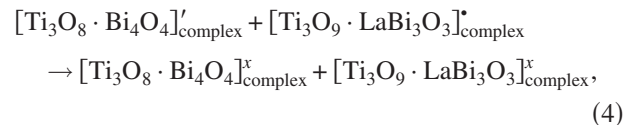
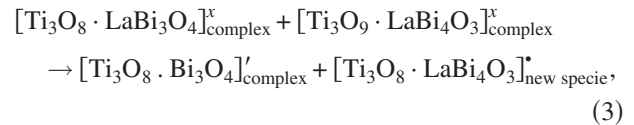
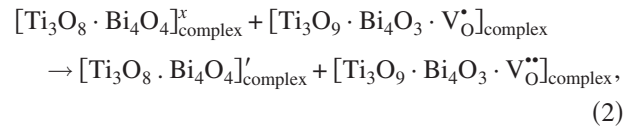
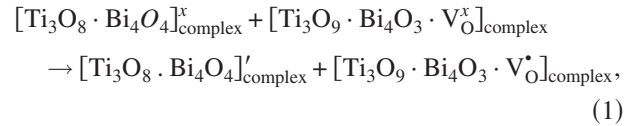


FIG. 5. XPS spectra of (a) Bi 4*f*, (b) Ti 2*p*, and (c) O 1*s* peaks for  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  thin films deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si and annealed at 700 °C for 2 h in static air: with  $x=0.00, 0.25, 0.50,$  and  $0.75$ .

present in the bismuth titanate lattice. These experimental results imply that oxygen vacancies could be induced in the neighborhood of the Bi and the Ti ions in BIT. Therefore, the oxygen atom in the stronger Ti–O bond carries a higher effective negative charge than in a weaker Bi–O bond. So

compared with the Bi–O bond, the Ti–O bond is not easily broken by a lanthanum addition. The electronic structure of [TiO<sub>6</sub>] is favored by three factors: lack of oxygen vacancies, small amount of lanthanum ions for charge compensation, and abundance of [Ti<sub>3</sub>O<sub>9</sub>·LaBi<sub>3</sub>O<sub>4</sub>]<sup>x</sup> complex. If lanthanum ions substitute the bismuth site, the presence of [Ti<sub>3</sub>O<sub>8</sub>·Bi<sub>4</sub>O<sub>4</sub>]<sup>x</sup> and [Ti<sub>3</sub>O<sub>9</sub>·LaBi<sub>3</sub>O<sub>3</sub>V<sub>O</sub>]<sup>x</sup> complexes will stabilize defects domains by charge compensation according to the following equations:



The line shape of the O 1*s* core level photoemission reveals two peaks [Fig. 5(c)]. The first one at the low binding energy side corresponds to the Ti–O bond while the second peak is ascribed to oxygen attached to bismuth. The oxygen atom in a stronger Ti–O bond carries a more effective negative charge than in a weaker Bi–O bond. The correlation between the effective charge of an oxygen atom and the binding energy of oxygen core electrons has been well-documented in the literature.<sup>21</sup> There is no evidence of a third peak in the O 1*s* photoemission that could be ascribed to OH groups likely to be present on the surface of the films. The OH groups 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.

#### IV. CONCLUSIONS

Pure and lanthanum-doped bismuth titanate thin films were prepared by the polymeric precursor method through annealing at 700 °C for 2 h. Lanthanum improved the fatigue resistance and ferroelectric properties of the films changing the structure from orthorhombic to tetragonal. XPS data reveal that oxygen vacancies are responsible for the unstable phase in the BIT films. On the other hand, when the La content is superior of 0.25 the phase can be stabilized. The XPS data reveal a nominal valence state of bismuth lower

than 3+ and for the Ti cations were found to be in the 4+ state. The oxygen vacancies are preferentially sited in the vicinity of bismuth ions, i.e., most probably confined in the Bi<sub>2</sub>O<sub>2</sub> layer, within the perovskite layer structure of BIT.

## ACKNOWLEDGMENTS

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

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