

A comparative study on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ferroelectric thin films derived by metal organic decomposition

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The crystal orientations and electrical properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) ferroelectric thin films were studied and compared. Stoichiometric BIT and BLT samples were deposited on Pt(111) substrates and crystallized at 750 °C to get mixed orientations. The BIT sample exhibited a/b axes orientation with (117) component, while the BLT sample was more c -axis oriented. The 2Pr values of such BIT and BLT were 34.3 $\mu\text{C}/\text{cm}^2$ and 25.7 $\mu\text{C}/\text{cm}^2$, respectively. Nevertheless, BLT has much better leakage current and polarization saturation properties. In order to obtain c -axis oriented BIT thin films, excess bismuth was used. BIT with 15% excess bismuth processed at 750 °C was purely c -axis oriented and only possessed a 2Pr value of 4.9 $\mu\text{C}/\text{cm}^2$, while that of 15% excess bismuth BLT sample was 18.3 $\mu\text{C}/\text{cm}^2$. This can be attributed to the large polarization anisotropy in BIT, and this anisotropy is reduced by lanthanum doping. © 2010 American Institute of Physics. [doi:10.1063/1.3428968]

I. INTRODUCTION

The polarization cycling reliability¹ is an important property for ferroelectric materials, especially when it comes to ferroelectric memories.^{2,3} In solving the “fatigue” problems in ferroelectric thin films, much attention has been paid to Bi-based layered perovskite materials that belong to the Aurivillius phase.⁴ $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT), as a member of $m=2$ Aurivillius family, was discovered to possess excellent polarization cycling property on Pt electrodes.⁵ This does not necessarily imply that all Aurivillius phase ferroelectric materials are fatigue-free since $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), as a member of $m=3$ Aurivillius family, suffers from fatigue problems nevertheless.⁶

One may believe that the stronger bonding of Ta^{5+} in comparison to Ti^{4+} should account for this discrepancy. The different fatigue resistance between SBT and BIT could possibly be ascribed to the B site difference. Kang *et al.*,⁷ however, studied this issue by making $\text{Bi}_3\text{TiTaO}_9$, which belongs to $m=2$ Aurivillius family. This material could be regarded as substituting a Bi cation for each Sr cation in SBT, and introducing a Ti instead of Ta for charge neutrality. Nevertheless, if we neglect the structural difference ($m=2/m=3$), the concept of $\text{Bi}_3\text{TiTaO}_9$ also emerges when some of the B site Ti cations in BIT are replaced by Ta cations. They found though the remanent polarization value of $\text{Bi}_3\text{TiTaO}_9$ was similar to SBT, it indeed suffered from fatigue problems. According to this fact they concluded that the A site cation does affect the fatigue properties of Aurivillius phase ferroelectric materials. The high volatility of Bi is the major reason why BIT is not fatigue-free. In addition, by substituting some La for the Bi in BIT, Park *et al.*⁸ achieved a fatigue-free ferroelectric material $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT). The fa-

tigue improvement was due to the introduction of less volatile La cations into the pseudoperovskite layers (see Fig. 1) and hence stabilizing the oxygen anions.

While many works have confirmed the fatigue improvement in BLT, there has been no common understanding on the magnitude and direction of the polarization vector in BLT. It is well known that pure BIT has a polarization vector in the $b-c$ axes plane and makes a 4.5° angle to the b -axis.⁹ When doped with La, the La cations will take up some of the Bi cations within the pseudoperovskite layers because the ion radius of La^{3+} (136 pm) (Ref. 10) is very similar to that of Bi^{3+} (130 pm),¹¹ as illustrated in Fig. 1(b). Hence, the polarization direction of BLT could possibly resemble that of BIT. Nevertheless, Chon *et al.*¹² have pointed out that the different bonding influence of La compared with Bi may affect and stretch the polarization vector of BIT. Although the c -axis component of BIT's polarization is only 4 $\mu\text{C}/\text{cm}^2$,⁹ Chon has achieved high 2Pr values in highly c -axis oriented BLT,¹² $\text{Bi}_{3.15}\text{Sm}_{0.85}\text{Ti}_3\text{O}_{12}$,¹³

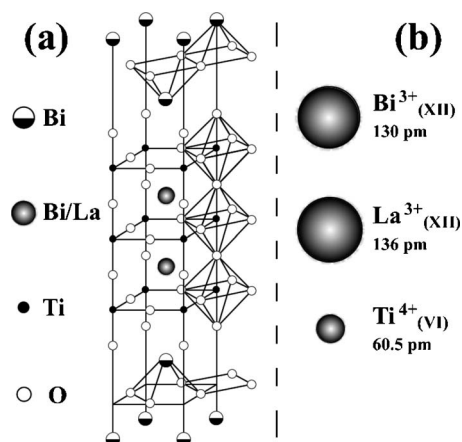


FIG. 1. (a) The structure of BLT; (b) comparison of some cations' radii.

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$\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_3\text{O}_{12}$ (BNdT),¹⁴ etc. Hou and Shen's work on BNdT¹⁵ also implies that higher c -orientation leads to higher polarization. However, the works of Lee and Hesse,¹⁶ Sun *et al.*,¹⁷ Garg *et al.*,¹⁸ and Lu *et al.*¹⁹ do not support Chon's conclusion. Many of such works were done on BNdT because BNdT was claimed to possess an unexpected giant 2Pr value ($103 \mu\text{C}/\text{cm}^2$) along the c -axis.¹⁴ The controversy on the polarization direction of BLT and other rare earth (Ln) substituted BIT (BLnT) has not been clarified yet.

In addition, a systematic comparison on the electrical properties between BIT and BLnT is still lacking. Although there seem lots of works on this already,^{12,20} the ferroelectric properties of BIT in those researches were generally very poor. We argue that, lanthanum doping cannot improve the 2Pr value of BIT for two reasons. First, given that the giant spontaneous polarization of BIT stems from the $6s^2$ lone pair electrons of Bi^{3+} ,²¹ the substitution of lanthanum for bismuth tends to diminish this polarization origin. Second, the ionic radius of La^{3+} is larger than Bi^{3+} on the A site, and in Aurivillius phase layered perovskites this usually reduces the Curie point and polarization, in contrary to cubic perovskites.²² The discrepancy between our argument and the experimental results may be attributed to the large polarization anisotropy in BIT, since a c -axis oriented BIT sample only possesses extremely low polarization. To avoid the inequity, a non- c -orientation BIT sample should also be fabricated and compared.

In the present study, we report the differences in ferroelectric properties between mixed (with a/b -axes) oriented BIT and BLT, and also between c -axis oriented BIT and BLT. Remanent polarization, coercive field, leakage current, and polarization saturation properties are compared. The control of crystal orientation is done by varying the thermal procedure, as well as allowing certain amount of excess bismuth.

II. EXPERIMENTAL

Both BIT and BLT thin films were prepared on Pt(111) substrates using a metal organic decomposition (MOD) technique. The solutions for MOD were made by Kojundo Chemical Laboratory, Japan. Stoichiometric BIT and BLT were deposited on Pt (200 nm) substrate using a spinner. The as-deposited films were pyrolyzed at 160°C for 1 min and then 260°C for 4 min. Such a coating process was referred to as one deposition and all the films were deposited by three depositions. The speeds of these spinning steps were 3500 rpm, 4000 rpm, and 4000 rpm, respectively. Subsequently, decarbonization was performed in a 450°C oxygen furnace for 1 h. Ferroelectric capacitor structure (Pt/FE/Pt) was set up by 3 steps: (1) deposition of 200 nm platinum on BIT/BLT; (2) top electrode photolithography; and (3) ion-etching and photoresist strip to fabricate separate Pt/FE/Pt capacitors. The structure for the ferroelectric capacitors is illustrated in Fig. 2. The typical area of a capacitor is $7850 \mu\text{m}^2$. Finally, a 750°C , 1 min rapid thermal annealing (RTA) step in oxygen ambient was performed on all the wafers in order to crystallize the ferroelectric thin films.

For comparative reasons, BIT and BLT solutions with

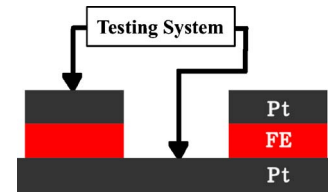


FIG. 2. (Color online) The structure of a ferroelectric capacitor.

15% excess bismuth were deposited as well, following the same procedure above. Various annealing temperatures were used during the post-RTA step.

The crystal orientations of the BIT/BLT films were examined by x-ray diffraction (XRD) technique with $\text{Cu } K\alpha$ radiation. The ferroelectric hysteresis loops of the capacitors were tested using triangular waves at 10 kHz. The leakage current was tested up to an electric field of 450 kV/cm.

III. RESULTS AND DISCUSSIONS

A. Stoichiometric BIT and BLT

The XRD results of stoichiometric BIT and BLT are shown in Fig. 3. Both of the samples exhibit mixed orientations. However, the BLT thin film is more c -axis oriented. The inclusion of La favors c -axis orientation, which is in accordance to Chon's results.¹² An equivalent statement is that c -axis components emerge at a lower temperature in BLT than in BIT.²³

The hysteresis loops tested on pristine $\text{Pt}/\text{Bi}_4\text{Ti}_3\text{O}_{12}/\text{Pt}$ and $\text{Pt}/\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}/\text{Pt}$ ferroelectric capacitors are shown in Figs. 4(a) and 4(b). At 300 kV/cm, the BIT capacitor has an abnormal hysteresis loop that resembles the antiferroelectricity to some extent, while that of BLT is fairly well. In history, Pulvari and De la Paz²⁴ showed that BIT thick film is antiferroelectric in its virgin state but very easily transformed to be ferroelectric by a high electric field. Here when the BIT thin film is prepolarized by a field of 700 kV/cm and retested at 300 kV/cm, the hysteresis loop becomes normal, as also shown in Fig. 4(a). Such phenomenon is not discovered in BLT samples. At 700 kV/cm, both capacitors exhibit good hysteresis loops. The saturated 2Pr values of BIT and BLT are $34.3 \mu\text{C}/\text{cm}^2$ and $25.7 \mu\text{C}/\text{cm}^2$, respectively. BIT possesses larger 2Pr value than BLT.

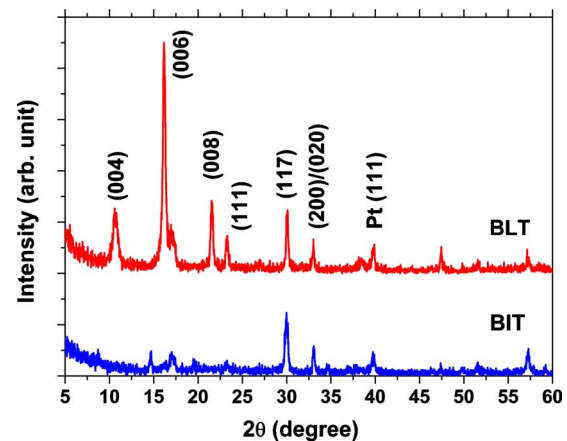


FIG. 3. (Color online) XRD results of stoichiometric BIT and BLT.

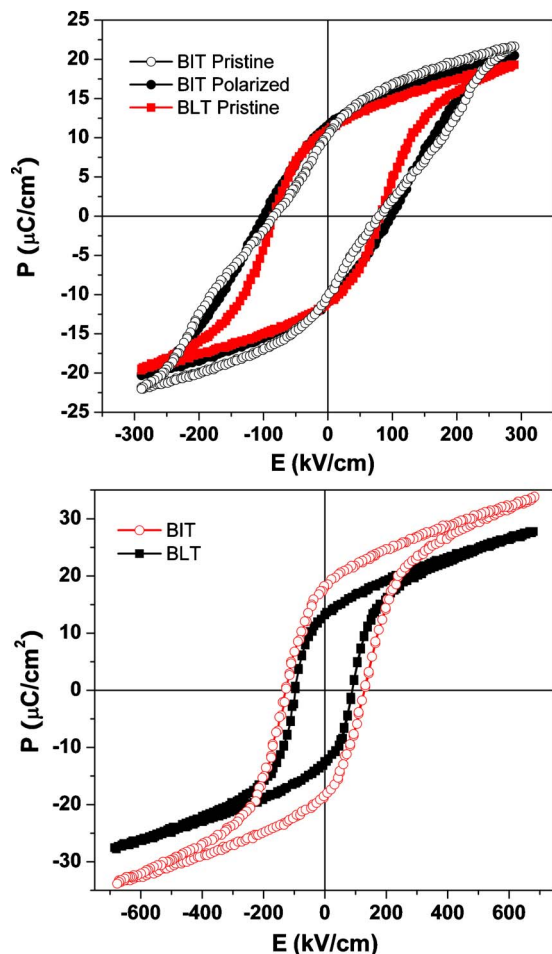


FIG. 4. (Color online) The hysteresis loops of Pt/BIT/Pt and Pt/BLT/Pt capacitors tested at: (a) 300 kV/cm and (b) 700 kV/cm.

The dc leakage test results are demonstrated in Fig. 5. The leakage current of BIT is two decades higher than BLT at 450 kV/cm. A scrutiny into the two curves reveals that BIT is not inferior to BLT until about 200 kV/cm. Nevertheless, BIT suffers from a shoot of leakage after 200 kV/cm, while BLT does not. The small chart (i) inside Fig. 5 is in linear scale where the current density of BIT after 200 kV/cm fits well the modified Child–Langmuir’s law^{25,26} (dotted curve).

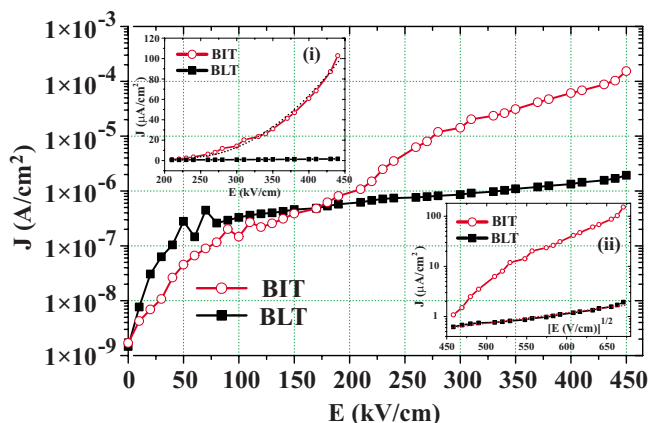


FIG. 5. (Color online) Leakage current results of BIT and BLT. Small charts: (i) linear scale plot for $E > 200$ kV/cm and (ii) $\log(J)$ vs \sqrt{E} for $E > 200$ kV/cm.

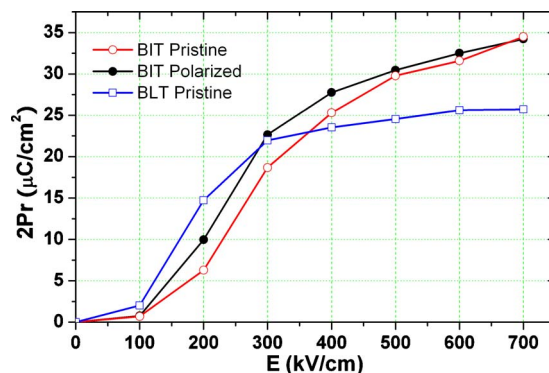


FIG. 6. (Color online) Test results of remanent polarization vs applied electric field.

$$J(E) = aE + bE^2. \tag{1}$$

This implies the leakage shoot of the BIT sample at high field is due to space-charge-limited current. On the other hand, the small chart (ii) demonstrates the relationship between $\log(J)$ and \sqrt{E} after 200 kV/cm. The BLT curve fits the law of Poole–Frenkel emission²⁶ (dotted line)

$$\log[J(E)] = \beta_{pf} \frac{\sqrt{E}}{k_B T}, \tag{2}$$

where $\beta_{pf} = \sqrt{e^3 / \pi \epsilon}$. Here e , ϵ , k_B , and T are elementary charge, dynamic permittivity, Boltzmann constant, and temperature, respectively. Consequently, the leakage improvement of BLT compared with BIT at high field is due to the abatement of space-charge effects.

Figure 6 illustrates the remanent polarizations versus electric fields. Considering the huge difference between pristine and polarized BIT thin films, we also measured polarized BIT thin films, which were prepolarized by an electric field of 700 kV/cm. Comparing the three lines in Fig. 6, BLT saturates much better than BIT. Once the applied electric field reaches 300 kV/cm, the 2Pr value changes very little when applied electric field increases further. This is not the case for BIT, in which the 2Pr value keeps rising with the electric field. A possible reason is that there exist certain oxygen vacancies inside BIT and they tend to pin the ferroelectric domains. Once the thin films are prepolarized, these domains become free to switch, which adds to the 2Pr value.

Figure 7 demonstrates the dependence of coercive field

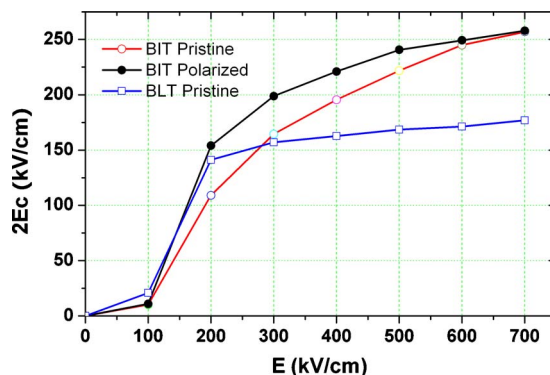


FIG. 7. (Color online) Test results of coercive field vs applied electric field.

on the applied electric field. The $2E_c$ value of BLT is 68.8% that of BIT at 700 kV/cm. Note that in Fig. 4(b) the $2P_r$ value of BLT is 74.9% that of BIT at the same applied field. These two percentages look not so different at first glance. Nevertheless, if considering in BIT the $2P_r$ value does not saturate well, we should be aware that the drop of $2E_c$ in BLT, compared with BIT, is much larger than the drop of $2P_r$. This may raise a question whether the polarization mechanism in BLT is still similar to BIT. Another question lies in why BLT can maintain high $2P_r$ value even if it is mainly grown along the c -axis. To ascertain these issues, highly c -axis oriented BIT and BLT should be prepared and compared. Experimentally, we found it difficult to grow highly c -axis oriented BIT with the procedure described above. Yet, our previous work²³ reveals that excess bismuth would help promote c -axis orientation. Such pursuits will be discussed in Sec. III B.

B. BIT and BLT with 15% excess bismuth

The XRD results 750 °C post-RTA processed $\text{Bi}_{4.6}\text{Ti}_3\text{O}_{12.9}$ and $\text{Bi}_{3.85}\text{La}_{0.75}\text{Ti}_3\text{O}_{12.9}$ thin films are shown in Fig. 8. The diffraction peaks of BLT are lower than BIT. In addition, the BLT sample also has a tiny (117) peak. Nevertheless, both of them possess strong c -axis orientation. The hysteresis loops of both samples are demonstrated in Fig. 9. Note that the $2P_r$ of purely c -axis oriented BIT is only $4.9 \mu\text{C}/\text{cm}^2$, while the highly c -axis oriented BLT possesses a $2P_r$ value of $18.3 \mu\text{C}/\text{cm}^2$. The dc leakage current results are shown in Fig. 10. Both samples suffer from a slight breakdown at around 150–200 kV/cm. This phenomenon could be attributed to the diffusion of excess bismuth into the electrodes during thermal processes.

A more interesting phenomenon arises if we reduce the processing temperature of 15% bismuth excess BIT. When the post-RTA temperature became 600 °C, the $2P_r$ value of BIT was tested to be $19.4 \mu\text{C}/\text{cm}^2$, much higher than $4.9 \mu\text{C}/\text{cm}^2$. The strong polarization anisotropy in BIT was clearly manifested in this experiment.

The BLT sample with 15% excess bismuth contains, however, certain (117) orientation component. It is difficult to obtain epitaxial c -axis oriented BLT on Pt(111) substrates

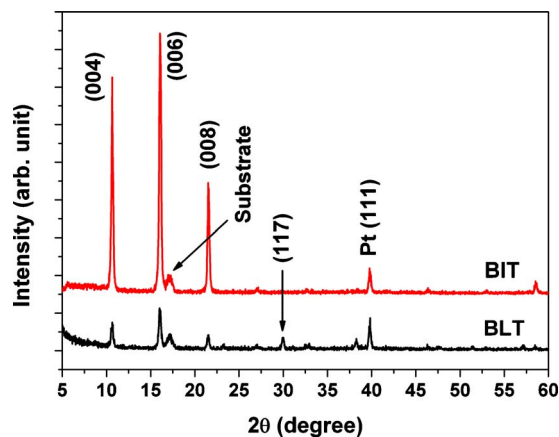


FIG. 8. (Color online) XRD results of BIT and BLT with 15% excess bismuth.

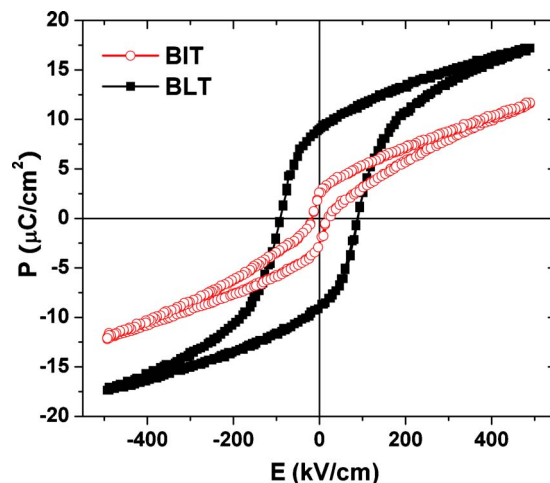


FIG. 9. (Color online) Hysteresis loops of $\text{Pt}/\text{Bi}_{4.6}\text{Ti}_3\text{O}_{12.9}/\text{Pt}$ and $\text{Pt}/\text{Bi}_{3.85}\text{La}_{0.75}\text{Ti}_3\text{O}_{12.9}/\text{Pt}$ capacitors.

without damaging the film. We believe that the inclusion of La cations reduces the polarization anisotropy of BIT. In a strongly c -axis oriented BLT thin films, considerable $2P_r$ value can still be attained. For epitaxial BLT thin films grown along the c -axis, Chon's result on Pt(100) substrate gave high $2P_r$ value ($27 \mu\text{C}/\text{cm}^2$),²⁷ while those researchers using SrRuO_3 bottom electrodes reported almost no ferroelectric property along the c -axis.¹⁶ To get an explanation we may resort to the work of Dorrian *et al.*,²¹ who attributed the finite c -axis polarization in BIT to the reorientation of lone pair electrons in Bi^{3+} . In case of BLT, certain amount of Bi^{3+} within the pseudoperovskite layer is replaced and hence c -axis polarization due to the shift in lone pair electrons should be reduced or even annihilated. Nevertheless, the mismatch of cation radii now causes local distortions and breaks the symmetry, especially when La^{3+} cations are randomly distributed. Besides, the capability of 12-fold coordination for La^{3+} influences the bonding in the solid. Hence, polarization due to the displacement of ions tends to shift its direction, a certain proportion of which may be projected along the c -axis. Yet, it should be noted that the ferroelectricity of c -axis oriented BLT could also depend on the preparation procedure and substrates which may determine, for example, structure distortions and the distribution of La cations.

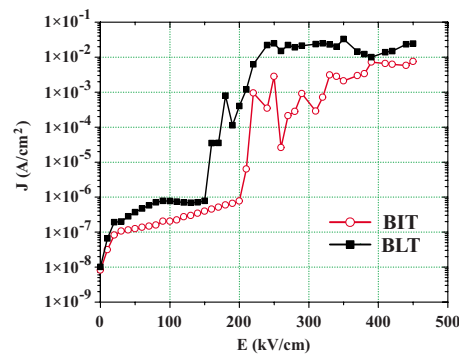


FIG. 10. (Color online) Leakage current results of BIT and BLT with 15% excess bismuth.

IV. SUMMARY

The present work examined the electrical properties of MOD derived BIT and BLT thin films on Pt(111) substrates. The following conclusions can be drawn.

- (1) Compared with BIT, BLT thin film favors the mixed orientations. While the stoichiometric BIT samples only show *a/b*-axes and (117) orientations, the stoichiometric BLT samples contain considerable *c*-axis components under the same conditions. Excess bismuth promotes pure *c*-axis orientation in BIT, while for BLT samples they remain in mixed orientations.
- (2) Non-*c*-orientation BIT thin film possesses higher 2Pr value (34.3 $\mu\text{C}/\text{cm}^2$) than BLT (25.7 $\mu\text{C}/\text{cm}^2$), though its saturation and leakage properties are not so good as BLT.
- (3) The polarization anisotropy in BIT is reduced by lanthanum doping.
- (4) A sharp polarization decrease may occur in BIT (rather than BLT) as the processing temperature increases, since high temperature favors *c*-axis orientation.

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