Orientation dependence of ferroelectric properties of pulsed-laser-ablated Bi4–xNdxTi3O12 films — Source link ↗

Ashish Garg, Zoe H. Barber, Matthew Dawber, James F. Scott ...+2 more authors

Related papers:

- Lanthanum-substituted bismuth titanate for use in non-volatile memories

- Layered perovskites with giant spontaneous polarizations for nonvolatile memories.

- Fatigue-free ferroelectric capacitors with platinum electrodes

- Ferroelectric Bi3.25La0.75Ti3O12 Films of Uniform a-Axis Orientation on Silicon Substrates

- Electrical and Optical Properties of Ferroelectric Bi4Ti3O12 Single Crystals

Orientation dependence of ferroelectric properties of pulsed-laser-ablated $Bi_{4-x}Nd_xTi_3O_{12}$ films

A. Garg[a)] and Z. H. Barber
Department of Materials Science and Metallurgy, Pembroke Street, University of Cambridge, Cambridge CB2 3QZ, United Kingdom

M. Dawber and J. F. Scott
Department of Earth Sciences, Downing Street, University of Cambridge, Cambridge CB2 3EQ, United Kingdom

A. Snedden and P. Lightfoot
School of Chemistry, University of St. Andrews, St. Andrews, KY16 9ST, United Kingdom

Epitaxial (001)-, (118)-, and (104)-oriented Nd-doped $Bi_4Ti_3O_{12}$ films have been grown by pulsed-laser deposition from a $Bi_{4-x}Nd_xTi_3O_{12}$ ($x=0.85$) target on $SrRuO_3$ coated single-crystal (100)-, (110)-, and (111)-oriented $SrTiO_3$ substrates, respectively. X-ray diffraction illustrated a unique epitaxial relationship between film and substrate for all orientations. We observed a strong dependence of ferroelectric properties on the film orientation, with no ferroelectric activity in an (001)-oriented film; a remanent polarization $2P_r$ of 12 $\mu C/cm^2$ and coercive field E_c of 120 kV/cm in a (118)-oriented film; and $2P_r=40$ $\mu C/cm^2$, $E_c=50$ kV/cm in a (104)-oriented film. The lack of ferroelectric activity along the c-axis is consistent with the orthorhombic nature of the crystal structure of the bulk material, as determined by powder neutron diffraction. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1613052]

SrBi$_2$Ta$_2$O$_9$ (SBT) films were the first of the Bi-layered oxides to show promise for ferroelectric random access memory applications, due to their excellent fatigue resistance on Pt electrodes.[1] However, growth of SBT films requires high temperatures ($>750\,°C$, and typically $850\,°C$ or higher for epitaxial films[2–4]), and films show low remanent polarization P_r (typically $2P_r \approx 10$ $\mu C/cm^2$ on Pt). The emergence of La-doped bismuth titanate (Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ or BLT)[5] as a possible substitute has fueled considerable research to find other variants and further enhance film properties. BLT can be deposited at lower temperatures ($\leqslant 750\,°C$) on Pt electrodes and shows a higher $2P_r$ (~ 24 $\mu C/cm^2$) than SBT, as well as excellent fatigue resistance.

Bi$_4$Ti$_3$O$_{12}$ (BTO) is an Aurivillius-phase Bi-layered oxide, and can be denoted by the formula $(Bi_2O_2)^{2+}$ $(Bi_2Ti_3O_{10})^{2-}$, in which perovskite units of Ti–O octahedra are sandwiched between Bi$_2$O$_2$ layers. Bulk undoped BTO shows a very high $2P_r$ (about 100 $\mu C/cm^2$),[6] but thin films have much lower values of switching polarization and suffer from fatigue upon bipolar switching.[7] It was proposed that doping with La led to improved oxygen ion stability in the lattice and hence improved fatigue resistance because some of the Bi ions in the pseudoperovskite layers containing Ti–O octahedra were substituted by La ions. Substitution of the nonspherical Bi^{3+} cation with La^{3+}, however, reduces the structural distortion of the perovskite block, thereby reducing P_r. Substitution by lanthanide ions having smaller ionic radii than Bi, such as Nd or Sm (comparative ionic

radii for eight-coordination: Bi^{3+} 0.117 nm, La^{3+} 0.116 nm, Nd^{3+} 0.111 nm, Sm^{3+} 0.108 nm) should maintain a more significant structural distortion and improved ferroelectric properties, in particular P_r.

Recently, Chon *et al.*[8] have reported very high values of remanent polarization in sol–gel-derived, lanthanide-doped bismuth titanate thin films, with $2P_r$ values as high as ~ 100 $\mu C/cm^2$ in highly c-axis-oriented Nd-doped (BNdT) films. The authors attributed this rather unexpected result to the development of the polarization vector along the c-axis of the BNdT unit-cell: in undoped Bi$_4$Ti$_3$O$_{12}$, the polarization is almost exclusively along the a-axis. Based on this explanation, we would expect BNdT films of the same composition with orientations further away from the c-axis (or closer to the a-axis) to exhibit lower P_r. In order to investigate this issue, we have deposited epitaxial BNdT films and measured the dependence of P_r upon film orientation.

In this letter, we report on the properties of epitaxial BNdT films of various crystallographic orientations (c-axis and non-c-axis oriented), grown by pulsed laser deposition (PLD) from a target of composition Bi$_{3.15}$Nd$_{0.85}$Ti$_3$O$_{12}$ on single crystal (100)-, (110)-, and (111)-oriented SrTiO$_3$ (STO) substrates. BNdT films, 300 nm thick, were deposited in 200 mTorr oxygen, at a substrate temperature of $750\,°C$, and were subsequently cooled to room temperature (in ~ 45 min) at an oxygen pressure of $\frac{1}{2}$ atm. The laser fluence during the deposition was approximately 2.8 J/cm^2 at a repetition rate of 5 Hz. The target was fabricated by cold pressing and sintering ($1100\,°C$ for 1 h in air) a powder compact prepared by a conventional solid-state reaction route. Prior to BNdT film deposition, conducting 50-nm-thick SrRuO$_3$ films were deposited on the STO substrates to act as a lower elec-

[a)]Present address: Dept. of Materials and Metallurgical Engg., Indian Institute of Technology, Kanpur-208016, India; electronic mail: ashishg@iitk.ac.in
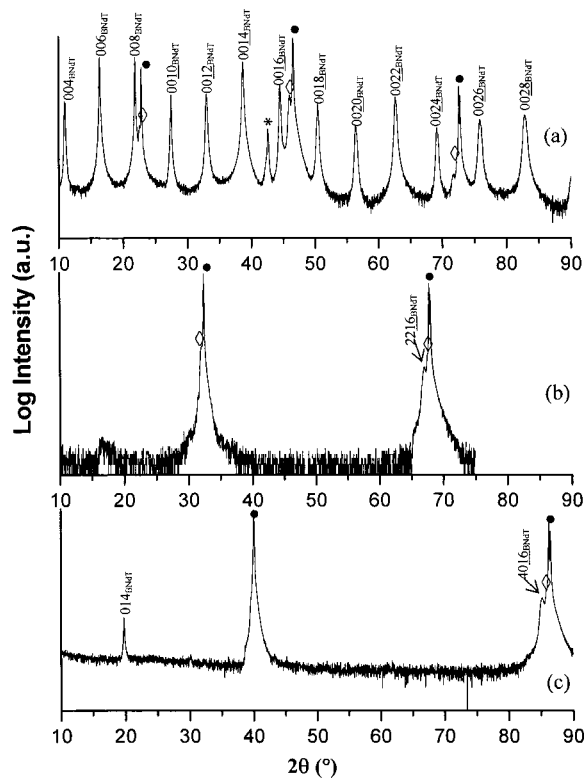
FIG. 1. 2θ scans of BNdT films on STO substrates of various orientations: (a) (100)-, (b) (110)-, and (c) (111)- oriented. ● - STO $K_{\alpha 1}$, ◇ - SrRuO$_3$ $K_{\alpha 1}$, * - unidentified.
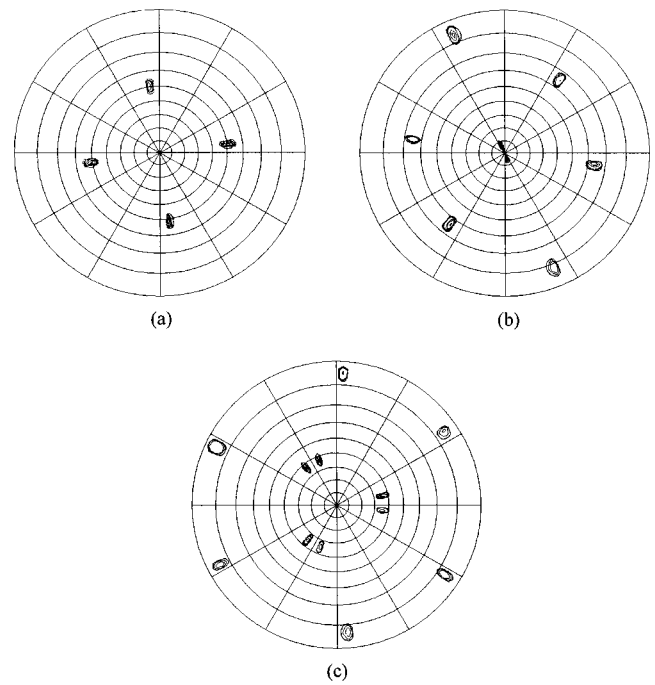

FIG. 2. (117) Pole figures of (a) (001)-oriented, (b) (118)-oriented, and (c) (104)-oriented BNdT Film. Pole figures are plotted on Wulff Scale and each division corresponds to 10° along the radii (ψ) and 30° along the circumference (ϕ).

trode: these films were deposited at 650 °C in 110 mTorr oxygen (laser fluence≃2.5 J/cm^2; repetition rate=4 Hz). Pseudocubic SrRuO$_3$ has a very low lattice mismatch with STO and hence maintains the substrate orientation.

The structure of the films was studied by x-ray diffraction (XRD). For ferroelectric characterization, Pt top contacts (area=8.1×10^{-5} cm^2) were deposited by sputter deposition through a shadow mask. Ferroelectric properties were measured using a Radiant Precision Pro. ferroelectric tester. Crystallographic studies were also made on bulk powder specimens by neutron diffraction.

A BNdT film on STO (100) was highly c-axis- or (001)-oriented, as shown by very strong 00l peaks on an XRD 2θ-scan [Fig. 1(a)]. A (117) pole figure [Fig. 2(a)] shows fourfold symmetry with four sharp peaks at $\psi \approx 50°$ (angular spread <5°), illustrating a very highly c-axis-oriented film with excellent in-plane orientation. The orientation relationship between the film and substrate is $(001)_{film} \| (100)_{substrate}$ and $[100]_{film} \| [110]_{substrate}$.

A BNdT film deposited on STO (110) was (118)-oriented, as shown by the XRD 2θ-scan in Fig. 1(b) and confirmed by a (117) pole figure scan, showing two sets of three peaks at $\psi \approx 5°$, 65°, and 85° corresponding to 117, $1\bar{1}7/\bar{1}17$, and $\bar{1}\bar{1}7$ reflections [Fig. 2(b)]. These two sets of peaks, related by mirror symmetry, indicate the presence of double-twin in the film, as previously reported for BLT on a similar substrate.[9] This twinning is due to two possible c-axis growth directions of BNdT perpendicular to the (100) planes of STO, which are at 45° to the (110) substrate plane.

A BNdT film deposited on STO (111) was (104)-oriented as shown by the 2θ-scan in Fig. 1(c). It should be noted that only the 014 peak is present, as 104 is prohibited due to

systematic absences. A (117) pole figure of this film showed a threefold symmetry with three sets of peaks at $\psi \approx 35°$ (117 and $1\bar{1}7$ reflections) and 85° ($11\bar{7}$ and $1\bar{1}\bar{7}$ reflections), confirming good quality in-plane orientation. This pole figure can be interpreted in terms of the formation of three in-plane orientations due to c-axis BNdT growth along three directions [perpendicular to the STO (100) planes], separated by azimuthal angles of 120° leading to a triple-twin situation, also reported for BLT films on STO (111) substrates.[9]

These results show that BNdT grows with a epitaxial relationship to the underlying SrRuO$_3$/STO substrate, with the c-plane of BNdT parallel to the (100) plane of STO, as previously reported for BLT film growth[9] and maintaining a similar orientation relationship on all substrate orientations.

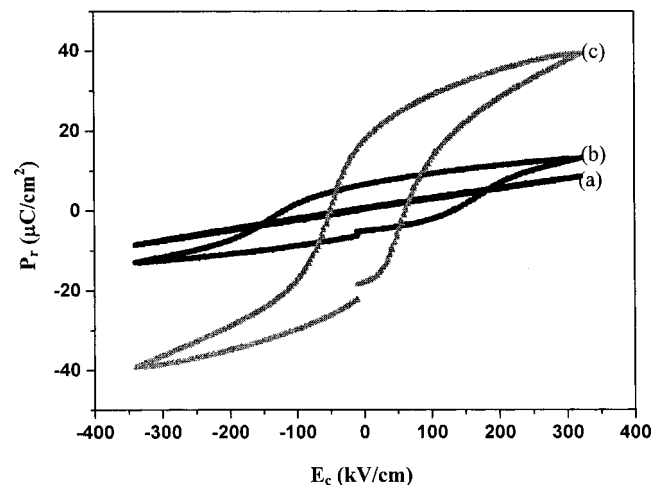Figure 3 shows the ferroelectric hysteresis loops for the

FIG. 3. $P-E$ Loops for (a) (001)-oriented, (b) (118)-oriented, and (c) (104)-oriented BNdT film. The applied voltage was 10 V at a frequency of 200 Hz.

three film orientations described above. A c-axis-oriented BNdT film [on (100) STO] did not show any ferroelectric activity, as demonstrated by a linear dielectric response and the absence of any hysteresis loop in Fig. 3(a). A (118)-oriented film [on (110) STO] showed a $2P_r$ of ~ 12 μC/cm^2 and coercive field E_c of 120 kV/cm at an applied voltage of 10 V and a frequency of 200 Hz [Fig. 3(b)], while a (104)-oriented film [on (111) STO] showed a $2P_r$ value of approximately 40 μC/cm^2 and an E_c of 50 kV/cm using the same parameters. Results for the (104)-oriented film are in agreement with the results obtained by Kojima *et al.*[10] for BNdT films grown by metalorganic chemical vapor deposition.

Although we have shown that doping with Nd leads to an increase in P_r as compared to La-doped films, due to increased lattice distortion, we do not see the dramatic increase in the remanent polarization along the c-axis, as observed by Chon *et al.*[8] On the contrary, our results suggest that P_r is 0 in c-axis oriented films, and the polarization increases on moving away from the BNdT c-axis.

In support of our thin-film results, we have carried out a careful Rietveld analysis of the crystal structure of our $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ sample in bulk polycrystalline form using powder neutron diffraction.[11] This analysis clearly shows that $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ adopts an orthorhombic structure, space group $B2cb$, rather than the higher symmetry tetragonal possibility recently suggested by Chon *et al.*[12] The orthorhombicity is confirmed by the presence of key superlattice reflections such as 014, 125, and 034; no significant peak splitting is observed, due to the similarity of the a/b lattice parameters. Moreover, there is no evidence for reduction of crystal symmetry to monoclinic (although we cannot rule out a very small distortion), as suggested for BTO itself. These subtle features are key, since both tetragonal and monoclinic groups naturally allow a c-axis component to P_r, whereas the orthorhombic $B2cb$ model necessitates only an a-axis polarization. Although there is evidence that the bulk and thin-film crystal structures of ferroelectric materials may differ due to epitaxial constraints (e.g., $BiFeO_3$ thin films[13]), in this case we have direct evidence for the preservation of orthorhombic symmetry in the thin-film: the presence of the 014 peak in Fig. 1(c) negates tetragonal symmetry.

Although the results of Chon *et al.* remain unexplained, the situation in strontium bismuth niobate described by Watanabe *et al.*[14] may be analogous; in that case they found that small deviations from stoichiometry, linked to preferred orientation, led to changes in P_r along the c-axis by as much as 70%.

Another interesting observation from these results is that the coercive voltage (which was not observed in the BLT thin films) of the (118)-oriented film is much larger than (104)-oriented film.[9] Reasons for this are not clear at the moment, but one possibility may be that Nd doping can lead to different magnitudes of distortions along different crystallographic directions due to the size difference between Nd and La, making some directions more easily switched than others.

In summary, we have found that (001)-oriented BNdT films deposited by PLD do not show ferroelectric activity. A (118)-oriented film showed a $2P_r$ value of 12 μC/cm^2 at a coercive field of 120 kV/cm, whereas a (104)-oriented film had a much higher $2P_r$ value of ~40 μC/cm^2 and lower E_c of ~50 kV/cm. These results are consistent with the proposed model of the crystal structure for $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ derived from neutron diffraction results.

[1] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, Nature (London) **374**, 627 (1995).

[2] J. Lettieri, M. A. Zurbuchen, Y. Jia, D. G. Schlom, S. K. Streiffer, and M. E. Hawley, Appl. Phys. Lett. **76**, 2937 (2000).

[3] H. N. Lee, A. Visinoiu, S. Senz, C. Harnagea, A. Pignolet, D. Hesse, and U. Gösele, J. Appl. Phys. **88**, 6658 (2000).

[4] A. Garg, S. J. Lloyd, and Z. H. Barber, Integr. Ferroelectr. **44**, 1 (2002).

[5] B. H. Park, B. S. Kang, S. D. Bu, T. W. Noh, J. Lee, and W. Jo, Nature (London) **401**, 682 (1999).

[6] S. E. Cummins and L. E. Cross, J. Appl. Phys. **39**, 2268 (1968).

[7] P. C. Joshi and S. B. Krupanidhi, Appl. Phys. Lett. **62**, 1928 (1993).

[8] U. Chon, H. M. Jang, M. G. Kim, and C. H. Chang, Phys. Rev. Lett. **89**, 087601 (2002).

[9] H. N. Lee and D. Hesse, Appl. Phys. Lett. **80**, 1040 (2002).

[10] T. Kojima, T. Sakai, T. Watanabe, H. Funakubo, K. Saito, and M. Osada, Appl. Phys. Lett. **80**, 2746 (2002).

[11] Powder neutron diffraction data were collected on the high resolution powder diffractometer (HRPD) instrument at the ISIS facility, UK. Rietveld refinement used our previous model for BTO in space group $B2cb$ [C. H. Hervoches and P. Lightfoot, Chem. Mater. **11**, 3359 (1999)]. The final structural model showed a considerable reduction in the orthorhombic distortion as compared to BTO, with lattice parameters $a = 5.3978(3)$ Å, $b = 5.4039(3)$ Å, $c = 32.8393(8)$ Å. Final agreement factor R_{wp} is 15.5% for full isotropic refinement.

[12] U. Chon, J. S. Shim, and H. M. Jang, J. Appl. Phys. **93**, 4769 (2003).

[13] 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).

[14] K. Watanabe, M. Tanaka, M. Sumitomo, K. Katori, H. Yagi, and J. F. Scott, Appl. Phys. Lett. **73**, 126 (1998).