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Morphology and mobility of 90° domains in La-substituted bismuth titanate

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Abstract

The domain structures of $Bi_{4-x}La_xTi_3O_{12}$ (BLT) ceramics (where $x = 0$, 0.5, 0.75, and 1.0) have been investigated by transmission electron microscopy. The morphology of the 90° domain walls were found to be curved due to a decrease of the spontaneous strain energy after doping with La. Movement of the 90° domain walls was observed *in situ* under electron beam irradiation. It is indicated that the irregular and active 90° domain walls in BLT0.75 result from a decrease in internal stress. It is suggested that the existence of irregular and active 90° domains in BLT0.75 has an important effect on the remanent polarization, and fatigue properties.

1. Introduction

Ferroelectric thin films have attracted much attention for their application in microelectromechanical systems, ferroelectric field-effect transistors, and ferroelectric random access memories (FeRAMs) [1–5]. Perovskites are the most intensively studied material: examples are $BaTiO_3$, $(BaSr)TiO_3$, and $Pb(Zr_xTi_{1-x})O_3$ (PZT) [1–3], for FeRAM applications. However, these thin films, sandwiched between metal electrodes, suffer a severe reduction of remanent polarization (fatigue) after repetitive polarization. Recently, Bi-layered structured ferroelectrics (BLSFs) have raised wide interest due to the observation of fatigue-free characteristics in $SrBi_2Ta_2O_9$ (SBT) thin films [4]. $Bi_4Ti_3O_{12}$ (BTO) is another BLSF with a relative high remanent polarization, high Curie temperature, and high breakdown strength [6]. After the bismuth element in its perovskite layer is partly substituted by a lanthanum element, BTO also show a fatigue-free behaviour. As to the origin of this fatigue-free behaviour, Park and his

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co-workers [7] suggested that it is due to the chemical stability of the perovskite layers to oxygen vacancies. Most recently, there has been experimental evidence about the contributions of internal stress and chemical nonstoichiometry to ferroelectric fatigue [8, 9]. However, there is still controversy about the common origin of fatigue-free behaviour in ferroelectric materials. In our previous papers, different viewpoints on fatigue behaviour were also proposed based on transmission electron microscopy (TEM) studies [10, 11].

There have already been some reports published on the domain structure of bismuth titanate [13–15]. Landuyt *et al* studied the domain structure of BTO by transmission electron microscopy and observed 90° and 180° domain walls. Ding *et al* found that an anti-phase boundary (APB) appeared in BTO after the La element was partly doped in it, and the domain wall morphology also changed. Recently, Pan and his co-workers observed 90° domains and an APB in the epitaxial BTO thin films on $SrTiO_3$ substrates. These studies had been done on the domain structure in bismuth titanate; however, little systemic work concerning the mobility of domain walls was reported. In addition, the published reports studied even less the effects between the domain structure and the physical properties. So, we attempt to give an insight into the La doping contribution to properties from a domain structure study in this work.

The domain structures in $Bi_{4-x}La_xTi_3O_{12}$ (BLTx, where x is the amount of La substitution $x = 0$, 0.5, 0.75, or 1, respectively) were investigated using TEM. After La doping in BTO, APBs appear and the 90° domain walls (DWs), originally straight, become curved. The movement of the 90° domain walls was observed *in situ* by TEM. The origin of the different morphology and mobility of 90° domains are discussed. Their special effects on the remanent polarization and the fatigue property are suggested.

2. Experiments

Ceramics of $Bi_{4-x}La_xTi_3O_{12}$ (BLTx, where $x = 0.0$, 0.5, 0.75, and 1.0) were prepared using the conventional solid-state reaction method, including a powder mixing technique and a sintering process. Pure phases were characterized in all samples by a Rigahu x-ray diffractometer with Cu Kα radiation (as shown in figure 1). The TEM specimens were prepared by mechanical thinning down to 20–40 μm, followed by Ar^+-ion milling at 4 kV with 10°–12°. A Philips CM12, operated at 120 kV and equipped with a double-tilt specimen stage, was used for the diffraction contrast. The ferroelectric properties of BLTx were measured with an RT6000HVS test system at the same voltage after the samples were polished to 0.15 mm thickness and after silver plating on both surfaces.

3. Results and discussion

In [16], it is reported that there are three types of domains in the ferroelectric phase of the bismuth-layered compound: 90° domain, 180° domain and anti-phase domain. In the view of structure, 90° domains belong to rotation twins, which can be identified from their different electron diffraction patterns or the fringe symmetry character of their boundary [17]. 180° domains originate from a 180° directional rotation of the polarization vector and do not lead to lattice distortion in the a–b plane, which could only be seen in this situation as the failure of Friedel's Law. The method of identifying 180° domain walls was reported by Tanaka [18]. Antiphase boundaries are one type of translational domain and they show π fringes in the bright and dark field images [19], which are only seen in the dark-field images using a superlattice diffraction spot.

The physical property aspect of La doping in bismuth titanate has been investigated in previous papers. A Raman study as well as neutron structure refinement showed that when $x < 1.0$, the La selectively substitutes for Bi ions in the perovskite layer instead of those

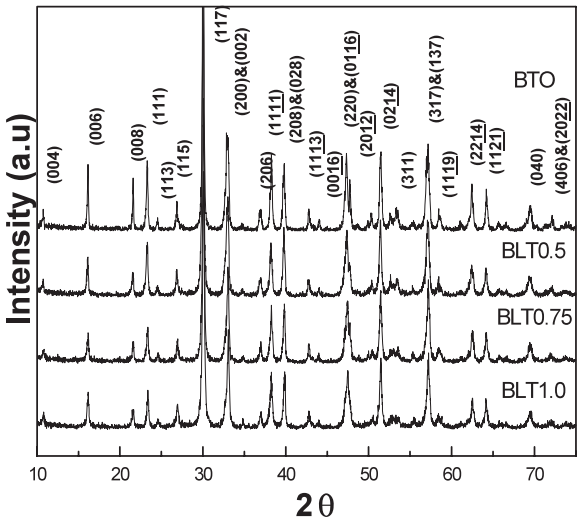

Figure 1. XRD patterns of BTO, BLT0.5, BLT0.75, and BLT1.0 with Cu Kα irradiation.

in the bismuth oxygen layer [12, 20]. As suggested by [7], La doping in the perovskite layer efficiently increases the chemical stability against oxygen vacancies which results in an improvement in the fatigue property. It is also reported that the remanent polarization increases after La doping in BTO. Our recent study shows that the activation energy associated with the hopping of oxygen vacancies increases from 0.69 (BTO) to 0.83 eV (BLT0.75) [21]. The changes in properties and activation energy lead us to want to understand the change of domain structure in BLTx.

3.1. Morphology of 90° domains

A series of TEM images of BLTx are shown in figure 2. Figures 2(a) and (b) show the bright-field (BF) image and the corresponding dark-field (DF) image of BTO, respectively, using the (020) diffraction spot. The boundary between domains I and II is a 90° domain wall, which shows δ fringes (i.e. the fringe in BF image is asymmetric, while the fringes in the DF image are symmetric) [17]. It is shown that the boundary is straight and parallel to the $\{110\}$ planes. The morphology of the 90° domain walls in BTO is as same as that reported in PZT [22]. Figures 2(c) and (d) show two DF images of BLT0.5 using the (125) and $(2\bar{1}4)$ superlattice diffraction spots respectively. The (125) and $(2\bar{1}4)$ superlattice diffraction spots belong to these two types of domains respectively, and have a 90° rotational relationship between them. After a 90° rotation around the c axis, the (125) spot transfers to the $(2\bar{1}5)$ spot position in reciprocal space. However, the $(2\bar{1}5)$ reflection is not allowed. Instead, the $2\bar{1}4$ superlattice diffraction spot is used to obtain the DF image (figure 2(d)). So, it is identified that the dark areas and the bright areas form 90° domain walls, where the contrast is reversed. The boundaries are almost straight and parallel to the $\{110\}$ planes. Since the two DF images are obtained using superlattice diffractions, APBs should be observed if they exist. Dozens of grains have been examined and no clue to the existence of APBs has been found as in the cases of BLT0.5 and BTO. This is in agreement with the previous reports [13, 14]. Figure 2(e) shows a DF image of BLT0.75 using a superlattice diffraction, in which the contrast of APBs can clearly be seen. The bright and dark areas form 90° domain walls, in contrast to the straight 90° domain walls in

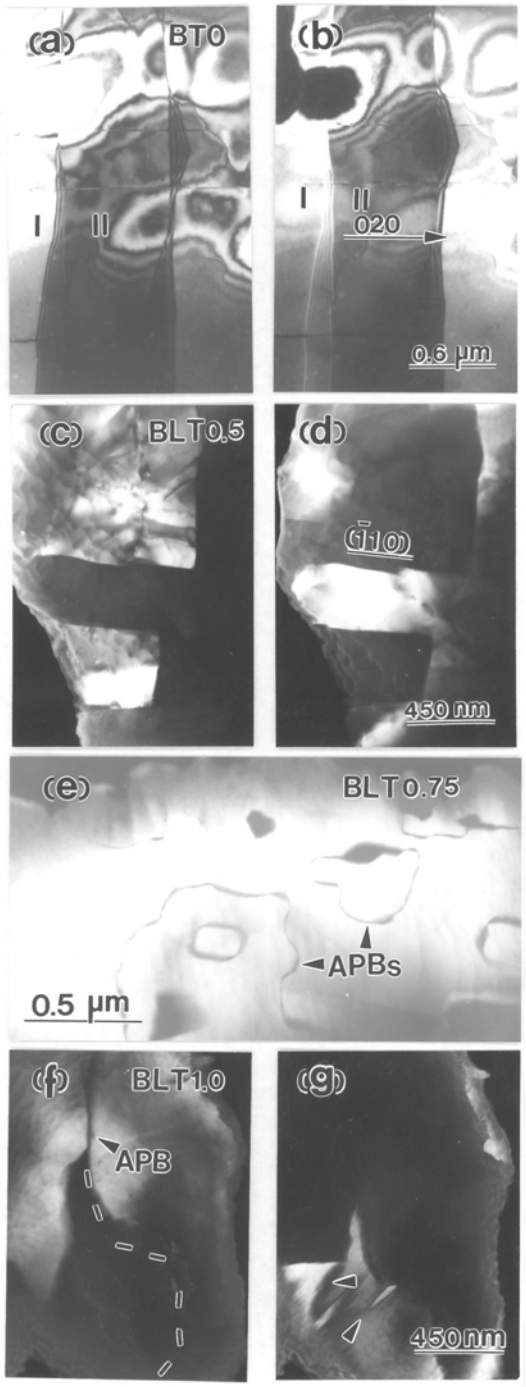

Figure 2. BF (a) and DF (b) images of the BTO sample using the (020) diffraction spot. The 90° domain walls are straight. (c) and (d) are two DF images of the sample of BLT0.5 using the (125) and (2$\bar{1}$4) diffraction spots, respectively. The bright and dark areas are 90° domains. (e) DF image of BLT0.75 using a superlattice diffraction spot; the curved lines are APBs. (f) and (g) are two DF images of the sample of BLT1.0 using the (125) and (2$\bar{1}$4) diffraction spots, respectively; the arrows in (g) mark the 180° domain walls.

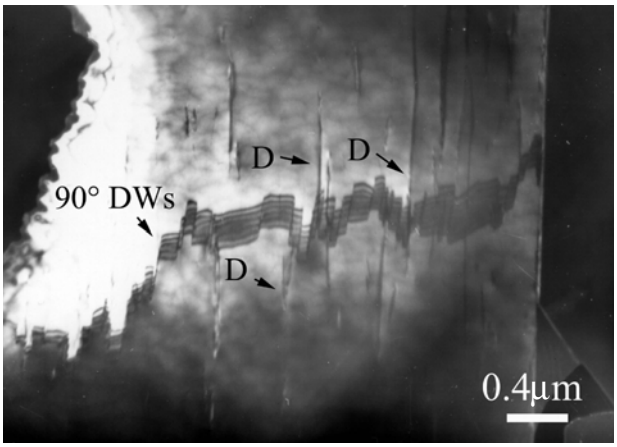

Figure 3. A dark field image of BTO shows several dislocations (marked as 'D') congregating about the 90° domain walls.

BTO, PZT and BTN [23], and the 90° domain walls show curved morphology similar to those of SBT. Figures 2(f) and (g) also show two DF images of BLT1.0 using the (125) and $(2\bar{1}4)$ superlattice diffractions, respectively. The APB is marked and the observed 180° domain walls are marked by arrows in figure 2(g). The failure of Friedel's Law in the 180° domains results in the small difference in contrast. A high density of APBs is observed in BLT0.75. But when x exceeds 1.0, the density of APBs, as well as 90° DWs, is decreased. This trend may be due to the decrease of T_c.

Three types of domain wall are observed in BLTx ceramics. The 180° domains do not lead to lattice distortion in the a–b plane and are only ferroelectrics. However, the 90° DWs are both ferroelectric and ferroelastic. The morphology of the 90° DWs is affected by the total free energy including strain energy, dipole–dipole interaction and electrostatic energy. In BTO, the strain energy dominates the free energy, and hence the 90° DWs are straight due to the demand of minimizing the magnitude of the strain energy. When a Bi ion at an A site is substituted by La in BTO, the strain energy suddenly decreases in BLT0.75, and then dipole–dipole interactions and electrostatic energy are dominant in the free energy [8]. Both of them are independent of the area of the domain wall; therefore, the 90° DWs become curved, possibly from the inhomogeneity of the dipole–dipole effects, the same as the case in $SrBi_2Ta_2O_9$ reported by Zurbuchen *et al* [24].

Figure 3 shows a dark field image taken from another BTO specimen, and dislocations are found in it. These dislocations are in the c plane and have been suggested to result from the mismatch between the Bi_2O_2 layer and the perovskite layer. It is found that the 90° DW changes its usual configuration when meeting with vertical dislocations. This indicates that there are strong interactions between the 90° DW and dislocations. We do not find this phenomenon in other BLTx samples. Our results suggest that dislocations could also pin down domain walls; in addition, x-ray photoemission spectroscopy has revealed domain wall pinning by oxygen vacancies in BTO [25].

3.2. Mobility of 90° domains

Figures 4(a)–(d) show a series of DF images from a grain of BLT0.75, using a superlattice diffraction. The images were taken at intervals of about 1 min. The polarization directions in the domains are marked by arrows. As seen in figures 4(a)–(d), under the irradiation of the

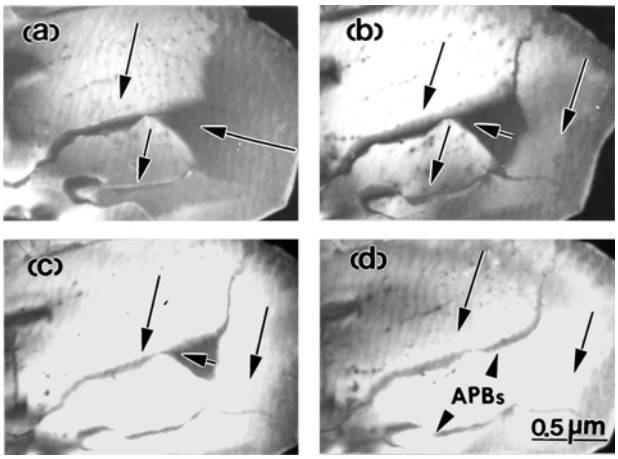

Figure 4. A series of DF images of the sample of BLT0.75 using a superlattice diffraction. Arrows mark the polarization directions in these domains. The movement of the 90° domain wall is recorded, just under the electron beam irradiation.

electron beam, the 90° domain wall moves step by step and completely disappear in figure 4(d). Those images show the mobility of the 90° domain after La doping. The effects of the electron beam on 90° domains includes thermal effects and the effect from accumulated charge on the specimen surface as suggested in [26]. We believe that the accumulated charge effect is most important because the domain wall would be stable after depositing carbon on the specimen surface. In contrast with the 90° DWs, APBs are observed to be stable.

There are three possible reasons for the higher mobility of 90° DW in BLT0.75. The first is the lower P_s in BLT0.75, the second is its lower distortion energy, and the third is attributed to the different nature in pinning 90° DWs. According to the equation proposed by Merz [27], the domain wall velocity can be given by $v = v_\infty \exp(-\delta/E)$, where δ is the activation energy and E is the applied electric field that depends on the interactions inside the TEM. Lines and Glass gave the formula $\delta = \text{constant} \times P_s^3/T$ [28]. P_s is 36.3 μC cm^{-2} along the a axis in BTO and it is 44% more than that in BLT. This shows that the lower P_s leads to higher mobility of 90° DWs. On the other hand, as we know, the distortions of the 90° DWs in BTO is larger than that in BLT0.75. Therefore, the movement of 90° DWs should be able to overcome a higher potential hill in BTO, which leads to its stability in the electron beam irradiation. So, the higher mobility of 90° DWs in BLT0.75 could also result from the lower relative strain energy contribution. Finally, with regard to the crystal structure, the formation of 90° domains in BTO (or BLT) is caused by exchanging the a axis with the b axis (oxygen octahedrals tilting with vertical axis), which differs from ionic distortion in PZT (the B site ions displacing in the vertical direction). At the 90°-domain walls, lattice mismatching leads to some interspaces. And the interspaces are ideal sites for charged defects. In BTO, there are larger deformations resulting in a bigger defects capability. Furthermore, the density of the charged defects in BTO is more than that in BLT due to the higher Bi volatility in BTO [29]. Consequently, more charged defects will be assembled at 90° DWs in BTO than in BLT. Such defects could also pin down the 90° DWs and depress their mobility in BTO. In agreement with this, we see that dislocations interact with 90° DWs in BTO (figure 3), which is not the case in BLT.

3.3. The effects of 90° DW morphology and mobility on ferroelectric properties

In BLTx thin films, the largest remanent polarization was observed with $x = 0.75$ [29]. This enhanced P_r has been interpreted as being due to the effect of lattice distortion induced by La

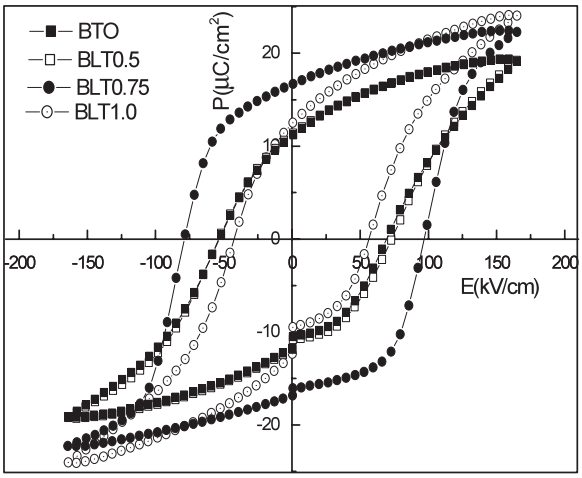

Figure 5. P–E loops of BLTx ceramics with $x = 0$, 0.5, 0.75, 1.

substitution. However, Shimakawa *et al* found that La substitution at an A site would reduce the internal tension in the a–b plane, leading to a decrease of T_c and the spontaneous polarization in BLT [12]. The grain orientation of ferroelectric thin films could strongly influence the magnitude of P_r. To exclude this effect, BLT ceramics with different La contents, instead of thin films, were selected to be measured, in which no orientation difference was found from their XRD patterns (see figure 1). The P–E loops of the ceramic samples are shown in figure 5. BLT0.75 was found to have the largest P_r, which is in agreement with the results in thin films [30]. This could be considered as resulting from the movement of 90° domain walls: 90° domain wall switching needs longer relaxation time due to the existence of the strain. In contrast, no strain is formed in the case of 180° domain walls. In PZT, within the frequency range of application, polarization reversal of the 90° domains is always ignored due to its low responsive velocity, and 180° domain reversal is considered to be the main contribution to the switching process [31]. With depression of strain in BLT0.75, the responsive velocity of the 90° domains increases. The reversal of 90° DWs is suggested to have an additional contribution to P_r in BLT0.75.

In our previous work, we discussed the relations between the fatigue properties and the morphology of 90° DWs [10, 11]. Our most recent results suggested that the curved 90° DWs could reduce the charged defects in SBT, contributing to a fatigue-free behaviour. In this section, an additional reason for the fatigue-free properties related to stress is proposed: in the process of switching, an additional stress induced by the relaxation of the straight 90° domains could pin 180° domains [16]. On the other hand, in BLT0.75, no stress was produced in the moving of curved 90° DWs, because the movement of opposite domains counteracts the stress. So, the pinning of 180° domains by stress is reduced. Until now, all experimental results support the conclusion that curved 90° DWs correspond to fatigue-free properties. Comprehensive work on the effects of domain structures on the physical properties in BLSFs is in progress.

4. Conclusions

In summary, two types of 90° domain wall are found in BLTx ceramics: one type is straight and parallel to the {110} planes in BTO and BLT0.5; another type in BLT0.75 is observed

to be curved and active. The different morphology and mobility of 90° domains in BLT0.75 originate from the decrease in strain energy and the pinning effect of charged defects after La doping. The P–E loops of BLTx ceramics have also been measured, and the enhancement of the P_r in BLT0.75 was interpreted as due to the movement of 90° DWs. Relaxation of curved 90° DWs, absorbing the stress by opposite movements, is suggested as improving the fatigue properties.

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