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Domain Observations of As-grown and Annealed Bismuth Titanate-Based Crystals

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ABSTRACT

Domain structures of bismuth titanate (BiT) and rare-earth (La and Nd)-substituted BiT crystals (BLT or BNT) before and after annealing were investigated by optical microscope and piezoresponse force microscope (PFM). Annealing of BiT at 950°C in air significantly decreased the number of striped 90° domain walls, while charged 180° domain walls were still observed in the crystals after the annealing. The annealing for the crystals of BLT and BNT at the same condition did not change their 90° domain structures. PFM observations of BLT crystals indicate that antiphase domain boundaries play an important role in the formation of 90° domain structures. These results suggest that the 90° domain structures of BiT-based crystals are influenced by external stress, spontaneous strain and antiphase domain boundaries.

Key words: bismuth titanate, single crystals, rare earth substitution, piezoresponse force microscopy

1. INTRODUCTION

Ferroelectric bismuth titanate ($Bi_4Ti_3O_{12}$, BiT) has been regarded as a promising candidate material for many applications such as nonvolatile memories and lead-free piezoelectric devices, because of its high Curie temperature (T_C) of 675°C and its spontaneous polarization (P_s) of as large as50 μC/cm^2 along the ***a*** axis [1,2]. It is, however, known that BiT ceramics and thin films show a small remanent polarization (P_r) and that they are prone to fatigue after repetitive polarization switching [3]. The small values of P_r are considered to be the decrease in reversible domains, i.e., domain pinning. Since the poor polarization property of BiT-based materials is closely related to domain structures [4], understanding the behavior of domain structures is essentially important for the applications of BiT.

One of the most effective ways for improving polarization properties of BiT is the substitution of Bi by rare-earth elements such as La and Nd. La-substituted BiT (BLT) and Nd-substituted BiT (BNT) have shown a relatively large P_r and high fatigue endurance [5,6]. We have previously reported the domain structures of as-grown crystals of BiT, BLT and BNT in the ***a-b*** plane, and antiphase domain boundary (ADB) was observed in BLT crystals [7,8]. However, the changes in domain structures of BLT and BNT crystals by annealing have not been understood yet.

In this study, the influence of thermal annealing in air or in high pressure oxygen on the domain structures is reported for BiT crystals. The effects of La and Nd substitution on the domain structures are also discussed.

2. EXPERIMENTAL

BiT crystals were grown by a self-flux method from a powder mixture of Bi_2O_3 (flux) with 99.9999% purity and TiO_2 with 99.99% purity. The mixture was melted at 1200°C for 10 h, and then cooled to 1000°C at a rate of 4-7°C/h. The obtained plate-like crystals had the dimensions of about 10 mm by 10 mm in the ***a-b*** plane, with the thickness of 0.1-0.2 mm along the *c* axis. After mechanical polishing of surfaces, the 90° domain structures in the ***a-b*** plane of the crystals were observed by optical microscope using transmitted light. Observations by piezoresponse force microscope (PFM, SII SPI3800N + SPA400) were conducted for the detailed visualizations of 90° and 180° domain structures. For the PFM measurements, Rh-coated Si cantilevers (SII SI-DF40R) with a spring constant of 38 N/m^{-1} and a resonance frequency of 316 kHz were employed, and an oscillation voltage of 20 V at a frequency of 5-10 kHz was applied between the

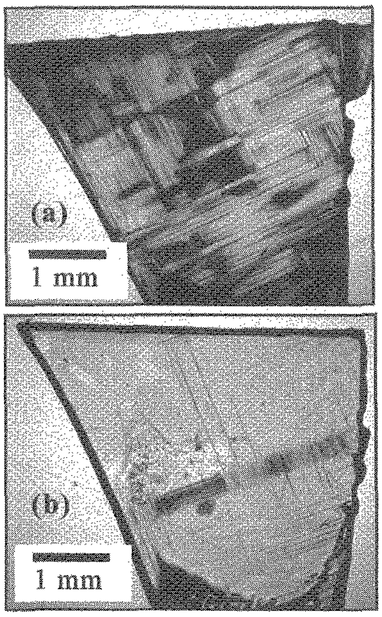

Fig.1 Optical microscope images of the BiT crystal (a) before and (b) after annealing at 950°C for 10 h in air.

cantilever and gold electrode sputtered to the backside of the crystals. The domain observations were conduced before and after annealing at 950°C for 10 h in air. Some of the BiT crystals annealed in air were subsequently annealed at 700°C for 10 h at a high oxygen pressure of 35 MPa, and their domain structures were also observed by PFM. $Bi_{3.54}La_{0.46}Ti_3O_{12}$ [BLT (0.46)] and $Bi_{3.54}Nd_{0.48}Ti_3O_{12}$ [BNT (0.48)] crystals were also grown by a self-flux method from the polycrystalline powders, which were prepared by the conventional solid-state reaction method. The details of the growth of BLT and BNT crystals are described in Refs. [8,9]. The content of rare earth in the crystals was determined by inductively coupled plasma emission spectroscopy. The domain observations of BLT (0.46) and BNT (0.48) crystals were also conduced before and after the annealing at 950°C for 10 h in air, by the same method as the observations of BiT.

3. RESULTS AND DISCUSSION

Figure 1 shows the optical microscope images of BiT crystal before and after annealing in air. For as-grown samples, striped 90° domain walls were observed throughout the crystal. The width of 90° domains was about 10 μm. After annealing in air, the amount of 90° domain walls was significantly reduced and the transparency of crystals became higher. The annealing resulted in the formation of larger 90° domains from 10 μm to more than 1 mm in width.

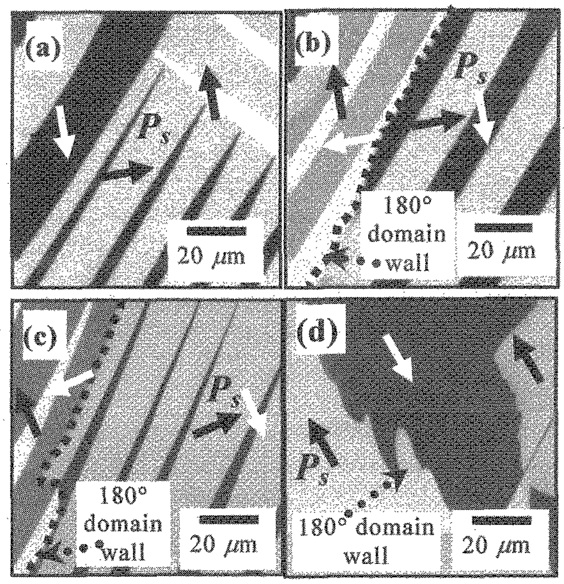

Fig. 2 PFM images of the (a), (b) as-grown and (c), (d) annealed BiT crystals. Arrows indicate the directions of P_s.

Figure 2 shows the in-plane PFM images of as-grown and air-annealed BiT crystals. The directions of P_s of domains are indicated by the arrows. Along with the striped 90° domain walls [Fig. 2(a)], 180° domain walls with tail-to-tail configuration of P_s were found in the as-grown crystals [Fig. 2(b)]. These charged (head-to-head or tail-to-tail) domain walls are known to interact strongly with charged defects such as oxygen vacancies [10], and this interaction causes a pinning of domains. The domain structures of the 90° domain wall-rich region of the annealed crystals [Fig. 2(c)] were similar to the image of the as-grown crystal [Fig. 2(b)]. The charged 180° domain walls were still observed after the annealing. Fig. 2(d) shows the PFM image of another region of the annealed crystal. Although there were no 90° domain walls, irregular shaped 180° domain walls with charged (head-to-head or tail-to-tail) configurations existed in the area. Unlike 90° domain walls, the density of 180° domain walls did not change remarkably by the annealing.

When BiT crystals are cooled in flux (Bi_2O_3) with a solid state, ferroelectric phase transition occurs under high mechanical stress. The change in the size of crystals by the phase transition is strongly restricted by the adjacent solid-state flux. To minimize the change of macroscopic external form, which requires a much higher energy, many 90° domain walls are introduced in spite of having a high strain energy. For the crystals annealed above T_C, however, the structural phase transition occurs without external stress. In this stress-free state, the energy required for changing

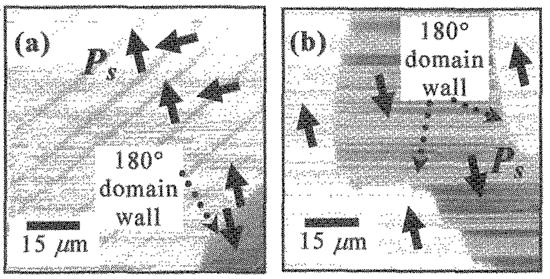

Fig. 3 PFM images of the BiT crystal after annealing in high-pressure oxygen.. Arrows indicate the directions of P_s.

external form becomes much lower, and then the formation of 90° domain walls, which is energetically unfavorable, is suppressed. Thus, the annealing of the BiT crystals greatly decreases 90° domain walls with the ferroelastic strain energy. On the contrary, since 180° domain walls are non-ferroelastic walls, 180° domain structures are less affected by the external strain when ferroelectric phase transition takes place, as can be seen in Fig. 2. Our results indicate that charged 180° domain walls act as a strong pinning site during polarization switching even for the BiT crystals annealed above T_C. The domain pinning by the charged 180° domain walls is a reason that the reported values of P_r in annealed BiT crystals [1,7] is much lower than the predicted P_s value of BiT [2].

Figure 3 shows in-plane PFM images of a BiT crystal annealed in air and then in the high-pressure oxygen. Like the crystals annealed only in air [Fig. 1], the density of 90° domain walls was not uniform. However, the overall amount of 90° domain walls of the crystal was slightly increased by subsequent annealing in oxygen, which originates from relatively high pressure of the ambient oxygen. Figure 3(a) shows the region with a high density of 90° domain walls, and Fig. 3(b) shows the region without 90° domain walls. Charged 180° domain walls were shown in both the images and significant influence on local domain structures of the annealing in oxygen was not observed. Therefore the domain pinning by the charged walls is not reduced markedly after the annealing in high-pressure oxygen. In fact, the reported P_r value of BiT crystals annealed in high-pressure oxygen is slightly larger than that of the crystals annealed in air [7,10].

Figure 4 shows the optical microscope images of (a)(b) BLT (0.46) and (c)(d) BNT (0.48) crystals before and after annealing in air. These crystals exhibited no recognizable change in 90° domain structures after the annealing in air, which made a great contrast to the BiT crystals. The substitutions of La and Nd in BiT has been reported to decrease spontaneous strain (S), which is

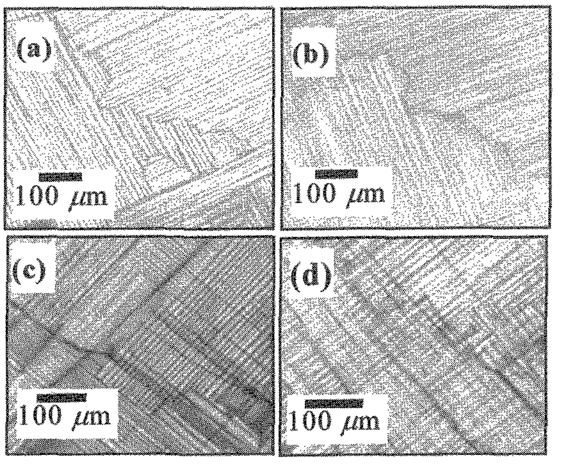

Fig. 4 Optical microscope images of the BLT (0.46) crystal (a) before and (b) after annealing, and the BNT (0.48) crystal (c) before and (d) after annealing.

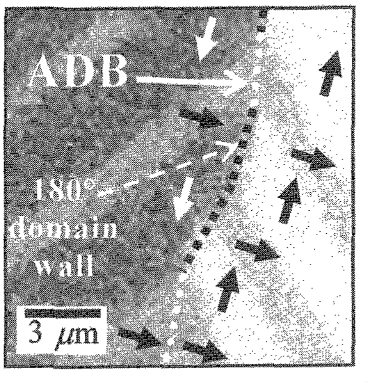

Fig. 5 PFM image of annealed BLT (0.46) crystal. Arrows indicate the directions of P_s.

defined by $S = \boldsymbol{a}/\boldsymbol{b} - 1$, from 0.007 for BiT to 0.004 for BLT (0.50) and BNT (0.50) [7,8]. The lower values of S decrease the energy for the formation of 90° domain walls, where the exchange of the ***a*** and ***b*** axes occurs. Therefore, the rare-earth substitution stabilizes the 90° domain walls compared with the case of BiT, and many 90° domain walls can be formed even under stress-free condition.

The PFM image of annealed BLT (0.46) crystal is shown in Fig. 5. BLT (0.46) crystal had striped 90° domains with a smaller average domain width of 4 μm than that of BiT. Unlike the domain structures of BiT, adjacent 90° domain structures were terminated at a curved boundary. PFM observations of as-grown BLT (0.46) crystals by Soga *et al.* [7] have demonstrated that the curved boundary consists of 180° domain walls and antiphase domain boundaries (ADB). In Fig. 5, the black dotted lines indicate 180° domain walls where the ***a*** axis have an antiparallel (uncharged) configuration, and the white dotted lines indicate ADB where the directions of the ***a*** axes are the same and the ***b*** axes have an antiparallel configuration. The translational phase shift of the unit cell by [1/2 1/2 0] occurs at the ADB [4]. Across the ADB, the ***a*** axis does not change, whereas the ***b*** axis rotates by 180°. Since the structural distortion of BLT is much larger along the ***b*** axis than along the ***a*** axis, a high strain energy is stored around the ADB. The results shown in Fig. 5 suggests that the deformation of the crystals is restricted by the ADB, leading to the formation of striped 90° domain structure surrounded by the ADB. Further study on the phase transition of BLT and the formation mechanism of ADB is required for elucidating the domain structure. It is concluded that the 90° domain structures of BiT-based crystals are influenced by external stress, *S* and ADB.

4. CONCLUSION

Influence of annealing on the domain structures of BiT, BLT and BNT crystals were investigated by optical microscope and PFM. The annealing of BiT crystals above T_C decreased 90° domain walls, whereas the density of 180° domain walls remained unchanged even after annealing in air and in high-pressure O_2. Unlike BiT, 90° domain structures of annealed BLT (0.46) and BNT (0.48) crystals were almost the same as those of as-grown crystals. These results suggest that not only external stress, spontaneous strain but also ADB play an important role in the formation of 90° domain structures of BiT-based crystals.

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