

## Domain Observation of Rare-earth-substituted Bismuth Titanate Single Crystals

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### ABSTRACT

Bismuth titanate ( $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , BiT) and rare-earth (RE=La, Nd)-substituted BiT single crystals were grown by a self-flux method. La-substituted BiT ( $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ , BLT) and Nd-substituted BiT ( $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ , BNT) showed a smaller remanent polarization ( $P_r$ ) than BiT, and the decrease in  $P_r$  arises from smaller ferroelectric distortions. In polarizing microscopy images, striped  $90^\circ$  domain walls were observed for all crystals, and La or Nd-substitution led to a noticeable decrease in average domain width from  $8.5 \mu\text{m}$  for BiT to  $2.5 \mu\text{m}$  for BLT ( $x=1.20$ ) and  $2.7 \mu\text{m}$  for BNT ( $x=1.24$ ). Piezoelectric force microscope observations of BLT demonstrate the presence of antiphase domain boundary (ADB), which was not observed in BiT. These results suggest that the ADB plays an important role in the formation of the  $90^\circ$  domain structure and the domain dynamics during polarization switching.

Key words: bismuth titanate, single crystals, domain switching, piezoelectric force microscopy

### 1. INTRODUCTION

Bismuth titanate (BiT,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ) has received a great deal of attention for its applications to nonvolatile memories and electromechanical devices because of its large spontaneous polarization ( $P_s$ ) and lead-free nature.[1, 2] However, ceramics or thin films of BiT show a much smaller remanent polarization ( $P_r$ ) than its single crystals. Moreover, they suffer from fatigue, *i.e.* a  $P_r$  decrease with repeated switching of polarization.[3,4]

Ceramics and thin films of rare-earth (RE)-substituted BiT, such as lanthanum-substituted BiT (BLT,  $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ ) [5, 6] and neodymium-substituted BiT (BNT,  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$ ) [7, 8], have been reported to show a larger  $P_r$  and better fatigue durability than BiT counterparts. Although RE substitution is demonstrated to improve the memory properties of BiT thin films, details of lattice parameters and domain structure remain uncertain. For further understanding of the effects of RE substitution, studies using single crystals of RE-substituted BiT are crucially important.

In the present study, we have grown BLT and BNT single crystals with various RE content  $x$ . The domain structures of these single crystals were investigated through piezoelectric force microscopy (PFM) [9, 10] as

well as optical microscopy, and the origin of the improved properties by RE substitution is discussed.

### 2. EXPERIMENTAL

$\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$  [BLT ( $x$ )] and  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  [BNT ( $x$ )] ceramics were synthesized by a solid-state reaction from  $\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{La}_2\text{O}_3$  (or  $\text{Nd}_2\text{O}_3$ ). Their x-ray diffraction patterns were obtained and analyzed by the Rietveld method (the RIETAN 2000 program [11]) based on  $B2cb$  orthorhombic symmetry. BLT and BNT single crystals were grown by a self-flux method using the ceramics powder and  $\text{Bi}_2\text{O}_3$  as a flux.[12] The content of RE ( $x$ ) in the crystals was determined by inductively coupled plasma atomic emission spectrometry. For electrical measurements, the crystals were embedded in resin and cut so that electric field is parallel to the crystallographic  $a$  or  $b$  axis. After polishing the surfaces of crystals well, domain structures in the  $a$ - $b$  plane of the as-grown crystals were observed with polarizing microscope. For the detailed investigations of the domain structures, in-plane PFM measurements were performed using conductive cantilever. The PFM can not only visualize  $180^\circ$  domain boundaries but also determine the direction of

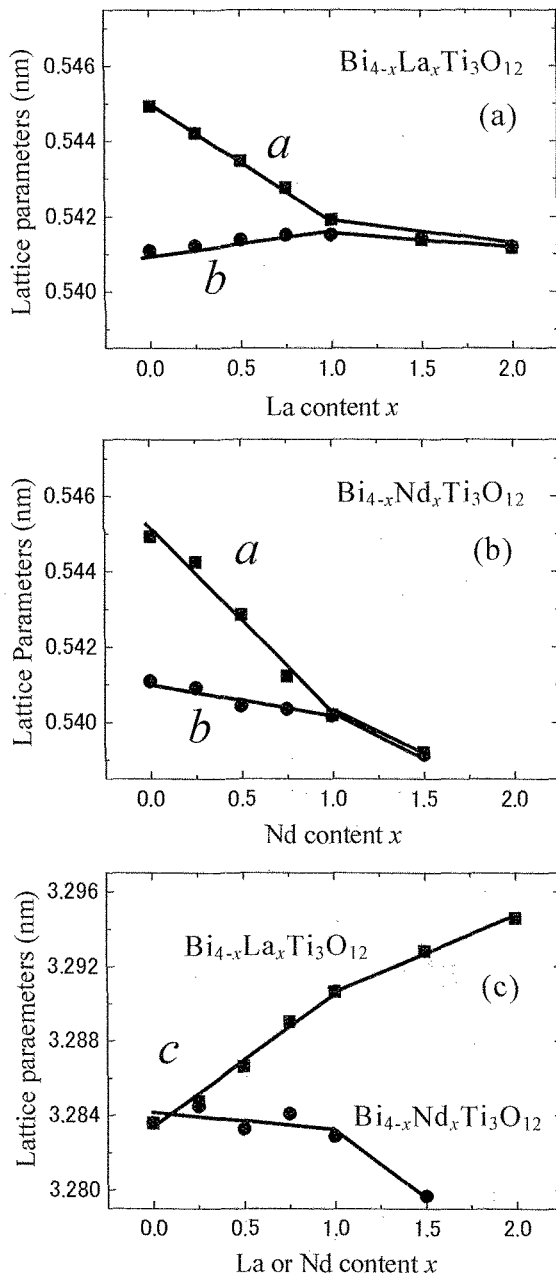


Fig.1 Lattice parameters  $a$ ,  $b$  and  $c$  of BLT and BNT ceramics with various compositions.

spontaneous polarization ( $P_s$ ).

### 3. RESULTS AND DISCUSSION

The lattice parameters  $a$ ,  $b$  and  $c$  refined by the Rietveld method as a function of RE content  $x$  are shown in Fig. 1. In both series, parameter  $a$  decreased with increasing  $x$ . Parameters  $b$  and  $c$ , however, showed different trend due to a smaller ionic radius of  $\text{Nd}^{3+}$  than  $\text{La}^{3+}$ : La substitution increased  $b$  and  $c$  while Nd substitution resulted in a monotonic decrease in  $b$  and  $c$ . The substitution of RE led to a decrease of orthorhombic

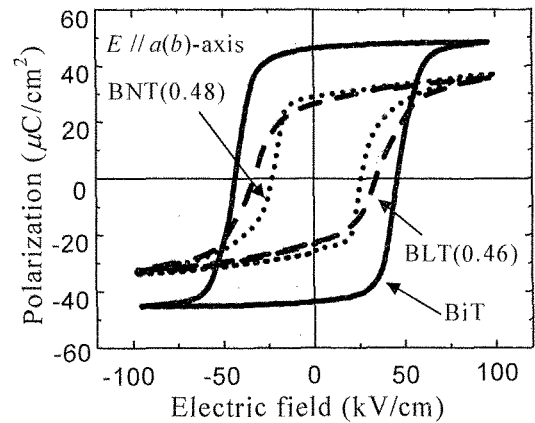


Fig.2 Polarization hysteresis loops for BiT, BLT(0.46) and BNT(0.48) single crystals measured at room temperature.

lattice distortion  $a/b$  in both cases, which suggests the smaller  $P_s$  in RE-BiT. All fitted lines in Fig. 1 had a change in slope near  $x = 1.0$ . These results imply that the substitution site of RE changes from the perovskite  $A$  site for  $x < 1.0$  to both the  $A$  site and Bi site in the  $\text{Bi}_2\text{O}_2$  layers for  $x > 1.0$ .

Figure 2 shows the polarization hysteresis loops of BiT, BLT(0.46) and BNT(0.48) crystals measured at room temperature. The  $P_r$  and coercive field ( $E_c$ ) of BiT were  $46 \mu\text{C}/\text{cm}^2$  and 45 kV/cm, respectively. The RE substitution resulted in a significant decrease in  $P_r$ , and the values of which were  $26 \mu\text{C}/\text{cm}^2$  for BLT(0.46) and  $29 \mu\text{C}/\text{cm}^2$  for BNT(0.48). The  $E_c$  values were also decreased by RE substitution to 33 kV/cm for BLT(0.46) and 24 kV/cm for BNT(0.48), respectively. The smaller ionic displacements of constituent ions along the  $a$  axis (polarization direction) [13] induce the smaller  $a/b$  caused by the RE substitutions, which are responsible for the smaller  $P_r$  observed for BLT and BNT crystals. The increase in  $P_r$  by RE substitution has been reported for ceramics or thin films, whereas our polarization measurements using single crystals showed poor polarization properties for BLT and BNT. This discrepancy seems to be closely related to domain structure and its dynamics.

Figure 3 indicates the polarizing micrographs of the crystals (the incident light was normal to the  $a$ - $b$  plane). All the crystals showed striped  $90^\circ$  domain boundaries in the  $a$ - $b$  plane. The domain structures of both BLT and BNT crystals were found to be finer than those of BiT. The average domain width of the crystals is plotted as a function of RE content  $x$  (Fig. 4). The average domain width decreases gradually with an increase in  $x$ . Since RE substitution decreases orthorhombic distortion ( $a/b$ ), the wall energy for  $90^\circ$  domain formation is reduced. As

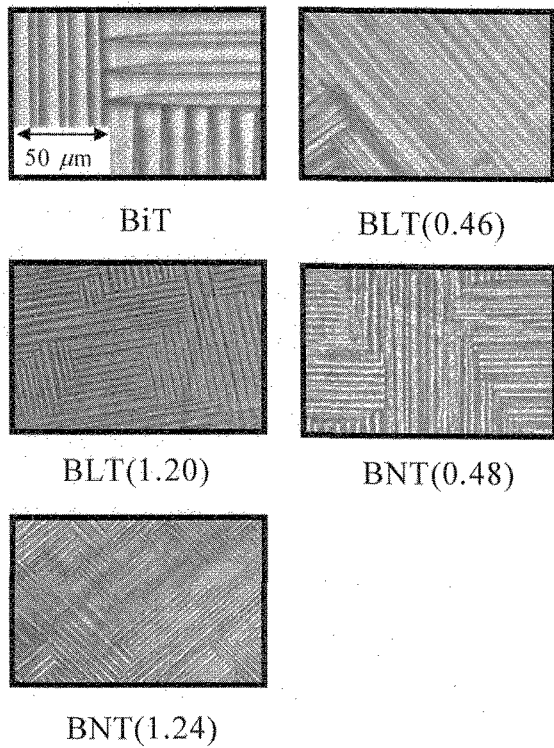


Fig.3 Polarizing microscope images of BiT, BLT and BNT single crystals in the *a-b* plane. All images are shown to the same scale.

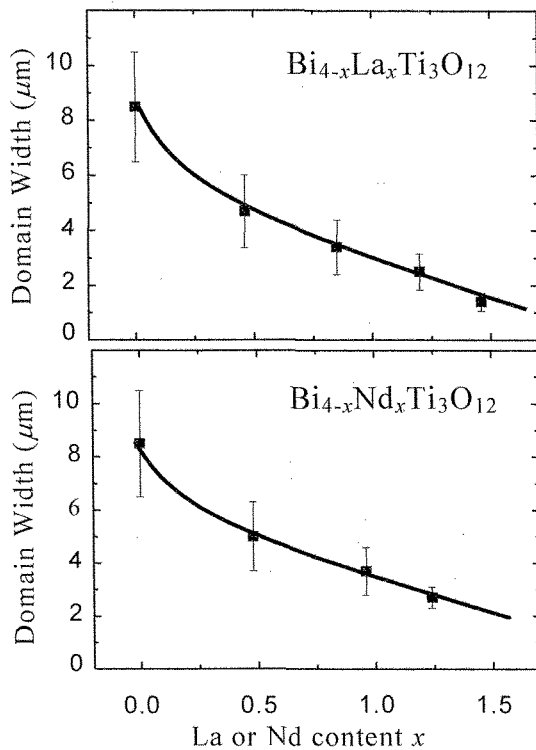


Fig.4 Average widths of 90° domains as a function of La or Nd content (*x*).

RE content *x* increases, it is energetically easier to form domain boundaries than smaller domain width for BLT and BNT crystals.

The PFM images of BiT single crystals are shown in Figs. 5(a) and (b). The arrow in the figures indicates the direction of *P<sub>s</sub>*. The striped region is composed of 90° domains and their widths are consistent with the results of the optical observations. The 90° domains connected perpendicularly at the needle-like domain ends. In the images obtained from another sample, there were randomly shaped 180° domain structures as well as striped 90° domain structures. Most of these 180° domain walls had head-to-head or tail-to-tail configurations of *P<sub>s</sub>* with electric charge. These results indicate that, in addition to typical charge-free 90° domain walls, the charged 180° domain walls are present in BiT crystals in spite of having an extremely high energy compared with charge-free walls. First-principles calculation study in perovskite

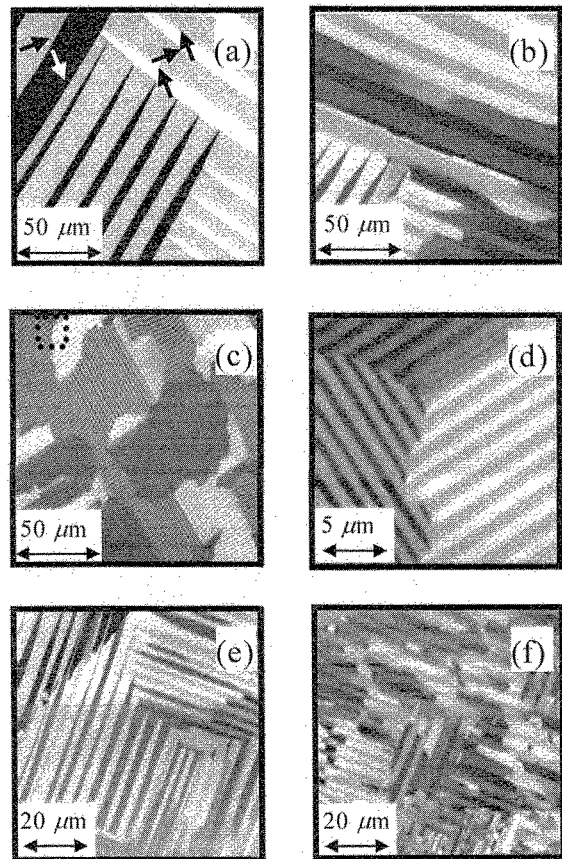


Fig.5 Piezoelectric force microscope images of BiT [(a) and (b)], BLT(0.46) [(c) and (d)] and BNT(0.48) [(e) and (f)] single crystals (*a-b* plane). Scales are shown below each image. Arrows indicate the directions of spontaneous polarization (*P<sub>s</sub>*).

ferroelectrics has showed strong interaction of charged domain walls with oxygen vacancies.[14] Furthermore, oxygen vacancies have reported to give rise to a poor polarization properties in BiT ceramics.[15, 16] These charged domain structures interact strongly with oxygen vacancies and are pinned during polarization reversals, which are responsible for a degradation of polarization and fatigue properties in BiT thin films and ceramics.

Figures 5 (c) and (d) show the PFM images of BLT(0.46) single crystals. In contrast to the PFM images of BiT, the domain structures were separated by irregular curves. Figure 5 (d) indicates the enlarged image of the dashed area in Fig. 5 (c). The irregular boundaries are the ends of regular 90° domains, which are composed of alternate sequence of uncharged (antiparallel configuration of  $P_r$ ) 180° domain walls and regions without change in PFM signal. These boundaries are antiphase domain boundaries (ADB) [13, 17], which can be superimposed on each other by a  $[1/2 \ 1/2 \ 0]$  translation operation. Ding *et al.* [17] have reported that the ADB exists in BLT ceramics and the ADB was not observed for BiT ceramics, which agrees with our present observations of single crystals. Ding *et al.* [18] suggest that, in addition to electrodes, the ADB plays the role of nuclei for domain formation during polarization reversal. It is suggested that only the sample/electrode interface acts as nuclei of new domain for BiT while domain switching occurs from the ADB as well as the electrode interface for BLT, leading to superior polarization properties of BLT thin films and ceramics.

The results of PFM observations of BNT single crystals are shown in Figs. 5 (e) and (f). Contrary to our expectation, no ADB were found in PFM images for BNT crystals. Whether BNT single crystals contain ADB or not is still unclear. Compared with BLT, BNT crystals exhibited a higher density of 180° domain walls with and without electric charge. Detailed analysis of the domain structure in BNT crystals is required for elucidating the effects of Nd substitution.

#### 4. CONCLUSIONS

BLT and BNT single crystals were grown by a self-flux method. The RE substitution resulted in a smaller  $P_r$  than BiT crystals, which originates from the decrease in ferroelectric distortion (ionic displacement of constituent ions along the  $a$  axis). Polarizing microscopy showed that both BLT and BNT had 90° domains with smaller width than BiT. The in-plane PFM observations revealed that BiT single crystals have

charged 180° domains with tail-to-tail and head-to-head  $P_r$  configurations as well as striped 90° domains. BLT had antiphase domain boundaries (ADB), which were not observed for BiT and BNT crystals. It is suggested that the ADB acts as nuclei of new domain during polarization switching, which is partly responsible for the better memory properties in BLT thin films.

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