

Domain Dynamics in Unpoled and Poled Bismuth Titanate Crystals

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ABSTRACT

Domain switching process of bismuth titanate single crystals was investigated under application of electric field along the crystallographic c axis through polarization measurements and domain observations by optical microscope and piezoelectric force microscope. While unpoled crystals exhibited a poor polarization hysteresis, the crystals which were poled at 150°C showed a well-saturated polarization hysteresis with a remanent polarization of 4.4 $\mu\text{C}/\text{cm}^2$ and a coercive field of 4.7 kV/cm. Domain observations reveal that lenticular domain acts as an initial nucleus both in the poled and unpoled crystals during polarization switching of the c -axis component. The sidewise motion of the lenticular-domain walls and resultant single domain state were easily established for the poled crystals, while the lenticular domains observed in unpoled crystals were clamped even though a high electric field was applied to them.

Key words: Bismuth Titanate, Ferroelectrics Properties, Domain Dynamics, Domain Clamping

INTRODUCTION

Bismuth layer-structured ferroelectrics (BLSFs) have attracted much attention for applications to ferroelectric non-volatile memories and lead-free piezoelectric devices [1, 2]. Bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT), a typical member of BLSFs, is known to show a large spontaneous polarization (P_s) mainly along the a axis [3, 4]. Figure 1(a) shows the crystal structure of ferroelectric BiT. Since BiT in a ferroelectric state has $B1a1$ monoclinic structure [5] and its P_s vector lies away from the a axis to the c axis by 4-5°, P_s appears along the c axis ($P_{s(c)}$) as well as along the a axis ($P_{s(a)}$). The switching of $P_{s(c)}$ occurs under a low electric field along the c axis without the change in the direction of $P_{s(a)}$. Since this $P_{s(c)}$ switching is accompanied with a large change in the orientation of the optical indicatrix (shown in Fig. 1(b)) [6], BiT has been regarded as a candidate material for optoelectronic devices [7, 8]. Although controlling the domain structure in BiT by applying an external electric field is essential for the applications, domain dynamics in BiT has not yet been clarified. The present paper describes the domain dynamics of BiT crystals under alternating electric field along the c axis, and the effects of electric poling at 150 °C [9] on the room-temperature polarization properties along the c axis are investigated.

EXPERIMENTAL

BiT crystals were grown by a flux method. Powders of Bi_2O_3 (with a purity of 99.9999 %) and TiO_2 (with a purity of 99.99 %) were mixed in the stoichiometric composition. The calcination of the mixed powder at 800°C for 4 h led to a single phase of BiT powder. Mixtures of the BiT powder and Bi_2O_3 powder as a flux were melted at 1200°C in platinum

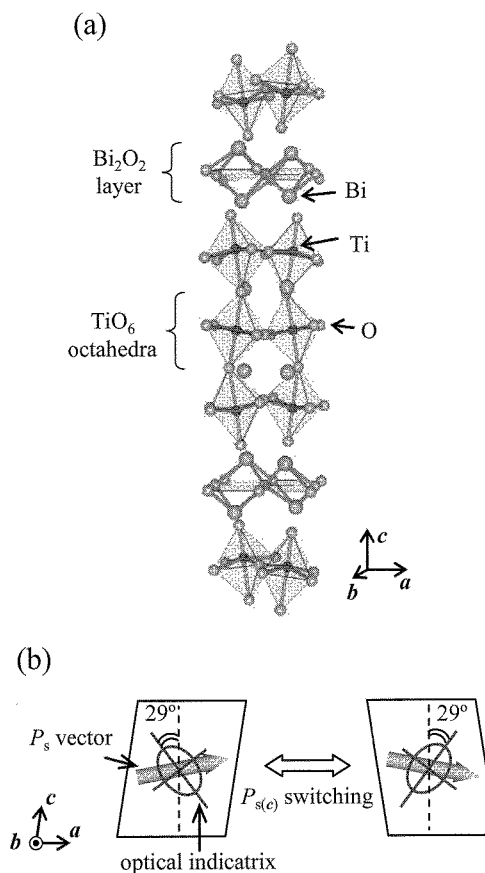


Fig.1 (a) Crystal structure of BiT and (b) the direction of optical indicatrix shifted by $P_{s(c)}$ switching (the monoclinic tilt angle β is shown exaggerated).

crucibles, and then slowly cooled down to 1100°C at a rate of 4°C/h. In the temperature range from 1100°C to 1000°C, the cooling rate was changed to 7°C/h. The BiT crystals obtained were thin plate-like sheets with lateral dimensions of about 10 mm × 10 mm and with a thickness of 0.1-0.3 mm along the *c* axis. After heat treatment at 900°C for 10 h in air was performed to reduce physical stress during crystal growth, these crystals were annealed under high-pressure oxygen atmosphere ($P_{O_2} = 35$ MPa) at 700°C for 10 h. Both major surfaces (the *a-b* planes) of the annealed crystals were mechanically polished, and then gold electrodes were sputtered on the polished surfaces. The thickness of the electrodes was adjusted to be 20 nm for optical observations of domain dynamics through the electrodes. This electrode thickness allows us to perform simultaneous investigations of polarization properties and optical-microscope observations. Polarization properties were measured at 25°C with an alternating field of 60 kV/cm (10 Hz). Some crystals were subjected to electrical poling treatment before measurements. The poling treatment is a method to align the direction of P_s by applying a high field. In our study, an electric field of 60 kV/cm was applied to the crystals along the *c* axis at 150°C. Optical observations of the domain dynamics were performed on the poled and unpoled crystals under application of alternating field along the *c* axis. Either the tilted-extinction-angle method or the differential-retardation method was employed on the observations so that domains with different directions of $P_{s(c)}$ were distinguishable [10]. In the differential-retardation method, white light was used as a light source [11], and retardation of crystals was subtracted with a Berek compensator for observing $P_{s(c)}$ switching as a change in interference color. Piezoelectric force microscopy was performed on the polished *a-b* surface to observe the detailed domain structures [12].

RESULTS AND DISCUSSION

Figure 2(a) shows the polarization hysteresis loops measured on unpoled BiT crystals (without the poling process at 150°C). The unpoled crystals exhibited a poor polarization hysteresis when the number of electric-field cycling was less. The remanent polarization (P_r) at the initial stage of cycling was quite small compared with the value reported for $P_{s(c)}$ of 4 $\mu\text{C}/\text{cm}^2$ [3, 13]. As shown in Fig. 2(b), the P_r rose gradually as the number of cycling increased, and finally reached a steady value of around 5 $\mu\text{C}/\text{cm}^2$ (this larger P_r is possibly overestimated due to the influence of leakage current or capacitance). A coercive field (E_c) of 7-8 kV/cm was obtained for the unpoled crystals after 10^3 cycles. This behavior of polarization properties shown in Fig.2 is quite similar to the deaging behavior reported in some aged ferroelectric materials [14, 15]. The increase in P_r by repetitive polarization switching suggests that $P_{s(c)}$ switching was clamped in the initial stage of cycling, and that the domain clamping results in the poor polarization properties as in the case of the aged ferroelectric materials [16].

Figure 3 shows the polarization hysteresis loops for the crystals before and after poling. The P_r and E_c of the poled crystals were 4.4 $\mu\text{C}/\text{cm}^2$ and 4.7 kV/cm,

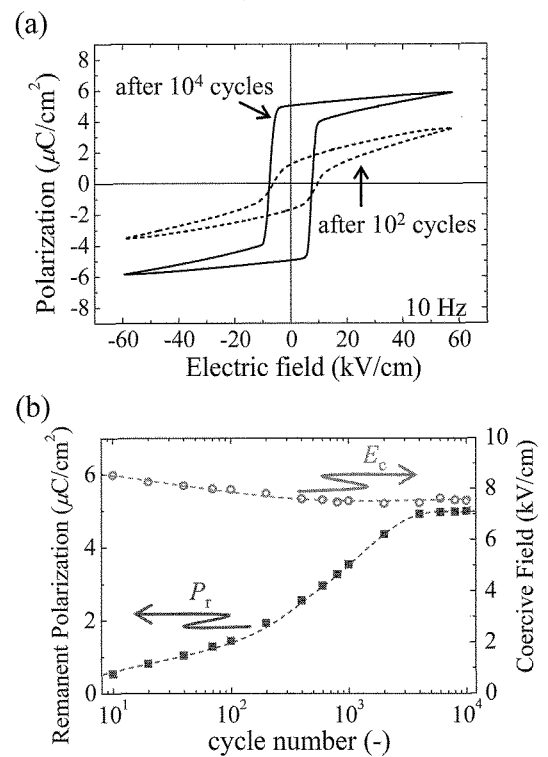


Fig.2(a) Polarization hysteresis loops after 10^2 and 10^4 electric-field cycles and (b) P_r and E_c as a function of the cycle number of electric field applied for unpoled BiT crystals.

respectively. The poling treatment led to an increase in P_r and to a decrease in E_c . In addition, the poling process enhanced the squareness of hysteresis loop which is determined by the mobility of domain walls. These results suggest that the poling treatment, as well as repetitive application of ac field, can unclamp the domains in unpoled crystals. The shift of the hysteresis loop observed for the poled crystals is attributed to the internal bias field established in the crystals due to the alignment of defect dipoles through the poling treatment [17, 18].

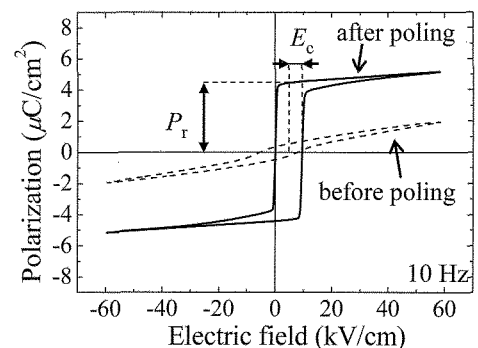


Fig.3 Polarization hysteresis loop along the *c* axis of poled BiT crystals (dashed line is a polarization hysteresis loop measured on the same crystal before poling).

Optical observations of domain dynamics in unpoled crystals reveal that most of the domains was strongly clamped and not switched at the beginning of repetitive application of ac field. It is also confirmed that the repetitive application induces small lenticular domains along the b axis in the clamped region and that these lenticular domains are switchable in the ac field. As the cyclic application of ac field was repeated, the switchable lenticular domains spread gradually. Figure 4(a) shows a piezoelectric force microscope (PFM) image of the lenticular domains observed on the a - b surfaces of unpoled crystals, in which a large number of the lenticular domains were induced by the repetitive application of ac field. This PFM image represents the vertical component of P_s on the surfaces namely the signal intensity and phase are determined by the vector of $P_{s(c)}$. Figure 4(b) shows the schematic representation of the lenticular domain. The deep-colored areas (with upward $P_{s(c)}$) in these figures denote the lenticular domains induced by external field, and neighboring light-colored areas (with downward $P_{s(c)}$) are strongly clamped region in which $P_{s(c)}$ cannot be switched by an ac field much higher than E_c . These results of optical and PFM observations provide direct evidence that the clamping of lenticular domain leads to the poor polarization properties in unpoled crystals as shown in Figs.2(a) and (b).

In poled crystals, domain switching by ac field was accomplished in the whole electrode area, and clamped domains were not observed. Figure 5 shows the switching process of $P_{s(c)}$ observed on the poled crystals.

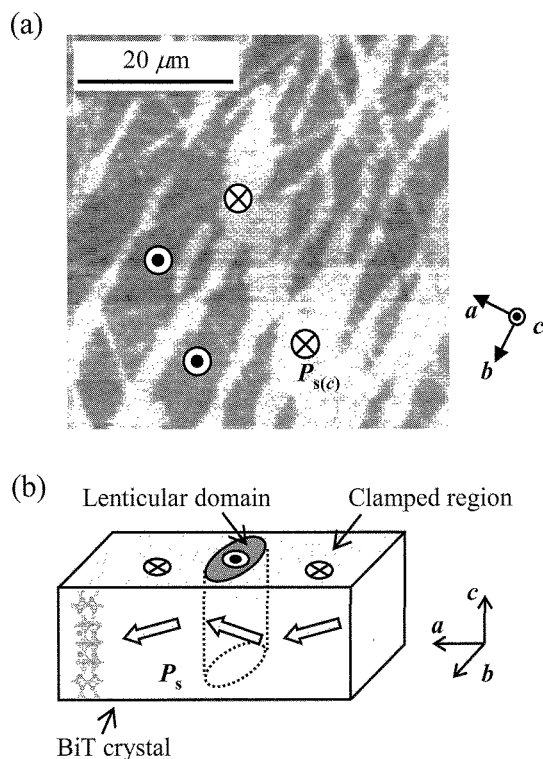


Fig.4 (a) PFM image in a - b surface of unpoled BiT crystals and (b) the schematic representation of the lenticular domain observed in (a).

Figures 5(a)-(c) indicate the optical micrographs of the domain states, which correspond to the closed circles denoted in the polarization hysteresis in Fig. 5(d). The $P_{s(c)}$ in the bright and dark areas seen in Figs. 5(a) and (b) were thoroughly reversed by applying an electric field, which shows that $P_{s(c)}$ switching is achieved in the whole region. The dashed lines which run vertically between bright and dark areas in Figs.5 (a) and (b) were

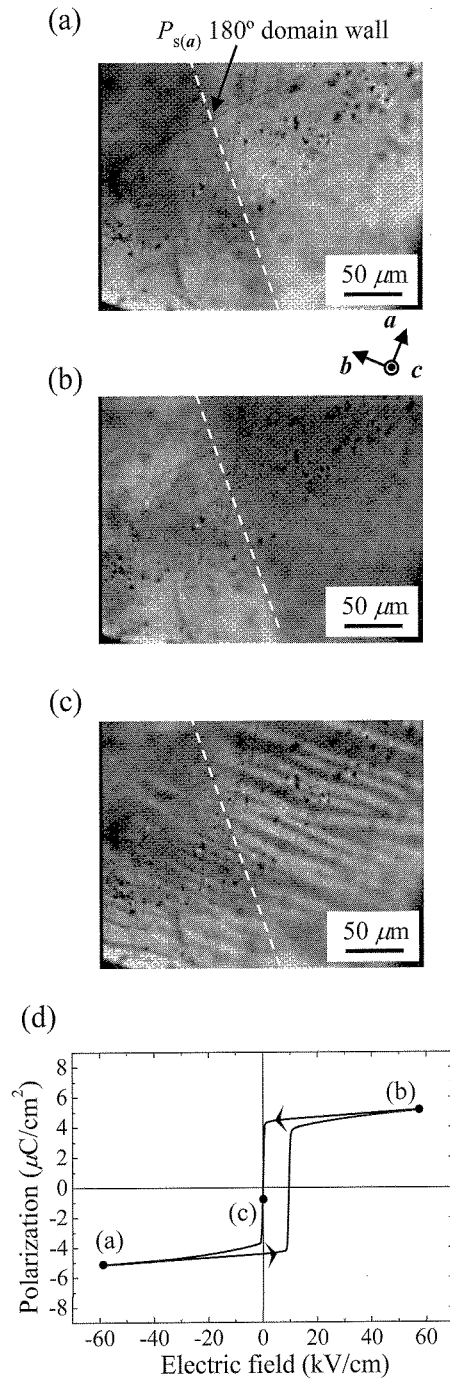


Fig.5 Domain structures of the poled crystals under (a) -60 kV/cm, (b) $+60$ kV/cm and (c) 0 kV/cm. (d) shows the polarization hysteresis along the c axis. The closed circle in (d) corresponds to the electric field at which the domain structure was observed ((a)-(c)).

$P_{s(a)}$ -180° domain wall ($P_{s(a)}$ directions of left and right sides were opposite). The lenticular domains are found to act as initial nuclei of $P_{s(c)}$ switching shown in Fig.5(c) [19, 20]. Note that the multidomain structure at 0 kV/cm was formed by spontaneous backswitching of $P_{s(c)}$ due to the internal bias field. These optical observations indicate that the poling treatment can make the clamped domains switchable, resulting in the well-saturated hysteresis shown in Fig.3.

The comparative study of the domain dynamics in unpoled and poled BiT crystals leads to the conclusion that the poor polarization properties of unpoled crystals originate from the clamping of the sidewise motion of lenticular domains. While the sidewise motion was easily achieved in poled crystals, as can be shown in Figs. 5(a)-(c), the sidewise motion was inhibited in unpoled crystals (see Fig. 4(a)). It is found that electric-field cycling as well as poling treatment is effective for enhancing polarization switching of $P_{s(c)}$ [14]. However, it should be noted that there is a difference in the stability of domain structures formed by these two electric treatments. The domain structures established by the cycling were in an unstable state, because the unpoled crystals showing a well-saturated hysteresis loop were aged and the P_r value returned to a lower one after a few days. On the other hand, poled crystals did not show the aging behavior after the poling treatment. These results clearly show that the domain structure established by the poling treatment is more stable than that formed by the repetitive switching as shown in Fig. 2.

CONCLUSIONS

Behavior of domain switching by applying an electric field along the c axis was investigated in unpoled and poled bismuth titanate crystals. The unpoled crystals show an unsaturated polarization hysteresis at the initial stage of electric field cycles. Observations of domain dynamics reveal that the poor polarization properties result from domain clamping. It is found that lenticular domains act as initial nuclei for domain switching both in poled and unpoled crystals. While the sidewise motion of the lenticular domains was prevented for the unpoled crystals, the sidewise motion easily occurred and a single domain state was established for the poled crystals. The single domain state produced in the poling process was stable compared with that formed in the unpoled crystals by applying an electric field cycling at room temperature.

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