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Effects of oxidation and reduction on the ferroelectric properties of superlattice-structured $Bi_4Ti_3O_{12}$-$PbBi_4Ti_4O_{15}$ single crystals

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ABSTRACT

Superlattice-structured $Bi_4Ti_3O_{12}$- $PbBi_4Ti_4O_{15}$ single crystals were grown, and the effects of oxidation and reduction of the polarization hysteresis and leakage current along the ***a*** axis were investigated at room temperature. High P_{O2} annealing gave rise to an increase in leakage current, while annealing in N_2 atmosphere yielded a marked decrease in leakage current. These results show that electron hole is the dominant carrier for the leakage current. A well-saturated polarization hysteresis with a remanent polarization of 41 $\mu C/cm^2$ was observed for air-annealed crystals, which is suggested to originate from the peculiar ferroelectric displacement of Bi in the Bi_2O_2 layers.

Key words: single crystals, bismuth layer-structured ferroelectrics, superlattice structure, polarization hysteresis

1. INTRODUCTION

Bismuth layer-structured ferroelectrics (BLSFs) [1] have been intensively studied for the applications to nonvolatile memories [2, 3] and piezoelectric devices [4, 5]. Compared with perovskite ferroelectrics such as $BaTiO_3$ and $Pb(Ti,Zr)O_3$, BLSFs have a high Curie temperature (T_C), which enables us to achieve the piezoelectric sensors and actuators operating at higher temperatures. [6, 7] Since the relatively high T_C and high fatigue endurance are considered to originate from the layered structure [3]. In the crystal structure, perovskite layers ($A_{m-1}B_mO_{3m+1}$) are sandwiched between Bi_2O_2 layers along the ***c*** axis: *A* is mono-, di-, and trivalent ions; *B* is tetra-, penta-, and hexavalent ions; *m* is the number of BO_6 octahedral layers in the perovskite layers (m = 1, 2, 3, 4, and 5). The Bi_2O_2 layers play a role not only in the polarization properties but also in the high durability of ferroelectric capacitor [3]. Furthermore, spontaneous polarization (P_s) and insulating properties are dependent on *m* of the perovskite blocks. [8] The BLSFs with even number of *m* show no ferroelectric polarization along the ***c*** axis due to the mirror plane perpendicular to the ***c*** axis. [9, 10] In contrast, the crystals of BiT with odd number of *m* exhibit a small P_s (4 $\mu C/cm^2$) along the ***c*** axis as well as a large P_s (50 $\mu C/cm^2$) along the ***a*** axis. [8, 11]

Superlattice-structured BLSFs first discovered by Kikuchi *et al.* have received a renewed interest as a candidate for ferroelectric materials with a relatively large remanent polarization (P_r) [12-14]. The superlattice -structured ferroelectrics have two kinds of BLSFs with difference number of *m*. BiT-SBTi consists of alternate stacking of BiT (m = 3) and $SrBi_4Ti_4O_{15}$ (SBTi, m = 4), and these two kinds of perovskite layers with different *m* are present in the structure. [13, 15] A lattice mismatch between the two kinds of perovskite blocks and their chemical character induce a large structural distortion in the Bi_2O_2 layers. This structural feature in the superlattice-structured BLSFs leads to a distinct type of ionic displacement of Bi in the Bi_2O_2 layers, [15] which is not common for the normal BLSFs. The displacement of the Bi in the Bi_2O_2 layers is suggested to contribute to a larger P_r observed for the ceramics [15, 16] and films [16] of BiT-SBTi than those of ceramics of the constituent BiT and SBTi. Although the superlattice-structured BLSFs with the form of ceramics and films have been extensively studied to elucidate their ferroelectric features, the properties are influenced strongly by microstructure, morphology, and orientation etc. It seems that investigations on single crystals are advantageous to know the fundamental ferroelectric properties, which has rarely been conducted for the superlattice-structured BLSFs, probably due to difficulty in crystal growth. Recently, Kobayashi *et al.* [17, 18] have reported that the superlattice-structured crystals composed of BiT (m = 3) and $BaBi_4Ti_4O_{15}$ (BBTi, m = 4) show a larger P_s compared with the crystals of the constituent BiT and BBTi.

In this paper, we show the effects of oxidation and reduction on the properties at room temperature of polarization hysteresis and leakage current for the superlattice-structured crystals composed of BiT and $PbBi_4Ti_4O_{15}$ (PBTi, m = 4). Although the polarization hysteresis of BiT-PBTi crystals has been reported, [19] polarization switching by applying an electric field was not achieved yet and a minor polarization loop with a small P_r of 12 $\mu C/cm^2$ was presented. Here, the properties along the ***a*** axis (the major polarization direction) are focused, and a well saturated polarization

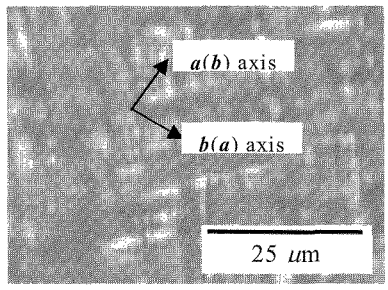

Fig. 1. 90° domain structure of BiT-PBTi in the ***a-b*** plane.

hysteresis with a P_r of 41 $\mu C/cm^2$ is reported for air-annealed crystals. Furthermore, electron-hole conduction is shown to be a detrimental carrier for the leakage current in this system.

2. EXPERIMENTS

Powder samples of BiT-PBTi were prepared by a solid-state reaction. Raw materials of PbO (99.99% purity), Bi_2O_3 (99.9999%), and TiO_2 (99.99%) were mixed for 1h using planetary ball milling. To compensate for the vaporizations of Pb and Bi during high-temperature process, excess powders of 2 at. % of PbO and of 1 at. % of Bi_2O_3 were added to the starting powder, i.e., the powder with a nominal composition of $Pb_{1.02}Bi_{8.08}Ti_7O_x$ was prepared for crystal growth. The powder mixture was calcined at 1100°C for 5 h in air.

Single crystals of BiT-PBTi were grown by a melting-slow cooling method [19]. The powder of BiT-PBTi was melted at 1230°C for 5 h in a Pt crucible, slowly cooled to 1050°C at a rate of 5 °C/h, and then furnace cooled to room temperature. The crystals were annealed in air at 950°C for 18 h (air-annealed crystals). Some of the crystals annealed in air were further annealed at a high oxygen partial pressure (Po_2) of 35 MPa at 700°C for 10 h to reduce oxygen vacancies in the crystals. Other crystals were annealed in N_2 atmosphere at 700°C for 10 h to investigate the effects of reduction treatment. The crystal structures of the calcined powder and the crystals obtained were investigated by X-ray diffraction (XRD). The powder XRD data were analyzed by the Rietveld method using the program RIETAN-2000 [20] on the basis of $P2_1am$ symmetry [15]. For electric measurements, the crystals embedded in resin were cut to have 0.15 ~ 0.2 mm thickness along the ***a(b)***-axis, and Au electrodes were sputtered onto both surfaces of the crystals. The properties of polarization hysteresis and leakage current were measured at 25°C along the ***a*** axis

3. RESULTS AND DISCUSSION

Figure 1 exhibits the optical microscope of a BiT-PBTi crystal. The crystals obtained were plate-like thin sheets, with thickness of approximately 0.2 mm along the ***c*** axis and dimensions of 3 mm square along the ***a-b*** plane. The crystals were light yellow in color. The fine 90° domain structure with a domain width of about ~2 μm were observed.

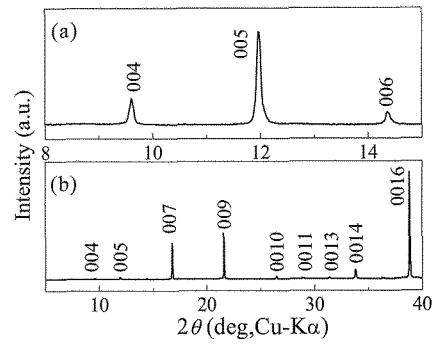

Fig.2. XRD patterns observed from the ***a-b*** crystal surface of the BiT-PBTi crystals in the 2θ range of (a) 8-15° and (b) 5-40°.

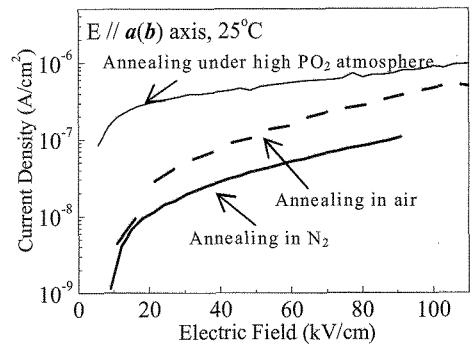

Fig.3. Leakage current properties of BiT-PBTi crystals along ***a*** axis at 25°C.

Figure 2 shows the XRD profiles of 00*l* reflections from the crystal surface. The XRD patterns (Fig. 2(b)) is similar to that of BiT-$BaBi_4Ti_4O_{15}$ [18]. The peculiar XRD peak of 005 originating from the superlattice structure composed of the alternate stacking of BiT (m = 3) and PBTi (m = 4) layers, is clearly seen at around 15°. Conventional BLSFs such as BiT (m = 3) and PBTi (m = 4) exhibit the 00*l* peaks only with even number of *l* due well as even numbers of *l*. [15] The appearance of the 00*l* with odd number of *m* is direct evidence that the superlattice structure with the alternate stacking of two kinds of perovskite layers (m = 3 and 4) is established in the BiT-PBTi crystals.

Figure 3 shows the leakage current properties as a function of dc electric field for the BiT-PBTi crystals along the ***a(b)*** axis. Compared with the air-annealed crystals with a leakage current density (***J***) of ~10^{-7} A/cm^2, the crystals annealed under high pressure oxygen showed an increase ***J*** of ~10^{-6} A/cm^2. Note that the high-Po_2 annealing leads to an increase in ***J*** in spite of decreasing oxygen vacancies ($V_O^{\bullet\bullet}$). These results provide evidence that electron hole ($h^{\bullet}$) arising from oxygen absorption in the crystals is the dominant carrier for the leakage current and hence plays a detrimental role in the electrical conduction at room temperature. The oxidation reaction by the annealing is expressed by the following equation:

$$1/2O_2 + V_O^{\bullet\bullet} \rightarrow O_O^{x} + 2h^{\bullet}, \qquad (1)$$

where O_O^{x} denotes the oxide ion at the O site.

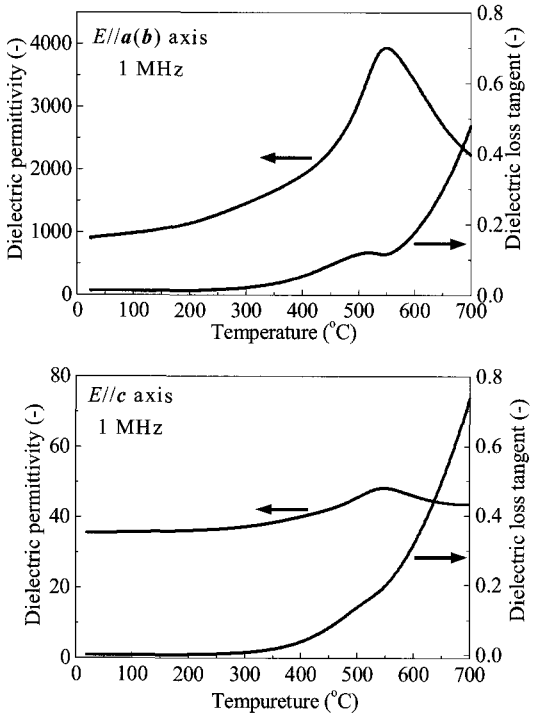

Fig.4. Temperature dependence of dielectric permittivity and loss tangent along the *a*(*b*) axis (a) and along the *c* axis (b) for the BiT-PBTi crystals.

Figure 4 exhibits the temperature dependence of dielectric permittivity (ε_r) of the BiT-PBTi crystals along the *a*(*b*) axis and *c* axis at a frequency of 1MHz. The ε_r along the *a*(*b*) axis was about 750 at 25°C, while that along the *c* axis 35 at 25°C. The Curie temperature (T_C) estimated from the ε_r peak was 550°C, and this T_C of the crystals was the same as that of BiT-PBTi dense ceramics with the stoichiometric composition. This T_C is lower than those of BiT (T_C = 675°C [8, 11, 21] and PBTi (T_C = 570°C [19]). For the temperature dependences of ε_r for the superlattice-structured ceramics with m = 1-2 [13, 14] and m = 2-3 [13, 22], dielectric anomaly (ε_r peak) has appeared twice above room temperature. These two peaks of ε_r suggest that two ferroelectric phase transitions occur during cooling from the high-symmetry (*P4/mmm*) paraelectric phase. The temperature dependences for the samples with m = 1-2 and m = 2-3 exhibit two ε_r peaks, and the peak temperatures coincide well with T_C's of the constituent BLSFs. [13] In contrast, the crystals of BiT-PBTi show one dielectric anomaly at 550°C above room temperature despite having two kinds of perovskite layers in the structure. The one dielectric anomaly has been reported also for BiT-BBTi and BiT-SBTi.[13, 17, 15]

The T_C at 550°C (one dielectric anomaly) of the BiT-PBTi crystals suggest that a strong ferroelectric interaction between two kinds of perovskite layers through the Bi_2O_2 layers induce simultaneous ferroelectric phase transition of these two perovskite layers in the superlattice structure. The T_C of BiT-SBTi has been reported to be 610°C [13, 15], which lies an intermediate temperature between T_C's of BiT (675 °C [8, 11, 21]) and $SrBi_4Ti_4O_{15}$ (520°C [23]), which is different from the tendency observed for the BiT-PBTi crystals. The lower T_C of BiT-PBTi than those of BiT and PBTi seems to be attributed to the cation disordering of isoelectronic Bi^{3+} and Pb^{2+} in the Bi_2O_2 layers and in the perovskite layers as has been observed for $PbBi_2Nb_2O_9$ [24].

Figure 5 shows the polarization hysteresis loops along the *a*(*b*) axis of the BiT-PBTi crystals (25°C, 0.5 Hz). The air-annealed crystals exhibited a well-developed hysteresis loop with a P_r of 41μC/cm^2 and a coercive field (E_c) of 103 kV/cm. This P_r value of the BiT-PBTi crystals is much larger than that of PBTi crystals (8 μC/cm^2 [25]) and slightly smaller than that of BiT (48μC/cm^2 [26]). If the ferroelectric distortions of the constituent BiT and PBTi are assumed to be preserved in the superlattice structured BiT-PBTi, the BiT-PBTi should have an averaged P_s of BiT and PBTi. The averaged P_s is roughly estimated to be 28 μC/cm^2. Note that the BiT-PBTi crystals exhibited a much higher P_r of 41μC/cm^2 than the averaged P_s value, which suggests that the superlattice stacking enhances the ferroelectric distortions in the structure of BiT-PBTi.

The high-P_{O_2} annealing led to a suppressed polarization hysteresis with a P_r of 14 μC/cm^2. Although the concentration of $V_O^{\cdot\cdot}$ seems to be reduced by the high-P_{O_2} annealing, the polarization switching by applying an electric field is restricted, probably due to the higher J for the crystals due to the oxidation [see Eq. (1)] by the high-P_{O_2} annealing. The P_r of the crystals annealed in N_2 atmosphere was 33 μC/cm^2. Although the N_2-annealed crystals exhibited a lower J than the air-annealed crystals, a large amount of $V_O^{\cdot\cdot}$ is still present in the crystals annealed in N_2 atmosphere. For

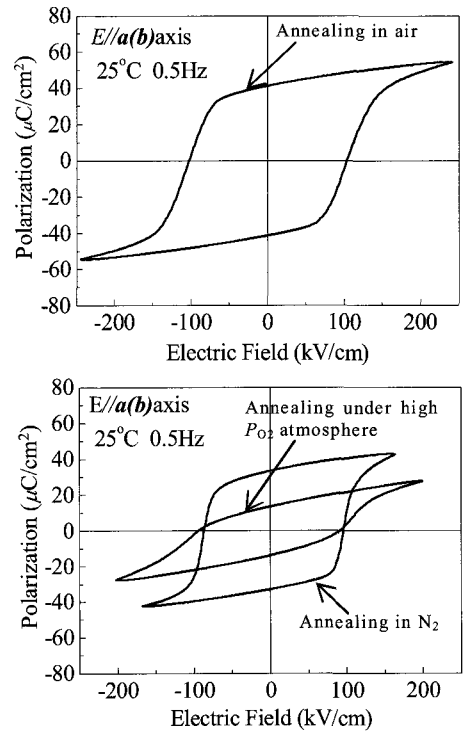

Fig.5 Polarization hysteresis loops of the BiT-PBTi crystals along *a* axis at 25°C.

the samples with a relatively high ***J***, nucleation of new domain and the following domain wall motion are restricted due to leakage current flow and the volume of switchable domains are reduced, leading to a lower P_r , as observed for the high-P_{O2} annealed crystals.

Here we discuss the origin of the large P_s observed for the BiT-PBTi crystals. The lattice parameters have been reported as follows: a = 0.544 668(4), b = 0.540 865(4), c = 3.283 48(4) for BiT [17], and a = 0.542 67(1), b = 0.544 58(1), c = 4.14 12(1) for PBTi [19]. The lattice mismatch between the BiT and PBTi is estimated to be 0.37% along the ***a*** axis and 0.67% along the ***b*** axis. It is considered that the lattice mismatch, *i.e.*, the lattice distortion caused by the superlattice stacking of BiT (m = 3) and PBTi (m = 4) layers, plays an important role in the ferroelectric distortion of the BiT-PBTi (m = 3-4). This crystallographic environment induces a local symmetry breaking of the Bi_2O_2 layers. Two Bi ions of the Bi_2O_2 layers in BiT and PBTi are identical from the structural point of view, while the Bi ions of the Bi_2O_2 layers in BiT-PBTi are regarded as crystallographically different cations; one is connected to the perovskite layers with m = 3, and the other is adjacent to those with m = 4. The symmetry breaking results in a peculiar ferroelectric displacement of the Bi ions of the Bi_2O_2 layers, as has been reported for BiT-SBTi [15] and BiT-BBTi [17]. It has been reported that the Bi ions of the Bi_2O_2 layers in BiT-SBTi are displaced along the ***a*** axis (the polar direction) by 2 % of the parameter a from the corresponding positions of the high-temperature tetragonal structure [15]. The similar displacements of the Bi ions are expected for BiT-PBTi. The larger P_r observed for the BiT-PBTi crystals is suggested to originate from the ferroelectric Bi displacements of the Bi_2O_2 layers caused by the superlattice stacking composed of two kinds of perovskite layers.

4. SUMMARY

The polarization properties and leakage current, dielectric permittivity of superlattice-structured BiT-PBTi crystals were investigated along the ***a*** axis. Measurements of dielectric permittivity revealed that the Curie temperature of the crystals was 550°C, which was lower than those of the constituent crystals of $Bi_4Ti_3O_{12}$ and $PbBi_4Ti_4O_{15}$. Annealing under high-pressure oxygen led to a marked increase in leakage current, showing that electron-hole plays a detrimental carrier for the electrical conduction at room temperature. The P_r (41 $\mu C/cm^2$) of BiT-PBTi crystals was larger than the average of P_r of BiT crystals and PBTi crystals, which is suggested to originate from the peculiar ferroelectric displacement of Bi in the Bi_2O_2 layers induced by the alternate stacking of two kinds of perovskite layers.

5. REFERRENCE

[1] B Aurivillius, *Arkiv Kemi*, **1**, 499 (1949).
[2] J. F. Scott and C. A. Paz de Araujo, *Science*, **246**, 1400 (1989).
[3] C. A. Paz de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, *Nature*, **374**, 627 (1995).
[4] K. Sakata, T. Takenaka, and K. Shoji, *Ferroelectrics*, **22**, 825 (1978).
[5] T. Takenaka and K. Sakata, *Jpn. J. Appl. Phys.*, **19**, 31 (1980).
[6] D. Damjanovic, *Curr. Opin. Solid State Mat. Sci.*, **3**, 469 (1998).
[7] H. X. Yan, H. T. Zhang, M. J. Reece, and X. L. Dong, *Appl. Phys. Lett.*, **87**, 82911 (2005).
[8] H. Irie, M. Miyayama, and T. Kudo, *J. Appl. Phys.*, **90**, 4089 (2001).
[9] A. D. Rae, J. G. Thompson, and R. L. Withers, *Acta Crystallogr, Sect B*, **48**, 418 (1992).
[10] K. Ishikawa and H. Funakubo, *Appl. Phys. Lett.*, **75**, 1970 (1999).
[11] S. E. Cummins and L. E. Cross, *J. Appl. Phys.*, **39**, 2268 (1968).
[12] T. Kikuchi, *Journal of the Less-Common Metals*, **52**, 163 (1977).
[13] T. Kikuchi, A. Watanabe, and K. Uchida, *Mater. Res. Bull.*, **12**, 299 (1977).
[14] T. Kikuchi, *Journal of the Less-Common Metals*, **48**, 319 (1976).
[15] Y. Noguchi, M. Miyayama, and T. Kudo, *Appl. Phys. Lett.*, **77**, 3639 (2000).
[16] A. Shibuya, M. Noda, M. Okuyama, H. Fujisawa, and M. Shimizu, *Appl. Phys. Lett.*, **82**, 784 (2003).
[17] T. Kobayashi, Y. Noguchi, and M. Miyayama, *Appl. Phys. Lett.*, **86**, 12907 (2005).
[18] T. Kobayashi, Y. Noguchi, and M. Miyayama, *Jpn. J. Appl. Phys.*, **43**, 6653 (2004).
[19] Y. Goshima, Y. Noguchi, and M. Miyayama, *Appl. Phys. Lett.*, **81**, 2226 (2002).
[20] F. Izumi and T Ikeda, *Mater. Sci. Forum*, **321-324**, 198 (2000).
[21] Y. Noguchi, I. Miwa, Y. Goshima, and M. Miyayama, *Jpn. J. Appl. Phys.*, **39**, L1259 (2000).
[22] P. Duran, F. Capel, C. Moure, M. Villegas, J. F. Fernandez, J. Tartaj, and A. C. Caballero, *J. Eur. Ceram. Soc.*, **21**, 1 (2001).
[23] H. Irie and M. Miyayama, *Appl. Phys. Lett.*, **79**, 251 (2001).
[24] Y. Noguchi, M. Soga, M. Takahashi, and M. Miyayama, *Jpn. J. Appl. Phys.*, **44**, 6998 (2005).
[25] M. Miyayama and I. S. Yi, *Ceram. Int.*, **26**, 529 (2000).

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