Electric-field-induced giant strain in $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based single crystals: Influence of high-oxygen-pressure annealing

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Influences of high-oxygen-pressure (350 MPa) annealing on the properties of leakage current, polarization, and strain were investigated for single crystals of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – BaTiO_3 with $P4mm$ tetragonal structure. The oxygen annealing led to a marked increase in leakage current, showing that the oxidized crystals have a high concentration of electron hole (carrier) and a low concentration of oxygen vacancy compared with the crystals annealed in air. While the air-annealed crystals exhibited a giant strain up to 0.8% at an electric field of 40 kV/cm, the oxidized crystals showed a small strain less than 0.3%. The results can be explained by the interaction between ferroelectric domains and charged defects.

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1. Introduction

There is an urgent demand for the development of lead-free ferroelectric/piezoelectric materials from environmental and economical points of view. Lead-free perovskite ferroelectrics of BaTiO_3 (BT)-based materials,^{1)–11)} $(\text{Bi},\text{K},\text{Na})\text{TiO}_3$ ^{12)–21)} and $(\text{Ag},\text{K},\text{Li},\text{Na})\text{NbO}_3$,^{22)–41)} and layered ferroelectrics of $\text{SrBi}_2(\text{Ta},\text{Nb})_2\text{O}_9$,^{42)–54)} $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BiT),^{55)–64)} $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$,^{50),65)–68)} and their derivatives^{69)–71)} have attracted a great deal of attention as alternative materials of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT). $(\text{K},\text{Na})\text{NbO}_3$ (KNN)-based solid solution^{22)–25)} has been considered as a promising lead-free material because of its high Curie temperature (T_C) of 300–400°C and superior piezoelectric properties. Recent investigations^{2)–5),72)} have shown that BT ceramics with a grain size of ~100 nm show a large piezoelectric strain constant (d_{33}) in which engineered domain configurations^{72)–75)} probably enhance the piezoelectric properties. Since materials properties show a marked temperature dependence near the transition temperature; phase transitions occurring near room temperature restrict the practical applications of BT.

Since Takenaka et al.^{12)–14)} demonstrated that $(\text{Bi},\text{Na})\text{TiO}_3$ (BNT) is an attractive piezoelectric material because of its high T_C of 320°C and a large spontaneous polarization, considerable attention has focused on BNT-based solid solution system. The piezoelectric properties of BNT-based materials are lost or drastically deteriorated above the depolarization temperature (T_d) around 200°C^{20),76),77)} due to the structural phase transition from rhombohedral $R3c$ to tetragonal $P4bm$.⁷⁶⁾ Tremendous efforts have been devoted to increase the T_d for solid solutions of BNT with other perovskite materials.^{20),77)}

Polarization and piezoelectric properties are closely linked to domain structure and its dynamics in ferroelectric crystals. It is likely that the domain behaviors are strongly influenced by defects. Especially, oxygen vacancies ($\text{V}_\text{O}^\bullet$) in ferroelectric oxides play an active role in domain dynamics.^{42),78),79)} At rela-

tively high temperatures at which $\text{V}_\text{O}^\bullet$ has a sufficient mobility to move, $\text{V}_\text{O}^\bullet$ interacts not only with 180° domain⁸⁰⁾ but also with non-180° domain.^{81),82)} The interaction between $\text{V}_\text{O}^\bullet$ and the ferroelectric domains determines the ferroelectric and piezoelectric behaviors of ferroelectric ceramics.⁸³⁾ At low temperatures near room temperature at which $\text{V}_\text{O}^\bullet$ has a low mobility, the defect dipoles (D), composed of $\text{V}_\text{O}^\bullet$ and negatively-charged defects such as cation vacancies or lower-valent cations, form. Since D in ferroelectric oxides introduces structural inhomogeneity as well as charge inhomogeneity in nanometer scale in the host crystal lattice, D is expected to play an important role in the domain dynamics. Recently, Teranishi et al.⁸⁴⁾ have reported that the defect dipoles ($D_{\text{A-O}}$) composed of A-site vacancy and $\text{V}_\text{O}^\bullet$ interact with 90° domain structure and that this interaction results in an extremely large strain up to 0.87% for BNT-based single crystals.

In this study, the influences of oxygen annealing on the leakage current, polarization, and strain properties for BNT-based single crystals have been investigated. The annealing at a high-oxygen pressure of 350 MPa led to a marked decrease in remanent polarization and electric-field-induced strain. The results can be explained by the interaction between ferroelectric domains and charged defects.

2. Experimental procedure

Single crystals of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ – BaTiO_3 (BNT–BKT–BT) were grown by the flux method in air.⁸⁴⁾ Bi_2O_3 (99.9999%), Na_2CO_3 (99.999%), BaCO_3 (99.99%), and TiO_2 (99.99%) were used as raw materials. The calcined powder of BNT–BKT–BT with Bi_2O_3 and KF as fluxes was soaked at 1300°C for 30 h in a Pt crucible, and subsequently cooled to 1200°C at a rate of 3.3°C/h. All the crystals were annealed in air at 950°C for 10 h to reduce mechanical stress induced during crystal growth. Thermogravimetric analysis confirmed that the air annealing at 950°C did not decrease weight of the crystals, i.e., the evaporation of Bi and/or K did not occur during this annealing. To investigate the influences of oxidation treatment on the electrical properties, high- P_{O_2} annealing at 700°C for 20 h

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($P_{O_2} = 350$ MPa) was performed. Hereafter, the crystals annealed at $P_{O_2} = 350$ MPa is abbreviated as oxidized crystals. Since the temperature of the high- P_{O_2} annealing is much lower than that at which defect formation of cations occurs, it is reasonable to consider that the high- P_{O_2} annealing does not lead to a change in metal composition but does decrease the concentration of $V_O^{\bullet\bullet}$ ($[V_O^{\bullet\bullet}]$), where the brackets denote the concentration inside it.

The chemical composition of the air-annealed and oxidized crystals determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) was $Bi_{0.50(1)}Na_{0.34(2)}K_{0.07(1)}Ba_{0.06(1)}TiO_3$ (BNT-BKT-BT), where the standard deviation is given in parenthesis. This composition analysis suggests that the crystals contain A-site vacancy ($V_A^{\prime\prime}$) of approximately 3%, where double primes represent two negative charge. Since the standard deviation of the metal composition is from one to two percent, the accuracy of the absolute value of $[V_A^{\prime\prime}]$ of 3% is not high. Our composition analysis suggests that the crystals have a A-site-deficient composition. Although A-site vacancy probably consists both of Bi vacancy ($V_{Bi}^{\prime\prime\prime}$) and K vacancy ($V_K^{\prime\prime}$), averaged A-site vacancy of $V_A^{\prime\prime}$ is considered for the sake of argument.

Transmission electron microscope observations have shown that the average size of 90° domains in the air-annealed crystals is approximately 10 nm.⁸⁴⁾ The air-annealed crystals were prepared by the same procedure,⁸⁴⁾ but the properties were slightly different from the earlier report,⁸⁴⁾ probably due to the difference in the initial 90° domain structure. In this paper, the difference in properties is not addressed hereafter.

For electric characterizations, the crystals were sliced parallel to $[100]_{cubic}$ into plates 250 μm in thickness and gold electrodes were sputtered on both sides of the specimens. Hereafter, cubic notation is used for describing crystal orientation throughout the manuscript. Polarization (P)-electric field (E) hysteresis loops and E -induced strains (S) were measured at $25^\circ C$ at a frequency of 0.5 Hz using a ferroelectric test system (Toyo Corporation; Model 6252 Rev. B). Leakage current density (J) as a function of E was also evaluated. In all the measurements, E was applied along $[100]_{cubic}$ and thus the properties of the crystals were investigated along $[100]_{cubic}$.

3. Results and discussion

Figure 1 shows the $J(E)$ along $[100]_{cubic}$ at $25^\circ C$. The air-annealed crystals had a low J on the order of 10^{-8} A/cm². Note that the high- P_{O_2} annealing led to a marked increase in J by approximately one order of magnitude. At high temperatures

Fig. 1. Leakage current density as a function of applied electric field along $[100]_{cubic}$ measured at $25^\circ C$.

during crystal growth, volatile elements such as Bi and K inevitably evaporate from the crystals, and $V_A^{\prime\prime}$ is created. The formation of $V_A^{\prime\prime}$ is accompanied by the formation of $V_O^{\bullet\bullet}$ due to charge compensation.^{85)–88)} The vacancy formation at high temperatures is expressed by

For Bi-based ferroelectrics such as $Bi_4Ti_3O_{12}$ ^{86)–88)} and BNT,⁸⁹⁾ it is shown that adsorbed Bi does not react with adsorbed O on the crystal surface and that these species leave the surface separately, which is probably due to a low possibility of the encounter between them. During cooling or annealing process below $1000^\circ C$, in which the vacancy formation of Eq. (1) does not occur, the crystals absorb oxygen from ambient and the following oxidation reaction produces electron hole ($h^\bullet$) as follows:

The carrier of the leakage current for BNT⁸⁹⁾ and BNT-BT⁹⁰⁾ has been reported to be $h^\bullet$ generated by the oxidation reaction (Eq. (2)). Since the high- P_{O_2} annealing does not change $[V_A^{\prime\prime}]$ but decrease $[V_O^{\bullet\bullet}]$, the resultant $[h^\bullet]$ is higher for the oxidized crystals. The experimental fact of the higher value of J shown in Fig. 1 is direct evidence that the oxidized crystals have low $[V_O^{\bullet\bullet}]$ and high $[h^\bullet]$ compared with the air-annealed crystals.

Figure 2(a) exhibits the $P(E)$ hysteresis loop of the crystals measured along $[100]_{cubic}$. For the air-annealed crystals, the samples showed a peculiar $P(E)$ loop with a remanent polarization (P_r) of $10 \mu C/cm^2$. The apparent value of P_r indicates that BNT-BKT-BT is categorized not as an antiferroelectric (AFE) but as

Fig. 2. (a) Polarization hysteresis loops and (b) strain curves induced by applying an electric field measured along $[100]_{cubic}$ at $25^\circ C$ (0.5 Hz).

a ferroelectric crystal.⁸⁴⁾ As E increased, a jump in P was observed at $E = 23$ kV/cm, which was confirmed by the peak in the switching current vs. E .⁸⁴⁾ The high- Po_2 annealing led to a suppressed polarization at a high E around 40 kV/cm as well as a decreased P_r of $5 \mu\text{C}/\text{cm}^2$ (the averaged value of $+P_r$ and $-P_r$). The suppressed value of the high- E polarization is attributed to a very small or a lack of P jump in the E range of 20–35 kV/cm.

Figure 2(b) shows the strain curve $S(E)$ along $[100]_{\text{cubic}}$. It should be noted that a large jump in S up to 0.6% was observed at $E = 23$ kV/cm at which the P jump was observed. These behaviors driven by E application were reproducibly observed. The value of S reached 0.8% at $E = 40$ kV/cm, which was about five times as large as that of PZT ceramics.⁸⁴⁾ It is noteworthy that the S value was markedly reduced by the high- Po_2 annealing. A very small or a lack of S jump is responsible for the smaller S value for the oxidized crystals.

We discuss the origin of the large S observed for the air-annealed crystals. The properties of $P(E)$ and $S(E)$ are governed by the dynamics of ferroelectric domains induced by E application. Here, tetragonal crystals with $P4mm$ symmetry are assumed, because the crystals of BNT–BKT–BT has a tetragonal $P4mm$ structure with lattice parameters of $a = 0.3901$ nm and $c = 0.3935$ nm (tetragonal distortion (c/a) of 1.008) at 25°C .⁸⁴⁾ In these crystals, two kinds of domain wall are present: one is 180° domain wall across which P_s are antiparallel, and the other is 90° domain wall across which P_s rotates by approximately 90° . It is considered that 180° domains can be easily switched by E application compared with 90° domains. In contrast, 90° domains play a dominant role in the values of P_r and S , as a result of the reorientation of the 90° domain configurations as shown in Fig. 3. The crystal structures shown in Fig. 3 are drawn by using the program VESTA (Visualization for Electronic and Structural Analysis) developed by Momma and Izumi.⁹¹⁾

It has been reported that the reorientation of the 90° domains originates from the interaction between P_s and defect dipole (D).^{79,92)} Figure 3 depicts the schematics of the reorientation of the 90° domains, i.e., the reversible rotation of the 90° domains, in BNT–BKT–BT crystals. At intermediate temperatures in the range of 400°C to 800°C , it is likely that V_A'' and V_O'' do not form defect dipole due to the contribution of entropy term to total free energy, and that V_O'' takes a random walk. With decreasing temperature, the defect dipoles (D_{A-O}) composed of V_A'' and V_O'' becomes energetically favorable to form due to the attractive interaction between them.

Noguchi et al. have performed *ab initio* electronic calculations of the interaction between P_s and defect dipole (D_{A-O}) in tetragonal BaTiO_3 ($P4mm$ symmetry).⁹⁰⁾ The calculations suggest that the configuration of D_{A-O} normal to P_s (Fig. 3(c), stable configuration) is energetically preferred compared with those of D_{A-O} parallel (Fig. 3(d)) and antiparallel to P_s (the configurations of D_{A-O} parallel/antiparallel to P_s are metastable). After the 90° domain structure is established below T_C (Fig. 3(a)), V_O'' hops into the adjacent O site even near room temperature^{79,92)} to form the stable D_{A-O} configuration in each 90° domain (Fig. 3(c)). This redistribution of D_{A-O} resulting from the V_O'' hopping further stabilizes the 90° domain structure.^{79,92)} When E is applied along $[100]_{\text{cubic}}$ to the crystals with this 90° domain structure, the domains with P_s normal to E are rotated by 90° so that the P_s vector becomes parallel to E (Fig. 3(b)). As a result, the 90° domains rotate and the metastable single domain state (Figs. 3(b) and (d)) is established by E application. Note that the rotation of 90° domains simultaneously leads to a drastic increase in S , because the longer axis of c becomes parallel to E direction. The increase in S by the 90° domain rotation is expected to be as high as $(c/a - 1)$. For the crystals of BNT–BKT–BT, the S value increased by approximately 0.6% at around 23 kV/cm, which is

Fig. 3. Schematics of the configuration of P_s and defect dipole (D_{A-O}) composed of A-site vacancy (V_A'') and oxygen vacancy (V_O'') (a) before and (b) after the rotation of 90° domains by E application. Metastable single domain state (b) is established only during E application, and the 90° domains are recovered to the initial state (a) after removing E . Compared with the configuration of D_{A-O} parallel to P_s (d), the configuration of D_{A-O} normal to P_s (c) yields a lower total energy. With increasing E , the 90° domain structure (a) transforms to the single domain state (b), leading to a strain jump (e), while the single domain state (a) is reversed to the initial 90° domain structure (a) associated by a drastic decrease in strain (f) with decreasing E .

in good agreement with the value of $(c/a - 1)$ of 0.8% determined by X-ray diffraction measurements. In-situ X-ray diffraction measurements have demonstrated that the S jump observed for the air-annealed crystals (Fig. 2 (b)) originates from the rotation of nanosized 90° domains.⁸⁴⁾

With decreasing E , the reorientation of the 90° domains from the metastable single domain state (Fig. 3(b)) to the multidomain state (Fig. 3(a)) occurs due to the stabilization by the interaction between P_s and D_{A-O} , because the energetically-favorable defect configuration with D_{A-O} normal to P_s (Fig. 3(c)) is almost frozen in the time range of the measurements. The results shown in Fig. 2 indicate that the back rotation of the 90° domains from the single domain state (Fig. 3(b)) to the multidomain state (Fig. 3(a)) occurs near $E = 5$ kV/cm. The origin of the reversible 90° domain rotation induced by E application is suggested to be the interaction between P_s and D_{A-O} for BNT-BKT-BT crystals.

Here, the influence of the high- P_{O_2} annealing on the $S(E)$ properties is discussed. Two possible reasons for the markedly reduced S for the oxidized crystals are considered: one is the decrease in the volume fraction of a domains (P_s normal to the E direction) and the other is the clamping of 90° domain walls. While c domains (P_s parallel to the E direction) do not contribute to the rotation of 90° domains by E application, a domains can rotate by E application, which leads to a marked increase in S . The decrease in the volume fraction of a domains should increase P_r , but the P_r value observed for the oxidized crystals was lower than that of the air-annealed crystals (Fig. 2(a)). This experimental fact excludes the former reason (the decrease in the volume fraction of a domains). It is reasonable to consider that the clamping of 90° domain walls reduces the S value as well as the P_r value for the oxidized crystals.

It has been reported that 90° domain walls have built-in electric field.^{81),82),90)} The direction normal to 90° domain walls is defined by the x axis. In the profile of the P_s component along x , $P_{s(x)}$ is suppressed near the domain walls due to the spatial modulation of the P_s vector caused by ferroelastic distortion inside the 90° domain walls.^{81),82),90)} The lower value of $P_{s(x)}$ at the domain walls leads to an electrostatic potential drop across the domain walls. This potential drop induces a charged double layer⁸¹⁾ and the depolarization field near the domain walls exceeds 1 MV/cm in $BaTiO_3$.⁹³⁾ This built-in electric field near the 90° domain walls is expected to strongly interact with mobile charge such as $V_o^{\bullet\bullet}$ and h^+ .⁸²⁾ The mobility of the 90° domain walls appears to be markedly reduced for the crystals with high $[V_o^{\bullet\bullet}]$ or high $[h^+]$.⁸²⁾ The results of the leakage current density (Fig. 1) suggest that the high- P_{O_2} annealing not only decreases $[V_o^{\bullet\bullet}]$ but also increase $[h^+]$. Since the oxidized crystals seem to have high $[h^+]$ and low $[V_o^{\bullet\bullet}]$ compared with the air-annealed crystals, the domain clamping by $V_o^{\bullet\bullet}$ cannot explain the experimental results. The clamping of the 90° domain walls by h^+ provide reasonable explanation of the reduced S value as well as the smaller P_r observed for the oxidized crystals.

4. Conclusions

Single crystals of $(Bi_{0.5}Na_{0.5})TiO_3-(Bi_{0.5}K_{0.5})TiO_3-BaTiO_3$ with tetragonal $P4mm$ structure were grown by the flux method and the influence of high-oxygen-pressure (350 MPa) annealing on the properties of leakage current, polarization, and electric-field-induced strain were investigated. The oxygen annealing led to a marked increase in leakage current by approximately one order of magnitude, showing that the oxidized crystals have a high concentration of electron hole (carrier) and low concentration of oxygen vacancy compared with the crystals annealed in air.

While the air-annealed crystals exhibited a giant strain up to 0.8% at an electric field of 40 kV/cm, the oxidized crystals showed a small strain less than 0.3%. The giant strain has been demonstrated to originate from the reversible rotation of nanosized 90° domains, and the reversibility of 90° domain rotation can be explained by the interaction between spontaneous polarization and the defect dipole composed of A-site vacancy and oxygen vacancy.⁸⁴⁾ The suppressed strain observed for the oxidized crystal is suggested to be caused by the clamping of the 90° domain walls by electron hole.

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