High-quality single crystal growth of Bi-based perovskite ferroelectrics based on defect chemistry

Yuji NOGUCHI,[†] Ichiro TANABE, Muneyasu SUZUKI and Masaru MIYAYAMA

Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8904

We present the O₂-blowing method for the growth of high-quality single crystals of Bi-based perovskite ferroelectrics, in which O₂ gas is directly introduced inside crucibles during crystal growth. The O₂-blowing method is demonstrated to be effective for enhancing polarization and piezoelectric properties as well as reducing leakage current for (Bi,Na)TiO₃–BaTiO₃ crystals. The superior properties are suggested to originate from the reduced reorientation of non-180° domains. *Ab initio* calculations suggest that the interaction between spontaneous polarization and defect dipole composed of Bi vacancy and O vacancy is the origin of the reorientation of non-180° domains.

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1. Introduction

In view of a worsening global environment posing serious problems, the environmental preservation of the earth and symbiosis with nature are the primary purpose of our industrial activities. Perovskite ferroelectric Pb(Zr,Ti)O₃ and related Pb-based materials including toxic lead have been used exclusively as the active material of sensors, transducers, actuators and non-volatile memories.^{1)–17)} Since the use of Pb(Zr,Ti)O₃ in electronic materials would be restricted in the near future, the development of lead-free ferroelectric materials with sufficient ferroelectric and piezoelectric properties has been strongly demanded from the environmental and economical points of view. In recent days, lead-free perovskite ferroelectrics of BaTiO₃(BT),^{18)–23)} (Bi,K,Na)TiO₃,^{24)–32)} (K,Na)NbO₃(KNN)^{33)–39)} and layered ferroelectrics of SrBi₂Ta₂O₉,^{40)–47)} Bi₄Ti₃O₁₂(BiT),^{48)–55)} CaBi₄Ti₄O₁₅^{56)–62)} and their derivatives⁶³⁾ have attracted much attention as alternative materials of Pb(Zr,Ti)O₃.

Potassium sodium niobate (KNN)^{33)–35)} has been regarded as a promising lead-free piezoelectric material, because of its high Curie temperature (*T*_C) of 420°C and superior piezoelectric properties. KNN shows a consecutive structural phase transition from cubic to tetragonal around 420°C and tetragonal to orthorhombic around 200°C. Although piezoelectric properties are markedly enhanced by the presence of tetragonal-orthorhombic phase transition,^{33),34)} the temperature dependence of materials-properties near the transition temperature becomes extremely high.⁶⁴⁾ The superior properties near phase-transition temperature are tricky to use for practical applications, in which temperature stability of the materials properties are strongly demanded in a wide range of temperature from –50 to 120°C. Recently, this problems related to the tetragonal-orthorhombic phase transition of KNN have been overcome by doping technique.⁶⁴⁾ Nevertheless, the expensiveness of Nb is still considered a barrier for the bulk applications of KNN-based devices.

Ti-based perovskite ferroelectrics such as BT^{18)–23)} and

(Bi,Na,K)TiO₃^{24)–32)} have recognized as cost-effective lead-free piezoelectric materials. Recent investigations^{18),22),23)} have demonstrated that fine-grained BT ceramics with a grain size of ~100 nm show a large piezoelectric strain constant *d*₃₃, in which engineered domain configurations^{22),23)} probably enhance the piezoelectric properties. However, *T*_C of BT is as low as 135°C, and furthermore fine-grained BT ceramics exhibit a tetragonal-orthorhombic transition temperature around room temperature.¹⁹⁾ These phase transitions constitute an obstacle to the practical applications of BT.

Pioneering works by Takenaka et al.^{24)–26)} have shown that (Bi,Na)TiO₃(BNT) is an attractive piezoelectric material because of a high *T*_C of 320°C and a large spontaneous polarization. One of the problems to be overcome is that depolarization temperature (*T*_d), i.e., piezoelectric activities disappear or are markedly reduced at *T*_d, lies around 200°C for BNT^{65)–68)} for BNT due to structural phase transition from rhombohedral (*R*3*c* symmetry: ferroelectric) to tetragonal (*P*4*bm* symmetry: weak ferroelectric).^{67),68)} It is widely accepted that the use of BNT-based ferroelectrics for piezoelectric materials opens up the possibility of lead-free piezoelectric devices in views of properties and cost-effectiveness.

It is well known that rhombohedral BNT constitutes a morphotropic phase boundary (MPB) with tetragonal BT. The piezoelectric properties have been enhanced for the ceramics of BNT–BT solid solutions near the MPB composition.²⁶⁾ Although BNT–BT ceramics near the MPB composition have been intensively studied, marked enhancement in piezoelectric properties has not been achieved to date as well as the reported values of the piezoelectric constants etc. are scattered,^{26),69)–79)} which seems to be ascribed to the multiple influences of microstructure, grain size and orientation, nonstoichiometry, and defects.

Defects in ferroelectric materials play an important role in their properties of leakage current, ferroelectric and piezoelectric properties. The control of polarization states is the underlying basis of ferroelectric and piezoelectric devices. Polarization switching is achieved through nucleation of domains and subsequent domain-wall motion by applying an electric field (*E*). Leakage current arising from defects, however, interferes with

[†] Corresponding author: Y. Noguchi; E-mail: ynoguchi@crm.rcast.u-tokyo.ac.jp

the polarization switching of Bi-based perovskites.^{80)–83)} In addition, oxygen vacancies are known to act as an obstacle to the polarization switching,^{84)–86)} and a resultant remanent polarization (P_r) is suppressed by the clamping of the domain walls by oxygen vacancies. The leakage current and domain clamping by oxygen vacancies make ferroelectric materials unsuitable for practical applications.^{42),87)–95)} Thus, a guiding principle of defect control is required to be established for obtaining high-quality Bi-based devices with superior piezoelectric properties. Investigations on single crystals seem advantageous to know the influences of defects on the properties of ferroelectric materials, in which microstructure and grain size does not affect the properties.

In this study, the single crystals of BNT–BT near the MPB composition (91%BNT–9%BT) is selected as a model material for Bi-based ferroelectrics, and the defect chemistry during crystal growth is investigated to obtain a materials processing leading to high-quality Bi-based perovskite ferroelectrics. The O₂-blowing method,^{96),97)} in which O₂ gas is introduced directly to the melt surface in crucible during crystal growth, is demonstrated to be effective for obtaining high-quality BNT–BT crystals with superior piezoelectric properties. The blowing of O₂ gas during crystal growth suppresses the defect formation reaction leading to Bi vacancy and oxygen vacancy, which is the origin of the enhanced piezoelectric properties for the high-quality BNT–BT crystals.

2. Experiments and *ab initio* electronic calculations

Single crystals of BNT–BT were grown by the O₂-blowing method based on high-temperature flux technique.⁹⁸⁾ The schematic image of the furnace used in this study is illustrated in Fig.

1(a). Pt crucibles with 30 cc were used, and the crucible was covered with alumina lid at the center of which the hole with 6.2 mm diameter was present. Alumina tube with an inner diameter of 4 mm (wall thickness of 1 mm) was placed in the hole of the alumina lid for O₂ blowing, and O₂ gas was introduced through the alumina tube to the melt surface. The distance between the melt surface and the forefront of the alumina tube was critical for crystal growth. This distance was fixed at 1 mm in our experiments.

High purity powders of Bi₂O₃ (99.9999%), Na₂CO₃ (99.999%), BaCO₃ (99.99%) and TiO₂ (99.99%) were used as raw materials. The mixed powders with the composition of 0.88BNT–0.12BT were calcined at 850°C for 4 h in air, which led to single-phase powder with perovskite structure. 0.88BNT–0.12BT powder mixed with Bi₂O₃ and NaF as fluxes were soaked at 1300°C for 5 h in the Pt crucible. The profiles of temperature and O₂-flow rate during crystal growth are illustrated in Fig. 1 (b). For the last 1 h during the soaking, the flow rate of O₂ gas increased linearly from zero to a certain value (50 ml/min, 100 ml/min and 150 ml/min). The temperature decrease at the melt surface by the blowing of O₂ was about 30°C (50 ml/min), 70°C (100 ml/min) and 110°C (150 ml/min). The blowing of O₂ to the melt surface was kept at the flow rate described above during crystal growth. The temperature of the furnace was slowly cooled from 1300°C to 1100°C for 10 h with the O₂ blowing. Single crystals of BNT–BT with a maximum size of 5 × 5 × 3 mm³ were obtained just beneath the alumina tube and small-sized crystals (2 × 2 × 2 mm³) were present at around the edge of the crucible (Fig. 1(c)). When the flow rate of O₂ increased to 200 ml/min, the melt surface was rippling and then crystals were not obtained. The crystals were annealed at 950°C for 10 h in air

Fig. 1. (a) Electric furnace used for the crystal growth based on the O₂-blowing method, (b) the profiles of temperature and O₂-flow rate during crystal growth and (c) the crystals obtained by the O₂-blowing method with a flow rate of 150 ml/min.

before electrical measurements. The chemical composition of the crystals determined by inductively coupled plasma atomic emission spectrometry was 0.91BNT–0.09BT, which did not depend on the O₂ flow rate during crystal growth. The composition of BT of the crystals was smaller than that of the starting powder (0.88BNT–0.12BT).

For electric characterizations, the crystals were sliced parallel to (001)_{cubic} into plates 250 μm in thickness and gold electrodes were sputtered on both sides of the specimens. Polarization (P)–electric field (E) hysteresis loops and E -induced strains (S) at a frequency of 0.5 Hz were measured using a ferroelectric test system (Toyo Corporation; Model 6252 Rev. B) at 25°C.

In order to obtain an insight into the interaction between P_s and defect dipole, *ab initio* density functional theory (DFT)^{(99), (100)} calculations of tetragonal BaTiO₃ were conducted within the generalized gradient approximation (GGA-PBE)^{(101), (102)} using the all-electron projector augmented wave (PAW) method⁽¹⁰³⁾ implemented in VASP.^{(104), (105)} As a model material of perovskite ferroelectric oxide with a tetragonal $P4mm$ structure, we selected tetragonal BaTiO₃ to calculate the total energies of the crystals with different defect dipole configurations. We created a $2 \times 2 \times 3$ supercell using the optimized tetragonal BaTiO₃ unit cell, and then generated the vacancies of Ba and O. After relaxing the lattice parameters and the fractional coordinates of all atoms of the supercell with defect dipole (D_{A-O}) composed of A-site (Ba) vacancy and O vacancy, the total energies were compared in order to investigate a stable configuration of D_{A-O} with P_s . A cutoff kinetic energy was set as 400 eV throughout the calculations.

3. Results

Figure 2 shows the leakage current density (J) at 25°C as a

Fig. 2. Leakage current density as a function of applied electric field along the [100]_{cubic} direction measured at 25°C.

Fig. 3. Polarization hysteresis loops measured along the [100]_{cubic} direction at 25°C (1 Hz).

function of E applied along the [100]_{cubic} direction. Hereafter, cubic notation is used for describing crystal orientation throughout the manuscript. The value of J in the low E region below 40 kV/cm was almost the same for all the crystals with different O₂ flow rate, while J in the higher E region decreased markedly with increasing O₂ flow rate. At an E of 80 kV/cm, the crystals (50 ml/min) showed a high J of 10^{-5} A/cm². It is interesting to note that the crystals (150 ml/min) exhibited a J of $\sim 10^{-7}$ A/cm², which was by about two orders of magnitude lower than those of the crystals (50 ml/min). When Pt electrodes were used for the measurements, a significant change in J was not observed. These results demonstrate that the leakage current properties for BNT–BT crystals obtained in this study are not influenced by the interface between the electrodes and the ferroelectrics but determined by defects inside the crystals.

Figure 3 indicates the P – E hysteresis loop measured along the [100]_{cubic} direction at 25°C. The crystals (50 ml/min) showed a small hysteresis with a P_r of 8 $\mu\text{C}/\text{cm}^2$. This small P_r seems to be attributed to domain reorientation^{(11), (106), (107)} with decreasing E , as discussed below. Polarization properties were drastically improved with increasing O₂ flow rate during crystal growth, and the P_r value of the crystals (150 ml/min) was as large as 20 $\mu\text{C}/\text{cm}^2$. The crystals (100 ml/min) had a P_r of 10 $\mu\text{C}/\text{cm}^2$. The polarization and leakage current properties are summarized in Table 1.

Figure 4 shows the S induced by E application measured along the [100]_{cubic} direction at 25°C. Before measurements, a unipolar E of 60–80 kV/cm was applied to the crystals at 25°C several times for electrical poling. For the crystals (50 ml/min), S gradually increased with increasing E in the low E region below 20 kV/cm, which was due to their small piezoelectric

Table 1. Polarization and Piezoelectric Properties of 0.91BNT–0.09BT Crystals Grown by the O₂ Blowing Method

O ₂ flow rate during crystal growth	50 ml/min	100 ml/min	150 ml/min
P_r ($\mu\text{C}/\text{cm}^2$)	8	10	20
Leakage current density (A/cm^2) at 80 kV/cm	7.8×10^{-6}	$9. \times 10^{-7}$	6.9×10^{-8}
$S_{\text{max}}/E_{\text{max}}$ (pm/V)	337	295	368
Dominant contribution to E -induced strain	non-180° domain rotation	non-180° domain rotation	inverse piezoelectric effect
Piezoelectric strain constant ^a d_{33} (pm/V)	6	66	242

^a The value of d_{33} was determined by the slope in the S – E curve below $E = 10$ kV/cm.

Fig. 4. Strain curves induced by applying an electric field measured along the [100]_{cubic} direction at 25°C (1 Hz).

strain constant (d_{33}). The value of d_{33} determined by the slope below 10 kV/cm was 6 pm/V for the crystals (50 ml/min). Above E of 20 kV/cm, S showed a quadratic increase with E , which does not originate from inverse piezoelectric effects but probably from the rotation of non-180° domains^{(11),(106),(107)} induced by E application. An E application over 70 kV/cm led to a dielectric breakdown of the crystals (50 ml/min). A strain constant defined by $S_{\max}/E_{\max}$ was 337 pm/V for the crystals (50 ml/min). The value of S during E decreasing was larger than that during E increasing at the same E value, and S became almost zero at $E = 0$ kV/cm. The hysteresis in the S - E curve has been reported to originate from the reorientation of non-180° domain due to defects,^{(106),(107)} as discussed below. Almost the same S - E properties with difference strain constants were observed for the crystals (100 ml/min), which showed a d_{33} of 14 pm/V and an $S_{\max}/E_{\max}$ of 295 pm/V. These strain data are also listed in Table 1.

It is noteworthy that the crystals (150 ml/min) showed a linear increase in S with E even in the low E region. The d_{33} value estimated from the slope below 10 kV/cm was 242 pm/V, which was 20 times as large as that of the crystals (100 ml/min). The S - E curve of the crystals (150 ml/min) was similar to those of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics,⁽¹¹⁾ and the strain behavior is mainly ascribed to inverse piezoelectric effects. The $S_{\text{max}}/E_{\text{max}}$ value of the crystals (150 ml/min) was 368 pm/V.

4. Discussion

4.1 Defect formation at high temperatures

We consider the effects of the O_2 blowing to the melt surface during crystal growth. Since the O_2 blowing decreases the temperature just beneath the forefront of the alumina tube by some degree, the process of crystal growth is influenced by the O_2 blowing. In fact, the O_2 blowing method provides larger single crystals of BNT-BT. It is, however, apparent that the properties shown in Figs. 2-4 are not directly related to the size of the crystals. Here, defects which strongly affect the electrical properties are focused.

At high temperatures, elements with a high vapor pressure such as Bi are apt to evaporate from the surface of solid as well as liquid. BNT–BT crystals are floating in the melt (see Fig. 1(a)) due to the low specific gravity of BNT–BT compared with the melt, and the crystals are obtained from the upper part of the flux. Therefore, the evaporation of Bi from the crystal surface at high temperatures plays a critical role in the properties at room temperature of the resultant crystals. It has been reported for Bi-based layered ferroelectric of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ that the trigger of defect formation is the generation of Bi vacancy ($V_{\text{Bi}}^{\prime\prime\prime}$), which is accompanied by the formation of oxygen vacancy ($V_{\text{O}}^{\prime\prime}$) due to charge compensation.^{89,95,108} The vacancy formation at high temperatures is expressed by

where $\text{Bi}_{\text{Bi}}^{\times}$ is $\text{Bi}^{3+}(\text{lattice})$ at the Bi site and $\text{O}_{\text{O}}^{\times}$ denotes $\text{O}^{2-}(\text{lattice})$ at the O site. Noguchi et al.^{(108),(109)} have indicated that the vacancy formation of Bi proceeds preferentially in the perovskite layers rather than in the Bi_2O_2 layers. The reaction of the vacancy formation (Eq. (1)) has been reported to occur above 1000°C in air.^{(108),(109)}

It is interesting to note that the weight loss due to the formation of $V_{\text{Bi}}^{\bullet\bullet}$ and $V_{\text{O}}^{\bullet\bullet}$ at high temperatures are reduced under a higher P_{O_2} atmosphere.^{(108),(109)} The P_{O_2} dependence of weight loss demonstrates that the limiting factor of the vacancy formation is not diffusion of the vacancies inside the crystals but surface reaction

on the crystal surface. The following model of the vacancy formation of Bi-based perovskite oxides (**Fig. 5**) is proposed.^{(108),(109)} Two $\text{Bi}_{\text{Bi}}^{\times}$ and three $\text{O}_{\text{O}}^{\times}$ migrate to the surface of crystals, but do not react with each other because of the low possibility of Bi_{ad} to meet O_{ad} on the surface, where Bi_{ad} and O_{ad} are adsorbed Bi and O on the surface. Bi_{ad} detaches from the surface as $\text{Bi}(\text{gas})$ and then $\text{Bi}(\text{gas})$ promptly reacts with $\text{O}_2(\text{gas})$ to form $\text{Bi}_2\text{O}_3(\text{gas})$ in the atmosphere, as expressed by the following equations;

These reactions proceed quickly and do not limit the vacancy formation of Eq. (1). In contrast, O_{ad} has to meet another O_{ad} on the surface to form an O_2 molecule. The reaction related to O_{ad} that is suppressed at a higher P_{O_2} is the limiting factor of the vacancy formation as follows:

Therefore, the defect formation of Eq. (1) is suppressed under higher- P_{O_2} atmosphere, because the equilibrium point of Eq. (4) moves to the left side, *i.e.*, the rate-limiting reaction is prevented at a higher P_{O_2} . The defect formation during crystal growth is sensitive to P_{O_2} just above the crystals inside the Pt crucible. Under low P_{O_2} atmosphere, the defect formation of Eq. (1) is easy to proceed, and then low-quality crystals with high concentrations of V_{Bi}''' and V_O'' are grown (**Fig. 6(a)**).

Fig. 5. Defect formation at high temperatures of BNT–BT crystals. The reaction related to Bi rapidly proceeds, while the transformation from adhesive O (O_{ad}) on the crystal surface to O_2 (gas) is the rate-limiting reaction for the overall defect formation.

Fig. 6. Schematic images of the defect-formation reactions at (a) lower P_{O_2} and (b) higher P_{O_2} .

For the O₂-blowing method, fresh O₂ gas is introduced directly inside the crucible, and a high P_{O_2} is maintained even at the crystal surface (Fig. 6(b)). The higher P_{O_2} atmosphere prevents the progress of the rate-limiting reaction of Eq. (4), and then the overall defect formation of Eq. (1) is suppressed. The O₂-blowing method is an effective technique for obtaining high-quality Bi-based perovskite crystals with the low concentrations of V_{Bi}''' and V_O'' .

4.2 Effects of O₂ blowing during crystal growth on the leakage current properties

The dependence of O₂-flow rate on the leakage current properties (Fig. 2) can be explained by $[V_O'']$ in the crystals, where brackets indicate concentration. During cooling or annealing process below 1000°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') as follows:

The carrier of the leakage current for BNT crystals has been reported to be h' generated by the oxidation reaction (Eq. (5)).⁹⁸ As discussed above, the crystals grown at a lower P_{O_2} have a higher $[V_O'']$, because the vacancy formation of Eq. (1) is accelerated under a lower P_{O_2} atmosphere. Thus, the crystals (150 ml/min) with a lower $[V_O'']$ have a lower $[h']$, leading to a lower J than other crystals.

4.3 Reorientation of domain structure leading to poor properties

We discuss the reasons of the poor polarization and piezoelectric properties observed for the crystals with lower O₂-flow rates. The properties of P and S are governed by domain dynamics induced by E application. Here, tetragonal crystals with $P4mm$ symmetry are assumed for simplicity. 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 about 90°. 180° domains can be easily

switched by E application compared with 90° domains and the volume of the backswitched 180° domains is small.⁹⁵ In contrast, 90° domains play a dominant role in the values of P_r and d_{33} , as a result of the reorientation of 90° domain configurations in BNT–BT crystals (see Fig. 7). The crystal structure shown in Figs. 7 and 8 are drawn by using the program VESTA (Visualization for Electronic and STructural Analysis) developed by Momma and Izumi (Ref. 110).

The polarization measurements show that the value of P at $E = 80$ kV/cm was almost the same for both the crystals (50 ml/min and 150 ml/min) (Fig. 3). These results demonstrate that the rotation of 90° domains is induced, *i.e.*, almost the single domain state (Fig. 7(b)) is established by E application. With decreasing E , the reorientation of the 90° domains, *i.e.*, the rotation of the domains by 90°, gradually takes place and finally initial 90° domain structure (Fig. 7(a)) is recovered. This reorientation of the 90° domains is the reason why the crystals (50 ml/min) showed a smaller P_r in spite of having a large P value at $E = 80$ kV/cm.

The reorientation of the 90° domains deteriorates the piezoelectric properties in addition to the polarization properties. Piezoelectric strain originating from inverse piezoelectric effects is defined as the deformation of crystals induced by applying E application without the change in domain structure. For ferroelectric materials, piezoelectric strain tensor is defined unambiguously for the crystals with the single domain state (here, we do not consider the cooperative effect of 90° domain walls in engineered domain configurations.^{21),22}) When the reorientation of the 90° domains occurs and the value of P_r decrease, effective strain induced by E application becomes smaller, leading to a lower d_{33} . It is considered that the low d_{33} values for the crystals (50 ml/min and 100 ml/min) are attributed to the reorientation of the 90° domains.

It has been reported that the reorientation of the 90° domains originates from the interaction between P_s and defect dipole (D).^{106),107} Figure 7 depicts the schematics of the reorientation of the 90° domains, *i.e.*, the reversible 90° domain rotation, in BNT–BT crystals. At intermediate temperatures in the range of 400°C

Fig. 7. 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 90° domain rotation 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 .

Fig. 8. Supercells of tetragonal BaTiO_3 for *ab initio* calculations of the interaction between spontaneous polarization (P_s) and defect dipole (D_{A-O}) composed of A-site vacancy (V_A'') and oxygen vacancy (V_O''). There are three possible configurations of D_{A-O} and P_s : (a) D_{A-O} parallel to P_s ; (b) D_{A-O} antiparallel to P_s ; (c) D_{A-O} normal to P_s . *Ab initio* calculations show that the configuration of (c) D_{A-O} normal to P_s leads to a lowest total energy.

to 800°C, V_{Bi}''' and V_O'' do not form defect dipole due to the contribution of entropy term to total free energy, and V_O'' takes a random walk. With decreasing temperature, the defect dipoles (D_{A-O}) composed of V_{Bi}''' and V_O'' becomes energetically favorable to form due to the attractive interaction between them. In Fig. 7, the vacancy at the A site including V_{Bi}''' is expressed as V_A'' .

4.4 *Ab initio* calculations of the interaction between P_s and defect dipole

To perform *ab initio* calculations of the interaction between P_s and D , we have selected a model material of tetragonal BaTiO_3 with D_{A-O} composed of Ba vacancy (V_A'') and V_O'' . At first, the structure optimization of tetragonal BaTiO_3 with $P4mm$ space group was performed. The resultant structural parameters are $a = 0.397144 \text{ nm}$, $c = 0.408949 \text{ nm}$, which quantitatively agree well with the experimental structural data.¹¹¹⁾ A supercell with $2a \times 2a \times 3c$ was built up using the optimized BaTiO_3 , in which the c axis of the supercell is set to be long to reduce ferroelectric cell-to-cell interaction.

In view of the directions of D_{A-O} with respect to P_s , there are three kinds configuration, as schematically illustrated in Fig. 8. The directions of P_s and D shown in Figs. 8(a) and (b) are designated as parallel: (a) P_s parallel to D_{A-O} and (b) P_s antiparallel to D_{A-O} . The rest depicted in Fig. 8(c) is the configuration with P_s normal to D_{A-O} . After these vacancies are created in the supercell, a higher crystal symmetry is imposed for each cell: (a) P_m , (b) P_m and (c) C_m . Structural optimization was again performed for all atoms with the fixed lattice parameters and then total energies (E_{total}) of the optimized cell were calculated. Since the configuration of P_s antiparallel to D_{A-O} (Fig. 8(b)) shows the highest E_{total} , this value is set to the standard for comparison. The configuration of P_s parallel to D_{A-O} (Fig. 8(a)) exhibits a lower E_{total} by 0.29 eV ($\Delta E_{\text{total}} = -0.29 \text{ eV}$), which is quite reasonable in view of electrostatic interaction. Note that an E_{total} of the configuration with P_s normal to D_{A-O} (Fig. 8(c)) becomes the smallest ($\Delta E_{\text{total}} = -0.59 \text{ eV}$), which indicates that this D_{A-O} configuration with respect to P_s is the grand state for tetragonal BaTiO_3 .

These calculations suggest that the configuration of D_{A-O} perpendicular to P_s (Fig. 7(c), stable configuration) is energetically

preferred compared with those of D_{A-O} parallel (Fig. 7(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 , V_O'' hops into the adjacent O site even near room temperature^{106,107)} to form the stable D_{A-O} configuration in each 90° domain (Fig. 7(c)). This redistribution of D_{A-O} resulting from the V_O'' hopping further stabilizes the 90° domain structure.^{106,107)} When E is applied along the $[100]_{\text{cubic}}$ direction 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 . As a result, the 90° domains rotate and the metastable single domain state (Figs. 7(b) and (d)) is established by E application. With decreasing E , the reorientation of the 90° domains from the metastable single domain state (Fig. 7(b)) to the multi-domain state (Fig. 7(a)) occurs due to the stabilization by the interaction between P_s and D_{A-O} , because the defect configuration with D_{A-O} normal to P_s (Fig. 7(c)) is energetically favorable compared with D_{A-O} parallel/antiparallel to P_s . It is concluded that the interaction between P_s and D_{A-O} is the origin of the reorientation of the 90° domains leading to poor polarization and piezoelectric properties observed for BNT–BT crystals.

5. Conclusions

To establish a guiding principle of defect control during crystal growth for obtaining high-quality Bi-based ferroelectric single crystals, we selected perovskite BNT–BT near the MPB composition as a model material. The O_2 -blowing method was developed for high-quality BNT–BT single crystals based on defect chemistry. The properties of leakage current, remanent polarization and piezoelectric constants were markedly improved by increasing O_2 -flow rate during crystal growth. The piezoelectric strain constant (d_{33}) of 288 pm/V was achieved along the $[100]_{\text{cubic}}$ direction for the crystals obtained by the O_2 -blowing method. The vacancies of Bi and O formed during crystal growth are shown to originate from poor properties of BNT–BT crystals. The reorientation of non-180° domains is indicated to deteriorate remanent polarization and d_{33} for the crystals with high concentrations of the vacancies. *Ab initio* calculations suggest that the interaction between spontaneous polarization and defect dipole composed of

Bi vacancy and O vacancy is the origin of the reorientation of non-180° domains. The O₂-blowing method is demonstrated to be effective for growing high-quality BNT–BT single crystals with low concentrations of Bi vacancy and O vacancy.

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