Function Design of Bismuth Layer-Structured Ferroelectrics

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Recent research activities of the author’s group concerning the structure-property relationship and property design by defect control of bismuth layer-structured ferroelectrics (BLSFs) are described. The polarization measurements for various single-crystal BLSFs showed that the remanent polarization $P_r$ and the coercive field $E_c$ of these ferroelectrics are related to Curie temperature and the number of perovskite units in one layer, $m$, respectively. For SrBi$_2$Ta$_2$O$_9$ (SBT), Bi substitution at the A site increased $P_r$, and rare-earth-element substitution at the A site decreased or increased $E_c$ depending on the type and amount of rare-earth element used. These property changes were due to changes in lattice distortion induced by the substitution, and the softening and hardening of polarization property were attained in SBT. A decrease in the concentration of oxygen vacancies was found to be very effective in improving the polarization and insulating properties of Bi$_2$Ti$_2$O$_7$ (BIT). Conductivity analysis and ab initio band-structure calculations showed that the doping of higher-valence cations at the B site and the substitution of rare-earth elements for Bi at the A site decrease the concentration of oxygen vacancies, which cause domain pinning, by charge compensation and lattice stabilization, respectively. Such defect control was demonstrated to be a promising approach to designing the polarization properties of BLSFs.

Key-words: Ferroelectrics, Layer structure, Anisotropy, Defect control, Lattice distortion, Single crystal

1. Introduction

Layer-structured compounds show anisotropic electronic, dielectric, optical and ionic properties. In addition, novel functions not observed in isotropic-structured materials can appear due to interactions between the electronic, mechanical and chemical properties of constituent layers. Regarding ferroelectric oxides, perovskite oxides with fundamentally isotropic but slightly distorted structures, represented by lead zirconate titanates, occupy the major position nowadays for various ferroelectric and piezoelectric applications. Recently, the use of ferroelectrics in high-speed switching memory devices and electrooptic devices including photonic crystals has become important. For such devices, directional signal propagation is one of the key factors, and layer-structured ferroelectrics with anisotropic properties are promising in this respect. In addition, with increasing worldwide interest in environmental problems, lead-free ferroelectrics are strongly demanded. Although many types of lead-free ferroelectrics have been studied, those that can be used in practical applications are limited.

Bismuth layer-structured ferroelectrics (BLSFs) have a crystal structure in which pseudo-perovskite blocks are sandwiched between bismuth oxide $\text{Bi}_2\text{O}_3$ layers along the $c$ axis, as shown in Fig. 1. The perovskite blocks have the formula of $\left(\text{A}_{m-\frac{1}{2}}\text{B}_2\text{O}_{3m+1}\right)^{2+}$, where $\text{A}$ is $1+$ to $3+$ ions, $\text{B}$ is $4+$ to $6+$ ions, and $m$ is the number of BO$_6$ octahedra in each perovskite block.$^1$ Ferroelectricity arises mainly in the perovskite blocks along the $a$ axis, parallel to the bismuth oxide layers.$^{1,2}$ The bismuth oxide layers act as insulating paraelectric layers and affect the structural distortion and electronic properties of the perovskite blocks.$^3$ Since Araujo et al. reported fatigue-free behavior in repetitive switching of polarization in SrBi$_2$Ta$_2$O$_9$ (SBT),$^4$ BLSFs have occupied an important position among nonvolatile ferroelectric memory materials as well as among lead-free piezoelectrics. Owing to their layered structure, BLSFs have ferroelectric, piezoelectric and electrically conducting properties with a large anisotropy.$^5$ The high fatigue endurance of SBT is also believed to originate from its anisotropic nature. Thus, the orientations of crystal axes are important in most applications using thin films and ceramics. However, the effects of a layered crystal structure, especially $m$, on ferroelectricity have not yet been clarified for lack of single-crystal data.

For the application in ferroelectric memories, the remanent polarization ($P_r$) of SBT is not sufficient. In contrast, Bi$_2$Ti$_2$O$_7$ (BIT), another typical BLSF material, has a large spontaneous polarization ($P_s$)$^6,^7$ but the $P_r$ observed in thin films and ceramics is small owing to the high leakage current and large $E_c$. To overcome these disadvantages, the control of lattice defects is very effective. Defects in crystals, such as...
substituted aliovalent cations and vacancies of oxygen and cations, significantly affect ferroelectric properties through changes in electronic structure, domain wall movement and lattice distortion. Defect control for improving various properties, called “defect engineering,” is becoming a promising approach to the design of polarization properties.8)

The understanding of the effects derived from a layered structure and the control of lattice defects are indispensable for designing the polarization properties of BLSFs and developing these ferroelectrics as key materials in novel applications. In the present paper, the structure-property relationship and the property design by defect control in BLSFs are described.

2. Structure dependences of polarization properties

In this section, the relationship between polarization properties (P and E) and the Curie temperature (Tc) or m is described for various BLSF single crystals.9) Figure 2 shows a list of single-crystal samples and an example of a polarization hysteresis loop of BBT. The BIT single crystal was grown by a flux method using Bi2O3 as a flux, and the other crystals were grown by a melting and slow-cooling method.10) For structural analysis, the Rietvelt analysis using the RIETAN program11,12) was performed on X-ray diffraction patterns or synchrotron radiation diffraction patterns obtained with a multiple-arm system of the Photon Factory in KEK. Polarization measurements were conducted along the a(b) axis and c axis separately.

Figure 3(a) shows the relationship between the remanent polarization (Pr) and the difference between the Curie temperature and the measuring temperature (20 and 110°C) along the a(b) axis. For PBN and PBT, Pr values were estimated from the relative atomic displacements of B-site ions13) because saturated hysteresis curves were not obtained. Pr was larger in BLSFs with a higher Tc. BIT with the highest Tc was found to show the largest Pr, reaching 46 μC/cm². This relationship holds true not only in BLSFs but also in typical perovskite-type compounds, if they are displacive ferroelectrics.14) However, P with no linear relationship with m.

In general, displacive ferroelectrics with a large Pr have a large Ec. However, this relationship does not hold true strictly for BLSFs. Figure 3(b) shows the relationship between Ec, Em, and the number of BO6 octahedra (m) at 20°C, where Em is the minimum electric field at which a saturated hysteresis curve is obtained. Ec and Em were smaller in BLSFs with a larger m. Different from ABO3-type ferroelectrics whose BO6 octahedra are distorted, perovskite blocks of BLSFs have BO6 octahedra that rotate in the a-b plane.15) Such rotation brings about the movement of B cations and the surrounding oxygen ions, which mainly contributes to spontaneous polarization. On the other hand, the bismuth layer is considered to be paraelectric, and it is difficult for bismuth ions in the bismuth layer to move in the direction of an external electric field. Therefore, the BO6 octahedra receive strain energy from the bismuth layers. Because the strain energy decreases with increasing m, the rotation of the octahedra and the movement of constituent ions become easier with increasing m. Polarization reversal velocity also increases with increasing m for the same reason.16)

Along the c axis, the ferroelectric properties of BLSFs with an odd m showed the same relationship as those along the a(b) axis, although the Pr values were very small. There was no polarization along the c axis in BLSFs with an even m, because they have a mirror plane by which the polarizations cancel each other along the c axis.17)

3. Property design by defect control in SrBi2Ta2O9

3.1 Bi-substituted SrBi2Ta2O9

As described above, SBT has a high fatigue endurance but its remanent polarization (Pr) is not sufficient for application in ferroelectric memories. Many studies have been conducted to increase Pr, and thin films with the Sr-deficient and Bi-excess composition Sr1−xBixTa2O9 were reported to show Pr larger than that of stoichiometric SBT.18) However, different valences of Sr and Bi ions should bring about other types of defect for charge neutrality. To clarify the effects of Bi substitution at the A site, structure refinement was conducted for Sr5.7Bi12.1Ta2O9 (A-dif. SBT) and SrBi13.6Ta2O9 (stoichiometric SBT, to which a slight excess of Bi was added for sinterability) by the Rietvelt analysis of synchrotron-radiation diffraction data and their polarization properties were compared.19,20) Ceramic samples were prepared by a conventional solid-state reaction.

The calculated diffraction pattern obtained by the Rietvelt analysis of Sr5.7Bi12.1Ta2O9 fitted the observed pattern fairly well, under the condition that excess Bi is substituted at the A site with cation vacancies. This indicates the A-site composition to be (Sr5.7Bi12.1V0.05), where V denotes cation vacancies, satisfying the charge neutrality. The polarization measurements showed that A-dif. SBT has a Pr of 13 μC/cm², much larger than that of stoichiometric SBT (7 μC/cm²).21)

In the SBT structure with A2Tta orthorhombic symmetry, the a axis is the polar axis, and displacements along the a axis of constituent ions contribute to the spontaneous polarization P. P can be calculated using

\[
P = \Sigma (m_i \times \Delta x_i \times Qe) / V,
\]

where \(m_i\) is the site multiplicity, \(\Delta x_i\) is the atomic displacement...
along the $a$ axis from the corresponding position in the parent tetragonal ($I4/mmm$) structure, $Q_{fe}$ is the ionic charge for the $i$th constituent ion, and $V$ is the volume of the unit cell. Using the formal charges of constituent ions and atom positions determined by the Rietveld analysis, the $P_{r}$ of A-diff. SBT was calculated to be $20 \mu C/cm^{2}$, larger than the $16 \mu C/cm^{2}$ of stoichiometric SBT. This result is consistent with the $P_{r}$ increase, and indicates that the Bi substitution with cation vacancies enhances the intrinsic ferroelectricity of SBT.

The ferroelectric distortion in SBT consists of the tilting and rotation of TaO$_6$ octahedra, as shown in Fig. 4. The principal change in ferroelectric distortion caused by the substitution was found to be on the rotation. The tilt angle ($\alpha$) from the $c$ axis for stoichiometric SBT was about 8$^\circ$ which is mostly to the $b$ axis; it was almost the same for A-diff. SBT. On the other hand, the average octahedral rotation angle ($\beta$) increased from 4.3 to 5.4$^\circ$ by the Bi substitution with A-site vacancies. The enhanced octahedral rotation accompanied with the whole shift of the octahedra was found to be responsible for a larger $P_{r}$ and increased $P_{r}$ in A-def. SBT.

3.2 Rare-earth-element-substituted SrBi$_2$Ta$_2$O$_9$

The rare-earth (RE) cations La, Nd and Sm were substituted at the A site with Sr vacancies in SBT, and polarization properties were examined. Ceramic samples of $M_{1-x}Sr_xBi_2Ta_2O_9$ (M-SBT: M = La, Nd, Sm) were prepared by a solid-state reaction. To obtain dense samples over 95% relative density for electrical measurements, excess Bi$_2$O$_3$ of 2 at.-% of the stoichiometric composition was added to the starting powders. Time-of-flight neutron powder diffraction data and powder XRD data were collected and structural parameters were refined by the Rietveld method.

Single-phase solid solutions were obtained at compositions $x \sim 0.5$ for La- and Sm-SBTs, and $x \sim 0.7$ for Nd-SBT. The rare-earth elements were also confirmed to be substituted at the A site with A-site vacancies. For example, La substitution at $x = 0.5$ resulted in the formation of 17% cation vacancies at the A site. This vacancy formation compensates for the difference in valence between Sr$^{2+}$ and M$^{3+}$. The Curie temperature ($T_{C}$), estimated from the peak temperature of dielectric permittivity, decreased with increasing La content from 295$^\circ$C of SBT to 180$^\circ$C of La-SBT ($x = 0.5$). For Nd- and Sm-SBTs, the $T_{C}$ change was similar to that of La-SBT in the low-$x$ region, but further substitution led to a increase in $T_{C}$ giving the minimum of $T_{C}$.

Figure 5 shows polarization hysteresis loops for La-SBT ($x = 0.5$) and Nd-SBT ($x = 0.5$) at 25$^\circ$C. The La substitution improved the squareness of hysteresis, and led to an increase in $P_{r}$ from 6.4 $\mu C/cm^{2}$ ($x = 0$) to 9.0 $\mu C/cm^{2}$ ($x = 0.2$), which slightly decreased at $x = 0.5$, $E_{r}$ decreased linearly from 28 $kV/cm$ ($x = 0$) to 21 $kV/cm$ ($x = 0.5$). For Nd-SBT, the $P_{r}$ change was almost the same as that in La-SBT, but $E_{r}$ increased markedly above $x = 0.2$ from 30 $kV/cm$ ($x = 0.2$) to 79 $kV/cm$ ($x = 0.7$). As a result, “softening” and “hardening” in ferroelectric behavior were attained by La and Nd substitutions, respectively, as shown in Fig. 5.

La-SBT has a high concentration of dipolar defects composed of substituted La$^{3+}$ at the Sr site ($La_{8-x}^{3+}$) and Sr vacancies ($V_{Sr}^{0}$) in the perovskite blocks. The “random field” around the dipolar defects significantly lowers the activation barrier required for the nucleation of new domains. For La-SBT, it is assumed that the random field assists the nucleation and switching of domains by an applied field, leading to a lower $E_{r}$. In addition, from results of structural analysis, an almost linear relationship between $E_{r}$ and $\alpha_{r}$ (tilting component along the polarization direction, as shown in Fig. 4) is observed for various samples with A-site vacancies. This suggests that the tilting reversal along the $a$ axis induced by an applied field requires a large energy and determines polarization-switching behavior. The $\alpha_{r}$ of La-SBT ($x = 0.5$) was confirmed to be much lower than that of SBT ($x = 0$), and this structural change may be another reason for the low $E_{r}$ of La-SBT.

The high $E_{r}$ of Nd-SBT with $x > 0.5$ is due to the B-site substitution of Nd and subsequent domain pinning by oxygen vacancies. When a high Nd ion concentration is substituted in SBT, a low Nd ion concentration is likely to occupy the B (Ta) site, as well as the A (Sr) site, due to the relatively small ionic radius of Nd ion. For charge compensation, the B-site substitution generates oxygen vacancies, which assemble close to charged domain walls and induce domain pinning.

Figure 6 shows the composition dependences of $P_{r}$ and $E_{r}$ for the solid solution system of La- and Nd-SBTs, expressed as $(La_{1-x}Nd_{x})_{0.5}Sr_{0.5}Bi_2Ta_2O_9$. With increasing Nd content ($y$), $E_{r}$ increased markedly but $P_{r}$ remained fairly constant. This is due to the markedly different $E_{r}$'s and the same $P_{r}$ of La- and Nd-SBTs. This result indicates that the $E_{r}$ of SBT can be controlled by La and Nd cosubstitution while maintaining $P_{r}$ unchanged.

4. Property design by defect control in Bi$_4$Ti$_3$O$_{12}$

4.1 B-site modified Bi$_4$Ti$_3$O$_{12}$

Bismuth titanate (Bi$_4$Ti$_3$O$_{12}$, BIT) has been regarded as a promising ferroelectric material because of its high Curie temperature, large spontaneous polarization and large electrooptic coefficient. However, its leakage current arising from defects often interferes with polarization switching and poling, and its poor insulation property makes BIT unsuitable for practical applications. In this section, effects of the doping of higher-valence cations such as W and V ions at the B site (Ti site) on polarization and conduction properties are shown,
and the crucial role of oxygen vacancies in these properties is described.

Figure 7 shows polarization hysteresis loops of BIT and tungsten-doped BIT (W-BIT, Bi$_{1-2x}$Ti$_x$W$_x$O$_{2+2x}$; $x=0.015$) ceramics, prepared by a solid-state reaction. For only BIT, excess Bi of 5 at. % of the stoichiometric composition was added to decrease leakage current. The observed $P$ is below 10 $\mu$C/cm$^2$ and the squarness of hysteresis is poor in BIT. In contrast, W-BIT showed a large $P$ of 21 $\mu$C/cm$^2$. Considerable decreases in leakage current and dielectric loss by V and W doping were also confirmed. 

Figure 8 shows oxide-ion conductivity ($\sigma_{\text{ion}}$) and hole conductivity ($\sigma_{\text{hole}}$) along the $a$ and $b$ axes for single crystals of BIT and vanadium-doped BIT (V-BIT, Bi$_{0.96}$Ti$_{1.2}$V$_{0.04}$O$_{12}$). The single crystals were grown by a self-flux method using Bi$_2$O$_3$ as a flux. Total conductivity ($\sigma_{\text{total}}$) was measured by the complex impedance method in the oxygen partial pressure ($P_O$) range of 20 Pa–0.1 MPa along the $a$ and $c$ axes. Ionic and hole conductivities were estimated as the $P_O$-independent and $P_O$-dependent parts of total conductivity, respectively, on the basis of

$$\sigma_{\text{total}} = \sigma_{\text{ion}} + \sigma_{\text{hole}} (P_O/0.1 \text{ MPa})^{1/6},$$

where $\sigma_{\text{hole}}$ is the hole conductivity at 0.1 MPa of $P_O$. In BIT shown in Fig. 8(a), the conductivities along the $a$($b$) axis are 1.5–2.5 orders of magnitude larger than those along the $c$ axis, indicating a large anisotropy, and $\sigma_{\text{ion}}$ is larger than $\sigma_{\text{hole}}$ along the $a$($b$) axis. It is expected that Bi and O in the perovskite blocks preferentially evaporate during crystal growth, as described in Section 4.2. The oxygen vacancies move easily in the perovskite blocks in the $a$-$b$ plane, but their migration along the $c$ axis is inhibited by the Bi$_2$O$_3$ layers. In V-BIT shown in Fig. 8(b), $\sigma_{\text{ion}}$ and $\sigma_{\text{hole}}$ along the $a$($b$) axis were largely decreased by vanadium doping. The vanadium incorporation into BIT and hole generation are assumed to occur through the following reactions.

$$2\text{TiO}_2 + V_0 \rightarrow 2V_{Ti}^+ + 5O_2^*$$

(3)

$$1/2O_2 + V_0 \rightarrow O_0^* + 2h^+$$

(4)

Here, $V_0$ is an oxygen vacancy, $O_0^*$ is lattice oxygen, $V_{Ti}^+$ is vanadium at the Ti site and $h^+$ is an electron hole. The vanadium doping efficiently decreases oxygen vacancy concentration, resulting in a lower $\sigma_{\text{ion}}$ as observed in Fig. 8(b). Subsequently, the hole generation induced by the incorporation of oxygen into oxygen vacancies is inhibited, resulting in a lower $\sigma_{\text{hole}}$.

Many investigations on oxide ferroelectrics have shown that oxygen vacancies assembled at domain boundaries act as a space charge causing domain pinning. The vanadium doping effectively decreases the concentrations of oxygen vacancies and electron holes, and reduces the influences of domain pinning and leakage current. This results in very large $P$’s of V-BIT and W-BIT. Decreases in the oxygen-vacancy concentration and leakage current can also be attained by sintering or crystal growth under a high-$P_O$ condition. Figure 9 shows polarization hysteresis loops along the $a$($b$) axis for BIT single crystals. The crystal grown in $O_2$ atmosphere at $P_O$ of 0.1 MPa showed a $P$ of 48 $\mu$C/cm$^2$, larger than that of the crystal grown in air.

4.2 Rare-earth-element-substituted Bi$_{1-x}$Ti$_x$O$_{12}$

La- and Nd-substituted BITs (BLT and BNT) have received much attention because rare-earth substitutions lead to better memory properties of thin films such as a large $P$, a high fatigue endurance and excellent insulating properties. La and Nd ions preferentially occupy the perovskite A site and suppress lattice distortion in the perovskite blocks, resulting in a smaller spontaneous polarization $P_s$ than that of nonsubstituted BIT. It is not clear why thin films and polycrystals of BLT and BNT show better polarization properties than BIT, in spite of their smaller $P_s$. Here, the results of defect structure analysis through ab initio band structure calculations and domain structure analysis using piezoresponse force microscope (PFM) are described.

Single crystals of BIT, BLT (La$_{1-x}$Bi$_x$Ti$_x$O$_{12}$: BLT($x$), $x=$
0–2.0) and BNT (Nd$_{2}$Bi$_{4-x}$Ti$_{2}$O$_{12}$: BNT(x), x = 0–1.5) were grown by a self-flux method using Bi$_{2}$O$_{3}$ as a flux. Chemical composition was determined by inductively coupled plasma (ICP) analysis.

Ab initio band structure calculations were performed to estimate the vacancy formation energy ($E_{\text{vacancy}}$) of Bi and O.\textsuperscript{28} The calculations were conducted within the density functional theory \textit{via} generalized gradient approximations using a plane wave basis set.\textsuperscript{29} First, we optimized the crystal structure of Bi$_{2}$Ti$_{3}$O$_{12}$ (BIT) and La$_{2}$Bi$_{4}$Ti$_{12}$O$_{24}$ (BLT; 2.0) with I4/mmm tetragonal symmetry, in which all La atoms occupy the A site. An atom was deleted at a specific site from the 2a×2b×1c supercell of the optimized structure, and then the total energy of the cell was calculated. \textit{E}_{\text{vacancy}} was estimated from the difference in total energy between the defective cell and the optimized unit cell.

Figure 10 indicates the relative $E_{\text{vacancy}}$ of Bi and O in each site.\textsuperscript{28} Since Bi1 and O2 show the lowest \textit{E}_{\text{vacancy}} in Bi and O, these values are set as the standard for comparison. The \textit{E}_{\text{vacancy}} of Bi1 is lower than that of Bi2 by about 2 eV. This indicates that Bi vacancies are generated preferentially in the perovskite blocks rather than in the Bi$_{2}$O$_{3}$ layers. For oxygen vacancies, O1, O2 and O3 in BIT showed similar \textit{E}_{\text{vacancy}} values within 0.2 eV, which are lower by about 0.4–0.6 eV than those of O4 and O5. Furthermore, the nuclear-density analysis revealed that oxygen vacancies preferentially localize at the O1 site. From these results, the following reaction in the perovskite blocks can be concluded for principal defect formation

\[2\text{Bi}_{\text{Bi1}}^+ + 3\text{O}_{\text{O1}}^* = 2V_{\text{Bi1}}^{\prime\prime\prime} + 3V_{\text{O1}}^{\prime\prime\prime} + \text{Bi}_2\text{O}_3(g)\]  

Here, $V_{\text{Bi1}}^{\prime\prime\prime}$ and $V_{\text{O1}}^{\prime\prime\prime}$ are vacancies at the Bi1 and O1 sites, respectively. In BLT, the \textit{E}_{\text{vacancy}} values of the adjacent oxygen atoms, O1, O3 and O5, are larger than those in BIT by about 1 eV. This suggests that La substitution improves the chemical stability of oxygen in the perovskite blocks. Results of total/partial density of states (DOS) analysis of BLT (x = 2.0) suggested that the La 5$d$ is hybridized with the O 2$p$ of the adjacent oxygen. This may be the origin of the high chemical stability of oxygen in BLT. The conductivity at high temperatures and leakage current at 25°C along the a axis of BLT were lower than those of BIT.\textsuperscript{30} These results support the notion that La substitution suppresses the formation of defects (oxygen vacancies and electron holes) by improved stability. The lowered defect concentration will be the reason for the excellent insulating property and the large \textit{P}$_c$ of BLT, regardless of relatively small \textit{P}$_r$. This effect was also confirmed in thin films.\textsuperscript{31}

Figure 11 shows PFM images of (a) BIT and (b) BLT (x = 0.46). The white and black areas are the domains with \textit{P}$_c$ oriented upward and downward, respectively, whereas the neutral-color area indicates the domain with \textit{P}$_r$ in the right direction. In BIT, a striped 90° domain structure is clearly observed, and 180° domain walls can be recognized in some needle-like 90° domains. In BLT, domain size significantly decreased and irregular curved boundaries were observed. There are boundary parts without a change in PFM signal in the curved boundaries, thus the presence of antiphase domain boundaries (ADB) is suggested.\textsuperscript{32} Because the ADB can act as a nucleus of a new 90° domain, it may contribute to a relatively large \textit{P}$_c$ with a fatigue-free feature in BLT thin films.

5. Superlattice-structured BLSFs

A family of intergrowth BLSFs has a crystal structure in which one-half of the unit cells of the BLSFs with different \textit{m} numbers are alternately stacked in the structure along the c axis, that is a natural superlattice structure. Intergrowth compounds with \textit{m} = 1–2, 2–3, and 3–4 have been reported.\textsuperscript{33} Intergrowth compounds with \textit{m} = 1–2 and 2–3 undergo phase transitions twice at approximately the $T_c$'s of constituent BLSFs, whereas those with \textit{m} = 3–4 undergo ferroelectric phase transition once at a temperature between the $T_c$'s of constituent BLSFs.\textsuperscript{34–37} A lattice mismatch and related interactions between two perovskite blocks induce a large lattice distortion, and thus novel polarization properties can be expected. In this section, the enhanced polarization properties of intergrowth Bi$_{2}$Ti$_{3}$O$_{12}$–BaBi$_{4}$Ti$_{12}$O$_{24}$ (BIT-BBT; \textit{m} = 3–4) single crystals are described.\textsuperscript{36,37}
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and good agreement with half the lattice parameters permittivity, measurements of the Bi ions in the Bi P T alternate stacking of Ba site, as observed in SBT with excess Bi and Sr deficiency. BBT, respectively, indicating the alternative stacking of of single-crystal BIT, BBT and BIT-BBT along the a axis. and BBT, tensile and compressive stresses built up in the a b c axis.

One reason for the large strain energy but contributes to the insulating property and defects. The former gives spontaneous polarization and the latter restricts the structural distortion of the perovskite blocks by strain energy but contributes to the insulating property and structural stability. It is important to understand these roles for selecting BLSFs as a suitable mother material for various applications. As for polarization properties, defect control is very effective in improving them. Bi substitution in SBT enhances lattice distortion, which is, increases intrinsic ferroelectricity, resulting in a large P,. In BIT, the doping of high-valence cations at the B site compensates for oxygen vacancies formed in sample processing, and the substitution of rare-earth cations at the A site stabilizes the perovskite lattice and suppresses the formation of oxygen vacancies. Such modifications release domain walls from pinning by oxygen vacancies, resulting in a large P, and a small E,.

By applying the concept of defect control to BLSFs with a suitable layered structure, we can realize further improvement in their ferroelectric properties and the discovery of novel functions.

Acknowledgements

The author sincerely thanks all his coworkers for their contribution to experiments and discussion in this work, particularly Dr. Yuji Noguchi, an assistant professor at the University of Tokyo.

References


Figure 12 shows a transmission electron microscope (TEM) image of BIT-BBT in the a(b)–c plane.③ The thicknesses of the constituent layers were about 1.5 and 2.0 nm, which are in good agreement with half the lattice parameters c of BIT and BBT, respectively, indicating the alternative stacking of m = 3 and 4 layers. From the temperature dependence of dielectric permittivity, Tc was determined to be 540°C, which was intermediate between the Tc of BIT (576°C) and the Tc of BBT (395°C). Figure 13 indicates the polarization hysteresis loops of single-crystal BIT, BBT and BIT-BBT along the a(b) axis at 25°C. The hysteresis loops showed a very good squareness, and the P, of BIT-BBT was 52 μC/cm², which is larger than those of BIT (46 μC/cm²) and BBT (16 μC/cm²) crystals.③④

One reason for the large P, may be the Bi substitution at the Ba site, as observed in SBT with excess Bi and Sr deficiency. However, in BIT-BBT, the lattice distortion induced by the alternate stacking of m = 3 and m = 4 layers is assumed to play a predominant role in the enhanced P,. Because the lattice parameters a and b of BIT-BBT were averages of those of BIT and BBT, tensile and compressive stresses built up in the m = 3 and m = 4 layers, respectively. This environment induces a local symmetry breaking of the BiO₂ layers, and the displacements of the Bi ions in the BiO₂ layers contribute to the enhanced P,, as reported for BIT-SrBi₄Ti₄O₁₅ ceramics.③⑤

6. Summary

The electrical properties of BLSFs are characterized as the interactions between perovskite blocks and bismuth oxide layers; the former gives spontaneous polarization and the latter restricts the structural distortion of the perovskite blocks by strain energy but contributes to the insulating property and structural stability. It is important to understand these roles for selecting BLSFs as a suitable mother material for various applications.
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