

Defect Engineering for Control of Polarization Properties in Bismuth Layer-Structured Ferroelectrics

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ABSTRACT

A defect engineering approach for SrBi₂Ta₂O₉ (SBT), the introduction of cation vacancies at the Sr site (*A* site) by Bi or La substitution, is shown to be useful for polarization-property control. The Rietveld analysis of neutron powder diffraction has demonstrated that Bi and La are substituted at the *A* site as trivalent cations accompanied with *A*-site vacancies. The substitution of Bi and La enhances P_r , and a very low E_c of 20 kV/cm is attained for La-SBT. The presence of *A*-site vacancies is crucially important for polarization reversal by applied electric field.

1. INTRODUCTION

There has been an increasing interest in ferroelectric materials because of their application to nonvolatile random access memories. Ferroelectric SrBi₂Ta₂O₉ (SBT) is considered as a promising candidate due to its excellent fatigue endurance.[1] In the crystal structure of SBT, perovskite blocks, (SrTa₂O₇)²⁻, composed of double TaO₆ octahedra with Sr at the *A* site, are interleaved with (Bi₂O₂)²⁺ layers. The (Bi₂O₂)²⁺ layers act as insulating paraelectric layers and largely control the electronic response (electrical conductivity, band gap, etc.), [2] while the ferroelectricity arises mainly in the perovskite blocks. [3-5] The ferroelectricity is attributed to the rotation and tilt of TaO₆ octahedra accompanied with the entire shift of octahedra along the polarization direction. [5,6] It is expected, therefore, that *A*-site ions positioned in the cavities between two TaO₆ octahedra play a crucial role in determining the ferroelectric properties of SBT.

Polarization-switching characteristics of ferroelectrics are known to be strongly influenced by the presence of defects.[7] For lanthanum-modified Pb(Zr,Ti)O₃, La³⁺ is substituted preferentially at the Pb²⁺ site, and cation vacancies are created to satisfy the requirement of charge neutrality.[8] Such higher valent substituents and associated cation vacancies would form dipolar defects which are quenched above the ferroelectric transition temperature due to their extremely low mobility. [9] Since random field near the quenched dipolar defects weakens long-range ferroelectric order, La modification decreases the ferroelectric transition temperature.[8] Furthermore, the dipolar defects act as

nuclei for the formation of twinned structures, thus the experimentally measured coercive field (E_c) is usually much lower than the intrinsic value predicted by the Landau-Ginzburg mean field theory.[10]

Recently, structure investigations of SBT using neutron [4] and synchrotron-radiation diffraction [5] have verified that cation vacancies can be introduced by the substitution of higher valent Bi³⁺ at the Sr²⁺ site. The substitution of Bi³⁺ at the Sr²⁺ site induces *A*-site vacancies to satisfy the requirement of charge neutrality. [5] In this paper, we describe a defect engineering, the introduction of cation vacancies at the Sr site (*A* site) by Bi or La substitution, is useful for polarization-properties control of SBT. The presence of *A*-site vacancies is shown to be crucially important for nucleation-growing processes of domains by applied electric field.

2. EXPERIMENTAL PROCEDURE

Ceramic samples of M_{2x/3}Sr_{1-x}Bi₂Ta₂O₉ (M=La and Bi, $x=0 \sim 0.5$) were prepared by a conventional solid-state reaction from ground powders of La₂O₃, SrCO₃, Bi₂O₃, and Ta₂O₅ of 99.99% purity. The details of the preparation condition of bulk ceramics are described in Ref.5. For powder diffraction measurements, the mixed powder was calcined at 800-1050°C for 4 h, and then fired at 1100°C for 4 h with intermediate grindings. Time-of-flight neutron powder diffraction data were collected at 25°C using the Vega diffractometer at KENS [11]. Structure parameters were refined by the Rietveld method using the program RIETAN-2001T [12] based on $A2_1am$ orthorhombic symmetry.

To obtain dense samples for electrical and

polarization measurements, 2-at.% excess Bi_2O_3 powder was added to the starting powders with the stoichiometric composition. For example, dense SBT ceramics were obtained from the powders with the nominal composition of $\text{SrBi}_{2.04}\text{Ta}_2\text{O}_9$. Uniaxially pressed pellets were followed by a cold isostatic press (CIP) treatment at 300 Mpa. The final sintering was performed at 1200 °C for $M=\text{Bi}$ and 1250°C for $M=\text{La}$ for 1 h. X-ray diffraction measurements on the polished surface of the dense samples revealed no preferred orientation.

3. RESULTS AND DISCUSSION

In our previous study [5], the synchrotron-radiation diffraction data was analyzed using Rietveld method, for the sample obtained from the powder prepared from the mixture with the nominal composition of $\text{Sr}_{0.73}\text{Bi}_{2.18}\text{Ta}_2\text{O}_9$. The following possibilities were considered in the analysis; (1) $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (stoichiometry), (2) $\text{Sr}_{0.73}\text{Bi}_{2.27}\text{Ta}_{1.946}\text{O}_9$ (Bi^{3+} substitution at the A site (Sr site) for SBT with Ta vacancies), (3) $\text{SrBi}_2(\text{Ta},\text{Bi})_2\text{O}_9$ (Bi^{5+} substitution at the Ta site), (4) $\text{Sr}_{0.73}\text{Bi}_{2.27}\text{Ta}_2\text{O}_9$ (Bi^{2+} substitution at the A site), and (5) $\text{Sr}_{0.73}\text{Bi}_{2.18}\text{Ta}_2\text{O}_9$ (Bi^{3+} substitution at the A site with A -site vacancies). The results indicated that the conditions of (4) and (5) were superficially plausible [R -weighted pattern (R_{wp}) was around 13~14%]. Thus, we checked the diffraction pattern of the powder obtained from the mixture with the nominal composition of $\text{Sr}_{0.73}\text{Bi}_{2.27}\text{Ta}_2\text{O}_9$. Several peaks of second phase(s) were observed, and R_{wp} was very large (32%), leading to the conclusion that the possibility of (4) was eliminated in non-stoichiometric SBT.

Figure 1 shows neutron powder diffraction data (\times) of $\text{Sr}_{0.73}\text{Bi}_{2.18}\text{Ta}_2\text{O}_9$ (Bi-SBT; $x=0.27$) powder. The peaks observed were almost the same as those of stoichiometric SBT, and no second peak was detected. The Rietveld analysis of the neutron data was carried out in a similar manner. The value of R_{wp} was smallest

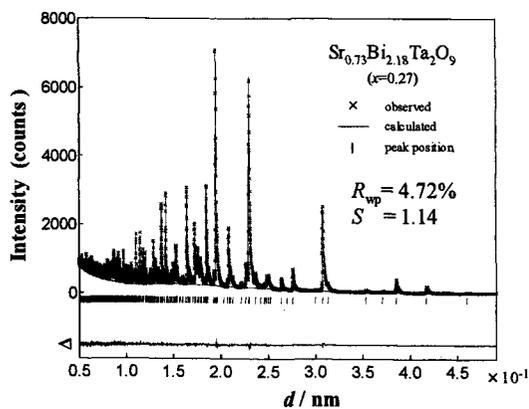


Fig. 1 Fitting result of the Rietveld analysis of the neutron powder diffraction for $\text{Sr}_{0.73}\text{Bi}_{2.18}\text{Ta}_2\text{O}_9$ ($x=0.27$).

(4.29%) in the condition (5). A fitting result of the Rietveld analysis under the condition (5) is indicated in Fig. 1. In the analysis, excess Bi was assumed to be substituted with cation vacancies at the perovskite A site. The calculated pattern fits the observed data fairly well. The composition at the A site determined by the Rietveld analysis was $(\text{Sr}_{0.73(2)}\text{Bi}_{0.18(2)}\square_{0.09})$, where \square indicates A -site vacancies. The results of both synchrotron-radiation and neutron diffraction data reveals that the charge neutrality in the crystal of $\text{Sr}_{1-x}\text{Bi}_{2+2x/3}\text{Ta}_2\text{O}_9$ is satisfied through the substitution of Bi with cation vacancies at the A -site. We conclude that excess Bi is substituted as *trivalent cations* with A -site vacancies. The substitutions of rare-earth cations such as La^{3+} , Nd^{3+} , and Sm^{3+} with A -site vacancies were also confirmed by X-ray and/or neutron diffraction analyses.

Figure 2 shows the refined lattice parameters as a function of the degree of Bi substitution (x). Unit-cell volume (V) decreased with an increase in x due to the smaller ionic radius (r_i) of Bi^{3+} than Sr^{2+} ($r_i=0.144$ nm) at the 12-coordinated site, while the change in a and b was not straightforward as expected in a simple solid solution. The cause of the decreasing-tendency change in a and b at around $x=0.11$ remains unclear. In the SBT system with $A2_1am$ orthorhombic symmetry, spontaneous polarization (P_s) appears and constituent ions are displaced cooperatively along the a axis.[3-6] The entire shift of perovskite blocks along the a axis

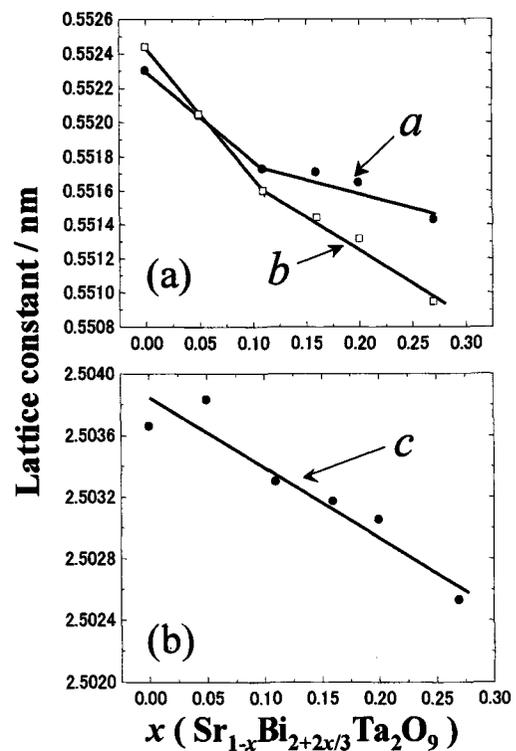


Fig. 2 Lattice constants as a function of Bi content (x) at the A site for Bi-SBT.

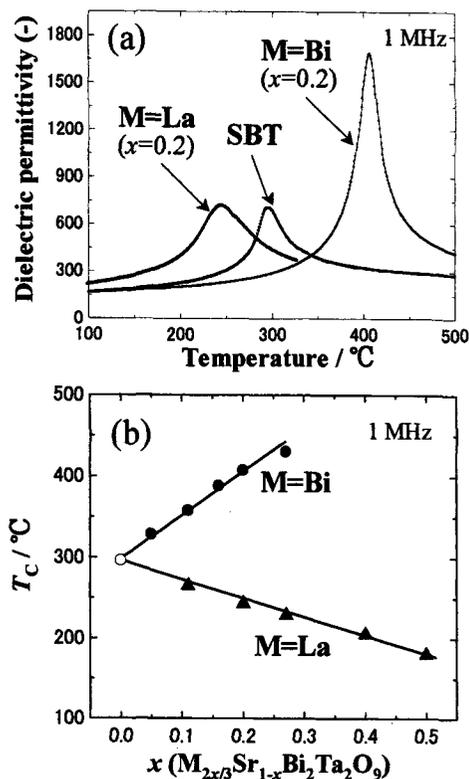


Fig. 3 (a) Temperature dependence of dielectric permittivity (at 1 MHz) and (b) T_C vs. x .

mainly contributes to P_s . [5,6] The TaO₆ octahedral tilt along the b axis (about 8 deg) is much higher than that along the a axis (less than 1 deg), leading to the large distortion along the b axis. [6] For the stoichiometric SBT, a was shorter than b . The Bi substitution resulted in a large decrease in b compared with that in a , leading to the change in the longer axis of the unit cell. With increasing Bi content (x) at the A site, the orthorhombic distortion (a/b) was enhanced.

For La-modified SBT, V and lattice parameters decreased with an increase in La content (x), while a/b remained constant at around 0.99975. The r_i of La³⁺ ($r_i = 0.136$ nm) is smaller than that of Sr, and La is substituted with A -site vacancies. When Ca²⁺ ($r_i = 0.134$ nm) with smaller r_i than Sr²⁺ was substituted at the A site of SBT, V decreased and a/b was changed to 1.001 for $A = \text{Ca}_{0.3}\text{Sr}_{0.7}$ [6]. Although the occupation of smaller La³⁺ at the A site is directly responsible for the overall structure change, the unchanging behavior of a/b cannot be explained in terms of only the effects of ionic size. Thus, the presence of A -site vacancies would play an important role in ferroelectric distortion for La-SBT.

Figure 3 (a) shows the temperature dependence of dielectric permittivity at a frequency of 1 MHz. The Bi substitution lead to a shift of T_C from 295°C (SBT) to 400°C (M=Bi; $x=0.27$), while T_C decreased with La substitution to 180°C (M=La; $x=0.5$). It is clearly seen that T_C for SBT can be controlled from 150 to 420°C by

the substitution of Bi- and La substitution with A -site vacancies. Since r_i of Bi³⁺ is almost the same as that of La³⁺, the large difference in T_C between Bi- and La-substituted samples cannot be explained by the size effect of trivalent cations. In general, bismuth layer-structured ferroelectrics (BLSFs) with smaller A -site cations tend to show a higher T_C . For the SBT system, the 30% substitution of smaller Ca²⁺ than Sr²⁺ increases T_C from 295°C to 420°C and promotes the displacements of oxide ions of TaO₆ octahedra. [6] Furthermore, SrBi₂Nb₂O₉ has a higher T_C (440°C) than BaBi₂Nb₂O₉ (200°C) because of smaller r_i of Sr²⁺ than Ba²⁺ ($r_i = 0.161$ nm). [13,14] However, La-SBT showed a lower T_C than SBT in spite having a smaller La³⁺ at the A site. These results lead to a conclusion that A -site vacancies weakens a long-range ferroelectric order of perovskite blocks resulting in a lower T_C as observed for La-substituted PbTiO₃ [8].

When Bi³⁺ and Pb²⁺ with 6s² lone-pair electrons occupy the A site of perovskite blocks, T_C tends to rise. In fact, PbBi₂Nb₂O₉ has a high T_C (560°C) compared with SrBi₂Nb₂O₉ ($T_C = 440^\circ\text{C}$) in spite of having larger r_i of Pb²⁺ than Sr²⁺. [13,14] Electron structure calculations [15] suggest for PbTiO₃ that the hybridization of electron orbitals Pb(6s)-O(2p) as well as Ti(3d)-O(2p) plays an important role in the ferroelectricity. The difference between La and Bi ions is bonding characteristics to oxide ions; Bi ions have partial covalent bonding to oxide ions of TaO₆ octahedra, as is observed between Pb and oxide ions for PbTiO₃, [15] whereas La³⁺ would act as an almost pure ions at the A site. This kind of covalent nature between A -site cations and oxide ions enhances long-range ferroelectric order, and promotes lattice distortions in perovskite blocks. Thus, there are two factors affecting T_C in Bi-SBT; partial covalent bonding Bi(6s)-O(2p) leading to a higher T_C , and A -site vacancies resulting in a lower T_C . The resultant high T_C in Bi-substituted samples suggests that the effect of the partial covalent bonding on ferroelectric distortions is dominant over that of A -site vacancies.

Figure 4 indicates the polarization hysteresis loops at a drive field of 200 kV/cm measured at 25°C. For SBT, P_r was 6.5 $\mu\text{C}/\text{cm}^2$, while La-SBT ($x=0.5$) had a larger P_r of 8.5 $\mu\text{C}/\text{cm}^2$. La-SBT ($x=0.5$) showed a E_c of 20 kV/cm, which is much smaller than those of SBT (33 kV/cm) and SBT thin films [1]. For La-SBT polarization switching began at an E_m of 15-20 kV/cm and P_r values were large in both low and high E_m regions compared with SBT. It is clearly seen for Bi-SBT that polarization properties were enhanced by Bi substitution. Bi-SBT ($x=0.2$) had a large P_r of 10.5 $\mu\text{C}/\text{cm}^2$. On the other hand, Bi-SBT ($x=0.2$) showed a slightly higher E_c of 40 kV/cm than SBT ($x=0$).

Since the dipole moment of each ion is estimated from the ionic displacement along the a axis from the

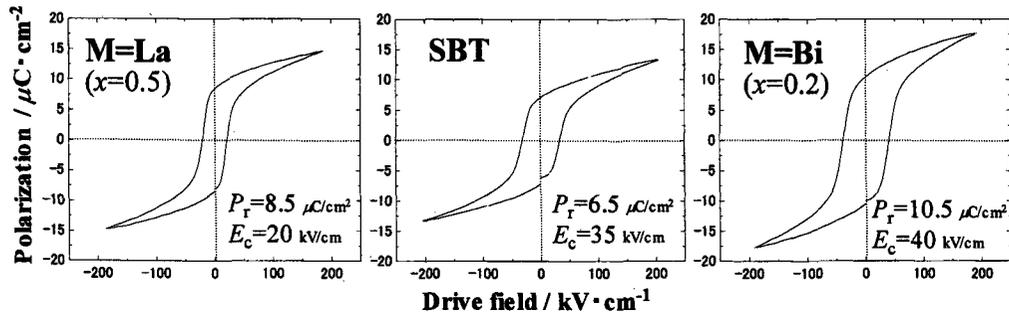


Fig. 4 Polarization hysteresis loops measured at 25 °C using dense ceramics.

corresponding position in the parent tetragonal ($I4/mmm$) structure, P_s can be calculated as the sum of the dipole moments of the constituent ions per V . [3-6] As a result of the structure analysis by neutron powder diffraction, P_s for SBT was calculated to be $16.7 \mu\text{C}/\text{cm}^2$ using the formal charges. In the perovskite blocks, the entire TaO_6 octahedra are greatly displaced along the a axis with respect to Bi_2O_2 layers. The displacements of oxide ions of TaO_6 octahedra along the a axis and the opposite movement of Bi ions are mainly responsible for P_s . [5,6] For La-modified SBT, P_s decreases slightly with increasing La content, and La-SBT ($x=0.5$) has a smaller P_s of $13.3 \mu\text{C}/\text{cm}^2$ than SBT, as expected from the lower T_C . On the other hand, polarization measurements indicated that SBT exhibits a smaller P_r than La-SBT. For Bi-SBT, P_s was found from calculation to be $19 \mu\text{C}/\text{cm}^2$ using the result of our Rietveld analysis, and this increase in P_s is practically consistent with our polarization hysteresis measurements shown in Fig. 4. This improvement in P_s is mainly attributed to the enhanced displacements of oxide ions along the a axis with respect to Bi_2O_2 layers.

Although the Ca-substituted samples with $A=\text{Ca}_{0.3}\text{Sr}_{0.7}$ and Bi-SBT ($x=0.2$) showed almost the same T_C (420°C for the Ca-SBT), and had comparable degrees of A -site modification, a very high E_c of over $75 \text{ kV}/\text{cm}$ was observed for Ca-SBT [6] compared with Bi-SBT ($x=0.2$; $40 \text{ kV}/\text{cm}$). Furthermore, La substitution led to a much smaller E_c than SBT. These experimental results indicate that Bi- and La-substitution with A -site vacancies lowers E_c and the presence of A -site vacancies facilitates nucleation-growing processes of domains by applied electric field. The origin of low E_c for A -site deficient SBT would be I: random field [10, 16] around dipolar defects composed of trivalent cations and A -site vacancies, and II: the relief of lattice distortion along the a axis (the decrease in TaO_6 tilt angle (α_x) along the a axis) [5,6]. The mechanism of polarization reversal and the effects of A -site vacancies in the SBT system still remain unclear. It is verified that a defect engineering approach is useful for the design of the dielectric and polarization properties in the SBT system.

4. CONCLUSIONS

The Rietveld analysis of neutron diffraction for SBT has demonstrated that Bi and La are substituted at the A site as trivalent cations with A -site vacancies. T_C can be controlled from 150°C (La-SBT) to 420°C (Bi-SBT) by the trivalent-cation substitution with A -site vacancies. The substitution of Bi and La enhances P_r . A very low E_c of $20 \text{ kV}/\text{cm}$ is attained for La-SBT, which is attributed to the presence of A -site vacancies. It is shown that A -site vacancies play an important role in the ferroelectricity and a defect engineering approach is useful for the design for the dielectric and polarization properties in the SBT system.

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REFERENCES

- [1] C. A-Paz de Araujo, J. D. Cuchiaro, L. D. Mcmillan, M. C. Scott and J. F. Scott, *Nature (London)* **374**, 627 (1995).
- [2] M. Stachiotti, C. Rodriguez, C. A.-Draxl and N. Christensen, *Phys. Rev. B* **61**, 14434 (2000).
- [3] A. D. Rae, J. G. Thompson, and R. L. Withers, *Acta Crystallogr., Sect. B* **48**, 418 (1992).
- [4] Y. Shimakawa, Y. Kudo, Y. Nakagawa, T. Kamiyama, H. Asano, and F. Izumi, *Appl. Phys. Lett.* **74**, 1904 (1999).
- [5] Y. Noguchi, M. Miyayama, and T. Kudo, *Phys. Rev. B* **63**, 214102 (2001).
- [6] Y. Noguchi, M. Miyayama, K. Oikawa, and T. Kamiyama, *Jpn. J. Appl. Phys.*, **40**, 5812-5815 (2001).
- [7] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1979).
- [8] T.-Y. Kim and H. M. Jang, *Appl. Phys. Lett.* **77**, 3824 (2000).
- [9] Q. Tan, J. Li and D. Viehland, *Appl. Phys. Lett.* **75**, 418 (1999).
- [10] R. Ahluwalia and W. Cao, *Phys. Rev. B* **63**, 012103 (2001).
- [11] T. Kamiyama, K. Oikawa, N. Tsuchiya, M. Osawa, H. Asano, N. Watanabe, M. Furusawa, S. Satoh, I. Fujikawa, T. Ishigaki and F. Izumi, *Physica B* **213-214**, 875 (1995).
- [12] T. Ohta, F. Izumi, K. Oikawa and T. Kamiyama, *Physica B* **234-236**, 1093 (1997).
- [13] E. C. Subbarao, *J. Phys. Chem. Solids* **23**, 665 (1962).
- [14] G. A. Smolenskii, V. A. Isupov, and A. I. Agranovskaya, *Sov. Phys. Solid State* **3**, 651 (1961).
- [15] R. E. Choen, *Nature (London)* **358**, 136 (1992).
- [16] D. Viehland and Y.-H. Chen, *J. Appl. Phys.* **88**, 6696 (2000).