

Enhanced polarization properties by the introduction of cation vacancies in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ polycrystals

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ABSTRACT

The effects of Bi substitution on the polarization properties in $\text{Ba}_{1-x}\text{Bi}_{4+2x/3}\text{Ti}_4\text{O}_{15}$ (BBTi) were investigated using dense ceramics. The Rietveld analysis of powder x-ray diffraction data suggested that cation vacancies were introduced by the substitution of Bi^{3+} for Ba^{2+} . Dielectric measurements revealed that Curie temperature (T_C) for BBTi($x=0.1$) was 440°C , which was higher than that for BBTi($x=0$) [$T_C=415^\circ\text{C}$]. The Bi substitution enhanced remanent polarization ($2P_r$) from 13.8 to $18.0 \mu\text{C}/\text{cm}^2$, which is attributed to a larger spontaneous polarization and to the assistance of random field around cation vacancies for domain switching.

1. INTRODUCTION

Defects in ferroelectric crystals play an important role in the polarization properties, and the influence of various kinds of defects has been investigated for BaTiO_3 and $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ [PZT]. [1,2] The substitution of higher-valent cations such as La and Nd etc. compared with constituent ions leads to cation vacancies for the requirement of charge neutrality. The cation vacancies disturb the ordering of ferroelectric dipoles, and thus the presence of cation vacancies leads to a decrease in Curie temperature (T_C). When electric field is applied to ferroelectric crystals with cation vacancies, nanometer-sized clusters with reversed polarization are nucleated in the vicinity of "random field" around cation vacancies within micrometer-sized domains.[2] The random field significantly lowers the activation barrier required for nucleation of new domains, and the polarization switching easily occurs compared with cation-vacancy free crystals.

Recently, bismuth layer-structured ferroelectrics (BLSFs) have received considerable interest for Pb-free piezoelectrics[3-5] as well as ferroelectric memory materials[6-11]. The general formula of BLSFs is expressed by $(\text{Bi}_2\text{O}_2)(A_{m-1}B_m\text{O}_{3m+1})$, where A is mono-, di- or trivalent ions such as Na^{1+} , Sr^{2+} and Bi^{3+} etc., B is tetra-, penta- or hexavalent ions such as Ti^{4+} , Ta^{5+}

and W^{6+} etc. with appropriate size and valency, and m is the number of BO_6 octahedra in the perovskite layer ($m=1, 2, 3, 4$ and 5). In the crystals of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ (BBTi) with $m=4$, one of the members of BLSFs, as shown in Fig. 1, perovskite blocks ($\text{BaBi}_2\text{Ti}_4\text{O}_{13}$) are sandwiched between bismuth oxide (Bi_2O_2) layers. The Bi_2O_2 layers act as insulating paraelectric layers and affect the electronic response (electrical conductivity, band

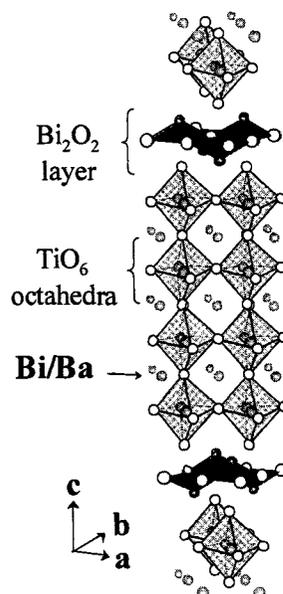


Fig. 1 Schematic crystal structure of $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$.

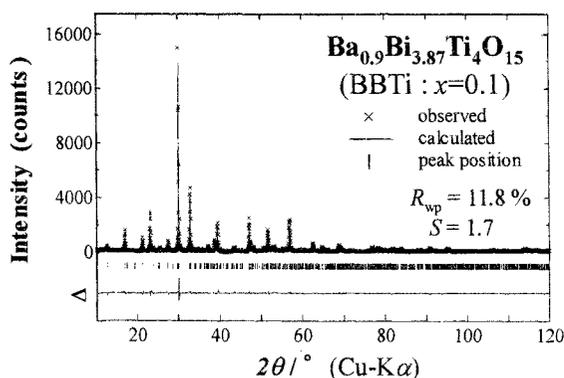


Fig. 2 The result of the Rietveld refinement for BBTi ($x=0.1$).

gap, etc.), [12,13] while the ferroelectricity arises mainly in the perovskite blocks.[14-16] The polarization properties of $SrBi_2Ta_2O_9$ (SBT: $m=2$) are strongly affected by composition, and defects[7,8,15,16] have been recognized as a crucially important factor. Noguchi *et al.* [8] reported that remanent polarization (P_r) of the films with Sr-deficient and Bi-excess strontium bismuth tantalate ($Sr_{0.8}Bi_{2.2}Ta_2O_9$) is much larger than that of stoichiometric SBT. It has been demonstrated from neutron[15] and synchrotron-radiation[16] diffraction studies that the substitution by Bi^{3+} at Sr^{2+} site induces Sr vacancies to satisfy the requirement of charge neutrality. However, the reports on the effects of cation vacancies on the polarization properties are few for BLSFs with $m=4$. [17]

In this letter, we show that cation vacancies could be introduced at perovskite A site in $BaBi_4Ti_4O_{15}$ by the substitution of Bi^{3+} for Ba^{2+} , and that the substitution is effective for the improvement of P_r . The effects of Bi substitution accompanied by cation vacancies are discussed in terms of lattice distortion and electric field randomly generated around cation vacancies.

2. EXPERIMENTAL PROCEDURE

Ceramic samples of $Ba_{1-x}Bi_{4+2x/3}Ti_4O_{15}$ (BBTi: $x=0, 0.1$) were prepared by a solid-state reaction. Powders of $BaCO_3$, Bi_2O_3 and Ti_2O_2 of 99.99 % purity were mixed with the stoichiometric composition. The mixed powder was calcined at $800^\circ C$ for 7 h, and then fired at $1050^\circ C$ for 4 h for powder diffraction measurements. X-ray diffraction (XRD) data measured using Cu-K α radiation were analyzed by the Rietveld method (the RIETAN program[18]) on the basis of $A2_1am$ orthorhombic symmetry. The sample with the nominal composition of $Ba_{0.9}Bi_{4.1}Ti_4O_{15}$ was also prepared and the XRD data

was analyzed in the same manner.

To obtain dense samples for electrical measurements, excess Bi_2O_3 of 2 at.% was added to the starting powders, and then sintered at $1150^\circ C$ for 1 h. This excess- Bi_2O_3 addition led to a high relative density of over 95 %. The lattice constants and Curie temperature (T_c) for the samples with excess Bi_2O_3 were practically the same as those for the stoichiometric samples. XRD data on the polished surface of the dense samples showed no preferred orientation. The polarization properties were measured at $25^\circ C$ using an RT6000 ferroelectric tester (Radiant Technologies) operating in the virtual ground mode.

3. RESULTS AND DISCUSSION

The phase identification was carefully carried out through the Rietveld analysis. The XRD data of BBTi($x=0.1$) was almost the same as that of $Ba_{0.9}Bi_{4.1}Ti_4O_{15}$. The Rietveld analysis revealed that both samples were assumed to be a single phase and the R -weighted pattern (R_{wp}) was around 12%. Since the leakage-current density was below $10^{-8} A/cm^2$ up to an applied electric field of 200 kV/cm, electronic defect such as electron or hole seems not to be relevant to the charge neutrality condition in the crystal lattice. Thus, when excess Bi is substituted at the A site, the following three cases that meets the condition are considered; ① the Bi^{2+} substitution, ② the Bi^{3+} substitution with the formation of Ti^{3+} , ③ the Bi^{3+} substitution accompanied by cation vacancies.

For SBT with Sr-deficient and Bi-excess composition, it has been reported that excess Bi is substituted at the A site. X-ray photoelectron spectroscopy investigations[19] did not show the result that suggests the presence of Bi^{2+} . The Rietveld analysis of neutron[15] and synchrotron x-ray diffraction[16] data indicated that Bi is substituted as trivalent cations accompanied by Sr vacancies rather than Ta vacancies. Furthermore, for rare-earth substituted SBT largely deviating from the stoichiometry, the single phase was obtained for $La_{0.33}Sr_{0.5}Bi_2Ta_2O_9$ and $Nd_{0.33}Sr_{0.5}Bi_2Ta_2O_9$, [20] and the apparent impurity phase(s) was detected for $La_{0.5}Sr_{0.5}Bi_2Ta_2O_9$. These results clearly show that, for SBT, excess Bi is substituted as trivalent cations at the A site and the charge neutrality is satisfied through the formation of the A site vacancies to compensate the charge difference between Sr^{2+} and Bi^{3+} . For La-substituted $PbTiO_3$, La is substituted for the A site, and not Ti^{3+} but cation vacancies are formed for charge neutrality requirement.[21] When excess Pb was not added to the starting powder, A -site vacancies are preferentially generated rather

than Ti vacancies. These results indicate that, for BBTi, excess Bi is substituted as trivalent cations at the *A* site accompanied by cation vacancies (the case ③), and *A*-site vacancies seem to be preferentially formed for the charge neutrality requirement.

Figure 2 shows the result of Rietveld analysis for BBTi($x=0.1$). In the analysis, Ba, Bi and vacancies at the *A* site are assumed to be randomly distributed, because the accuracy of XRD data obtained in this study was not sufficient to determine the cation distribution at the *A* site. The calculated pattern fitted fairly well with the observed data. The *R*-weighted pattern (R_{wp}) and goodness of fit (*S*) were 11.8% and 1.7, respectively. The single phase was not obtained for BBTi($x=0.2$). The refined unit-cell volume (*V*) for BBTi($x=0.1$) was 1.2489(10) nm³, which was smaller than that of BBTi($x=0$) [1.2524(13) nm³]. The decrease in *V* is attributed to the smaller ionic radius (r_i) of Bi³⁺ than Ba²⁺ and to the introduction of cation vacancies. The substitution of smaller Bi³⁺ led to a decrease also in lattice parameters; from 0.5473(2) nm to 0.5466(3) nm for *a*, from 0.5460(2) nm to 0.5454(3) nm for *b* and from 4.191(2) nm to 4.189(3) nm for *c*.

Figure 3 shows the temperature dependence of dielectric permittivity at a frequency of 1 MHz. It was found that Bi substitution led to an increase in T_C from 415°C to 440°C. In general, 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.[21] Ferroelectric SrBi₂Nb₂O₉ has a higher T_C (440 °C) than BaBi₂Nb₂O₉ (200 °C) because of the smaller r_i of Sr²⁺ than Ba²⁺. [22,23] Furthermore, Bi³⁺ with lone-pair electrons at 6*s* orbital tend to have partial covalent bonding to oxide ions of TiO₆ octahedra, as is suggested

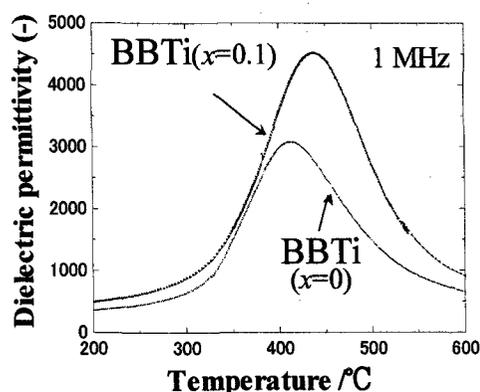


Fig. 3 Temperature dependence of dielectric permittivity at a frequency of 1 MHz.

between Pb²⁺ and oxide ions for PbTiO₃. [24] It is likely that the covalent nature contributes to the higher T_C observed for BBTi($x=0.1$). These results imply that Bi substitution with cation vacancies promotes lattice distortion of TiO₆ octahedra in perovskite blocks.

Figure 4 indicates the polarization hysteresis loops measured at 25°C. The substitution of Bi resulted in an improvement of the squareness of the hysteresis loop, and enhanced $2P_r$ from 13.8 to 18.0 $\mu\text{C}/\text{cm}^2$. The values of coercive field ($2E_c$) for the samples with $x=0$ and 0.1 were 100 and 142 kV/cm, respectively. The enhancement of P_r observed for BBTi($x=0.1$) is considered to be attributed to the following two factors. One is a larger spontaneous polarization (P_s) caused by Bi substitution. The Landau-Ginzburg mean field theory [25] suggests that P_s increases monotonically with decreasing temperature. This implies that the ferroelectric crystal with a higher T_C has a larger P_s at room temperature for the system with the similar lattice distortion. Since Bi substitution resulted in a higher T_C , BBTi($x=0.1$) is suggested to have a larger P_s than BBTi($x=0$).

The other is the effect of “*random field*” around cation vacancies. As mentioned above, Bi³⁺ substitution for Ba²⁺ is accomplished by the formation of cation vacancies (probably at the *A* site). Due to the strong interaction between the cation vacancies (V_{Ba}) and the substituted Bi³⁺ (Bi_{Ba}), the defect dipoles composed of V_{Ba} and Bi_{Ba} seems to be formed during sintering. Since the mobility of the cation vacancies (V_{Ba}) and the substituted Bi³⁺ (Bi_{Ba}) are extremely low below T_C , these defects are randomly quenched. The defect dipoles generate electric field *randomly* in the crystal, thus disturb the ordering of ferroelectric ordering. Before electric field reaches the value at which domain walls move cooperatively, nanometer-sized clusters with reversed polarization are nucleated under an applied field in the vicinity of *random field* around cation vacancies within micrometer-sized domains. [2,26,27] The random field lowers the activation barrier required for nucleation of new domains, leading to a lower E_c . In fact, La-substituted SBT (La_{0.33}Sr_{0.5}Bi₂Ta₂O₉) with lower T_C showed a lower E_c compared with non-modified SBT. [26] For BBTi($x=0.1$), there are two factors affecting E_c ; one is the effect of cation vacancies (leading to a lower E_c and T_C) and the other is the effects of the hybridization of Bi 6*s* and O 2*p* (resulting in a higher E_c and T_C). The effects of the orbital hybridization dominantly determine the polarization properties, thus the Bi substitution enhanced the lattice distortion (leading to a higher

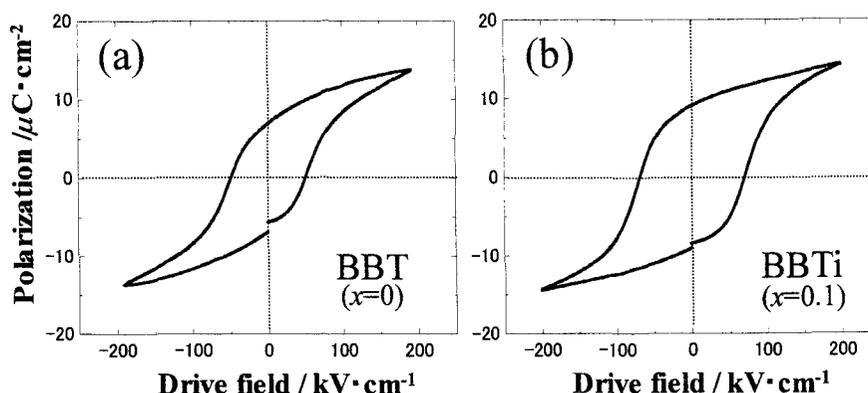


Fig. 4 Polarization hysteresis loops measured at 25°C for (a) BBTi ($x=0$) and (b) BBTi ($x=0.1$)

T_C), and then increased E_c .

For the polarization hysteresis of BBTi($x=0$), a gradual change in polarization was seen at around E_c . The declined hysteresis is probably attributed to an incomplete domain switching. In contrast, the substitution of Bi^{3+} improved squareness of hysteresis, and P_r and E_c were well saturated, as can be seen in Fig. 4(b). Since cation vacancies act as nuclei of reversed domains, the random field assists polarization switching by applied field. This is likely to result in a complete domain switching and larger P_r . It is indicated that the cation vacancies play an important role in polarization properties, and that defect engineering is the promising approach to improve the ferroelectric properties for $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$.

4. CONCLUSIONS

The Rietveld analysis of powder x-ray diffraction data indicated that cation vacancies could be introduced in $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ by the substitution of Bi^{3+} for Ba^{2+} . The Bi substitution led to an increase in T_C and improvement of P_r . It is suggested that the enhanced P_r observed for Bi-substituted samples with cation vacancies is attributed to a larger spontaneous polarization and to the assistance of random field around cation vacancies for domain switching.

REFERENCES

- [1] Berlincourt, D., Curran, D. and Jaffe, H., in *Physical Acoustics*, edited by W. Cady (Academic, New York, 1964), Vol.1.
- [2] Viehland, D., Chen, Y.-H., *J. Appl. Phys.* **88**, 6696-07 (2000).
- [3] Hirose, M., Suzuki, T., Oka, H., Itakura, K., Miyauchi, Y. and Tsukada, T., *Jpn. J. Appl. Phys.* **38** 5561-63 (1999).
- [4] Kimura, M., Sawada, T., Ando, A. and Sakabe, Y., *Jpn. J. Appl. Phys.* **38**, 5557-60 (1999).
- [5] Takeuchi, T., Tani, T. and Saito, Y., *Jpn. J. Appl. Phys.* **39**, 5577-80 (2000).
- [6] Araujo, C. A-Paz de, Cuchiaro, J. D., Mcmillan, L. D., Scott, M. C. and Scott, J. F., *Nature*, **374** 627-29 (1995).
- [7] Nagata, H., Chikushi, N. and Takenaka, T., *Jpn. J. Appl. Phys.*, **38** 5497-99 (1999).
- [8] Noguchi, T., Hase, T. and Miyasaka, Y., *Jpn. J. Appl. Phys.*, **35** 4900-04 (1996).
- [9] Kato, K., Zheng, C., Finder, J. M., Dey, S. K. and Torii, Y., *J. Am. Ceram. Soc.* **81**, 1869-75 (1998).
- [10] Park, B. H., Kang, B. S., Bu, S. D., Noh, T. W., Lee, J. and Joe, W., *Nature* **401**, 682-84 (1999).
- [11] Ishikawa, K. and Funakubo, H., *Appl. Phys. Lett.*, **75**, 1970-72 (1999).
- [12] Kim, S.-K., Miyayama, M. and Yanagida, H., *Mater. Res. Bull.*, **31**, 121-31 (1996).
- [13] Stachiotti, M., Rodriguez, C., Draxl, C. A. and Christensen, N., *Phys. Rev. B* **61**, 14434-39 (2000).
- [14] Rae, A. D., Thompson, J. G. and Withers, R. L., *Acta Crystallogr. B*, **48**, 418-28 (1992).
- [15] Shimakawa, Y., Kudo, Y., Nakagawa, Y., Kamiyama, T., Asano, H. and Izumi, F., *Appl. Phys. Lett.*, **74**, 1904-06 (1999).
- [16] Noguchi, Y., Miyayama, M., and Kudo, T., *Phys. Rev. B*, **63**, 214102 (2001).
- [17] Yn, H., Li C., Zhou, J., Zhu, W., He, L. and Song, Y., *Jpn. J. Appl. Phys.*, **39**, 6339-42 (2000).
- [18] Izumi, F., "The Rietveld method" ed. by R. A. Young, Oxford University Press, Chap. 13 (1993).
- [19] Asami, K., Koiwa, I., and Yamanobe, T., *Jpn. J. Appl. Phys.*, **38**, 5423-27 (1999).
- [20] Noguchi, Y., Miyayama, M., Oikawa, K., Kamiyama, T., Osada, M., and Kakihana, M., *Jpn. J. Appl. Phys.*, in press.
- [21] Kim, T.-Y., and Jang, H. M., *Appl. Phys. Lett.*, **77** 3824-26 (2000).
- [22] Noguchi, Y., Shimizu, H., Miyayama, M., Kudo, T., Oikawa, K., and Kamiyama, T., *Jpn. J. Appl. Phys.*, **40**, 5812-15 (2001).
- [23] Subbarao, E. C., *J. Phys. Chem. Solids.*, **23**, 665-76 (1962).
- [24] Smolenskii, G. A., Isupov, V. A., and Agranovskaya, A. I., *Sov. Phys. Solid State*, **3**, 651-55 (1961).
- [25] Choen, R. E., *Nature*, **358**, 136-38 (1992).
- [26] Tan Q., Li J. and Viehland D., *Appl. Phys. Lett.*, **75**, 418-20 (1999).
- [27] Ahluwalia, R., and Cao, W., *Phys. Rev. B*, **63**, 12103 (2000).