PHYSICAL REVIEW B, VOLUME 63, 214102

Direct evidence of *A*-site-deficient strontium bismuth tantalate and its enhanced ferroelectric properties

Yuji Noguchi*
Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Masaru Miyayama and Tetsuichi Kudo
Institute of Industrial Science, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106-8558, Japan

(Received 19 September 2000; published 30 April 2001)

The Rietveld refinement of synchrotron-radiation diffraction has been performed to investigate the displacive-type ferroelectricity and crystal chemistry for Sr-deficient and Bi-excess strontium bismuth tantalate. The analysis of $Sr_{0.73}Bi_{2.18}Ta_2O_9$ demonstrates that excess Bi ($Bi_{0.18}$) is substituted at the perovskite *A* site (Sr site) as trivalent ions and that the charge neutrality in the crystal is satisfied through the introduction of cation vacancies at the *A* site. The substitution of Bi with the *A*-site vacancies led to a marked increase in Curie temperature (T_C), and resulted in a twofold remanent polarization without sacrificing the polarization switching properties. The structure refinement revealed that the rotation of TaO_6 octahedra in the a-b plane accompanied with the whole shift of the octahedra along the a axis is largely enhanced by the Bi substitution with *A*-site vacancies, which is responsible for the higher T_C and giant polarization.

DOI: 10.1103/PhysRevB.63.214102 PACS number(s): 77.84.Dy, 61.10.Nz

Displacive-type ferroelectricity originates from displacements of constituent ions from the corresponding positions in high-symmetry structure. For simple perovskites such as $BaTiO_3$ and $Ba_{1-x}Sr_xTiO_3$, the polarization is attributed mainly to the displacement of Ti ion (*B*-site ion) from the center of TiO_6 octahedra. The substitution of the alkaline-earth ions at the perovskite *A* site by Pb ions induces another soft mode in which the *A*-site ions participate, resulting in an enhancement of ferroelectric polarization.[1]

Ferroelectric $SrBi_2Ta_2O_9$ (SBT), one of the promising candidate materials for nonvolatile random-access memories, has a layered structure.[2] In the crystal, pseudoperovskite blocks, $(SrTa_2O_7)^{2-}$, composed of double TaO_6 octahedra with Sr at the *A* site are interleaved with $(Bi_2O_2)^{2+}$ layers. The $(Bi_2O_2)^{2+}$ layers act as insulating layers[3,4] and largely control the electronic response, while the ferroelectricity arises mainly in the pseudoperovskite blocks.[5,6] Even when in the form of thin films with Pt electrodes, SBT shows high fatigue endurance against the repetitive switching of polarization.[2] It is argued that the $(Bi_2O_2)^{2+}$ layers perform a primary function in preventing degradation of remanent charge. On the other hand, the ferroelectricity is attributed to the rotation and tilting of TaO_6 octahedra as well as the displacement of Ta ions in the octahedra.[5] It is expected therefore that the *A*-site ions positioned at the cavities between two TaO_6 octahedra play a crucial role in the ferroelectric properties of SBTs caused by the revolution of the octahedra.

Thin films with compositions deviating from the stoichiometry of SBT have been extensively studied to improve ferroelectric properties.[7–9] Noguchi *et al.*[8] reported that the remanent polarization (P_r) of the films with Sr-deficient and Bi-excess composition, $Sr_{0.8}Bi_{2.2}Ta_2O_9$, is larger than that of stoichiometric SBT. In spite of extensive effort to improve the ferroelectric properties of thin films,[10–12] the fundamental nature and the crystal structure of Sr-deficient and Bi-excess SBT have not yet been elucidated. Miura *et al.*[13] examined the substitution of Bi at the *A* site in $Sr_{1-x}Bi_{2+x}Ta_2O_9$ on the basis of an electronic state calculation by the discrete variational $X\alpha$ method and suggested the possibility that Bi ions occupy the *A* site as divalent ions. Shimakawa *et al.*[14] carried out the Rietveld analysis of powder neutron-diffraction patterns for $Sr_{0.8}Bi_{2.2}Ta_2O_9$, and proposed a model in which some excess Bi is substituted at the *A* site with cation vacancies. Compared with neutron diffraction, synchrotron-radiation diffraction is very sensitive to the metal composition in crystals. Structure refinement using high-resolution synchrotron-radiation diffraction therefore enables us to investigate not only ferroelectric displacements but also crystal chemistry.

This paper describes the results of the structure refinement for stoichiometric SBT and $Sr_{0.73}Bi_{2.18}Ta_2O_9$ through the Rietveld analysis of synchrotron-radiation diffraction. Direct evidence that excess Bi ($Bi_{0.18}$) in $Sr_{0.73}Bi_{2.18}Ta_2O_9$ is substituted as trivalent ions with cation vacancies at the perovskite *A* site is adduced. The Bi substitution with cation vacancies results in giant remanent polarization without sacrificing the polarization switching properties, which originates from an enhancement of TaO_6 octahedral rotation accompanied with the whole shift of the octahedra along the *a* axis.

Ceramic samples with nominal compositions of $SrBi_2Ta_2O_9$ (stoichiometric SBT), $SrBi_{2.04}Ta_2O_9$ (Bi-ex. SBT), $Sr_{0.73}Bi_{2.27}Ta_2O_9$, and $Sr_{0.73}Bi_{2.18}Ta_2O_9$ were prepared by conventional solid-state reaction from ground powders of $SrCO_3$, Bi_2O_3, and Ta_2O_5 of 99.99% purity. The details of the preparation condition of bulk ceramics are described in Ref. 15. The final sintering was performed at 1200 °C for 4 h. The samples obtained had a density of over 98% of the theoretical density, except for stoichiometric SBT whose relative density was 78%. The lattice constants and Curie temperature (T_C) of Bi-ex. SBT were exactly the same as those of stoichiometric SBT, revealing that excess Bi in

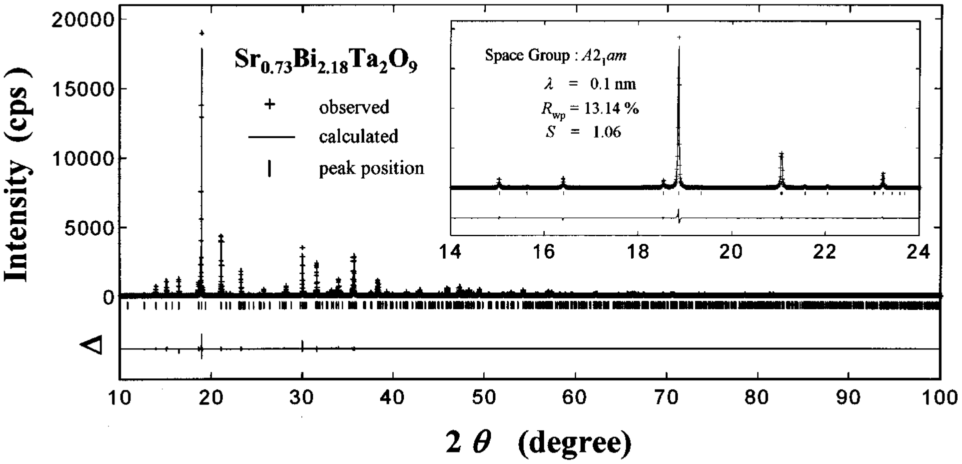


FIG. 1. Fitting result of the Rietveld analysis of the powder synchrotron-radiation diffraction pattern for $Sr_{0.73}Bi_{2.18}Ta_2O_9$. A wavelength of 0.1 nm was used to collect the diffraction data. △ indicates the difference between the observed and calculated values.

$SrBi_{2.04}Ta_2O_9$ facilitated densification and did not change the intrinsic nature of stoichiometric SBT. Scanning electron microscopy observations revealed that the ceramic samples of Bi-ex. SBT and $Sr_{0.73}Bi_{2.18}Ta_2O_9$ had almost the same microstructure. For diffraction measurements, the calcined powder was fired at 1100 °C for 4 h to prevent grain growth and preferred orientation.

Synchrotron-radiation diffraction patterns were obtained using a powder diffractometer for synchrotron radiation with a multiple-arm system at BL-4B2 of the Photon Factory in KEK.[16] The crushed powder was mounted on a flat plate holder and rotated so as to decrease the effect of preferred orientation. The wavelength of synchrotron radiation was chosen to be 0.1 nm, and data of the powder patterns were collected from 10 to 120 (2θ) using steps of 0.004° and counting 4 s at each step. The patterns obtained were analyzed by the Rietveld method (the RIETAN program[17]) on the basis of $A2_1am$ orthorhombic symmetry. For the values of anomalous scattering factors, f' and f'', a table calculated by Sasaki[18] was used.

The synchrotron-radiation diffraction of the sample obtained from the powder prepared from the mixture with the nominal composition of $Sr_{0.73}Bi_{2.18}Ta_2O_9$ was shown in Fig. 1 (observed). The peaks observed were almost the same as those of stoichiometric SBT, and no second peak was detected. The Rietveld analysis of the diffraction pattern ($Sr_{0.73}Bi_{2.18}Ta_2O_9$) was carried out under the following conditions: (i) $SrBi_2Ta_2O_9$ (stoichiometry), (ii) $Sr_{0.73}Bi_{2.27}Ta_{1.946}O_9$ (Bi^{3+} substitution at the A site with Ta vacancies), (iii) $SrBi_2(Ta,Bi)_2O_9$ (Bi^{5+} substitution at the Ta site), (iv) $Sr_{0.73}Bi_{2.27}Ta_2O_9$ (Bi^{2+} substitution at the A site), and (v) $Sr_{0.73}Bi_{2.18}Ta_2O_9$ (Bi^{3+} substitution at the A site with A-site vacancies). The accuracy of the analysis was estimated from the value of R-weighted pattern (R_{wp}). For the conditions of (i)–(iii), R_{wp} was over 16%. On the other hand, the values of R_{wp} for the conditions of (iv) and (v) were 13.95 and 13.14%, respectively. These analyses indicate that the conditions of (iv) and (v) are superficially plausible. Thus we checked the diffraction pattern of the powder obtained from the mixture with the nominal composition of $Sr_{0.73}Bi_{2.27}Ta_2O_9$ in a similar manner, and the diffraction pattern was analyzed by the Rietveld method. Several peaks of second phase(s) were observed, and the value of R_{wp} was very large (32%). The diffraction result for $Sr_{0.73}Bi_{2.27}Ta_2O_9$ clearly indicates that excess Bi was not substituted at the A site as *divalent ions* and that the Bi left over formed the second phase(s). Figure 1 shows a fitting result of the Rietveld analysis of the powder-diffraction pattern under the condition (v). 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, confirming a single phase with SBT structure. The composition at the A site determined by the Rietveld analysis was ($Sr_{0.73(3)}Bi_{0.18(3)}\square_{0.09}$), where □ indicates cation vacancies. This analysis reveals that the charge neutrality in the crystal of $Sr_{0.73}Bi_{2.18}Ta_2O_9$ is satisfied through the substitution of Bi with cation vacancies at the A site. Thus these Rietveld results become direct evidence that Bi ions are substituted as *trivalent ions* with cation vacancies at the A site. In other words, the Bi substitution can be accomplished only by the formation of cation vacancies at the A site so as to compensate the difference between valences of Sr^{2+} and Bi^{3+}. The refined lattice parameters a and b, decreased by the Bi substitution, from 0.552 318 (14) to 0.551 878 (2) nm for a and from 0.552 474 (14) to 0.551 366(2) nm for b, while c remained constant at around 2.504 nm, revealing that the structural change mainly occurred in the a-b plane in the A-site-deficient samples. There are two factors that reduce the a-b plane in the crystal: the smaller ionic radius of Bi^{3+} than Sr^{2+} and the cation vacancies at the A site. It is not clear which factor causes this structural change. The refined structure parameters of stoichiometric SBT was practically the same as the results of the neutron-diffraction study by Shimakawa *et al.*[14] Table I lists the final structure parameters for A-site-deficient $Sr_{0.73}Bi_{2.18}Ta_2O_9$.

Figure 2 shows the temperature dependence of dielectric permittivity at a frequency of 1 MHz. The T_C of Bi-ex. SBT was 300 °C, which is exactly the same as the reported T_C of stoichiometric SBT.[14] On the other hand, A-site-deficient $Sr_{0.73}Bi_{2.18}Ta_2O_9$ (A-def. SBT) had a higher T_C of 420 °C. This marked increase in T_C is a result of Bi substitution with cation vacancies. When Bi^{3+} and Pb^{2+} with $6s^2$ electrons occupy the A site of the perovskite blocks, T_C tends to rise.[19,20] In fact, $PbBi_2Ta_2O_9$ has a higher T_C of 430 °C in

TABLE I. Structure refinement results for *A*-site deficient $Sr_{0.73}Bi_{2.18}Ta_2O_9$ at 25 °C, space group $A2_1am$, lattice parameters $a = 0.551878(2)$ nm, $b = 0.551366(2)$ nm, and $c = 2.504026(10)$ nm. Numbers in parentheses indicate standard deviations of the last significant digit. Final agreement factors are as follows: $R_{wp} = 13.14\%$, $R_p = 9.49\%$, $R_I = 3.89\%$, $R_F = 2.61\%$, and $S = 1.06(R_{wp}/R_c)$.

Atoms	Position	*x*	*y*	*z*	Occupancy	$B_{eq} \times 10^{-2}$ (nm^2)
Sr/Bi	4*a*	0	0.261 3(12)	0	0.73(3)/0.18(3)	1.18(8)
Bi	8*b*	0.471 37(88)	0.773 52(36)	0.200 45(8)	1	1.65(5)
Ta	8*b*	0.516 26(93)	0.748 64(55)	0.414 83(6)	1	0.22(2)
O(1)	4*a*	0.535 3(11)	0.297 57(98)	0	1	0.9(3)
O(2)	8*b*	0.529 4(10)	0.695 76(64)	0.341 57(8)	1	1.1(2)
O(3)	8*b*	0.743 7(10)	0.991 76(53)	0.250 24(11)	1	0.6(2)
O(4)	8*b*	0.759 1(10)	0.979 33(58)	0.069 62(8)	1	0.5(2)
O(5)	8*b*	0.806 7(9)	0.970 55(59)	0.584 23(9)	1	0.7(3)

spite of having almost the same ionic radii of Sr^{2+} and Pb^{2+}. Considering a high T_C of 625 °C for $CaBi_2Ta_2O_9$,[20] the smaller ions occupying the *A* site cause a shift of T_C to higher temperature. The substitution of smaller Bi ions at the *A* site would contribute to an increase in T_C to some extent. However, Bi^{3+} occupies only 18% of the *A* site in *A*-def SBT; these two factors related to Bi^{3+} at the *A* site are not sufficient to explain the drastic increase of 120 °C in T_C. Not only the substitution of smaller Bi^{3+} with $6s^2$ electrons but the introduction of cation vacancies at the *A* site could lead to an enhancement of ferroelectric structure distortion, thus resulting in a higher T_C.

Figure 3 indicates the polarization hysteresis loops measured at 25 °C. For Bi-ex. SBT, $2P_r$ was 14 μC/cm^2, which is more or less equivalent to the optimally synthesized stoichiometric thin films with random orientation.[21,22] Note that *A*-def. SBT had a very large $2P_r$ of 26 μC/cm^2. This $2P_r$ value is about twofold that of Bi-ex. SBT and is larger than the optimal value of the randomly oriented thin films with Sr-deficient and Bi-excess composition.[7–9] On the other hand, *A*-def. SBT had a slightly higher coercive field ($2E_c$) of 90 kV/cm compared to 65 kV/cm of Bi-ex. SBT. The higher $2E_c$ is expected to lead to difficulty of polarization switching, however, this was not the case. Figure 4 shows $2P_r$ as a function of maximum drive field (E_m). The $2P_r$ of Bi-ex. and *A*-def. SBTs rose at the same E_m of around 25 kV/cm, and showed a saturation tendency over 100 kV/cm. It is worth noting that $2P_r$ of *A*-def. SBT was much larger than that of Bi-ex. SBT in both low and high E_m regions. These results demonstrate that *A*-def. SBT would exhibit a larger remanent charge in the form of thin films in low-voltage operation. On the other hand, the stoichiometric SBT was porous (78% of its theoretical density), and the $2P_r$ value was very small, 4 μC/cm^2, as shown in Fig. 4. The Bi addition of 2 at. % of the stoichiometry was effective for densification which resulted in proper polarization properties. For *A*-def. SBT, dense ceramic samples were easily obtained under the same preparation condition, which indicates a possibility of lower temperature preparation of thin films with *A*-site-deficient composition. This improved densification is probably due to cation vacancies at the *A* site in the crystal, which facilitates diffusion of constituent ions in the sintering process. Namely, *A*-def. SBT has crucial advantages of lower temperature synthesis and enhanced ferroelectric properties without sacrificing the polarization switching.

In the SBT structure with $A2_1am$ orthorhombic symmetry, the *a* axis is the polar axis, and constituent ions are displaced along the *a* axis. The spontaneous polarization (P_s) can be calculated by

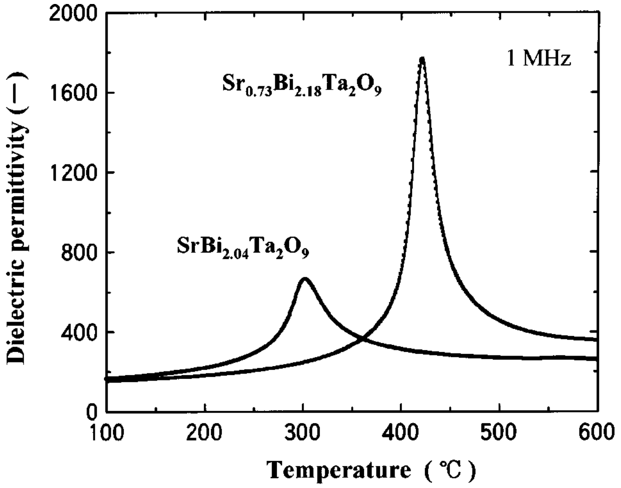


FIG. 2. Temperature dependence of dielectric permittivity at a frequency of 1 MHz for $SrBi_{2.04}Ta_2O_9$ and $Sr_{0.73}Bi_{2.18}Ta_2O_9$.

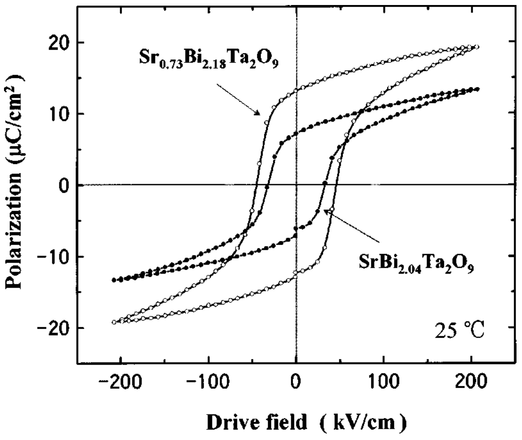


FIG. 3. Polarization hysteresis loops measured at 25 °C using dense ceramics.

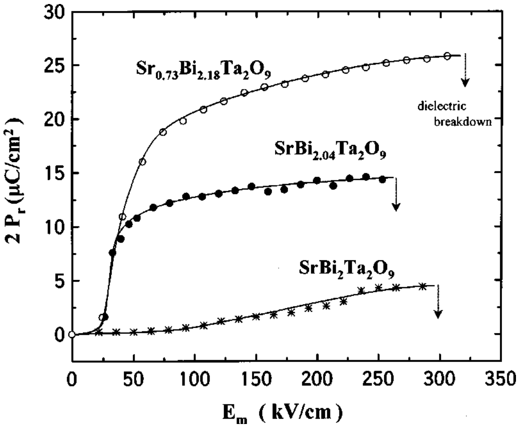


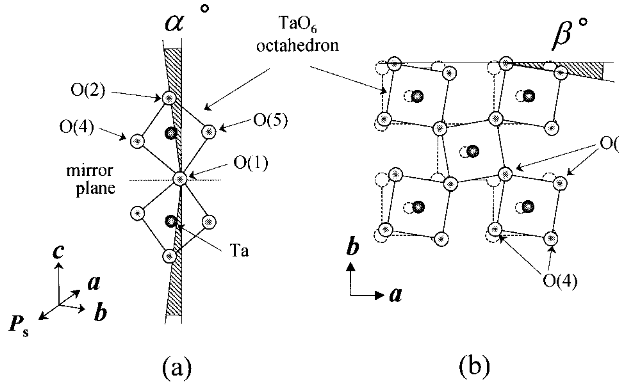
FIG. 4. Maximum drive electric-field (E_m) dependence of remanent polarization ($2P_r$) measured at 25 °C.

$$P_s=\Sigma_i(m_i\times\Delta x_i\times Q_{ie})/V, \qquad (1)$$

where m_i is the site multiplicity, Δx_i is the atomic displacement along the *a* axis from the corresponding position in the parent tetragonal ($I4/mmm$) structure, Q_ie is the ionic charge for the ith constituent ion, and V is the volume of the unit cell. Using the formal charge ($+2$ for Sr, $+3$ for Bi, $+5$ for Ta, -2 for O) in the calculation, P_s of stoichiometric SBT was estimated to be 16 μC/cm^2, which agrees well with the value determined from the data on the basis of the single-crystal structure analysis performed by Rae *et al.*[5] For *A*-def. SBT, P_s was found from calculation to be 20 μC/cm^2 using the result of our Rietveld analysis, and this increase in P_s is consistent with our polarization hysteresis measurements shown in Fig. 3. The structure analysis indicates that the Bi substitution with cation vacancies at the *A* site enhances the intrinsic ferroelectricity of SBT.

The displacement of Ta ions from the center of octahedra along the *a* axis was estimated to be 3×10^{-4} nm for stoichiometric SBT. This value was practically the same as that for *A*-def. SBT, indicating that the Bi substitution with cation vacancies does not affect Ta ions in octahedra. The contribution of the Ta displacements in octahedra is about 15% of P_s, which is not the main origin of the ferroelectric polarization of SBT.

The principal change in ferroelectric distortion caused by the substitution was found to occur in perovskite blocks composed of TaO_6 octahedra. The tilting and rotation of the octahedra are schematically shown in Figs. 5(a) and (b), respectively. For stoichiometric SBT, the tilt angle (α) from the *c* axis, was about 8° [O(2)–O(1)–O(2) bond angle: 164°], which is consistent with the earlier reports.[5,14] The tilt along the *a* axis, i.e., the component in the *a*-*c* plane (α_x) was about 0.4°, while α_y (in the *b*-*c* plane) was 7.9°. The tilting feature of the octahedra for *A*-def. SBT was almost the same as for stoichiometric SBT. This result indicates that the tilting of TaO_6 octahedra did not make a main contribution to the ferroelectricity for both SBTs. In fact, the displacements of O(1) and (2) are not the major element of P_s. On the other hand, the TaO_6 octahedra largely rotated in the *a*-*b* plane accompanied with the whole shift of the octahedra along the *a* axis as schematically indicated in Fig. 5(b). The average octahedral rotation angle (β) increased from 2.8 to 5.4° by the Bi substitution with *A*-site vacancies. While the displacement of O(4) was not affected largely by the substitution, the polarization due to the displacement of O(5) was drastically promoted [see Fig. 5(b)]. The enhanced octahedral rotation accompanied with the whole shift of the octahedra is responsible for a larger P_s, resulting in both the higher T_C and giant $2P_r$ found for *A*-def. SBT.



(a) (b)

FIG. 5. Schematic representations of TaO_6 octahedral distortions in perovskite blocks: (a) tilting from the *c* axis and (b) average rotation in the *a*-*b* plane. O(1) and O(2) are apex oxygen atoms. O(1) is shared by two TaO_6 octahedra, while O(2) bonds to the Bi in $(Bi_2O_2)^{2+}$ layers. The $(Bi_2O_2)^{2+}$ layers contain a plane composed of O(3), which is not depicted in this figure. The dashed circles show the oxygen atoms in a paraelectric state.

In conclusion, the Rietveld analysis of synchrotron-radiation diffraction has yielded direct evidence that excess Bi($Bi_{0.18}$) in $Sr_{0.73}Bi_{2.18}Ta_2O_9$ is substituted at the perovskite *A* site as trivalent ions and that the charge neutrality in the crystal is satisfied through the introduction of cation vacancies at the *A* site. While the tilting of TaO_6 octahedra from the *c* axis was unchanged by the substitution, the rotation in the *a*-*b* plane of octahedra for $Sr_{0.73}Bi_{2.18}Ta_2O_9$ was twice as large as that of stoichiometric SBT. The enhanced rotation of TaO_6 octahedra accompanied with the whole shift of the octahedra along the *a* axis caused by the Bi substitution with the *A*-site vacancies could lead to a marked increase in T_C and a giant $2P_r$, as observed for $Sr_{0.73}Bi_{2.18}Ta_2O_9$.

The authors thank Professor Toraya, Dr. Yamasaki, and Dr. Tanaka for helpful support in data collection and Rietveld analysis of synchrotron-radiation diffraction.

---

*Present address: The University of Tokyo RCAST Intelligent Lab., 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan. Email address: ynoguchi@iis.u-tokyo.ac.jp

[1] R. E. Choen, Nature (London) **358**, 136 (1992).
[2] C. A-Paz de Araujo, J. D. Cuchiaro, L. D. Mcmillan, M. C. Scott, and J. F. Scott, Nature (London) **374**, 627 (1995).
[3] S.-K. Kim, M. Miyayama, and H. Yanagida, J. Ceram. Soc. Jpn. **102**, 722 (1994).
[4] S.-K. Kim, M. Miyayama, and H. Yanagida, Mater. Res. Bull. **31**, 121 (1996).

[5] A. D. Rae, J. G. Thompson, and R. L. Withers, Acta Crystallogr., Sect. B: Struct. Sci. **48**, 418 (1992).
[6] J. Robertson, C. W. Chen, W. L. Warren, and C. D. Gutleben, Appl. Phys. Lett. **69**, 1704 (1996).
[7] T. Atsuki, N. Soyama, T. Yonezawa, and K. Ogi, Jpn. J. Appl. Phys., Part 1 **34**, 5096 (1995).
[8] T. Noguchi, T. Hase, and Y. Miyasaka, Jpn. J. Appl. Phys., Part 1 **35**, 4900 (1996).
[9] M. Noda, Y. Matsumuro, H. Sugiyama, and M. Okuyama, Jpn. J. Appl. Phys., Part 1 **38**, 2275 (1999).
[10] A. Furuya and J. D. Cuchiaro, Jpn. J. Appl. Phys., Part 2 **39**, L371 (2000).
[11] M. J. Forbess, S. Seraji, Y. Wu, C. P. Nguyen, and G. Z. Cao, Appl. Phys. Lett. **74**, 1904 (2000).
[12] K. Aizawa, E. Tokumitsu, K. Okamoto, and H. Ishiwara, Appl. Phys. Lett. **76**, 2609 (2000).
[13] K. Miura and M. Tanaka, Jpn. J. Appl. Phys., Part 1 **37**, 2554 (1998).
[14] Y. Shimakawa, Y. Kudo, Y. Nakagawa, T. Kamiyama, H. Asano, and F. Izumi, Appl. Phys. Lett. **74**, 1904 (1999).
[15] Y. Noguchi, M. Miyayama, and T. Kudo, J. Appl. Phys. **88**, 2146 (2000).
[16] H. Toraya, H. Hibino, and K. Ohsumi, J. Synchrotron Radiat. **3**, 75 (1996).
[17] F. Izumi, *The Rietveld Method*, edited by R. A. Young (Oxford University Press, Oxford, 1993), Chap. 13.
[18] S. Sasaki, Rev. Sci. Instrum. **66**, 1573 (1995).
[19] E. C. Subbarao, J. Phys. Chem. Solids **23**, 665 (1962).
[20] G. A. Smolensikii, V. A. Isupov, and A. I. Agranovskaya, Fiz. Tverd. Tela (Leningrad) **3**, 895, (1961) [Sov. Phys. Solid State **3**, 651 (1961)].
[21] A. C. Rastogi, S. Tirumala, and S. B. Desu, Appl. Phys. Lett. **74**, 3492 (1999).
[22] B. S. Kang, B. H. Park, S. D. Bu, S. H. Kang, and T. W. Noh, Appl. Phys. Lett. **75**, 2644 (1999).