Ferroelectricity in intergrowth $\text{Bi}_3\text{TiNbO}_9\text{--Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics

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Monophase intergrowth $\text{Bi}_3\text{TiNbO}_9\text{--Bi}_4\text{Ti}_3\text{O}_{12}$ (BTN-BIT) ceramics were synthesized by solid-state reaction method. In the temperature dependence of dielectric permittivity, two anomalies appeared at 945 and 1114 K, respectively. The ferroelectric hysteresis loop measurement revealed that the $2P_r$ is $20\text{ }\mu\text{C}/\text{cm}^2$, nearly as twice as that of the BTN ceramic. The crystal structure analysis indicated that the enhanced octahedral distortion along the a axis is the main contribution to the ferroelectricity of BTN-BIT. The increased $2P_r$ for the BTN-BIT ceramics is ascribed to its larger P_s than that of the BTN and easier domain switching under electric field than that of the BIT.

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I. INTRODUCTION

The intergrowth bismuth layer-structured ferroelectrics (IBLSFs) were reported by Kikuchi¹ in 1976 and henceforth have attracted considerable attentions. The relation of the crystal structure and its properties has been widely studied for the past several decades.^{2–7} This type of materials are usually made up of an intergrowth of one-half the unit cell of the usual bismuth layer-structured oxide (BLSO), and one-half the unit cell of another BLSO along the c axis, with the difference of the numbers of perovskitelike layers that sandwiched between $(\text{Bi}_2\text{O}_2)^{2+}$ layers equals unity ($m-n=1$). For example, the IBLSF $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ (BTN-BIT) is made up of alternate arranged $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($m=3$) and $\text{Bi}_3\text{TiNbO}_9$ ($n=2$) along the c axis.⁴ Their potentially superior ferroelectric properties are recognized only recently.^{8–10}

To this kind of natural superlattice structures, some unique characteristics compared to the normal BLSFs, has been reported. For example, the remanent polarization (P_r) was observed along the c axis,⁹ there are two distinct crystallographic sites of bismuth in $(\text{Bi}_2\text{O}_2)^{2+}$ layers^{4,8} and the dielectric anomalies,^{3,5} etc. However, the origin of the enhanced ferroelectric property is not fully understood yet. Noguchi *et al.* proposed in their paper that the displacement of Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ along the a axis is partially responsible for the larger remanent polarization P_r of intergrowth ferroelectrics.⁸ Since the displacement of Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ will inevitably affect the coordinate oxygen ions and thus adjust the rotation and tilting of perovskitelike layers. In this article, the enhanced ferroelectric properties of a typical intergrowth $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ ferroelectric originating from octahedral distortion caused by lattice mismatch was reported.

II. EXPERIMENT

The pellet specimens of BTN-BIT with a diameter of 13 mm and a thickness of 1 mm were prepared by conven-

tional solid-state reaction method. Appropriate amounts of high purity raw materials were first mixed and presintered at 1123 K for 7 h, then pressed into pellets and sintered at 1373 K for 2 h in air. The x-ray diffraction (XRD) patterns of sintered specimens were recorded using $\text{Cu K}\alpha$ radiation in a Rigaku D/max-2550V. For electrical measurements, platinum electrodes were applied after pellet surfaces being polished (~ 0.4 mm thickness for the hysteresis loop measurement). The dielectric properties of the specimens were measured by an HP4194A in air at a heating rate of 3 K/min. The ferroelectric properties were evaluated by a standard ferroelectric test system (TF Analyzer 2000 FE-Module).

III. RESULTS AND DISCUSSION

Figure 1 shows the Rietveld refined results for the XRD patterns of the BTN-BIT powders. The XRD pattern was calculated according to Ref. 4. It can be seen that all diffraction peaks can be well indexed by the space group $I2cm$. The refined lattice constants a , b , and c are 0.5441, 0.5403, and 5.799 nm, respectively. The R -weighted pattern (R_{wp}) was 12.1% and the goodness of fit (S) was 0.6. These parameters

FIG. 1. X-ray diffraction pattern and the Rietveld refinement for $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$ powders, where the solid circles are data points, the thin solid line is the refinement result, the short bars are the position of the diffraction peaks predicted from the space group $I2cm$, and the thick line below is the difference between the data points and the fitted line.

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FIG. 2. The temperature dependence of dielectric permittivity and dielectric dissipation for intergrowth $\text{Bi}_3\text{TiNbO}_9\text{-Bi}_4\text{Ti}_3\text{O}_{12}$ (BTN-BIT), measured at 1 MHz. The inset is the temperature dependence of the reciprocal of the dielectric permittivity around T_C . The straight line is deduced according to the Curie-Weiss law.

are inconsistent with the previously reported results⁴ and demonstrate that the monophasic intergrowth BTN-BIT ferroelectric was obtained.

The temperature dependence of the dielectric permittivity ϵ' and dielectric loss, $\tan \delta$, of the BTN-BIT ceramic at a frequency of 1 MHz is shown in Fig. 2. Two dielectric anomalies were observed. The second anomaly around 1114 K is attributed to the ferroelectric-paraelectric transition (T_C), while the first one, around 945 K, is associated with the regularization of the “BIT part” of the intergrowth structure.⁵ Inset in Fig. 2 shows the temperature dependence of the reciprocal of the dielectric permittivity around Curie temperature T_C . From it the Curie-Weiss temperature T_0 (1087 K) was deduced. The dielectric loss of the BTN-BIT ceramic is prominent at high temperatures. However, at the temperatures below 700 K, the $\tan \delta$ is lower than 0.01, which is of benefit to high electric field polarization experiment.

Figure 3 shows the P - E hysteresis loop measured at 423 K. Figure 4 shows the maximum electric field (E_m) de-

FIG. 3. Polarization hysteresis loop of intergrowth BTN-BIT ceramic measured at 423 K.

FIG. 4. Remanent polarization ($2P_r$) and coercive field ($2E_c$) vs maximum applied electric field (E_m) measured at 423 K.

pendence of the remanent polarization $2P_r$ and the coercive field $2E_c$. The nearly saturated $2P_r$ and $2E_c$ are $20.1 \mu\text{C}/\text{cm}^2$ and $184.6 \text{ kV}/\text{cm}$, respectively. It is known that the $2P_r$ of the constituent BTN ceramic is very low and is only $\sim 11 \mu\text{C}/\text{cm}^2$ even for hot-press textured ceramic.¹¹ Whereas the $2P_r$ of the constituent BIT ceramic is only $16 \mu\text{C}/\text{cm}^2$.⁸ Though the $2P_r$ of the BTN-BIT ceramic here is just a little larger than that of the BIT ceramic, Zhang *et al.* reported previously that the $2P_r$ of the BTN-BIT ceramic can reach $28 \mu\text{C}/\text{cm}^2$.¹² As a result, it can be concluded that the P_r of the BTN and the BIT ceramics can be enhanced by constructing an intergrowth structure.

According to the crystal structures of the BTN-BIT compound and the BTN compound,^{4,13} the spontaneous polarization (P_s) can be calculated by

$$P_s = \sum_i (m_i \Delta x_i Q_i e) / V, \quad (1)$$

where m_i is the site multiplicity, Δx_i is the atomic displacement from the corresponding position in the tetragonal ($I4/mmm$) structure, $Q_i e$ is the ionic charge of the i th constituent ion, and V is the unit-cell volume. Using the formal charge (+3 for Bi, +4 for Ti, +5 for Nb, and -2 for O) in the calculation, P_s of BTN and BTN-BIT along the a axis were estimated to be 14.3 and $24.3 \mu\text{C}/\text{cm}^2$, respectively. Therefore, the intrinsic ferroelectric property of BTN-BIT is considered larger than that of the BTN. However, it is known that the P_s of BIT single crystal along the a axis is $\sim 46 \mu\text{C}/\text{cm}^2$.¹⁴ The larger P_r of the BTN-BIT ceramic means that the domain switching of BTN-BIT under electric field is easier than that of the BIT.

The contribution of the Ti/Nb ion displacements along the a axis in octahedra is about 14% of the P_s for the BTN-BIT compound, which is just a little larger than that of the BTN compound (12%). Additionally, the contribution of the Bi ion displacements along the a axis in $(\text{Bi}_2\text{O}_2)^{2+}$ is just 1% of the P_s for the BTN-BIT compound, which is quite different with the suggestions proposed by Noguchi *et al.*⁸ These results indicate that neither Ti/Nb nor Bi displacements is the main cause of the ferroelectric polarization of BTN-BIT.

FIG. 5. Schematic representations of octahedral tilting from the c axis in perovskite blocks: along the a axis for (a) BTN-BIT, (b) BTN, and (c) BIT; along the b -axis for (d) BTN-BIT, (e) BIT, and (f) BTN.

It should be noted that the two kinds of Bi^{3+} ion in the $(\text{Bi}_2\text{O}_2)^{2+}$ layers of intergrowth ferroelectrics bond to the apex oxygen of two adjacent Ti/NbO_6 octahedra, respectively, the adjustment of $(\text{Bi}_2\text{O}_2)^{2+}$ induced by lattice mis-

FIG. 6. Schematic representations of octahedral rotation in the a - b plane for (a) outer layer of the BIT part in BTN-BIT; (b) middle layer of the BIT part in BTN-BIT; (c) the BTN part in BTN-BIT; (d) outer layer of the BIT; (e) middle layer of the BIT; (f) the BTN.

match affect inversely the two adjacent Ti/NbO_6 octahedra.

The principal ferroelectric distortion, i.e., tilting and rotation of the octahedra, for the intergrowth BTN-BIT ferroelectric⁴ and its constituent BTN and BIT compounds,^{13,15} are schematically shown in Figs. 5 and 6. The tilting of the octahedra can be depicted by the tilt angle (α) from the c axis, which can be further reduced to the tilt along a and b axes, i.e., the component in the a - c plane (α_x) and in the b - c plane (α_y). The rotation of the octahedra can be represented by the octahedral rotation angle (β) along the b axis, in the a - b plane. The values of these parameters for the compounds are summarized in Table I. It can be seen from these parameters that the tilting extent for the octahedra of the intergrowth BTN-BIT ferroelectric is more apparent than that of the constituent BTN and BIT compounds. Since the ionic displacements along the b axis cancel each other out due to the presence of the glide plane perpendicular to the b axis, the lattice distortion related to α_y does not contribute to the spontaneous polarization. In the a - b plane parallel to $(\text{Bi}_2\text{O}_2)^{2+}$ layers, the rotation content for the octahedra of the intergrowth BTN-BIT ferroelectric decreases on the whole. Therefore, the enhanced lattice distortion related to α_x is responsible for the larger P_s than that of the BTN.

TABLE I. Summarization of the tilt angle (α) of the octahedra from the c axis, the tilt in the a - c plane (α_x) and in the b - c plane (α_y), and the octahedral rotation angle (β) along the b axis in the a - b plane.

	α (deg)	α_x (deg)	α_y (deg)	β (deg)
BTN	13.41	3.28	46.768	9.287
BTN part in BTN-BIT	13.95	22.41	68.46	8.51
	9.12	15.896	46.575	8.39
BIT	10.13	0.24	47.57	6.29
	9.12	16.48	39.91	5.89
BIT part in BTN-BIT	11.7	41.64	61.43	7.77
	11.7	0	68.38	0
	11.7	41.64	61.43	7.77

IV. CONCLUSIONS

In summary, monophasic intergrowth BTN-BIT ceramics were obtained by conventional solid-state reaction method. Two dielectric anomalies were observed at 945 and 1114 K, respectively. The ferroelectric property measurement revealed that the $2P_r$ is $20 \mu\text{C}/\text{cm}^2$ and the $2E_c$ is 184.6 kV/cm. The crystal structure analysis indicates that the lattice distortion related to α_x is responsible for the ferroelectricity of BTN-BIT. The larger P_s than that of the BTN and the easier domain switching under electric field than that of the BIT result in the increased $2P_r$ for the BTN-BIT ceramics.

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