Ferroelectric state in lead-free mixed-oxide system 
\((1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3\) having high Ba contents

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The ferroelectric state in a simple-perovskite mixed-oxide system \((1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3\) (NBT–xBT) for \(0.30 \leq x \leq 1.0\) was investigated primarily via in situ transmission electron microscopy observation. Dielectric permittivity measurements reveal that the NBT–xBT samples for \(0.30 \leq x < 0.80\) exhibited hysteresis with a temperature width of approximately 20–50°C. This result suggests that a successive phase transition was present and that the ferroelectric state at room temperature was not a simple tetragonal symmetry. In situ transmission electron microscopes observation reveals that the ferroelectric state in the BT-rich end had an M\(_C\)-type monoclinic symmetry with \((201)\_C\) polarization vectors in \([100]_C\) planes. The ferroelectric M\(_C\) state was characterized by a 79° (pseudo 90°) domain with a \((110)\_C\) twin structure and 180° domain. Thus, the continuous change at room temperature from the ferroelectric tetragonal state in BT for \(x = 1.0\) to the monoclinic M\(_C\) state for \(x = 0.30\) can be explained by the introduction of a \((100)\_C\) component perpendicular to the original \([001]_C\) polarization vector in the tetragonal system.

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1. Introduction

In a mixed-oxide system having a simple perovskite structure \(A\text{BO}_3\), substitution of cations that occupy \(A\) or \(B\) sites can lead to the appearance of various dielectrics such as a ferroelectric phase and an antiferroelectric phase. \(\text{Pb(Zr}_{1-x}\text{Ti})_x\text{O}_3\), \(\text{Pb(Zn}_{1-x}\text{Nb}_{2/3})_{x}\text{O}_3\)–\(\text{PbTiO}_3\), \(\text{Pb(Mg}_{1/3}\text{Nb}_{2/3})_{x}\text{O}_3\)–\(\text{PbTiO}_3\), and \(\text{Ba(Zr}_{1-x}\text{Ti})_x\text{O}_3\) are typical examples. The notable feature of these mixed-oxide systems is the presence of a morphotropic phase boundary (MPB) that is nearly parallel to the temperature axis.¹–⁶ Commonly, conspicuous dielectric and piezoelectric responses have been reported near the MPB. These origins have been explained in terms of the rotation of the polarization vector in the ferroelectric monoclinic (FM) state.⁷⁻⁸ It is worth noting that there are generally three types of monoclinic states. In ferroelectric \(M_{\_A}\)-type and \(M_{\_B}\)-type monoclinic states, polarization vectors lie in \([100]\) planes. By contrast, polarization vectors lie in \([100]\) planes in the ferroelectric \(M_{\_C}\)-type (FM\(_C\)) monoclinic state.

The mixed-oxide system \((1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3\) (NBT–xBT) is an \(A\)-site substitution-type ferroelectric mixed-oxide system having \((\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\) (NBT) and \(\text{BaTiO}_3\) (BT) as end materials. According to previous studies, when temperature is gradually reduced, BT exhibits successive ferroelectric cubic transitions from the paraelectric cubic (PC) state to the tetragonal (FT) state at around 393 K, orthorhombic (FO) state at around 278 K, and then rhombohedral (FR) state at around 183 K.⁹⁻¹⁰ On the other hand, NBT exhibits the successive ferroelectric transitions from the PC state to the antiferroelectric state at around 623 K and further to the FR state at around 473 K.¹¹ The dielectric properties and structures of NBT–xBT for \(0 \leq x \leq 0.30\) have been investigated by Takenaka et al. According to their experimental data, when the BT content increases from \(x = 0\) at 300 K, the FR state is transformed into the FT state at around \(x = 0.07\).¹¹ The FR/FT boundary can be identified as MPB, at which remarkable physical properties were reported.¹²⁻¹⁶ For the ferroelectric state on the BT end, however, few researches have been conducted for \(0.30 \leq x \leq 1.0\).

In the present work, to clarify the features of the FT state on the BT end, the crystallographic features of the ferroelectric states and dielectric properties of NBT–xBT with \(0.30 \leq x \leq 1.0\) were investigated. Ferroelectric domain structures and polar state were examined by in situ transmission electron microscopes (TEM) observations with the help of the failure of Friedel’s law in electron diffraction.

2. Experimental procedure

NBT–xBT samples with \(0.30 \leq x \leq 1.0\) were prepared from \(\text{Bi}_2\text{O}_3\) (5 wt% excess), \(\text{BaCO}_3\), \(\text{TiO}_2\), and \(\text{Na}_2\text{CO}_3\)
powders by a solid-state reaction. Na$_2$CO$_3$ was pre-heated at 150$^\circ$C for 2 h before weighing. These powders were first mixed for 16 h using the ball milling technique. After calcination at 1073 K for 3 h, the powders were mixed again for another 16 h and pressed into pellets. Sintering procedures were then conducted at 1423 K for 12 h. The characterization of each prepared sample was conducted by measuring its dielectric permittivity using a usual LCR method. Powder X-ray diffraction (XRD) profiles were obtained utilizing Cu K$\alpha$ radiation with the wavelength of $\lambda = 1.5406$ Å. To accurately examine temperature dependence of the lattice constant as well as ferroelectric transition behavior, Lorentzian peak fitting was applied to experimentally obtained XRD profiles (Supplementary Fig. S1).

The features of the ferroelectric states were examined at room temperature via TEM (JEM-3010, JOEL) at an accelerating voltage of 300 kV. The ferroelectric domain structures and polar state of NBT$\_x$BT samples were studied by examining their electron diffraction (ED) patterns and bright- and dark-field (DF) images. To clarify the polar direction in each ferroelectric domain, the help of the failure of Friedel’s law in a two-beam condition was utilized. The specimens for in situ TEM observations were prepared using the Ar-ion thinning technique.

### 3. Results and discussion

The crystal structures of NBT$\_x$BT polycrystalline samples with $0.30 \leq x \leq 1.0$ at 300 K were investigated using conventional powder XRD measurements. Figure 1 shows the powder XRD profiles obtained from the samples of NBT$\_x$BT with $x = 1.0$, 0.80, 0.65, 0.50 and 0.30. Since no impurity peaks were observable, all the samples were confirmed to have a single phase of the simple perovskite structure. The fitting of a conventional crystal structure refinement was carried out for all the samples using the tetragonal space group $P4mm$. Figures 2(a) and 2(b) show the variations in the unit lattice parameters ($a$, $c$) and cell volume ($V$) as functions of the BT content ($x$) for $0.30 \leq x \leq 1.0$. All the unit lattice parameters and the cell volume changed uniformly with increases in the BT content ($x$). These indicate that all the samples were successfully prepared with the desired compositions.

The temperature dependence of real dielectric permittivity $\varepsilon'$ in each NBT$\_x$BT sample was then evaluated. Figures 3(a)–3(e) show the temperature dependence of the measured $\varepsilon'$ values with 100 kHz for $x = 1.0$, 0.80, 0.65, 0.50, and 0.30, respectively, in heating and cooling processes. Among the prepared NBT$\_x$BT samples, the dielectric behavior can be generally classified into two types. For $0.80 \leq x \leq 1.0$, the dielectric behavior in the heating process is almost the same as that in the cooling process. The behavior of $\varepsilon'$ for $x = 0.80$ is similar to that for BT ($x = 1.0$), implying that the peak for $x = 0.80$ seems to be attributed to the Curie temperature $T_C$ for the (PC$\leftrightarrow$FT) ferroelectric transition. For $0.30 \leq x < 0.80$, however, hysteresis appeared by increasing NBT substitution contents, as indicated by the double arrows in Figs. 3(c)–3(e). Here we focused on the dielectric behavior in the cooling process. The samples for $x = 0.50$ and 0.30 exhibited sharp decreases of $\varepsilon'$ at $T_1$ and the maximum dielectric constant at $T_2$. Although $T_2$ is likely to be assigned to the Curie temperature $T_C$ for the (PC$\leftrightarrow$FT) ferroelectric transition, the presence of a hysteresis and $T_1$ indicates that successive phase transition existed below $T_2$. In other words, the ferroelectric state at room temperature would

**Fig. 1.** Powder XRD profiles obtained at 300 K in NBT$\_x$BT for $x = 1.0$, 0.80, 0.65, 0.50 and 0.30.

**Fig. 2.** The variations in (a) the lattice parameters ($a$, $c$) and (b) cell volume ($V$) as functions of the BT content ($x$).
not be the FT state. To clarify the ferroelectric transition behavior, the temperature dependence of XRD profile was then investigated. Figure 4 shows the temperature dependence of the XRD profile and the lattice constant for \(x = 0.30\). Each XRD profile was obtained in the cooling process. To accurately determine the unit lattice parameters, Lorentzian peak fitting was conducted. When the temperature was lowered from the paraelectric cubic state, the 200 peak at 46° began to split at approximately 473 K, as indicated by the arrow in Fig. 4(a). Temperature dependence of the corresponding unit lattice parameter in Fig. 4(b) indicated that the ferroelectric transition occurred at approximately 493 and 403 K. This suggests that \(T_2\) is the Curie temperature \(T_C\) for the (PC->FT) ferroelectric transition, while \(T_1\) is the temperature for the (FT->FM or FO) transition. To further understand the ferroelectric state at room temperature, in situ TEM observations were then conducted for the prepared NBT-xBT samples with \(0.30 \leq x \leq 1.0\).

Figure 5 shows the results of the analysis for the ferroelectric domain structure in a typical FT state for BT (\(x = 1.0\)). Two DF images and a corresponding ED pattern of a BT sample at room temperature are shown, together with a schematic diagram of the determined domain structure. The electron beam incidence is parallel to the [001]C direction, where subscript C denotes the PC state. In Fig. 5(a), we observed the splitting of [550] fundamental reflections attributable to the simple perovskite structure. Because the splitting derived from the 90° domain structure, the ED images in Figs. 5(c) and 5(d) were taken using \(g = 020\) and \(020\) for one variant, respectively. Large banded structures having an average width of approximately 500 nm were

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**Fig. 3.** Temperature dependence of \(\varepsilon'\) with 100 kHz in the heating and cooling process for \(x = (a) 1.0, (b) 0.80, (c) 0.65, (d) 0.50, and (e) 0.30.**
observed. The boundary between two neighboring bands is parallel to the (1/C2210)C plane. The {110}C twin boundary is consistent with the cubic-to-tetragonal transition based on the Sapriel theory concerning ferroelastic transitions. Note here that the Friedel’s law of \(F_{hkl} = F_{hk}l\) is satisfied in the kinematical theory. Therefore, features of a ferroelectric domain having no central symmetry can be investigated. When the dynamical effect that produces the failure of the Friedel’s law was utilized, DF images were taken under the two-beam condition. In other words, a ferroelectric domain with \(g \cdot P > 0\) generates a bright contrast in DF images, where \(g\) and \(P\) denote the scattering and polarization vectors, respectively. As shown in Figs. 5(c) and 5(d), the bright- and dark-contrast reversal occurred for one variant region, indicating that the bright- and dark-contrast regions in Fig. 5(c) had polarization vectors parallel to the \([010]_C\) and \([00T]_C\) directions, respectively. On the basis of these results, the ferroelectric domain structure of the FT state, which consists of 90 and 180° domain walls, can be determined and is shown in Fig. 5(b).

Figure 6 shows DF images for \(g = 020\) as a function of BT content. The electron beam incidence for all images was parallel to the \([001]_C\) direction. The images in Figs. 6(a)–6(c) were taken at 300 K for NBT–xBT samples with \(x = 0.80, 0.50,\) and \(0.30,\) respectively. In all images, banded structures with an average width of approximately 200 nm were observed. The boundary between two neighboring bands is parallel to the (1/C2210)C plane, which is identical to that in BT, as shown in Fig. 5. In terms of the Sapriel theory concerning ferroelastic transitions, the \([110]_C\) domain boundary is attributable to the cubic-to-tetragonal. As shown in Figs. 6(a)–6(c), however, only a uniform contrast can be detected, which is considered as the notable feature. In other words, in spite of the same imaging conditions as in Fig. 5(c), the \([100]_C\) polarization component regions were not observed in the bands. Thus, the polarization direction is not parallel to the \([100]_C\) direction of the FT state.

To clarify the polarization direction of each ferroelectric domain, the \(g\)-vector dependence of DF images for \(0.30 < x < 0.80\) was then investigated. Because the ferroelectric domain structures for \(0.30 < x < 0.80\) were fundamentally the same, the experimental results for \(x = 0.50\) are shown here. Figure 7 shows the results of the analysis for the ferroelectric domain structure for \(x = 0.50\). Two DF images and a corresponding ED pattern at room temperature are shown, together with a schematic diagram of the determined domain structure. The electron beam incidence is parallel to the \([112]_C\) direction. In Fig. 7(a), splitting of fundamental reflections was observed as indicated by the arrows, which was derived from the 90° domain structure.
state. The FM_C domain structure as shown in Fig. 7(b) is exactly the same as that reported in the FT phase of Pb(Mg_{1/3}Nb_{2/3})O_3–PbTiO_3 and Pb(Sc_{1/2}Nb_{1/2})O_3–PbTiO_3.

In this study, in situ TEM observation revealed that the ferroelectric state for 0.30 ≤ x < 0.80 had an M_C-type monoclinic symmetry with (201)_{C} polarization in {100}_{C} planes. The average structure and ferroelastic domain are tetragonal, while the polarization deviates slightly from the [001]_{C} direction of the FT state. The feature of the FMC state is that the (201)_{C} polarization was produced by introducing extra perpendicular (100)_{C} components to the original [001]_{C} polarization in the FT state. The introduction of extra (100)_{C} components likely had a significant influence on lattice distortion. As shown in Figs. 6(b) and 6(c) for x = 0.50 and 0.30, the twin boundaries were seen to be curved and dissimilar compared with Fig. 6(a) for x = 0.80 and Fig. 5(c) for BT, as indicated by the arrows.

The increase in BNT substitution contents could lead to the lattice distortion. Therefore, the FT state for BT at room temperature continuously transformed into the FMC state by introducing the (100)_{C} components normal to the [001]_{C} polarization in the FT state. On the basis of this result, T_1 of samples for x = 0.50 and 0.30 likely corresponds to the transition temperature of the (FM_C→FT) ferroelectric transition. To clarify the feature of the (FM_C→PC) transition for 0.30 ≤ x < 0.80, the temperature variation of the ferroelectric domain structure in heating and cooling processes will be investigated via in situ TEM observation as the next step.

4. Conclusions

In the mixed-oxide system NBT–xBT for 0.30 ≤ x ≤ 1.0, the ferroelectric features at room temperature were investigated by in situ TEM observations with the help of the failure of Friedel’s law. In terms of the average structure and ferroelastic domain, NBT–xBT samples have a tetragonal symmetry. However, in terms of the ferroelastic domain structure, the polarization vector is not parallel to the (100)_{C} directions in the FT state. The ferroelectric state for 0.30 ≤ x < 0.80 could be characterized by an M_C-type monoclinic symmetry with (201)_{C} polarization in {100}_{C} planes. The appearance of the FM_C state seems to be attributable to the introduction of (100)_{C} components to
the [001]_C polarization in the FT state. In addition, the curved twin boundaries that were observed in the NBT–xBT samples for 0.30 ≤ x < 0.80 implied that the additional introduction of ⟨100⟩_C components induced lattice distortion. As a result, the ferroelectric state at room temperature in the NBT–xBT binary system was transformed from the FT to FM_C state by increasing the BNT substitution content.

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