The crystallographic features of the ferroelectric tetragonal (FT) state in $(1-x)$Pb(Sc$_{1/2}$Nb$_{1/2}$)$_2$O$_3$–xPbTiO$_3$ (PSN–xPT) were investigated between 300 and 700 K, primarily using transmission electron microscopy (TEM) with the help of the failure of Friedel’s law in electron diffraction. The ferroelectric state for $0.60 \leq x < 1.0$, which has been recognized as the normal FT state thus far, was found to have M$_c$-type monoclinic symmetry with $(201)_c$ polarization vectors in the $\{100\}_c$ planes. Notably, the ferroelectric M$_c$ state (FM$_c$) was characterized by pseudo 90° and 180° domain structures, in which the polarization rotates slightly from the $\{010\}_c$ direction of the FT state. In addition, in situ TEM observation during heating and permittivity measurement revealed that the (FM$_c \rightarrow$ FT) transition occurred at below $T_c$ for $0.60 \leq x < 1.0$. The FT/FM$_c$ phase boundary, which is nearly perpendicular to the temperature axis, was therefore present at approximately 560 K.

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Key-words : Ferroelectrics, Domain structure, Phase transition, Transmission electron microscopy

[Received November 24, 2017; Accepted December 27, 2017]
the ferroelectric orthorombic state, occurs by sequential freezing of the triple degenerated $T_{uu}$ mode. That is, the FM$_C$ state can be understood as the transition state from the FR or FO state to the FT state. To clarify the features of the (FM$_C$ $\rightarrow$ FT) transition with increases in PT content, the crystallographic features of ferroelectric states for $0.60 \leq x < 1.0$ were investigated in this study using in situ TEM observations with the help of the failure of Friedel’s law in electron diffraction. Notably, the in situ TEM observations revealed that the ferroelectric state for $0.60 \leq x < 1.0$, which has been recognized as the FT state thus far, could be identified as the FM$_C$ state with (201)$_C$ polarization vectors in the [100]$_C$ planes. In addition, the (FM$_C$ $\rightarrow$ FT) phase transition could be detected at approximately 560 K. The FT/FM$_C$ phase boundary that is nearly perpendicular to the temperature axis is therefore located below $T_C$.

2. Experimental procedure

PSN–xPT polycrystalline samples with $0.60 \leq x < 1.0$ (interval of $x = 0.05$) were prepared using a solid-state-reaction method. To obtain ScNbO$_4$, Sc$_2$O$_3$ (>99.9% purity) and Nb$_2$O$_5$ (>99.9% purity) powders were first mixed for 1 h and calcined in air at 1553 K for 1 h. Initial powders of PbO (>99.9% purity), TiO$_2$ (>99.9% purity), and the obtained ScNbO$_4$ were then mixed for 1 h and calcined at 1223 K for 3 h. To prevent PbO loss during the calcinating and sintering processes, 2 wt % excess PbO was added. After calcination, the mixed powders were pressed into pellets and sintered at 1473 K for 3 h. To avoid PbO loss, this sintering process was performed in a PbO-rich atmosphere using a covered crucible. Characterization of the sintered samples was conducted by measuring their dielectric permittivity using the standard LCR method. The crystallographic features of the prepared PSN–xPT samples, including their ferroelectric domain structures, were examined by obtaining their electron diffraction patterns and bright- and dark-field images using a JEOL JEM-3010 TEM with an accelerating voltage of 300 kV. During the heating experiments, the temperature was controlled via a heating control unit (EM-SHU2, JEOL Co. Ltd.). To determine the direction of the polarization vector in each ferroelectric domain, we utilized the FEI Tecnai G2 F20 S-Twin TEM with an accelerating voltage of 200 kV. The specimens for in situ observation were prepared using the Ar-ion thinning technique. Here, the theoretical background for the failure of Friedel’s law in electron diffraction is described. According to the dynamical theory proposed by Fujimoto, the failure of Friedel’s law occurs under a transmission diffraction conditions. When intensities of reflections with scattering vectors of $g = [hkl]$ and $-g = [-hkl]$ are written as $I_g$ and $I_g$, respectively, the intensity ratio $I_g/I_g$ is given by

$$I_g/I_g = \frac{|v_g|^2 + (D/2k)\overline{\vartheta}(v_g \sum_{m} v_{-m}v_{m-g}) + \cdots}{|v_g|^2 - (D/2k)\overline{\vartheta}(v_g \sum_{m} v_{-m}v_{m-g}) + \cdots} \tag{1}$$

In this equation, $D$ is the thickness of a crystal, $k$ is the wave number of an electron, and $v_i$ is the Fourier coefficient of a crystal potential. The prim in the sum $\sum$ means the absence of zero and $g$ terms. The symbol $\overline{\vartheta}$ indicates the imaginary part of $(v_g \sum_{m} v_{-m}v_{m-g})$. The point to note here is that the asymmetry of the intensity first appears in the second terms in the numerator and the denominator. That is, the two-beam condition was utilized in our observation, but the second term shows that weak reflections for $v_{-m}$ play an essential role in the failure of Friedel’s law.

3. Experimental results and discussion

We first examined the crystal structures of PSN–xPT for $0.60 \leq x < 1.0$ at 300 K using conventional powder X-ray diffraction (XRD) measurements. Figure 1 presents the powder XRD profiles obtained from the samples of PSN–xPT with $x = 0.95$, 0.85, 0.75, and 0.65. Because no impurity peaks were detected, all the samples were confirmed to have a single phase of the simple perovskite structure. The fitting of a conventional crystal structure refinement was performed for all the samples using the space group $P4mm$. Figures 2(a) and 2(b) show the variations in the unit lattice parameters ($a$, $c$, cell volume ($V$), and axial ratio ($c/a$) as functions of the PT content ($x$) for $0.60 \leq x < 1.0$. All the unit lattice parameters and the axial ratio changed linearly with increases in the PT content ($x$). These findings indicate that all the samples were successfully prepared with the desired compositions. Here we focused on the variations in the various unit lattice constants, $\Delta a$ and $\Delta c$, as shown in Fig. 2(a). In the typical tetragonal distortion, $\Delta c$ is generally larger than $\Delta a$ according to the following relational expression: $\Delta c/\Delta a \approx 2.6$–29 In the present case of PSN–xPT, however, $\Delta a$ is slightly larger than $\Delta c/\Delta a \approx 0.6$. This result implies that the ferroelectric state for $0.60 \leq x < 1.0$
is not the simple FT state. Further investigation was thus conducted.

Figure 3 shows the temperature and frequency dependence of the real dielectric permittivity $\varepsilon'$ for $x = 0.65$, 0.7, 0.85, and 0.95 during the heating process. The heating rate was approximately 1 K/min. All the PSN–xPT samples showed a peak and dielectric anomaly for temperature dependence, as indicated by the arrows, with the temper-
For $0.60 \leq x < 1.0$, which was determined based on our experimental data. In the diagram, $T_C$ (= $T_1$) and $T_2$ for $0.60 \leq x \leq 0.95$ were determined from the temperature dependencies during the heating process. The PC, FT, and FM$_C$ states are present in the diagram. The boundary present at approximately 560 K was identified as the phase boundary between the FT and FM$_C$ states. To clarify the ferroelectric state below $T_1$ and between $T_1$ and $T_2$, in situ TEM observations were carried out in the temperature range from 300 and 720 K.

First, we checked whether the PSN–xPT samples for $0.60 \leq x < 1.0$ had a simple tetragonal symmetry. The four dark-field images in Fig. 5 were obtained at room temperature from PSN–xPT samples with $x = 0.60$ (low PT content) and 0.95 (high PT content). The images in Figs. 5(a) and 5(a') and Figs. 5(b) and 5(b') were obtained under two-beam conditions using $g = 020$ and 020, respectively. The electron beam incidence for all the images was parallel to the [001]$_C$ direction, where the subscript C denotes the PC state. In this study, both the reflections and electron incidences in the electron diffraction patterns were indexed in terms of the pseudocubic notation. Note that all the dark-field images were obtained under two-beam conditions using the dynamical effect that induces the failure of Friedel’s law. Under these conditions, a ferroelectric domain with $g \cdot P > 0$ exhibits bright contrasts in images, where $g$ and $P$ represent the scattering and polarization vectors, respectively. In all four images, banded structures with widths of approximately 200 nm on average and a boundary between two neighboring bands parallel to the (110)$_C$ plane are observed. This {110}$_C$ domain boundary results from a cubic-to-tetragonal transition based on the Sapriel theory on ferroelastic transitions.30) In the [001]$_C$ diffraction patterns in the insets of Figs. 5(a) and 5(b), a splitting of the 220 fundamental reflections can be detected, indicating the presence of the 90° domain structure characterizing the FT state. In addition, boundaries parallel to the (100)$_C$ plane can be observed in each band, as indicated by the white arrows. These boundaries appear to be the 180° domain walls. Note here that the typical FT state has 180° domain structures with {100}$_C$ polarization vectors. Hence, if the ferroelectric state below $T_2$ could be identified as the FT state, bright and dark contrast regions with the (100)$_C$ polarization vector should be observed in the bands using $g = 020$, while those in (a') and (b') were taken using $g = 020$. In these images, however, only a uniform contrast could be detected. The direction of the polarization vector in each ferroelectric domain apparently deviates from the (100)$_C$ direction of the FT state as described in the Sapriel theory concerning ferroelastic domains.

To examine the features of the ferroelectric state below $T_2$, we further evaluated the $g$-vector dependence of dark-field images for $0.60 \leq x < 1.0$. The ferroelectric domain structures below $T_2$ for $0.60 \leq x < 1.0$ were found to fundamentally exhibit the same features. Thus, the experimental results for $x = 0.65$ are shown here. The images in Figs. 6(a)–6(d) were taken using $g = 201$, 201, 021, and 021, respectively. The corresponding [112]$_C$ electron diffraction pattern is shown in the inset of Fig. 6(d). In Figs. 6(a)–6(d), banded structures can be observed, and the neighboring bands are parallel to the (110)$_C$ plane. Here, the wide and narrow bands are called variants A and B, respectively. In variant A, contrast reversal occurs in the $g = 201$ and 201 images, as shown in Figs. 6(a) and 6(b).
This indicates that the bright- and dark-contrast regions in (a) have polarization vectors parallel to the [201]₀ and [201]₀ directions, respectively. In variant B, on the other hand, contrast reversal occurs in the g = 021 and 021 images, as shown in Figs. 6(c) and 6(d). Thus, the bright- and dark-contrast regions in (c) have polarization vectors parallel to the [021]₀ and [021]₀ directions, respectively. The ferroelectric domain model below T₂ was constructed based on the g-vector dependence of contrasts in DF images as shown in Fig. 6(e). It is understood that the polarization vectors in each domain are parallel to the (201)₀ direction in the [100]₀ planes. Because the adjacent (201)₀ polarization vectors are not orthogonal, this domain structure can be characterized by non-180° domain walls. Thus, the ferroelectric state below T₂ can be identified as the M₀-type monoclinic state. The FMC domain structure determined here is identical to that reported in the FT phase of PMN–xPT.32

To reveal the origin of the dielectric anomaly at T₂, in situ TEM observation was carried out during heating. The heating rate of the samples was estimated to be approximately 1 K/min. Figure 7 presents a series of dark-field images of the same area in an x = 0.95 sample (high PT content), together with a corresponding [001]₀ electron diffraction pattern, as well as showing the temperature dependence of ε’ in the inset. T_C (= T₁) and T₂ for x = 0.95 were estimated to be approximately 730 and 560 K, respectively, from the state diagram in Fig. 4. The images in Figs. 7(a) and 7(a’), 7(b) and 7(b’), 7(c) and 7(c’), and 7(d) and 7(d’) were taken at 300 K (room temperature), 523, 563, and 633 K, respectively, upon heating. The scattering vectors of g = 020 and 020 were used for the images in Figs. 7(a)–7(d) and for those in Figs. 7(a’)–7(d’). Among these images, the images at 300 K, Figs. 7(a) and 7(a’), exhibit a relatively uniform contrast, indicating that the ferroelectric state below T₂ is not the FT state. When the temperature was raised above 300 K, a change in contrast was detected near T₂. Here, we focused on the variants, in which 180° domain boundaries could be observed, as indicated by the yellow arrows in Figs. 7(a) and 7(a’). In Figs. 7(b)–7(d) and 7(b’)–7(d’), bright- and dark-contrast regions denoted by A and B are seen. Notably, the bright-contrast regions A in the image for g = 020 are observed as dark-contrast regions in the image for g = 020. That is, contrast reversal occurs in the g = 020 and g = 020 images. This suggests that regions A and B have polarization vectors parallel to the [010]₀ and [010]₀ directions, respectively, as indicated in Figs. 7(c) and 7(c’). These results demonstrate that T₂ corresponded to the (FMC → FT) transition.

In addition to an x = 0.95 sample with high PT contents, we investigated the (FMC → FT) transition in an x = 0.65 sample with low PT contents. Figure 8 presents a series of dark-field images of the same area in an x = 0.65 sample, together with a corresponding [001]₀ electron diffraction pattern, as well as showing the temperature dependence of ε’ in the inset. The heating rate of the samples was approximately 1 K/min. T_C (= T₁) and T₂ for x = 0.65 were estimated to be approximately 650 and 550 K, respectively, from the state diagram in Fig. 4. The images in Figs. 8(a) and 8(a’), 8(b) and 8(b’), 8(c) and 8(c’), and 8(d) and 8(d’) were taken at 300, 600, 650, and 720 K, respectively, upon heating. The scattering vectors of g = 200 and 200 were used for the images in Figs. 8(a)–8(d) and for those in Figs. 8(a’)–8(d’), respectively. A uniform contrast is observed over the entire region at 300 K, despite the presence of the 180° domain boundaries indicated by the arrows. That is, the initial state at 300 K was not the FT
state but the FM\textsubscript{C} state. When the temperature was increased above 300 K, no change in contrast was detected in the temperature range between $T_2$ and $T_1$, as observed in Figs. 8(b)–8(d) and 8(b')–8(d'). This result is entirely different from the aforementioned result for an $x=0.95$ sample. It is additionally notable that banded contrasts remained even at a temperature approximately 70 K higher than $T_C$, as observed in Figs. 8(d) and 8(d'). This finding indicates that the FM\textsubscript{C} state remained even above $T_C$.

The present experimental data revealed that the ferroelectric state for $0.60 \leq x < 1.0$ had an M\textsubscript{C}-type monoclinic symmetry with [201]\textsubscript{C} polarization in the \{100\}\textsubscript{C} planes. Notably, the FM\textsubscript{C} state could be characterized by pseudo 180 and 90° domain structures, in which the polarization rotated slightly from the (001)\textsubscript{C} direction of the FT state. In situ TEM observation for $x=0.95$ during heating revealed, moreover, that the (FM\textsubscript{C} $\rightarrow$ FT) transition occurred at around $T_2$, at which a dielectric anomaly could be detected. For $x=0.65$, however, the (FM\textsubscript{C} $\rightarrow$ FT) transition could not be observed near $T_2$, and the domain structure exhibiting banded contrasts did not disappear even above $T_C$. In other words, despite using the same heating rate conditions, neither the (FM\textsubscript{C} $\rightarrow$ FT) nor (FT $\rightarrow$ PC) transition occurred. The differences in the phase transition behaviors for $x=0.65$ (low PT content) and 0.95 (high PT content) are discussed below based on the features of the domain structures of the FM\textsubscript{C} state.

As mentioned above, the polarization vector in the FM\textsubscript{C} state is parallel to the (201)\textsubscript{C} directions in the \{100\}\textsubscript{C} planes. The (201)\textsubscript{C} polarization vector appears to be pr-
tering vector with $x$ in (a), (b), (c), and (d) were taken at 300 K for PSN–xPT samples with $x = 0.95, 0.90, 0.75$, and $0.65$, respectively, using the scattering vector $g = 110$.

duced by the introduction of [100]$C$ or [010]$C$ components to the original [001]$C$ polarization in the FT state. This introduction of [100]$C$ or [010]$C$ components could have a significant effect on lattice distortion. Figure 9 presents dark-field images indicating the changes of 180° domain boundaries as a function of PT content. The images in (a), (b), (c), and (d) were taken at 300 K of PSN–xPT samples with $x = 0.95, 0.90, 0.75$, and $0.65$, respectively, using the scattering vector $g = 110$. Observation of Fig. 9(a) for $x = 0.95$ shows that the 180° domain boundaries are relatively rectilinear compared with the other samples. In Figs. 9(b)–9(d), however, the boundaries are seen to be curved, and complex contrasts indicating the presence of lattice distortion are observed, as indicated by the arrows and dotted circles. That is, these images demonstrate that as the PT content decreased, the lattice became more distorted. This lattice distortion likely plays a role in restricting the structural change.

In the FT state, twin structures are formed and each unit lattice fits between twin interfaces. When the (FT $\rightarrow$ FM$_C$) transition occurs, however, the [001]$_C$ polarization vector in the FT state rotates to the [100]$_C$ or [010]$_C$ direction in the [100]$_C$ planes together with elongation of the lattice. These changes could cause distortion at the twin interface. That is, the crystal stabilizes the monoclinic state by relaxing the interface instead of eliminating the distortion. This phenomenon might explain why no changes in the ferroelectric domain structure could be detected during the heating process in an $x = 0.65$ sample containing large lattice distortions. To ease the internal crystal structures for $x = 0.65$ to enable the polarization vector to be rotated, it may be necessary to raise the temperature more slowly to allow sufficient time for in situ TEM observation at each temperature. It was eventually understood that the difference in the (FT $\rightarrow$ FM$_C$) transition behavior for $x = 0.65$ and 0.95 could be explained as being due to the associated degree of polarization rotation and lattice distortion, both of which were caused by PT substitution.

4. Conclusions

To clarify the features of the FT state in PSN–xPT, the crystallographic features of the ferroelectric states for $0.60 \leq x < 1.0$ were examined using TEM with the help of the failure of Friedel’s law. In situ TEM observations revealed that the ferroelectric state for $0.60 \leq x < 1.0$ was the monoclinic M$_C$ state with (201)$_C$ polarization vectors in the [100]$_C$ planes. The FM$_C$ state was characterized by pseudo 90 and 180° domain structures, in which the polarization rotated slightly from the [001]$_C$ direction of the FT state. As the PT content decreased, the polarization rotation and associated lattice distortion increased. Based on in situ TEM observation and permittivity measurement, furthermore, it was found that the (FM$_C$ $\rightarrow$ FT) transition occurred at approximately 560 K below $T_C$ for $0.60 \leq x < 1.0$. In an $x = 0.65$ sample containing large lattice distortions, lattice distortions significantly contributed to the suppression of the (FM$_C$ $\rightarrow$ FT) transition. In an $x = 0.95$ sample with smaller lattice distortions, on the other hand, the (FM$_C$ $\rightarrow$ FT) transition could be detected at around $T_C$.

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