Tetragonal Distortion of a BaTiO$_3$/Bi$_{0.5}$Na$_{0.5}$TiO$_3$ Nanocomposite Responsible for Anomalous Piezoelectric and Ferroelectric Behaviors

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1. INTRODUCTION

Ferroelectric materials are commonly used in sensors, actuators, and transducer technologies due to their unique ability to couple electrical- and mechanical-energy transformations. In recent years, lead-free piezoelectric materials have drawn significant attention due to their eco-friendly nature. Up to now, the lead-free piezoelectric materials have been competitive for some specific properties but still not good enough to replace the lead-based one (Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$, PZT). In the lead-free piezoelectric families, Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT) is a promising candidate for the replacement of PZT materials because of its high Curie temperature ($T_c$) of 320 °C and relatively large remanent polarization ($P_r$) of 38 μC/cm$^2$. However, difficulty in poling limits its application as a basic material for device manufacture. On the other hand, BaTiO$_3$ (BT) exhibits a much higher piezoelectric response ($d_{33}$) than commercialized PZT, while its $T_c$ (120 °C) still restrains its application range. The formation of solid solutions for perovskite ferroelectric materials has frequently been utilized to improve their dielectric, piezoelectric, and ferroelectric properties. Specifically, (1 − x)BNT−xBT solid solution with formation of the morphotropic phase boundary (MPB) at $x = 0.07$ exhibited a highly elevated $d_{33}$ of ∼322 pC/N compared with ∼78 pC/N of BNT, but it showed a lower $T_c$. To solve the problem, strain engineering has been applied to 2D ferroelectric materials to improve the $T_c$ by using the lattice mismatch between the thin film and its substrate with different lattice constants, which creates the 2D heteroepitaxial interface. The $T_c$ of BT has been dramatically increased to over 540 °C, while the improvement of $d_{33}$ has not yet been reported. Researchers have concentrated more on making use of the lattice mismatch between two different ferroelectric materials with different lattice constants, such as BT/SrTiO$_3$, BT/KNbO$_3$ and BT/BiFeO$_3$. Recently, both the $d_{33}$ and $T_c$ of mesocrystalline BT/BNT nanocomposite have been successfully improved by introducing strain engineering with a 3D heteroepitaxial interface. The increase in the $T_c$ of BT/BNT nanocomposite could be attributed to the highly tetragonal distortion of BT or BNT that originated from the interface. The $T_c$ of BT/BNT solid solution is expected to be enhanced with the introduction of the 2D heteroepitaxial interface.
and Mastelaro et al. used XAS to detect the change of tetragonality in PbTiO$_3$ compounds with the replacement of Pb by Ca and La, respectively.\textsuperscript{19,23} Herein, to better understand the tetragonal distortion of a ferroelectric perovskite BT/BNT nanocomposite, X-ray diffraction (XRD) and Ti $L_{2,3}$ edge XAS analyses were employed to verify the role of the heteroepitaxial interface in the anomalous ferroelectric behavior of mesocrystalline ferroelectric BT/BNT nanocomposites.

2. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of perovskite BT obtained from the hydrothermal treatment of HTO and Ba(OH)$_2$ at 200 °C for 12 h and BT samples obtained after heating treatment at different temperatures for 3 h. It can be clearly seen that the pure BT phase was obtained after the hydrothermal reaction, which seems to show the cubic structure has a centrosymmetric TiO$_6$ octahedron without Ti $\hat{o}$ (Figure 1f), which exhibits paraelectric behavior.\textsuperscript{24} To increase the crystalline size and the crystallinity of the BT sample, the heating treatment was applied. By increasing the heating temperature, the crystalline size increased to 100, 200, and 400 nm for BT-700, 1000, and 1200, respectively (Figure 2b–e). Moreover, the plate-like morphology of BT was maintained until 1000 °C. By further increasing the heating temperature up to 1200 °C, the splitting of the (200) peak into (002) and (200) peaks appeared (Figure 1e), indicating the formation of the tetragonal structure of the BT sample ($a' = b' = 3.994$ Å, $c = 4.038$, $c'/a = 1.011$).\textsuperscript{25} The Ti off-center displacement of TiO$_6$ formed the dipoles, where all the cations moved slightly toward the [001] direction, and the two oxygen anions along [001] moved toward the opposite direction, as shown in the right ball model of Figure 1f.\textsuperscript{25} It shows a macroscopic $P_s$ along the [001] direction, namely, ferroelectricity. It is well known that ferroelectric perovskite oxides with giant tetragonality ($c/a$) have large polarization values and high $T_c$ as a result of the large dipolar moment.\textsuperscript{12}

For comparison, the BNT sample was also successfully fabricated. The same amount of BNT and the aforementioned BT powders obtained at 700 °C were physically mixed for the XRD measurement (Figure 3a). Based on the XRD analysis, both individual BT-700 and BNT-700 samples seemed to exhibit the cubic structure with lattice parameters of $a = 4.006$ and 3.890 Å, respectively. In addition, they are both mesocrystals constructed from corresponding nanocrystals with the same orientation direction along [110] with plate-like morphology as shown in Figures 2b,e and 3d\textsuperscript{9,27} and single-crystal-like selected area electron diffraction patterns.\textsuperscript{16,22} Mesocrystals are polycrystals constructed from the uniform distribution of nanocrystals, and each nanocrystal shows the same orientation direction and single-crystal-like selected area electron diffraction (SAED) pattern.\textsuperscript{9,16,27} For the formation of the plate-like BT/BNT nanocomposite, a two-step reaction process was employed. In the first step, the plate-like HTO crystals were solvothermally reacted with Ba(OH)$_2$ (Ba/Ti = 0.5) to obtain a BT/HTO nanocomposite.\textsuperscript{16,17,28} In the second step, a mixture of BT/HTO, 20% excess Bi$_2$O$_3$, and 40% excess Na$_2$CO$_3$ was calcined to obtain the BT/BNT nanocomposite. The excess of Bi$_2$O$_3$ and Na$_2$CO$_3$ not only guarantees the complete reaction with residual HTO in BT/HTO but also avoids their evaporation loss during the heating treatment.\textsuperscript{17} After the heating treatment at 700 °C, a mixture of BT and BNT phases was seen, as shown in Figure 3b. In the meantime, the plate-like morphology of BT/BNT-700 was seen from the FE-SEM image (Figure 2f). Moreover, the plate-like particle was the polycrystalline particle constructed from nanocrystals, which was confirmed by the transmission electron microscope (TEM) image (Figure 4a). Moreover,
two sets of SAED patterns corresponding to the BT phase and the BNT phase were observed simultaneously in one plate-like particle (Figure 4b). The SAED result also revealed that the BT and BNT nanocrystals in the mesocrystalline BT/BNT-700 had the same crystal-axis orientation direction in the [110]-zone axis, and the lattice constant of the BT phase was slightly larger than that of the BNT phase, which also agrees well with the XRD result in Figure 3. The chemical composition distributions in the plate-like particle were investigated using energy dispersive X-ray spectroscopy (EDS) analysis (Figure 4c).28,29 Three positions (labeled “①”, “②”, and “③” in Figure 4a) in the BT/BNT-700 particle presented almost the same EDS spectra, suggesting a homogeneous chemical composition distribution in the plate-like particle. The C and Cu elements were from the copper grid used for the sample holder, but all the remaining elements corresponded to BT/BNT-700, suggesting no impurities.

BT in the BT/BNT-700 mesocrystal exhibited the same cubic structure as the individual BT-700 mesocrystal based on the XRD analysis in Figure 3. However, the structure of BNT in the BT/BNT-700 mesocrystal could not be confirmed from the XRD analysis.16 It can be clearly seen from Figure 3c (scanning range of 31°–33°) that the (110) peak of BNT in BT/BNT-700 shifted to a lower diffraction angle compared with the individual BNT-700, indicating the increase in the lattice constant due to the tensile strains from the larger lattice constant of neighboring BT. However, the (110) peak of BT in BT/BNT-700 showed no peak shifting toward a higher angle,

Figure 3. XRD patterns of (a) physically mixed BT and BNT powder samples with the same weight and the (b) BT/BNT-700 sample. Panel (c) is from the range (31° to 33°) of (a) and (b). (d) Schematic images of BT-700, BNT-700, and BT/BNT-700 mesocrystals and heteroepitaxial interfaces in the BT/BNT-700 mesocrystal. (e) Polarization–electric field (P–E) hysteresis loops of pellet samples of BT-700, BNT-700, and BT/BNT-700. Adapted with permission from ref 16. Copyright 2018 Royal Chemical Society.

Figure 4. (a) TEM image, (b) SAED pattern, and (c) EDS spectra of the BT/BNT-700 mesocrystal.
which can be explained by the fact that the BT nanocrystals in the BT/BNT-700 mesocrystal formed in the first step of the solvothermal reaction and the BNT nanocrystals formed and coherently grew on the BT nanocrystals during the second step of the heating treatment. Furthermore, the continuous area between BT and BNT was the heteroepitaxial interface area of BNT growth on BT, which is schematically described in Figure 3d. Subsequently, the tensile force to BNT caused the transition formation of BNT by gradually decreasing the lattice constant, as shown in Figure 3d, suggesting the expansion of the (110) plane of BNT according to the crystallographic relationship. To determine the crystalline sizes of the BT and BNT nanocrystals in the BT/BNT-700 mesocrystal and further confirm its strains, the Williamson–Hall equation was utilized, which is simply expressed as follows: \[ \beta_{hkl} \cos \theta = \frac{K \lambda}{D} + 4 \sin \varepsilon \theta \] where \( \beta_{hkl} \) is the full width at half maximum (FWHM) value for each diffraction peak, \( K \) is the shape factor (0.89), \( \lambda \) is the wavelength of Cu K\( \alpha \) (0.154 nm) radiation, \( D \) is the crystalline size, and \( \varepsilon \) is the integral breadth related to the strain. Hence, by plotting the graph of \( \beta_{hkl} \cos \theta \) against \( 4 \sin \theta \), the crystalline size and the lattice strain of samples can be estimated from the intercept and slope of the Williamson–Hall plot, respectively. Figure 5 shows the Williamson–Hall plots of BT and BNT in ferroelectric but not paraelectric responses, suggesting that they were not cubic structures, which contradicted the XRD results. Moreover, the converse piezoelectric responses of BT-700, BNT-700, and BT/BNT-700 were measured by the piezoresponse force microscopy (PFM) technique, where BT/BNT-700 showed a large piezoelectric response of 408 pm/V, suggesting its ferroelectricity. In the meantime, BT-700 and BNT-700 showed weak piezoelectric responses, revealing their weak ferroelectricity.\(^{16}\) Actually, it is well known that BT and BNT perovskites prepared by low-temperature processes, such as hydrothermal, solvothermal, and sol–gel processes, have pseudo-cubic structures, which are almost cubic with very little distortion at the crystal plane angle and are difficult to distinguish from XRD results. The lattice defects, low crystallinity, and small crystal sizes are responsible for the formation of the pseudo-cubic BT and BNT phases.\(^{28,35}\) The results demonstrated that both the BT-700 and BNT-700 samples showed pseudo-cubic structures (\( c/a = 1.000 \)).

The strain induced by the lattice mismatch between BT and BNT can generally lower the crystal symmetry from cubic (\( O_h \)) to tetragonal (\( D_{4h} \)). Therefore, Ti L\( \alpha \)-edge XAS can be employed to determine the actual symmetry of the TiO\( _6 \) octahedron of BNT in the BT/BNT nanocomposite and elucidate the anomalous ferroelectric behavior.\(^{19,36,37}\) Figure 6 shows Ti L\( \alpha \)-edge XAS spectra for the BT-500, BT-700, and BT-1200 samples. These spectra have L\( _3 \) and L\( _2 \)

![Figure 5. Williamson–Hall plots of BT/BNT-700 samples (BT in BT/BNT-700 and BNT in BT/BNT-700); SrTiO\(_3\) standard was analyzed for instrumental calibration.](image)

the BT/BNT-700 mesocrystal. The instrumental broadening was determined by the SrTiO\(_3\) standard. The crystalline size of SrTiO\(_3\) was 80 nm by the calculation and was obviously independent of the d-spacing (\( 4 \sin \theta \)), which suggests that the instrumental broadening and strain in the sample were negligible.\(^{32,33}\) The crystalline sizes of BT and BNT in BT/BNT-700 were calculated to be 39 and 46 nm, respectively. The positive slope value for BNT in BT/BNT-700 confirmed the existence of tensile strain. On the other hand, BT in BT/BNT-700 showed a very small negative value within the error bars, making it difficult to confirm the strain type.

In order to obtain convincing evidence to identify the intrinsic ferroelectric properties of the materials, we measured their \( P–E \) hysteresis.\(^{14}\) Figure 3e shows the \( P–E \) hysteresis loops of the pellet samples of BT-700, BNT-700, and BT/BNT-700. The BT/BNT-700 nanocomposite showed ferroelectric behavior with a large \( P \) value of 2.4 \( \mu \)C/cm\(^2\), whereas the BT-700 and BNT-700 samples showed very weak regions created by the spin–orbit interaction, and each region contains \( t_2g \) and \( e_g \) peaks separated by approximately 2.10 eV by crystal-field splitting (\( \Delta L_3 \)). The \( L_3 \) \( e_g \) state, which consists of 3\( d_{x^2−y^2} \) and 3\( d_{xy−yz} \) orbitals, is directed toward ligand anions and is therefore more sensitive to deviations from the Ti octahedral symmetry, which means the \( e_g \) orbital is expected to split and shift to lower energy for tetragonal distortion in the symmetry of the TiO\(_6 \) octahedron.\(^{36}\) By increasing the heating temperature, the area intensity of the spectra was increased. Based on the XRD results (Figure 1), BT-500 and BT-700 showed pseudo-cubic structures with nearly centrosymmetric TiO\(_6 \) octahedra, resulting in no decrease in \( \Delta L_3 \) or splitting of the \( e_g \) orbital. The BT-1200 sample showed a tetragonal structure (\( c/a = 1.011 \)) with a non-centrosymmetric TiO\(_6 \) octahedron. However, there was no peak splitting or shifting of the \( e_g \) orbital, suggesting that the tetragonal distortion of the TiO\(_6 \) octahedron was not obvious. Similar behavior has also been found when Ba atoms are substituted for Sr atoms in the Ba\(_{1−x}\)Sr\(_x\)TiO\(_3\) ceramic system.\(^{37}\) Torres-Pardo et al. demonstrated that significant Ti off-centering is only observed once the tetragonality exceeds \( c/a = 1.020 \) for SrTiO\(_3\), confirming the paraelectric state \( c/a = 1.000 \) as the predicted ground state.
by local density approximation (LDA) calculations. It is similar to the case of PbTiO$_3$ where the bulk phase with a tetragonal structure ($c/a = 1.030$) exhibited L$_3$ eg peak splitting with a $\Delta L_3$ of 1.80 eV, and a PbTiO$_3$ thin film ($c/a = 1.063$) deposited on the SrTiO$_3$ substrate exhibited L$_3$ eg peak splitting with an even smaller $\Delta L_3$ of 1.65 eV.

Figure 7a shows the Ti L-edge XAS spectra for BT-700, BNT-700, and BT/BNT-700. The L$_3$-edge eg orbital centered at 460 eV for BT-700 reveals the centrosymmetry of the TiO$_6$ octahedron; that is, the structure of BT-700 is pseudo-cubic. Similarly, the TiO$_6$ octahedron in BNT-700 also keeps the pseudo-cubic centrosymmetric structure. They are all consistent with the XRD results in Figure 3a.

For the BT/BNT-700 sample, on the other hand, the L$_3$-edge eg peak has an asymmetric profile tailing toward high energy and peaking at lower energy than BT-700 and BNT-700 (Figure 7a). The asymmetric profile of the eg peak directly indicates the tetragonal distortion of the TiO$_6$ octahedron of BNT in BT/BNT-700, as revealed by the XRD result. We investigated the tetragonal distortion in detail by a Gaussian fitting of the eg peak. The BT/BNT-700 sample should have had the BT-700 region without tetragonal distortion as well as the BNT region with tetragonal distortion. Then, we assumed a fixed Gaussian (peak 3 in Figure 7e) peaking at the same energy as BT-700, and two Gaussians (peaks 1 and 2) representing the split eg peaks originated from the distorted BNT-700. Figure 7e shows the three Gaussian fittings of the eg peak of BT/BNT-700. The relatively higher intensity of peak 1 than peak 2 is consistent with previous results on Fe implanted SrTiO$_3$ and TiO$_2$ anatase. A recent Ti 2p XAS calculation for rutile and anatase TiO$_2$ using a sizable supercell and the Bethe–Salpeter equation reproduced not only the splitting of the eg peak (peaks 1 and 2) distributed across the single peak 3 but also the enhancement of peak 1 for anatase and peak 2 for rutile TiO$_2$. The different eg peak profiles between anatase and rutile TiO$_2$ can be explained largely by differences in the binding energies of the excitons for the corresponding eg peaks. The enhancement of peak 1 in the present case may have a connection with the localized character of the eg state for the highly defective structure typical for anatase, which constructs the asymmetric profile peaking at a lower energy than that of BT-700 and BNT-700. This also leads to the observed reduction in $\Delta L_3$ from 2.00 eV (e.g., BNT-700) to 1.85 eV.

The Gaussian fitting of the eg peak also allowed us to estimate the volume ratio of BT-700 and BNT-700 by comparing the area intensity ratio of the sum of peaks 1 and 2 with that of peak 3. The obtained value of 1.18 is close to the expected volume ratio (1.23) of BNT and BT in BT/BNT-700. The slightly lower than expected value may be due to the less heteroepitaxial interface depicted in Figure 3d.

As shown in Figure 7b–d, the ratio of the area intensity of the eg and t$_{2g}$ peaks ($A_{eg}/A_{t_{2g}}$) for BT-700, BNT-700, and BT/BNT-700 were estimated to be 2.71, 2.83, and 3.24 by simply fitting the L$_3$-edge using two Gaussians and background subtractions. According to the configuration interaction (CI) cluster model calculations by Wu et al., simulated eg peaks in Ti 2p XAS spectra for tetragonally distorted SrTiO$_3$-based thin films by the strain from the substrate shift to lower energy (corresponding to the smaller $\Delta L_3$) and the increased $A_{eg}/A_{t_{2g}}$.  

Figure 7. (a) Ti L$_3$-edge XAS spectra and (b–d) their peak fitting of Ti L$_3$ edge by Gaussian after background subtraction with two arctangent functions in the form of $y = \arctan \left(\frac{x + x_0}{y_0}\right) + y_0$ shown as dashed lines for BT-700, BNT-700, and BT/BNT-700. (e) Peak fitting of the L$_3$ eg peak by Gaussians after same background subtraction. (f) Symmetry transformation of a TiO$_6$ octahedron from cubic to tetragonal by (110) plane tensile strains.
Thus, it can be concluded that the BNT phase subjected to tensile strain in a (110) plane from the BT phase caused a tetragonal distortion with the expansion of the [001]-axis Ti–O bond length, as shown in Figure 7f. Otosuki et al.45 reported the ΔL1 and the tetragonal distortion (c/a) of a TiO6 octahedron by employing different strains, where the c/a ratio was estimated to be 1.020 in BNT of BT/BNT-700. On the other hand, the lattice mismatch between BT and BNT in BT/BNT-700 was calculated to be 2.14% from the XRD result, suggesting that the tensile strains almost contribute to the tetragonal distortion of BNT in BT/BNT-700. Tensile strains often lead to the improvement of the ferroelectricity of the ferroelectric material or turn paraelectric behavior into ferroelectric behavior.10−12 The present result explains how the tensile strain causes the tetragonal distortion only in the BNT phase, which is responsible for the anomalous ferroelectric properties of the BT/BNT nanocomposite. Now, we know that the tetragonal distortion can be well confirmed, and its c/a ratio can be estimated using XAS. The increasing shifts and split of the Ti L3 edge peak for the BT/BNT nanocomposite indicate larger tetragonal distortion at the BNT site. Ferroelectricity with larger tetragonality (c/a) exhibits improved ferroelectric and piezoelectric behaviors of materials.69 In this paper, we identified the connection between the tetragonal distortion and the corresponding modification in the electronic structure only at the BNT site that is responsible for the change of ferroelectricity in the BT/BNT nanocomposite.

3. CONCLUSIONS

BT-700, BNT-700, and BT/BNT-700 mesocrystal samples were successfully synthesized, and their structures were confirmed by XRD measurement. Both BT-700 and BNT-700 showed weak-ferroelectric pseudo-cubic structures (c/a = 1.000). BT with a tetragonal structure (c/a = 1.011) was obtained after heating treatment up to 1200 °C. In the BT/BNT-700 nanocomposite, the BT phase did not suffer strain from the neighboring BNT phase, while the BNT phase was highly tetragonally distorted, which was also confirmed by the Williamson–Hall method. The electronic structure of the corresponding samples was also confirmed by Ti 2p XAS. The Ti 3d(e_g) peak shift and splitting of the BT sample heated at 1200 °C could not be detected due to insignificant tetragonal distortion. Ti 3d(e_g) peak shift and splitting were observed for the BT/BNT-700 nanocomposite, which is ascribed to a significant tetragonal deformation (c/a = 1.020) of the TiO6 octahedron of BNT in the BT/BNT nanocomposite caused by the lattice mismatch between BT and BNT. That is, the tetragonally distorted BNT in BT/BNT should be responsible for the improved ferroelectric behavior of the mesocrystalline BT/BNT nanocomposite.

4. EXPERIMENTAL SECTION

4.1. Fabrication of Perovskite Mesocrystals. The mesocrystalline BT/BNT nanocomposite was prepared from an HTO powder sample as reported in our previous study.16 For the synthesis of the plate-like mesocrystal samples of BT and BNT for comparison, the plate-like HTO crystals (0.4 g) and Ba(OH)2·8H2O (mole ratio of Ba/Ti = 1.2) were hydrothermally treated in 30 mL of distilled water under stirring conditions at 200 °C for 12 h. Then, the obtained samples were washed with distilled water and dried at 60 °C. Finally, the obtained BT samples were heat treated at different temperatures for 3 h at a heating rate of 10 °C/min. The BNT was prepared according to the reference.47 The samples obtained by heat treatment were designated as BT/BNT-X, BT-X, and BNT-X, where X represents the heating temperature.

4.2. Characterization. The structures of powder samples were investigated using a powder X-ray diffractometer (Shimadzu, XRD-6100) with Cu Kα (λ = 0.154 nm) radiation. The particle size and morphology of the samples were observed using FE-SEM (Hitachi, S-900).

The P–E loops of the pellet samples were measured using a ferroelectric testing system (Toyo Corporation, FCE3-4KVSY) at room temperature. XAS measurement was carried out at BL07LSU of SPring-8. The Ti L3-edge XAS spectra for the samples fabricated in this research were obtained in the total-electron-yield detection mode. Note that XAS in the total-electron-yield mode is not as surface sensitive as photoelectrons, and although all the samples in this study have a mesocrystalline structure with uniform distribution of nanocrystals, it is safe to say that we can mostly probe the characteristics of the entire particle using XAS in the total-electron-yield mode.

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Notes
The authors declare no competing financial interest.

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