In-situ electric field induced lattice strain response observation in BiFeO$_3$–BaTiO$_3$ lead-free piezoelectric ceramics

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The electric field-dependent crystal structures and electrical properties were investigated in the 0.67BiFeO$_3$–0.33BaTiO$_3$ (BF33BT) lead-free piezoelectric ceramics. The room temperature synchrotron radiation X-ray diffraction (SR-XRD) patterns measured, without the application of an electric field, revealed all the peaks to be single suggesting the cubic-like crystal structure of the BF33BT system. The domain switching was ascertained in the $P$–$E$ hysteresis loop and $S$–$E$ curve meanwhile, SR-XRD patterns exhibited beyond doubt single peak. In order to study the electric field induced structural phase transition, SR-XRD was measured in BF33BT ceramics as a function of electric field. The electric field applied up to 40 kV/cm with bipolar cycling was parallel along the longitudinal lattice response direction that was similar for the piezoelectric response measuring method. The shift of SR-XRD peaks to lower and/or higher angle in comparison to the peak position of zero field-SR-XRD was found to depend on the direction and intensity of the applied electric field. The peak shape under maximum electric field was quite same that of SR-XRD patterns at zero electric field. Importantly, the single peak shape was maintained for all the SR-XRD measured under the electric field. Therefore, the electric field induced structural phase transition did not occur in the BF33BT ceramics.

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1. Introduction

Lead-based piezoelectric ceramics, such as lead zirconate titanate [Pb(Zr,Ti)TiO$_3$, PZT], in the original or various modified forms, have been widely used for actuators, transducers, and sensors applications due to their excellent electrical properties around the morphotropic phase boundary (MPB) composition. However, the lead-free piezoelectric materials have been attracting lots of attention due to the increased awareness of environmental safety of regarding the toxic nature of lead and lead-oxide.$^{1-3}$

The various lead-free piezoelectric ceramics have been studied for potential applications and the good performances comparable to those of PZT ceramics has been obtained for (K,Na)NbO$_3$ (KNN)-based piezoelectric system.$^{4}$ Among the various lead-free piezoelectric ceramics, the Bi-based systems have attracted attention due to their high spontaneous polarization and large piezoelectric response.$^{5,6}$

It has been reported that the pure (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (BNT) has a large remanent polarization ($P_r = 38 \mu \text{C/cm}^2$)$^{7}$ and a low piezoelectric coefficient ($d_{33} = 58 \text{ pC/N}$)$^{8}$ Moreover, a large piezoelectric coefficient was observed at MPB compositions of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$–BaTiO$_3$ (BNT–BT)$^{9,10}$ and (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$–(Bi$_{0.5}$K$_{0.5}$)TiO$_3$ (BNT–BKT) solid solutions. Because of the large piezoelectric coefficients of BNT-based materials, they were studied extensively for possible replacements of PZT. The BNT-based piezoelectric ceramics, however, are limited in real applications due to the presence of depolarization temperature ($T_d$)$^{11}$

On the other hand, BiFeO$_3$-based materials are being studied as substitutes for lead-based materials due to the prominent electrical properties, high Curie temperature, and absence of $T_d$.$^{12-14}$ Recently, it was reported that the large piezoelectric coefficient were 420 and 324 pC/N in 0.67Bi$_{1.05}$(Fe$_{0.95}$Ga$_{0.05}$)O$_3$–0.33BaTiO$_3$ and 0.97$\cdot$[0.67Bi$_{1.05}$FeO$_3$–0.33BaTiO$_3$]$\cdot$0.03Bi$_{1.05}$(Zn$_{0.5}$Ti$_{0.5}$)O$_3$ ceramics with Curie temperature above 450°C.$^{15}$

One of the peculiarities of the Bi-based lead-free piezoelectric ceramics is their large spontaneous polarization and piezoelectric response in the slightly distorted cubic structure; pseudo-cubic structure. For example, the strain is 0.45% in the 0.92(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$–0.06BaTiO$_3$–

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$0.02(K_{0.5}Na_{0.5})NbO_3$ with pseudo-cubic structure.\textsuperscript{16}) Likewise, the large spontaneous polarization and large piezoelectric response has been reported for the BiFeO$_3$–BaTiO$_3$ (BFBT) ceramics with pseudo-cubic structure.\textsuperscript{23} The remnant polarization and strain are 15.2 $\mu$C/cm$^2$ and 0.16%, in Mn-doped 0.67BiFeO$_3$–0.33BaTiO$_3$ ceramics with pseudo-cubic structure.\textsuperscript{17} The large electrical properties (spontaneous polarization and piezoelectric response) observed in the pseudo-cubic structure, however, cannot be explained with small crystal structure distortion. The demonstration of the electrical properties by a pseudo-cubic structured system might be related to a structural phase transition under a large applied electric field. The electric-field-induced structural phase transition has been observed in the Bi-based lead-free piezoelectric ceramics.\textsuperscript{18} J. E. Daniels et al. reported that the electric-field-induced strain in 0.93(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$–0.07BaTiO$_3$ lead-free piezoelectric ceramics was originated due to the electric-field-induced crystal structure transformation from a pseudo-cubic structure to a tetragonal one.\textsuperscript{19} The electric field induced structural phase transition in the BNT–BT lead-free ceramics is well reported. However, existence of a structural phase transition under an applied electric field is not clear in the BFBT system.

In this study, the 0.67BiFeO$_3$–0.33BaTiO$_3$ (BF33BT) lead-free piezoelectric ceramics were prepared by a solid-state reaction method. The crystal structure under various electric fields in the BFBT lead-free piezoelectric ceramics was investigated by synchrotron radiation X-ray diffraction (SR-XRD).

2. Experiment

The 0.67BiFeO$_3$–0.33BaTiO$_3$ (BF33BT) lead-free ceramic was fabricated by a conventional solid-state reaction method using BiFeO$_3$ (BF, Nippon Chemical Industrial) and BaTiO$_3$ (BT, Sakai Chemical Industry Co. Ltd.) powders. The powders were ball-milled with zirconia ball and ethanol for 24 h. The wet powders were dried in the oven, and then they were calcined at 800°C for 6 h. The calcined powders were again ball-milled and dried. A polyvinyl butyral (PVB) binder was added for uniaxial pressing. The pellets were formed with 10 mm diameter and 1 mm thickness. The pellets were then burned for removing the PVB binder at 700°C for 10 h, and sintered at 1000°C for 4 h. Both surfaces of the sintered pellets were polished and cut into samples with two types of geometry for measuring electrical properties (1.50 mm × 4.00 mm × 0.40 mm) and SR-XRD measurements (0.30 mm × 0.30 mm × 7.50 mm) under electric fields. After annealing of the as-prepared samples (polished and cut) at 800°C for 20 h, the samples were taken out from furnace and quenched into water. The annealing and quenching process were performed in order to achieve to enhanced electrical properties (ferroelectric and piezoelectric) by a domain wall de-pinning and mechanical stress relaxation.\textsuperscript{20,21} The electrical properties of the quenched samples were successfully enhanced compared with those of virgin samples. The crystal structure of BF33BT with quenching and without quenching was investigated by a laboratory X-ray diffractometer (Ultima IV, Rigaku). The lattice constant of quenched sample was increased compared with that of virgin sample, meanwhile crystal symmetry was maintained, which is similar exhibited in the 0.80BiFeO$_3$–0.20BaTiO$_3$ ceramics.\textsuperscript{21}

The density of BF33BT ceramic is 92.5%, which was investigated by an Archimedes method. The Au electrodes were coated in samples surfaces for electrical properties and electric field induced synchrotron radiation X-ray diffraction measurement. The ferroelectric and electric-field-induced strain properties were investigated by a ferroelectric and strain measuring system (JP005-SE, Kitamoto Denshi) and the linear variable differential transformer (LVDT, Milltron 1202 IC, Mahr). The crystal structures were identified with high energy synchrotron radiation X-ray diffraction with transmission geometry at BL02B2 beam line in SPring-8.\textsuperscript{22} An X-ray beam with energy of 35 keV, wavelength of 0.354924(1) Å, and a size of 0.5 mm (vertical) × 3.0 mm (horizontal) was irradiated on the BF33BT samples. The sample was enrooted on the sample holder, and the Au electrodes were placed in the longitudinal direction of the incident X-ray beam. The sample was rotated along $\omega = -5.08^\circ$. The X-ray was exposed to the sides of samples which was uncoated by Au electrodes. The sample was rotated by $\Delta \omega = 5.00^\circ$ from $\omega = -7.58^\circ$ for 4 times along anticlockwise direction with maintaining continuous X-ray exposure on the sample. Diffraction X-ray was detected by a one-dimensional silicon sensor system (a MYTHEN X-ray detector system, Dectris). During the measurement procedure of SR-XRD, the electric field was increased from zero kV/cm to 40 kV/cm by 5 kV/cm and the SR-XRD patterns were measured for BF33BT ceramics at each applied electric field.

3. Results and discussion

The crystal structure of the 0.67BiFeO$_3$–0.33BaTiO$_3$ (BF33BT) ceramics investigated by a SR-XRD is shown in Fig. 1, which was measured at room temperature. The SR-XRD patterns clearly revealed ABO$_3$ type perovskite crystal structure without secondary phases.

The SR-XRD patterns with selected 2$\theta$ angles from 7.0 to 7.4° for (110), from 8.6 to 9.0° for (111), and from 10.0 to 10.4° for (200) peaks are shown in Figs. 1(b)–(d), respectively. It is worthy to notice that the diffraction peaks seem to exhibit cubic symmetry. The (110), (111) and (200) peaks are displayed in a single peak shape that can be observed only in the cubic structure. It is in agreement with the result that reported the crystal structure of BF33BT ceramics to have cubic structure with small distortion; a pseudo-cubic structure,\textsuperscript{17} which might be related to orbitals of A-site (Bi$^{3+}$ and Ba$^{2+}$) ions. It is well known that the interaction between 6p and 6s orbitals in Bi$^{3+}$ ion plays an important role for the octahedron distortion. The Ba$^{2+}$ ions with empty 6p orbital can inhibit the movement of Bi$^{3+}$ ions and thereby reducing structural distortion due to coexistence of Bi$^{3+}$ and Ba$^{2+}$ ions at A-site.\textsuperscript{23}

Figure 2 shows ferroelectric and electric-field-induced
strain properties of the BF33BT lead-free piezoelectric ceramics. The ferroelectric property was investigated by a polarization-electric field ($P-E$) hysteresis loop, which was measured by an AC bias with a frequency of 0.1 Hz at room temperature is shown in Fig. 2. The remanent polarization ($P_r$) of BF33BT was 19.9 $\mu$C/cm$^2$, while the coercive field ($E_c$) was 12.3 kV/cm under the applied electric field of 40 kV/cm.

The electric-field-induced strain property was investigated from strain-electric field ($S-E$) curve that was measured under the bipolar cycling with an AC bias of 0.1 Hz at room temperature. The maximum positive strain ($S_{P_{\text{max}}}$) is 0.15% at 40 kV/cm. The high field piezoelectric constant ($d_{33}$) for BF33BT was 375 pm/V, which was calculated as $S_{P_{\text{max}}}/E_{\text{max}}$. The maximum negative strain ($S_{N_{\text{max}}}$) of BF33BT was 0.04%.

The obtained large spontaneous polarization and piezoelectric response in the BF33BT ceramics is the most important point in our results despite the crystal structure of cubic-type symmetry as shown by SR-XRD in Fig. 1. A similar phenomenon has been observed in other Bi-based lead-free piezoelectric ceramics, which was strongly related to a structural phase transition under an applied electric field that was applied during the electrical property measurement. The electric-field-induced structural phase transition from pseudo-cubic crystal structure to tetragonal structure under the presence of external electric field in BNT–BT ceramics was well reported.

In order to study the crystal structure under the electric field, the SR-XRD was measured with various electric fields at room temperature. During the electric-field-dependent SR-XRD measurement, the electric field was applied along the longitudinal direction that was parallel to the lattice response direction and the direction of the applied electric field during SR-XRD measurement was similar to that of the piezoelectric response measuring system. The external electric field was applied with bipolar cycling from zero field up to ±40 kV/cm. The (110), (111), and (200) peaks of BF33BT as function of electric field are shown in Figs. 3(a)–3(c), respectively. The (110), (111), and (200) peaks were shifted to lower angles, while applying initial electric field from zero to the maximum electric field (+40 kV/cm). Then, the diffraction peaks were shifted to higher angles with decreasing electric field from 40 kV/cm to zero electric field. The shift of the diffraction peaks was saturated at the maximum diffraction angle and then shifted to lower angles again with the application of the electric fields in the opposite direction. The peak shift behaviors observed under the electric fields were similar to those of the 0.86BNT–0.14KNN and 0.3BaTiO$_3$–0.1(Mg$_{1/2}$Ti$_{1/2}$)$_2$–0.6BiFeO$_3$ lead-free piezoelectric materials.

It is worthy to mention that the shape of the diffraction peaks observed with and without the application of the electric fields, were exactly the same; single peak. Single peak for the zero electric field XRD patterns were reported to separate with the application of electric fields in BNT–BT and BNT–BT–KNN ceramics. The peak shape
behaviors under the electric field in BF33BT ceramics, however, showed distinct differences from those of BNT-based piezoelectric ceramics under the electric field. The single peak shape was maintained while applied electric field with bipolar cycling as shown in Fig. 3. Therefore, the electric field induced structural phase transition did not occur in the BF33BT ceramics.

The lattice strain response curves of the BF33BT ceramics was calculated with the amount of peak shift from the reference value (the peak position of the initial SR-XRD without applying electric field) by using each (110), (111), and (200) reflection peak as shown in Fig. 4. The obtained lattice strain response curves were similar to that of bulk S–E curve as shown in Fig. 2, however, the magnitude was slightly higher for lattice strain response because of difference measurement frequency as strain response depends on frequency.\(^{26}\) The maximum lattice strain response (\(LS_{\text{max}}\)) of BF33BT at an electric field of 40 kV/cm was 0.185% for (110), 0.206% for (111), and 0.296% for (200), respectively.

It is noteworthy that the hysteric lattice stain response curves were observed in the BF33BT ceramics. A hysteric lattice strain response curve is also observed in the BiScO\(_3\)–PbTiO\(_3\) ceramics,\(^{26}\) which is related to domain switching. The domain switching could be confirmed in the P–E hysteresis loop and S–E curve as shown in Fig. 2. However, the evidence of domain switching that is shown by change of intensities ratios of (111) and (1-11) peaks of rhombohedral structure\(^{26}\) was invisible in the electric-field-dependent SR-XRD pattern of the BF33BT ceramics.

The domain switching (in P–E hysteresis loop and S–E curve) and hysteric lattice strain observation in BF33BT ceramics with pseudo-cubic structure could be considered as a result of coexisting distorted polar crystal structure and non-polar crystal structure. It is reported that the local polar distorted rhombohedral structure is existed within non-polar cubic matrix in BFBT ceramics.\(^{27}\) The domain switching could be revealed under the external electric field by a nano-scale polar domain formation in BFBT ceramics with local distorted rhombohedral structure. However, the locally distorted rhombohedral structure within cubic matrix in BFBT ceramics is difficult to detect from the X-ray diffraction patterns, because of the inhomogeneous locally distorted structure. The exhibited pseudo-cubic X-ray diffraction pattern was caused by a homogeneous cubic matrix in the BFBT ceramics. Therefore, it is suggested that domain switching in the P–E hysteresis loop and the S–E curve and hysteric lattice strain revelation might be related to nano-scale domain structure formation in pseudo-cubic structured BF33BT system that was observed from SR-XRD patterns due to the presence of homogeneous cubic matrix.

4. Conclusion

In this work, the structural and electrical properties under the electric field were investigated in 0.67BiFeO\(_3\)–0.33BaTiO\(_3\) (BF33BT) lead-free ceramics. The crystal structure was investigated from SR-XRD at room temperature. The SR-XRD pattern exhibited diffraction patterns...
with single peak suggesting the crystal structure to be cubic. However, the ferroelectric and electric-field-induced strain properties were revealed by the $P$–$E$ hysteresis loop and $S$–$E$ curve. The remanent polarization was 19.90 μC/cm$^2$ under the 40 kV/cm applied electric field. Moreover, the hysteretic $S$–$E$ curves was observed with large positive strain (0.15%) and small negative strain (0.04%). The domain switching was observed in the $P$–$E$ hysteresis and $S$–$E$ curve of BF33BT ceramics with pseudo-cubic structure.

In order to investigate the electric-field-induced structural phase transition, the SR-XRD was measured under the electric field. The domain switching was observed in the ferroelectric and electric-field-induced phase transition in BF33BT ceramics. The hysteretic lattice strain calculated using peak shift of SR-XRD under the electric field and domain switching as observed in the ferroelectric properties evaluation might be related to nano-scale domain structure caused by local structure distortion in BFBT ceramics.

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