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Original Article

Anomalously large lattice strain contributions from rhombohedral phases in BiFeO₃-based high-temperature piezoceramics estimated by means of in-situ synchrotron x-ray diffraction



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<i>Keywords:</i> High-temperature piezoceramics BiFeO ₃ solid solution Morphotropic phase boundary Strain contribution	Thermally-stable (0.75- <i>x</i>)BiFeO ₃ -0.25PbTiO ₃ - <i>x</i> Ba(Zr _{0.25} Ti _{0.75})O ₃ (0.1 $\leq x \leq$ 0.27) piezoelectric ceramics were reported to have excellent dielectric and electromechanical properties of d ₃₃ ~405 pC/N, k _p ~46%, $\varepsilon_{33}^{T/}$ ε_0 ~1810, tanδ~3.1% and T _c ~421 °C close to tetragonal (T)-rhombohedral (R) morphotropic phase boundary. The dielectric measurement indicates that R ferroelectric phase is gradually transformed into relaxor ferro- electric across the phase boundary due to the substitution of BZT for BF. The transmission electron microscopy and convergent beam electron diffraction provide clear evidences that both the R-T phase coexistence and polar nanodomains contribute to enhanced piezoelectric properties at $x = 0.19$ through cooperatively facilitating polarization orientation. In combination with the macroscopic piezoelectric coefficient measurement, the quantitative analysis of synchrotron diffraction data under electric fields suggests that extremely large lattice strain contribution predominantly from R phases plus little extrinsic domain switching contribution should dominate the piezoelectric response of the $x = 0.19$ sample, mainly owing to both irreversible field-induced T to R phase transition and irreversible non-180° domain switching.

1. Introduction

Pb-based perovskite piezoelectric solid solutions have been widely applied in industry owing to their excellent electromechanical properties in the proximity of morphotropic phase boundary (MPB) between rhombohedral (R) and tetragonal (T) normal ferroelectric phases (MPB-I) [1] or between T normal ferroelectric phase and R/pseudo-cubic (PC) relaxor ferroelectric phases (MPB-II) [2]. The former mainly includes donor or acceptor doped PbZrO₃-PbTiO₃ (PZT) binary solid solutions. The latter is involved with solid solutions of PT/PZT and Pb-based complex perovskites such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $Pb(Zn_{1/3}Nb_{2/3})O_3$. Particularly, the latter systems usually exhibit obviously enhanced dielectric and piezoelectric responses due to the formation of polar nanoscale domains [3] in addition to the flattening of the free energy profile from the ferroelectric phase coexistence [4].

However, Pb-based perovskite piezoelectrics have met a big challenge as used at high temperatures of above 200 °C due to their limited de-poling temperatures. There are actually very limited material choices for piezoelectric devices working at high temperatures, where high Curie temperatures (T_c) and desirable piezoelectric performances are needed simultaneously. So far, (1-x)BiFeO₃-xPbTiO₃ (BF-PT) perature piezoelectric solid solutions [5-7], showing large potentials in the field of automotive, aerospace and so on. It exhibits nearly the highest T_c value (~632 °C) in all of PT-relaxor MPB systems [8]. However, the high c/a ratio, large coercive field ($E_c \sim 100 \text{ kV/cm}$) and large leakage current have made it difficult to be poled sufficiently and achieve well-saturated polarization vs. electric field (P-E) loops [5,9]. The substitution of Ga^{3+} , La^{3+} , and Ba^{2+} at A-sites or Sc^{3+} and Zr^{4+} at B-sites, or the combination of PZ or BaTiO₃ was applied to reduce the loss and Ec values of the BF-PT binary system and simultaneously to improve piezoelectric properties [10–12]. Nevertheless, these ceramics still show much inferior piezoelectric properties to conventional Pbbased MPB ceramics probably because of their specific domain structures [6,13]. There are generally two types of contributing mechanisms including intrinsic and extrinsic contributions with regards to the piezoelectric response in ferroelectrics [14]. The intrinsic contribution mainly involves the piezoelectric lattice distortion and lattice deformation from ferroelectric phase transformation under an external field, while the extrinsic contribution results from the interphase boundary motion, domain wall motion or domain switching. Khansur et al. recognized that the piezoelectric response in pure bulk BF is

system has been considered as one of the most promising high-tem-

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primarily due to non-180° ferroelectric domain switching with no observable change in the phase symmetry [15]. Zeches et al. found a similar MPB between T- and R-like phases induced by epitaxial strain in BF thin film, which consequently resulted in the enhancement of piezoelectric properties owing to the inter-ferroelectric phase transition [16]. An ultrahigh electrostrain of 1.3% was obtained in La-modified BF-PT ceramics owing to the combination of a large spontaneous lattice strain and a large reversible non-180° domain switching through domain miniaturization [17].

Ba(Zr_{0.25}Ti_{0.75})O₃ (BZT) is an important B-site complex perovskite with a space group (Pmm) and exhibits a typical relaxor ferroelectric characteristic [18]. In this work, a ternary system of (0.75-*x*)BF-0.25PT*x*BZT was fabricated via a solid-state reaction method. A special aim is to achieve enhanced piezoelectric responses by introducing the relaxor feature in a typical R-T MPB-I composition. Excellent piezoelectric properties and desirable thermal stability were at the same time obtained as the composition is close to a mixed phase boundary of MPB-I and MPB-II. The underlying mechanism of high piezoelectric responses was especially explored by means of in-situ high-resolution synchrotron x-ray diffraction (XRD) and transmission electron microscopy (TEM).

2. Experimental

The (0.75-x)BF-0.25PT-xBZT (BF-PT-xBZT, $0.1 \le x \le 0.27$) ceramics were prepared by a traditional mixed-oxide route. The stoichiometric powder mixture was calcined at 820 °C for 2 h after thorough mixing. Followed by a grinding process in a planetary mill, the powder was granulated, then uniaxially pressed into discs and finally sintered in the temperature range of 1000-1140 °C for 2 h. The phase structure was analyzed by an x-ray diffractometer (D/Mzx-rB; Rigaku, Tokyo, Japan) with Cu Ka1 radiation. The microstructure of the polished and thermally-etched specimens was observed using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6490LV, Tokyo, Japan). Dielectric properties were measured at various frequencies using an LCR meter (Agilent E4980A, Santa Clara, CA). The quasi-static d₃₃ of the samples was measured using a Berlincourt-meter (YE2703A, Sinocera, Yangzhou, China) after being poled under a dc field of 4 kV/ mm for 15 min at room temperature. The planar electromechanical coupling factor kp was determined by a resonance-antiresonance method with an impedance analyzer (PV70A; Beijing Band ERA Co. Ltd., Beijing, China). A ferroelectric test system (Precision LC, Radiant Technologies, Inc. Albuquerque, NM) was used to measure P-E and strain vs. electric field (S-E) loops. The domain morphology observation and selected area electron diffraction (SAED) were performed on a TEM (JEM-ARM200F, JEOL, Japan) operated at 200 kV. In addition, convergent beam electron diffraction (CBED) patterns were recorded at 120 kV. For TEM examination, samples were first mechanically polished to a thickness of $\sim 20\,\mu m$ and then ion-milled on a Precision Ion Polishing System (PIPS, Model 691, Gatan Inc., Pleasanton, CA) at 5 kV. All specimens were annealed at 80 °C for at least one day to release the mechanical stress before the observation. In-situ synchrotron XRD measurement was carried out under various electric fields at Shanghai Synchrotron Radiation Facility (SSRF) using beam line 14B1 $(\lambda = 1.2378 \text{ Å})$ in a symmetric reflection geometry. Measurements were performed by high-resolution θ -2 θ step-scans using a Huber 5021 six-circle diffratometer with a NaI scintillation detector. The angle between the detector and the sample surfaces is θ . For in-situ diffraction measurement, the sample surface was perpendicular to the applied electric field.

3. Results and discussion

Fig. 1(a) shows XRD patterns on $(111)_{pc}$ and $(200)_{pc}$ reflections of BF-PT-*x*BZT ceramics. It can be seen that the x = 0.1 sample owns a single R structure, as evidenced by a single (200) peak and a split (111) peak. With the substitution of BZT for BF, the (200) peak is gradually



Fig. 1. (a) The evolution of $(111)_{pc}$ and $(200)_{pc}$ reflections of BF-PT-*x*BZT ceramics, (b) the c/a value and phase volume fraction as a function of *x*, and (c) phase diagram of BF-PT-BZT ternary system in which blue lines stand for the possible phase boundaries between R and T, and red points indicate the composition points investigated in this work (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

split into three peaks of $(002)_T/(200)_T$ and $(200)_R$ and simultaneously the splitting of the (111) diffraction lines gradually becomes vague as $0.1 < x \le 0.26$. This indicates that the lattice distortion of R phases becomes smaller with increasing x. According to the fitting result of diffraction profiles, the tetragonality (c/a) and phase volume fraction could be obtained for BF-PT-xBZT ceramics, as shown in Fig. 1(b). The volume fraction of the T phase (F_T) was calculated by using the equation: $F_T = SI_T/(SI_T + SI_R)$ in which SI_T and SI_R are the sums of the peak integrated intensities of (200)pc reflections for T and R phases, respectively. The volume fraction of the R phase was accordingly given by $F_R = 1 - F_T$. F_T first increases up to a maximum value of 84.8% approximately at x = 0.18, and then decreases with further increasing x. Finally, the T phase completely disappears as $x \ge 0.27$, meaning that two-phase coexistence occurs within a wide composition range of 0.1 < x < 0.27. Moreover, the lattice distortion of both T and R phase declines with x at the same time, probably because of the decreased hybridization between A-site ions and O ions and the substitution of non-ferroelectric active cations such as Zr^{4+} [19]. The average structure of the R phase seemingly changes into a PC phase as $x \ge 0.185$ owing to the formation of relaxor ferroelectrics (as discussed in the permittivity property part infra), illustrating that the local symmetry of the unit cell is still R. This also suggests that the phase boundary should evolve gradually from MPB-I to MPB-II with increasing the BZT content, leading to a wide phase coexistence zone. The evolution law of the crystal structure in BF-PT-xBZT ceramics was mainly ascribed to the special compositional design in this study, as shown in Fig. 1(c).

Fig. 2 shows the grain morphology of a few BF-PT-*x*BZT ceramics with increasing *x* as sintered at their optimal temperatures. All samples exhibit dense and uniform microstructure with a relative density of over 96%. Compared with the binary BF-PT ceramic [6], the substitution of BZT for BF does not have an obvious effect on its sintering behavior. The optimal sintering temperature varies with x in the range of 1000–1100 °C. Nevertheless, the grain size of the sintered ceramic was found to increase from $\sim 3 \,\mu\text{m}$ at x = 0.1 to $\sim 8 \,\mu\text{m}$ at x = 0.26



Fig. 2. The grain morphology of a few typical BF-PT-xBZT ceramics with (a) x = 0.1, (b) x = 0.15, (c) x = 0.19 and (d) x = 0.26.

probably because of slightly increased sintering temperature. The x = 0.19 sample sintered at 1030 °C has an average size of 5 µm.

The dielectric permittivity as a function of temperature (25-600 °C) and frequency (100 Hz-1 MHZ) was measured for BF-PT-xBZT ceramics, through which the diffuse degree $\boldsymbol{\gamma}$ can be obtained according to the modified Curie-Weiss law, as well as another parameter ΔT_{relax} defined as the difference between two temperature values (Tm) at the dielectric maximum measured at 1 MHz and 1 kHz. As shown in Fig. 3(a), both γ and ΔT_{relax} very slightly increase with x before x = 0.18 ($\gamma = 1.3$ –1.39 and ΔT_{relax} is nearly 0 °C). Afterwards, both of them increase quickly with increasing x from 0.185 to 0.27 ($\gamma = 1.46-1.74$ and $\Delta T_{relax} = 10-39$ °C), suggesting that the substitution of BZT for BF has induced a typical normal ferroelectric to relaxor phase transition at room temperature. This observation keeps a good agreement with the XRD result in Fig. 1(a). The typical feature of a relaxor ferroelectric is the formation of polar nanoregions (PNRs) with an R local distortion in the non-polar cubic matrix as a result of local random fields. Moreover, the decline of the lattice distortion of R or T phases was also reflected by the decreased T_m values (see Fig. 3(a)).

Fig. 3(b) shows the variation of the remanent polarization P_r and the coercive field E_c with *x*, as obtained from P-E loops of BF-PT-*x*BZT ceramics at room temperature. The gradually decreased E_c might be attributed to the decrease in the lattice distortion of T and R phase as



Fig. 3. (a) Two relaxor parameters $\Delta T_{relaxor}$ and γ , and T_m , (b) P_r and E_{cs} (c) d_{33} , k_p and $\epsilon_{33}^{-T}/\epsilon_0$ as a function of *x* for BF-PT-*x*BZT ceramics, and (d) room-temperature d_{33} , k_p and $\epsilon_{33}^{-T}/\epsilon_0$ of the *x* = 0.19 ceramics after exposure to the annealing temperature. The inset in (b) shows second-cycle P-E loops of several representative compositions.

mentioned above. Moreover, the reduction of domain size, which is in fact related with a decrease in domain wall energy, would facilitate the alignment of polarization vectors in response to external electric fields [20]. It is to be noted that the E_c value of this system is far lower than that of BF-PT binary system [7,9], which would benefit to the improvement of piezoelectric properties owing to an easier electric poling process. P_r was found to reach its maximum value at x = 0.19 owing to relatively low energy barrier for polarization switching as the composition is located in the proximity of MPB [21,22]. The decline of P_r as x > 0.19 should be because the increased random field can suppress long-range ferroelectric interaction, such that the ferroelectric ordering becomes instable upon removal of electric field, as can be seen from the inset of Fig. 3(b) (note that a relatively small P_r is observed in the x = 0.1 sample because it has a very large E_c value).

For the same reason, the d_{33} , k_p and $\varepsilon_{33}^{T}/\varepsilon_0$ values of poled BF-PTxBZT ceramics reach their maxima values of $d_{33} \sim 405$ pC/N, $k_p \sim 46\%$ and $\varepsilon_{33}^{T}/\varepsilon_0 \sim 1810$ at x = 0.19, as shown in Fig. 3(c). Therefore, it is believed that the MPB plays a crucial role in improving dielectric, ferroelectric and piezoelectric properties. Compared with previously reported Bi-based high-T_c perovskite ceramics, the overall properties of the x = 0.19 sample in this study are advantageous [12,23–25]. Most importantly, these property values remain almost constant up to a higher temperature of ~ 350 °C, which is close to its T_c (T_m) of 421 °C, as shown in Fig. 3(d). Excellent piezoelectric properties and desirable thermal stability demonstrate that BF-PT-*x*BZT ceramics would be a promising candidate for high-temperature piezoelectric applications.

Fig. 4(a) illustrates the domain morphology within one grain in the x = 0.19 sample. One can see that it mainly consists of lamellar (A) (the width is in the range of 30-100 nm), tweed-like (B) and polar nanoscale (C) domains, further suggesting the coexistence of normal ferroelectric and relaxor ferroelectric states in this sample. Because of long-term heat-treatment at 80 °C as mentioned in the experimental procedure, the effect of mechanical stress during sample preparation on grain morphology may not occur [6]. In order to further identify its local structure, the < 001 > c zone axis CBED patterns were obtained, as shown in Fig. 4(b and c). The incidence direction was determined by the corresponding SAED pattern, as shown in the inset of Fig. 4(a). It can be seen from Fig. 4(b) that there are two mirror planes parallel to the [001] and [110], respectively, between which the angle is 45°, indicating a typical T symmetry with a 4 mm point group. However, only one mirror plane parallel to the [110] can be observed in Fig. 4(c). This should be because of the projection of [111] ionic displacements in the R phase with a 3 m point group onto a cubic (111) plane, as viewed along the [001] axis. These results clearly demonstrate the coexistence



Fig. 4. (a) Bright-field image of the x = 0.19 sample, the inset shows the SAED pattern taken along < 001 > zone axis, (b, c) CBED patterns of the x = 0.19 sample taken along < 001 > zone axis.

of T (4 mm) and R (3 m) phases in the x = 0.19 sample. In addition, the existence of a large amount of nanodomains conforms to the observation of the dielectric relaxor behavior (Fig. 3(a)). The results indicate that the R-phase domains are miniaturized into nanoscales as the composition is across the R-T phase boundary with increasing the BZT content. By comparison, typical T-phase domains of small coherence length were reported in La-modified BF-PT with high PT content, causing a reproducible ultrahigh electrostrain [17].

Fig. 5(a) shows the evolution of $(111)_c$ and $(200)_c$ reflections for the x = 0.19 sample at the virgin state, poling state (in-situ fields from 1 to 4 kV/mm) and the poled state (after being poled at 4 kV/mm). These diffraction lines were fitted by a pseudo-Voigt function in order to further analyze the electric field induced phase transition and domain switching. It is evident that virgin samples exhibit R and T phase co-existence. The R distortion in this sample was clearly identified through irradiation of synchrotron x-ray, compared to conventional XRD in Fig. 1(a). Moreover, the application of external fields was found to induce the variation of both diffraction peak position and intensity, particularly as $E \ge 2 \text{ kV/mm}$ which approximates to the E_c value of this composition. Moreover, the electric field induced changes can be mostly maintained after removal of the electric field (the poled state).

According to the fitting results of XRD data, apart from F_T and F_R values under different field conditions, the volume fraction of domains (f) parallel to the field direction for T and R phases can be estimated by using the following equations: $f_T = I_{(002)T}/(I_{(002)T} + I_{(200)T})$ and $f_R = I_{(111)R}/(I_{(111)R} + I_{(11-1)R})$, respectively. As shown in Fig. 5(b), with increasing the field up to 4 kV/mm, f_R increases from 38.4% to 81% and f_T rises from 31.3% to 50%, indicating a significantly preferential (111)



Fig. 5. The evolution of $(111)_{pc}$ and $(200)_{pc}$ reflections for the x = 0.19 ceramics at the virgin state, poling state under different electric fields from 1 to 4 kV/mm and poled state after removal of electric field, as fitted by using Peakfit software, and (b) domain switching fraction (f_R and f_T) and (c) volume fraction of R and T phases (F_R and F_T) varying with increasing electric fields on a virgin sample and then releasing the field up to zero. The inset in (b) shows bipolar S-E loops of the first (black line) and the second cycle (red line); the inset in (c) is the sketch of the crystallographic relationship between T and R phase (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

domain orientation for R phases compared with T phases. After removal of electric fields, f_R and f_T exhibit only a slight decrease from 81% to 78%, and from 50% to 43%, respectively, suggesting that an irreversible non-180° domain switching is dominant for both phases. This judgment conforms to the fact that an anomalously large negative strain S_{neg} , accounting for ~58% of the total poling strain, was observed in bipolar S-E loops (see the inset of Fig. 5(b)). In addition, both F_R and F_T in Fig. 5(c) exhibit a drastic change with changing the electric field. F_T decreases from $\sim 61\%$ at the virgin state to $\sim 35\%$ at the poling state (4 kV/mm), but F_R increases accordingly from ~39% to ~65%, meaning that $\sim 26\%$ of T phases are electrically forced into R phases. Compared with the poled state ($F_{\rm R} \sim 64\%$, $F_{\rm T} \sim 36\%$), the electric field induced T to R phase transition proves to be basically irreversible. The irreversibility of the T-R phase transition can well interpret the difference between S_{neg} and the remanent strain S_{rem} obtained from the nonfirst cycle and the first cycle bipolar S-E loops (see the inset of Fig. 5(b)), respectively.

The field induced phase transition was also observed in near-MPB compositions in traditional PZT as well as some Bi-based perovskites [26-29]. Hinterstein et al. have shown evidence of field-induced T to R transformation in a soft PZT [26]. Similar phase transition phenomenon has been recently found in (Bi_{0.5}Na_{0.5})TiO₃-BaTiO₃ single crystal [29], where the phase transition from R + T to T occurs when an electric field is applied along < 001 > direction, whereas the R + T to R phase transition happens as an electric field is along < 111 > direction. This might be because the activation energy required for the phase transition in the vicinity of the R and T phase boundary is so low that the applied electric field can induce the phase transition in both directions. A T to R phase transformation in BF-PT-xBZT ceramics should occur through the polarization rotation from $[100]_T$ to $[111]_R$ (as sketched in the inset of Fig. 5(c)), suggesting the existence of a low-energy polarization rotation pathway along the $[111]_c$ direction in the $(1-10)_c$ plane of the T phase. This might be inherently associated with the crystal structure of BF, in which both a huge shift of Bi³⁺ and Fe³⁺ ions and a counter rotation of oxygen octahedron were believed to occur along the (111) direction [30].

It is generally believed that intrinsic lattice strains (Slatt.) can be evaluated using the change of the lattice spacings ($\Delta d/d$) along nonpolar directions ((111)_c for T phases and (200)_c for R phases) between the poling state (4 kV/mm) and the poled state (after poling). In the case of two-phase coexistence, the total lattice strain (Slatt.-total) should be the sum of the lattice strain of each phase weighted with the corresponding phase fraction. According to the peak position variation in Fig. 5(a), $S_{latt,T}$ and $S_{latt,R}$ were estimated to be 0.06% and 0.21%, respectively. It is evident that R phases can exhibit nearly four times intrinsic strains of T phases, as observed between orthorhombic phases and T phases in alkaline niobate ceramics [31]. Large lattice strain was also found in the R phase of BiScO3-PT system [28]. Considering the irreversibility of T-R phase transition, the $S_{\rm latt.-total}$ of $\sim\!0.156\%$ was then achieved using $S_{latt.-total} = F_T \cdot S_{latt.,T} + F_R \cdot S_{latt.,R}$ under assumption of an Reuss model with iso-stress [32], as an electric field of 4 kV/mm was applied on a poled sample. This calculated lattice strain value was found to approximate to the product ($\sim 0.162\%$) of the measured d₃₃ value and the applied electric field magnitude, meaning little domain wall motion contribution in the piezoelectric response. As obtained from the bipolar S-E curve in the inset of Fig. 5(b), the unipolar strain at 4 kV/mm reaches 0.195%. This result demonstrates that high-field electromechanical strains in the x = 0.19 sample should be dominated by intrinsic lattice strains, particularly from the R phase, which is closely correlated with irreversible domain switching of either R or T phases and irreversible T-R phase transformation. Similar phenomenon has been found in PZT-based ceramics [33].

4. Conclusions

R ferroelectrics in a wide composition range, in which the lattice distortion of both T and R phases declines with *x* together with the formation of relaxor R phases. The optimum dielectric, ferroelectric and piezoelectric properties of $d_{33} \sim 405$ pC/N, $k_p \sim 46\%$, $\varepsilon_{33}^{-1}/\varepsilon_0 \sim 1810$, $\tan \delta \sim 3.1\%$ and $T_c \sim 421$ °C were obtained at x = 0.19, together with excellent high-temperature stability of piezoelectric properties. The high piezoelectric activity was ascribed to both the two-phase structural coexistence and nanoscale domain morphology. The quantitative analysis of the diffraction data suggests that high piezoelectric response of the x = 0.19 composition mainly originate from an extremely large lattice strain contribution of R phases. Little extrinsic contribution from domain switching was observed because of the clamping of domain reorientation caused by both irreversible non-180° domain switching and the irreversible T to R phase transition.

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BF-PT-xBZT ceramics were found to exhibit an MPB between T and

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