Giant strain with low hysteresis in A-site-deficient $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ -based lead-free piezoceramics

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ABSTRACT

We report a giant strain (0.72 %) with a low degree of hysteresis (*ca.* 36.2 %) and a giant $S_{\max}/E_{\max}$ ratio (916 pm V⁻¹, $S_{\max}$ and $E_{\max}$ denote the maximum strain and the corresponding electric field, respectively) for lead-free (1- x)(0.8Bi_{0.5}Na_{0.5}TiO₃-0.2Bi_{0.5}K_{0.5}TiO₃)- x Sr_{0.8}Bi_{0.1}□_{0.1}Ti_{0.8}Zr_{0.2}O_{2.95} piezoceramics with $x = 0.06$. The giant strain originates from a reversible transition between the ergodic relaxor and ferroelectric states under applied electric fields. A-site vacancies (V_A) and oxygen vacancies (V_O), *deliberately* introduced to the system, induce a randomly distributed local polarization field. The local field induces embryonic polarization domains that have a broad distribution of maturity and thus smears the transition between the ferroelectric and relaxor states. This leads to a narrow hysteresis loop. The poling field required for the relaxor-to-ferroelectric transition is reduced significantly, due to the remanent ferroelectric phase at zero field acting as the seed, and the point defects synergistically facilitating the nucleation and growth of the ferroelectric phase. Our work provides a novel route for designing piezoelectric materials with both a giant strain and a narrow hysteresis for practical actuator applications.

Keywords: BNT-based piezoceramics, Strain, Relaxor, A-site and oxygen vacancies

1. Introduction

Piezoelectricity is a physical phenomenon that manifests mutual conversion between electrical energy and mechanical energy. Piezoelectric materials have been used in many electronic device applications, such as actuators, sensors, ultrasonic motors and imaging devices [1-3]. Due to their high strain, lead-based piezoelectric ceramics, exemplarily lead zirconate titanate $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT), have been widely used in actuators [4]. This, however, has brought serious environmental concerns due to the toxicity of lead. Recently, tremendous effort has been devoted to developing competitive lead-free piezoelectric ceramics [5]. Among all the lead-free materials developed, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) is considered to be one of the most promising candidates due to its high electric-field-induced strain level [6,7]. Although a high strain and good fatigue resistance could be both achieved in BNT-based piezoceramics, their strain loops show a larger hysteresis in comparison with the lead-based systems [6-10]. Therefore, how to reduce the strain hysteresis of BNT materials while maintain their high strain level and favorable fatigue-resistance remains a big challenge for practical actuator applications.

Proper selections of base compositions, chemical modifiers and the configurable design of composites (*e. g.*, 0-3 type composite ceramics) play key roles in achieving giant strain and low hysteresis. To maintain high strain levels, the base composition is supposed to have a relatively high strain. Then, the long-range ferroelectric order of the base composition can be disrupted by chemical modifiers in a way that the long-range ferroelectric order could be readily recovered by an external electric field.

For example, compositions around the morphotropic phase boundary (MPB) of BNT-BaTiO₃ (BNT-BT) and BNT-Bi_{0.5}K_{0.5}TiO₃ (BNT-BKT) where rhombohedral (R) and tetragonal (T) phases coexist have been generally chosen as the base compositions [11-14]. Indeed, these MPB compositions exhibit relatively large strains due to the existence of nanotwins with monoclinic symmetry as an intermediate bridging phase, which facilitates polarization reorientation [15,16]. However, they also show a large negative strain, along with a large hysteresis. In order to address these problems, chemical modifiers, such as KNN and SrTiO₃, are often used as dopants to disrupt the long-range ferroelectric order and nurture the ergodic relaxor state, thereby reducing the negative strain [6,17,18]. The strategy of forming ergodic/nonergodic composites has been shown to be effective in reducing the negative strain [19,20]. Meanwhile, both the critical field for triggering the large strain and the strain hysteresis are also reduced in a composite material because the residual ferroelectric phase facilitates the relaxor-to-ferroelectric phase transformation [19,20]. However, it should be kept in mind that a strong internal bias field induced by defects or defect dipoles, manifested by the presence of a strong asymmetry in strain values, should be avoided with the aim of maintaining a high fatigue resistance of the material [9].

In this work, 0.8BNT-0.2BKT is chosen as the base composition and Sr_{0.8}Bi_{0.1}□_{0.1}Ti_{0.8}Zr_{0.2}O_{2.95} (SBTZ) as the modifier. Sr_{0.7}Bi_{0.2}□_{0.1}TiO₃ is a recently reported lead-free ferroelectric relaxor [21,22]. Thus, the combination of a ferroelectric and a ferroelectric relaxor can help form an ergodic relaxor and reduce

the negative strain. An appropriate amount of Zr^{4+} substitution was found to be beneficial for significantly enhancing the electric-field-induced strain level of BNT-BKT ceramics [23]. V_A and V_O are *deliberately* introduced to the system, as they induce local polarization fields, which break the symmetry of the Landau free energy with regard to polarization and hinder the formation of the long-range ferroelectric order, according to our earlier work [24]. This methodology has been proved to be beneficial for reduction of strain hysteresis, as seen previously in other ferroelectric and ferroelastic systems [25,26]. Systematic structural and electrical characterizations of the BNT-BKT-SBTZ100 x ceramics (abbreviated as BNKT-SBTZ100 x , $x = 0.00, 0.02, 0.04, 0.06, 0.08$) were then carried out in order to develop lead-free piezoelectric materials with excellent properties for actuator applications. In this work, we demonstrate that the BNKT-SBTZ6 sample shows a giant strain (0.72 %) with a low degree of hysteresis (36.2 %) and a giant $(S_{\text{max}}/E_{\text{max}})_{\text{max}}$ ratio (916 pm V⁻¹).

2. Experimental

$(1-x)(0.8\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.2\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3)-x\text{Sr}_{0.8}\text{Bi}_{0.1}\square_{0.1}\text{Ti}_{0.8}\text{Zr}_{0.2}\text{O}_{2.95}$ ($\square$ represents A-site vacancies; $x = 0.00, 0.02, 0.04, 0.06$ and 0.08 ; abbreviated as BNKT-SBTZ100 x , *e. g.*, BNKT-SBTZ0, BNKT-SBTZ2, BNKT-SBTZ4, BNKT-SBTZ6 and BNKT-SBTZ8, respectively) were prepared by using the traditional solid-state process with appropriate amounts of Bi_2O_3 (99.975 %), TiO_2 (99.6 %), ZrO_2 (99.99 %), Na_2CO_3 (99.997 %), K_2CO_3 (99.997 %) and SrCO_3 (99.99 %) as the raw materials (all from Alfa Aesar GmbH). These raw powders were

dried at 200 °C for 24 h and weighed, and then mixed by a ball milling method in ethanol for 12 h. The mixtures were then dried, sieved and calcined at 850 °C for 4 h in air. The calcined powders were milled again for 12 h, dried and sieved, and then formed into pellets (diameter: 12 mm, thickness: 4 mm) using cold isostatic pressing at 300 MPa. These green pellets were embedded in precursor powders and sintered at 1160 °C for 2 h in air. The sintered pellets were polished to ~0.8 mm in thickness. Silver paint electrodes were coated on the surface of pellets and fired at 600 °C for 20 min.

Powder X-ray diffraction (XRD) data of BNKT-SBTZ100 x were collected by using a diffractometer (XRD-7000, Shimadzu, Kyoto, Japan) with Cu K α radiation at ambient temperature at the 2 θ range of 10°-90° with a step size of 0.01°, and Rietveld refinements for BNKT-SBTZ100 x were carried out by using the Fullprof program. Raman spectra of BNKT-SBTZ100 x ceramics were obtained by using an instrument (LabRam HR800, Horiba Jobin Yvon, Lyon, France) in a backward scattering geometry (a 514 nm argon laser as excitation). For the temperature-dependent Raman measurements, a heating-cooling stage (HFS600E-P, Linkam, Surrey, UK) was used in the temperature range of 30-330 °C. Surface morphologies of BNKT-SBTZ100 x ceramics were revealed by scanning electron microscopy (SEM; JSM-5610, JEOL, Tokyo, Japan). The selected-area electron diffraction (SAED) patterns and atomic-resolution high-angle annular dark field (HAADF) images for the BNKT-SBTZ6 powder (to avoid the introduction of defects caused by argon ion-beam thinning) and the ceramic were obtained by using an aberration-corrected scanning

transmission electron microscopy (STEM, JEM-ARM200F, JEOL, Tokyo, Japan) with a probe aberration corrector, operated at 200 kV. For dielectric and Raman measurements, BNKT-SBTZ100x samples were poled under a dc field of 50 kV cm^{-1} in a silicone oil bath at ambient temperature for 30 min, and BNTK-SBTZ6 was also poled at $-50 \text{ }^{\circ}\text{C}$. Dielectric permittivity (ϵ') and dielectric loss ($\tan\delta$) of the poled BNKT-SBTZ100x ceramics were detected by using a precision impedance analyzer (4294A, Agilent, Santa Clara, CA, USA) with the discrete frequencies: 100 Hz, 1 kHz and 10 kHz. Ferroelectric and electrostrain properties of the BNKT-SBTZ100x ceramics, namely electric-field-induced polarization (P - E) and electric-field-induced strain (S - E) loops, were measured by using a ferroelectric analyzer (TF-2000, Aix ACCT, Aachen, Germany) linked an accessory laser interferometer vibrometer (SP-S120/500, SIOS Mebtechnik GmbH, Jena, Germany). For the fatigue test of BNKT-SBTZ6, a triangular wave signal with bipolar electric field of $\pm 50 \text{ kV cm}^{-1}$ at 1 Hz up to 10^5 cycles was applied. X-ray photoelectron spectroscopy (XPS) of the BNKT-SBTZ100x ceramics were examined with a spectrometer (VG ESCALAB220i-XL, Thermo Scientific, Surrey, UK) with Al $K\alpha$ radiation, and all the peaks were calibrated with respect to C 1s peak at 284.8 eV. Temperature-dependent impedance spectra (IS) of BNKT-SBTZ100x ceramics were performed in air, oxygen and nitrogen by using an impedance test unit (Solartron, SI 1260, Hampshire, UK).

3. Results

Fig. 1(a) shows the hysteresis loops (P - E) and electric-field-induced strain loops (S - E) of the BNKT-SBTZ100x samples at 50 kV cm^{-1} . It shows that the P - E loops

change from well-saturated loops (*i. e.*, BNKT-SBTZ0 and BNKT-SBTZ2), characteristic of normal ferroelectrics, to pinched loops (*i. e.*, BNKT-SBTZ4, BNKT-SBTZ6, BNKT-SBTZ8), characteristic of ferroelectric relaxors, with increasing x . Fig. 1(b) shows that the strain level first increases, reaches the maximum of 0.458 % at BNKT-SBTZ6, and then decreases as x increases. Fig. 1(c) displays the P - E and S - E loops of BNKT-SBTZ6 measured at different electric fields. It is seen that the strain reaches 0.72 % at 110 kV cm^{-1} with a hysteresis of 36.2 % (the strain hysteresis is defined as $\Delta S/S_{\max}$, calculated in the same way as that in the reference [27]). The evolution of P_r , $P_{\max}$ and $S_{\max}$ of BNKT-SBTZ6 with the increasing number of fatigue cycles (fatigue measurements were conducted at 1 Hz, under 50 kV cm^{-1}) at ambient temperature is presented in Fig. 1(d). Obviously, BNKT-SBTZ6 shows excellent fatigue resistance and displays no obvious change in P_r , $P_{\max}$ and $S_{\max}$ values after 10^5 cycles.

Table 1 gives the comparison of $S_{\max}$, $S_{\max}/E_{\max}$ and strain hysteresis ($\Delta S/S_{\max}$) of BNKT-SBTZ6 and other ceramics reported in the literature. It is seen that our BNKT-SBTZ6 samples possess the highest strain, a modest $S_{\max}/E_{\max}$ ratio and a low hysteresis, demonstrating the best *comprehensive* properties ever achieved in lead-free piezoceramics. For example, BNT-2.5Nb shows a high strain (0.7 %) and a high $S_{\max}/E_{\max}$ ratio (1400 pm V^{-1}), but it also demonstrates a large hysteresis (68.9 %) and poor fatigue resistance [9]. The KNN-based ceramic shows a low hysteresis (9.2 %), but it also exhibits a relatively small strain (0.16 %) and a small $S_{\max}/E_{\max}$ ratio (400 pm V^{-1}) [28].

4. Discussion

As can be seen from the S - E loop of BNKT-SBTZ0 in Fig. 1(a) and also the reference [29], the base composition demonstrates a high strain with a typical butterfly shape under an electric field. With increasing SBTZ concentration, the negative strain (S_{neg}) decreases in general, except that BNKT-SBTZ2 exhibits a slight increase in S_{neg} as compared to BNKT-SBTZ0. The maximum strain (S_{max}) of BNKT-SBTZ2 reaches about 0.287 % and its S_{neg} is around 0.221 %. The BNKT-SBTZ2 sample therefore exhibits improved ferroelectric properties due to the introduction of SBTZ, in which a softened ferroelectric behavior and easy polarization reorientation is favored. When the SBTZ concentration reaches 6 %, the S_{max} reaches 0.458 % and there is almost no S_{neg} because of the dominant ergodic state. Such a high strain level observed in the present study is mainly attributed to the reduction in S_{neg} caused by the transition from the nonergodic to ergodic states with increasing x . With further doping (*e. g.*, BNKT-SBTZ8), the S_{neg} remains near zero, but the S_{max} decreases because the relaxor phase becomes more stable and requires an increase in the critical bias field for the relaxor-to-ferroelectric transition.

From the above analysis, it is important to notice that the base composition of BNKT-SBTZ0 has a relatively high strain level (S_{max}). The effect of dopants is to reduce S_{neg} and then increase S_{max} . The reason why the base component BNKT-SBTZ0, as well as BNKT-SBTZ2, BNKT-SBTZ4, BNKT-SBTZ6, has such a high strain level is due to the coexistence of T and R phases in these specific compositions, as illustrated below.

4.1. The composition-induced phase evolution

Fig. 2(a) shows the room-temperature XRD patterns of the unpoled BNKT-SBTZ100 x samples, revealing a single-phase perovskite structure without any secondary phases. Our XRD data indicate that SBTZ has been incorporated into the BNKT lattices and forms solid solutions. The diffraction peaks can be indexed as a pure Bi_{0.5}Na_{0.4}K_{0.1}TiO₃ with both an R phase (space group $R3c$) and a T phase (space group $P4bm$) [33]. The insets of Fig. 2(a) show an enlarged view of the characteristic 1/2(310) and 1/2(311) superlattice reflections, (021)_T/(202)_R peaks and (220)_T/(002)_T/(024)_R peaks, respectively, all of which indicate the coexistence of T and R phases.

To further verify the presence of both T and R phases in BNKT-SBTZ100 x , the selected-area electron diffraction (SAED) pattern of BNKT-SBTZ6 in the grain taken along the [013] zone axis was recorded, as displayed in the inset of Fig. 2(b). Superlattice spots of the 1/2{*ooe*}-type, indicative of the T phase, and the 1/2{*ooo*}-type, signifying the presence of the R phase, are visible. The electron diffraction result is hence in support to the XRD data. Additionally, the 1/2(311) superlattice reflection becomes weaker with increasing x , indicating a decrease in the fraction of the R phase with increasing x .

The Raman spectra of BNKT-SBTZ100 x also exhibit the typical vibrational modes of both T and R phases, and the fraction of the T phase increases with increasing x (see Supplementary Fig. S1). Table S1 lists the phase fraction and the Rietveld refined agreement factors of BNKT-SBTZ100 x , roughly providing the structural information of phase transition with increasing x . Such T and R coexistence

in BNKT-SBTZ100 x lowers systematic energy barriers. This is beneficial for polarization reversal and polarization extension. As a result, these compositions demonstrate a large strain.

4.2. *The temperature-induced phase evolution*

In BNT-based systems, the origin of the large strain is attributed to a reversible electric-field-induced relaxor-to-ferroelectric phase transition. To investigate the nonergodic and ergodic relaxor states for BNKT-SBTZ100 x , temperature-dependent Raman spectra on BNKT-SBTZ0 and BNKT-SBTZ6 were conducted, as shown in Fig. 3. From the contour plots of BNKT-SBTZ0, a sudden change in Raman shifts (70-130 cm^{-1} , 220-320 cm^{-1} and 470-640 cm^{-1}) of the poled BNKT-SBTZ0 sample can be observed below $\sim 110^\circ\text{C}$, in comparison with that of the unpoled BNKT-SBTZ0 sample. This is in agreement with the dielectric anomalies of BNKT-SBTZ0 and its transition point from the ferroelectric to a relaxor state ($T_{\text{F-R}}$, 108°C) (see Supplementary Fig. S2). However, no drastic change is detected above $T_{\text{F-R}}$. Particularly, Fig. 3(b) displays the Raman spectra of the poled BNKT-SBTZ0 sample upon heating and subsequently cooling below $T_{\text{F-R}}$ (100°C) and above $T_{\text{F-R}}$ (110°C). It suggests that the phase structure of BNKT-SBTZ0 at temperatures above 110°C is nearly uniform either in the poled state or the thermally depoled state. By contrast, electric poling changes the phase structure of BNKT-SBTZ0 at temperatures below 110°C . An electric-field-induced irreversible transformation occurs from the mixed R and T phases to an R phase-dominant structure. This poled state persists until the temperature of $T_{\text{F-R}}$. Therefore, BNKT-SBTZ0 is predominantly a nonergodic relaxor

in its original state.

In contrast, BNKT-SBTZ6 is largely an ergodic relaxor, and it is characterized by the nearly identical contour plots of Raman spectra from the poled BNKT-SBTZ6 and unpoled BNKT-SBTZ6. Fig. 3(b) displays the Raman spectra of the poled BNKT-SBTZ6 upon heating and subsequently cooling at 30 °C and 50 °C, indicating that the phase structure in the poled BNKT-SBTZ6 is almost the same as in the thermally depoled BNKT-SBTZ6 at both temperatures. Close examination indicates that the Raman vibrational peaks of the poled BNKT-SBTZ6 at $\sim 116\text{ cm}^{-1}$, $\sim 309\text{ cm}^{-1}$ and $\sim 614\text{ cm}^{-1}$ become slightly weakened upon poling. The minor changes suggest the presence of a small amount of the nonergodic relaxor phase in the unpoled BNKT-SBTZ6.

4.3. The presence of lattice vacancies

The $T_{\text{F-R}}$ decreases with increasing SBTZ content, as mentioned in Fig. S2 in the Supplementary Materials, and the giant strain appears when the $T_{\text{F-R}}$ is lower than ambient temperature. BNKT-SBTZ6 is an ergodicity-dominant relaxor under ambient condition and its $T_{\text{F-R}}$ is 17 °C (see Fig. S2(d)). The application of a large-enough electric field can reversibly induce a ferroelectric long-range order that is only stable under the electric field. Therefore, the reversible electric-field-induced relaxor-to-ferroelectric phase transition is one of the main reasons for the observed high electric-field-induced strain in BNKT-SBTZ6. This process is accompanied by the reduced energy barriers for polarization extension from the relaxor to ferroelectric states and the reorientation of ferroelectric domains upon the application of the

external electric field. This mechanism is similar to those reported in other BNT-based ceramic systems [6,29,34]. However, both the $S_{\max}$ and $S_{\max}/E_{\max}$ of BNKT-SBTZ100x in this work are higher than those in other BNT-based materials reported in the literature, and the strain hysteresis $\Delta S/S_{\max}$ is lower. Here, we argue that point defects caused by the existence of V_A and V_O may explain the origin of the giant $S_{\max}$ and $S_{\max}/E_{\max}$ and the low $\Delta S/S_{\max}$.

Fig. 4(a) shows a typical atomic-resolution HAADF-STEM image of the BNKT-SBTZ6 ceramic, viewed along the [001] zone axis. Under the HAADF-STEM conditions, the A-site (Bi/Na/K/Sr) atom columns appear as brighter dots while the B-site (Ti/Zr) atom columns appear as less bright ones. The O atom column is too weak to be seen because of its low nuclear charge values. It is noted that the existence of V_O is indirectly identified by using XPS (Supplementary Fig. S3) and IS measurements (Supplementary Fig. S4) and the changes of surface morphologies of the BNKT-SBTZ100x ceramics (Supplementary Fig. S5). During HAADF-STEM analysis, some fluctuations in the intensity of the A-site atom columns are observed, which is ascribed to the different nuclear charge values for Bi/Na/K/Sr and A-site disordering structure in BNT-based ceramics [35,36]. Notably, some atomic columns display an exceptionally low intensity beyond the normal fluctuation, marked with yellow circles in Fig. 4(a). The representative intensity profiles in Fig. 4(b) are measured along the atom plane highlighted by the rectangle box in Fig. 4(a). The intensity profile denoted by the yellow circle clearly suggests the existence of V_A in the atom columns. The HAADF-STEM experimental results shown in Fig. 4(a) are

reproducible, as exemplified by the observation on other areas in the same sample (Supplementary Fig. S6).

4.4. The phenomenological model

Combining structure refinement profiles with the HAADF-STEM image, a model of BNKT-SBTZ6 for the representative T phase can be proposed in Fig. 4(c), containing (I) the defect-free state and (II) the state with defects. In the BNKT-SBTZ6 ceramic, V_A and V_O are randomly distributed in the perovskite structure, causing local distortions in the crystal lattices. According to the Landau-Devonshire theory and the relation of polarization and local fields [37,38], the free energy of the defect-free state and state with defects can be described, respectively, by the following Landau polynomials:

$$F = aP^2 + bP^4 + cP^6 \quad (1)$$

$$F = aP^2 + bP^4 + cP^6 - E_D P \quad (2)$$

where a , b and c are the expansion coefficients and E_D is the local field caused by the point defects (V_A and V_O). Fig. 4(d) and 4(e) show schematically the Landau free energy curves as a function of the order parameter P at different electric fields and with and without the local field effect, respectively. It can be readily seen that the introduction of E_D breaks the symmetry of the F - P curves.

4.5. The trend in critical fields

The poling field (E_{pol}) and depoling field (E_{dep}) are key parameters for the achievement of the large strain because the electric-field-induced ferroelectric order is established and disrupted at these two fields, respectively. Here, E_{pol} and E_{dep} are

defined at the inflection point during uphill cycle and downhill cycle, respectively [19]. E_{dep} of BNKT-SBTZ0, BNKT-SBTZ2 and BNKT-SBTZ4 is negative due to the stable ferroelectric phase while that of BNKT-SBTZ6 and BNKT-SBTZ8 is positive due to the stable relaxor phase (Fig. 5). E_{dep} lies near 0 kV cm^{-1} in BNKT-SBTZ6, for which the maximum $S_{\text{max}}/E_{\text{max}}$ is obtained. With increasing SBTZ content, E_{dep} monotonically increases and $E_{\text{pol}}-E_{\text{dep}}$ decreases, suggesting that the emergent ergodic state not only delays the relaxor-to-ferroelectric transition but also favors early disruption of the ferroelectric order during unloading. E_{pol} decreases first and then increases. In relaxor/ferroelectric composites, E_{pol} increases monotonically with increasing relaxor concentration [19]. In this work, with increasing SBTZ content the ergodic state is gradually formed, and a monotonic increase in E_{pol} is anticipated. However, the presence of V_A and V_O facilitates the nucleation and growth of the ferroelectric phase, because defects are known to lower the free energy [39]. These potent sites with the lowest potential barriers associated with V_A and V_O are activated first under a given electric field. A coupled contribution to E_{pol} between the ergodic state and potent sites occurs in BNKT-SBTZ100x. As a result, E_{pol} of BNKT-SBTZ2 is lower than that of BNKT-SBTZ0 because the effect to E_{pol} of potent sites is dominant when the ergodic state fraction is low (*i. e.*, BNKT-SBTZ2). With increasing ergodic state fractions, the effect to E_{pol} of the ergodic state prevails, leading to the increase in E_{pol} . This can help reduce the magnitude of the electric field required for the relaxor-to-ferroelectric transition compared with those BNT-based ceramics without defects [23,29].

4.6. The development of giant strain with low hysteresis in BNKT-SBTZ6

For BNKT-SBTZ6, an ergodicity-dominant relaxor, the reversible phase transitions from relaxor to ferroelectric and ferroelectric to relaxor take place during electrical loading and unloading, respectively. In particular, BNKT-SBTZ6 in its original state, corresponding to point P_0 on the S - E curve shown in Fig. 6(a), contains both R ($R3c$) and T ($P4bm$) phases. And it is T phase-dominant with many nanodomains and a few lamellar domains, as shown in the inset of Fig. 6(a). Upon electric loading, the system transforms gradually from an ergodic state into a ferroelectric state, forced by the electric field. A gradual increase of strain takes place from point P_0 to point P_1 . The residual ferroelectric phase in the virgin state, manifested as those lamellar domains, serves as the seed for the transition. Also, at a given electric field, the most potent sites with the lowest potential barrier associated with V_A and V_O are activated first. Therefore, E_{pol} is reduced significantly, thereby leading to a giant S_{max}/E_{max} . From point P_1 to point P_2 , there is no a sharp jump of the S - E curve because it is difficult for the system to achieve only lamellar domains after electric loading due to the existence of E_D which prevents the sudden formation of a long-range order.

Upon electric unloading, the system transforms gradually from a ferroelectric-dominant state into an ergodicity-dominant state, and the E_D tends to gradually restore the original ergodic state. This process does not need to nucleate new lamellar domains because the embryos of these domains already exist. At point P_4 where the applied electric field returns to 0 kV cm^{-1} , BNKT-SBTZ6 returns to the T

phase-dominant relaxor state, and the remanent strain observed at zero field correlates well with the presence of small amount of the residual ferroelectric phase in the sample.

Importantly, during the electric loading and unloading processes, the E_D breaks the symmetry of the Landau free energy with regard to polarization, as shown in Fig. 6(b). The E_D induces embryonic polarization domains that have a broad distribution of maturity and thus smears the transition between the ferroelectric and relaxor states. As a consequence, there is no abrupt jump in the S - E curve shown in Fig. 6(a) and the curve has a narrow hysteresis. We have previously investigated the effect of point defects on the properties of a generic ferroelectric relaxor by phase field simulations and the results show a slim P - E loop with small P_r , a “sprout” S - E loop with large $S_{\max}$ and a narrow hysteresis [24]. These results are in good agreement with the experimental results obtained for the BNKT-SBTZ100x ceramics in this work.

Doping SBTZ to the base composition has several effects. First of all, after doping, the sample remains the mixed R and T phases, which benefits polarization reversal and polarization extension, the reversible transition between the ergodic relaxor and ferroelectric states under an applied electric field and the increase in $S_{\max}$. Secondly, a small amount of V_A and V_O is *deliberately* designed in the system, as we mentioned previously. The poling field for the relaxor-to-ferroelectric transition decreases, because the most potent sites associated with V_A and V_O are activated first due to their lowest potential barrier, and the remanent ferroelectric phase at zero field also favors this transition due to skipping the nucleation stage. Thirdly, E_D induced by

these defects breaks the symmetry of the Landau free energy and lowers the potential barrier. It can induce embryonic polarization domains that have a broad distribution of maturity and thus smear the transition between the ferroelectric and relaxor states, leading to a narrow hysteresis S - E loop. Note that the low defect concentration in our composition was not detrimental to the fatigue resistance of the sample, as experimentally demonstrated in Fig. 1(d).

5. Conclusion

In summary, the lead-free BNKT-SBTZ6 piezoceramic is developed in this work and it shows a giant strain (0.72 %) with a low hysteresis (36.2 %), and a giant $(S_{\max}/E_{\max})_{\max}$ ratio (916 pm V⁻¹). The superior comprehensive properties in this composition are believed to benefit from the T and R phase coexistence, the formation of an ergodic state induced by dopants, and a small concentration of A-site and oxygen vacancies (V_A and V_O). Our findings could stimulate further research on lead-free piezoelectric materials with a large strain and a narrow hysteresis for actuator applications.

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Fig. 1 (a) The bipolar P - E and bipolar S - E curves of the BNKT-SBTZ100 x ceramics and the unipolar S - E curve of BNKT-SBTZ6 (the dashed line), measured at ambient temperature and 1 Hz. (b) The evolution of P_r , $P_{\max}$, $S_{\max}$, S_{neg} and $S_{\max}/E_{\max}$ as a function of SBTZ content. (c) The bipolar P - E and bipolar S - E curves of the BNKT-SBTZ6 ceramic at various electric fields ranging from 30 kV cm⁻¹ to 110 kV cm⁻¹. (d) The change in P_r , $P_{\max}$ and $S_{\max}$ of BNKT-SBTZ6 as a function of the number of electrical fatigue cycles (measured up to 10⁵ cycles at 1 Hz under 50 kV cm⁻¹) at ambient temperature, and the inset shows the bipolar P - E and bipolar S - E hysteresis loops of BNKT-SBTZ6 measured at 1 Hz after the first and 10⁵th cycles, respectively.

Fig. 2 (a) X-ray diffraction patterns of the BNKT-SBTZ100 x powder with $x = 0.00-0.08$, and the insets of Fig. 2(a) show the enlarged view. (b) The Rietveld refinement of the data for BNKT-SBTZ6 at ambient temperature, with the inset showing the SAED pattern of the sample recorded along the [013] zone axis. Superlattice diffraction spots of $1/2\{00\}$ -type, marked by the red circle, and $1/2\{000\}$ -type, marked by the white circle, are visible.

Fig. 3 (a) Raman spectra mapping of the poled BNKT-SBTZ0 and BNKT-SBTZ6 upon heating and subsequently cooling process at 30-330 °C; the cooling Raman spectra of poled specimens can be approximately equal to the heating Raman of the unpoled specimens because the poling state of the poled specimens is disrupted by heating to 330 °C. (b) Raman spectra at 100 °C and 110 °C (below and above T_{F-R}) of the poled BNKT-SBTZ0 and the Raman spectra at 30 °C and 50 °C of the poled BNKT-SBTZ6 at the heating and subsequently cooling process.

Fig. 4 (a) Atomic-resolution HAADF-STEM image of the BNKT-SBTZ6 ceramic along the [001] zone axis, showing the existence of A-site vacancies (V_A) marked by yellow circle. (b) The representative intensity trace along the yellow rectangular frame in Fig. 4(a). (c) Structure model for the BNKT-SBTZ6 ceramic along the [001] zone axis, including (I) the defect-free state and (II) the state with defects due to the existence of V_A and oxygen vacancies (V_O). (d) and (e) Landau potential corresponding to two different states, including (I) the defect-free state and (II) the state with defects.

Fig. 5 (a) A part of bipolar P - E of the BNKT-SBTZ100x ceramics measured at ambient temperature, 50 kV cm^{-1} and 1 Hz. (b) The variation of poling field (E_{pol}) and depoling field (E_{dep}) for BNKT-SBTZ100x.

Fig. 6 (a) The unipolar S - E curve of the BNKT-SBTZ6 ceramic, and the inset shows the TEM image of the sample with nanodomains and lamellar domains. The schematic microstructure evolution of domain states upon electric loading and unloading is also shown. Black dots represent point defects; Nanodomains are transparent and lamellar domains are in yellow. (b) The schematic Landau free energy curves of five representative states on the S - E curve, that is, P_0 , P_1 , P_2 , P_3 , and P_4 .

Table 1 Comparison of $S_{\max}$, $(S_{\max}/E_{\max})_{\max}$ and $\Delta S/S_{\max}$ of the BNKT-SBTZ6 ceramic and the other representative ceramics reported in the literature.

Materials	$S_{\max}$ (%)	$(S_{\max}/E_{\max})_{\max}$ (pm V ⁻¹)	$\Delta S/S_{\max}$ (%)
BNKT-SBTZ6^[This work]	0.72	916	36.2
BNKT-5ST ^[29]	0.36	600	66.8
BNKTZ-3 ^[23]	0.43	614	52.6
BNKLiTN-ST ^[30]	0.40	800	69.1
BNT-2.5Nb ^[9]	0.70	1400	68.9
BNBT6-2FS ^[10]	0.57	713	69.7
Textured KBT-BT-NBT ^[27]	0.48	400	17.2
92BNT-6BT-2KNN ^[6]	0.45	563	68.6
BNT-BT Composite ^[20]	0.33	824	69.1
KNN-based ^[28]	0.16	400	9.2
BT-based ^[31]	0.07	1444	21.9
Pb-based ^[32]	0.39	650	39.1