Creating Adjoining Polymorphic Phase Transition (PPT)

Regions in Ferroelectric (Ba,Sr)(Zr,Ti)O₃ Ceramics

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Abstract: In this work, we report the polymorphic phase transitions(PPT) in ferroelectric Ba_{0.95}Sr_{0.05}Zr_xTi_(1-x)O₃ (BSZT, $x=0.01\sim0.10$) ceramics synthesized by using a solid-state reaction method. The doping elements and composition ratios were selected to create adjoining PPT phase boundaries near room temperature, hence to achieve a broadened peak of piezoelectric performance with respect to composition. The temperature-composition phase diagram was constructed and the effects of PPT on the electromechanical and ferroelectric properties of the ceramics were investigated. It was revealed that the two adjacent PPT regions at room temperature showed different characteristics in property enhancement. However, due to the proximity of the phase boundaries, Ba_{0.95}Sr_{0.05}Zr_xTi_(1-x)O₃ ceramics in a fairly broad range of compositions ($0.02\leq x\leq 0.07$) showed excellent piezoelectric properties,

¹ Certain commercial equipment, instruments, or materials are identified in this paper to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

including a large piezoelectric constant ($312 \text{ pC/N} \leq d_{33} \leq 365 \text{ pC/N}$) and a high electromechanical coupling coefficient k_p ($0.42 \leq k_p \leq 0.49$).

Keywords: Ferroelectric ceramics; Solid solution; Polymorphic phase transition; Piezoelectricity; Barium titanate

1. Introduction:

Electromechanical performance of ferroelectric ceramics has a close relationship with their phase structures[1-8]. The high d_{33} piezoelectric coefficients in PZT ceramics are results of the effect of a morphotropic phase boundary(MPB) created by a proper Zr/Ti atomic ratio[9, 10]. A MPB was initially defined as a vertical or near-vertical phase boundary in the temperature-composition (T - x) diagram which separates two polymorphic phases. It represents a very narrow composition region wherein two different phases coexist over a range of temperatures. On the other hand, for many other piezoelectric ceramics, the concept of polymorphic phase transition (PPT) instead of MPB has been used. For example, it is well known that a undoped BaTiO_3 (BT) ceramic have a rhombohedral-(R) $\rightarrow$ Orthorhombic (O) $\rightarrow$ Tetragonal(T) polymorphic phase transition sequence when it is heated from a low temperature to room temperature (RT) before it finally transforms into the paraelectric cubic phase above the Curie temperature T_C ($\sim 130^\circ\text{C}$). This temperature sensitive polymorphism is associated with enhanced electromechanical properties in ferroelectric ceramics[6, 11-13], i.e., when the temperatures are near the PPT temperatures (T_{PPT}), such as $T_{\text{O-T}}$ or $T_{\text{R-O}}$, the ferroelectric ceramics demonstrate

performance peaks in their piezoelectric and dielectric responses.

L. E. Cross proposed five types of control in the engineering of ferroelectric phase transitions, including both MPB and PPT approaches, in his famous tutorial review on tailoring the properties of ferroelectric ceramics for specific applications[14]. He presented in the review the change of T_{PPT} and T_{C} in BaTiO₃-based ceramics with different doping elements. Adapted from Ref. [14], Fig. 1(a) to 1(c) describe the effects of a doping element on phase transition behavior of the BT ceramic in the case of a decreasing tolerance factor t . A single doping element will stabilize the lower symmetry phases of O and R near RT, if the curves of T_{PPT} vs. doping concentration are sloping up (Fig 1a), leading to the formation of a “pinch-off” region between the two T_{PPT} curves and a sloping-down T_{C} curve (Fig. 1a). This type of phase transition behavior takes place in some doping elements including Zr, Sn and Hf[4, 14], all of which substituting the B-site Ti ions with larger ionic radius. Fig 1(b) (c) show another type of commonly observed phase transition behavior: both the T_{C} curve and the T_{PPT} curves slope down but with different slopes. Fig 1(b) shows a much slower ramping-down of the T_{PPT} with the doping concentration as compared with that of T_{C} , while Fig. 1(c) illustrates the opposite scenario with a much slower decreasing T_{C} . Sr and Ca are representative elements of the two scenarios of phase transition behavior with doping elements, respectively. Sr²⁺ ions have the smallest radius difference among di-valence cations that can replace Ba²⁺ in BT, therefore it produces the smallest perturbation on the stability of the low symmetry phases, especially on that of the R phase which is induced by a

rotation of the oxygen octahedral, a lattice distortion sensitive to the stacking density (hence ionic radii) of the perovskite structure.[1, 15] On the other hand, Ca^{2+} ions have a much larger size difference with Ba^{2+} , therefore the stabilities of low symmetry phases are perturbed more prominently, as shown in Fig. 1(c). For an increasing tolerance factor t due to doping with larger A-site ions, Fig 1(d) illustrates the composition-dependent T_{PPT} and T_{C} . It is noted that the three phase transition behaviors demonstrated in Fig. 1b through 1d correspond to stabilization of high symmetry phases (either C or T phases) near RT instead of low symmetry ones.

In recent years, a lot of research efforts have been made to construct rhombohedral–orthorhombic(R–O), orthorhombic–tetragonal(O–T) and tetragonal–rhombohedral (T–R) phase boundaries near room temperature in BaTiO_3 - and (K, Na) NbO_3 - based ceramics[3-5, 7, 16-18]. These efforts are mostly concentrated in obtaining discrete PPT or MPB regions near RT in the T - x diagram. This goal has been achieved by taking advantage of the phase transition behavior shown in Fig 1a for single-element doped BT ceramics[4, 16], where the O-T and R-O PPT regions are usually well defined and separated by a sizable composition difference. Moreover, by constructing a complex phase diagram with multiple doping elements differing in the induced phase transition behaviors, it is possible to create a MPB-like phase boundary under a tricritical point[7, 17], or a 3-phase PPT region near the convergent (composition) point of two phase boundaries [5, 18], leading to greatly enhanced electromechanical properties. However, the major drawback of a discrete PPT or MPB region, whether it is a two-phase region or a three-phase one, is the lack of

compositional stability of the enhanced properties. Just like in the case of MPB-PZT materials, a slight deviation from the PPT or MPB composition will lead to a rapid deterioration of the electromechanical properties[6, 7, 9, 10, 16, 18].

In the present work, we start with a general design approach to bring two discrete PPT regions close to each other, so that the electromechanical properties will show a broadened peak with respect to the composition. We use BaTiO₃-based solid solutions as the model system and propose the following design principles:

- (1) Both PPT phase boundaries need to move towards room temperature with an increasing doping concentration, i.e., low symmetry phases need to be stabilized near RT. This is in accordance with the approach to obtain discrete PPT regions. Doping elements with the induced phase transition behavior as shown in Fig. 1(a) meet this requirement to create PPT regions near RT in BT-based ceramics.
- (2) In order to merge two PPT regions near room temperature, it is necessary to generate a sharper “pinch-off” in the T-x diagram than those producing discrete PPT regions as shown in Fig. 1(a), i.e., the PPT temperature closer to RT (T_{PPT}^1) needs to move towards RT at an decelerated rate while the T_{PPT} further away from RT (T_{PPT}^2) does the opposite. Alternatively, a sharper “pinch-off” can be created by having a smaller baseline T_{PPT}^1 and/or a larger baseline T_{PPT}^2 than those in Fig. 1(a). These changes in the slope or the intercept of a T_{PPT} curve can be combined to produce a more prominent effect.

In the case of BT-based ceramics, a natural pinch-off by single-element doping as shown in Fig 1(a) is not sharp enough to generate adjoining R-O and O-T PPT regions.

It is necessary to combine an element from Fig 1(a) with that of Fig 1(b), so the stable region of the intermediate O phase will shrink and hence the two phase boundaries can be brought close to each other (Fig. 1(e)).

2. Design of Compositions

In our work, we selected Sr and Zr as the two doping elements with the former replacing Ba (the A-site ions) and the latter Zr (B-site ions). In the periodic table of elements, Sr is right above Ba and Zr is right under Ti, hence doping of the two in a BaTiO₃ ceramic would form a continuous solid solution with a good chemical stability. More importantly, with their individual doping effects reflected in Fig. 1(a) and Fig. 1(b), a combination of the two will meet the two principles stated above for merging of the two PPT regions. On one hand, Zr doping can rapidly increase the T_{O-T} and T_{R-O} [14, 19, 20] of the BT ceramic, which means that the PPT temperatures of (Ba,Sr)(Zr,Ti)O₃ ceramics (BSZT) could move to RT with a small amount of Zr (Fig. 1a). On the other hand, Sr has a weaker effect on shifting the PPT temperatures at the same doping level (Fig. 1b). Therefore, we chose to fix the Sr concentration at a nominal level of 5% and vary the Zr concentration (x) in our experimental investigations.

In our previous work[21], Ba_{0.95}Sr_{0.05}Zr _{x} Ti_(1- x)O₃ (BSZT, x = 0.05, 0.08, 0.10, 0.15, 0.20) ceramics were synthesized by using a solid-state reaction method and a PPT temperature was revealed at about 50°C in the BSZT ceramic with 5% Zr. This temperature moved up towards T_C and became indistinguishable from T_C when the Zr

concentration reached 10% or above[21]. This result indicates that a rich collection of polymorphs exists in the BSZT ceramics near RT with the Zr concentration between 1% and 10%[4]. To validate the above-mentioned design principles and explore these PPT regions, we prepared $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ (BSZT) ceramics with a composition interval of 1% in the Zr compositions of interest, i.e., $x=0.01\sim0.10$. These ceramics were synthesized by using the solid-state reaction method described in Ref. [21]. The composition-tunable phase structures, as well as the effects of T_{PPT} on the electrical properties, are investigated for the BSZT ceramics.

3. Experimental procedures:

For the preparation of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics (BSZT, $x=0.01\sim0.10$), strontium carbonate (SrCO_3 , 99%, Sinopharm Chemical Reagent Co.,Ltd), titanium oxide (TiO_2 , 98%, Sinopharm Chemical Reagent Co.,Ltd), zirconium oxide (ZrO_2 , 99%, Sinopharm Chemical Reagent Co.,Ltd) and barium carbonate (BaCO_3 , 99%, Sinopharm Chemical Reagent Co.,Ltd) powders were used as raw materials in a solid-state reaction process. The sintering temperature was set at 1400 °C and pellet samples of 10 mm in diameter and 1 mm in thickness were prepared for analysis[21].

Relative densities of the ceramic samples were measured by using the Archimede's method. Surface morphology and crystalline structures of as-sintered ceramics were analyzed via Scanning Electron Microscopy (SEM, SU-70, Hitachi) and X-Ray Diffraction ($\lambda=1.5406\text{ \AA}$, Rigaku Dmax-rc diffractometer with Ni-filtered Cu K α radiation), respectively. The results were shown in Fig. 2 (SEM images) and

Fig. 3 (XRD 2 θ scan spectra). Temperature dependent dielectric properties of the ceramics were measured by using a Broadband Dielectric/Impedance Spectrometer (Novocontrol CP-80) in a temperature range of [-100°C, 150°C] (Fig. 4). Ferroelectric hysteresis loops were measured by using a ferroelectric tester (Radiant Precision Multiferroic PMF0513-330) (Fig. 6) and the results were summarized in Fig. 7. Lastly, the piezoelectric properties of the BSZT ceramics were measured and the results were summarized in Fig. 8. The longitudinal piezoelectric modulus d_{33} was measured by using a quasi-static piezoelectric d_{33} meter. Prior to the measurement, the samples were poled under a dc field of 1 kV/mm at room temperature for 40 min in a silicone oil bath. The planar electromechanical coupling coefficient k_p and the mechanical quality factor Q_m were determined by using the resonance-antiresonance method[22]. For all electrical/electromechanical measurements, silver paste electrodes were painted on both sides of the samples to make contacts.

4. Results and discussion:

Representative SEM micrographs of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics are shown in Fig. 2 (a)-(e). The samples showed a densely-packed, large-grained morphology, typical of the sintered ceramics via solid-state reaction. The relative densities of these samples are about the same, which is ~98%. The average grain size measured from the SEM micrographs decreased from 79.9 μm , to 79.6 μm , 75.6 μm , 61.1 μm and 47.5 μm with the Zr concentration increasing from 1 % to 3%, 5%, 7% and 9%, respectively, (Fig. 2 (f)). This compositional dependence of grain

size can be attributed to the mobility difference between the host Ti^{4+} ions and the substitutional Zr^{4+} ions. Because of the larger ionic radius and atomic weight compared with those of Ti^{4+} , Zr^{4+} has a smaller mobility than Ti^{4+} at the same temperature. With an increasing amount of Zr^{4+} ions, the mobility of grain boundaries was reduced, which slowed down the inter-grain diffusion process and hence decreased the grain size[21, 23].

Fig. 3 shows the room temperature XRD 2θ spectra of the BSZT ceramics. In order to highlight the process of phase evolution with the Zr concentration, the zoomed-in XRD spectra near $2\theta = 45^\circ$ were also displayed. All the XRD spectra showed the characteristic peaks of a perovskite structure, which overlapped with those of the standard BaTiO_3 2θ spectrum. This implies that a stable solid solution has formed by the substitution of Ba^{2+} , Ti^{4+} with Sr^{2+} , Zr^{4+} , respectively. In addition, the diffraction peaks of the BSZT ceramics shifted to the lower angle side of 2θ with an increasing Zr concentration, which can be explained by an increasing lattice parameter with the addition of larger Zr^{4+} ions. Moreover, the (200) peaks of the BSZT ceramics at $2\theta \sim 45^\circ$ showed an evolution of the phase structure. When the Zr concentrations were 1% and 2%, the XRD spectra corresponded to a single tetragonal (T) phase. With the increase of the Zr concentration, an orthorhombic (O) phase appeared and a mixed phase of T+O became dominant at room temperature (Zr%=3%, 4% and 5%). Further increase of the Zr concentration led to the formation of a mixed phase of O+R (Zr%=6% and 7%), and at last, the ceramics with Zr%>7% stabilized in the rhombohedral (R) phase.

To confirm the existence of adjoining PPT regions, temperature dependent dielectric properties of the ceramics were measured from -100°C to 150°C. Fig. 4 shows the temperature dependent dielectric constants (ϵ_r) and losses ($\tan\delta$) of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics ($x= 0.01\sim 0.10$) measured at 1 kHz. T phase was identified in the ceramic with $x= 0.01$ at room temperature, matching the phase structure of pure BaTiO_3 . With an increasing Zr concentration, $T_{\text{O-T}}$ and $T_{\text{R-O}}$ moved up towards T_{C} , which was ramping down towards the room temperature. When the Zr concentration increased to 10%, $T_{\text{O-T}}$ and $T_{\text{R-O}}$ merged into one point. This tricritical point ($x\sim 10\%$) appeared much earlier than those reported for single element Zr-doped BT ceramics ($x\sim 15\%$)[4, 14, 20], indicating that co-doping with Sr successfully reduced the stability region of the O phase, and, therefore, the two PPT regions (T-O and O-R) have been brought close to each other. With the Zr concentration increasing from 1% to 10%, T_{C} of the BSZT ceramics decreases from 106°C to 73°C, which is consistent with a decreasing tolerance factor (t) toward $t=1$ [21, 24, 25]. The maximum dielectric constant, ϵ_r^{peak} , increased from 8300 to 14000 with the Zr concentration increasing from 1% to 9%. The ϵ_r^{peak} fell back to ~ 10400 at $\text{Zr}\%=10\%$ where $T_{\text{O-T}}$ and $T_{\text{R-O}}$ merged into one point[26].

Based on the XRD and dielectric data, the temperature-composition (T-x) phase diagram of our BSZT ceramics was constructed (Fig. 5). Stable regions of different phases were determined by using T_{C} , $T_{\text{O-T}}$ and $T_{\text{R-O}}$ curves as function of the Zr concentration. Comparing with the T-x diagram for $\text{Ba}(\text{Zr}, \text{Ti})\text{O}_3$ (superimposed in Fig.5), double doping with both Zr and Sr has successfully brought the O-T (x

$=0.03\pm0.01$) and R-O ($x =0.06\pm0.01$) PPT regions together, forming a fairly wide composition range ($0.02\leq x\leq0.07$) where the three polymorphic phases- tetragonal, orthorhombic, and rhombohedral phases have very close bulk free energies at room temperature.[27] Consequently, BSZT ceramics in this composition range can easily adapt to an external electric field or mechanical load by switching between the different phases and associated domain states, and, therefore, they should demonstrate a broadened peak in their electromechanical performance with respect to composition.

P-E hysteresis loops of the BSZT ceramics are given in Fig. 6. The saturated and remnant polarizations (P_s , P_r), as well as coercive fields (E_c) are summarized in Table 1 and plotted as functions of the Zr concentration in Fig. 7. All ceramics exhibit typical ferroelectric *P-E* loops. The saturated polarization showed two peaks near the PPT boundaries, one at $x= 0.03$ (T/T-O) and the other at $x= 0.07, 0.08$ (O-R/R). The first P_s peak can be attributed to an enhanced ferroelectricity at the T-O PPT boundary (P_r peaked at $\sim12.0\mu\text{C}/\text{cm}^2$), while the second P_s peak is mostly due to a large contribution from the dielectric constant ε_r , which peaked at the O-R PPT boundary ($P_s\sim P_r+\varepsilon_0\varepsilon_rE_s$, where ε_0 and ε_r are the dielectric constant of the vacuum, relative dielectric constant of the ceramic, respectively, and E_s is the saturation electric field). On the other hand, the polarizations showed small values near the two ends of the composition range ($x= 0.01$ and $x= 0.10$), indicating a reduced polarizability in stable single phase states (T and R). Lastly, the coercive field E_c varied little across the T and T-O phase regions ($E_c \sim2.0$ kV/cm when $x\leq0.05$), and it plummeted at the O-R phase boundary ($E_c \sim1.5$ kV/cm at $x=0.06$). With a further

increase of the Zr concentration, E_c decreased and reached its minimum at $x=0.08$ before it finally went up with the composition in the single R phase region. It is noted that high P_s and low E_c were simultaneously achieved for $x = 0.07, 0.08$, compositions near the R-O phase boundary, which indicates that this boundary between lower symmetry phases can effectively soften the ceramic and improve its polarizability [1, 3]. It has been reported that an intermediate monoclinic phase (M) may exist in the process of a R-O phase transition, which could help soften the domain walls and re-arrange the polar phases under an external field[16, 28, 29]. Based on these results, an enhanced piezoelectric performance is expected near the R-O phase boundary.

Fig. 8 shows the composition dependent piezoelectric performance, i.e., Q_m , k_p and d_{33} , for the BSZT ceramics. The mechanical quality factor Q_m showed a weak composition dependence. The measured Q_m values are in the range of ~200-250, typical of piezoelectric ceramics sintered via the regular, single-step solid state reaction method. On the other hand, d_{33} and k_p showed strong composition dependence with similar trends, which first increase with the Zr concentration and reach a plateau for a fairly broad composition range. Further increase of the Zr concentration leads to declines in both parameters. The characteristic performance levels at their plateaus are $d_{33} \sim 312$ to 365 pC/N and $k_p = 0.42$ to 0.49. The composition range corresponding to the performance plateaus correlates well with that of the merged PPT regions shown in Fig. 5, i.e., $0.02 \leq x \leq 0.07$. All the piezoelectric property data were summarized in Table 1, together with the data from the electrical

measurements. Ceramics at the O-T phase boundary where $x \sim 0.03$ showed a large d_{33} value of ~ 357 pC/N, a Curie temperature T_C of $\sim 99^\circ\text{C}$ and the largest remnant polarization of ~ 12.0 $\mu\text{C}/\text{cm}^2$. On the other hand, ceramics at the O-R phase boundary ($x \sim 0.06$) gave the best electromechanical performance with $d_{33} \sim 365$ pC/N, $\epsilon_r \sim 2000$ and $k_p \sim 0.48$ at the cost of a reduced Curie temperature ($T_C \sim 90^\circ\text{C}$). These experimental observations are consistent with our expectations on the two engineered phase boundaries.

5. Conclusion:

We successfully merged the Orthorhombic-Tetragonal (O-T) and Rhombohedral-Orthorhombic (R-O) PPT regions near room temperature in the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ (BSZT, $x = 0.01 \sim 0.10$) ceramics sintered via a solid-state reaction method. Although the two PPT regions of the ceramics showed different characteristics in property enhancement, the proximity of the phase boundaries created a compositional stability for the piezoelectric properties. In general, $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics with Zr concentrations in the two adjoining PPT regions ($0.02 \leq x \leq 0.07$) showed large d_{33} piezoelectric constants ($312 \text{ pC/N} \leq d_{33} \leq 365 \text{ pC/N}$) and high electromechanical coupling coefficients k_p ($0.42 \leq k_p \leq 0.49$). Our design approach can be applied to other ferroelectric ceramics with multiple doping elements, where a concerted effect can be obtained to bring two phase boundary compositions close to each other near the temperature of application interest, and, therefore, an enhanced electromechanical performance can be achieved and stabilized in a fairly broad composition range.

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Table 1 The room temperature electrical and electromechanical properties of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics with different Zr concentrations ($x=0.01\sim 0.10$).

Zr concentrations (%)	1	2	3	4	5	6	7	8	9	10
T_C ($^{\circ}\text{C}$)	105.6	102.9	99.0	95.7	92.6	89.8	85.4	81.2	75.6	72.8
ε_r	1536	1875	1718	1586	1665.	2005	2079	2131	2122	1654
$\tan\delta$	0.02	0.02	0.04	0.04	0.03	0.03	0.04	0.04	0.04	0.03
P_s ($\mu\text{C}/\text{cm}^2$)	10.9	12.8	16.6	13.9	13.9	13.7	15.5	16.0	13.2	13.4
P_r ($\mu\text{C}/\text{cm}^2$)	5.4	6.7	12.0	8.6	9.3	7.0	9.2	9.3	6.8	7.9
E_c (kV/cm)	2.10	1.94	2.14	2.08	2.26	1.51	1.40	1.30	1.37	1.77
d_{33} (pC/N)	181	312	357	319	349	365	328	247	241	238
k_p	0.28	0.42	0.46	0.49	0.49	0.48	0.47	0.34	0.32	0.30
Q_m	232.9	241.7	228.6	248.6	189.3	220.5	223.4	235.2	174.0	264.2

Fig. 1 The phase transition behavior of BT ceramics doped with: (a) a larger B-site ions, such as Zr, Sn and Hf, (b) a slightly smaller A-site ion, such as Sr, (c) a much smaller A-site ion, such as Ca, (d) a larger A-site ion, such as Pb; (e) the effect of co-doping with a larger B-site ion and a slightly smaller A-site ion on bringing together the two polymorphic phase transition regions. ((a)-(d) adapted from Ref. 14.)

Fig. 2 The SEM micrographs of polished then thermally etched surfaces of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ (BSZT) ceramics sintered at 1400 °C : (a) $x= 0.01$; (b) $x= 0.03$; (c) $x= 0.05$; (d) $x= 0.07$; (e) $x= 0.09$; (f) the average grain size of the BSZT ceramics as a function of the Zr concentration.

Fig. 3 The XRD 2θ-scan spectra of the Ba_{0.95}Sr_{0.05}Zr_xTi_(1-x)O₃ ceramics ($x=0.01\sim0.10$)

Fig. 4 Temperature dependent (a) dielectric constants and (b) dielectric losses of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics ($x = 0.01 \sim 0.10$), measured at 1 kHz.

Fig. 5 Temperature-Composition (T-x) phase diagram of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ (BSZT) ceramics; solid symbols are data points of the phase transition temperatures, those at $x=15\%$ and $x=20\%$ are taken from Ref. 21, while the solid lines are guide for the eyes; the dashed lines give the phase transition temperatures of $\text{BaZr}_x\text{Ti}_{(1-x)}\text{O}_3$ (BZT) ceramics as functions of Zr%, taken from Ref. 20.

Fig. 6 The P - E hysteresis loops of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics

($x=0.01\sim 0.10$) measured at 1 Hz.

Fig. 7 The saturated and remnant polarizations (P_s , P_r), as well as the coercive field (E_c) of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics, as functions of the Zr concentration ($x=0.01\sim0.10$).

Fig. 8 Composition dependent piezoelectric properties (Q_m , k_p and d_{33}) of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics ($x=0.01\sim0.10$).