Electromechanical Properties of (Ba,Sr)(Zr,Ti)O₃ Ceramics

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Abstract: In this work, we report dielectric, piezoelectric and ferroelectric properties of perovskite Ba_{0.95}Sr_{0.05}Zr_xTi_(1-x)O₃ (BSZT, $x=0.05, 0.10, 0.15, 0.20$) ceramics synthesized by using a solid-state reaction method. It is demonstrated that when the Zr concentration was 5 at% and the sintering temperature was 1400 °C, the BSZT ceramic gives the best overall electromechanical performance, including a large remnant polarization of $\sim 12.1 \mu\text{C}/\text{cm}^2$, large dielectric constants ($\epsilon_r^{\text{peak}} \approx 12600$, $\epsilon_r^{\text{RT}} \approx 3500$) and

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.

an excellent d_{33} value of ~ 355 pC/N. Curie temperature of this ceramic is about ~ 100 °C.

The enhanced electromechanical properties of the BSZT ceramics as compared with $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{TiO}_3$ (BST) can be explained by optimization of the tolerance factor and shift of ferroelectric polymorphic phase transition temperatures (T_{PPT}).

Keywords: Lead-free piezoceramics; Phase structure; Polymorphic phase transition; Piezoelectricity; Barium titanate

1. Introduction:

Lead–zirconate–titanate-based (PZT) ceramics are widely used in sensing and actuating devices because of their excellent piezoelectric properties[1]. However, there is a rising concern about recycling and disposal of devices containing lead due to its toxicity, especially those used in consumer electronics including cars, smart systems and sound generators[2]. Furthermore, applications of piezoelectric ceramics in the biomedical field is highly restricted due to the same reason. Therefore, development of high performance lead-free piezoelectric ceramics has become a consensus among world-wide ceramic researchers.

As a famous ferroelectric and piezoelectric material, barium titanate (BT) as early as in 1942 was synthesized by the scientists of United States and Soviet Union. Pure BT ceramics have a moderate d_{33} of ~ 190 pC/N [3], while this number for PZT ceramics is up to 500–600 pC/N due to the effect of a morphotropic phase boundary created by a proper Zr/Ti atomic ratio [4]. From the PZT experience, it came naturally to place the composition to the proximity of a transition between two ferroelectric phases[4] to

achieve high piezoelectricity in a BT-based solid solution ceramic. In the periodic table of elements, Sr is right above Ba and Zr right under Ti. Either of the two elements can be added to barium titanate to form complete solid solutions, (Ba,Sr)TiO₃ (BST) or Ba(Zr, Ti)O₃ (BZT). Studies of BST and BZT solid solutions have shown improved electromechanical properties, including an enhanced dielectric constant and a reduced dielectric loss in BST [5], and improved piezoelectric properties (electromechanical coupling coefficient k_{33} =56.5%, piezoelectric stain coefficient d_{33} =236 pC/N) in BaZr_{0.05}Ti_{0.95}O₃ ceramics [7]. However, there are very few reported investigation focusing on the design of phase structures in (Ba,Sr)(Zr,Ti)O₃ (BSZT) ceramics to achieve optimal electromechanical properties, which is the topic of the present work.

Manipulating stability of the perovskite phases by varying the type and amount of dopants is the key to obtain desirable co-existing phase structures with optimized electromechanical properties. It has been reported that the Curie temperature (T_C) drops with Sr or Zr doping, while temperatures of the ferroelectric polymorphic phase transitions (O→T and R→O), i.e., T_{O-T} and T_{R-O} , move up towards the room temperature with an increasing amount of Zr/Sr in BT ceramics. [5-7] Some researchers indicated that coexistence of multiple phases at room temperature can help to improve the dielectric and piezoelectric performance of these solid solution ceramics [6, 8, 9]. However, there have been very few reported studies in correlating a detailed phase structure analysis with electrical property data, i.e., demonstrating the relationship between electrical properties of a perovskite ferroelectric, and the composition of its phase structure. In this study, we will not only present the structure and property data of the BSZT ceramics, but also

explain the evolution of the microstructure and properties with dopant amount (Zr%) and temperature.

2. Design of Ceramics via the Tolerance Factor (t)

Goldschmidt's tolerance factor, t , is usually used to describe the stability of a perovskite structure [10]. When t is close to 1, the perovskite structure becomes less distorted from a cubic lattice and hence is more stable. In contrast, with tolerance factor deviating from 1, the structural instability increases and low symmetry phases become dominant [10]. Therefore, Curie temperature of a doped ceramic will fall below that of the undoped one if its t value is closer to 1. This has been verified in numerous research reports [11-14].

The tolerance factor (t) of a perovskite oxide is computed using the formula below:

$$t = (R_A + R_O) / \sqrt{2}(R_B + R_O) \quad (1)$$

where R_A , R_B and R_O are the ionic radii of the A-site, B-site, and oxygen atoms, respectively [10]. The t values of pure BT and 5% Sr doped BT are 1.062 and 1.059 based on the ionic radii data from Refs. 13 and 14. With the doping amount of Zr% increasing from 5% to 10%, 15% and 20%, the t value is reduced to 1.055, 1.052, 1.050, and 1.047, respectively (Table 1). Therefore, we can expect a continuous decreasing of Curie temperature with the increasing amount of Zr% in $\text{Ba}_{0.95}\text{Sr}_{0.05}(\text{Zr,Ti})\text{O}_3$ ceramics. On the other hand, according to the research by Yu Z. et al[6], the temperatures of polymorphic phase transitions (T_{PPT}) will increase with an increasing Zr concentration. The movement of phase boundaries towards each other from both sides of the temperature axis expands

the spectrum of possible phases existing in the ceramics, hence making it difficult to determine the optimal composition for electromechanical performance without a systematic study of structure-property relations.

Table 1 The tolerance factor and T_C of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics *

x	Tolerance factor (t)	T_C (°C)
0	1.059	114 ^[15]
0.05	1.055	100
0.10	1.052	80
0.15	1.050	56
0.20	1.047	28

*: The ionic radii: Ba^{2+} : 1.61 Å, Sr^{2+} : 1.44 Å, Ti^{4+} : 0.605 Å, Zr^{4+} : 0.72 Å, O^{2-} : 1.40 Å [16, 17]

3. Experimental procedures:

Strontium carbonate (SrCO_3 , 99%), titanium oxide (TiO_2 , 98%), zirconium oxide (ZrO_2 , 99%) and barium carbonate (BaCO_3 , 99%) powders were used as raw materials. They were weighted according to the compositions of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics (BSZT, $x=0.05, 0.10, 0.15, 0.20$). The powders were mixed and ball-milled in an ethanol solution. After 12 hours of ball milling, the slurries were air-dried at 120 °C.

The calcination temperature was determined via a DSC analysis. As shown in Fig. 1, there was a significant endothermic peak at ~830 °C, which corresponded to the decomposition of SrCO_3 and BaCO_3 near this temperature. Moreover, there was a

significant exothermic peak near 1050 °C, above which a proper synthesis process can be carried out. To make sure all the raw materials completely convert to BSZT, we set the calcination temperature to be 1150 °C. The dried powders were heated to 850 °C at 5 °C/min and held at 850 °C for 1 hour in an alumina crucible for decomposition. Then the temperature was raised to 1150 °C at 5 °C/min and the powders were held at this temperature for 6 hours. After cooling down to room temperature, the calcined powders were milled in an ethanol solution for 12 hours and air-dried again at 120 °C. The dried powders were then prilled at 75 MPa using a binder of 5 wt% polyvinyl alcohol (PVA). Then the prilled powders were compacted at 180 MPa to form pellets (Φ = 12 mm, t = 1.5 mm). These pellets were heated to 600 °C at 5 °C/min and held at 600 °C for 2 hours to remove the binder. The resulting samples were sintered in air at 1300 °C, 1350 °C and 1400 °C for 2 hours, respectively. The ramping rate was again set at 5 °C/min.

Density of the ceramic samples were measured by using the Archimedes method. To measure the grain size, surfaces of as-sintered samples were analyzed via Scanning Electron Microscopy (SEM). Crystalline structures of the ceramics were analyzed via X-Ray Diffraction. Moreover, to determine the phase compositions and their relative stabilities in these ceramic samples, temperature-dependent Raman scattering measurements were carried out by using a micro-Raman spectrometer (Jobin-Yvon LabRAM HR 800 UV) and a heating/cooling stage (Microstat HiRes, Oxford). A laser with a wavelength of 632.8 nm was used as the excitation source and an air-cooled charge coupled device (CCD) was used to collect the scattered signals dispersed on an 1800 grooves/mm grating in the frequency range of 50-650 cm^{-1} .

For electrical measurements, silver paste electrodes were painted on both sides of the sintered ceramic samples. The piezoelectric properties of the BSZT ceramics were 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 15 min in a silicone oil bath. The planar electromechanical coupling coefficient k_p was determined by using the resonance-antiresonance method. Temperature dependent dielectric properties of the ceramics were measured by using an LCR meter (Quadtech 7400 plus) connected with a programmable furnace in a temperature range of [25°C, 130 °C]. Lastly, ferroelectric hysteresis loops of the BSZT ceramics were measured by using a ferroelectric tester (Radiant WS-2000).

4. Results and discussion:

4.1 Optimal Sintering Temperature

Fig. 2 (a)-(c) are the SEM micrographs of BSZT ceramics with 5 % Zr concentration sintered at different temperatures. The ceramic sintered at 1300 °C has the minimum relative density (96.1 %) with an average grain size of $\sim 1.3 \mu\text{m}$. As the sintering temperature was increased to 1350 °C and 1400 °C, the density and grain size increased to 96.8 %/ $81.6 \mu\text{m}$, 98.2 %/ $109.7 \mu\text{m}$, respectively. To achieve a good densification, an optimal sintering temperature of 1400 °C was selected for all ceramic specimens. In the following discussions, all the structure and property data were measured from the 1400 °C sintered samples.

4.2 Microstructure Analysis

SEM micrographs of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics with different Zr concentrations sintered at 1400 °C are shown in Fig. 2 (c)-(f). The average grain sizes were $\sim 109.7\text{ }\mu\text{m}$, $\sim 76.2\text{ }\mu\text{m}$, $\sim 55.1\text{ }\mu\text{m}$ and $\sim 19.5\text{ }\mu\text{m}$ as the Zr concentration was increased from 5 at% to 10 at%, 15 at% and 20 at%, respectively. This suggests that the incorporated Zr^{4+} ions restrained grain growth in the BSZT ceramics. The difference between the sizes of Ti^{4+} and Zr^{4+} ions can be used to explain the decrease of grain size with Zr doping. Since Zr has a larger ionic radius and atomic weight than those of Ti, it has a smaller mobility than the latter at the same temperature. An increasing amount of Zr^{4+} ions would reduce the mobility of grain boundaries in the process of inter-grain diffusion, and hence decreases the grain size[18].

Fig. 3 shows the XRD patterns of the BSZT ceramics from the 2θ scans. Firstly, the four XRD patterns have the same characteristic peaks of a perovskite structure. This is consistent with the nature of a complete solid solution. Secondly, the diffraction peaks moved to the lower angle side of 2θ with the increase of Zr concentration, which can be explained by an increasing lattice parameter with the addition of larger Zr^{4+} ions. Lastly, the (200) peak of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ showed a split which indicates the existence of a tetragonal phase, while all other three ceramics did not show such a characteristic pattern (see the right-hand inset of Fig. 3).

To confirm the structural changes of BSZT ceramics with an increasing amount of Zr, Raman scattering measurements were carried out for the two BSZT ceramics with 5% and 20% Zr in a broad temperature range (- 190 °C ~150 °C). Due to lattice distortions

from the incorporation of Zr and Sr atoms, positions and intensities of the characteristic Raman peaks are slightly different from those of pure BaTiO₃ [19, 20]. Room temperature Raman spectra for the two compositions, and those measured at different temperatures (-190 °C ~150 °C), are shown in Fig. 4 and Fig. 5, respectively. The bands were labeled based on bibliographical data of BaTiO₃ ceramics [20-22]. In Fig. 4, the dip at 178 cm⁻¹ in the Raman spectrum of 5% Zr sample is absent in that of the 20% Zr sample. In addition, the Raman peak corresponding to the A₁+E(TO+LO) mode observed in the 5% Zr sample disappeared in the Raman spectrum of the sample with 20% Zr. It is well known that the disappearance of the dip at ~178 cm⁻¹ and the A₁+E(TO+LO) peak at ~301 cm⁻¹ is characteristic of the cubic-to-tetragonal phase transition [19]. Hence it can be concluded that the amount of tetragonal phase in the 20% Zr BSZT ceramic is negligible at room temperature.

Raman spectra of the 5% and 20% Zr samples were collected from -190 °C to 150 °C and compared in Fig. 5. For the 5% Zr BSZT ceramic at -190 °C, characteristic Raman peaks existed for all three polymorphic phases, i.e., orthorhombic (“O”), rhombohedral (“R”) and tetragonal (“T”) phases. As the temperature was increased, the Raman peak for the “O” phase (~490 cm⁻¹) shrank and eventually disappeared at ~-50 °C. In addition, the two strong peaks characteristic of the “R” phase (A₁ (TO₁) at ~161 cm⁻¹ and A₁ (LO₁) at ~189 cm⁻¹), levelled off with an increasing temperature, and disappeared at ~50 °C, i.e., the PPT temperature. Lastly, the characteristic features of the “T” phase, i.e., the dip at 178 cm⁻¹ and the A₁+E(TO+LO) mode at 301 cm⁻¹, disappeared in the spectra taken at temperatures above the Curie point (~100 °C). When it comes to the BSZT ceramic with

20% Zr, the A_1 (TO_1) and A_1 (LO_1) peaks, as well as the dip at $\sim 178\text{ cm}^{-1}$ can all be observed in the $-190\text{ }^\circ\text{C}$ Raman spectrum. The O phase did not show a separate characteristic Raman peak due to its structure similarity with the R phase at this composition[21, 22]. These two sets of characteristic peaks for the R/O and T phases shrank simultaneously in the Raman spectra collected at higher temperatures, and they almost disappeared at the same temperature, which indicates that the T_{PPT} and T_C have merged into one temperature (28°C from the dielectric measurement). These results are consistent with those reported for BT-based ceramics[20, 22, 23].

4.3 Electrical Properties

Temperature dependent dielectric properties of the BSZT ceramics were measured and the representative results are shown in Fig. 6. Curie temperatures (T_C) of these ferroelectric ceramics correspond to the locations on the temperature axis where the maximum dielectric constants appeared. With an increasing Zr concentration from 5% to 20%, T_C continuously decreases from $101\text{ }^\circ\text{C}$ (5% Zr) to $80\text{ }^\circ\text{C}$ (10% Zr), $56\text{ }^\circ\text{C}$ (15% Zr) and $28\text{ }^\circ\text{C}$ (20% Zr). This is consistent with our prediction based on the comparison of tolerance factors (see Table 1). Another possible source of contribution to the reduced T_C of the BSZT ceramics with a high Zr concentration comes from their reduced grain size, according to the study by Reddy et al. [24]. On the other hand, the polymorphic phase transition temperature T_{PPT} can only be observed in the BSZT ceramics with $\text{Zr}\% \leq 10\%$. This is due to the up-shifting of T_{PPT} with the addition of Zr, which eventually merges with the down-shifting Curie temperature. Such a process is better illustrated in Fig. 7.

With data points from 3% and 8% Zr doped BST ceramics in addition to those obtained from Fig. 6, Fig. 7 demonstrates the relationship between T_{PPT} and Zr% in our BSZT ceramics. It should be noted that for the BSZT ceramics with a 5% and 20% Zr concentration, the temperature-dependent dielectric properties agreed well with their Raman scattering data. Overall, the dielectric constants of these ceramics are very high (several thousands at room temperature, and approaching 10000 to 15000 near T_c), indicating that the A, B co-doping method with strontium and zirconium is effective on improving the dielectric properties of BT-based ceramics.

P-E hysteresis loops of the BSZT ceramics are given in Fig. 8, and the remnant polarizations (P_r) and coercive fields (E_c) are summarized in Table 2. With the increase of Zr concentration, the P - E loop shrinks due to smaller E_c and P_r . This is consistent with a decreasing tolerance factor (see Table 1) [10-12] and an evolving phase structure with the addition of Zr in the BSZT ceramics [6, 25]. For the BSZT ceramic with a 5% Zr concentration, the remnant polarization (P_r) is at the maximum of 12.1 $\mu\text{C}/\text{cm}^2$ while the coercive field (E_c) is about 2.7 kV/cm.

Table 2 The remnant polarizations (P_r) and coercive fields (E_c) of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics

Zr (x)	0.05	0.10	0.15	0.20
P_r ($\mu\text{C}/\text{cm}^2$)	12.1	10.4	6.7	4.0
E_c (kV/cm)	2.7	2.4	1.7	1.8

Table 3 presents the piezoelectric properties of our BSZT ceramics. The BSZT

ceramic with 5% Zr shows the maximum d_{33} ~355 pC/N and the best k_p value at 46.6%. This is consistent with its Raman and dielectric characteristics, both of which indicate a microstructure of multi-phase coexistence at room temperature[6, 21, 26]. In other words, by doping with Zr, we successfully created a polymorphic phase transition (PPT) region near room temperature, which has significantly enhanced the piezoelectric properties of our BST-based ceramics. The PPT causes instability of the polarization vector, which can be easily rotated under an external field and hence results in an improved piezoelectricity. [27, 28]

Table 3 Piezoelectric Properties of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics

Zr (x)	0.05	0.10	0.15	0.20
k_p	46.6%	31.9%	19.9%	6.2%
Q_m	249.0	297.5	437.2	405.5
d_{33} (pC/N)	355	227	134	106

4. Conclusion:

In this work, we systematically investigated effects of Zr doping on stability of the perovskite phases existing in the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ferroelectric ceramics, i.e., shifts of polymorphic phase transition (PPT) and paraelectric-ferroelectric phase transformation temperatures with a varying Zr% concentration (5%, 10%, 15%, 20%). It was revealed that a 5% Zr addition shifted the PPT region of $\text{R} \rightarrow \text{T}$ of the BST ceramic to near room temperature and significantly improved its piezoelectric property (d_{33} ~355 pC/N and k_p ~46.6%), while increasing the Zr concentration to 10% or above will cause the merge of

PPT temperature with the Curie point (T_c), deteriorating the room-temperature ferroelectric and piezoelectric properties. On the other hand, T_c decreases with the doping concentration of Zr, resulting in large dielectric constants of these BSZT ceramics. A 20% Zr doping brought down T_c to room temperature and the dielectric constant reached a maximum of ~15000.

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Figure captions

Fig. 1 DSC analysis of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_{0.10}\text{Ti}_{0.90}\text{O}_3$, the other three ceramics showed similar DSC curves

Fig. 2 The SEM micrographs of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics sintered at (a) 1300 °C, $x=0.05$; (b) 1350 °C, $x=0.05$; (c) 1400 °C, $x=0.05$; (d) 1400 °C, $x=0.10$; (e) 1400 °C, $x=0.15$; (f) 1400 °C, $x=0.20$.

Fig. 3 The XRD 2θ -scan patterns of $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics ($x=0.05, 0.10, 0.15, 0.20$)

Fig. 4 Room temperature (25 °C) Raman spectra of BSZT ceramics with compositions $x=0.05$ and $x=0.20$.

Fig. 5 Temperature-dependent Raman spectra of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics (a) $x=0.05$; (b) $x=0.20$.

Fig. 6 Temperature dependent dielectric constants of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics ($x=0, 0.05, 0.10, 0.15, 0.20$) measured at 1 kHz. Data points for $x=0$ come from Ref.15. The inset shows the dielectric constants measured near the Curie point (~ 28 °C) of the BSZT ceramic with 20% Zr.

Fig. 7 Phase transition temperatures of the $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_x\text{Ti}_{(1-x)}\text{O}_3$ ceramics with $0 < x \leq 0.2$.

Fig. 8 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 measured at 1 Hz.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8