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# Ferroelectric and piezoelectric properties of SrZrO<sub>3</sub>-modified Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> lead-free ceramics

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Abstract: The lead-free SrZrO<sub>3</sub>-modified  $Bi_{0.5}Na_{0.5}TiO_3$  (BNT-SZ100x, with x=0-0.15) ceramics were fabricated by a conventional solid-state reaction method. The effects of SZ addition on BNT ceramics were investigated through X-ray diffraction (XRD), scanning electron microscopy (SEM), ferroelectric and electric field-induced strain characterizations. XRD analysis revealed a pure perovskite phase without any traces of secondary phases. Ferroelectric and bipolar field induced-strain curves indicated a disruption of ferroelectric order upon SZ addition into BNT ceramics. A maximum value of remnant polarization (32 µC/cm<sup>2</sup>) and piezoelectric constant (102 pC/N) was observed at 5% (mole fraction) of SZ. Maximum value of the electric field-induced strain (S<sub>max</sub>=0.24%) corresponding to normalized strain ( $S_{max}/E_{max} = d_{33}^* = 340 \text{ pm/V}$ ) was obtained at BNT-SZ9. Key words: lead-free ceramics; BNT; perovskite structure; field induced strain

## **1** Introduction

Lead-based ceramics with perovskite structure, such as Pb(Zr,Ti)O<sub>3</sub> (PZT) and PZT-based multicomponent materials are widely used for actuators, sensors and micro-electromechanical devices owing to their superior piezoelectric properties [1-3]. However, the use of lead-based materials produces serious lead pollution and environmental problems due to high toxicity of lead oxide. Therefore, legislations such as RoHS/WEEE demand for development of high performance lead-free materials for electronic industry. In this scenario, the development of new environment-friendly materials for the replacement of PZT-based materials has become one of the most important issues.

Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> (BNT) is considered one of the most promising candidate materials for the piezoelectric applications. It has ABO<sub>3</sub> perovskite structure with a ferroelectric rhombohedral symmetry (R3C) at room temperature [4,5]. As temperature increases, the phase of BNT transform from rhombohedral to tetragonal and finally into cubic phase [6]. BNT shows strong ferroelectricity ( $P_r$ =38  $\mu$ C/cm<sup>2</sup>), but also has drawbacks such as a large coercive field  $(E_c)$  of approximately 7.3 kV/mm and a high conductivity [7,8]. To decrease its conductivity and improve its piezoelectric properties, it has been modified with various types of perovskite materials, such as CaTiO<sub>3</sub> (CT) [9], BaTiO<sub>3</sub> (BT) [10-13], SrTiO<sub>3</sub> (ST) [7,14,15], BiAlO<sub>3</sub> (BA) [16-18], (Bi<sub>0.5</sub>K<sub>0.5</sub>)TiO<sub>3</sub> (BKT) [19,20], NaNbO<sub>3</sub> (NN) [21], KNbO<sub>3</sub> (KN) [22] and BaSrTiO<sub>3</sub> (BST) [23,24]. Furthermore, it has also been modified with divalent (Ca, Sr, Ba) [25] and trivalent (La, Nd, Ho, Yb) [26] ions. Above studies [7-26] revealed that the formation of a new solid solution is an effective way to improve the ferroelectric and piezoelectric properties of the BNT ceramics.

Strontium zirconate (SrZrO<sub>3</sub>) belongs to the perovskite family and has an orthorhombic structure at room temperature, with space group Pbnm [27]. Due to its high dielectric constant, high breakdown strength and low leakage current density, SrZrO<sub>3</sub> has been extensively investigated as a possible candidate material for highk gate dielectrics ( $E_g$ =5.6 eV) [28,29]. In the present work, new SZ-modified BNT ceramics were produced

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by continues solid solution reaction and its ferroelectric and piezoelectric properties were investigated systemically.

### 2 Experimental

A conventional mixed oxide method was utilized to prepare SrZrO<sub>3</sub>-modified Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub> (BNT-SZ100x with x=0-0.15) ceramics. The commercially available reagent grade oxide or carbonate powders of Bi<sub>2</sub>O<sub>3</sub> (99.90%), Na<sub>2</sub>CO<sub>3</sub>(99.95%), TiO<sub>2</sub>(99.90%), SrCO<sub>3</sub> (99.90%) and ZrO<sub>2</sub>(99.0%) of Sigma Aldrich Co. St. Louis, MO, were used as starting raw materials. Prior to measuring the weighs, the powders were dried in an oven at 100 °C for 24 h. For each composition, the starting materials were weighed according to the stoichiometric formula and ball-milled for 24 h in ethanol. The dried slurries were calcined at 850 °C for 2 h and then ball-milled again. After calcinations, the mixture was ball milled for 24 h, and then dried. The powders were pulverized, mixed with an aqueous polyvinyl alcohol (PVA) solution as a binder for granulation and passed through a sieve of 63 µm. The granulated powders were subsequently pressed into green discs of diameter 10 mm. The compacts were sintered at 1150 °C for 2 h in a covered alumina crucible. To minimize the evaporation of the volatile elements Bi and Na, the disks were embedded in the powder for same composition. Silver paste was coated on both faces of the sintered samples and fired at 650 °C for 0.5 h to form electrodes. The specimens for measurement of piezoelectric properties were poled in silicone oil bath with a DC field of 4 kV/mm for 15 min. All the electrical measurements were performed after aging for at least 24 h.

The crystal structure was characterized using X-ray diffractometry (XRD, X'pert MPD 3040, Phlips, Netherland) using unpoled crushed sintered samples. 5 N Si (Alfa Aesar, USA) powder was used as an internal standard to calibrate XRD patterns obtained using X-ray diffractometer of Cu K<sub> $\alpha$ </sub> lines. Surface morphology was checked through scanning electron microscope (SEM, JP/JSM 5200, Japan). The piezoelectric properties were measured using a Berlincourt  $d_{33}$  meter (IACAS, ZJ-6B). The dependence of the electric polarization (*P*) under an external electric field (*E*) was measured in a silicon oil bath by using Precision Material Analyzer (Radiant Technologies, Inc. Albuquerque, NM). Field induced strain (*S*) was measured using a contact type displacement sensor (Millitron, Model 140).

# **3** Results and discussion

#### 3.1 Phase and microstructure analysis

The XRD patterns of sintered SZ-modified BNT

ceramic samples are shown in Fig. 1. No significant changes or extra phases in the crystallographic structure were identified in the studied composition range. Patterns of all samples revealed a pure perovskite phase with pseudocubibic symmetry, indicating that SZ successfully diffused into the lattice structure of the BNT ceramics to form complete solid solutions. The overall effect of SZ substitution on the XRD patterns of BNT ceramics is the slight shifting of intensity peaks towards lower angle. This peak shifting behavior increase with increasing SZ concentration. This may be due to replacement of small ions with the larger ionic radii  $Sr^{2+}$ (0.144 nm) on A site (for  $Bi^{3+}$ , 0.136 nm; and  $Na^{+}$ , 0.139 nm) and  $Zr^{4+}(0.072 \text{ nm})$  on B site (for  $Ti^{3+}$ , 0.0605 nm) in BNT ceramics. Similar peaks shifting behavior was also observed in Zr-modified BNT ceramics [30,31] and in BST-modified BNT ceramics [23,24].



**Fig. 1** XRD patterns of BNT–SZ100*x* ceramics in  $2\theta$  range of  $20^{\circ}$ – $80^{\circ}$  (a) and  $46^{\circ}$ – $48^{\circ}$  (b)

Figure 2 presents the SEM micrographs of the polished and thermally etched surfaces of SZ-modified BNT ceramics with x = 0, 0.02, 0.05, 0.07, 0.09 and 0.10. All ceramics were uniformly distributed and tightly bound with homogeneous macrostructures of similar grain morphology. SZ had small influence on the grain morphology of the BNT ceramics. The grain size decreased with an increase in the SZ concentration. Using a linear intercept method, the average grain size was found to decrease from 25.2 µm for x=0 to 2.4 µm for x=0.10.

#### **3.2 Electric properties**

3.2.1 P-E ferroelectric hysteresis

The measurement of polarization versus electric field (P-E) hysteresis loops was conducted to investigate the ferroelectric properties of BNT-SZ ceramics. Figure 3(a) shows the room temperature P-E hysteresis loops of the BNT-SZ ceramics with different SZ content measured at 20 Hz. Pure BNT ceramics without SZ



Fig. 2 SEM micrographs of thermally etched samples of BNT-SZ ceramics with different SZ contents: (a) x=0; (b) x=0.02; (c) x=0.05; (d) x=0.07; (e) x=0.09; (f) x=0.10

content show a typical saturated ferroelectric behavior (FE), which is characterized by definite squareness in the P-E hysteresis loop with a remanent polarization ( $P_r$ ) of 30 µC/cm<sup>2</sup> and a coercive field ( $E_c$ ) of 5.5 kV/mm. It can be clearly seen in Fig. 3(a) that SZ exerts significant influence on the loop shape and polarization values. Similar behavior is also perceived in ST and BA-modified BNT ceramics [15–17]. A significant reduction in the  $E_c$  is observed at SZ5 along with the clear increase in the  $P_r$  and  $P_m$ . However, at SZ7 the  $P_r$  drastically decreased from 32 to 22 µC/cm<sup>2</sup>, and the  $E_c$  decreased from 3.5 to 2.4 kV/mm. At higher SZ concentrations i.e. for SZ10, both  $P_r$  and  $E_c$  drastically decreased, indicating the material became electrostructive without any apparent switching.

The characteristic values of  $P_r$ ,  $P_m$ , their difference  $(P_m-P_r)$  and  $E_c$  are shown in Fig. 3(b). At higher SZ concentrations  $P_r$  and  $E_c$  significantly decreased with increasing SZ content which is characterized by a slim P-E hysteresis loop. The large difference between the

 $P_{\rm m}$  and  $P_{\rm r}$  at SZ9 indicates the large filed induced strain response which is similar to other reports on BNT-based ceramics [11,14,15]. This significant decrease in  $P_{\rm r}$  and  $E_{\rm c}$  along with concurrent minor decreases in  $P_{\rm m}$  implies that the long-range FE order dominant in BNT is disrupted and ferroelectric relaxor-type (FER) behavior become dominant with the addition of SZ.

3.2.2 Bipolar and unipolar S-E curves

Figure 4(a) shows the bipolar field-induced strain curves of BNT-SZ ceramics with different SZ contents measured at room temperature under an applied electric field of 8 kV/mm at 50 mHz. Pure BNT ceramics exhibit a butterfly shaped curve typical of a ferroelectric material with maximum ( $S_{max}$ =0.08%) and negative strain ( $S_{neg}$ =0.13%). However, SZ-modified samples show disrupted curves, i.e., deviated from the butterflyshape. At small amount of SZ substitution (i.e., x=0.05), the curve change shape, resulting in an increase in  $S_{max}$ value. However, above this critical composition, drastic changes from the typical FE order were observed. This



**Fig. 3** Effect of SZ-modification on P-E hysteresis loops (a) and characteristic values of  $P_{\rm m}$ ,  $P_{\rm r}$ , their difference  $(P_{\rm m}-P_{\rm r})$  and  $E_{\rm c}$  as function of SZ content (b)

was evidenced by a small  $S_{\text{neg}}$  value and is closely related to domain back-switching during bipolar cycles [11, 22]. The decreasing trend for the  $S_{\text{neg}}$  of SZ-modified BNT ceramics is presented in Fig. 4(b). The significant enhancement in bipolar strain at SZ9 attributed to the FE to FER phase transition corroborates the polarization hysteresis loop (Fig. 3), where the relatively slim loops indicates the coexistence of FE and FER phases [11,14,15].

The unipolar electric field-induced strain curves of the BNT ceramics with different amounts of SZ concentration measured at room temperature are depicted in Fig. 5(a). The unipolar field-induced strain increased significantly with increase in SZ concentration. The highest strain value ( $S_{max}=0.24\%$ ) is obtained for composition with SZ9. However, further increase in SZ concentration i.e., for SZ10 and above the strain level drops. The field-induced strain  $S_{max}$  and normalized strain  $d_{33}^*$  of BNT-SZ ceramics as a function of SZ content are presented in Fig. 4(b) and Fig. 5(b), respectively. An enhanced strain ( $S_{max}=0.24\%$ ) nearly three times more than that of pure BNT and the normalized strain ( $d_{33}^*=S_{max}/E_{max}=340$  pm/V) was obtained for SZ9 at an applied electric field of 7 kV/mm.



**Fig. 4** Field induced bipolar S-E loops of BNT ceramics with different SZ contents (a) and maximum and negative strain ( $S_{\text{max}}$  and  $S_{\text{neg}}$ ) of BNT ceramics as function of SZ content (b)

Recently, similar normalized strain behaviors were also observed in other BNT-based systems, such as BNT-BA [16–18], BNT-BKT [20], BNT-BT [11,12] and BNT-ST [14,15].

Figure 5(b) shows the piezoelectric constant  $d_{33}$  of the BNT ceramics as a function of SZ content. The  $d_{33}$ parameter increases with an increase in the SZ content, reaches a maximum value of  $d_{33}$ =102 pC/N at SZ5. Further increase in SZ concentration resulted in a significant reduction in  $d_{33}$  values. The observed trends in  $d_{33}$  are in good agreement with the polarization hysteresis loops in Fig. 3. Similar behavior is also shown in Refs [16,17]. The significant improvement observed in  $d_{33}$  at SZ5 is attributed to a large  $P_r$  and a lower  $E_c$ . This is because a lower  $E_c$  enables the ceramics to be more easily poled, while a large  $P_r$  and  $P_m$  favors piezoelectricity.

This enhancement in the field-induced strain and corresponding  $d_{33}^*$  is due to replacement of small ions with the larger ionic radii  $\text{Sr}^{2+}(0.144 \text{ nm})$  on *A* site (for Bi<sup>3+</sup>, 0.136 nm; and Na<sup>+</sup>, 0.139 nm) and Zr<sup>4+</sup>(0.072 nm) on *B* site (for Ti<sup>3+</sup>, 0.0605 nm) in BNT ceramics. Furthermore, the FER phase dominated at higher SZ concentrations (i.e., *x*=0.09 and above), which delays the



**Fig. 5** Effect of SZ-modification on unipolar *S*–*E* loops of BNT-SZ ceramics with different SZ contents (a); Piezoelectric constant ( $d_{33}$ =pC/N) and normalized strain ( $d_{33}^*$ = $S_{max}/E_{max}$ ) as function of SZ content (b)

transformation from the FER phase to the FR phase based on the significant decrease in the polarization response. The free energy of the FR phase was comparable to that of the FER phase under zero field, such that it can be easily induced by an external electric field and becomes saturated, as shown in Fig. 3(b). Similar to previous works [14–17], the results of this study suggest that high unipolar strain, located only in a narrow region around SZ9 in which both ferroelectric and FER phases coexist in the BNT ceramic system. Beyond this narrow region, either the ferroelectric or FER phase dominates. Neither of the phases can solely deliver a strain as large as that measured from compositions (x=0.07-0.10) near the boundary between polar and FER phases. The P-E hysteresis loops and S-E curves suggest that the large strain at SZ9 can be attributed to the coexistence of ferroelectric and FER phases.

# **4** Conclusions

1) The influence of SZ-substitution on crystal structure, microstructure, ferroelectric and field-induced

strain behavior of BNT ceramics was investigated. XRD analysis revealed that SZ addition had no remarkable effect on the crystal structure of BNT ceramics and a single perovskite phase was observed in the studied composition range. SEM analysis revealed a decrease of the grain size for increasing SZ content.

2) Deformed hysteresis loops at small SZ concentrations were observed, suggesting the coexistence of ferroelectric and relaxor phases for modified BNT ceramics. At SZ7, the slim hysteresis curve with low remnant polarization (22  $\mu$ C/cm<sup>2</sup>) and a small piezoelectric constant (37 pC/N) was observed. Encouraging results of unipolar large strain of 0.24%  $(S_{\text{max}}/E_{\text{max}}=340 \text{ pm/V})$  were obtained in BNT-SZ at SZ9. It was found that SZ induced a ferroelectric-to-relaxor transition which was accompanied by a large enhancement in electric field induced strain. This significant strain enhancement is a result of the reversible phase transition between a FER phase in a zero field and a field-induced ferroelectric phase.

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# Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-SrZrO<sub>3</sub>无铅陶瓷的铁电和压电性能

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**摘 要:**采用固相反应法制备 Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-SrZrO<sub>3</sub>(BNT-SZ100*x*, *x*=0-0.15)无铅陶瓷,通过 XRD、SEM 和电致 应变等手段对其进行表征。XRD 分析表明样品的第二相为纯钙钛矿型。铁电致应变曲线表明:当 SZ 添加到 BNT 陶瓷中,铁电顺序被破坏。当添加 5% (摩尔分数)SZ 时,剩余极化强度和压电常数的最大值分别为 32 μC/cm<sup>2</sup> 和 102 pC/N。BNT-SZ9 样品的电致应变(*S*<sub>max</sub>)和归一化应变(*S*<sub>max</sub>/*E*<sub>max</sub>=*d*<sup>\*</sup><sub>33</sub>)的最大值分别为 0.24%和 340 pm/V。 关键词:无铅陶瓷; BNT;钙钛矿结构;场诱导应变