Structure and temperature dependent electrical properties of lead-free Bi0.5Na0.5TiO3- SrZrO3 ceramics

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Abstract. Lead-free SrZrO3-modified Bi0.5Na0.5TiO3 (BNT-SZ) ceramics were fabricated by a conventional solid state reaction method. X-ray diffraction analysis reveals a pure perovskite phase without any traces of secondary phases. Scanning electron microscopy images depicts dense grain morphology. The temperature dependences of the dielectric behavior was measured in the temperature range of 50–500 °C at 100 kHz. With the increase in SZ content, the dielectric constant ($\varepsilon_r$) constantly decreased and the maximum dielectric constant temperature ($T_m$) shifted towards lower temperatures. In addition to this, ferroelectric hysteresis loops indicated a disruption of ferroelectric order and increase in the relaxor character of BNT ceramics with increase in SZ concentration. A maximum values of remnant polarization (32 µC/cm2) and piezoelectric constant (100 pC/N) were observed at SZ5 and SZ4, respectively.

1. Introduction

Lead-based ceramics with perovskite structure, such as Pb(Zr,Ti)O3 (PZT) and PZT-based multicomponent materials are widely used for actuators, sensors and micro-electromechanical devices owing to their superior piezoelectric properties [1]. However, the use of lead-based materials produce serious lead pollution and environmental problems due to high toxicity of lead oxide.

In lead-free materials, Bi0.5Na0.5TiO3 (BNT) is considered one of the most promising candidate materials for the piezoelectric applications. It has ABO3 perovskite structure with a ferroelectric rhombohedral symmetry (R3C) at room temperature [2, 3]. As temperature increases, the phase of BNT will transform from rhombohedral to tetragonal and finally into cubic phase [4]. The transition temperatures of rhombohedral-tetragonal phase ($T_{R-T}$) and tetragonal-cubic phase ($T_{T-C}$) are 300 and 540 °C, respectively. BNT shows strong ferroelectricity ($P_r = 38 \mu$C/cm$^2$), but also has drawbacks such as a large coercive field ($E_c$) of approximately 7.3 kV/mm and a high conductivity. To decrease its conductivity and improve its piezoelectric properties, it has been modified with various types of perovskite materials, such as CaTiO3 (CT) [5], BaTiO3 (BT) [6-8], BaZrO3 [9], SrTiO3 (ST) [4, 10, 11], BiAlO3 (BA) [12, 13], (Bi0.5K0.5)TiO3 (BKT) [14, 15], NaNbO3 (NN) [16], KNbO3 (KN) [17, 18] and BaSrTiO3 (BST) [19, 20]. Furthermore, it has been also modified with divalent (Ca, Sr, Ba) [21] and trivalent (La, Nd, Ho, Yb) ions [22].

Hiruma et al. [18] have fabricated BNT-based solid solutions, such as BNT-NN, BNT-KN and BNT-BKT and demonstrated relationship between the phase diagrams and their electrical properties. They...
reported that piezoelectric properties and strain response increased at the phase boundary between the ferroelectric rhombohedral phase and the ferroelectric relaxor phase with the mixed pseudocubic tetragonal phase. In addition, Krauss et al. [10] studied the piezoelectric properties and phase transition temperatures of the solid solution of (BNT-ST) ceramic system. From their X-ray diffraction (XRD) measurements a broad maximum of the lattice parameter was observed around $x = 0.5$, but no structural evidence for a morphotropic phase boundary was found. Above studies [4-8, 10-24] revealed that formation of a new solid solution is an effective way to improve the piezoelectric properties of the BNT ceramics.

Strontium zirconate (SrZrO$_3$) belongs to the perovskite family and has an orthorhombic structure at room temperature, with space group Pb$_{n}$mm [25]. Due to its high dielectric constant, high breakdown strength and low leakage current density, SrZrO$_3$ has been extensively investigated as a possible candidate material for high-k gate dielectrics ($E_g = 5.6$ eV) [26, 27]. In the present work, new SZ-modified BNT ceramics were produced 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$_3$-modified Bi$_{0.5}$Na$_{0.5}$TiO$_3$ (BNT-SZ100 with $x = 0-0.15$) ceramics. The commercially available reagent grade oxide or carbonate powders of Bi$_2$O$_3$ (99.90%), Na$_2$CO$_3$ (99.95%), TiO$_2$ (99.90%), SrCO$_3$ (99.90%) and ZrO$_2$ (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 $^\circ$C for 24 hrs. For each composition, the starting materials were weighed according to the stoichiometric formula and ball-milled for 24 hrs in ethanol. The dried slurries were calcined at 850 $^\circ$C for 2 hrs and then ball-milled again. After calcinations, the mixture was ball milled for 24 h, dried. The powders were pulverized, mixed with an aqueous polyvinyl alcohol (PVA) solution as a binder for granulation and passed through a sieve of 250 mesh. The granulated powders were subsequently pressed into green discs of diameter 10 mm. The compacts were sintered at 1150 $^\circ$C for 2 hrs in 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 $^\circ$C for 0.5 hrs 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 of sintered samples was characterized using X-ray diffractometry (XRD, X'pert MPD 3040, Philips, Netherland). Surface morphology was checked through scanning electron microscope (SEM, JP/JSM 5200, Japan). Dielectric constant and loss of the specimens were measured using an automatic acquisition system using an impedance analyzer (Agilent HP4292A, USA) in 25-500 $^\circ$C temperature range at different frequencies. 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 ($E$) were measured in a silicon oil bath by using Precision Material Analyzer (Radiant Technologies, Inc. Albuquerque, NM).

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. Patterns of all samples revealed a pure perovskite phase, indicating that SZ successfully diffused into the lattice.
structure of the BNT ceramics to form complete solid solutions. Pure BNT ceramics revealed the characteristic rhombohedral structure. With increasing SZ content, the rhombohedral structure gradually transforms to the pseudo-cubic symmetry. 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$^{2+}$ (1.44 Å) on A site (for Bi$^{3+}$ = 1.36 Å and Na$^{+}$ = 1.39 Å) and Zr$^{4+}$ (0.72 Å) on B site (for Ti$^{3+}$ = 0.605 Å) in BNT ceramics. Similar peaks shifting behavior was also observed in Zr and BZ-modified BNT ceramics [9, 28] and in BST-modified BNT ceramics [19, 20].

Figure 2 presents the SEM micrographs of the polished and thermally etched surfaces of SZ-modified BNT ceramics with $x = 0, 0.02, 0.04, 0.05, 0.07$ 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 Dielectric constant and loss
The temperature dependent dielectric constant ($\varepsilon_r$) and loss ($\tan\delta$) for the BNT-SZ ceramics measured at 100 KHz are presented in Fig. 3. It can be observed that with increase in measuring frequency, the observed dielectric constant decrease for all the samples similar to other BNT-based relaxor ferroelectric materials [10, 11, 18]. For pure BNT ceramics, the maximum dielectric constant ($T_m$) peak is observed at highest value 3600 at 10 KHz. The curves of temperature dependence of relative dielectric constant for different samples look similar, as indicated in Fig. 3. By the substitution of SZ, $T_m$ gradually decreases and peaks become much broader. The decrease of $T_m$ can be associated with the structural transition point from the rhombohedral to pseudo-cubic phase, as discussed in XRD analysis. The dielectric loss slightly increased with increasing SZ content in the BNT. The dielectric loss has not change much at room temperature because of the less distortion in the crystalline structure and then
increase around $T_m$ due to increase in the conductivity of the conductivity of SZ-modified ceramics. The dielectric loss slightly decreased with increasing SZ content and varied from of SZ7-10.

![Figure 2. SEM micrographs of thermally etched samples of BNT-SZ ceramics with different SZ content.](image)

![Figure 3. Direct comparisons of the dielectric constants and losses of all the samples of BNT-SZ ceramics at 100 kHz](image)
3.3 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. Fig. 4(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 content show a typical saturated FE behavior, which is characterized by definite squareness in the P–E hysteresis loop with a remanent polarization ($P_r$) of 30 µC/cm$^2$ and a coercive field ($E_c$) of 5.5 kV/mm. It can be clearly seen in Fig. 4(a), SZ exerts significant influence on the loop shape and polarization values, similar behavior is also perceived in ST and BA-modified BNT ceramics [11, 13]. 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$^2$, 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 electrostrictive 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. 4(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 $P_m$ and $P_r$ at SZ9 indicates the large filed induced strain response which is similar to other reports on BNT-based ceramics [7, 10, 11]. This significant decrease in $P_r$ and $E_c$ along with concurrent minor decreases in $P_m$ implies that the long-range FE order dominant in BNT is disrupted and FER type behavior become dominant with the addition of SZ.

3.4 Temperature dependent P–E loops

To better understand the temperature stability and ferroelectric behavior of BNT-SZ ceramics, the temperature dependent polarization hysteresis loops were illustrated in detail in Fig. 5. For pure BNT ceramics, $P_r$ decreases slightly however sharp reduction in $E_c$ is observed with the increase in the temperature. For SZ-modified ceramics, with increase in temperature a sharp reduction in $P_r$ and $E_c$ is observed, indicating the disappearance of FE order and appearance of a relaxor phase [7, 29, 30]. For SZ4 and SZ5, a pinched-type character is also observed at elevated temperatures. In case of pure BNT, no pinched-type loop is revealed even at 175 °C. However, pinched-type characteristic can be easily seen around 100 °C for SZ4 and 75 °C for SZ5 samples. In SZ4 and SZ5, at elevated temperature around 150 °C, P–E loops become very slim and narrow but still pinched-type character is not completely vanished. However, SZ9 ceramics exhibited like the linear dielectric materials at elevated temperature. Similar results of the temperature dependent P–E loops have been reported for other BNT-based ceramics [7]. This change of the P–E loops are well consistent with the temperature dependence of dielectric properties. As suggested by literature, it can be concluded that pinched type anomalies in P–
E loops resulted from the electromechanical interaction between the polar and non-polar regions which coexisted in the ceramics at high temperatures.

3.5 Piezoelectric constant

Figure 6 shows the piezoelectric constant $d_{33}$ and $K_p$ of the BNT ceramics as a function of SZ content. The $d_{33}$ and $K_p$ both enhance with an increase in the SZ content, reaches a maximum value of $d_{33} = 100$ pC/N and $K_p = 0.19$ at SZ4. Further increase in SZ concentration resulted in a significant reduction in $d_{33}$ and $K_p$ values. The observed trends is in good agreement with polarization hysteresis loops in Fig. 4(a), similar behavior is also in other studies [12, 13]. The substantial increase observed in $d_{33}$ and $K_p$ at SZ4 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.

4. Conclusions

The influence of SZ-substitution on crystal structure, microstructure, dielectric, ferroelectric piezoelectric behavior of BNT ceramics was investigated. XRD revealed that rhombohedral structure gradually transforms to the pseudo-cubic symmetry with increasing SZ. SEM-analysis revealed a decrease of the grain size for increasing SZ-content. The maximum dielectric constant temperature $T_m$ gradually decreased and shift toward lower temperature with increasing SZ content. Deformed hysteresis loops at small SZ concentrations were observed, suggesting the coexistence of ferroelectric and relaxor phases for modified BNT ceramics. A significant reduction in the $E_c$ is observed at SZ5 along with the clear increase in the $P_r$ and $P_m$. At SZ5, the slightly deformed hysteresis curve with high remnant polarization (32 $\mu$C/cm$^2$) and at SZ4 high piezoelectric constant (100 pC/N) was observed. In
temperature dependent $P$–$E$ loops, pinched type behavior were revealed which indicated the coexistence of polar and non-polar regions in the ceramics at high temperatures.

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6. References
[1] Jaffe B, Cook W R and Jaffe H 1971 Piezoelectric ceramics vol 1 (New York: Academic Press)
[2] Smolenskii G A, Isupov V A, Agranovskaya A I and Krainik N N 1961 New ferroelectrics of complex composition Sov. Phys. Solid State 2 2651-4
[3] Rödel J, Jo W, Seifert K T, Anton E M, Granzow T and Damjanovic D 2009 Perspective on the Development of Lead-free Piezoceramics J. Am. Ceram. Soc. 92 1153-77
[4] Sakata K and Masuda Y 1974 Ferroelectric and antiferroelectric properties of (Na$_{0.5}$Bi$_{0.5}$)TiO$_3$-SrTiO$_3$ solid solution ceramics Ferroelectrics 7 347-9
[5] Takenaka T, Sakata K O and Toda K O 1990 Piezoelectric properties of (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$-based ceramics Ferroelectrics 106 375-80
[6] Takenaka T, Maruyama K I and Sakata K 1991 (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$–BaTiO$_3$ system for lead-free piezoelectric ceramics Jpn. J. App. Phys. 30 2236-9
[7] Zhang S-T, Kounga A B, Aulbach E and Deng Y 2008 Temperature-Dependent Electrical Properties of 0.94Bi$_{0.5}$Na$_{0.5}$TiO$_3$–0.06BaTiO$_3$ Ceramics J. Am. Ceram. Soc. 91 3950-4
[8] Xu C, Lin D and Kwok K W 2008 Structure, electrical properties and depolarization temperature of (Bi$_{0.5}$Na$_{0.5}$)TiO$_3$–BaTiO$_3$ lead-free piezoelectric ceramics Solid State Sci. 10 934-40
[9] Rahman J U, Hussain A, Maqbool A, Song T K, Kim W J, Kim S S and Kim M H 2014 Dielectric, ferroelectric and field-induced strain response of lead-free BaZrO$_3$-modified Bi$_{0.5}$Na$_{0.5}$TiO$_3$ ceramics Curr. Appl. Phys. 14 331-6

![Figure 6. Piezoelectric constant ($d_{33}$) and coupling coefficient ($K_p$) of BNT-SZ100x ceramics.](image)
[10] Krauss W, Schütz D, Mautner F A, Feteira A and Reichmann K 2010 Piezoelectric properties and phase transition temperatures of the solid solution of (1−x)(Bi0.5Na0.5)TiO3–xSrTiO3 J. Eur. Ceram. Soc. 30 1827-32

[11] Hiruma Y, Imai Y, Watanabe Y, Nagata H and Takenaka T 2008 Large electrostrain near the phase transition temperature of (Bi0.5Na0.5)TiO3–SrTiO3 ferroelectric ceramics Appl. Phys. Lett. 92 262904

[12] Watanabe Y, Hiruma Y, Nagata H and Takenaka T 2009 Fabrication and electrical properties of (Bi1/2Na1/2)TiO3-BiAlO3 ferroelectric ceramics Key Eng. Mater. 388 229-32

[13] Ullah A, Ahn C W, Jang K B, Hussain A and Kim I W 2010 Phase Transition and Electrical Properties of BiAlO3-Modified (Bi0.5Na0.5)TiO3 Piezoelectric Ceramics Ferroelectrics 404 167-72

[14] Sasaki A, Chiba T, Mamiya Y and Otsuki E 1999 Dielectric and Piezoelectric Properties of (Bi0.5Na0.5)TiO3–(Bi0.5K0.5)TiO3 Systems Jpn. J. App. Phys. 38 5564

[15] Yoshi K, Hiruma Y, Nagata H and Takenaka T 2006 Electrical Properties and Depolarization Temperature of (Bi1/2Na1/2)TiO3–(Bi1/2K1/2)TiO3 Lead-free Piezoelectric Ceramics Jpn. J. App. Phys. 45 4493-6

[16] Wada T, Toyoike K, Imanaka Y and Matsuo Y 2001 Dielectric and piezoelectric properties of (A0.5Bi0.5)TiO3–ANbO3 (A= Na, K) systems Jpn. J. App. Phys. 40 5703

[17] Kounga A B, Zhang S-T, Jo W, Granzow T and Rödel J 2008 Morphotropic phase boundary in (1-x)Bi0.5Na0.5TiO3–xK0.5Na0.5NbO3 lead-free piezoceramics Appl. Phys. Lett. 92 222902-3

[18] Hiruma Y, Nagata H and Takenaka T 2008 Phase transition temperatures and electrical properties of divalent ions (Ca2+, Sr2+ and Ba2+) substituted (Bi1/2Na1/2)TiO3 ceramics Ceram. Int. 34 761-4

[19] Yu H and Ye Z-G 2008 Dielectric, ferroelectric, and piezoelectric properties of the lead-free (1-x)Na0.5Bi1.5TiO3–xBiAlO3 solid solution Appl. Phys. Lett. 93 112902-3

[20] Parija B, Rout S K, Cavalcante L S, Simões A Z, Panigrahi S, Longo E and Batista N C 2012 Structure, microstructure and dielectric properties of 100-x(Bi0.5Na0.5)TiO3–x[SrTiO3] composites ceramics Appl. Phys. A 109 715-23

[21] Ahtee A, Ahtee M, Glazer A and Hewat A 1976 The structure of orthorhombic SrZrO3 by neutron powder diffraction Acta. Crystallogr. B 32 3243-6

[22] Popescu B, Enache S, Ghica C and Valeanu M 2011 Solid-state synthesis and spark plasma sintering of SrZrO3 ceramics J. Alloys Compd. 509 6395-9
[27] Chen C, Zhu W, Yu T, Chen X and Yao X 2003 Preparation of metal–organic decomposition-derived strontium zirconate dielectric thin films Appl. Surf. Sci. 211 244-9

[28] Rachakom A, Jaiban P, Jiansirisomboon S and Watcharapasorn A 2012 Crystal structure and electrical properties of bismuth sodium titanate zirconate ceramics Nanoscale Res. Lett. 7 57

[29] Hussain A, Ahn C W, Lee J S, Ullah A and Kim I W 2010 Large electric-field-induced strain in Zr-modified lead-free Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_{3} piezoelectric ceramics Sens. Actuator A-Phys. 158 84-9

[30] Hussain A, Ahn C W, Ullah A, Lee J S and Kim I W 2012 Dielectric, ferroelectric and field-induced strain behavior of K_{0.5}Na_{0.5}NbO_{3}-modified Bi_{0.5}(Na_{0.78}K_{0.22})_{0.5}TiO_{3} lead-free ceramics Ceram. Int. 38 4143-9