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# Relaxor and field-induced strain behavior in lead-free Bi<sub>0.5</sub>(Na<sub>0.82</sub> K<sub>0.18</sub>)<sub>0.5</sub>TiO<sub>3</sub> ceramics modified with BaZrO<sub>3</sub>

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The crystal structure, microstructure, dielectric, ferroelectric and field-induced strain properties of lead-free (1-x)(Bi<sub>0.5</sub>  $(Na_{0.82}K_{0.18})_0$ , TiO<sub>3</sub>)-xBaZrO<sub>3</sub> (x = 0-0.05) ceramics (BNKT-BZ) were investigated. X-ray diffraction analyses revealed that a phase transformation occurred at x = 0.02 from a coexistence of rhombohedral and tetragonal symmetry to another mixed state of pseudocubic and tetragonal symmetry. The temperature and frequency dependence of dielectric constant and loss showed strong frequency dispersive behaviors for all BZ-modified specimens. The polarization and strain hysteresis loops suggested that the addition of BZ signicantly disrupted the ferroelectric order accompanied by an enhancement in fieldinduced strain up to 0.26 % at x = 0.02.

Key words: Lead-free ceramics, Strain, BNKT-BZ, Relaxor ferroelectric.

#### Introduction

The relaxor ferroelectrics are known to reveal strong dielectric dispersions as a function of temperature and frequency. The peculiar dielectric, electromechanical, and polarization mechanisms make the relaxors and their solid solutions as high performance materials for various applications [1]. The relaxation behavior in lead magnesium niobate (PMN) was firstly reported by Smolensky and Agranovskaya [2]. Since the discovery of relaxation behavior, much attention was focused on lead-based ceramics such as (Pb,La)(Zr,Ti)O<sub>3</sub>, Pb(Zn<sub>1/</sub> <sub>3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-PbTiO<sub>3</sub> and Pb(Co<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> [3, 4]. However, the studies on lead-free relaxor ferroelectrics are rarely encountered. Therefore, there is a great need to investigate new lead-free relaxor ferroelectric materials with superior piezoelectric properties for various applications.

Nowadays, (Bi1/2Na1/2)TiO3-(Bi1/2K1/2)TiO3 solid solutions (BNKT) attract great attention as promising candidates for lead-free piezoelectric ceramics owing to their strong ferroelectricity, high electromechanical coupling factor, and piezoelectric constant near the rhombohedraltetragonal morphotropic phase boundary (MPB) [5]. Various BNKT-based solid solutions have been investigated such as BNKT-SrTiO<sub>3</sub> [6], BNKT-BiAlO<sub>3</sub> [7], BNKT-K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>(KNN) [8] and BNKT-Ta<sub>2</sub>O<sub>5</sub> [9] for their ferroelectric, piezoelectric and electromechanical properties. Recently, a couple of studies reported the relaxor behavior of BNKT-based lead free system such as Sb-doped [10] and CeO<sub>2</sub>-doped BNKT [11] ceramics. Furthermore, relaxor behaviors were also reported in BaTiO3-based lead-free ceramics including Ba(Ti1-x  $Zr_x$ )O<sub>3</sub> [12, 13] and Ba(Ti<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub> [14]. Recently, Zuo et al. [15] reported a normal to relaxor ferroelectric transition in (Na<sub>0.52</sub>K<sub>0.40</sub>)(Nb<sub>0.84</sub>Sb<sub>0.08</sub>)O<sub>3</sub>-(0.08-x)LiTaO<sub>3</sub> $xBaZrO_3$  lead free ceramics. However, to the best of our knowledge, there is little report on dielectric, ferroelectric and electric-field-induced strain behavior of (1-x)Bi<sub>0.5</sub> (Na<sub>0.82</sub>K<sub>0.18</sub>)<sub>0.5</sub>TiO<sub>3</sub>-xBaZrO<sub>3</sub>(BZ) ceramics to date. Therefore, this work aims to investigate the microstructure, ferroelectric, dielectric and electric-fieldinduced strain behavior of BZ-modified BNKT ceramics.

## **Experimental**

The  $(1-x)Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}TiO_3 - xBaZrO_3$  (x = 0-0.05) ceramics were synthesized by a conventional solid state reaction method using Bi<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, TiO<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub> (99.9% High Purity Chemicals, Japan), BaCO3 and ZrO<sub>2</sub> (99.9% Cerac Specialty Inorganics, USA) as starting materials. Before weighing, the powders were dried in an oven at 100 °C for 24 hrs to make them moisture-free. Starting materials were weighed according to the stoichiometric formula and ball-milled for 24 hrs in ethanol with zirconia balls. The dried slurries were calcined at 800 °C for 2 hrs and then ball-milled again for 24 hrs. The powders were pulverized, mixed with an aqueous polyvinyl alcohol (PVA) solution, and pressed into green discs with a diameter of 12 mm at 98 MPa. Sintering was carried out at 1200 °C for 2 hrs in a covered alumina crucible. To prevent the vaporization of Bi, Na, and K, the discs were embedded in a powder with the corresponding composition.

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The crystal structure was characterized by an X- ray diffractometer (XRD, RAD III, Rigaku, Japan). A field-emission scanning electron microscope (FE-SEM, Jeol, JSM-65OFF, Japan) was used to examine the surface morphology of samples. Silver paste was applied on both surfaces of the disc as electrodes, and then fired at 700 °C for 30 minutes. Polarization (*P-E*) hysteresis loops were measured in silicon oil using a conventional Sawyer-Tower circuit. The electric field-induced strain (*S-E*) loop was measured with a linear variable differential transducer (LVDT, Mitsutoyo MCH-331 & M401). The temperature dependence of the dielectric properties was recorded using an impedance analyzer (HP4192A, USA) over a temperature range of 30-550 °C.

#### **Results and discussion**

Fig. 1 presents the XRD patterns of BZ-modified BNKT ceramics sintered at 1200 °C for 2 hrs for different BZ concentrations. All compositions exhibit a single phase perovskite structure without any traces of secondary phases. This means that Ba<sup>2+</sup> and Zr<sup>4+</sup> ions diffused into the BNKT lattice to form a homogeneous solid solution. Expanded XRD patterns in the  $2\theta$ ranges of 39 °-41 ° and 45 °-47 ° are shown in Fig. 1(b) and (c), respectively. It was reported that the rhombohedral BNT and tetragonal BKT formed a MPB region when the BKT concentration was in the range of 0.16-0.20 [5]. In Figs. 1(b) and (c), at x = 0, the exhibits features of both unmodified BNKT rhombohedral and tetragonal symmetry evidenced by the splitting of (111)/(11) peaks at 20 of around 40 ° and (002)/(200) peaks at 20 of around 46 ° [9]. However, it is noted that the net effect of BZ modification on the XRD patterns is a gradual vanishing of rhombohedral phase and the shift of tetragonal peaks towards a lower angle, leading to a coexistence of pseudocubic and tetragonal symmetry at x = 0.05. Such a peak shift increased with raising the



**Fig. 1.** X-ray diffraction patterns of the (1-x)BNKT-xBZ ceramics in the 2 $\theta$  ranges of (a) 20 ° - 80 °, (b) 39 ° - 41 °, and (c) 45 ° - 48 °.

BZ content, which was due to the substitution of bigger ions (Ba<sup>2+</sup> = 1.61 Å and Zr<sup>4+</sup> ~ 0.72 Å) into smaller ions (Bi<sup>3+</sup> = 1.36 Å, Na<sup>+</sup> = 1.36 Å and Ti<sup>4+</sup> = 0.605 Å), respectively [16]. Similar peak shifts were also reported by Hussain *et al.* [17] in Zr-doped BNKT and Kuang *et al.* [13] in BZ-modified BaTiO<sub>3</sub>.

Fig. 2 shows FE-SEM micrographs of BZ-modified BNKT ceramics with x = 0, 0.01, 0.02 and 0.04 after sintering. All specimens showed dense microstructures like a previous report on BNKT ceramics doped with Zr [17]. It is seen that the addition of BZ brings insignificant effect on grain morphology but the average grain size decreases with increasing BZ concentration, resulting in a highly dense microstructure.

Fig. 3 shows the temperature dependence of dielectric constant of BZ-modified BNKT ceramics at 1, 10, and 100 kHz between room temperature and 500 °C. As can be seen in Fig. 3(a), there are two distinct anomalies in the  $\varepsilon_r$  - T curve of the unmodified BNKT; the hump at about 130 °C that is known as the depolarization temperature  $T_d$  and the peak at about 260 °C (the maximum dielectric constant temperature  $T_{\rm m}$ ). The dielectric spectra were clearly affected by BZ modification, as seen in Figs. 3(b)-(d). The transition at  $T_{\rm d}$  became unclear in BZ-modified specimens, whereas the  $T_{\rm m}$  decreased with increasing the BZ content. It is obvious that all the samples exhibit relaxation behavior (apparent from diffuse phase transition), which is similar to the Mn-doped BNKT system [18]. Such a relaxor behavior in BZ-modified specimens can be explained by compositional fluctuations or random local electric fields [19] and stress-induced phase transitions [20] due to randomly distributed cations. In the case of our specimens, K<sup>+</sup>, Na<sup>+</sup>, Bi<sup>3+</sup> and Ba<sup>+2</sup> ions can occupy A-sites, while Zr4+ and Ti4+ can be located in B-sites.

The diffuse phase transition was observed for all samples, as exemplified by broadening of dielectric peak. Hence the nature of diffusivity is examined here.



**Fig. 2.** FE-SEM micrographs of the (1-x)BNKT-*x*BZ ceramics; (a) x = 0 (b) x = 0.01 (c) x = 0.02, and (d) x = 0.04.



**Fig. 3.** The temperature-dependent dielectric constant and loss of the (1-x)BNKT-xBZ ceramics measured at 1, 10 and 100 kHz for (a) x = 0 (b) x = 0.01 (c) x = 0.02, and (d) x = 0.04.



**Fig. 4.** Plots of log  $(1/\varepsilon_r - 1/\varepsilon_m)$  vs. log  $(T - T_m)$  at 1 kHz for the (1-x)BNKT- *x*BZ ceramics.

Figure 4 shows the plot of log  $(1/\varepsilon_r - 1/\varepsilon_m)$  vs. log  $(T - T_m)$  at 1 kHz for x = 0, 0.01, 0.02, 0.03, 0.04 and 0.05. The equation  $1/\varepsilon_r = (T - T_m)^2$  has been shown to be valid over a wide temperature range instead of the normal Curie-Weiss law, where  $T_m$  is the temperature at which the dielectric constant reaches maximum. For the explanation of dielectric behavior with diffuse phase transition, the value of  $\gamma$  was calculated using the modified Curie-Weiss law [21].

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^{\gamma}}{c_2}, 1 \le \gamma \le 2$$
(1)

where  $\varepsilon_m$  is the maximum dielectric constant,  $\gamma$  the diffusivity for phase transition (which indicates the degree of dielectric relaxation), and  $C_2$  the Curie constant. If  $\gamma$  is 1 then the material belongs to a normal ferroelectric and for  $\gamma = 2$ , the material corresponds to an ideal relaxor ferroelectric. The values of  $\gamma$  and  $C_2$  are both materials constants that depend on the composition and structure of materials. After fitting the curve (Fig. 4), the slope of the curve was obtained at 1



**Fig. 5.** The polarization and strain hysteresis loops of the (1-x)BNKT- xBZ ceramics as a function of composition.

kHz for all samples. The  $\gamma$  was found to be 1.76, 1.92, 1.97, 1.92, 1.43 and 1.82 for x = 0, 0.01, 0.02, 0.03, 0.04 and 0.05, respectively, which confirmed the diffuse phase transition in BNKT system. Recently, Zuo *et al.* also found similar phenomena in BZ-modified ((Na<sub>0.52</sub>K<sub>0.40</sub>) (Nb<sub>0.84</sub>Sb<sub>0.08</sub>) O<sub>3</sub>-(0.08-*x*) LiTaO<sub>3</sub>) ceramics [15].

Fig. 5 shows the polarization-electric field (P-E) hysteresis loops and bipolar S-E loops of BZ-modified BNKT ceramics measured at room temperature. Both  $P_{\rm r}$  and  $E_{\rm c}$  values decreased gradually with increasing BZ content. The hysteresis curves showed that BZ exerted considerable effect on the polarization as well as  $E_{\rm c}$ . However, *P*-*E* loop measurements revealed that both  $P_r$  and  $E_c$  significantly decreased at x = 0.02, leading to a slimmed hysteresis loop. The remnant polarization ( $P_r$ ) decreased from 30  $\mu$ C/cm<sup>2</sup> for x = 0 to  $16 \,\mu\text{C/cm}^2$  for x = 0.02. The coercive field (E<sub>c</sub>) was also found to significantly decrease from 35 kV/cm to 10 kV/cm within the corresponding composition range. The transition point in the shape of P - E loops corresponded to the phase transition point in the XRD pattern as seen in Fig. 1. At higher BZ concentrations, both  $P_{\rm r}$  and  $E_{\rm c}$  were considerably decreased, suggesting a typically observed phenomenon in relaxors [22]. Similar results were reported by Seifert et al. in the KNN-modified BNKT, resulting in the destabilization of ferroelectric order of BNKT [23]. Therefore, the decrease in remnant polarization  $(P_r)$  with increasing the BZ content can be attributed to the growth of polar nanoregions induced by compositional disorder at the expense of the long-range polar order in BNKT.

From the bipolar *S*-*E* loop measurement, pure BNKT exhibited a butterfly-shaped curve with a maximum strain of 0.13%. The maximum strain was drastically increased up to 0.26% at x = 0.02, where a relaxor-ferroelectric crossover was believed to occur [24] because the negative strain induced by domain switching disappeared. The large enhancement in the field-induced strain at this crossover was also reported in other BNT-based ceramics [24, 25].

## Conclusions

The crystal structure of BNKT ceramics was changed from the coexistence of rhombohedral-tetragonal phases to another coexistence of pseudocubic-tetragonal symmetry by BZ-modification. However, temperature dependent dielectric properties revealed strong relaxor behaviors in all solid solutions. It is believed that such relaxor behaviors are not related with the phase transition but strongly associated with nanometer-scale compositional inhomogeneities in both *A*- and *B*-sites by BZsubstitution. The *P*-*E* and *S*-*E* loops demonstrated that the addition of BZ destabilized the ferroelectric order of BNKT ceramics and resulted in enhanced field-induced strains with a maximum strain of 0.26 % at x = 0.02.

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#### References

- 1. L.E. Cross, Ferroelectrics 76 (1987) 241-267.
- G.A. Smolensky and A.I. Agranovskaya, Sov. Phys. Tech. Phys. 3 (1958) 1380.
- D. Viehland, S.J. Jang, L.E. Cross and M. Wuttig, J. Appl. Phys. 68 (1990) 2916-2921.
- J.J. Lima-Silva, I. Guedes, J. Mendes-Filho, A.P. Ayala, M.H. Lente, J.A. Eiras and D.Garcia, Solid State Commun. 131 (2004) 111-114.
- A. Sasaki, T. Chiba, Y. Mamiya and E. Otsuki, Jpn. J. Appl. Phys. 38 (1999) 5564-5567.
- J. Yoo, J. Hong, H. Lee, Y. Jeong, B. Lee, H. Song and J. Kwon, Sens. and Actu. A 126 (2006) 41-47.

- A. Ullah, C.W. Ahn, A. Hussain, S.Y. Lee, H.J. Lee and I.W. Kim, Curr. Appl. Phys. 10 (2010) 1174-1181.
- 8. A. Hussain, C.W. Ahn, A Ullah, J.S. Lee and I.W. Kim, Ceramics International 38 (2012) 4143-4149.
- 9. N.B. Do, H.B. Lee, C.H. Yoon, J.K. Kang, J.S. Lee and I.W. Kim, Trans. Electr. Electron. Mater. 12 (2011) 64-67.
- K. Kumar and B. Kumar, Integrated Ferroelectrics, 121 [1] (2010) 99-105.
- 11. Y. Li, W. Chen, Q. Xu, J. Zhou, Y. Wang and H. Sun, Ceramics International 33 (2007) 95-99.
- A.A. Bokov, M. Maglione and Z.G. Ye, J. Phys.: Condens. Matter. 19 (2007) 092001-10.
- S.J. Kuang, X.G. Tang, L.Y. Li, Y.P. Jiang and Q.X. Liu, Script. Mater. 61 (2009) 68-71.
- 14. N.Yasuda, H. Ohwa and S. Asano, Jpn. J. Appl. Phys. 35 (1996) 5099-5103.
- 15. R. Zuo, J. Fu, S. Lu and Z. Xu, J. Am. Ceram. Soc. (2011) 1-6.
- 16. R.D. Shannon, Acta. Crystrallogr. A 32 (1976) 751-767.
- A. Hussain, C.W. Ahn, J.S. Lee, A. Ullah, and I.W. Kim, Sens. Actuators A 158 (2010) 84-89.
- X.P. Jiang, L.Z. Li, M. Zeng and H.L.W. Chan, Materials Letters 60 (2006) 1786-1790.
- I.G. Siny, E. Husson and J.M. Beny, Physica B 293 (2001) 382-389.
- J. Kreisel, A.M. Glazer, P. Bouvier and G. Lucazeau, Phys. Rev. B 63 (2001) 174106.
- 21. K. Uchino and S. Nomura, Ferroelectr. Lett. 44 (1982) 55-61.
- 22. V.V. Shvartsman and D.C. Lupascu, J. Am. Ceram. Soc. 95 [1] (2012) 1-26.
- 23. K.T.P. Seifert, W. Jo and J. Rödel, J. Am. Ceram. Soc. 93 [5] (2010) 1392-1396.
- 24. W. Jo, S. Schaab, E. Sapper, L.A. Schmitt, H.J. Kleebe, J. Appl. Phys. 110 (2011) 074106.
- S.T. Zhang, A.B. Kounga, E. Aulbach, T. Granzow, W. Jo, H.J. Kleebe and J. Rödel, J. Appl. Phys. 103 (2008) 034107.