

## Structures and piezoelectric properties of $(\text{NaKLi})_{1-x}(\text{BiNaBa})_x\text{Nb}_{1-x}\text{Ti}_x\text{O}_3$ lead-free ceramics

Ruzhong Zuo<sup>a)</sup> and Chun Ye

School of Materials Science and Engineering, Hefei University of Technology, Hefei, Anhui 230009, China

(Received 12 June 2007; accepted 19 July 2007; published online 10 August 2007)

Lead-free solid solution piezoelectric ceramics  $(1-x)(\text{Na}_{0.475}\text{K}_{0.475}\text{Li}_{0.05})\text{NbO}_3-x(\text{Bi}_{0.48}\text{Na}_{0.48}\text{Ba}_{0.04})\text{TiO}_3$  ( $x=0-0.15$ ) have been fabricated by traditional solid state sintering. All compositions studied have pure perovskite structures, showing an orthorhombic-tetragonal phase transition with increasing  $x$ . The tetragonality, however, declined with further increasing  $x$ . A morphotropic phase boundary (MPB) between orthorhombic and tetragonal ferroelectric phases was identified approximately at  $x=0.02$ , leading to enhanced electrical properties of the dielectric constant  $\epsilon_r/\epsilon_0 \sim 702$ , the piezoelectric constant  $d_{33} \sim 328$  pC/N, and the planar electromechanical coupling factor  $k_p \sim 48\%$ . The MPB composition has a higher Curie temperature (415 °C) than most  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  compositions. These solid solution ceramics look promising as potential lead-free candidate materials. © 2007 American Institute of Physics. [DOI: 10.1063/1.2769939]

Lead-based piezoelectric ceramics with perovskite structures, such as  $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$  (PZT), exhibit high relative permittivity, large remanent polarization, and high piezoelectric coefficients, and thus have been widely used in actuators, sensors, and transducers.<sup>1</sup> However, lead pollution problems have attracted extensive attention. Therefore, research on lead-free alternatives has been more and more concentrated nowadays.

There have been so far two main material systems with perovskite structure investigated for lead-free piezoelectric applications:  $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$  (BNT) based and  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  (NKN) based materials. BNT is a rhombohedral ferroelectric at room temperature and forms a morphotropic phase boundary (MPB) with  $\sim 6$  mol %  $\text{BaTiO}_3$  (BT), possessing enhanced piezoelectric and electromechanical properties.<sup>2</sup> The MPB was believed to play a crucial role in the enhancement of the dielectric, ferroelectric, piezoelectric, and electromechanical properties.<sup>3-6</sup>

By comparison,  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  ceramics (NKN) seem more attractive on the basis of better piezoelectric and electromechanical properties. However, NKN is rather difficult to densify by ordinary sintering. Although its densification was improved by a few processing methods, this did not significantly advance the properties.<sup>7-10</sup> The Li, Ta, and Sb substituted NKN ceramics were reported to have enhanced piezoelectric and electromechanical responses owing to the formation of MPBs.<sup>11-15</sup> However, these systems intrinsically have difficulty in processing and microstructure control, durability against water, reproducibility of the properties and fatigue lifetime, and so on.<sup>16</sup> Recently, NKN-BNT ceramics have been reported, exhibiting complex phase transition behavior, enhanced piezoelectric and electromechanical properties, and improved reliability,<sup>17</sup> compared to pure NKN ceramics. However, their electrical properties are still not enough to replace conventional PZT materials. In this work, solid solutions between Li doped NKN ceramics and BT-added BNT ceramics were investigated from the view-

point of structures and properties. The adoption of lithium was expected to enhance electrical properties and BT addition was anticipated to modify sintering and chemical reliability of alkaline niobates. The solid solution ceramics were structurally and electrically characterized and prepared by ordinary sintering.

Ceramics with compositions of  $(\text{Na}_{0.475}\text{K}_{0.475}\text{Li}_{0.05})_{1-x}(\text{Bi}_{0.48}\text{Na}_{0.48}\text{Ba}_{0.04})_x\text{Nb}_{1-x}\text{Ti}_x\text{O}_3$  [(1-x)NKL5N-xBNB4T] ( $x=0, 0.005, 0.01, 0.02, 0.03, 0.04, 0.08, 0.15$ ) were synthesized by means of a conventional mixed oxide route. The starting materials were  $\text{K}_2\text{CO}_3$  (>99.0%),  $\text{Na}_2\text{CO}_3$  (99.5%),  $\text{Li}_2\text{CO}_3$  (99.5%),  $\text{BaCO}_3$  (99.8%),  $\text{Bi}_2\text{O}_3$  (99.97%),  $\text{TiO}_2$  (99.9%), and  $\text{Nb}_2\text{O}_5$  (99.9%). A drying process and a sample preparation method similar to those described previously were employed.<sup>17</sup> The powder mixtures were calcined in the temperature range of 820–900 °C for 5 h, depending on  $x$ . After compaction, the disk specimens placed under a platinum foil were sintered in air in the temperature range of 1000–1100 °C for 2–4 h. The microstructure was observed by a scanning electron microscope (SEM) (Philips Electronic Instruments, Mahwah, NJ). A powder x-ray diffractometer (XRD) (Rigaku) with a  $\text{Cu } K\alpha$  radiation was utilized to identify the crystal structures. Densities of the samples sintered at different temperatures were measured by the Archimedes method.

After all samples were polished, silver paste was fired on two major sides as electrodes. The dielectric properties as a function of temperature were measured by a LCR meter (HP 4284). The piezoelectric and electromechanical properties were measured only 24 h after a poling treatment. The piezoelectric strain constant  $d_{33}$  was measured by a quasistatic Belincourt meter (YE2730 SINOCERA China). The planar electromechanical coupling factor  $k_p$  was obtained by a resonance-antiresonance method through an impedance analyzer (HP 4192A) on the basis of IEEE standards.

Figure 1 shows that NKN-0.05LiNbO<sub>3</sub> (NKL5N) has a typical perovskite structure with an orthorhombic symmetry as reported.<sup>11</sup> Moreover, the crystal symmetry starts to change due to the addition of BNT-0.04BT (BNB4T) which lies on the rhombohedral side of binary BNT-BT system.<sup>2</sup>

<sup>a)</sup> Author to whom correspondence should be addressed; electronic mail: piezolab@hfut.edu.cn

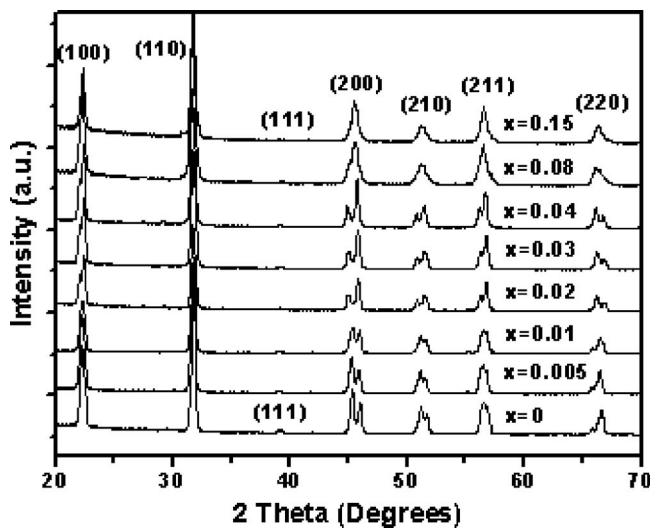


FIG. 1. XRD patterns of  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics.

The  $(1-x)\text{NKL5N}-x\text{BNB4T}$  solid solution ceramics begin to exhibit tetragonal structures approximately at  $x=0.02$ . A small amount of rhombohedral composition, BNB4T, can transform the crystal structure from orthorhombic to tetragonal, implying that these two crystal structures have similar energy states. However, the tetragonal symmetry remains in a limited composition range. This phase transition behavior is similar to that of NKN-BNT system.<sup>17</sup> The diffraction peak profiles in Fig. 1 were fitted to calculate the lattice parameters. The variation of lattice constants as a function of the BNB4T content is shown in Fig. 2. A MPB between ferroelectric orthorhombic and tetragonal phases should exist approximately at  $x=0.02$ . In the orthorhombic zone, the lattice constants  $c$  and  $a$  show very close values, explaining why there are only two peak splitting of (200) reflections for an orthorhombic structure, rather than three peak splittings. In the tetragonal zone, the tetragonality  $c/a$  declines rapidly with additional BNB4T compositions, indicating that the transitional tetragonal state is unstable. The curve of  $c/a$  values against the BNB4T content is also shown in the inset of Fig. 2. The  $c/a$  ratio of the composition with  $x=0.02$  is about 1.02. The tetragonality seems to disappear at  $x \sim 0.15$ . The compositions with  $x > 0.15$  were not reported

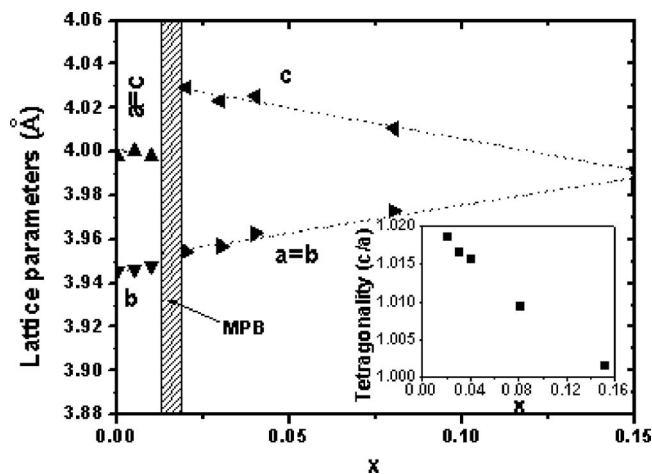


FIG. 2. Lattice parameters of  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics as a function of  $x$ . The insets are the  $c/a$  values in the tetragonal zone.

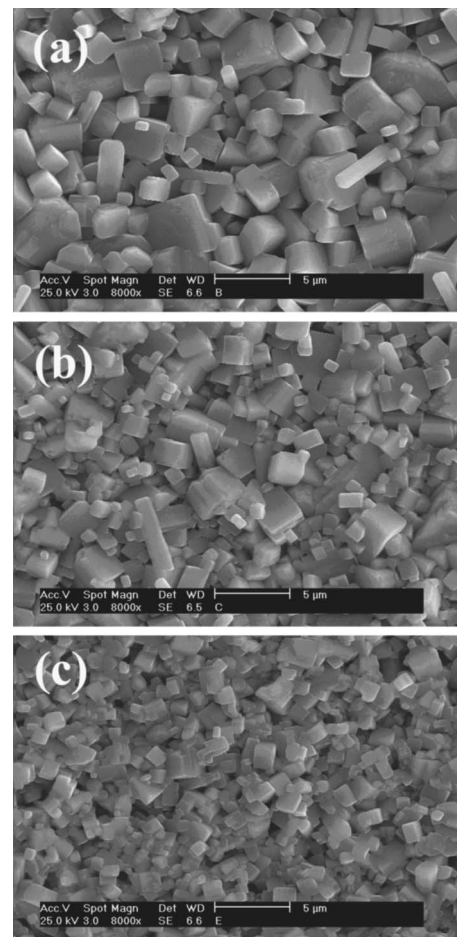


FIG. 3. SEM pictures of  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics sintered at  $1070\text{ }^\circ\text{C}$  for 2 h with  $x$  equals (a) 0.01, (b) 0.02, and (c) 0.04.

because the materials possess the best piezoelectric and electromechanical properties near the MPB.

The addition of BNB4T not only changes the crystal structures of NKL5N compositions but also influences their densification behavior. The NKL5N-BNB4T solid solutions can be highly densified at relatively low temperatures. The micrographs of  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics sintered at  $1070\text{ }^\circ\text{C}$  for 2 h are shown in Fig. 3. These samples have relative densities of  $>96\%$  theoretical values. Moreover, NKL5N-0.01BNB4T ceramics have an average grain size of  $\sim 3\text{ }\mu\text{m}$  and it drops to  $\sim 1\text{ }\mu\text{m}$  for NKL5N-0.04BNB4T ceramics. Moreover, a modified durability against water can be obtained by adding BT doped BNT, compared to pure NKN and NKN-BNT systems. No change in microstructure can be observed after the samples were immersed in water for weeks.

Figure 4 shows dielectric properties as a function of temperature for unpoled  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics. The NKL5N-0.005BNB4T ceramics show similar dielectric behavior to pure NKL5N.<sup>11</sup> They have two phase transitions at  $141$  and  $427\text{ }^\circ\text{C}$ , corresponding to the orthorhombic-tetragonal and tetragonal-cubic transitions, respectively. It should be noted that the addition of BNB4T causes both transitions to shift to lower temperatures. For the samples with  $x < 0.02$ , the two phase transitions are observed. When the BNB4T content is higher than 0.02 up to 0.15, only a cubic-tetragonal transition can be observed. Interestingly, with further increasing BNB4T content, the material shows

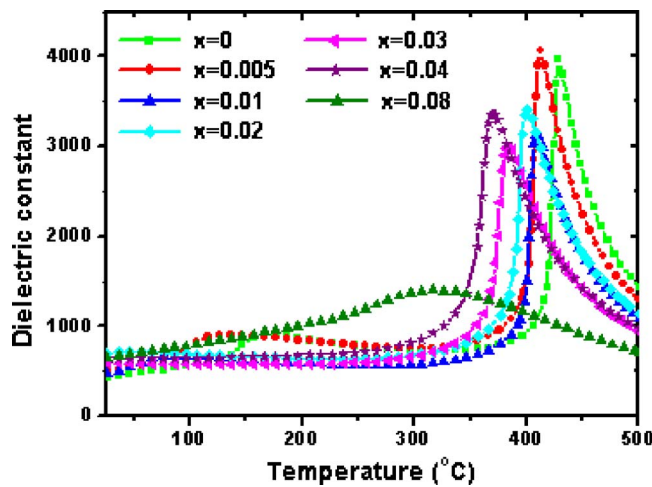


FIG. 4. (Color online) Dielectric constants at 1 MHz as a function of temperature for  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics.

much lower dielectric maxima and broad phase transition behavior. This can be attributed to the decreasing tetragonality and the finer grain morphology. More complex occupation at  $A$  or  $B$  site in a  $\text{ABO}_3$  perovskite structure may also contribute to the diffuse phase transition.

The various electrical properties of poled  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics are shown in Fig. 5. The materials show a strong compositional dependence of the properties near the MPB. The best properties of these materials exist near the MPB composition with  $x=0.02$ . Pure NKL5N ceramics have a room-temperature dielectric constant  $\epsilon_r/\epsilon_0$  of 430,  $d_{33}$  of 200 pC/N, and  $k_p$  of 38%. The addition of a few percent of BNB4T significantly increases the piezoelectric activities until they reach the best values of

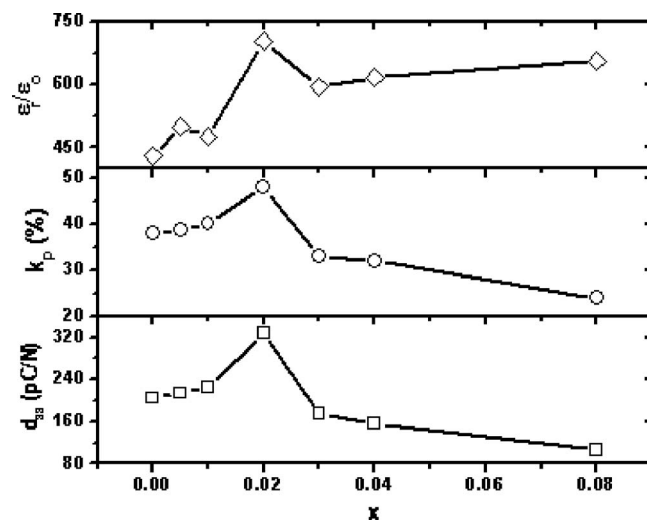


FIG. 5. Various electrical properties of  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics as a function of the BNB4T content  $x$ .

$\epsilon_r/\epsilon_0$  of 702,  $d_{33}$  of 328 pC/N, and  $k_p$  of 48%. Over this boundary, the piezoelectric and electromechanical properties decline rapidly with increasing BNB4T content. The dielectric constant first decreases after the boundary and then does not change significantly in a certain composition range, owing to a shift of dielectric peaks close to room temperature. Although the improvement of electrical properties might be partially due to the increase in density and the change in microstructure, it should be noted that the MPB plays the most important role in improving piezoelectric properties of NKL5N-BNB4T ceramics.

In summary,  $(1-x)\text{NKL5N}-x\text{BNB4T}$  ceramics were prepared by ordinary sintering at relatively low sintering temperatures, possessing an improved durability against water. Identification of crystal structures demonstrated a MPB between orthorhombic and tetragonal phases at  $\sim 2$  mol% BNB4T. The piezoelectric and electromechanical properties of solid solution ceramics exhibit a strong compositional dependence near the MPB. The best electrical properties  $d_{33} \sim 328$  pC/N and  $k_p \sim 48\%$  were obtained in the MPB composition which also has a Curie temperature of 415 °C higher than those of most PZT materials.

This work was financially supported by HFUT RenCai Foundation (No. 103-035006) and a special Program for Excellence Selection "R & D of Novel Lead-Free Piezoelectric Ceramics" (No. 103-035034).

- <sup>1</sup>B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic, New York, 1971), pp. 115–181.
- <sup>2</sup>T. Takenaka, K. Maruyama, and K. Sakata, *Jpn. J. Appl. Phys., Part 1* **30**, 2236 (1991).
- <sup>3</sup>H. Fu and R. E. Cohen, *Nature (London)* **403**, 281 (2000).
- <sup>4</sup>R. Guo, L. E. Cross, S. E. Park, B. Noheda, D. E. Cox, and G. Shirane, *Phys. Rev. Lett.* **84**, 5423 (2000).
- <sup>5</sup>J. M. Kiat, Y. Uesu, B. Dkhil, M. Matsuda, C. Malibert, and G. Calvarin, *Phys. Rev. B* **65**, 064106 (2000).
- <sup>6</sup>A. K. Singh and D. Pandey, *Phys. Rev. B* **67**, 064102 (2003).
- <sup>7</sup>M. Matsubara, T. Yamaguchi, K. Kikuta, and S. Hirano, *Jpn. J. Appl. Phys., Part 1* **43**, 7159 (2004).
- <sup>8</sup>S. H. Park, C. W. Ahn, S. Nahm, and J. S. Song, *Jpn. J. Appl. Phys., Part 2* **43**, L1072 (2004).
- <sup>9</sup>R. Z. Zuo, J. Rodel, R. Z. Chen, and L. T. Li, *J. Am. Ceram. Soc.* **89**, 2010 (2006).
- <sup>10</sup>R. Wang, R. Xie, T. Sekiya, and Y. Shimojo, *Mater. Res. Bull.* **39**, 1709 (2004).
- <sup>11</sup>Y. Guo, K. Kakimoto, and H. Ohsato, *Appl. Phys. Lett.* **85**, 4121 (2004).
- <sup>12</sup>Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, and M. Nakamura, *Nature (London)* **432**, 84 (2004).
- <sup>13</sup>E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, *Appl. Phys. Lett.* **87**, 182905 (2005).
- <sup>14</sup>S. J. Zhang, R. Xia, T. R. Shrout, G. Z. Zang, and J. F. Wang, *J. Appl. Phys.* **100**, 104108 (2006).
- <sup>15</sup>Z. P. Yang, Y. F. Chang, and L. L. Wei, *Appl. Phys. Lett.* **90**, 042911 (2007).
- <sup>16</sup>J. Yoo, K. Lee, K. Chung, S. Lee, K. Kim, J. Hong, S. Ryu, and C. Lhee, *Jpn. J. Appl. Phys., Part 1* **45**, 7444 (2006).
- <sup>17</sup>R. Z. Zuo, X. S. Fang, and C. Ye, *Appl. Phys. Lett.* **90**, 092904 (2007).