Phase structures and electrical properties of new lead-free $(Na_{0.5}K_{0.5})NbO_3-(Bi_{0.5}Na_{0.5})TiO_3$ ceramics

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Highly dense $(1-x)(Na_{0.5}K_{0.5})NbO_3-x(Bi_{0.5}Na_{0.5})TiO_3$ (NKN-BST) solid solution piezoelectric ceramics have been fabricated by ordinary sintering. All compositions show pure perovskite structures, showing room-temperature symmetries of orthorhombic at $x \leq 0.02$, of tetragonal at $0.03 \leq x \leq 0.09$, of cubic at $0.09 < x \leq 0.20$, and of rhombohedral at $x > 0.20$. A morphotropic phase boundary (MPB) between orthorhombic and tetragonal ferroelectric phases was identified in the composition range of $0.02 < x < 0.03$. The materials near the MPB exhibit a strong compositional dependence, owning peak values of the planar electromechanical coupling factor $k_p \sim 43\%$, the piezoelectric constant $d_{33} \sim 195$ pC/N, and the Curie temperature of 375 °C comparable to that of commercial lead zirconate titanate ceramics. The results indicate that NKN-BST ceramic is a promising lead-free piezoelectric candidate material. © *2007 American Institute of Physics*.
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Lead based piezoelectric ceramics, such as $Pb(ZrTi)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$, and $Pb(Zn_{1/3}Nb_{2/3})O_3-PbTiO_3$, have been widely applied in industry as sensor, actuator, and transducer materials due to their excellent electrical properties.[1] However, the toxicity of lead oxide has been considered to be a serious threat to the environment. Therefore, research on lead-free replacement has become more and more concentrated in the last few years. On the other hand, the high piezoelectric response was generally considered to stem from the so-called morphotropic phase boundary (MPB) between rhombohedral, tetragonal, and/or monoclinic ferroelectric phases where the polarization vector can rotate almost continuously under the external electric field.[2] Therefore, currently the main research activities in this area are to search for new lead-free compositions with MPBs by means of a huge amount of experimental work and theoretical calculation.[3–5] There have been so far two main material systems with perovskite structure studied for lead-free piezoelectric applications. $(Bi_{0.5}Na_{0.5})TiO_3$ (BST) was extensively investigated because of its good ferroelectricity, with a remnant polarization of 38 $\mu C/cm^2$.[6] It is a rhombohedral ferroelectric at room temperature, changes to tetragonal antiferroelectric at ~200 °C, and becomes cubic paraelectric at the Curie point of ~320 °C. Several solid solutions with ferroelectric $BaTiO_3$, $(Bi_{0.5}K_{0.5})TiO_3$, and antiferroelectric $NaNbO_3$ were studied for lead-free ferroelectric and piezoelectric compositions.[7–9] However, they were restricted by the high coercive electric fields and low depolarization temperatures. The MPB $(Na_{0.5}K_{0.5})NbO_3$ (NKN) ceramics appeared more attractive on the basis of better piezoelectric and electromechanical properties and comparable Curie temperature (T_c) to that of commercial lead zirconate titanate (PZT).[10,11] However, difficulty in sintering of the ceramics and control of stoichiometry leads to deviation from excellent properties. Hot pressed NKN ceramics were reported to have a high piezoelectric strain constant $d_{33} = \sim 160$ pC/N and a large coupling coefficient $k_p = \sim 45\%$.[12] However, ordinarily sintered NKN ceramics own relatively low electrical properties ($d_{33} = \sim 80$ pC/N, $k_p = \sim 36\%$).[10] A lot of processing procedures were used to promote its sintering, leading to a significantly enhanced densification, but their properties are still not as good as those of hot pressed samples. NKN-based ceramics doped with Li, Ta, and Sb show excellent piezoelectric and electromechanical properties due to the formation of a MPB between orthorhombic and tetragonal ferroelectric phases.[13–15] The textured NKN-based ceramics were reported to own comparable piezoelectric properties to a hard PZT.[14] However, these systems also show some disadvantages such as in some cases abnormal grain growth, low fatigue resistance, low stability of piezoelectric properties, and so on.[16–18] In this work, solid solution ceramics between these two typical lead-free candidates, bismuth sodium titanate BST and NKN, were investigated from the viewpoint of phase transitions and resultant electrical properties. The results demonstrate that NKN-BST ceramics possess significantly improved sintering behavior and excellent piezoelectric and electromechanical properties when BST is added in a small amount.

Ceramics with a series of compositions $(1-x) \times (Na_{0.5}K_{0.5})NbO_3-x(Bi_{0.5}Na_{0.5})TiO_3$ (x=0.005, 0.01, 0.02, 0.03, 0.05, 0.09, 0.15, 0.2, 0.8, 1.0) were manufactured by a conventional mixed oxide route. The raw materials used in the study were Bi_2O_3 (99.97% in purity), TiO_2 (99.9%), Nb_2O_5 (99.9%), K_2CO_3 (99%), and Na_2CO_3 (99.5%). Before weighing, all starting powders were placed in an oven at 100 °C for 2 days and then stored in a dry vessel for future use. The weighed powders according to the chemical formula were milled in a nylon jar with ZrO_2 balls for 24 h using anhydrous ethanol as the medium. After three time calcinations at 900 °C for 5 h, the synthesized powders were ball milled once again and sieved through 230 meshes. The dried powders were subsequently pressed into disks of 10 mm in diameter and 2–3 mm in thickness. These powder compacts were sintered in air in the temperature range of 1020–1150 °C for 3 h, depending on x. The Archimedes method was used to determine the bulk density. The microstructure was observed by a scanning electron microscopy

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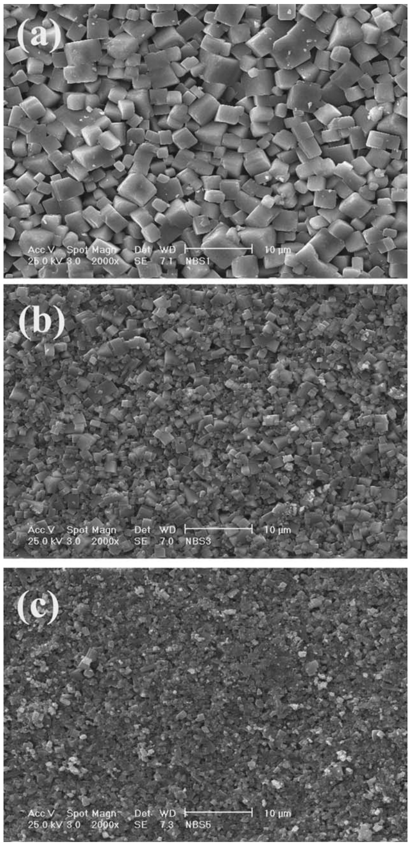

FIG. 1. SEM micrographs of $(1-x)$NKN-xBST ceramics sintered at 1090 °C with x equal to (a) 0.01, (b) 0.03, and (c) 0.05.

(SEM) (Philips Electronic Instruments, Mahwah, NJ). Powder x-ray diffraction (XRD) (Rigatu) patterns of crushed pellets using Cu $K\alpha$ radiation were recorded in the 2θ range of 20°–80°.

Silver paste was fired on two major sides of the specimens as electrodes after polishing. All polished disk specimens have an aspect ratio of 0.1. The dielectric properties were measured by an impedance analyzer (HP 4284A) at different frequencies from 100 Hz to 1 MHz in the temperature range of 25–500 °C. For measuring piezoelectric and electromechanical properties, samples were poled in stirring silicone oil at 100–130 °C applying 2–4 kV/mm for 30 min, and then cooled in the electric field. The piezoelectric strain constant d_{33} was measured 24 h after poling by a quasistatic Berlincourtmeter (YE2730 SINOCERA China). The planar electromechanical coupling factor kp was obtained by a resonance-antiresonance method through an impedance analyzer (HP 4192A) on the basis of IEEE standards.

Although sintering of pure NKN is known to be difficult owing to the volatilization of potassium at high temperature, the NKN-BST ceramics exhibit an improved sintering behavior. The densities up to 96% theoretical values can be reached at as low temperature at 1090 °C for 2 h. The SEM morphology of NKN-BST ceramics sintered at 1090 °C is shown in Fig. 1. It should be noted that the microstructure gets significantly finer with increasing the BST content. The grain size changes from 3–4 μm for NKN-0.01BST to ~0.6 μm for NKN-0.05BST.

The x-ray diffraction patterns of NKN-BST ceramics are shown in Fig. 2. It is clear that the crystal structure of pure NKN is changed by adding a small amount of BST. A series

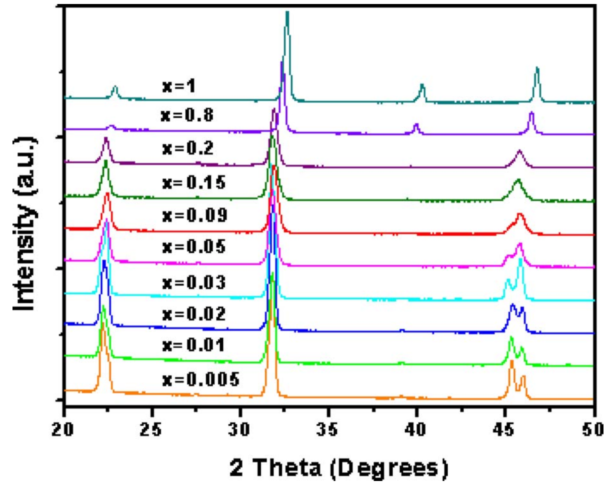

FIG. 2. (Color online) XRD patterns of $(1-x)$NKN-xBST ceramics with x, as indicated.

of continuous solid solutions between NKN and BST was formed because no trace of secondary phases was detected by XRD. $(1-x)$NKN-xBST ceramics at room temperature have orthorhombic structures similar to pure NKN, when $x \leqslant 0.02$. It becomes tetragonal when more BST is added. However, the tetragonal symmetry remains in a limited composition range within which the tetragonality decreases with increasing the BST content. The cubic structure starts to appear when x is greater than 0.09 until $x=0.20$ approximately. This is because the addition of BST shifts the Curie point of NKN ceramics below room temperature. However, when x continues to increase, NKN-BST solid solutions exhibit rhombohedral structures until pure BST composition which was known to be rhombohedral symmetry at room temperature. The MPB NKN ceramics[18] have orthorhombic symmetry at room temperature and tetragonal between about 200 and 420 °C (its Curie point). The structure of solid solutions transforms from orthorhombic to tetragonal probably due to a distortion of octahedra caused by smaller Ti^{4+} ions occupying the B site of NKN lattice, which slightly increases the tolerance factor of a ABO_3 perovskite structure, $t=(r_A-r_O)/\sqrt{2}(r_B-r_O)$ where r_A,r_B, and r_O are the radii of A, B, and O ions, respectively. This somewhat indicates that the orthorhombic and tetragonal structures in NKN have closer energy states. However, this transitional tetragonal state is unstable. The tetragonality declines rapidly with increasing the BST content. The lattice constants of NKN-BST ceramics as a function of the BST content are shown in Fig. 3. A MPB between ferroelectric orthorhombic and tetragonal phases should exist approximately at $0.02 \leqslant x \leqslant 0.03$. The c/a ratio for the composition with $x=0.03$ is 1.02. This decreases to 1.005 when $x=0.09$. Therefore, the Curie temperature continues to go down with increasing the BST content. The complex phase transition behavior of NKN-BST ceramics can be expected from both end members whose structures have been described above. However, the following electrical characterization was focused only on these compositions around the MPB because the material shows the best piezoelectric and electromechanical properties there.

The dielectric constants at the frequency of 100 kHz as a function of temperature for unpoled samples are shown in Fig. 4. As we know, pure NKN ceramics have two phase transitions at 420 and 200 °C, corresponding to the cubic-

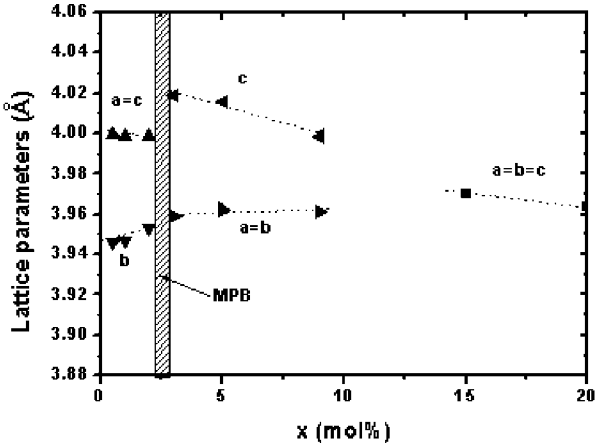

FIG. 3. Lattice parameters of NKN-BST ceramics as a function of the BST content.

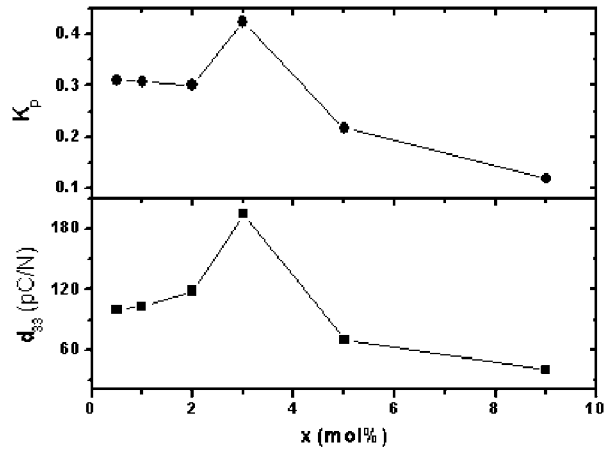

FIG. 5. Piezoelectric constants and electromechanical coupling factors of $(1-x)$NKN-xBST ceramics as a function of the BST content x.

tetragonal and tetragonal-orthorhombic transitions, respectively. For the samples with $x \leqslant 0.02$, the two phase transitions are observed, similar to those of pure NKN. However, the addition of a small amount of BST causes both transitions to shift to lower temperatures. When the BST content is higher than 0.03 up to 0.09, only a cubic-tetragonal transition can be observed. 0.80NKN-0.2BST ceramics have a flat dielectric-temperature curve, implying that it is possible to be a cubic above room temperature. This keeps consistency with the XRD result in Fig. 2. When x increases further, the materials become rhombohedral as discussed above, their Curie temperatures increase with increasing the BST content.

Figure 5 shows the piezoelectric and electromechanical properties of poled $(1-x)$NKN-xBST ceramics. The best properties of these materials exist in the MPB compositions with $x=0.03$ on the tetragonal side. For the pure NKN ceramic, it has d_{33} of 110 pC/N and k_p of 32%. The addition of a small amount of BST increases the piezoelectric activities significantly until they reach the best values at $x=0.03$. The MPB compositions show the properties of d_{33}, 195 pC/N, and k_p, 43%. Over this boundary, the properties decay very rapidly with increasing the BST content. So it is clear that the MPB plays an important role in improving the piezoelectric properties of NKN-BST ceramics, although only 2–3 mol % BST was added.

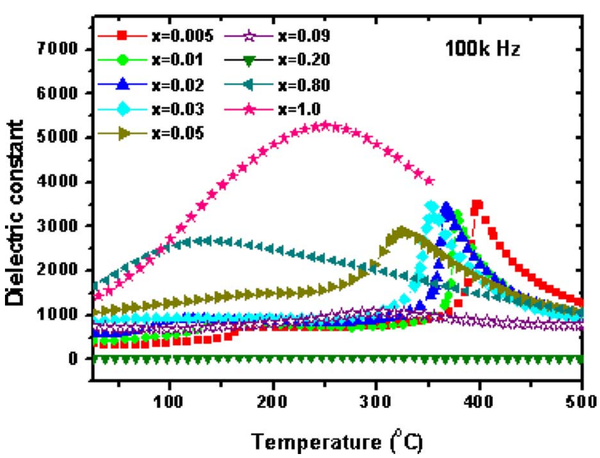

FIG. 4. (Color online) Temperature dependence of the dielectric constants of $(1-x)$NKN-xBST solid solution ceramics with different x, as indicated.

In summary, $(1-x)$NKN-xBST ceramics were investigated with their phase transition behavior and electrical characterization. A continuous phase transition was identified by adding a certain amount of BST into NKN compositions, bringing about a MPB existing at 2–3 mol % BST. Enhanced piezoelectric and electromechanical properties $d_{33} = 195$ pC/N and $k_p=43\%$ were obtained in the composition near the MPB. These compositions also have a comparable Curie temperature of 375 °C to that of PZT ceramics. These properties indicated that this system may be an attractive lead-free material for piezoelectric applications.

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