

## Morphotropic phase boundary in $(1 - x) \text{Bi}_{0.5} \text{Na}_{0.5} \text{TiO}_3 - x \text{K}_{0.5} \text{Na}_{0.5} \text{NbO}_3$ lead-free piezoceramics

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## Morphotropic phase boundary in $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ lead-free piezoceramics

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The electromechanical behavior of  $(1-x)\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (BNT-KNN) lead free piezoelectric ceramics is investigated for  $0 \leq x \leq 0.12$  to gain insight into the antiferroelectric-ferroelectric (AFE-FE) phase transition on the basis of the giant strain recently observed in BNT-based systems. At  $x \approx 0.07$ , a morphotropic phase boundary (MPB) between a rhombohedral FE phase and a tetragonal AFE phase is found. While the piezoelectric coefficient is largest at this MPB, the total strain further increases with increasing KNN content, indicating the field-induced AFE-FE transition as the main reason for the large strain. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938064]

During the last years, increased awareness for environmental topics has spurred considerable efforts to reduce the amount of hazardous substances in consumer products. Despite all this effort, there is so far no suitable material to replace piezoelectric ceramics containing the toxic heavy metal lead such as the ubiquitous  $(\text{Pb}, \text{Zr})\text{TiO}_3$  (PZT) in actuator or sensor applications. Research work is focused on lead-free systems with perovskite-type structure; compositions based on  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT) and  $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (KNN) are especially promising candidates.<sup>1-3</sup>

One of the criteria for piezoelectrics intended for actuator applications is the amount of strain  $S$  that can be induced with moderate electric fields. Recently, we reported a ternary system  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-\text{BaTiO}_3-\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (BNT-BT-KNN),<sup>4</sup> which exhibits  $S=0.45\%$  at 8 kV/mm, a level never achieved in any other lead-free piezoceramic and even surpassing that of standard PZT compositions. As this system has a lot of potential, a good understanding of its phase diagram is crucial for further development and improvement, especially since a large part of the observable strain is not due to the normal piezoelectric effect but to a phase transition from an antiferroelectric (AFE) to a ferroelectric (FE) phase induced by external electric fields. Some details of the phase diagram are already known. Guo *et al.* investigated structural and electrical properties of  $(1-x)\text{KNN}-x\text{BT}$ ,<sup>5</sup> with  $0 \leq x \leq 0.2$ . They found a transition from an orthorhombic to a tetragonal phase with higher BT content for  $x \approx 0.06$  and a transition to a cubic phase as the BT content reaches  $x=0.2$ . Choi *et al.*<sup>6</sup> started from the  $\text{BaTiO}_3$ -rich side and investigated different compositions of the  $(1-x)\text{BT}-x\text{KNN}$  with  $0 \leq x \leq 0.08$ . They obtained particularly good electrical properties for  $x=0.06$ . According to their x-ray diffraction (XRD) data, however, a morphotropic phase boundary (MPB) appears to be located at  $0.02 \leq x \leq 0.04$ .

On the other hand, Takenaka *et al.*<sup>7</sup> considered the binary system  $(1-x)\text{BNT}-x\text{BT}$  with  $0 \leq x \leq 1$ . They reported a MPB between a FE rhombohedral and a FE tetragonal phase for  $x=0.06-0.07$ . In the vicinity of this MPB, the material displayed very favorable electrical and piezoelectric properties; the Curie temperature  $T_C$  was about 280 °C. However,

the compound showed a transition from a FE to a AFE phase at the depolarization temperature  $T_d \approx 160$  °C, which can be a serious obstacle for applications. Recently, Zuo *et al.*<sup>8</sup> added a small amount of BNT to KNN. Their structural analysis revealed the coexistence of a rhombohedral and tetragonal phase for compositions of  $x=0.02-0.03$ . A piezoelectric coefficient  $d_{33}=196$  pC/N and  $T_c=370$  °C were reported for this MPB composition.

So far, the BNT-rich side of the binary system BNT-KNN has been largely ignored. The closure of this gap in the borderline of the phase diagram of the ternary system BNT-BT-KNN is essential to understand the physical properties of these promising materials. Therefore, the present work reports on the processing and properties of  $(1-x)\text{BNT}-x\text{KNN}$  ceramics with  $0 \leq x \leq 0.12$ . BNT displays rhombohedral crystal symmetry and, according to Zuo *et al.*, BNT-KNN with high KNN content is tetragonal.<sup>8</sup> Therefore, special attention was paid to a possible MPB in the investigated compositional range, since excellent piezoelectric properties are often found near such MPB.<sup>9</sup>

A series of ceramics of the compositions  $(1-x)\text{BNT}-x\text{KNN}$  ( $0 \leq x \leq 0.12$ ) was prepared by conventional solid state synthesis using  $\text{Bi}_2\text{O}_3$  (99.975% purity, Alfa Aesar),  $\text{Na}_2\text{CO}_3$  (99.5%, Alfa Aesar),  $\text{K}_2\text{CO}_3$  (99.0%, Alfa Aesar),  $\text{TiO}_2$  (99.9%, Alfa Aesar), and  $\text{Nb}_2\text{O}_5$  (99.9%, ChemPur). The powders were weighed according to the stoichiometric formula and ball milled in ethanol for 24 h. The dried slurries were calcined at 900 °C for 3 h, then ball milled again for 24 h. The powders were, subsequently, pressed into pellets with a diameter of 10 mm under 70 MPa and sintered at 1050 °C, except for the composition  $x=0$ , which was sintered at 980 °C in a covered alumina crucible. To prevent the loss of volatile Bi, Na, and K, the disks were embedded in the corresponding powders during sintering. The relative density of all samples was determined by the Archimedes method. The degree of densification was highest at 98% in the sample containing 6% KNN, while that of all other specimens was practically identical at 95%.

The crystal structures of the ceramics were characterized by powder XRD (D8 Advance, Bruker, Karlsruhe, Germany) with unpoled crushed sintered samples. For the microstructure characterization by scanning electron microscope (SEM)

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(XL 30 FEG, Philips), samples were polished and thermally etched for 45 min at 900 °C for samples with  $x > 0$  and 830 °C for pure BNT. Electric measurements were carried out on ground disk-shaped specimens about 500  $\mu\text{m}$  thick, electroded with a thin layer of silver paste and dried at 500 °C for 30 min. The dependence of the electric polarization  $P$  and the mechanical strain  $S$  on an external electric field  $E$  was measured in an oil bath using a modified Sawyer–Tower circuit and a mechanical displacement sensor. For hysteresis measurements, a triangular waveform was used for the field. The frequency was low at 50 mHz. The piezoelectric coefficient  $d_{33}$  at zero field was determined by using a Berlincourt meter after poling the samples with an electric field of 7 kV/mm for 5 min at  $T = 25$  °C. Dielectric permittivity and loss of unpoled specimens were measured by using an impedance analyzer (HP4284A, Hewlett-Packard) at frequencies ranging from 100 Hz to 1 MHz in a temperature range of 50–400 °C. The planar electromechanical coupling factor  $k_p$  was obtained by the resonance-antiresonance method by using an impedance analyzer (HP 4192A) according to IEEE standards.<sup>10</sup>

The XRD measurements showed no lines indicating secondary phases for any of the samples. Pure BNT displayed a single phase rhombohedral crystal structure, determined by the deconvolution of the (200) peak. Addition of a small amount of KNN did not change this until the KNN content reached 6%. Here, traces of the tetragonal phase start to appear, the volume ratio between rhombohedral and tetragonal phase was 66:34. At  $x = 0.075$ , the balance has tipped in favor of the tetragonal phase, the ratio now being 30:70. This implies that the MPB of the system is located at about 7% KNN. For even higher KNN content, only the tetragonal phase was observed. The SEM micrographs supported the conclusion that the matrix is uniform without any secondary phases. The most notable change was the decrease in grain size with increasing  $x$  from 1.2  $\mu\text{m}$  for pure BNT to 0.7  $\mu\text{m}$  for  $x = 0.12$ .

The polarization hysteresis  $P(E)$  for samples with  $x = 0$ ,  $x = 0.06$ , and  $x = 0.12$  is exemplarily shown in Fig. 1(a). Figure 1(b) summarizes the characteristic properties of all samples: maximum polarization  $P_m$  at 8 kV/mm, remnant polarization  $P_r$  at zero field, and coercive field  $E_c$ . Both  $P_m$  and  $P_r$  change only little until  $x$  exceeds 0.06; then, both values notably decrease, with the drop in  $P_r$  being significantly more pronounced. At the same time, the coercive field strongly decreases from 5.1 to 2.2 kV/mm with increasing  $x$ . The decrease in the coercive field indicates that a predominant FE ordering gradually decreases and is replaced by an AFE ordering with increasing  $x$ . A notable decrease in  $P_r$  and  $P_m$  as  $x > 0.06$  can be assigned to the point where the dominant state changes from an FE to an AFE at zero field. This assumption is supported by the fact that the decrease in  $P_r$  is more pronounced than that in  $P_m$ , since the presence of the AFE ordering is less influential to  $P_m$  than  $P_r$  in that AFE phases undergo a transition to FE phases in the application of electric field. This was also supported by the temperature dependent  $S(E)$  measurement. Similar to the previously reported BNT-KNN-BaTiO<sub>3</sub> system,<sup>11</sup> the temperature for the highest  $S_{\text{max}}/E_{\text{max}}$  decreased as  $x$  increased and reached near room temperature at  $x = 0.12$ . Figures 2(a) and 2(b) show the  $S(E)$  hysteresis of the three samples for bipolar and unipolar field cycling, respectively. The characteristic values of these curves, the difference between maximum and minimum

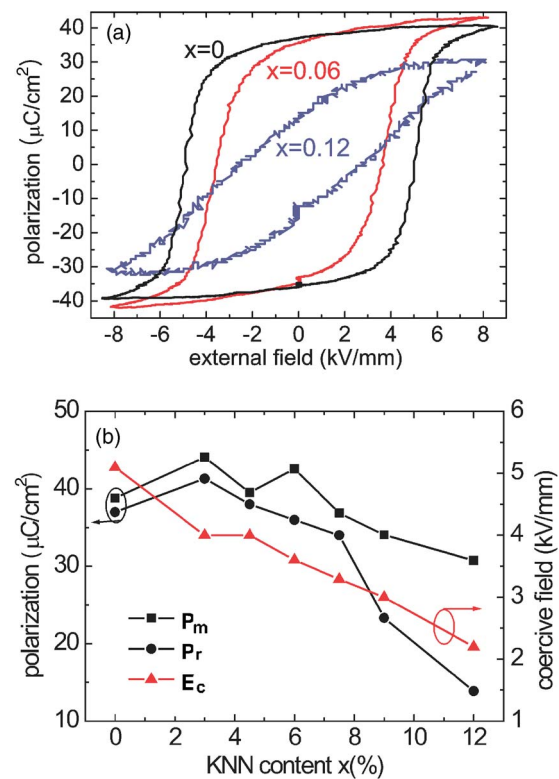


FIG. 1. (Color online) (a)  $P(E)$  hysteresis of  $(1-x)\text{BNT}-x\text{KNN}$  for  $x = 0$ , 0.06 and 0.12, and (b) composition-dependent maximum and remnant polarization  $P_m$  and  $P_r$ , and coercive field  $E_c$ .

strain, are shown for all compositions in Fig. 2(c), while Fig. 2(d) displays the  $d_{33}$  values measured at zero field and the planar coupling factor  $k_p$ . Contrary to expectations, the strain tends to increase with increasing  $x$  even beyond the MPB compositions; at the same time, the negative strain, i.e., the difference between the zero field values and the minima of the  $S(E)$  curves in the bipolar measurement, vanishes. On the other hand,  $d_{33}$  behaves as expected, reaching a peak value of 94 pm/V in the MPB region and nearly vanishing for  $x = 0.12$ . Due to this behavior,  $k_p$  could not be determined for the last sample. The dielectric permittivity  $\epsilon_r(T)$  of pure BNT showed a more or less well-defined maximum corresponding to  $T_c = 296$  °C. Addition of KNN shifts the maximum to lower temperatures and significantly broadens it, making the determination of its position practically impossible for the samples containing high concentrations of KNN.

The ceramics in the compositional range  $0 \leq x \leq 0.075$  show normal FE behavior at  $T = 25$  °C. The  $P(E)$  loops reveal polarization saturation at  $E = 8$  kV/mm,  $S(E)$  shows the usual butterfly shape. The decrease in  $E_c$  and the increase in maximum unipolar and bipolar strain as well as  $d_{33}$  fit well with the assumption that polarization alignment is easier in the vicinity of the MPB due to the increased number of degrees of freedom of domain orientation. One might also expect a corresponding increase in  $P_r$  or  $P_m$ , but apparently a field of 8 kV/mm is enough to align most domains even in samples far away from the MPB. Near the MPB, the domains align at lower fields, but the total number of domains is not increased, and neither is the total polarization. For  $x > 0.075$ , the  $P(E)$  loops appear to indicate merely partial polarization. At the same time, the total strain increases strongly, although  $d_{33}$  nearly vanishes. We suggest that the polarization in these compositions is not stable and therefore



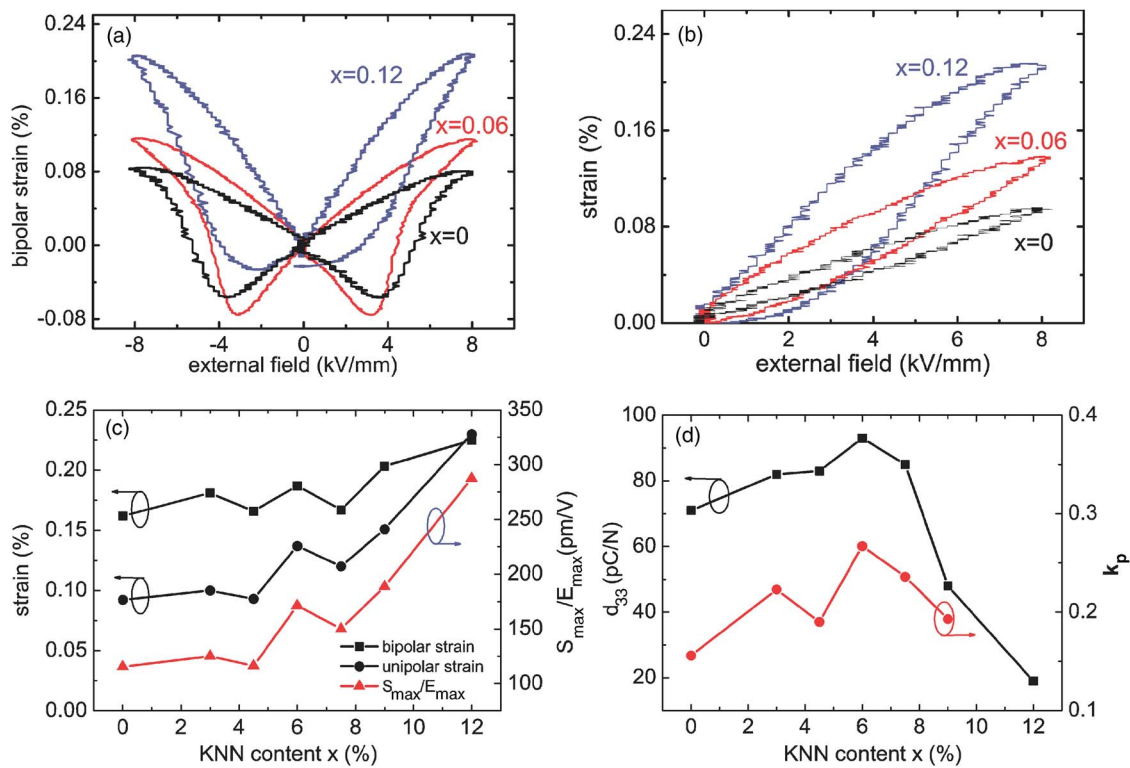


FIG. 2. (Color online) Strain hysteresis  $S(E)$  of  $(1-x)\text{BNT}-x\text{KNN}$  for  $x=0, 0.06$  and  $0.12$  for (a) bipolar and (b) unipolar cycling, (c) composition dependence of strain and (d) piezoelectric coefficient  $d_{33}$ , and planar coupling factor  $k_p$ .

the samples are poled from zero to the maximum value obtainable with each cycle. One way to obtain this polarization reduction is domain backswitching. It is possible that the majority of ferroelectric domains cannot be stably aligned by the external field and resume their original orientation when the field is removed. However, in light of the fact that BNT-based compositions undergo a FE-AFE phase transition at the depolarization temperature  $T_d$ ,<sup>4,7</sup> we suggest that a similar mechanism is at work in the BNT-KNN ceramics with high KNN content. We assume that these samples show a predominantly AFE domain structure at  $E=0$ ; application of a field causes a transition to a FE state, which is generally associated with a large change of strain.<sup>4</sup> When  $E$  is removed, the domains do not only switch back but vanish altogether as the material returns to its previous AFE state. As the small but measurable  $d_{33}$  values indicate traces of FE ordering even at  $E=0$ , this field-induced phase transition is not complete, and ordinary domain backswitching might also play a role, but the largest part of the observed effects can be assumed to be due to the AFE-FE transition. This assumption is supported by the dielectric measurements. The transition temperature  $T_d$  is usually accompanied by a local maximum of  $\epsilon_r$ . This feature is not clearly visible in any of the  $\epsilon_r(T)$  curves, as the broad maxima at higher values of  $x$  make a distinction between  $T_d$  and the temperature  $T_m$  of the transition to the paraelectric phase impossible. However,  $T_d$  of pure BNT is about  $185^\circ\text{C}$ , while for the samples with  $x > 0.075$ , the onset of the anomaly in the  $\epsilon_r(T)$  curve was well below  $150^\circ\text{C}$ . Hence, a reduction in  $T_d$  with increasing KNN content is rationalized, leading to the appearance of AFE ordering even at  $T=25^\circ\text{C}$ .

In summary,  $(1-x)\text{BNT}-x\text{KNN}$  ceramics with  $0 \leq x \leq 0.12$  have been prepared and electrically characterized. An MPB between a rhombohedral phase at low  $x$  and a tetrago-

nal phase at high  $x$  was found between  $x=0.06$  and  $x=0.075$ . Samples in this range exhibit the largest  $d_{33}$  and  $k_p$ . Nonetheless, the total strain at high fields was larger in samples with higher  $x$ ; samples with  $x=0.12$  yield a unipolar strain of  $0.22\%$  at  $E=8\text{kV/mm}$ . Possible sources for this behavior are domain backswitching at  $E=0$  and a field-induced AFE-FE phase transition. Both a high strain level and a relatively good temperature stability in the compositions with a higher  $x$  can make a potential candidate for actuator applications over a wide-temperature working range.

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<sup>1</sup>Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takator, T. Homma, T. Nagaya, and M. Nakamura, *Nature (London)* **432**, 84 (2004).

<sup>2</sup>E. Hollenstein, M. Davis, D. Damjanovic, and N. Setter, *Appl. Phys. Lett.* **87**, 182905 (2005).

<sup>3</sup>S. J. Zhang, R. Xia, T. R. Shrout, Z. G. Zang, and J. F. Wang, *J. Appl. Phys.* **100**, 104108 (2006).

<sup>4</sup>S.-T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg, and J. Rödel, *Appl. Phys. Lett.* **91**, 112906 (2007).

<sup>5</sup>Y. Guo, K. Kakimoto, and H. Ohsato, *Jpn. J. Appl. Phys., Part 1* **43**, 6662 (2004).

<sup>6</sup>C.-H. Choi, C.-W. Ahn, S. Nahm, J.-O. Hong, and J.-S. Lee, *Appl. Phys. Lett.* **90**, 132905 (2007).

<sup>7</sup>T. Takenaka, K. Maruyama, and K. Sakata, *Jpn. J. Appl. Phys., Part 1* **30**, 2236 (1991).

<sup>8</sup>R. Zuo, X. Fang, and C. Ye, *Appl. Phys. Lett.* **90**, 092904 (2007).

<sup>9</sup>L. E. Cross, *Jpn. J. Appl. Phys., Part 1* **34**, 2525 (1995).

<sup>10</sup>IEEE Standard on Piezoelectricity (IEEE, New York, 1988), ANSI/IEEE Std. 176-1987.

<sup>11</sup>S.-T. Zhang, A. B. Kounga, E. Aulbach, W. Jo, T. Granzow, H. Ehrenberg, and J. Rödel, *J. Appl. Phys.* **103**, 034108 (2008).