

Phase Transitional Behavior and Piezoelectric Properties of Lead-Free $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ Ceramics

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$(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ – $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ solid solution ceramics were successfully fabricated, exhibiting a continuous phase transition with changing x at room temperature from orthorhombic, to tetragonal, to cubic, and finally to tetragonal symmetries. A morphotropic phase boundary (MPB) between orthorhombic and tetragonal ferroelectric phases was found at 2–3 mol% $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT), which brings about enhanced piezoelectric and electromechanical properties of piezoelectric constant $d_{33} = 192$ pC/N and planar electromechanical coupling coefficient $k_p = 45\%$. The MPB composition has a Curie temperature of 370–380°C, comparable with that of the widely used PZT materials. These results demonstrate that this system is a promising lead-free piezoelectric candidate material.

I. Introduction

THE Pb-based perovskite ferroelectric ceramics and single crystals have been extensively investigated for piezoelectric applications.^{1–4} These materials contain about 70 wt% lead oxide, which has been believed to be a big threat to our environment. Therefore, an urgent task for scientific society is to search for alternative lead-free piezoelectric compositions with electrical properties comparable to those of commercial $\text{Pb}(\text{ZrTi})\text{O}_3$ (PZT) ceramics. Unfortunately, the best properties from the currently studied lead-free piezoelectric candidates are still not as good as expected. The focus of this field so far is still on looking for new lead-free ferroelectric ceramics with a so-called morphotropic phase boundary (MPB) where it is believed that the materials show superior dielectric, ferroelectric, piezoelectric, and electromechanical properties.^{5–8} Typical material systems currently investigated mostly are $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN)-based MPB ferroelectric compositions with perovskite structures,^{9–22} except for tungsten–bronze-type materials and bismuth-layer-structured materials. BNT, known to be strongly ferroelectric, was widely investigated in the early stage in a solid solution with BaTiO_3 (BT), $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (BKT), NaNbO_3 , BiFeO_3 ,^{9–16} etc. It has a rhombohedral structure with a strong ferroelectricity, a high Curie temperature ($\sim 320^\circ\text{C}$), as well as a relatively large remnant polarization of $38 \mu\text{C}/\text{cm}^2$ at room temperature.^{23–25} In spite of relatively simple processing conditions, its application was limited by some disadvantages such as a low-depolarization temperature (ferroelectric to antiferroelectric transition at

200°C), a relatively high-coercive field (73 kV/cm), and a medium piezoelectric coefficient, although its high-leakage current can be reduced by forming a solid solution with BT. By comparison, NKN was considered to be more promising because of its high Curie point up to about 420°C and adjustable electrical properties, particularly for modified NKN ceramics with Li, Ta, Sb, etc.^{17–21} However, difficulty in sintering, control of microstructure, and optimization of poling conditions have led to some misleading results in this field.^{26,27} Pure NKN ceramics are difficult to be fully densified. Several processing procedures such as sintering aids,^{28–30} high-energy milling,³¹ pressure-assisted sintering,^{32–36} etc., have been attempted to improve its densification. The electrical properties still required to be improved in order to replace such lead-based piezoelectric materials as PZT systems, even if the textured (Li, Ta, Sb)-modified NKN were reported to have piezoelectric properties ($d_{33} \sim 416$ pC/N) comparable to a hard PZT.¹⁷

The question nowadays comes back to why current lead-free compositions are still not as good as PZT from the viewpoint of overall properties. Except for some known reasons such as unique electronic structures of Pb ions contributing to a high coupling effect in PZT,^{37–39} a limited number of lead-free tetragonal ferroelectric phases with higher Curie temperatures might be another cause. BT is well-known to be tetragonal ferroelectric at room temperature and is widely used in a ceramic or single-crystal form.^{40–43} It has a high strain up to 1% under a high electric field; however, it has a large hysteresis, a Curie point of only 130°C , and also a complex phase transition with changing temperature. This makes solid solutions of other materials with BT display extremely complex phase structures.^{44–47} Its low Curie temperature also limits the depolarization temperature of BT-based MPB compositions whose value of application is thus significantly reduced.

BKT was demonstrated to be another tetragonal ferroelectric with a ferroelectric Curie point of 380°C .⁴⁸ It has thus been used to form an MPB piezoelectric composition with rhombohedral BNT, showing enhanced electromechanical properties. However, this material itself is difficult to densify.⁴⁹ Its sintering was significantly improved by adding a small amount of BT.⁵⁰ To our knowledge, it has never been used in NKN-based ceramics probably because it can bring some more potassium in the composition. The difficulty in sintering of NKN-based ceramics was believed to correlate with potassium in the composition. It can evaporate during sintering and is strongly deliquescent during the period of ball milling and weighing.

The intention of this study is to investigate the role of BKT in changing the phase transition and the electrical properties of NKN ceramics. High-energy attrition milling was used to achieve highly dense samples. The phase transition behavior of NKN–BKT ceramics was explored and an MPB was expected near which electrical properties were characterized.

D. Viehland—contributing editor

Manuscript No. 22672. Received January 10, 2007; approved March 22, 2007.

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.”

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II. Experimental Procedure

A series of $(1-x)\text{NKN}-x\text{BKT}$ ceramic compositions were synthesized by a conventional mixed-oxide route. The starting materials used in this study were potassium carbonate (K_2CO_3 , >99.0%), sodium carbonate (Na_2CO_3 , 99.5%), bismuth oxide (Bi_2O_3 , 99.97%), titanium oxide (TiO_2 , 99.9%), and niobium oxide (Nb_2O_5 , 99.9%). Before use, these powders were treated carefully by placing them in a dry box at 120°C for 2 days in order to remove almost all absorbed moisture, and then stored in a moisture-free vessel. After weighing according to the chemical formula, powders were ball milled in a nylon jar with ZrO_2 balls in anhydrous ethanol for 24 h. The dried powder mixtures were calcined in alumina crucibles at 850°C for 5 h. The calcination was repeated three times and after each time, the calcined powder was carefully milled in an agate mortar. Before compaction, powders were attrition milled for 6 h using anhydrous ethanol as the medium in order to improve the sintering activity and then sieved through 230 meshes. A stainless steel die was used to compact the powder into disc specimens under a uniaxial pressure of 50 MPa. No binder was used for compaction.

A platinum foil was used, on which samples were placed, to prevent them from reacting with the bottom alumina substrate because potassium vapor is strongly alkaline and corrosive. Other than that, an alumina crucible was placed on the top of the specimens to minimize the volatilization of potassium during sintering. Inside the crucible, some powder of the same composition as the specimens was placed around them to produce a potassium-rich atmosphere. Sintering was carried out in air in the temperature range of $1020^\circ\text{--}1090^\circ\text{C}$ depending on x . The heating rate was 300°C/h .

The Archimedes method was used to evaluate the density of the specimens sintered at different temperatures. The grain morphology of the samples was observed on natural surfaces by means of scanning electron microscopy (SEM, Philips Electronic Instruments, Mahwah, NJ). The phase structures were examined by a powder X-ray diffractometer (XRD, Rigaku, Tokyo, Japan) using a $\text{CuK}\alpha$ radiation.

Specific attention was paid to handling of the samples for electrical characterization. Careful polishing and grinding steps were taken for each sample to achieve parallel surfaces. The thickness of each sample was reduced to reach an aspect ratio of 0.1 with respect to the diameter. The silver paste was fired on two major sides as electrodes. Dielectric properties were measured as a function of both temperature and frequency by an impedance analyzer (HP4284A). For piezoelectric and electromechanical measurement, samples were first poled at 100°C in stirring silicone oil at 3 kV/mm for 30 min, and were then cooled to room temperature in the electric field. The piezoelectric strain constant d_{33} was measured only 24 h after poling by a quasi-static Belincourt-meter (Model YE2730, SINOCERA, Shanghai, China). The planar electromechanical coupling factor k_p was obtained by a resonance-antiresonance method through an impedance analyzer (HP4192A, Hewlett-Packard Co., Palo Alto, CA) on the basis of IEEE standards.

III. Results and Discussion

The phase structures of $(1-x)\text{NKN}-x\text{BKT}$ ceramics at room temperature are shown in Fig. 1. All compositions show pure perovskite structures. NKN and BKT were known to be orthorhombic and rhombohedral at room temperature, respectively. It can be seen that with increasing BKT content, NKN-BKT ceramics show changing crystalline structures, starting from orthorhombic ($0 \leq x \leq 0.02$), to tetragonal ($0.03 \leq x \leq 0.15$), to cubic (roughly $0.15 < x < 0.98$), and to tetragonal symmetry (roughly $x \geq 0.98$). The complex phase transition behavior of solid solution ceramics with changing BKT content was considered to stem from the respective phase structures of two end members with changing temperature. The MPB NKN ceramics show a complex phase transition sequence of rhombohedral-

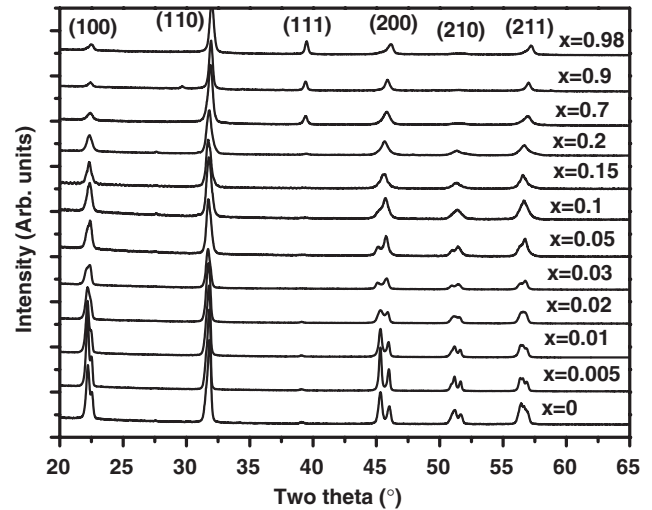


Fig. 1. X-ray diffraction patterns of the $(1-x)\text{NKN}-x\text{BKT}$ ceramics.

orthorhombic-tetragonal-cubic structures with increasing temperature,⁵¹ although BKT is simply tetragonal below its Curie point. The variation in lattice parameters as a function of the BKT content is shown in Fig. 2. A morphotropic phase boundary was pointed out in the plot, which lies close to 2–3 mol% of BKT. Interestingly, on further increasing the BKT content, the tetragonality decreased, rather than like other systems, such as PZT, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, and even NKN-LiNbO_3 where with increasing content of tetragonal phases, the tetragonality increases. When the content of BKT reaches about 10 mol%, it becomes a weak tetragonal perovskite ferroelectric that can be seen from the forthcoming dielectric property measurement as well. The addition of more than 15 mol% BKT transforms NKN ceramics into cubic paraelectrics at room temperature. This structure remains unchanged until it changes to a tetragonal ferroelectric once again when $x > 0.7$. Accordingly, the Curie points of NKN-BKT ceramics also decay with increasing BKT content up to $x = 0.7$. It can be expected that after $x = 0.7$, the tetragonal ferroelectrics show up with increased Curie temperatures up to 380°C (a Curie point of BKT). This part was not extensively focused upon in this study because of the main interest in creating a new MPB of importance to piezoelectric applications. This boundary is highlighted in Fig. 2. The following electrical characterization was also focused on those compositions around MPB.

Figure 3 shows SEM pictures of NKN-BKT sintered at 1080°C for 4 h. All samples reach densities of more than 97%

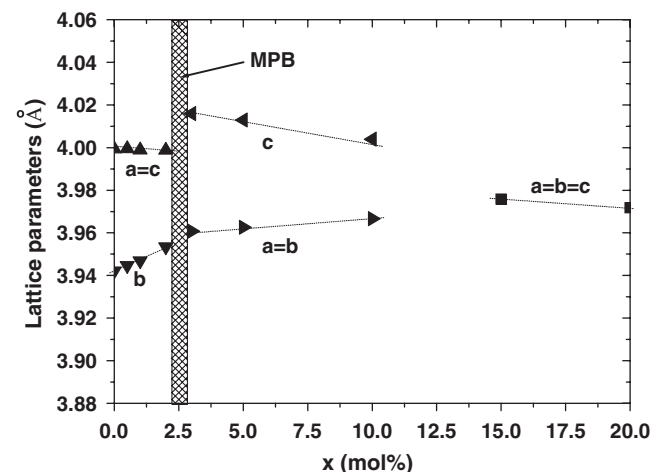


Fig. 2. Lattice parameters of the $(1-x)\text{NKN}-x\text{BKT}$ ceramics as a function of the BKT content x .

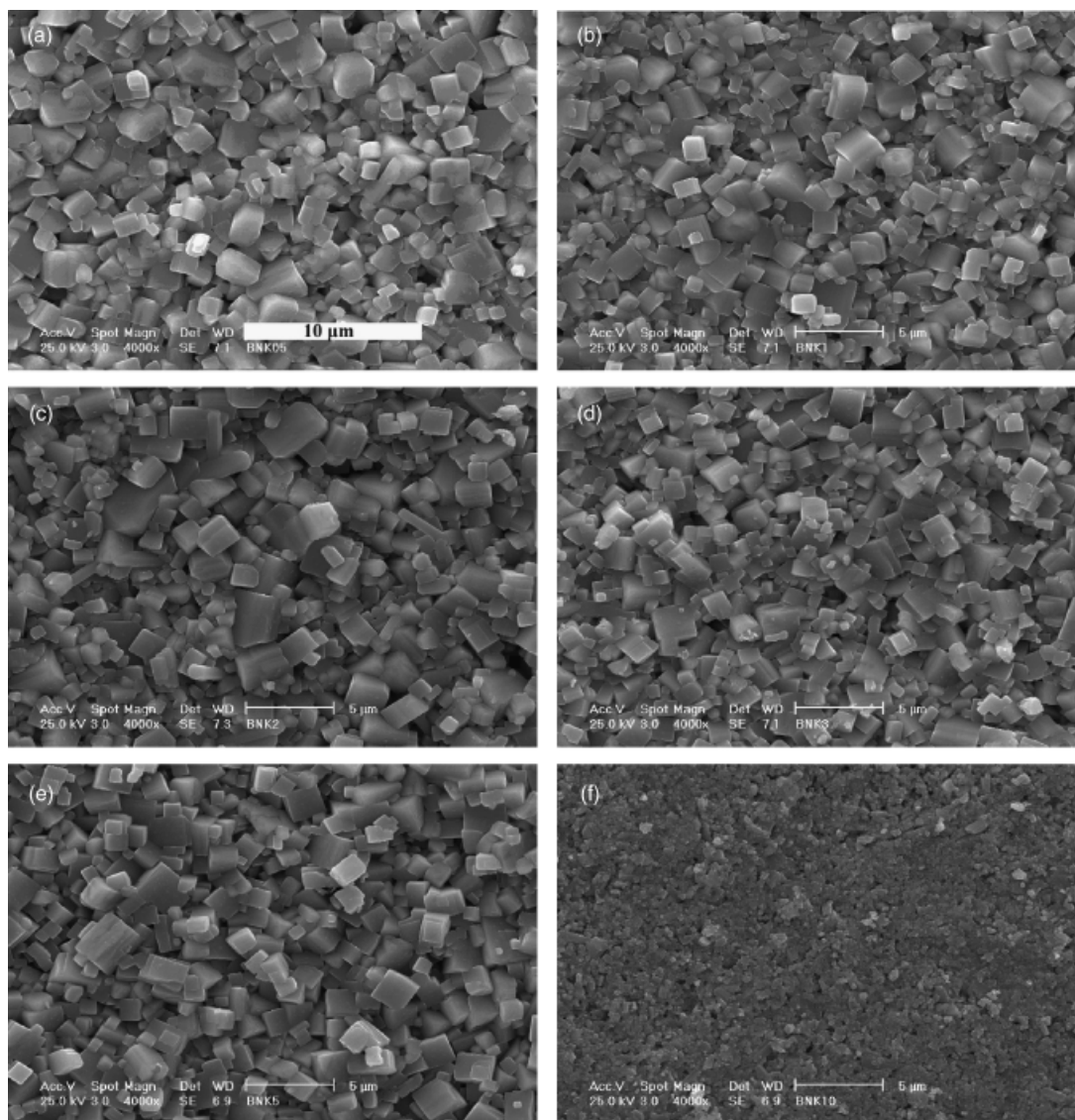


Fig. 3. Morphology on the natural surfaces of $(1-x)\text{NKN}-x\text{BKT}$ ceramics sintered at 1080°C with (a) $x = 0.005$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.05$, and (f) $x = 0.10$. (All pictures have the same scale bars.)

of the theoretical values. The average grain size decreases slightly with increasing BKT content; however, when the concentration of BKT is above 10 mol%, it becomes evidently smaller. The MPB composition has an average grain size of 2–3 μm . Also, too much BKT addition tends to degrade the sintering behavior of NKN ceramics. It was known that BKT ceramic itself has a difficulty in sintering. The low melting point of potassium was believed to be the reason for both BKT and NKN ceramics. In this study, high-energy attrition milling was applied to improve the sintering of the materials, which has proved to be an efficient way to enhance the sintering of pure NKN ceramics.³¹

The dielectric properties of NKN–BKT ceramics sintered at 1080°C are shown in Fig. 4. For pure NKN, there are two phase transition temperatures: one from orthorhombic to tetragonal at $\sim 200^\circ\text{C}$, and another from tetragonal to cubic at 420°C (its Curie point). It can clearly be seen that the addition of BKT shifts both transition temperatures of NKN ceramics to lower ones. At $x = 0.02$ – 0.03 , the second ferroelectric phase transition temperature between room temperature and the Curie point disappeared. The materials became solely tetragonal phases below the Curie point (see the inset of Fig. 4). This borderline is the so-called morphotropic phase boundary, as confirmed from XRD data in Figs. 1 and 2. The loss tangent at 1 MHz at

room temperature is in the range of 2%–9%, as indicated in Fig. 4(b).

The various piezoelectric and electromechanical properties are shown in Fig. 5. Similar to other MPB systems, like PZT, it can be seen that the properties exhibit a strong compositional dependence near the MPB. Poled specimens show peak values of piezoelectric constant $d_{33} = 192$ pC/N, planar electromechanical coupling coefficient $k_p = 45\%$, and room-temperature dielectric constant $K_r = 850$ for the sample with $x = 0.03$. Clearly, the formation of the MPB plays a significant role in the increase of electrical properties of NKN–BKT ceramics, although only 2–3 mol% BKT was added. Compared with ordinary sintered NKN ceramics, NKN–BKT ceramics show enhanced electromechanical properties, even if its sintering still needs to be improved by high-energy milling processing. Our results demonstrate that NKN–BKT ceramics near the MPB are promising piezoelectric materials for lead-free applications.

IV. Conclusions

Highly dense NKN–BKT solid solution ceramics were fabricated by means of high-energy attrition milling. The addition of BKT to NKN causes a continuous phase transition from

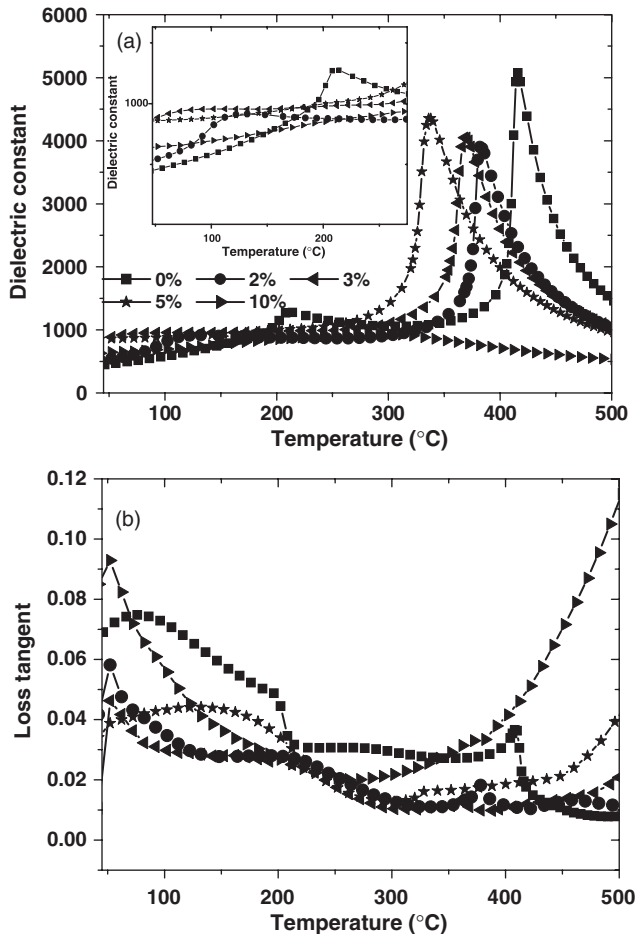


Fig. 4. Temperature dependences of (a) the dielectric constant and (b) loss tangent for the $(1-x)\text{NKN}-x\text{BKT}$ ceramics with different x as indicated.

orthorhombic, to tetragonal, to cubic, and finally to tetragonal symmetries. A morphotropic phase boundary between orthorhombic and tetragonal ferroelectric phases exists near 2–3 mol% BKT. The MPB compositions at $x=0.03$ show enhanced piezoelectric and electromechanical properties of $d_{33}=192\text{pC/N}$, and $k_p=45\%$, with a Curie temperature of $370\text{--}380^\circ\text{C}$ comparable with that of commercial PZT ceramics. These properties indicate that this system might be a promising

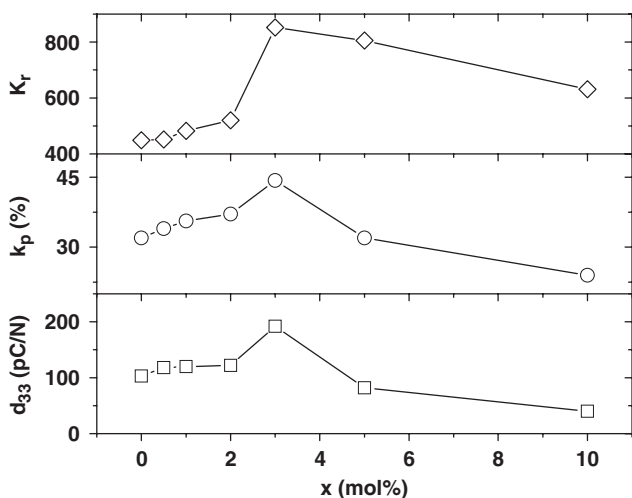


Fig. 5. Various electrical properties of $(1-x)\text{NKN}-x\text{BKT}$ ceramics as a function of the BKT content x .

lead-free piezoelectric material for various kinds of actuators and transducers.

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