



Phase transition and electrical properties of lead free $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--BiAlO}_3$ ceramics

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ABSTRACT

Lead free $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--}x\text{BiAlO}_3$ (NKN–BA) piezoelectric ceramics have been prepared by a solid-state reaction method. The phase transitional behavior and various electrical properties were investigated. A pure perovskite structure can be achieved when the content of BA is less than 5%. A morphotropic phase boundary between orthorhombic and tetragonal ferroelectric phases has been identified in the composition range of $0.005 \leq x \leq 0.01$. The enhanced ferroelectric and piezoelectric properties of a piezoelectric constant d_{33} of 202 pC/N, a planar electromechanical coefficient k_p of 46%, a remanent polarization P_r of 23.6 $\mu\text{C}/\text{cm}^2$ and a Curie temperature of 372 °C appear in the composition with $x=0.01$. These results indicate that the materials studied have potential as a candidate of lead free piezoelectric ceramics.

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1. Introduction

Alkaline niobate-based ferroelectric compositions have been paid much attention owing to their relatively good dielectric, ferroelectric and piezoelectric properties, becoming one of the most promising candidates for replacing traditional lead-based piezoelectric ceramics [1]. All studies on this system originate from a pure $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) composition near a morphotropic phase boundary (MPB) [2], which shows better overall properties compared with other lead free systems [3]. However, its processing difficulties have led to divergences in reported electrical properties. These difficulties are concerned with a narrow sintering window [4], the volatilization of K and Na [5], a poling barrier owing to high loss tangent [6] and the evolution of secondary phases [7], resulting in apparently poor piezoelectric properties of pure NKN ceramics.

Many attempts have been made in recent years toward solving the above-mentioned issues. Except for adopting special sintering techniques, such as pressure assisted sintering methods [8], developing new solid solutions with other phases have been mainly focused. The typical candidate is a solid solution between NKN and phases with a lithium niobate structure such as LiNbO_3 , LiSbO_3 , and LiTaO_3 , showing significantly improved sinterability

and electrical properties [1]. Another approach is through a partial substitution of NKN by other perovskite ferroelectric phases such as $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ [9], $\text{Ba}(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ [10], $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ [11], BiScO_3 [12], BiFeO_3 [13], and so on. The base for achieving intrinsically enhanced properties is on the formation of a MPB between orthorhombic and tetragonal (or rhombohedral) phases. It has been basically believed that more spontaneous polarization states are available owing to a coexistence of two kinds of ferroelectric phases [14].

A novel ferroelectric phase, BiAlO_3 (BA) has recently attained increasing attention due to potentially good electrical properties. Experimental [15–17] and theoretical [18] studies have been carried out on the structural analysis and preparation of BA thin films or bulk ceramics. Its extreme unstability has made it difficultly available under normal conditions. Moreover, its real crystal structure is still vague, being considered to own rhombohedral and $R3c$ symmetry through theoretical calculations [18], but a tetragonal perovskite from experimentally prepared films [17]. However, a high Curie temperature of ~ 530 °C has been confirmed [19].

In this study, this ferroelectric composition was used as a new end member to substitute for NKN. Considering its crystal structure different from that of NKN, a MPB can be expected with changing the content of BA. The phase transitional behavior and various electrical properties of NKN–BA ceramics as a function of the BA content were investigated. A discussion about the possible crystal structure of BA was made by means of the phase transition behavior of NKN–BA solid solutions.

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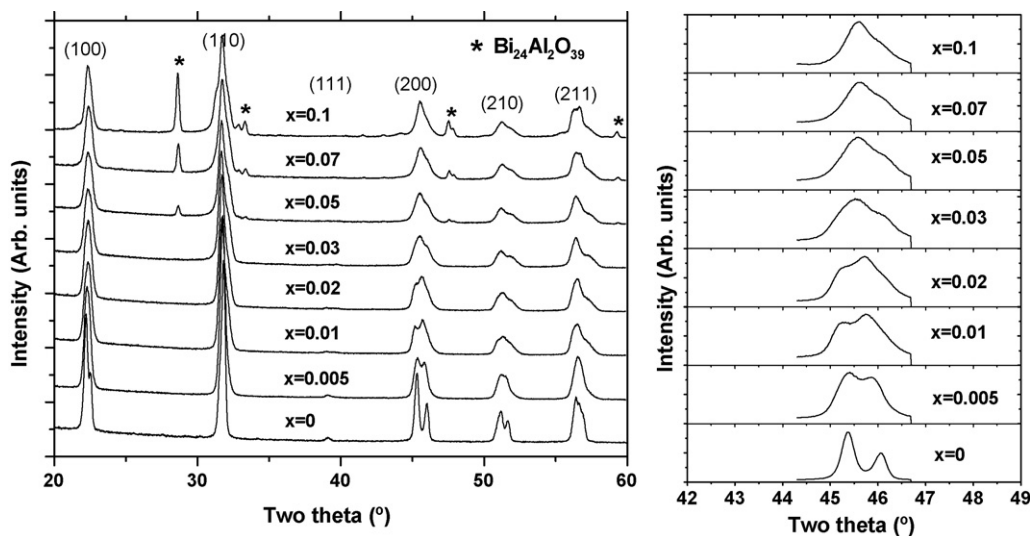


Fig. 1. XRD patterns of $(1-x)\text{NKN}-x\text{BA}$ ceramics; the locally magnified (200) peaks for all samples shown on the right side.

2. Experimental

$(1-x)\text{NKN}-x\text{BA}$ ($0 \leq x \leq 0.1$) powders were prepared from the constituent oxides and carbonates by a conventional solid-state reaction method. Appropriate mixtures of Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Nb_2O_5 (99.5%), Bi_2O_3 (99.5%) and Al_2O_3 (99.5%) were ball mixed in ethanol for 12 h. After mixing, the slurry was dried, crushed and then calcined in a lidded alumina crucible. The mixing and calcination were repeated two times for homogenization. A further milling process of the calcined powders together with 0.5 wt% PVA binder was finished in a nylon jar with ZrO_2 balls for 24 h. These powders were subsequently pressed into disks under a uniaxial pressure of 50 MPa. The powder compacts were sintered for 3 h in air. The microstructure was observed by a scanning electron microscope (SEM, JEOL6301F, Tokyo, Japan). The crystal structure was examined by means of an X-ray diffractometer (XRD, Rigaku, Japan). For electrical measurements, specimens were polished and painted with a silver paste on two major surfaces. The dielectric properties were measured by a LCR meter (HP4284A, Hewlett-Packard, USA) equipped with a programmable temperature box. Electric poling was done by immersing samples into silicone oil and then applying a dc field of 3 kV/mm for 20 min. After 24 h, the piezoelectric constant d_{33} was measured by a quasi-static Berlincourt meter (YE2730, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p was determined by a resonance-antiresonance method with an impedance analyzer (HP4192A, Hewlett-Packard, USA).

3. Results and discussion

Fig. 1 shows the crystal structure of $(1-x)\text{NKN}-x\text{BA}$ ceramics with changing the BA content. As reported, pure NKN ceramics have an orthorhombic perovskite structure at room temperature [3]. Pure perovskite structure for $(1-x)\text{NKN}-x\text{BA}$ ceramics can remain till $x = 0.05$. With further increasing x , a secondary phase was found as marked with stars. This phase can be identified to be $\text{Bi}_{24}\text{Al}_2\text{O}_{39}$ (PDF No. 42-0184). This is probably due to the instability of BA perovskite structure under normal conditions, although BA and NKN have the same ABO_3 perovskite structure. Moreover, the addition of BA induces a MPB between an orthorhombic phase and a weak tetragonal phase in the composition range of $0.005 \leq x \leq 0.01$. The emergence of a tetragonal phase due to the addition of BA implies that BA probably has a tetragonal structure, rather than a rhombohedral structure between room temperature and its Curie temperature. However, the tetragonal phase is very unstable and disappears rapidly with adding more BA. At $x = 0.03$ approximately,

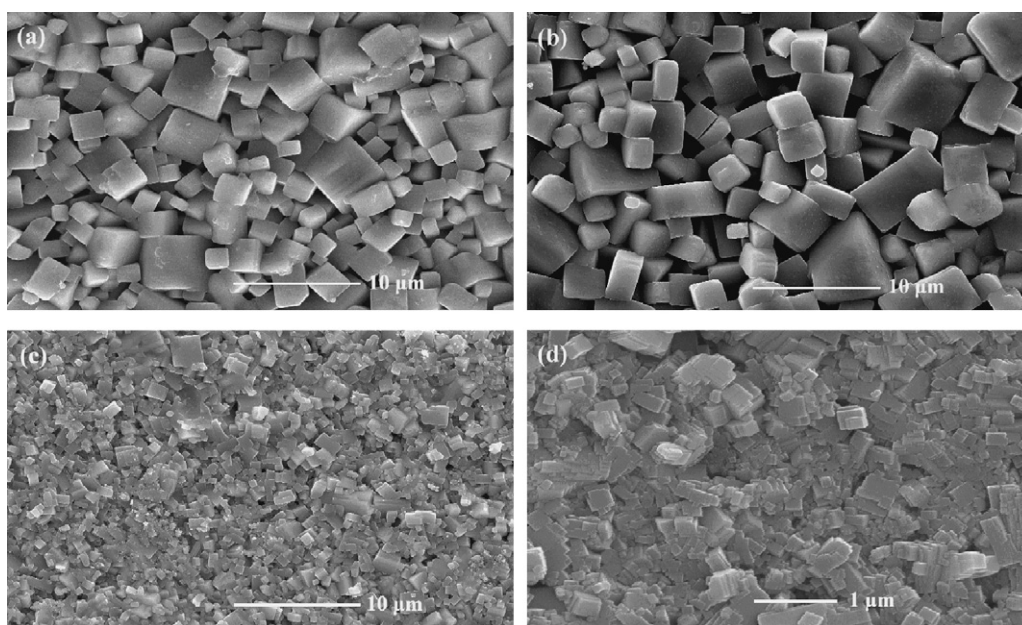


Fig. 2. SEM images on natural surfaces of $(1-x)\text{NKN}-x\text{BA}$ ceramics sintered at 1100°C for 3 h: (a) $x=0$, (b) $x=0.005$, (c) $x=0.01$ and (d) $x=0.02$.

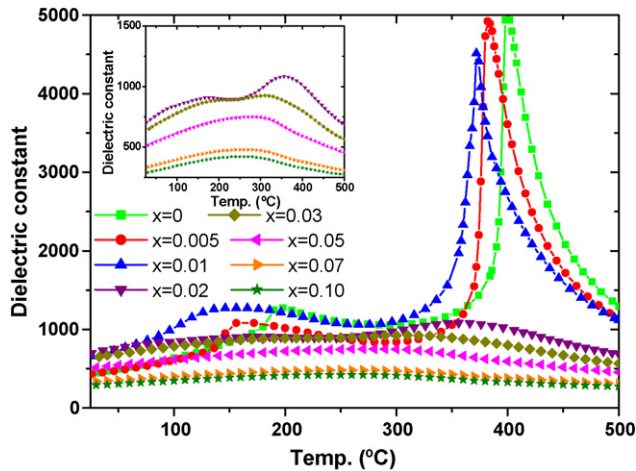


Fig. 3. Dielectric constants at 1 MHz as a function of temperature for $(1-x)\text{NKN}-x\text{BA}$ ceramics as indicated. Inset is the magnified dielectric constant vs. temperature curves only for samples with $x=0.02-0.10$.

it changes to a pseudo-cubic phase. Owing to the formation of a secondary phase, the phase transitional behavior was not investigated in the compositions with larger x . The above-mentioned phase transition within the studied composition range can be more clearly seen from the locally magnified (200) diffraction peaks.

The microstructure of $(1-x)\text{NKN}-x\text{BA}$ ceramics sintered at 1100°C is shown in Fig. 2. All samples have rectangular grains. The average grain size drops down with increasing the BA content. It is $\sim 4\ \mu\text{m}$ for pure NKN ceramics, decreases to $\sim 0.9\ \mu\text{m}$ for the 1% BA substituted NKN ceramics, and becomes even smaller for the 2% BA substituted NKN ceramics. In addition, the sinterability of NKN ceramics has been slightly improved only when the substitution level of BA is rather low, probably because BA in a small amount acts as an impurity. The 2% BA substituted NKN ceramics start to become difficultly densified, as seen from Fig. 2(d). The same phenomenon was found out in other Bi-containing perovskite substituted NKN ceramics [12,13]. This is probably related to the secondary phase appeared in the compositions with higher content of BA.

The dielectric properties of $(1-x)\text{NKN}-x\text{BA}$ ceramics as a function of temperature are shown in Fig. 3. Pure NKN ceramics indicate two phase transition temperatures: the orthorhombic–tetragonal polymorphic phase transition (T_{o-t}) and the tetragonal–cubic fer-

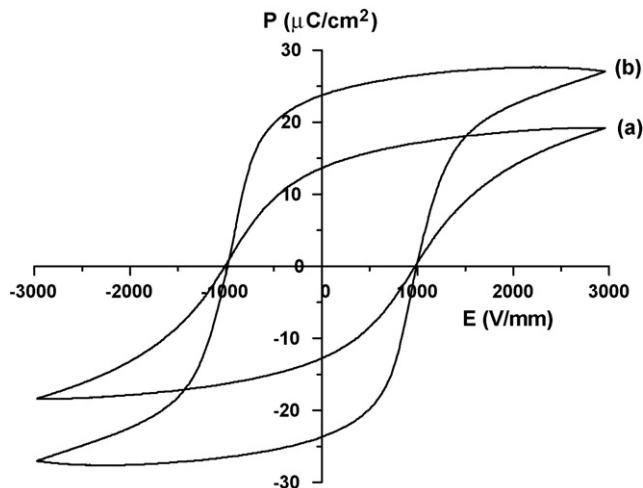


Fig. 4. Hysteresis curves of polarization vs. electric field at 50 MHz for (a) pure NKN ceramics and (b) 1 mol% BA substituted NKN ceramics, sintered at 1100°C for 3 h.

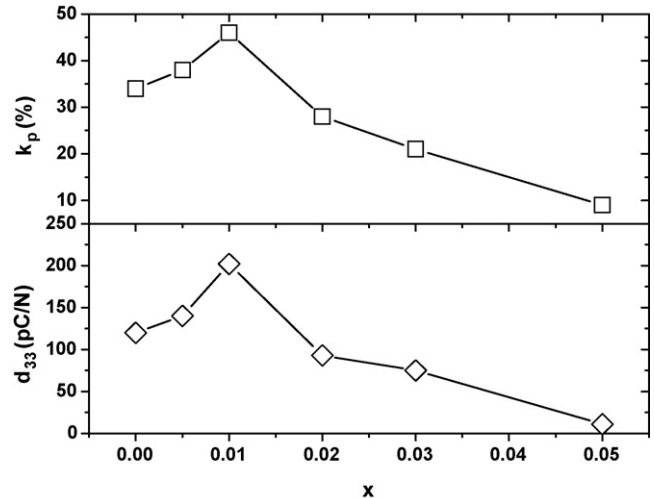


Fig. 5. Compositional dependence of piezoelectric constant d_{33} and electromechanical coupling factor k_p of poled $(1-x)\text{NKN}-x\text{BA}$ ceramics.

roelectric phase transition (T_c). With increasing the content of BA, both T_{o-t} and T_c are shifted to lower temperatures. When $x=0.01$, T_{o-t} is shifted close to room temperature so that only a tetragonal structure can be seen. When $x \geq 0.02$, the dielectric maxima drop down rapidly with further increasing x . Moreover, the dielectric peaks become extremely broad. This is partially ascribed to the fine grain morphology when the substitution level of BA is high. Additionally, the appearance of secondary phases and the formation of pseudo-cubic structures at higher level of substitution may also contribute to the weak dielectric properties. Noticeably, the polymorphic phase transition occurs around room temperature in the composition range of $0.005 \leq x \leq 0.01$ during which a coexistence of two kinds of ferroelectric phases should be expected. The 1-mol% substituted NKN ceramics have a Curie temperature of 372°C .

Fig. 4 compares the ferroelectricity of pure NKN and 1 mol% BA substituted NKN ceramics. It is obvious that the materials show soft properties with a coercive field of merely 1 kV/cm and a moderate remanent polarization P_r . The ferroelectricity is clearly enhanced after 1 mol% BA is added. P_r changes from $\sim 13.5\ \mu\text{C}/\text{cm}^2$ for a pure NKN to $\sim 23.6\ \mu\text{C}/\text{cm}^2$ for a 1-mol% BA substituted NKN. The enhancement of ferroelectricity can be ascribed to the formation of the MPB near $x=0.01$ where more spontaneous polarization states are available.

The piezoelectric and electromechanical properties of poled $(1-x)\text{NKN}-x\text{BA}$ ceramics with compositions near the MPB are shown in Fig. 5. The addition of a small amount of BA greatly enhances the piezoelectric activity of NKN ceramics. The best properties with a d_{33} of 202 pC/N and a k_p of 46% appear in the composition with $x=0.01$. With further increasing or decreasing x , the properties drop down rapidly. It is evident that a strong compositional dependence of piezoelectric properties exists near the MPB. It is evident that the MPB plays a crucial role in the enhancement of piezoelectric properties.

4. Summary

Lead free $(1-x)\text{NKN}-x\text{BA}$ piezoelectric ceramics have been manufactured by ordinary sintering. The results indicate that the addition of BA significantly influences the sintering, microstructure, phase transition and electrical properties of NKN ceramics. The identification of phase transitional behavior confirms the formation of a MPB between orthorhombic and tetragonal ferroelectric phases in the composition range of $0.005 \leq x \leq 0.01$. The enhanced

ferroelectric and piezoelectric properties with a d_{33} of 202 pC/N, a k_p of 46%, a P_r of 23.6 $\mu\text{C}/\text{cm}^2$ and a Curie temperature of 372 °C appear in the composition with $x=0.01$. The results indicate that $(1-x)\text{NKN}-x\text{BA}$ ceramics could be a potential candidate for lead free piezoelectric materials.

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