Dielectric and Piezoelectric Properties of Lead Free $Na_{0.5}K_{0.5}NbO_3$–$BiScO_3$ Ceramics

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A well-known Bi-containing perovskite ferroelectric, $BiScO_3$ (BS), was successfully utilized to develop $Na_{0.5}K_{0.5}NbO_3$ (NKN)-based lead-free piezoelectric ceramics, in which there is a morphotropic phase boundary (MPB) between ferroelectric orthorhombic and rhombohedral phases. The addition of a small amount of BS tends to promote the sinterability of NKN ceramics, and simultaneously, to retard the grain growth, and change the crystalline structures, resulting in a dense $(1 - x)$NKN–xBS solid-solution ceramic upon conventional sintering. Enhanced piezoelectric and electromechanical properties appear near the MPB composition with $x = 0.02$, the piezoelectric constant being $210\,pC/N$ and the planar electromechanical coupling factor being 45%. This material also has a comparable Curie temperature ($340\,°C$) to that of commercial $Pb(Zr,Ti)O_3$ as well. All these results reveal that BS-substituted NKN ceramics may become promising candidates for lead-free piezoelectric materials. [DOI: 10.1143/JJAP.46.6733]

KEYWORDS: lead-free material, piezoelectric, ferroelectric, ceramics

1. Introduction

An increasing amount of attention has been paid to lead-free or lead-content-reduced piezoelectric ceramics in recent years, in consideration of the protection of the environment. Actually, research on lead free dielectric or ferroelectric materials was begun a few decades ago. Unfortunately, the best properties from the currently investigated lead-free ferroelectric materials are still not as good as expected.

Since it was discovered by Smolenskii *et al.* in 1960,[1] $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) has attracted much attention due to its good ferroelectricity. Its piezoelectric and electromechanical properties were greatly enhanced by forming solid solutions[2–4] with, for example, $BaTiO_3$, $Bi_{0.5}K_{0.5}TiO_3$, and $KNbO_3$. These solid solutions exhibit a morphotropic phase boundary (MPB). It is believed that the MPB compositions provide for the possibility of polarization vectors to almost continuously rotate under an external electric field.[5] By comparison, more attention has recently been focused on another system, alkaline niobates ($ANbO_3$, A: Na, K, Li), particularly $Na_{0.5}K_{0.5}NbO_3$ (NKN) with a MPB. A conventionally sintered NKN ceramic may have a piezoelectric constant d_{33} of $\sim 80\,pC/N$ and a planar electromechanical coupling factor k_p of ~ 36–40%,[6] but it is rather difficult to densify by ordinary sintering. Densification was improved through some processing procedures,[7–10] however, changes in the properties were only minor. In recent years, the MPB compositions[11–14] between NKN, $LiTaO_3$, $LiNbO_3$, and $LiSbO_3$ were demonstrated to not only have enhanced sinterability, but greatly improved piezoelectric and electromechanical properties as well. The electrical properties can be further improved by the well-known templated grain growth processing.[12] However, a few problems have arisen concerning these novel materials, such as control of processing, reproducibility and stability of the properties, and fatigue lifetime.

$BiScO_3$ (BS) is a rhombohedral ferroelectric below its Curie point ($\sim 480\,°C$). It has been used to modify the sintering and electrical properties of BNT ceramics.[15] It has a different symmetry from NKN ceramics at room temperature, which allows one to anticipate a new MPB. The intention of the present study is to partially substitute BS into NKN ceramics to improve the processing of NKN ceramics. The influence of the BS addition on the sinterability, structures, and various electrical properties is reported. A MPB between ferroelectric orthorhombic and rhombohedral structures is confirmed, near which the electrical properties are characterized.

2. Experimental Procedure

A conventional mixed oxide route was employed to synthesize $(1 - x)$NKN–xBS ceramics ($x = 0$, 0.005, 0.01, 0.02, 0.03, 0.05, 0.1). High purity metal oxides and carbonates, $[Na_2CO_3$ (99.5%), K_2CO_3 (99.0%), Nb_2O_5 (99.9%), Bi_2O_3 (99.97%), Sc_2O_3 (99.9%)] were used as starting materials. A special drying process was performed before each powder was weighed, particularly for alkaline carbonates which may absorb moisture from the air, causing the deliquescence of carbonates. All powders were put in a dry oven at $120\,°C$ for 2 days and then stored in a moisture-free vessel. The weighed powders were mixed in a planetary ball mill in a nylon jar using anhydrous ethanol as the medium. The dried powder mixtures were calcined in covered alumina crucibles at 820–$900\,°C$ for 4 h depending on the composition. The same milling and calcination processes as described above were repeated three times to ensure the homogeneous distribution of each composition, and to reduce the amount of second phases as much as possible. Subsequently, the calcined powders were ball milled once again for 24 h in anhydrous ethanol. The dried powders sieved through a 230 mesh were compacted into disk specimens in a stainless-steel die under a uniaxial pressure of $\sim 50\,MPa$. The sintering of green specimens was carried out in air on platinum foil in the temperature range of 1000–$1150\,°C$ for 2–4 h at a heating rate of $3\,°C/min$.

An X-ray diffractometer (XRD; Automated D/Max B, Rigatu) was used to identify the crystalline structures of the synthesized powders. The grain morphology of the sintered samples was observed by a scanning electron microscope (SEM; XL 30 FEG, Philips Electronic Instruments). The Archimedes method was utilized to estimate the density of the samples sintered at different temperatures.

For electrical characterization, all samples were carefully polished to obtain parallel scratch-free surfaces. Silver paste
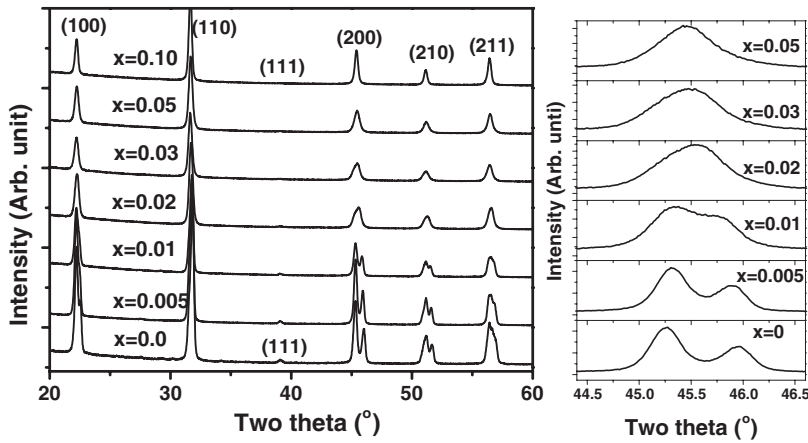
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Fig. 1.   XRD patterns of $(1-x)$NKN–xBS compositions synthesized at 1050 °C for 2 h; the local scans are provided on the right side.

was fired onto the two major sides of each specimen as electrodes. Dielectric constants as a function of temperature were measured using an impedance analyzer (HP 4284). Prior to the measurement of the piezoelectric and electromechanical properties, samples were poled in a silicone oil bath under a dc electric field. Depending on the composition, the poling temperature was varied in the range of 25–130 °C, the poling time was set for 20 min, and the poling electric field was in the range of 1.5–3 kV/mm. The poled samples were aged in air for 24 h at room temperature. The piezoelectric constant d_{33} was then measured using a Berlincourt meter (YE2730, Sinocera, Shanghai). A resonance-antiresonance method was utilized to determine k_p using an impedance analyzer (HP4192) on the basis of IEEE standards.

3.   Results and Discussion

The XRD patterns of $(1-x)$NKN–xBS ceramics synthesized at 1050 °C are shown in Fig. 1. It can be seen that all materials within the studied composition range have pure perovskite structures, yet show a changing symmetry with varying BS content. The solubility limit of BS in the NKN lattice should be more than 10% because no trace of secondary phases is detected. When $x = 0$, the material shows an orthorhombic structure at room temperature, as reported for pure NKN;[6] however, this structure changes rapidly with the addition of BS. The split (200) peaks for an orthorhombic phase are gradually combined into a single peak of a rhombohedral phase. This can also be seen from the local XRD data on the right side of Fig. 1. The transitional point for the structural change can be identified to be near $x = 0.02$. With further increase of the BS content, the structure becomes rhombohedral. Although the peak splitting of such reflections as (111) or (210) peaks typical of a rhombohedral structure is not detectable in Fig. 1, possibly causing a doubt as to whether the structure changes from orthorhombic phases to rhombohedral or cubic phases, an easy way to clarify this point is through the measurement of the dielectric and piezoelectric properties. The variation of lattice constants of $(1-x)$NKN–xBS solid solutions as a function of the BS content is shown in Fig. 2. When $x < 0.02$, the lattice parameters for an orthorhombic structure, a and c, become more similar with increasing amount of added BS; however, when $0.02 < x < 0.10$, the lattice parameters for a rhombohedral structure show a slight
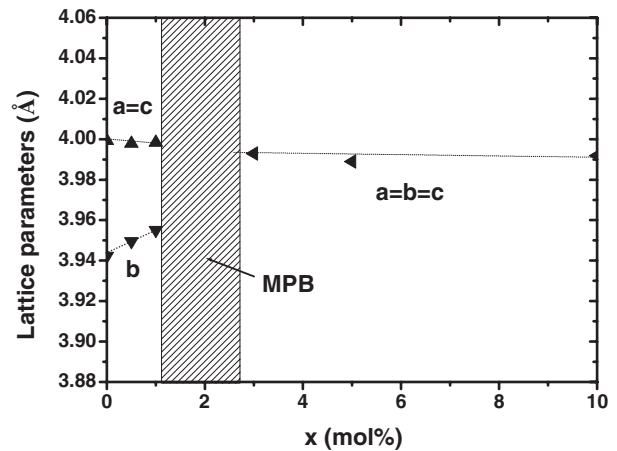

Fig. 2.   Lattice parameters of $(1-x)$NKN–xBS ceramics as a function of BS content x.

change within the studied composition range where BS and NKN can form continuous solid solutions. It is clear that a MPB should exist nearby at $x = 0.02$, as pointed out in the plot. This boundary is of importance because an enhanced piezoelectric activity can be expected there.

Not only is the crystalline structure changed by adding BS, but the densification can be influenced as well. The density of $(1-x)$NKN–xBS ceramics sintered at different temperatures as a function of BS content is shown in Fig. 3. Materials of all compositions show enhanced densification with increasing temperature. To attain the highest density, the optimum sintering temperature seems to be 1100 °C for the compositions with $x \leq 0.01$; however, for other compositions, it is necessary to increase the sintering temperature to 1120 °C. Samples sintered at 1120 °C for 3 h have densities of more than 96% of the theoretical values. This means that the addition of BS slightly affects the sintering of materials with NKN compositions. It seems that only a small amount of BS (0.5 mol % BS) can promote the densification of NKN. At this substitution level, BS may play a role similar to that of a dopant or an impurity. However, $(1-x)$NKN–xBS ceramics must be densified at higher temperatures when x is greater than 0.01. Although the sintering temperatures are not clearly reduced, the BS-substituted NKN ceramics can attain higher densities, probably because the melting points of the solid solutions
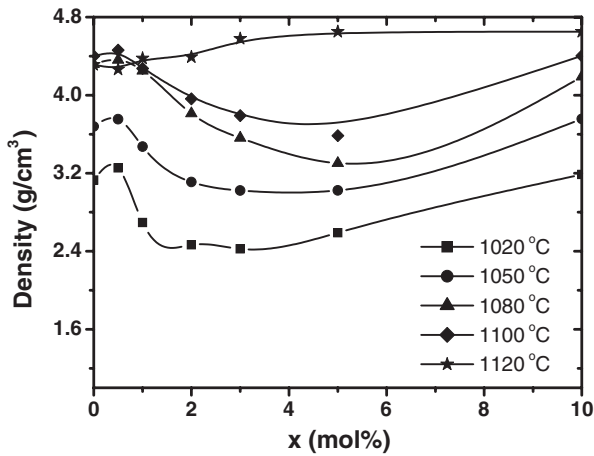
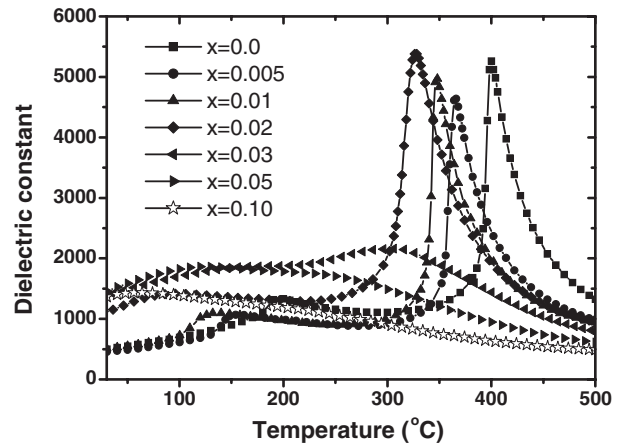Fig. 3. Sintering profiles of $(1 - x)$NKN–xBS ceramics sintered at different temperatures for 3 h.

Fig. 5. Dielectric constants at 100 kHz of $(1 - x)$NKN–xBS ceramics as a function of temperature.
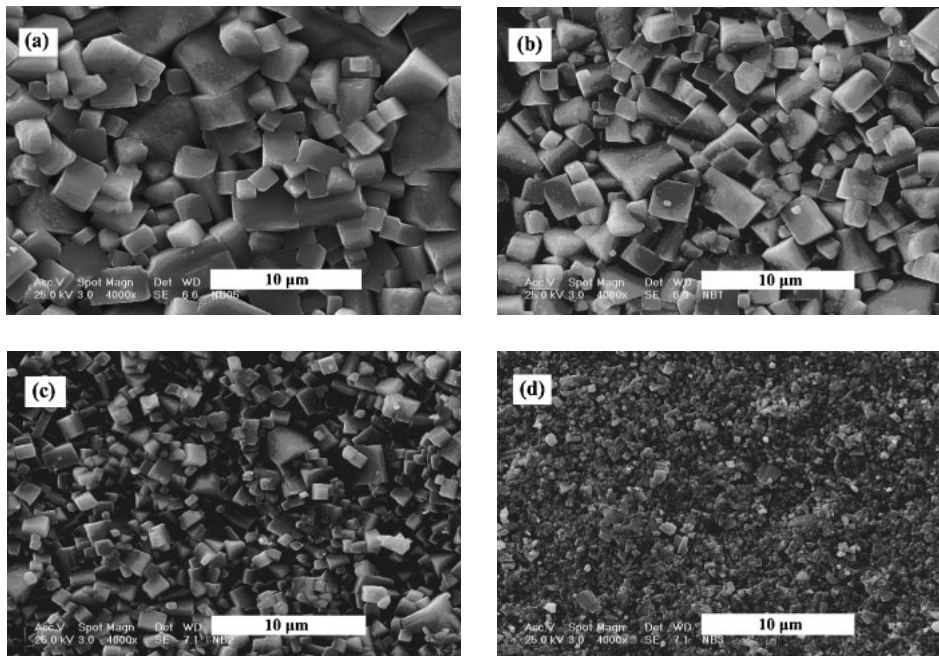

Fig. 4. SEM images of $(1 - x)$NKN–xBS ceramics sintered at 1120 °C for 3 h: (a) $x = 0.005$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.03$.

become higher compared with that of pure NKN. It was recognized that the low melting point of NKN, which is due to the presence of potassium and sodium ions, makes it impossible to improve densification by increasing temperature.

Figure 4 shows the effect of BS addition on the grain morphology of $(1 - x)$NKN–xBS ceramics sintered at 1120 °C for 3 h. It can be seen that the addition of BS significantly reduces the grain size. The 0.5-mol %-BS-substituted NKN ceramics have an average grain size of $\sim$5 µm; however, it drops to $\sim$1 µm for the sample substituted with 2 mol % BS. Although how BS addition influences the grain growth of $(1 - x)$NKN–xBF ceramics during sintering is not yet understood, the inhibition of grain growth is advantageous, because abnormal grain growth quite often occurs in NKN-based ceramics, particularly those doped with Li, Ta, or Sb.

The dielectric constants at 100 kHz of $(1 - x)$NKN–xBS

ceramics as a function of temperature are shown in Fig. 5. Pure NKN exhibits two ferroelectric phase transitions, one from the orthorhombic to the tetragonal phase at $\sim$200 °C and another from the tetragonal to the cubic phase at 420 °C. It is evident that the addition of BS shifts these two phase transitions to lower temperatures. When $x = 0.02$, the orthorhombic to tetragonal phase transition occurs at close to room temperature and the material starts to become rhombohedral above room temperature. When $x = 0.03$, the material becomes a solely rhombohedral structure and has a Curie temperature of $\sim$300 °C. These results confirm that the materials with x greater than 0.02 are rhombohedral ferroelectrics, not cubic paraelectrics. This finding is consistent with the above XRD results. The materials would be in the cubic phase when the Curie temperature moves below room temperature as a result of more BS addition. This further confirms that a MPB exists near $x = 0.02$. Notably, the materials with rhombohedral NKN-BS compositions show
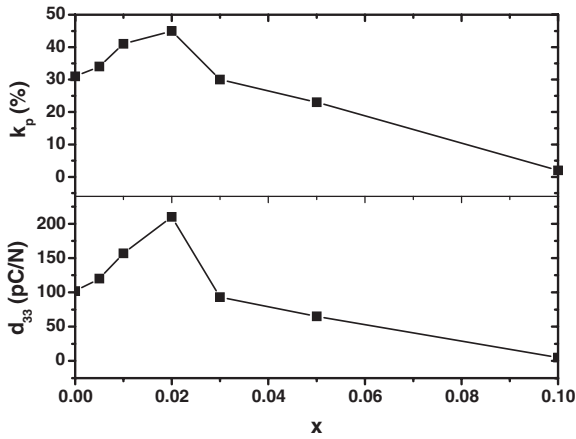
Fig. 6. Piezoelectric and electromechanical properties of $(1-x)$NKN–xBS ceramics as a function of BS content x.

much lower peak dielectric constants at the Curie temperature, than do those with the orthorhombic compositions. Simultaneously, the dielectric-temperature properties become broader with increasing BS content. The origin of such behavior may be closely associated with the more complex occupation of the A and B sites in an ABO_3 perovskite structure. Moreover, the low dielectric maxima and broad phase transitions can also be attributable to the small grain size at these compositions.

Figure 6 shows the piezoelectric and electromechanical properties of $(1-x)$NKN–xBS ceramics. It is evident that the properties exhibit a strong compositional dependence near the MPB. As expected, the best electrical properties of the poled solid solutions exist in the materials with the MPB composition with $x = 0.02$. It has piezoelectric constant $d_{33} = 210$ pC/N and planar electromechanical coupling factor $k_p = 45\%$. The pure NKN ceramic has a d_{33} of 102 pC/N and a k_p of 32%. These two values reach their peaks near the MPB and over this boundary, they decay very rapidly, regardless of the continuing decrease in grain size with further addition of BS. Clearly, the formation of the MPB plays an important role in the enhancement of various piezoelectric and electromechanical properties, similar to other MPB systems, such as Pb(Zr,Ti)O$_3$ (PZT). Although only 2–3 mol % percent of BS is needed to obtain the MPB, a large number of reversible polarization vectors will produce a high piezoelectric activity under an external electric field.

4. Conclusions

New lead free $(1-x)$NKN–xBS solid solution ceramics were manufactured by a conventional sintering technique. A morphotropic phase boundary between ferroelectric orthorhombic and rhombohedral phases exists in materials with the 2-mol %-BS-substituted NKN compositions. In addition, a small amount of BS addition tends to promote densification of NKN ceramics, and the addition of more BS greatly inhibits the grain growth. The materials with the MPB composition with $x = 0.02$ has a piezoelectric constant of 210 pC/N, and a planar electromechanical coupling factor of 45%, and a Curie temperature of 340 °C, which is comparable to those of some commercial PZT ceramics. These results indicate that NKN-BS systems can be promising candidates for lead-free piezoelectric materials.

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