Enhanced Electrical Properties of 3-0 Type Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$-BaTiO$_3$ Composite High-Temperature Piezoelectric Ceramics

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1. Introduction

Piezoelectrics have found a variety of applications in sensors, actuators, transducers and transformers, which are important in a wide range of industrial and scientific fields. For sensor applications, the piezoelectric materials convert the associated mechanical energy into electrical energy. With this direct piezoelectric effect, high temperature piezoelectric vibration sensors are of great significance for structural control and health monitoring in aerospace, nuclear plants and automotive industries.1-4

Aurivillius ferroelectrics with bismuth layered structure (BLSFs) have been of promising candidates for high temperature piezoelectric vibration sensors 1-5 due to their low dielectric permittivity, low aging rates, strong anisotropic electromechanical properties, high mechanical quality factors, high Curie point ($T_c$) and excellent fatigue endurance property. The general formula of BLSFs is (Bi$_2$O$_3$)(A$_{m}$B$_{2}$O$_{3m-1}$), with a structure of pseudo-perovskite block $m$(ABO$_3$)$^{2+}$ stacked alternately with (Bi$_2$O$_3$)$^{2+}$ layers.6-8 However, the piezoelectric activity of these materials is relatively low because of the two-dimensional orientation restriction of the rotation of their spontaneous polarization $P_s$ and their high coercive fields $E_c$ while their electrical resistivity decreased dramatically with elevated temperature,6-10 which limits their applications at higher temperature. Therefore, how to improve the piezoelectric activity and thermal stability of BLSFs is a key issue for their applications at high temperature.

A large amount of attempts using conventional methods based on chemical doping and/or texture techniques such as spark plasma sintering (SPS) and hot-pressing have been explored to improve the piezoelectric activity of BLSFs with enhancing the electrical resistivity and then achieving a compromise of good polarization and high Curie temperature. For example, the piezoelectric constant $d_{33}$ of Na$_{0.5}$Bi$_{2.5}$Nb$_2$O$_9$ (NBN, $m=2$) has been greatly improved from ~8 pC/N to ~22 pC/N and 25 pC/N by appropriate W$^{6+}$ and Li/’Ce$^{3+}$/Nd$^{3+}$ doping,11-12 respectively, together with excellent resistance to the thermal depolarization behavior. On the other hand, the $d_{33}$ of textured CaBi$_2$Nb$_2$O$_9$ ceramics by SPS has been reported to be three times (~20 pC/N)
of that of conventionally sintered ceramics and can be stable up to 800 °C.\textsuperscript{13}

Recently, it has been demonstralted that the formation of piezoelectric composites with suitable oxides is another effective approach to improve the piezoelctric properties as well as resistivity. In 2015, Zhang et al. reported that Bi\textsubscript{0.3}Na\textsubscript{0.7}TiO\textsubscript{3}-based 3-0 type composites showed remarkable piezoelectric properties of depolarization-free behavior by introducing ZnO particles at the grain boundaries,\textsuperscript{14} due to the semiconductor ZnO providing charges to partially compensate the ferroelectric depolarization field. Hussain et al. reported an improvement of \(d_{33}\) over 50% and thermal stability up to 600 °C for 3-0 type CaBi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{12}:BiFeO\textsubscript{3} composites owing to the embedded BiFeO\textsubscript{3} grains could introduce more bounded charge than CaBi\textsubscript{2}Ti\textsubscript{4}O\textsubscript{12}.\textsuperscript{15} Previously, we have managed to design 3-0 type Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3}:Al\textsubscript{2}O\textsubscript{3} composite piezocermics which showed increases in electrical resistivity over two orders of magnitude and \(d_{33}\) about 30%, due to the blocking effect on the electric current paths by the insulating Al\textsubscript{2}O\textsubscript{3} particles at the grain boundaries and higher poling electric field as a result of higher resistivity, respectively.\textsuperscript{16,17} Therefore, piezoelectric composites would be an effective way to tailor the microstructures and electrical properties of BLSFs.

It is well known that BaTiO\textsubscript{3} is a typical perovskite structured and commercially used ferroelectric material with a \(T_c\) value of \(\sim 120\) °C and \(d_{33}\) of \(\sim 180\) pC/N.\textsuperscript{18} The sintering temperature of BaTiO\textsubscript{3} ceramics is normally over 1300 °C which is much higher than that of NBN ceramics (\(<1100\) °C). Therefore, it could be expected that the large \(d_{33}\) of BaTiO\textsubscript{3} and high \(T_c\) of NBN may be inherited by designing a novel 3-0 type Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3}:BaTiO\textsubscript{3} composite piezocermics according to the composite effect. On the other hand, there has no information about the formation of Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3}:BaTiO\textsubscript{3} composite and subsequently the effect of BaTiO\textsubscript{3} addition on the structural and electrical properties of Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3} piezocermics. Therefore, the aim of this work is to explore the structural evolution and the electrical properties of NBN piezocermics by the formation Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3}:BaTiO\textsubscript{3} composite.

2. Experimental

Ceramic samples with compositions of (1-x)Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3}xBaTiO\textsubscript{3} (NBN-BT-100x, \(x = 0.0, 0.05, 0.08, 0.10, 0.12, 0.15\)) were prepared by solid state reaction method. Na\textsubscript{0.5}Bi\textsubscript{1.5}Nb\textsubscript{0.5}O\textsubscript{3} ceramic powdered was obtained by calcining appropriate amounts of raw materials [Bi\textsubscript{2}O\textsubscript{3} (99.99%), Nb\textsubscript{2}O\textsubscript{5} (99.99%) and Na\textsubscript{2}CO\textsubscript{3} (99.80%)] at 800 °C for 2 h. Commercial BaTiO\textsubscript{3} powder with nanometer-scale grains as evidenced in Figure 1 was used as raw material. The mixtures of stoichiometric NBN and BaTiO\textsubscript{3} powders were then milled in ethanol for 24 h. All samples with a dimension of 15 mm in diameter and 1.5 mm in thickness were sintered in air at 1100 °C for 2 h, followed by grinding to a final dimension of 12 mm in diameter and 0.5 mm in thickness for measurements.

The phase structure and natural surfaces of NBN-BT-100x ceramics were characterized by X-ray diffraction (XRD, D/max2550V; Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM; Hitachi, Tokyo, Japan), respectively. The element distribution of the polished and thermal etched NBN-BT-10 ceramics was analyzed by field-mission scanning electron microscope (FESEM, Magellan 400; Tokyo, Japan). Raman spectra were carried out using a Jobin–Yvon LabRAW HR 800 UV micro-Raman spectrometer (the exciting source was the 632.8 nm line from He-Ne laser). Electrodes for electrical measurements were made of fired-on platinum paste. The dielectric properties were measured with a LCR meter (Model E4980A; Keysight, USA). DC electrical resistivity at elevated temperature was measured with a high-resistance measurement system (Model HRMS-901, Partulab, Wuhan, China) over the temperature range from 200 to 725 °C with a heating rate 2 °C/min. Samples for piezoelectric measurement were poled in a silicone oil bath at 180 °C by applying a DC electric field of 13-16 kV/mm for 20 min. The piezoelectric constants \(d_{33}\) were measured using a \(d_{33}\) meter (Model ZJ-3, Institute of Acoustics, Chinese Academy of Sciences). Thermal depoling experiments were conducted by annealing the poled samples for 4h at various high temperatures, cooling to room temperature, re-measuring \(d_{33}\), and repeating the procedure at different temperatures up to over \(T_c\).

3. Results and discussion

The XRD patterns of NBN-BT-100x ceramics are plotted in Figure 2a. The diffraction peaks match the main phase of NBN

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**Figure 1.** XRD pattern of nanometer scale BaTiO\textsubscript{3} powder as raw material. Inset: SEM image of BaTiO\textsubscript{3} nanometer particles.
showing that all compositions belong to the typical Aurivillius phase structure with \( m = 2 \). The strongest diffraction peak is (115), which is consistent with the (112\(n+1\)) highest diffraction peak in BLSFs.\(^{37}\) There are no obviously additional diffraction peaks appearing after the introduction of BaTiO\(_3\) into NBN in this work. Moreover, it’s noted that the (0010) diffraction peaks shift towards to lower 2\(\theta\) angles as shown in Figure 2b. These indicate that BaTiO\(_3\) incorporates into the NBN lattice with A site (Na\(^{+}\), Bi\(^{3+}\)) substitution by Ba\(^{2+}\) and/or B site Nb\(^{5+}\) by Ti\(^{4+}\) according to ionic radius and coordination numbers.

To further investigate the substitutions and its effect on the vibration modes of NBN by the addition of BaTiO\(_3\), the room temperature Raman spectra of NBN-BT ceramics are characterized as shown in Figure 3. All the Raman spectra exhibit the intense phonon modes at about 60, 72, 110, 183, 214, 585, 830 cm\(^{-1}\) and some weak peaks. The features and the general spectral shape of NBN-BT ceramics are similar to some other Aurivillius ceramics with \( m = 2 \) such as Bi\(_3\)TiNbO\(_8\),\(^{20}\) SrBi\(_2\)Nb\(_2\)O\(_9\),\(^{21-22}\) and ABi\(_2\)Nb\(_2\)O\(_9\) (A=Ca, Sr, Ba).\(^{23}\)

According to these reported studies, the low-frequency modes are generally dominated by the motions of heavy Bi ions from the mass consideration of vibrational frequencies. Therefore, the modes below ~200 cm\(^{-1}\) are mainly related with the vibration of Bi\(^{3+}\) ions in the Bi\(_2\)O\(_3\) layers, while the internal modes appearing above 200 cm\(^{-1}\) stem from the vibrations of A site ions and BO\(_6\) octahedra. For NBN ceramics in this study, the peak at about 214 cm\(^{-1}\) can be attributed to the vibrations of A site (Na\(^{+}\), Bi\(^{3+}\)) ions. The peak at about 585 cm\(^{-1}\) can be assigned to the opposing excursions of the external apical oxygen atoms of the octahedral and indicates that the equivalent and opposite displacements of positive and negative ions are slightly changed, and the peak at about 830 cm\(^{-1}\) represents the symmetric stretching mode of the Nb–O–.\(^{20,22}\)

After composite with BaTiO\(_3\), it’s worth noting in Figure 3b that the intensity of the peak at about 214 cm\(^{-1}\) is increasing and the shape is becoming clearer, indicating that Ba\(^{2+}\) enters into the crystal lattice at A site. Meanwhile, the peak of Nb–O vibration mode at about 830 cm\(^{-1}\) shifts gradually to higher frequency, which means that B site Nb\(^{5+}\) is partially substituted by Ti\(^{4+}\). Consequently, the substitutions with Ba\(^{2+}\) and Ti\(^{4+}\) result in the rotation and/or tilting of the oxygen octahedral, leading to the peak at about 585 cm\(^{-1}\) shifting to the lower frequency. These Raman shifts confirm the substitutions at A and B sites in NBN-BT composites as evidenced by the above XRD results. Therefore, we can conclude that NBN and BT have formed a solid solution. In order to take deep insight into the structural evolution of NBN-BT composites during the grain growth and the formation of the solid solution, the morphology of natural sample surfaces are observed by SEM.

Figure 4 shows the SEM micrographs of natural surfaces of NBN-BT ceramics. As it can be seen that the majority grains are typically grey and plate-like shaped for all NBN-BT ceramics, which matches very well with the main phase of NBNO from the XRD analysis. It is interesting to note that the size distribution of plate-like grains are very similar in the cases of \( x \leq 0.08 \) as shown in Figure 4a-c, while an additional type of smaller and darker grains mainly locating at the grain boundaries of NBN can be observed and the aspect ratio of the plate-like grains.

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**Figure 2.** XRD patterns of NBN-BT composite ceramics with \( x = 0.00, 0.05, 0.08, 0.10, 0.12 \) and 0.15: (a) 2\(\theta\) angle of 20-50\(^\circ\) and (b) 2\(\theta\) angle of 25.2-36.8\(^\circ\).

**Figure 3.** Raman spectra of the NBN-BT composite ceramics at room temperature with the Raman shift (a) ranging from 50 to 1000 cm\(^{-1}\) and (b) selected regions for peaks at about 214 cm\(^{-1}\), 535 cm\(^{-1}\) and 830 cm\(^{-1}\).

**Figure 4.** SEM micrographs of natural surfaces of NBN-BT ceramics.
increases with the increasing amount of BaTiO$_3$ addition when $x > 0.08$ as shown in Figure 4d-f. These observations indicate that the solid solution limit of NBN and BT is about 0.08 and BaTiO$_3$ has a great effect on the grain growth during sintering when the amount of BaTiO$_3$ addition is over the solid solution limit. In other words, BaTiO$_3$ is preferable to form solid solution with NBN matrix, resulting in the formation of a secondary phase at the grain boundaries. In order to analyze the compositional distribution in the NBN-BT composites, the element mapping analyses were carried out.

Figure 5 shows the surface image and the element mappings of polished and thermal etched NBN-BT-10 ceramics. From the surface image in Figure 5a, it can be seen that there are mainly plate-like NBN grains and four darker areas of aggregated grains of the secondary phase. The detailed Bi, Nb, Ba and Ti element distributions recorded from the area scanning are provided in Figure 5b-e. We can see that Bi and Nb elements only distribute within the plate-like NBN grains as expected, and Ba element locates in the secondary phase area with a little in the matrix, while Ti element distribution is very uniform. These results further demonstrate that Ti$^{4+}$ ions substitute for Nb$^{5+}$ at B site and Ba$^{2+}$ ions for (Na$^+$, Bi$^{3+}$) at A site to form the NBN-BT solid solution and the secondary phase is mainly BaTiO$_3$ as designed, which are in accordance with the XRD and Raman analysis.

Figure 6 shows the dielectric properties measured at 1 MHz as a function of temperature for the NBN-BT ceramics. As it can be seen that BaTiO$_3$ addition has a great effect on the dielectric constant, loss and $T_c$ values of the NBN ceramics. $T_c$ values decrease almost linearly from 772 to 680 $^\circ$C and the dielectric constant increases with the increasing amount of BaTiO$_3$. For example, the room temperature $\varepsilon_r$ is 210 and 200 when $x$ is 0 and 0.15, respectively, which can be attributed to the substitutions and the composite effect by BaTiO$_3$ addition since BaTiO$_3$ has a much lower $T_c$ of 120 $^\circ$C and larger dielectric constant of several thousand. In previous study of NBN-Al$_2$O$_3$ composite piezocermics, $^{16}$ Al$_2$O$_3$ addition has no effect on the $T_c$ value of all samples (~790 $^\circ$C) because Al$^{3+}$ doesn’t enter into the crystal lattice of NBN, which is the opposite to the case in this work. It also can be seen that the dielectric loss of all NBN-BT ceramics is only below 5% and very stable until the temperature is 550 $^\circ$C. The low dielectric loss and temperature dependence of dielectric behavior of the NBN-BT ceramics suggest they have high stabilities in dielectric properties, which is of great importance for high temperature devices application.

In general, the conduction mechanism of BLSFs is a fabrication process and composition related issue. The former affects the grain orientation, density, pores and voids in the ceramics, which can construct the electric current path and then contribute to the conductivity. The latter is mainly associated with the compositional design by introducing the appropriate dopants, which can influence the types and concentration of charge carriers in the materials. In the case of the NBN-BT composite ceramics in this work, the formation of solid solution with BaTiO$_3$ in the matrix promotes the densification sintering
and then decrease the pores/voids in the bulk, which makes possible electric current paths getting less at the grain boundaries and consequently leads to the higher electrical resistivity. On the other hand, for Ti$^{4+}$ substituting for Nb$^{5+}$ as acceptor at B sites in the NBN-BT composite ceramics, a negative charge center in Nb sites and a hole are generated under charge neutrality restrictions, which will increase the concentration of hole carriers in NBN-BT as NBN piezoceramics is typically $p$-type conduction mechanism.$^{11}$ Therefore, it seems that there are two opposite contributions to the bulk electrical resistivity of NBN-BT composite ceramics.

Figure 7 shows the temperature dependence of $d_e$, electrical resistivity of the NBN-BT ceramics measured in the temperature range of 200 $\sim$ 725°C. It can be seen BaTiO$_3$ addition has significantly affected the electrical resistivity of NBN ceramics. The electrical resistivity increases 1~2 orders of magnitude in NBN after compositing with BaTiO$_3$ below 300°C for all compositions (region I), while decreases 1~2 orders of magnitude at higher temperature when $x > 0.10$ (region II). These observations can be attributed to that the contribution from decreasing electric current paths due to less pore/voids plays a dominant role in the higher electrical resistivity at lower temperature. With the increasing amount of BaTiO$_3$, the effect of Ti$^{4+}$ acceptor doping is getting substantial and more holes are generated, contributing to lowering the electrical resistivity. Thus, these two opposite effects reach a balance at about 300°C and with $x = 0.15$. With more amount of BaTiO$_3$, the doping effect is becoming dominant and results in a lower and lower electrical resistivity as shown in region II. It can also be seen that all the plots have a tendency to merge at high temperature and become more distinct after 600°C as shown in region III. All the samples have almost the same values of electrical resistivity at 700°C. This tendency can be due to that the conduction of NBN-BT is dominated by intrinsic contribution at higher temperature range as demonstrated in W$^{6+}$ donor and Ti$^{4+}$ acceptor doped Bi$_2$TiNbO$_6$ and W$^{6+}$ donor doped NBN piezoceramics.$^{11,23}$

Figure 8 shows the temperature stability and thermal depoling behaviors of the NBN-BT composite ceramics. Pure NBN piezoceramic has a relatively low $d_{33}$ of ~12 pC/N as other members of BLSFs when compared with lead zirconate titanate (PZT, typical $d_{33}$ value of 200~600 pC/N). This is because of the two-dimensional orientation restriction of the rotation of their spontaneous polarization and high coercive fields.$^9$ For the 3-0 type NBN-BT composite ceramics, the $d_{33}$ value is about 50% higher than that of pure NBN ceramics, which can be attributed to the increased piezoactivity from the rotation/tilting of oxygen octahedral as indicated by Raman analysis. As it can also be seen that the $d_{33}$ values of NBN-BT-5 and NBN-BT-10 ceramics show very little variation after thermal annealing until the $T_a$ is over 700°C ($\sim 0.9 T_c$), while that of NBN-BT-10 ceramic shows obvious degradation when $T_a$ higher than 500°C ($\sim 0.74 T_c$). All the $d_{33}$ values decrease rapidly when $T_a$ is close to $T_c$ and tends to zero when $T_a$ is increased above $T_c$. It is suggested that.
non-180° domain walls are thermally unstable well below the $T_c$, and give rise to the degradation of $d_{33}$.\textsuperscript{26}

4. Conclusions

Na$_{0.5}$Bi$_{2}$Nb$_3$O$_9$-based 3-0 type composite piezoelectric ceramics with composition of $(1-x)$Na$_{0.5}$Bi$_{2}$Nb$_3$O$_9$-xBaTiO$_3$ are prepared by solid state reaction method and their structural and electrical properties have been systematically investigated. XRD, SEM and Raman analysis demonstrate that BaTiO$_3$ is preferable to form solid solution with NBN matrix and the solid solution limit of NBN and BT is about $x = 0.08$. When $x > 0.08$, BaTiO$_3$ has a great effect on the grain growth during sintering and a secondary phase appears at the grain boundaries to form NBN-BT composite ceramics. The $d_{33}$ values of the 3-0 type NBN-BT composite ceramics are about 50% higher than that of pure NBN ceramics and with a high $T_c$ over 680 °C, which can be attributed to the substitutions and increased piezoelectricity from the rotation/tilting of oxygen octahedral. The electrical resistivity increases 1-2 orders of magnitude in NBN after composite with BaTiO$_3$ due to the formation of solid solution promoting the densification sintering and then decreasing the pores/voids in the bulk, which makes possible electric current paths getting less at the grain boundaries and consequently leads to higher electrical resistivity. Therefore, a compromise between enhanced electrical resistivity, large $d_{33}$ and high $T_c$, has been achieved by the formation of appropriate composites, which would shed light on how to obtain novel Aurivillius ferroelectrics for practical high-temperature applications.

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Notes and references
