Influence of Ba\textsuperscript{2+} Segregation on Microstructures and Electrical Properties of (Na,Bi)\textsubscript{1-x}Ba\textsubscript{x}TiO\textsubscript{3} Lead-free Piezoceramics Near MPB

Jingchang Zhao and Zhenlai Zhou

ABSTRACT

(Na\textsubscript{0.5}Bi\textsubscript{0.5})\textsubscript{1-x}Ba\textsubscript{x}TiO\textsubscript{3} (x=0.06, 0.07 and 0.10) lead free piezoelectric ceramics were fabricated to study their phase transition, microstructure and electrical properties near morphotropic phase boundaries. The obtained ceramics have the coexistence of tetragonal and rhombohedral phases at morphotropic phase boundaries, which is closely related to Ba\textsuperscript{2+} segregation during sintering. Meanwhile, morphologies and electrical properties of (Na\textsubscript{0.5}Bi\textsubscript{0.5})\textsubscript{1-x}Ba\textsubscript{x}TiO\textsubscript{3} ceramics evidently change with Ba\textsuperscript{2+} content. Samples with high tetragonal phase content exhibited large dielectric constant and low coercive field. An optimized ratio of rhombohedral and tetragonal phases at morphotropic phase boundaries is beneficial to improving the piezoelectric properties of (Na\textsubscript{0.5}Bi\textsubscript{0.5})\textsubscript{1-x}Ba\textsubscript{x}TiO\textsubscript{3} ceramics. Based on the results, the effect of Ba\textsuperscript{2+} segregation on microstructure and electrical properties of (Na\textsubscript{0.5}Bi\textsubscript{0.5})\textsubscript{1-x}Ba\textsubscript{x}TiO\textsubscript{3} ceramics was discussed.

INTRODUCTION

In recent decades, many lead-free or low-lead-content materials, such as (Na,Bi)TiO\textsubscript{3}(NBT), (K,Bi)TiO\textsubscript{3}(KBT), (K,Na)NbO\textsubscript{3}(KNN), (Ba,Ca)(Ti,Zr)O\textsubscript{3}(BCZT), SrBi\textsubscript{2}Nb\textsubscript{2}O\textsubscript{9}(SBN), BiFeO\textsubscript{3} etc. as well as their composite systems [1-8] have been actively studied to substitute the conventional lead-based piezoelectric materials [9-12] for reducing the release of hazardous substance-lead, which caused an increasing environmental pollution.

Among the lead-free piezoelectric materials, NBT is regarded as a promising candidate of lead-free piezoelectric devices due to its excellent piezoelectric properties (the curies temperature $T_c$=320°C, remanent polarization $P_r$=38\textmu C/cm$^2$, and coercive field $E_c$=73kV/cm) [13-18]. Furthermore, this system is intriguing because of its peculiar perovskite structure, NBT has relaxor ferroelectricity with an A-site complex perovskite structure, which shows a diffuse phase transition from

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Jingchang Zhao\textsuperscript{1, a}\textsuperscript{*} and Zhenlai Zhou\textsuperscript{1, b}

\textsuperscript{1}School of Materials Science and Engineering, Yunnan University, Kunming, 650091, P.R. China

\textsuperscript{*}jchzhao@ynu.edu.cn, \textsuperscript{b}zlzhou@ynu.edu.cn
rhombohedral to tetragonal phase between 200–320°C and from tetragonal to cubic phase at 540°C \[119,20\]. However, high volatility of Bi and Na ions during sintering as well as a high coercive field makes pure NBT materials difficult to reach saturation polarization due to their high leakage currents \[21,22\]. A-site or B-site substitutions by some nonvolatizing ions were adopted to improve the compositional stability and electrical properties of NBT-based materials \[23-25\]. In particular, NBT-BT system has received considerable attention because its phase structure gradually transforms from rhombohedral to tetragonal structure with increasing barium titanate content and large piezoelectric properties can be observed at the rhombohedral-tetragonal morphotropic phase boundaries (MPB) \[26-27\], similarly to PZT. Nowadays, numerous studies on NBT-BT still focus on the microstructure and properties of MPB to reveal the origin of electrical properties of NBT-BT systems.

In this paper, \((\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3\) ceramics with the composition near MPB were fabricated by solid state reaction and conventional ceramic technique. The phase structures, morphology and electrical properties were investigated to further understand the relaxor nature of NBT-BT system.

**EXPERIMENTAL**

Stoichiometric powders of reagent grade NaHCO\(_3\), Bi\(_2\)O\(_3\), BaCO\(_3\) and TiO\(_2\) were accurately mixed and wet-milled in propanol for 72h in a plastic jar. After drying and sifting, the mixed powders were calcined at 800°C for 2h to obtain \((\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3\) powders \((x=0.06, 0.07, 0.10)\). Subsequently, the calcined powders were pressed into disks with 8mm diameter and about 1mm thickness at a pressure of 200Mpa, then the green pellets were sintered at 1150°C for 2h in air and cooled at the rate of 5°C/min.

The phase structures of prepared ceramics were examined in the 2θ ranges of 20-80° and 44.5-48° by a Rigaku D/max IIIB X-ray diffraction meter using Cu radiation. The morphologies of ceramic samples were investigated by a Philip XL30 scanning microscope (SEM). After coating with silver electrodes, the dependence of dielectric properties on the temperature was measured by an impedance-frequency meter (HP4284). The measuring temperature range is from room temperature to 500°C and the frequency is at 100Hz, 1kHz, 10kHz, 100kHz and 1MHz, respectively. The polarization-electrical field (P-E) hysteresis loop was measured by a Radiant Precision workstation based on a standard Sawyer–Tower circuit at 50 Hz. After polarizing in a silicon oil bath at 60°C under 50kV/cm for 20 min, the piezoelectric constants \((d_{33})\) were measured using a quasistatic \(d_{33}\) meter based on the Berlincourt method at 200 Hz.

**RESULTS AND DISCUSSION**

Fig.1 gives XRD patterns of \((\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3\) \((x=0.06, 0.07, 0.10)\) ceramic. It can be seen that the obtained ceramics have perovskite structure without any distinct impurities phases in the 2θ ranges of 20-80°. Refined XRD patterns of \((\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3\) ceramics (scanned by 0.005°/step) in the 2θ ranges of 44.5-48° are shown at the right corner of Fig.1. It can be found that only one unsymmetric diffraction peak appears in the scanning region, showing that the phase structure of
(Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ is mainly rhombohedral symmetry at x=0.06. With increasing x value to 0.07, an obvious splitting of the (200) peak into two peaks of (002) and (200) reflections appears in Fig.1, showing that the phase structure of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ changes from rhombohedral to tetragonal symmetry at x=0.06-0.07, which is consistent with the conclusion in previous literatures [26]. Meanwhile, a small shoulder accompanying with (200) peak was also observed at x=0.07, indicating a small amount of rhombohedral phases still coexisted in system. When x>0.07, the small shoulder accompanying with (200) peak disappeared and the phase structure of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics completely transferred to tetragonal symmetry. Meanwhile, the distance of (002) and (200) peaks increases with increasing barium titanate content, showing the expansion of tetragonal lattices and the increase of c/a ratio.

Figure 1. XRD patterns of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ (x=0.06, 0.07, 0.10) in 2$\theta$ ranges of 20-80$^\circ$ and 44.5-48$^\circ$.

SEM micrographs of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ discs sintered at 1150$^\circ$C for 2 hours are shown in Fig.2 (x=0.06(a), 0.07(b), 0.10(c)). It can be seen that the microstructure of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics near MPB is sensitive to the variation of BT content. When x=0.06 and 0.07, it is obvious that the ceramic is composed of two type gains of different sizes. In Fig.2a, most grains are tiny with an average size of 1-3$\mu$m and a small darker area with much larger grains appears in the middle of SEM micrographs. With increasing x value to 0.07, the proportion of larger grains obviously increases in Fig.2b. According to the XRD results in Fig.1, it can be concluded that the small grains are rhombohedral phase and the large grains are tetragonal phase. Furthermore, it also can be found in Fig.2c that the ceramics completely transfer to a uniform phase and the corresponding grain sizes are less than 2$\mu$m when x value increases to 0.10. Above micrographs indicates that (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics have the coexistence of tetragonal and rhombohedral phases at morphotropic phase boundaries and the phase transition of from rhombohedral to tetragonal symmetry mainly occurs at x=0.06-0.07, which is consistent with the results of XRD in Fig.1.
Fig. 2. SEM micrographs of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ discs sintered at 1150°C for 2 hours.

Fig. 3 gives the curves of relative dielectric constant ($\varepsilon_r$)-temperature (T) for unpoled and poled (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ (x=0.06, 0.07 and 0.10) ceramics at the measuring frequency of 0.1, 1.0, 10, 100kHz and 1.0MHz, respectively. It can be observed in Fig. 3a, 3b and 3c that dielectric constant ($\varepsilon_{25}$) at room temperature for unpoled samples gradually increased with increasing x values from 0.06 to 0.07 and then dropped down at x=0.10. The value of $\varepsilon_r$ (1kHz) at room temperature reached the largest value of 1530 at x=0.07. Combining with the results of Fig. 1 and 2, it can assume that the dielectric constant will be significantly affected by the concentration of tetragonal phase and grain sizes in (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ system.
Figure 3. Dielectric constant-Temperature curves of unpoled and poled (Na0.5Bi0.5)1-xBaxTiO3 ceramics at measuring frequencies of 0.1kHz, 1.0kHz, 10kHz, 100kHz and 1.0MHz, respectively.

Meanwhile, it can also be found that the peak below 300°C, corresponding the transforming point from tetragonal to cubic phase (Curie temperature, Tc), moves to lower temperature with increasing x value, showing that the concentration of tetragonal phase becomes higher with increasing barium titanate content. At the same time, the dielectric constant of peak below 300°C becomes higher with increasing x value, showing the dielectric response of (Na0.5Bi0.5)1-xBaxTiO3 ceramics is gradually dominated by the increasing tetragonal phases. As known, the Curie point of barium titanate is about 120°C, lowering than that of pure (Na0.5Bi0.5)TiO3. Therefore, it is expected that the phase transformation of (Na0.5Bi0.5)1-xBaxTiO3 system from ferroelectric to paraelectric will move to lower temperature with increasing BT content.

The temperature dependences of dielectric constant ($\varepsilon_{33}/\varepsilon_0$) at different measuring frequencies for poled (Na0.5Bi0.5)1-xBaxTiO3 ceramics near MPB are shown in Fig.3d (x=0.06), Fig.3e (x=0.07) and Fig.3f (x=0.10), respectively. The dielectric constant ($\varepsilon_{33}/\varepsilon_0$, 1kHz) of all poled samples are lower than that of unpoled states comparing with Fig.3a-3c. An abrupt increase of dielectric constant ($\varepsilon_{33}/\varepsilon_0$) at different measuring frequencies near 100°C can be observed for poled state in fig.3d (x=0.06). However, these $\varepsilon_{33}/\varepsilon_0$ -T curves at the corresponding positions changed to a small bending angle in fig.3e (x=0.07) and then completely disappeared in fig.3f (x=0.10), which is originated from the transition of rhombohedral phase to tetragonal symmetry in (Na0.5Bi0.5)1-xBaxTiO3 coexist system of two phases.
P-E hysteresis loops of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics (x=0.06(a), 0.07(b), 0.10(c)) measured at room temperature are illustrated in Fig.4.

![Figure 4. P–E hysteresis loops of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics.](image)

It can be observed that all samples exhibit well-saturated P–E hysteresis loops, indicating a good ferroelectric properties. When x value changed from 0.06 to 0.07 and 0.10, the coercive field evidently decreased from 38.5kV/cm to about 24kV/cm. Comparing with the results in Fig.1 and 2, it can be found that the coercive field of NBT-BT ceramics decreases with increasing tetragonal phase content. In our experiments, the remnant polarization $P_r$ of samples increased from 27.8$\mu$C/cm$^2$ (x=0.06) to 30.0$\mu$C/cm$^2$ (x=0.07), and then rapidly decreased to 19.5$\mu$C/cm$^2$ (x=0.10). Meanwhile, the corresponding piezoelectric constant ($d_{33}$) reached the maximal value of 151pC/N at x=0.07, showing that an appropriate mixture of rhombohedral and tetragonal phases at MPB can make NBT-BT system have an excellent piezoelectric properties.

As known, a rhombohedral phase has eight possible polarization directions, and a tetragonal phase has six. Therefore, NBT-BT ceramics generally exhibit larger piezoelectric properties closed to the rhombohedral-tetragonal morphotropic phase boundaries, consisting of both phases.$^{[28]}$ Above results confirmed that the dielectric and piezoelectric properties of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics were evidently affected by the distribution of rhombohedral and tetragonal phases. Two phases with different polarization directions mixed at MPB, which formed the domain walls as well as the good isolating grain boundaries. Thus, it is expected that an optimized ratio of both phases at MPB is beneficial to improving the piezoelectric properties of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics.

Furthermore, it was reported in previous literature$^{[21]}$ that sintering of undoped NBT powder at the rather moderate temperature of 1000°C already caused strong thermal decomposition by evaporation of volatile Na and Bi oxide, forming paraelectric pyrochlore-phase Bi$_2$Ti$_2$O$_7$ and a ‘stuffed’ Ti oxide, BiNaTi$_6$O$_{14}$. According to defect chemistry, thermal decomposition increased cationic and oxygen vacancies by the formation of Schottky-like defects, which results in a high leakage current and a rise to ineffective poling. This drawback of NBT-based ceramics makes it difficult to satisfy the application on piezoelectric devices. Through replacing Bi and Na positions by non-volatile cationic ions of similar radius, it is expected to decrease the vacancies in NBT-based ceramics, which is beneficial to reducing the conductivity and to withstanding a higher poling field.
SUMMARY

(Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ lead free piezoelectric ceramics near MPB compositions were fabricated by solid state reaction routes. It was found that the phase structures, morphologies and electrical properties of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics near MPB are sensitive to variation of Ba$^{2+}$ content. The phase structure of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ transforms from rhombohedral to tetragonal symmetry at x=0.06~0.07 and Ba$^{2+}$ segregation forms the coexistence of both phases at morphotropic phase boundaries. With increasing tetragonal phase content, dielectric constant increased and coercive field decreased. It is expected that the piezoelectric properties of (Na$_{0.5}$Bi$_{0.5}$)$_{1-x}$Ba$_x$TiO$_3$ ceramics can be improved by optimizing the ratio of rhombohedral and tetragonal phases at MPB.

ACKNOWLEDGMENTS

This work was supported by Natural Science Foundation of China (No.51562037), Natural Science Foundation of Yunnan Province (No.2007E024M) and Program for Excellent Young Talents of Yunnan University (XT412003).

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