Synthesis of antiferroelectric ($\text{Bi}_{0.534}\text{Na}_{0.5}$) $_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method

LI XiaoJuan^{*}, XI ZengZhe, LONG Wei & FANG PinYang

School of Materials and Chemical Engineering, Xi'an Technological University, Xi'an 710021, China

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Antiferroelectric $0.94(\text{Bi}_{0.534}\text{Na}_{0.5})\text{TiO}_3$ - 0.06BaTiO_3 ceramics were prepared using a solid-state reaction method, involving the addition of excessive amounts of Bi_2O_3 . The resulting ceramics featured a very high phase transition temperature ($T_m \sim 330^\circ\text{C}$), from the antiferroelectric to the paraelectric phase, and a low depolarization temperature ($T_d < 25^\circ\text{C}$). The broad temperature range, within which antiferroelectric properties are retained, of the prepared materials indicates their higher potential over lead-based antiferroelectric ceramics such as PZT-based materials that exhibit a lower $T_m \leq 170^\circ\text{C}$. The lower T_d and higher T_m obtained values, relative to those reported in the literature, are believed to be due to the formation of A-site vacancies originating from the incorporation of excess Bi into the perovskite structure of the studied sample. In addition, the synthesized sample shows a high dielectric constant of ~ 1460 , in a temperature range of 50 – 150°C at 1 kHz , and a high energy storage density of 0.71 J/cm^3 , which is an asset in energy storage capacitor applications.

lead-free ceramics, antiferroelectric, high T_m , dielectric properties, energy-storage

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Antiferroelectric (AFE) materials have wide applications in high-energy storage capacitors [1], large strain actuators [2,3], explosive electrical transducers [4], and pyroelectric detectors [5] because of the electric field-induced phase transition between the ferroelectric (FE) and the AFE phase. To date, lead-based AFE materials including PZ [6], PZT [7], PLZT [8], and PLZST [9] have been extensively studied and applied. However, the restricted use and elimination of toxic lead in these materials is underway in accordance to environmental legislation. Moreover, most PZT-based materials show low AFE-paraelectric (PE) phase transition temperatures, typically $T_m \leq 170^\circ\text{C}$ [10,11]. The low transition temperature limits the use of these materials in high temperature-related applications, thereby directing research to lead-free AFE materials with higher AFE-PE phase transition temperatures.

In the past decades, $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $x\text{BaTiO}_3$ (BNT- $x\text{BT}$) lead-free ceramics have been thoroughly investigated [12–14]. Early studies showed that BNT- $x\text{BT}$ ceramics exhibit a morphotropic phase boundary (MPB) between the FE rhombohedral phase ($R3c$) and the FE tetragonal phase ($p4mm$) at $x \approx 6\text{ mol\%}$. Furthermore, phase transition from FE to AFE, at the MPB, has been reported to occur at a relatively high depolarization temperature $T_d \sim 140^\circ\text{C}$ [14]. Recently, Ma et al. [15] reported that at $x = 0.06$, phase segregation between the FE $R3c$ and relaxor AFE $P4bm$ phases preferentially takes place over phase separation between the FE $R3c$ and FE $P4mm$ phases. Also, transformation from the FE $R3c$ to the relaxor AFE $P4bm$ phase was reported to occur at a lower $T_d \sim 114^\circ\text{C}$ [15]. To further reduce T_d , Zhang et al. [16] studied $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN)-doped BNT-BT ceramics. Although the latter materials displayed AFE character at room temperature, the materials showed a low AFE-PE $T_m \sim 210^\circ\text{C}$. Recently, it was reported

^{*}Corresponding author (email: lixiaojuan28@163.com)

ed that by varying the $\text{Bi}^{3+}:\text{Na}^+$ molar ratio, modulation of the phase transition temperature was possible. For example, by adding excess amounts of Bi_2O_3 , during synthesis, a reduction in T_d from 85 to 65°C and an increase in T_m from 215 to 255°C were achieved in a studied $(\text{Bi}_x\text{Na}_{0.5})_{0.93}\text{Ba}_{0.07}\text{TiO}_3$ ($x = 0.500\text{--}0.510$) system, as reported by Xu et al. [17]. In another study, Guo et al. [18] examined the effect of decreasing the content of Na^+ , relative to the content of Bi^{3+} , in a lead-free $(\text{Bi}_z\text{Na}_y)\text{Ti}_{1-x}\text{O}_{3(1-x)}\text{-xBaTiO}_3$ system. At $x = 0.06$ and $z/y = 1.068$, the ceramics displayed a low $T_d \sim 38^\circ\text{C}$ and a high $T_m \sim 300^\circ\text{C}$.

In the present study, a solid-state reaction process was employed to prepare $0.94(\text{Bi}_{0.534}\text{Na}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics, with a $\text{Bi}^{3+}/\text{Na}^+$ molar ratio of 1.068. These materials were characterized and investigated as potential alternatives to lead-based AFE materials.

1 Experimental

$0.94(\text{Bi}_{0.534}\text{Na}_{0.5})\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ AFE ceramics were prepared using a solid-state reaction method. A mixture of Bi_2O_3 (99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), Na_2CO_3 (99.8%, Sinopharm Chemical Reagent Co., Ltd.), TiO_2 (99%, Kemiou Chemical Reagent Co., Ltd., Tianjin, China), and BaCO_3 (99.8%, Kemiou Chemical Reagent Co., Ltd.) were ball-milled in a polyethylene jar for 6 h using dehydrated ethanol as a medium. The resulting mixture was dried, then calcined in air at 850°C for 2 h. The calcined powders were ball-milled and mixed with a polyvinyl alcohol binder solution, pressed into discs (10 mm in diameter) using cold isostatic pressing, then sintered at 1150°C for 2 h in air.

The crystal structure and microstructure of the prepared sample were evaluated by X-ray diffraction (XRD, Shimadzu 6000) and scanning electron microscopy (SEM, FEI Quanta 400F), respectively. The polarization-electric field (P - E) hysteresis loops were obtained on a standardized ferroelectric test system (TF 2000) at 10 Hz. The dielectric properties were measured using an Agilent E4980A Precision LCR meter in a temperature range of 25–600°C and a frequency range of 1 kHz to 1 MHz. Prior to performing the electric properties measurements, the prepared pellets were polished to a thickness of ~ 1 mm, coated with a silver paste, and then fired as the electrodes at 550°C for 30 min.

2 Results and discussion

Figure 1 shows the XRD pattern of the powders calcined at 850°C for 2 h. The calcined powders feature a perovskite structure (JCPDS No. 36-0340) and a secondary phase at $2\theta \approx 30^\circ$. Figure 1 inset shows a SEM image of a fresh section of the 1150°C sintered ceramics, which feature a dense and void-free structure.

Figure 1 XRD pattern of the powders calcined at 850°C for 2 h. The main reflections correspond to perovskite and the secondary phase is marked by an asterisk. The inset shows a SEM image of a fresh section of the 1150°C sintered ceramics.

The P - E hysteresis loops of the sample measured at varying electric fields, at room temperature, are shown in Figure 2. The observed double hysteresis loops are associated with the onset of an AFE state. The nonzero remanent polarizations, $P_r \sim 2 \mu\text{C}/\text{cm}^2$, suggests the coexistence of the FE and AFE states. FE is a metastable state, which originates from the AFE parent matrix, as reported by Guo et al. [18] and Ma et al. [15]. A corresponding increase in maximum polarization (P_m) from 13 to 23 $\mu\text{C}/\text{cm}^2$ was observed with an increase in the electric field from 60 to 90 kV/cm, as shown in Figure 2. The considerable high observed values for P_m is believed to be due to the electric field-induced AFE to FE phase transformation [8]. During the phase transition, a large amount of electric energy is stored and released. Figure 2 inset shows the energy density-electric field (W - E) profile curve, as generated from the respective P - E hysteresis loops. A steady linear increase in W to 0.71 J/cm³,

Figure 2 P - E curves of the prepared sample measured at varying applied electric fields at room temperature. The inset shows the energy storage density under different applied electric fields.

which is higher than those of AFE BNT-BT-KNN [19] and PZST-based [20] ceramics, with an increase in the applied electric field was obtained.

Figure 3 shows the resulting P - E hysteresis loops measured at varying temperatures of 25, 60, and 120°C under a constant electric field of 50 kV/cm. The P - E hysteresis loops became slim and a decrease in P_r values were noted at increasing temperatures. The reduced P_r values indicated the higher abundance of the AFE state as a result of the relative decrease in the volume fraction of the FE state. At temperatures above 60°C, P_r essentially remained constant at $\sim 0.6 \mu\text{C}/\text{cm}^2$, as seen in Figure 3, suggesting that a threshold temperature of 60°C is sufficient for the formation of a stable AFE state. It should be noted that the current threshold temperature is considerably lower than the reported temperature in the literature that is typically $\sim 110^\circ\text{C}$ [17,19]. At 120°C, a slim double loop curve with a negligible hysteresis property was obtained. In contrast to PZT-based AFE materials, which display square-like hysteresis loops, the herein prepared $0.94(\text{Bi}_{0.534}\text{Na}_{0.5})\text{TiO}_3$ - 0.06BaTiO_3 ceramics featuring “slim” hysteresis loops are better suited for AC-related electric field applications [20].

To further ascertain the phase transition evolution, the temperature dependence of the relative dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of the sample were measured at frequencies of 1, 10, 100 kHz, and 1 MHz from 25 to 600°C, as shown in Figure 4. Two dielectric humps located at room temperature and T_m , respectively, were noted in the ε_r - T curves. T_m corresponds to the temperature at which ε_r exhibits a maximum value. However, the depolarization temperature T_d could not be clearly identified because of the absence of a hump in the dielectric loss tangent [21,22]. A similar phenomenon was reported by Ma et al. [15]. Using transmission electron microscopy techniques, the authors [15] reported the presence of AFE $p4bm$ nanodomains with no distinct T_d characteristics; the materials were coined as “relaxor AFE”. Based on these findings, the presence of relaxor AFE in the herein studied sample is also expected.

Figure 3 P - E curves of the sample measured at varying temperatures of 25, 60, and 120°C under a constant applied electric field of 50 kV/cm.

Only AFE nanodomains are observed at room temperature and the non-detectable T_d feature suggests that the onset of depolarization in our sample occurs below room temperature. The reduced T_d value is indicative of the formation of A-site vacancies. Because Bi^{3+} (added in excess) has an ionic radius of 1.03 Å, it can occupy the A-site of Bi^{3+} (1.30 Å) or Na^+ (1.39 Å), however, it is unlikely to substitute the B-site of Ti^{4+} (0.61 Å) [23]. The occupation of Bi^{3+} in the A-site of Na^+ leads to valence imbalance, thereby resulting in the creation of A-site vacancies [17,24]. According to the theory of dielectric response of relaxor ferroelectrics [25], when the coupling reaction between A-site cation and BO_6 octahedron decreases, the stability of the ferroelectric domain decreases. Thus the generation of A-site vacancies, in the studied sample, is likely to reduce the degree of the FE long-range coupling between the A-site cation and the BO_6 octahedron, thereby inducing the transformation of the FE to the AFE state, producing a lower T_d value [26]. The enhanced AFE state is likely to increase T_m to a higher value.

Strong dielectric relaxor properties (ε_r and $\tan\delta$) are observed at both room temperature and T_m . However, an increasingly weak frequency dispersion, becoming non-existent at increasing temperatures from 150 to 260°C, was also noted (Figure 4). The dielectric behavior at low temperatures may be due to the dynamic fluctuation of the nanodomains. As reported by Tan et al. [27], the displacements of A-site cations (Bi^{3+} , Na^+ , and Ba^{2+}) are antiparallel to those of B-site cations (Ti^{4+}) within each individual nanodomain. Thus, incomplete cancellation of the dipole moments will generate a net polarization effect. The dynamic fluctuation of the weakly polar nanodomains leads to the relaxor behavior. At temperatures above T_m , the frequency dispersion contributes to the space charge effect. As the polar time of space charge is longer, the dielectric constant is primarily influenced by the frequency: a decline in ε_r is observed as the frequency increases (Figure 4). Conversely, a rapid increase in $\tan\delta$ with increasing temperatures at low frequencies was obtained. At a constant frequency of 1 kHz, ε_r remains constant at ~ 1460 in the

Figure 4 Temperature and frequency dependence of the dielectric constant and loss of the sample.

temperature range of 50–150°C (Figure 4). The observed value is twice as high as that featured in FE BNT-based ceramics [28]. Materials exhibiting high dielectric constants are highly advantageous in energy-storage applications.

Both FE and relaxor AFE materials obey the Curie-Weiss law above the Curie temperature. Figure 5(a) shows the temperature dependence of $1/\varepsilon_r$ for the sample at 10 kHz, where T_{CW} denotes the onset temperature that the dielectric constant follows the Curie-Weiss law. The discrepancy between the observed T_{CW} (~490°C) and T_m (~330°C) values indicates the diffuse phase transition behavior.

The modified Curie-Weiss law was also applied to further study the degree of the diffuse phase transition:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C},$$

where C is the Curie constant, ε_m is the maximum value of dielectric constant, and the value of the dispersion factor γ ($1 \leq \gamma \leq 2$) is a measure of the degree of dielectric relaxor. The produced linearized plot, Figure 5(b), indicates the positive agreement of the dielectric constant with the modified Curie-Weiss law above the Curie temperature. The γ value (1.64), as deduced from the slope of the curve, is a measure of the degree of the dielectric relaxor property of the sample.

3 Conclusion

Antiferroelectric 0.94(Bi_{0.534}Na_{0.5})TiO₃-0.06BaTiO₃ ceramics, with a high T_m ~330°C and low T_d < 25°C, were prepared

Figure 5 (a) Relaxor properties of the sample measured as a function of temperature at 10 kHz and (b) the corresponding linearized plot.

using a solid-state reaction process. The low T_d and high T_m values were attributed to the formation of A-site vacancies upon addition of excess quantities of Bi₂O₃ during the synthesis. The generation of the A-site vacancies reduced the FE long-range interaction and increased the AFE short-range interaction. The dielectric relaxor properties at low temperatures were likely because of the dynamic fluctuations of weakly polar nanodomains. In addition, at 1 kHz, the ceramics displayed high ε_r (~1460) in the temperature range of 50–150°C and a positive linear response between W and the external electric field. W rose to a value of 0.71 J/cm³ when the external electric field was increased to 90 kV/cm. The current findings demonstrate the potential of AFE 0.94(Bi_{0.534}Na_{0.5})TiO₃-0.06BaTiO₃ ceramics as possible substitutes to PZT-based ceramics for electric field-related applications.

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