The dielectric and ferroelectric properties of $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ lead-free ceramics

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This work prepares $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ (BST)-doped $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (NBT) lead free ceramics through conventional solid reaction method and analyzes the doping effect of BST on phases, microstructure, dielectric and ferroelectric properties. The phase and structure of the NBT-BST ceramics were investigated through X-ray diffractometer (XRD) and Raman. The XRD results showed that BST has diffused into the NBT lattices to form a stable solid solution; while, Raman spectrum showed the bands at low frequency are different with that of pure NBT and divided into two ranges around 247 cm^{-1} and 303 cm^{-1} . Relative dense and homogeneous ceramic microstructures could be achieved, with the observation of a slight decrease in average grain size with the increase of BST doping content. The dielectric and ferroelectric properties were also investigated. The dielectric constant increases gradually with increasing the temperature to T_m , and then decrease. The temperature dependence property showed diffused phase transition near T_m . The polarization-electric field (P - E) hysteresis loops of BST-doped NBT ceramics showed typical ferroelectric or relaxor nature. Both the E_c and P_r increased first, then decreased with respect to the increase of the BST content.

Keywords: Lead-free; BST-doped; ferroelectric; dielectric.

1. Introduction

$\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)-based ferroelectric materials have been widely utilized in many fields like actuators, transducers, and so on for over 60 years because of their high piezoelectric and dielectric properties.^{1–6} However, in the past two or three decades, due to the health and environmental concerns, a variety of Pb-free perovskite ferroelectric materials have attracted a lot of positive attention.^{7–10} Among them, $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (NBT),^{11–16} BaTiO_3 (BT),^{17–22} and $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)^{23–26}-based systems therefore have been widely investigated, especially focusing on the compositions near morphotropic phase boundary (MPB) or polymorphic phase transition (PPT) in order to achieve superior dielectric and piezoelectric properties.^{2,3} For example, although NBT exhibits high piezoelectric properties and fascinating phase transition behavior, its low depolarization temperature, high ionic conductivity and huge coercive field (E_c) limit its application. Therefore, BT or SrTiO_3 (ST) has been adopted into NBT to form solid solutions, which usually exhibit a MPB and relaxor behaviors.^{27,28} However, the ternary systems formed by co-doping BT and ST into NBT are very rare in the literature and many systems are still unexplored. Moreover, Ba^{2+} and Sr^{2+} usually enter the

A-site of the ABO_3 perovskite, leading to a diffused phase transitions.^{29–31} How these two cations act within the NBT system remains unknown. Therefore, to understand the new ternary systems is of great interest from the view point of fundamental research and applications.

In the current paper, the ternary systems were fabricated by doping $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) into NBT through the conventional solid reaction method. A systematic investigation on the phase, microstructures, dielectric and ferroelectric properties of the system was conducted. The analysis of the results was also discussed in detail.

2. Experimental Procedure

Ceramic samples with a nominal formula as $\text{NBT-}x\text{BST}$ ($x = 0.25, 0.30, 0.35$, and 0.40) were prepared by a conventional solid state process using the standard mixed oxide route. High purity oxide powders of Bi_2O_3 (99%), Na_2CO_3 (99.8%), TiO_2 (99%), BaCO_3 (99.9%), and SrCO_3 (99.9%) (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) powders were used as raw materials. The starting powders were mixed according to the above nominal formulas and ball-milled for 24 h. Then, these compositions were calcined

at 850°C for 4 h. After ball-milling and sieving, the dried powders with 5 wt.% PVA were pressed into pellets, which were then debinded at 500°C in air, and heated up to 1150°C for 2 h.

Phase analyses were performed by an X-ray diffractometer (XRD, 6100, Shimadzu, Japan) with monochromatic Cu K α radiation. Lattice parameters were also extracted from the XRD data, and then were used to calculate theoretical density. The densities of studied samples were measured using Archimedes' method and the relative densities were calculated by using the measured density divided by the theoretical density. The microstructures of the fractured surfaces were observed by scanning electron microscope (JSM 6610, Jeol, Tokyo, Japan). The Raman spectra was recorded using Bruker instrument. For electrical properties characterization, silver paste was added onto both side of the pellets and sintered at 700°C for 10 min to form electrodes. The temperature-dependent dielectric properties at 1 kHz, 10 kHz and 100 kHz, were measured from room temperature to 450°C by a LCR meter (E4980AL, Keysight, USA) with a heating rate of 2°C/min. Polarization-electric field (*P-E*) hysteresis loops were measured based on a Sawyer–Tower circuit (TF analyzer 2000E, aixACCT, Aachen, Germany) at a frequency of 1 Hz.

3. Results and Discussion

Figure 1 shows the XRD spectrum of the sintered NBT-*x*BST ceramics measured at room temperature. All the prepared ceramics exhibit a single perovskite structure without any detectable secondary phase, indicating that BST has diffused into the NBT lattices to form a stable solid solution. Furthermore, with increasing the BST content, the intensities of peaks changed very little, indicating that the ratio of phase varied little.

The Raman spectra of BST-doped NBT ceramics at room temperature are shown in Fig. 2, which are similar to the previous published results of NBT.^{31,32} All the observed

Fig. 2. The Raman spectra of BST-doped NBT ceramics at room temperature.

Raman bands are broad and similar to each other but with different intensities. These features are related with A-site distortion, and also with the overlapping of Raman modes. According to the published literature about NBT,^{33,34} the Raman spectra normally exhibit several ranges which display scattering phenomenon roughly at 138 cm⁻¹, 272 cm⁻¹, 530 cm⁻¹ and 585 cm⁻¹. The difference between the pure NBT and BST-doped NBT in current study can be seen from the bands at low frequency, which is mainly attributed to the Na–O bonds in pure NBT. Because of the doping with Ba and Sr, the band at this range are divided into two ranges roughly located at 247 cm⁻¹ and 303 cm⁻¹, respectively, as shown in Fig. 2. Meanwhile, the bands at higher frequency are highly likely associated with the vibrations of TiO₆ octahedra and do not show much difference compared with that of pure NBT according to the reported literature.

Figure 3 shows the measured densities and relative densities of the sintered bulk ceramics as a function of BST doping content. Both of the curves show a very similar trend that all decreased with increasing the BST content. That is because the theoretical density of NBT is 5.976 g/cm³, while that of BST is 5.627 g/cm³. Therefore, the measured densities decreased as the BST content increased. The relative densities

Fig. 1. Room temperature XRD patterns for NBT-BST ceramic samples measured from 20° to 70° with a scanning step of 0.02°.

Fig. 3. Variation of the density as a function of the BST content for the NBT-BST ceramic samples.

Fig. 4. SEM micrographs of the fractured surface morphologies of the NBT-BST ceramic samples with different BST contents: (a) 0.25 mol, (b) 0.30 mol, (c) 0.35 mol, (d) 0.40 mol.

of all studied bulk ceramics are above 94%, indicating relatively dense structures, which can also be seen from the SEM images.

Figure 4 shows the SEM images of the bulk ceramics. Figure 4(a) is the fracture surface of pure BNT ceramic, while Figs. 4(a) to 4(e) are the fracture surfaces of the BNT ceramics doped with different amounts of BST. All the grain boundaries are clear and the pores in grain boundaries are few. These characters suggest that all the prepared bulk

ceramics show relatively dense microstructures, which are in good agreement with the observation of the relative densities. Moreover, with the increase of BST content from 0.25 mol to 0.40 mol, the ratio of small grains become larger, indicating that more BST can lead to more small grains.

Figure 5 shows the temperature-dependent dielectric permittivity and loss tangent of the BST-doped BNT samples measured at different frequencies from room temperature to 450°C. For each composition, the permittivity curves show

Fig. 5. Dielectric permittivity and loss tangent as a function of temperature for the NBT-BST ceramic samples measured at 100 Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz from room temperature to 450°C with a heating rate of 2°C/min.

Fig. 5. (Continued)

very similar trend. It is evident from the permittivity curves that the dielectric constant increases gradually with increasing the temperature to T_m (the transition temperature from a tetragonal to cubic phase^{35–37} where the dielectric peak also occurs), and then decrease. They also show diffused phase transition near T_m , which is well known as one of the

characteristic feature of relaxor ferroelectrics. Moreover, the composition-dependent T_m moves to lower temperature gradually as the BST content is increased; the dielectric maximum also becomes smaller with respect to the increase of the BST content, simultaneously. According to the published data, T_m of pure NBT is around 310°C,³⁸ while that of

Fig. 6. Room temperature P - E hysteresis loops for NBT-BST ceramic samples with different BST contents measured at 1 Hz. (a) 0.25 mol, (b) 0.30 mol, (c) 0.35 mol, (d) 0.40 mol.

pure BST is around -40°C .³⁹ The introduction of BST especially Sr^{2+} makes T_m move towards lower temperature.

Figure 6 shows the P - E hysteresis loops of BST-doped NBT ceramics. Relatively square loops can be observed within these compositions, indicating a typical ferroelectric nature of these ceramics.^{40,41} It is clear that both the E_c and remnant polarization (P_r) show a same variation trend with respect to the BST content. The E_c and P_r all increased first, then decreased with respect to the increase of the BST content. When the doping content of BST increased to 0.3 mol, E_c and P_r reached the maximum values, as shown in Fig 6(b). It is well known that a larger remnant polarization (P_r) can lead to better piezoelectricity, and a lower coercive field (E_c) can make polarization easier.⁴² Therefore, with increasing the BST content, the piezoelectricity can be enhanced with the doping level less than 0.2 mol; while, the polarization of these BST-doped NBT ceramics become better with further increase of BST content. That is because the pure NBT has high ionic conductivity.

4. Conclusion

In summary, the BST-doped NBT lead-free ceramics were prepared by conventional solid state reaction method. With increasing the BST content, the intensities of the XRD peaks changed very little, and BST has diffused into the NBT lattices to form a stable solid solution; while, the measured densities and relative densities of the sintered bulk ceramics all decreased with increasing the BST content. Because of the doping with Ba and Sr, the Raman spectra of BST-doped NBT ceramics show difference compared with that of pure NBT. The bands at low frequency, are divided into two ranges roughly located at 247 cm^{-1} and 303 cm^{-1} , respectively. The SEM images show that the grain boundaries are clear and the pores in grain boundaries are few, suggesting relatively dense microstructures. The composition-dependent T_m moves to lower temperature gradually as the BST content is increased; the dielectric maximum also becomes smaller with respect to the increase of the BST content, simultaneously. The P - E hysteresis loops of BST-doped NBT ceramics indicate ferroelectric or relaxor ferroelectric nature of these ceramics.

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