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Research Article

Structure and electrical properties of ternary $BiFeO_3$-$BaTiO_3$-$PbTiO_3$ high-temperature piezoceramics

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Abstract: In the current work, the bulk ternary (0.85-x) $BiFeO_3$-$x$$BaTiO_3-0.15PbTiO_3$ (BF-BTx-PT, x=0.08-0.35) system has been studied as a potential high-temperature piezoceramics. Samples with various content of BT were prepared via solid-state route, and pure perovskite phase was confirmed by X-ray diffraction. The temperature dependence of dielectric constants confirmed the decrease of Curie temperature with increasing BT content. It was found that the morphotropic phase boundary (MPB) composition of BF-BTx-PT ceramics was in the vicinity of x=0.15, which exhibits optimal properties with piezoelectric constant d_{33} of 60 pC/N, high Curie temperature of 550 ℃, and low sintering temperature of 920 ℃. Measurements also showed that the depoling temperature was 300 ℃, about 150 ℃ higher than that of commercialized PZT ceramics, which indicated good temperature stability. BF-BTx-PT ceramics are promising candidates for high temperature applications.

Key words: ceramics; piezoelectric materials; barium titanate; perovskite; ferroelectrics

1 Introduction

Many piezoelectric devices require piezoelectric ceramics with Curie temperatures higher than that of the most widely used lead zirconate titanate (PZT) in high temperature environment [1]. The recently-covered $BiMeO_3$-PT family of MPB containing materials has allowed the development of such solid solutions [2-12]. Among these systems, the $BiFeO_3$-$PbTiO_3$ (BF-PT) solid solution system is peculiar for its high Curie temperature (~700 ℃) and large tetragonality (c/a=1.16-1.18) at the morphotropic phase boundary (MPB) composition and thus promising for high temperature piezoelectric applications [12]. However, the applied field required to reorient domains is very high which results in the high dielectric loss (3.5% for 0.7BF-0.3PT at 1 MHz measured at room temperature) and high leakage current, and this makes it difficult to achieve good piezoelectric properties and well-saturated ferroelectric hysteresis loops [13-15]. The same difficulty also occurs in $BiFeO_3$-$BaTiO_3$ (BF-BT) solid solution system. Recently, Mn-doped $BiFeO_3$-$BaTiO_3$ (BF-BT) solid solution system was studied, and a small amount

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of Mn doping can greatly improve the resistivity of resultant ceramics [16-18]. Eitel et al reported that the optimal Mn-doped BF-BT solid solution system sintered in oxygen atmosphere exhibited excellent piezoelectric properties (d_{33}=116 pC/N) with high Curie temperature (T_c＞450 ℃) for 25 mol% $BaTiO_3$ content [16,17].

Here, the ternary (0.85-x)$BiFeO_3$-$x$$BaTiO_3-0.15PbTiO_3$ (BF-BTx-PT, x=0.08-0.35) solid-solution piezoceramics were chosen and prepared by conventional solid-state synthesis. It is possible for BF-BTx-PT system to obtain a MPB range and to own high Curie temperature (T_c) with excellent electrical properties suitable for high temperature application.

2 Experimental

Specimens with the compositions of (0.85-x)$BiFeO_3$-$x$$BaTiO_3-0.15PbTiO_3$ (BF-BTx-PT, x=0.08-0.35) were prepared by conventional solid-state synthesis. The reagent-grade materials of Bi_2O_3 (⩾99.5, Sinopharm Chemical Reagent Co., Ltd. or SCRC), Fe_2O_3(>99.5%, SCRC), PbO(yellow, >99.0%, SCRC), TiO_2 (>99.0%, SCRC), and $BaCO_3$ (>99.0%, SCRC) powders were weighed as starting powders according to the nominal compositions. The powders were re-mixed, calcined, ground, dried and then mixed with polyvinyl alcohol (PVA) binder. The powders were pressed into disks 12 mm in diameter and 1.2 mm in thickness at 200 MPa. Following binder burnout at 650 ℃, samples were sintered at 800-1100 ℃ (800-960 ℃ for $x \leqslant 0.15$ and 960-1100 ℃ for $x > 0.15$) for 2 h.

Density measurement was performed using the Archimedes method. Phase structures were measured by a Philips vertical X-ray diffractometer (PW3050/60, MPSS) using Cu Kα1 radiation. Sintered pellets were ground to the thickness of 0.5 mm, electroded with Ag-conductive paste, and fired at 800 ℃ for 40 min for electrical property characterization. The samples were poled under a field of 3-6 kV/mm for 15 min at 100 ℃. Temperature frequency dependence of dielectric properties of the ceramic samples was measured using an Agilent E4980A Precision LCR Meter from room temperature to 650 ℃. The piezoelectric constant d_{33} of the poled specimens were measured one day after poling using a quasi-static piezoelectric d_{33} meter (Model ZJ-3D, China). The thermal depoling experiments were performed by holding the poled specimens with Ag electrode for 30 min at various temperatures, then cooling to room temperature, measuring their piezoelectric constant d_{33}, and repeating the procedure up to the temperature above their Curie point.

3 Results and discussion

It is well known that BF-PT and BF-BT can form solid solution in the MPB region, respectively [12,19-22]. The MPB compositions were identified as the enhancement of piezoelectric properties due to the high polarizabilities resulting from the coexistence of tetragonal and rhombohedral phases. $BiFeO_3$-$PbTiO_3$ (BF-PT) has been reported to be a continuous solid solution across its entire composition range, with a rhombohedral-tetragonal morphotropic phase boundary (MPB) at 0.7-0.8 mol $BiFeO_3$ [19,20]. Similarly, it was reported that the $BiFeO_3$-$BaTiO_3$ system has three structural phase transitions at room temperature over the entire compositional range. Above 70 mol% of BF, the structure is in the rhombohedral and below 4 mol%, it is tetragonal [21]. The crystal structure changes from tetragonal to cubic phase at room temperature when 8 mol% of $BiFeO_3$ was added into $BaTiO_3$ for $x$$BiFeO_3$-(1-$x$)$BaTiO_3$ [22]. It can be predicted that there is a MPB region in the BF-BT-PT ternary system. The boundary of the tetragonal and cubic phase was not presented clearly enough yet. Figure 1 shows the compositional ternary diagram of BF-BT-PT in and around estimated MPB regions and the hatched part was the predicted MPB compositions in the BF-BT-PT ternary compounds.

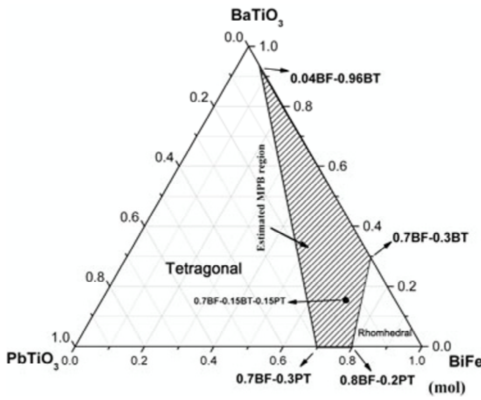

Fig. 1 Compositional ternary diagram of BF-BT-PT indicating compositions synthesized in this study. The estimated MPB region was marked by the shaded areas.

XRD of BF-BT*x*-PT-sintered pellets indicated high-purity perovskite structure without traces of secondary phases (Fig. 2) in the studied compositions. The lower symmetry phases, being either rhombohedral or tetragonal, are identified by splitting of perovskite peaks {hkl}, either {111} splitting for rhombohedral, or {110} and {100} splitting for tetragonal symmetry [23]. It is found from Fig. 2 that the crystalline symmetry of BF-BT*x*-PT shifts from rhombohedral to tetragonal with increasing *x* by the splitting of (002)/(200) peaks near 45°, indicating the existence of a MPB range near *x*=0.15. This result is in agreement with the result reported in $BiScO_3$-$PbTiO_3$ system [23,24].

Figure 3 shows the relative density of the ceramics of the BF-BT*x*-PT compositions near MPB with sintering temperatures. It can be seen that the addition of BF can effectively decrease the densified temperature of BF-BT*x*-PT compositions. Furthermore, high sintering temperature can deteriorate the density for high BF compositions. The optimal sintering temperature for *x*=0.15 near MPB is 920 ℃.

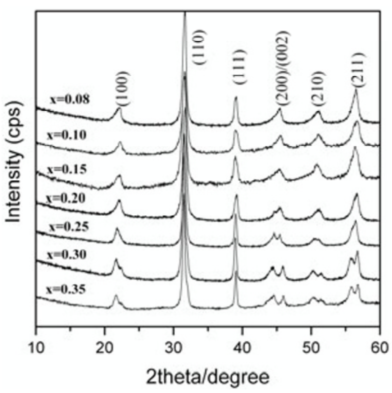

Fig. 2 XRD patterns of BF-BT*x*-PT ceramics for *x*=0.08-0.35.

Figure 4 shows the typical piezoelectric constant d_{33} of BF-BT*x*-PT ceramics poled under 3 kV/mm and saturated poling fields for the composition $x > 0.15$, respectively. The composition *x*=0.15 exhibited the highest d_{33} value (60 pC/N) under the same poling field (3 kV/mm). However, the compositions ($x > 0.15$) show higher piezoelectric properties when poled till to saturation (4-6 kV/mm) than that poled under 3 kV/mm. It is possible that more dipole orientations occurred under high poling fields (4-6 kV/mm) than that under low fields (3 kV/mm). Theoretically, the composition (*x*=0.15) near MPB owns more dipole orientations than that of far from MPB due to the mixed crystallite phases when poled till to saturation. However, the increase of BF content can result in the difficulty of poling due to the enhancement of leakage current and large tetragonality. The applied field required to reorient domains is very high. Therefore, the compositions of $x \leqslant 0.15$ with high BF content cannot be poled completely. To achieve high electrical fields across samples, materials have had to be doped reducing the possibility of electrical breakdown for $BiFeO_3$-based system [16-18,25].

The Curie temperature is an important factor for piezoelectric ceramics used in high working temperature. Figure 5 shows the variation of Curie temperatures with compositions in the BF-BT*x*-PT system. From Fig. 5, it is evident that the Curie temperature increases obviously with increasing BF content. All the studied compositions exhibit high

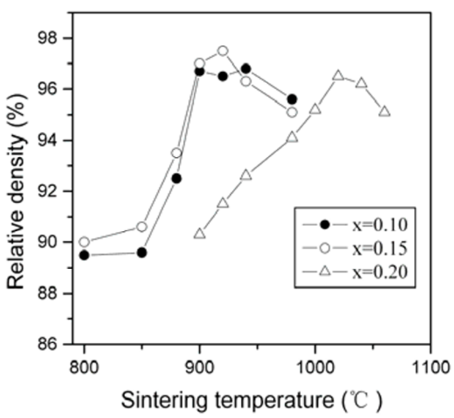

Fig. 3 Relative density of the ceramics with sintering temperatures of the BF-BT*x*-PT compositions near MPB.

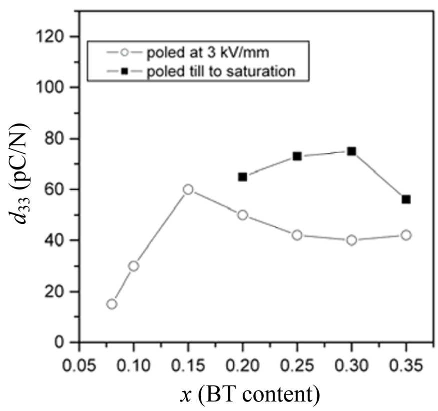

Fig. 4 Typical piezoelectric constant d_{33} of BF-BT*x*-PT ceramics poled under 3 kV/mm and saturated poling fields.

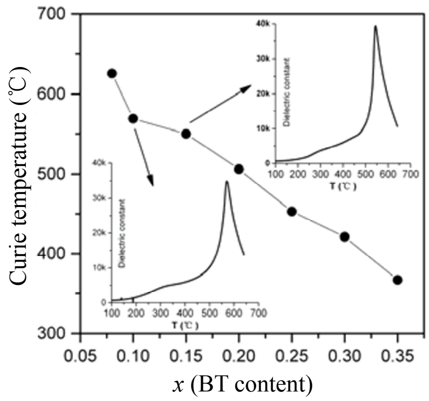

Fig. 5 The variation of Curie temperatures with compositions in the BF-BTx-PT system. The inset graphs are the dielectric temperature spectra of compositions x=0.10 and 0.15 measured at 1 kHz.

Curie temperatures compared to PZT system. The composition near MPB exhibited high Curie temperature of 550 ℃ for x=0.15 and 569 ℃ for x=0.10, respectively.

Thermal depoling temperature of ferroelectrics determines the usage range of their application in piezoelectric devices. It is well-known that there is a polymorphic phase transition for KNN-based lead-free piezoelectric ceramics which limits the applications at elevated temperature due to thermal instability at high temperatures [26]. The effect of thermal depoling on d_{33} values of poled BF-BTx-PT (x=0.15, 0.20, and 0.30) ceramics for different thermal treatments measured *ex situ* is shown in Fig. 6. As the temperature increases, d_{33} for the studied compositions remains almost constant and then drops dramatically above a critical temperature due to thermal depoling. This critical temperature can be defined as depolarization

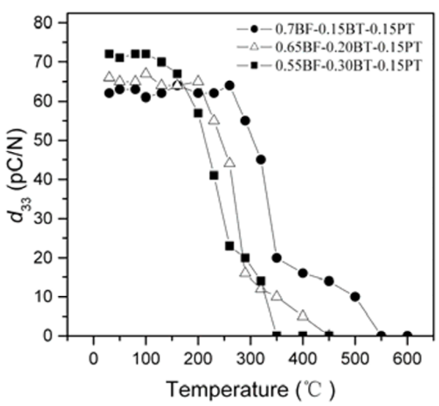

Fig. 6 Effect of thermal depoling on d_{33} values of poled BF-BTx-PT (x=0.15, 0.20, and 0.30) ceramics for different thermal treatments measured *ex situ*.

temperature (T_d). As shown in Fig. 6, d_{33} decreases at the temperature above the depolarization temperature T_d but not zero till to the Curie temperature. This remnant piezoelectric constant d_{33} can be ascribed to the asymmetry of crystal structure for the composition till to the symmetric cubic structure above Curie temperature. Also, T_d depends on BT content by the variation of the thermal depoling temperature. Based upon these results, the BF-BTx-PT (x=0.15) system shows potentialities as a new type of piezoelectric material used near 300 ℃, about 150 ℃ higher than that of commercialized PZT ceramics.

4 Conclusions

In conclusion, the structure and electrical properties of ternary $BiFeO_3$-$BaTiO_3$-$PbTiO_3$ high-temperature piezoceramics were investigated, focusing on the electrical properties of the compositions near MPB.

(1) The MPB region showing the coexistence of rhombohedral and tetragonal phases is confirmed near x=0.15.

(2) The composition 0.7$BiFeO_3$-0.15$BaTiO_3$-0.15$PbTiO_3$ exhibits a T_C=550 ℃, enhanced piezoelectric constant d_{33}=60 pC/N, and low sintering temperature (920 ℃), respectively.

(3) Thermal depoling measurement indicates that the BF-BTx-PT (x=0.15) composition can be used at the temperature near 300 ℃ as a new high temperature piezoelectric system.

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