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Enhanced piezoelectric properties of $Bi(Mg_{1/2}Ti_{1/2})O_3$ modified $BiFeO_3$–$BaTiO_3$ ceramics near the morphotropic phase boundary

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ABSTRACT

$(0.7\text{-}x)BiFeO_3$–$0.3BaTiO_3$–$xBi(Mg_{1/2}Ti_{1/2})O_3$ system was designed to obtain morphotropic phase boundary (MPB) between rhombohedral (*R*) phase and pseudocubic (*PC*) one to enhance the piezoelectric property. Their phase structures were investigated by the X-ray diffraction, temperature dependence of dielectric constant ε_r and Raman spectrum, which revealed that the phase transition exists from *R*–*PC* two-phase coexistence at $0.00 \le x \le 0.04$ to *PC*-phase at $0.06 \le x \le 0.08$ at room temperature. Due to coexisting *R*–*PC* two phases near MPB region and the improvement of polarization property, high $d_{33} = 154$ pC/N, $k_p = 28.5\%$ and $P_r = 16.2$ μm/cm^2 were achieved as $x = 0.04$. This research revealed the potential of $BiFeO_3$–$BaTiO_3$–$Bi(Mg_{1/2}Ti_{1/2})O_3$ system as promising lead-free piezoelectric ceramics with relatively high Curie temperature $T_C = 482$ °C.

1. Introduction

Lead-based piezoelectric materials such as $Pb(Zr,Ti)O_3$ (PZT) are widely used in electromechanical applications because of their excellent piezoelectric characteristics [1–3]. Apart from serious environmental problems in preparing and using PZT-based ceramics due to toxic Pb, the applications of commercial soft PZT are limited in high temperature sensors field, such as deep oil exploration, geothermal drilling and electric aircraft because their piezoelectric properties become unstable when the working temperature exceeds 200 °C [4–6]. The operation temperature for most piezoelectric ceramics is limited generally to one half of T_C because of thermal depolarization and increased conductivity at high temperatures [4]. Therefore, seeking an environment friendly piezoelectric ceramics with high T_C and d_{33} have received considerable attention, among which $BiFeO_3$–$BaTiO_3$ (BF-BT) system has received great attentions since it has higher $T_C > 580$ °C [7]. As to the inferior piezoelectric property of BF-*x*BT ($d_{33} = 33$–47 pC/N at $0.25 \le x \le 0.33$) [7], many efforts have been made to enhance d_{33} via increasing DC resistivity, improving polarization property and enhancing ferroelectric activity by adding small amount of MnO_2 [7] and/or introducing a complex perovskites system such as $Bi(Mg_{1/2}Ti_{1/2})O_3$ [8], $Bi(Ni_{1/2}Ti_{1/2})O_3$ [9], $Bi(Zn_{1/2}Ti_{1/2})O_3$ [10] and so on. Recently, Leontsev [7] reported that the direct current (DC) resistivity of 0.75BF-0.25BT ceramic increases effectively by five orders of magnitude from 2.7×10^7 to 7.6×10^{12} Ω m via MnO_2 doping. Because of the improvement of DC resistivity and polarization property with small amount of MnO_2 doping, a high piezoelectric property $d_{33} = 116$ pC/N was achieved in 0.75BF-0.25BT+0.1wt%MnO_2 ceramic, which is far higher than $d_{33} = 33$–47 pC/N in undoped BF-*x*BT ($0.25 \le x \le 0.33$) ceramics [7]. Besides, the high $d_{33} = 116$ pC/N in 0.75BF-0.25BT+0.1wt%MnO_2 ceramic is also related to phase structure which lies in the morphotropic phase boundary (MPB) between rhombohedral (*R*) and pseudocubic (*PC*) phases. This value is also higher than $d_{33} = 82$ pC/N in 0.69BF-0.31BT+0.1wt%MnO_2 ceramic which is a single *PC*-phase [7], further verifying the importance of MPB in enhancing the piezoelectric properties.

Early phase diagram of BF-*x*BT has shown *R*, cubic (*C*) and tetragonal (*T*) phases as $0.00 \le x \le 0.33$, $0.33 \le x \le 0.96$ and $0.96 \le x \le 1$, respectively [11]. The MPB between *R* and *PC* phases was also confirmed to be located in the 0.70BF-0.30BT composition [12]. Recently, a modified phase diagram of BF-*x*BT, in which the MPB composition between *R* and *PC* was found to be shifted to BF-rich side, lying in 0.75BF-0.25BT composition in Mn-doped counterparts, was reported by Leontsev et al. [7]. Hence, the addition of MnO_2 in BF-*x*BT system seems not only to increase DC resistivity but also to shift the MPB composition to BF-rich side. More evidences about the MPB composition shifting to BF-rich side could also be found in Mn-doped BF-BT-xBi(B_1B_2)O_3 systems (B_1=Zn^{2+},

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Mg^{2+}, Ni^{2+} etc., and B_2=Ti^{4+}, Zr^{4+}, Nb^{5+} etc.), such as (0.71-*x*)BF-0.29BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 [8], (0.71-*x*)BF-0.29BT-*x*Bi($Ni_{1/2}Ti_{1/2}$)O_3 [9] and (0.71-*x*)BF-0.29BT-*x*Bi($Zn_{1/2}Ti_{1/2}$)O_3 [10] in which 0.6wt% MnO_2 was doped. All of these samples show a pure *P*C-phase, which also means that the MPB composition is lower than 0.29BT in these Mn-doped counterparts. However, in the (0.71-*x*)BF-0.29BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3+0.6wt%MnO_2 system, the superior piezoelectric property d_{33} = 155 pC/N [8] was achieved at x = 0.03, which is attributed to the improvement of polarization property via introducing MnO_2 and Bi($Mg_{1/2}Ti_{1/2}$)O_3, although the sample shows a single *PC*-phase. In view of the important role of the phase structure especially the MPB in enhancing the piezoelectric properties [13–17], it is thus expectable that a higher d_{33} could be achieved in BF-BT system, whose composition lies in the MPB with introducing small amount of MnO_2 and Bi($Mg_{1/2}Ti_{1/2}$)O_3 additions. However, investigations on the effect of MPB on the electrical properties in BF-BT system are not fully understood so far, necessitating clarifying and further improving the piezoelectric properties.

In this work, (0.70-*x*)BF-0.30BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 ceramics were designed to seek MPB between *PC* and *R* phase to enhance the electrical properties. High piezoelectric properties of d_{33} = 154 pC/N and k_p = 28.5% were achieved in BF-BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 system because of the MPB effect with coexisting *R* and *PC* phases at x = 0.04. Moreover, a high T_C = 482 °C was also achieved in BF-BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 ceramics at x = 0.04, suggesting that the BF-BT-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 system has promising prospects in high-temperature piezoelectric devices.

2. Experimental procedure

$BaTiO_3$ (100 nm, 99%), Bi_2O_3 (99%), Fe_2O_3 (99%), MgO (99%) and TiO_2 (99%) were used as raw materials, which were weighed according to a composition of (0.7-*x*)$BiFeO_3$–0.3$BaTiO_3$-*x*Bi($Mg_{1/2}Ti_{1/2}$)O_3 ($0.00 \le x \le 0.08$ mol) (abbreviated as (0.7-*x*)BF-0.3BT-*x*BMT) and milled with alcohol (>99.7%). After dried and calcined at 780 °C for 4 h, the resultant powders were re-milled and pressed into disks of 10 mm in diameter and 1.5 mm in thickness under 80 MPa using 2 wt% polyvinyl alcohol (PVA) as the binder, followed by burning the binder at 650 °C for 1 h by 5 °C/min. Then the samples were cooled to room temperature and further heated up directly from room temperature to 1000 °C by 5 °C/min and held for 2 h. The sintered specimen was coated with silver on the upper and bottom surfaces and sintered at 600 °C for 30 min for the electrical measurement. The coated samples were poled under a DC field of 4 kV/mm at room temperature for 30 min in a silicone oil bath.

Bulk densities of sintered samples were measured using the Archimedes method. The crystallographic structures were studied by using X-ray diffraction (XRD: D/max-RB, Rigaku Inc., Japan) with a Cu Kα radiation (λ = 1.5406 Å) filtered through a Ni foil. Raman spectra were measured by HR800 Microscopic Confocal Raman spectrometer (Horiba Jobin Yvon Company, French), in which the light source of He–Ne gas laser, laser wavelength of 633 nm, using semiconductor cooling type of CCD detector. The temperature dependence of dielectric properties was examined using a programmable furnace with an LCR analyzer (TH2828S) at 1 kHz in temperature range of 25 °C–650 °C. The microstructure of the sintered samples was observed by field emission scanning electron microscopy (FESEM, SUPRATM 55, Japan). The piezoelectric properties were measured using a quasi-static piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The leakage current density was measured at 1000 V by AT683 insulation test instrument (Applent instruments Ltd, China). The planar electromechanical coupling coefficient k_p and the mechanical quality factor Q_m were determined by resonance-antiresonance method using an Agilent 4294A precision impedance analyzer (Hewlett–Packard, Palo Alto, CA). Ferroelectric hysteresis (*P*-*E*) loops were measured using a ferroelectric tester (RT6000HVA, Radiant Technologies, Inc., Albuquerque, NM).

3. Results and discussion

Fig. 1 shows room temperature XRD patterns of (0.7-*x*)BF-0.3BT-*x*BMT ($0.00 \le x \le 0.08$) ceramics. All ceramics exhibit a perovskite structure without any trace of impurity phase within the detectable limit of the XRD, suggesting the formation of a stable solid solution. The standard diffraction peaks cited from $BiFeO_3$ (BF) with *R*-symmetry (PDF#72-2112) are indicated by vertical lines for comparison. The diffraction peaks of the composition of x = 0.00 correspond well to *R*-symmetry PDF#72-2112. Unlike the PDF#72-2112, the composition of x = 0.00 in Fig. 1b has higher peak intensity of $(111)_R$ than that of $(1\bar{1}1)_R$, suggesting that its phase structure consists of *R* and *PC* two phases rather than a single *R* phase. This result is consistent with the correlation reported by Wei et al. [12], in which the 0.7BF-0.3BT composition lies in the phase boundary between *R*- and *PC*-phase. As increasing x, the $(111)_R$ peak and $(1\bar{1}1)_R$ one gradually merge into a single peak at $x \ge 0.06$ as shown in Fig. 1b, suggesting that the phase structure of samples from *R*–*PC* two-phase coexistence at $0.00 \le x \le 0.04$ turns into a single *PC*-phase at $x \ge 0.06$. Apart from the structural transition, a variation of peak position depending on x is also noticed in Fig. 1b. Although the 2θ angles of diffraction peaks for all samples are lower than those of the standard card of R_{BF} phase (PDF#72-2112), no obvious change on their values is observed as increasing x from 0.00 to 0.08. The constant 2θ angles of diffraction peaks at $0.00 \le x \le 0.08$ suggest that the replacement of B-site ions, such as Fe^{3+} with $(Mg_{1/2}Ti_{1/2})^{3+}$, has little effect on the variation of cell volume in (0.7-*x*)BF-0.3BT-*x*BMT system. Hence, the lower 2θ angles of diffraction peaks than those of the standard card of R_{BF} phase (PDF#72-2112) are due to the replacement of the small ion radius's Bi^{3+} (r = 1.03 Å) by the large ion radius's Ba^{2+} (r = 1.35 Å) in A-sites, making lattice enlarged for all the samples [13].

To be more accurate, Rietveld refinement (using Materials studio software) was performed on the XRD patterns of (0.7-*x*)BF-0.3BT-*x*BMT ceramics (x = 0.02, 0.04 and 0.08), and the observed, calculated and different XRD patterns are shown in Fig. 2. As can be seen, the experimental patterns (observed) are well fitted with the theoretically simulated ones, which were calculated by *R* symmetry

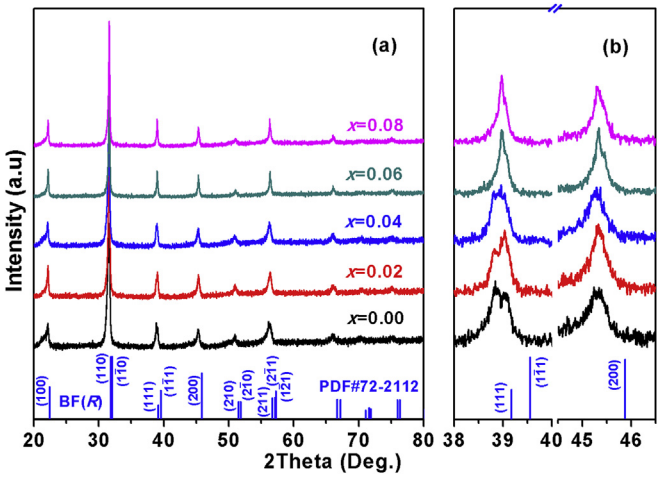

Fig. 1. X-ray diffraction patterns between the 2θ range of 20°-80° (a) enlarged ranges of 38°-40° and 44.5°-46.5° (b) for (0.7-*x*)BF-0.3BT-*x*BMT ceramics.