Large piezoelectric responses of Bi(Fe,Mg,Ti)O$_3$-BaTiO$_3$ lead-free piezoceramics near the morphotropic phase boundary

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A B S T R A C T

The $(1-x)Bi_{1+y}(Fe_{0.96}Mg_{0.02}Ti_{0.02})O_3$-$x$BaTiO$_3$ (abbreviated as B$_{1+y}$FMT-xBT) system was designed to explore the morphotropic phase boundary (MPB) separating rhombohedral (R) and tetragonal (T) phases, and the mechanism of performance enhancement. The phase structure of samples was discretely investigated by X-ray diffraction, and Rietveld refinement results of the XRD data revealed that the B$_{1+y}$FMT-xBT ceramics consist of an R phase at $x = 0.24$, two R and T phases at $0.26 \leq x \leq 0.32$, and a single T phase at $x = 0.34$. Because of the MPB and the improvement of resistivity with adding excess Bi compensation, excellent piezoelectric properties of $d_{33} = 198$ pC/N and $k_p = 30.9\%$, as well as high Curie temperature $T_C = 497$ °C were achieved in the B$_{1+y}$FMT-xBT system at $x = 0.30$ and $y = 0.02$. Here, the large $d_{33} = 198$ pC/N which is the maximum value for the BF-BT-Bi(Mg,Ti)O$_3$ system so far, and high $T_C = 497$ °C suggest that Bi(Fe,Mg,Ti)O$_3$-BaTiO$_3$ ceramics have good prospects in high-temperature piezoelectric devices.

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1. Introduction

Lead-based piezoelectric materials, such as Pb(Zr,Ti)O$_3$, Pb(Mg$_{1/3}$Nb$_{1/3}$)O$_3$-PbTiO$_3$, etc, are widely used in actuators, transducers and sensors, because of their excellent piezoelectric characteristics [1–3]. However, these lead-based ceramics are facing global restriction due to the strong toxicity of lead oxide. It is urgent to develop lead-free alternative materials with comparable piezoelectric and electromechanical properties to their lead-based counterparts. A series of typical lead-free piezoelectric systems such as BaTiO$_3$ (BT) [4–8], BiFeO$_3$-BaTiO$_3$ (BF-BT) [9–12], (1-x)Bi$_{0.5}$(Na,K)$_{0.5}$TiO$_3$-xBaTiO$_3$ [13,14] and (K$_{1-x}$Na$_x$)NbO$_3$ [15,16] based ceramics, have been highlighted to substitute for Pb-based piezoceramics. Among them, lead-free BF-BT solid solutions are considered as one of the most promising candidates for high-temperature piezoelectric applications due to their high T_C over 580 °C [9] and relatively high piezoelectricity [9–12,17–20]. Therefore, the BF-BT system has been extensively investigated in the past several years. Leontsev et al. [9] found that the piezoelectric coefficient d_{33} and DC resistivity (ρ) of BF-0.25BT ceramics increased from 47 pC/N and 2.7×10^7 Ω cm to 116 pC/N and 7.6×10^{12} Ω cm with addition of a small amount of MnO$_2$. Zhou et al. [17–19] reported that the polarization properties, ρ, d_{33} and ferroelectric activity of 0.71BF-0.29BT ceramics were improved by introducing a small amount of MnO$_2$ and complex perovskites of Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ [17], Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$ [18], Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ [19] and so on. The optimal d_{33} of 0.71BiFe$_{1-x}$(Mg$_{1/2}$Ti$_{1/2}$)$_x$O$_3$-0.29BT+0.6 wt%MnO$_2$ [17], 0.71BiFe$_{1-x}$(Ni$_{1/2}$Ti$_{1/2}$)$_x$O$_3$- 0.29BT+0.6 wt%MnO$_2$ [18] and 0.71BiFe$_{1-x}$(Zn$_{1/2}$Ti$_{1/2}$)$_x$O$_3$-0.29BT+0.6 wt%MnO$_2$ [19] ceramics is 155 pC/N, 156 pC/N and 163 pC/N at $x = 0.03$, 0.03 and 0.02, respectively. High $d_{33} = 180$ pC/N and 142 pC/N were achieved in the BF-BT system by adding excess Bi compensation [12,20]. Among those researches, most studies focused on the improvement of the polarization properties, ρ and d_{33} values by adding small amounts of MnO$_2$ and/or complex perovskites, and only a little attention was paid to the composition-induced phase transition between two ferroelectric phases, which has been known as the morphotropic phase boundary (MPB) in the phase diagram.

It is well known that the MPB separating rhombohedral (R) and tetragonal (T) phases plays an important role in enhancing piezoelectric properties in the PZT family [21] and lead-free Ba(Zr$_{0.2}$Ti$_{0.8}$)O$_3$- (Ba$_{0.7}$Ca$_{0.3}$)TiO$_3$ system [22]. The main reason is that the composition-induced ferro-ferro transition at the MPB can causes the instability of the polarization state so that the polarization

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direction can be easily rotated by an external stress or electric field [23,24], thereby resulting in a high piezoelectricity and permittivity. Therefore, the basic approach for achieving high piezoelectricity is to place the composition of the material in the proximity of a composition-induced phase transition between two ferroelectric phases. Early phase diagram of BF-xBT has shown R, cubic (C) and T phases at $0.00 \leq x \leq 0.33$, $0.33 \leq x \leq 0.96$ and $0.96 \leq x \leq 1$, respectively [25]. However, some reports [26,27] indicated that the C phase of BF-xBT at $x \geq 0.33$ is not really a paraelectric phase, but a ferroelectric pseudocubic (PC) or T phase. Recently, Lee et al. [27] reported that the MPB separating R and T phases was detected in BF-33BT, BF-33BT-3Bi($Zn_{0.5}Ti_{0.5}$)O$_3$ and BF-33BT-3BiGaO$_3$ systems, which exhibit excellent piezoelectric coefficients $d_{33} = 240$ pC/N, 324 pC/N and 402 pC/N, respectively. Mandal et al. [28] also indicated that an MPB was observed in the $(1-x)$BiTi$_{3/8}$Fe$_{2/8}$Mg$_{3/8}$O$_3$-xCaTiO$_3$ system, which has a maximum d_{33} value of 53 pC/N at $x = 0.1625$. Similarly, we believed that the composition-induced ferro-ferro transition at an MPB should also exist in the BF-BT-Bi(Mg,Ti)O$_3$ system. However, despite intense studies [10,17,29–34] of solid solutions in the BF-BT-Bi(Mg,Ti)O$_3$ system, few works disclosed the relationship between the phase structure and composition in detail, the piezoelectric properties of these materials have not yet been optimized, and the main mechanism behind their improved properties is not yet clear.

In this work, $(1-x)$Bi$_{1+y}$(Fe$_{0.96}$Mg$_{0.02}$Ti$_{0.02}$)O$_3$-xBaTiO$_3$ (abbreviated as B$_{1+y}$FMT-xBT) (at $0.24 \leq x \leq 0.34$ and $0.00 \leq y \leq 0.05$) ceramics were prepared to explore the relationship between the phase structure and compositions, as well as the mechanism of performance enhancement. However, the MPB between R and T phases was detected in the B$_{1+y}$FMT-xBT system located in the composition range of $0.28 \leq x \leq 0.32$ and $0.00 \leq y \leq 0.05$. Because of the R and T two phase coexistence and the improvement of resistivity with adding excess Bi compensation, excellent piezoelectric properties of $d_{33} = 198$ pC/N and $k_p = 30.9\%$, as well as high Curie temperature $T_C = 497$ °C were achieved in B$_{1+y}$FMT-xBT system at $x = 0.30$ and $y = 0.02$. This work suggests that the MPB region also exists in the B$_{1+y}$F-BT-xBMT system, which has promising prospects in high-temperature piezoelectric devices because of large $d_{33} = 198$ pC/N and high $T_C = 497$ °C.

2. Experimental procedure

Barium titanate (BaTiO$_3$, 99%, 100 nm, Aladdin Industrial Corporation), Bismuth oxide (Bi$_2$O$_3$, 99%, ShanTou Xilong Chemical Factory, GuangDong, China), Ferric oxide (Fe$_2$O$_3$, 99%, 1 μm, ShanTou Xilong Chemical Factory, GuangDong, China), Magnesium oxide (MgO, 99%, ShanTou Xilong Chemical Factory, GuangDong, China) and Titanium dioxide (TiO$_2$, 99%, ShanTou Xilong Chemical Factory, GuangDong, China) were used as raw materials, which were weighed according to a composition of $(1-x)$Bi$_{1+y}$(Fe$_{0.96}$Mg$_{0.02}$Ti$_{0.02}$)O$_3$-xBaTiO$_3$ (at $0.24 \leq x \leq 0.34$ and $0.00 \leq y \leq 0.05$ mol) (abbreviated as B$_{1+y}$FMT-xBT) and milled with alcohol (>99.9%) and Zirconium Oxide Spheres. After drying and calcining at 800 °C for 8 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 out the binder at 650 °C by heating at 5 °C/min and for 1 h. Then the samples were cooled to room temperature and further heated up directly from room temperature to 1000 °C at 5 °C/min and held for 3 h. The sintered specimen was coated with silver on the upper and bottom surfaces and fired at 600 °C for 30 min for the electrical measurement. The coated samples were poled under a DC field of 4 kV/mm at 120 °C for 30 min in a silicone oil bath.

Bulk densities of sintered samples were measured using the Archimedes method. Crystallographic structures were studied by using X-ray diffraction (XRD: D/max-RB, Rigaku Inc., Japan) with Cu Kα radiation ($\lambda = 0.15406$ nm) filtered through a Ni foil. The temperature dependence of dielectric properties was examined using a programmable furnace with an LCR analyzer (TH2828S) at 1 kHz in the temperature range of 20 °C–650 °C. The microstructure of the sintered samples was observed by field emission scanning electron microscopy (FESEM, SUPRATM 55, Japan), and average grain sizes of samples were calculated by the Nano Measurer software, which measured the grain of entire screen. Piezoelectric properties were measured using a quasi-static piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The planar electromechanical coupling coefficient k_p and the mechanical quality factor Q_m were determined by the 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 Bi(Fe$_{0.96}$Mg$_{0.02}$Ti$_{0.02}$)O$_3$-xBaTiO$_3$ (abbreviated as BFMT-xBT) ceramics at $0.24 \leq x \leq 0.34$. 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#73-0548) and BaTiO$_3$ (BT) with T phase (PDF#81-2202) are indicated by vertical lines for comparison. The diffraction peaks of the composition for $x = 0.24$ correspond well to that of R symmetry, suggesting that the crystalline structure of the sample at $x = 0.00$ is of single R symmetry, in which two peaks of $(111)_R$ and $(1\bar{1}1)_R$ as well as only one peak for (200) are visible around 39° and 45° in the enlarged Fig. 1 (b), respectively. with increasing x, the intensity of the $(111)_R$ peak increases, which is even higher than that of the $(1\bar{1}1)_R$ peak around 39°, along with the splitting of the $(200)_R$ peak around 45° to two peaks of $(002)_T$ and $(200)_T$ at $x \geq 0.26$, suggesting the phase structure consists of two R and T phases rather than a single R phase. As x further increases to 0.32, the $(111)_R$ peak and $(1\bar{1}1)_R$ peak merge into single (111) peak as shown in Fig. 1b, suggesting that the host phase structure of the sample turns from the R phase at $x \leq 0.24$ into the T one at $x \geq 0.32$.

The more detailed evidences are shown in the supporting information of Fig. S1, which plots the Rietveld refinement result of the XRD data. As can be seen, the experimental patterns (observed) are well fitted with the theoretically simulated ones, which were calculated with an R symmetry ($R3m$) corresponding to standard card (PDF#73-0548) and a T symmetry ($P4mm$) (corresponding to $a = b = 3.9925$, $c = 4.0365$ Å, $\alpha = \beta = \gamma = 90°$). The refined results further verify that the phase structure of the samples consists of an R phase at $x = 0.24$, two R and T phases at $0.26 \leq x \leq 0.32$, and a single T phase at $x = 0.34$ as shown in Fig. S1. The detailed variations of the lattice parameters, α, β, γ angles and the relative proportion between R symmetry and T symmetry are shown in Table SI (supporting information), which shows that the content of R phase monotonously decreases, and T phase increases with increasing x from 0.24 to 0.34, as well as that the MPB region of BFMT-xBT ceramics is located in the composition range of $0.26 \leq x \leq 0.32$.

According to the work of Grinberg et al. [35], the MPB of Bi(B'B'')O$_3$-PbTiO$_3$ system (x_{PT}^{MPB}) can be well predicted by Eq. (1). This equation was originally developed for systems with PbTiO$_3$ as an end member. However, since BaTiO$_3$ (BT) has a similar structure to PbTiO$_3$, which has Pb-B-cation repulsion which depends on interatomic distance and B-cation ionic size [35], it is considered that Eq. (1) is also suited to the Bi(B'B'')O$_3$-BaTiO$_3$ system. We can get that