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Novel high temperature ferroelectric single crystals 0.38Bi($Mg_{1/2}Ti_{1/2}$)O_3-0.62$PbTiO_3$ with good and temperature-stable piezoelectric properties

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Novel ferroelectric single crystals 0.38Bi($Mg_{1/2}Ti_{1/2}$)O_3-0.62$PbTiO_3$ have been successfully grown by flux method. The T_c and d_{33} are 520 °C and 208 pC/N, respectively. Good temperature stability, together with good piezoelectric properties and high T_c make the single crystals promising novel piezoelectric materials for high-temperature, high-performance actuators and transducers.

1. Introduction

With the rapid development of industry, there exists pressing demands for the piezoelectric devices such as actuators, transducers and sensors, which could be operated stably and reliably under temperature above 300 °C, especially in space exploration, aircraft, deep oil drilling rigs and automotive smart brakes[1-3]. Currently, the most widely used piezoelectric material is PZT ceramics[2, 4, 5]. However, the operating temperature of PZT ceramics is limited to one half of their T_c, usually lower than 180 °C [6], due to the depoling effect. In recent years, Bi(Me)O_3-$PbTiO_3$ piezoelectric materials, where Me can be a single cation of valency +3 (e.g., Sc^{3+} and Fe^{3+}) or a mixture of cations with an average valence of +3 (e.g., $Mg_{1/2}Ti_{1/2}$ and $Ni_{2/3}Nb_{1/3}$), become a research hotspot of high temperature piezoelectric materials because of their excellent piezoelectric properties and high Curie temperature[7-13].

In Bi(Me)O_3-$PbTiO_3$ system, (1-x)$BiScO_3$-$x$$PbTiO_3$(BS-PT) has the best piezoelectric performance and attracts much attention[8-10]. For BS-PT ceramics with the composition near the morphotropic phase boundary (MPB) (x=0.64), the d_{33}, planar coupling coefficient and T_c are 460 pC/N, 0.56 and 450 °C, respectively[11]. Meanwhile for BS-PT single crystals with the composition near MPB, the d_{33} of (001) orientation is as high as 1150 pC/N with the T_c of 402 °C[12] due to the anisotropy. However, too high cost of the scandium oxide as the major chemical constituent of BS-PT would seriously obstruct their widespread application in high temperature piezoelectric devices. Therefore, looking for an alternative is very urgent. As for Bi(Me)O_3-$PbTiO_3$ system, only few compounds can form a MPB with $PbTiO_3$, and most $BiMeO_3$ have limited solubility in $PbTiO_3$ so that the MPB is rarely reached, such as Bi($Zn_{1/2}Ti_{1/2}$)O_3-$PbTiO_3$[13] and $BiInO_3$-$PbTiO_3$[7]. Otherwise, except BS-PT[8], Bi($Ni_{1/2}Ti_{1/2}$)O_3-$PbTiO_3$(BNT-PT)[14] and Bi($Mg_{1/2}Ti_{1/2}$)O_3-$PbTiO_3$(BMT-PT)[13], other $BiMeO_3$-$PbTiO_3$-based materials have low or inferior piezoelectric properties near their MPB composition. However, due to the high conductivity and dielectric loss, BNT-PT is not a perfect piezoelectric material, either[14]. Therefore, BMT-PT is well worth investigating. The MPB of the (1-x)BMT-xPT ceramics is in the range of $0.36\leq x \leq 0.38$[15]. BMT-PT ceramics with the composition near MPB have relatively high T_c (430 °C) and comparable piezoelectric properties (d_{33} > 200 pC/N) [15]. Thus, BMT-PT were believed to be potential high-temperature piezoelectric materials. Up to present, almost all of the investigations related to BMT-PT focused on the ceramics and films, such as the preparation, structure, dielectric, ferroelectric and piezoelectric properties[15-19]. Little information could be found on the growth and piezoelectric properties of BMT-PT single crystals.

In this letter, the growth and piezoelectric properties of tetragonal BMT-PT single crystals will be delivered for the first time. The Curie temperature of 0.38BMT-0.62PT single crystals grown by a high temperature solution method is as high as 520 °C. The piezoelectric properties were good and almost unchanged until the temperature up to 520 °C. The results indicate that 0.38BMT-0.62PT single crystals may become novel high temperature piezoelectric materials with high performance and high usage temperature about 500 °C.

2. Experimental

BMT-PT single crystals have been grown by a high temperature solution method (flux method). High-purity powders Bi_2O_3, MgO, Pb_3O_4 and TiO_2 were selected as starting materials. PbO was selected as flux. The raw material powders were stoichiometrically weighed, mixed, and then calcined to form the desired perovskite phase. Afterwards, the calcined powders were mixed with flux and packed into a platinum crucible. The growth experiments were implemented in a box furnace. After completion of the growth, the crystals were detached with the platinum crucibles and immersed in acetic acid to dissolve the flux.

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The composition of the crystals was detected by Electron Probe Microanalysis (EPMA, JXA-8100). The crystal structure of the room temperature and high temperatures was performed by room temperature X-ray diffraction (XRD) analysis (Cu$_{k\alpha}$, Rigaku, Rint2000) and high temperature XRD analysis (Cu$_{k\alpha}$, Rigaku D/max 2550V). To measure the electrical properties, silver paste was coated on both sides of the (001) plane with thickness of 0.7 mm and fired for 30 min at 750 °C to form electrodes. The samples were poled at 135 °C in a silicon oil bath under a DC field of 5.5 kV/mm for 30 min. Dielectric properties were measured using an HP4284A LCR meter connected with a computer-controlled furnace. The temperature-dependent resonance-antiresonance frequency spectrum was measured using an HP4294 impedance analyzer (Hewlett-Packard, Palo Alto, CA). The d_{33} was measured by a piezoelectric d_{33} meter (Zj-4A, institute of Acoustics, Chinese Academy of Sciences, China). The thermal-depoling experiments were conducted by holding the poled samples with Ag electrodes for 2 h at various temperatures, cooling to room temperature, measuring d_{33}, and repeating the procedure up to 530 °C.

3. Results and discussion

The obtained (1-x)BMT-xPT crystals as shown in Fig. 1 were fulvous in color and 2-10 mm in size. The typical crystals are rectangular in shape with (001) faces in habit. A few flux inclusions can be observed in some samples.

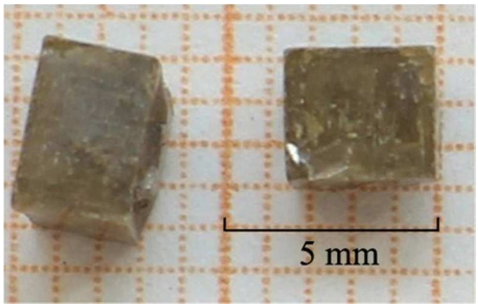

Fig. 1 Photograph of BMT-PT single crystals with rectangular shape.

Fig. 2 shows the XRD result of the emerged faces of the grown crystal, which revealed that the habitual faces of the grown crystals are {001}. The XRD result and the photograph of the crystals demonstrate that the samples are single crystals.

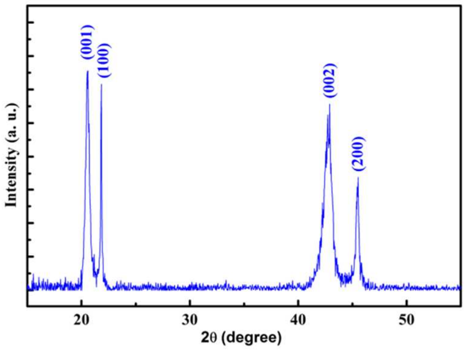

Fig. 2 XRD pattern for BMT-PT single crystal along the habitual face.

The XRD result of the powder grounded from BMT-PT single crystals at room temperature is shown in Fig. 3(b). It is apparent that the specimen exhibits a pure perovskite structure and no detectable traces of impurities are observed. The (001)/(100) and (002)/(200) peaks split at about 2θ = 22^o and 45^o, which means that the grown BMT-PT single crystals belong to tetragonal phase[16]. The actual composition of the single crystals is 0.38BMT-0.62PT determined by EPMA. The c/a ratio of 0.38BMT-0.62PT single crystals calculated from Fig. 2 is 1.061. Due to the composition largely deviating from the MPB, the value of c/a ratio is much larger than that of 0.62BMT-0.38PT. The c/a ratio of 0.62BMT-0.38PT is 1.034[19].

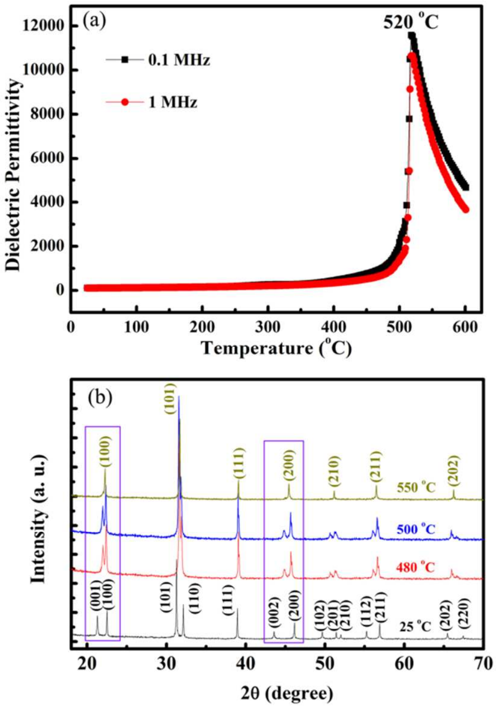

Fig. 3 (a) Temperature dependence of the dielectric permittivity (ε_r), and (b) high temperature XRD patterns of the samples.

The 0.38BMT-0.62PT single crystals for dielectric and piezoelectric measurements were oriented along their crystallographic direction (00l). The dielectric constant ε_r and dielectric loss tanδ at room temperature are about 108 and 0.4%, respectively. Fig. 3(a) shows the temperature dependence of ε_r for the crystal at 0.1 MHz and 1 MHz from room temperature to 600 °C. A dielectric peak is observed at 520 °C, which was assumed to be the Curie temperature T_c. In order to confirm it, the high temperature XRD was measured. Fig. 3(b) shows the high temperature XRD patterns of the 0.38BMT-0.62PT powder grounded from the single crystals. The (001)/(100) and (002)/(200) peaks at about 22^o and 45^o have a change from clear split to no split with increasing temperature, which signifies that the crystal structure of the sample undergo a phase transition from tetragonal phase to cubic phase. The crystal structure is still tetragonal phase at 500 °C, and then it becomes cubic phase at 550 °C. Therefore, the dielectric anomaly at 520 °C in Fig. 3(a) is the result of a transition from ferroelectric phase to paraelectric phase, and the T_c of 0.38BMT-0.62PT single crystal is 520 °C, which is 90 °C higher than that of the BMT-PT ceramics with the composition of MPB[15,20].

The piezoelectric coefficient d_{33} of the (001)-oriented 0.38BMT-0.62PT single crystals at room temperature is about 208 pC/N. As reported in reference 20, the d_{33} of 0.4BMT-0.6PT and 0.64BMT-0.36PT (MPB) ceramics is 34 pC/N and 220 pC/N, respectively, so the d_{33} value of 208 pC/N for 0.38BMT-0.62PT single crystals is much higher than that of BMT-PT ceramics with the similar composition (0.4BMT-0.6PT ceramics) and comparable to that of BMT-PT ceramics with composition of MPB (0.64BMT-0.36PT ceramics). As though 0.64BMT-0.36PT ceramics have good piezoelectric properties due to their composition near MPB, the existence of lower temperature phase transition or rhombohedral-tetragonal phase transition at about 350°C in 0.64BMT-0.36PT ceramics will make their usage temperature to be lower than 350 °C. Compared to the samples with the composition of MPB or the rhombohedral phase sample, the tetragonal phase avoids the rhombohedral-tetragonal phase transition within the temperature range from room temperature to Curie temperature, which overcomes the property fluctuation near phase transition temperature and greatly broadens the application temperature range of piezoelectric materials and devices. Therefore, in view of high temperature usage, tetragonal 0.38BMT-0.62PT single crystals are obviously better than rhombohedral 0.64BMT-0.36PT ceramics. The d_{33} of the (001)-oriented tetragonal 0.34BS-0.66PT single crystal is 200 pC/N, which is approximate to the value of (001)-oriented 0.38BMT-0.62PT single crystals. And it also avoids the rhombohedral-tetragonal phase transition. However, the price of the scandium oxide as a raw material of BS-PT is too high, and the T_c is 460 °C, which is 60 °C lower than that of the 0.38BMT-0.62PT crystals[21]. For systematic comparison, the T_c and d_{33} of the typical Bi(Me)O_3-PbTiO_3 piezoelectric materials are present in Table I. Taking into consideration various factors, such as application temperature, piezoelectric properties, cost of the raw materials and conductivity of the sample[14], the tetragonal 0.38BMT-0.62PT single crystal shows compositive advantages and a great research prospect.

TABLE I. Curie temperature T_c and piezoelectric coefficient d_{33} of the typical Bi(Me)O_3-PbTiO_3 piezoelectric materials.

Materials	MPB (x)	T_c (°C)	d_{33} (pC/N)
$(1\text{-}x)\mathrm{Bi(Zn_{1/2}Zr_{1/2})O_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[22]	0.67	668	27
$(1\text{-}x)\mathrm{BiFeO_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[23]	0.30	632	50
$(1\text{-}x)\mathrm{Bi(Mg_{1/4}W_{3/4})O_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[24]	0.62	220	150
$(1\text{-}x)\mathrm{Bi(Ni_{1/2}Ti_{1/2})O_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[14]	0.49	400	260
$(1\text{-}x)\mathrm{BiScO_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[8]	0.64	450	460
$(1\text{-}x)\mathrm{BiScO_3}\text{-}x\mathrm{PbTiO_3}$ (x=0.66, tetragonal crystal)[21]	—	460	200
$(1\text{-}x)\mathrm{BiScO_3}\text{-}x\mathrm{PbTiO_3}$ (x=0.57, rhombohedral crystal)[12]	—	404	1150
$(1\text{-}x)\mathrm{Bi(Mg_{1/2}Ti_{1/2})O_3}\text{-}x\mathrm{PbTiO_3}$ (ceramics)[15]	0.36-0.38	430	220
$(1\text{-}x)\mathrm{Bi(Mg_{1/2}Ti_{1/2})O_3}\text{-}x\mathrm{PbTiO_3}$ (x=0.60, ceramics)[20]	—	—	34
$(1\text{-}x)\mathrm{Bi(Mg_{1/2}Ti_{1/2})O_3}\text{-}x\mathrm{PbTiO_3}$(x=0.62, tetragonal crystal)[*]	—	520	184

[*] is the result of this work

From the viewpoint of application, it is necessary to study the sample's high-temperature stability of the piezoelectric properties. Fig. 4(a) shows the d_{33} of the 0.38BMT-0.62PT single crystal as a function of annealing temperature. The d_{33} were measured at room temperature after the sample underwent 2 h annealing under each temperature. It can be seen that the d_{33} values are stable with increasing temperature until up to the T_c (520 °C) of the sample. Fig. 4(b) exhibits the temperature dependence of electromechanical coupling factor k_{31} of the (001)-oriented 0.38BMT-0.62PT sample. The k_{31} is calculated according to the following equation:

$$k_{31} = \sqrt{\frac{\pi^2}{4}\frac{\Delta f}{f_r}\left[1+\left(\frac{4-\pi^2}{4}\right)\frac{\Delta f}{f_r}\right]} \qquad (1)$$

where Δf = f_r - f_a, f_a is the antiresonant frequency, and f_r is the resonant frequency. The k_{31} of the single crystal is about 0.45 at room temperature, and it is almost unchanged until the temperature up to 520 °C. As reported[20, 25], the T_c of 0.62BMT-0.38PT ceramics, 0.47BS-0.63PT ceramics, and 0.43BS-0.57PT single crystal is about 430 °C, 450 °C, and 402 °C, respectively. However, the rhombohedral-tetragonal phase transition temperature or depoling temperature of them is about 350 °C, 380 °C, and 340 °C, and it is much lower than its T_c. According to the results, we can conclude that the stability of the piezoelectric properties of 0.38BMT-0.62PT single crystal is better than that of BMT-PT ceramics and BS-PT (ceramics and single crystals). Therefore, the 0.38BMT-0.62PT single crystal is a kind of piezoelectric materials with high T_c and good temperature stability of piezoelectric properties, and may be suitable for high performance transducers and actuators at temperatures up to 500 °C.

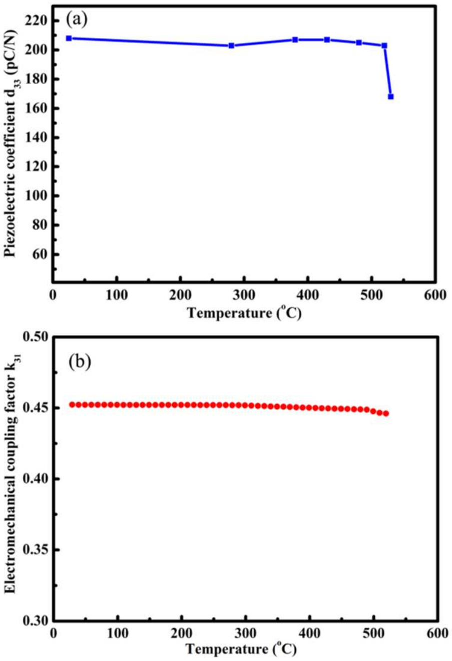

Fig. 4 (a) Piezoelectric coefficient d_{33} as a function of annealing temperature, and (b) electromechanical coupling factor k_{31} as a function of temperature for (001)-oriented 0.38BMT-0.62PT single crystals.

Conclusions

In summary, BMT-PT single crystals were grown by a high temperature solution method. The Curie temperature T_c, dielectric constant ε_r, dielectric loss tanδ, piezoelectric coefficient d_{33} and electromechanical coupling factor k_{31} of the obtained (001)-oriented tetragonal 0.38BMT-0.62PT crystals at room temperature are 520 °C, 108, 0.4%, 208 pC/N and 0.45, respectively. The results of high temperature experiments showed that the piezoelectric properties were almost unchanged until the temperature up to 520 °C. Together with the high T_c, large piezoelectric properties and good temperature stability of the properties, BMT-PT single crystals are the attractive material candidates for the next generation high-temperature, high-performance actuators and transducers.

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Novel 0.38BMT-0.62PbT single crystals with high T_c, good and temperature-stable piezoelectric properties have been grown by flux method.