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COMMUNICATION

Peculiar temperature-stable piezoelectric performance and strong self-poling effect in tetragonal phase $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-PbTiO}_3$ single crystals with high usage temperature

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Jinfeng Liu,^a Guisheng Xu,^a Yanfeng Tian^{ab} and Xiu Zhu^{ab}

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The peculiar temperature-stable piezoelectric performance and strong self-poling effect was observed in tetragonal phase ferroelectric single crystals $0.38\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-}0.62\text{PbTiO}_3$. The piezoelectric coefficient d_{33} of the as-prepared sample with self-poling is 158 pC/N, and it is as high as 75% of the value produced by an external electric field. The internal electric field E_i exists and the value is 4.34 kV/cm at the applied electric field of 40 kV/cm. The defect dipoles pin on the ferroelectric domains and stabilize the piezoelectric properties and the piezoelectric coefficient d_{33} at room temperature is nearly unchanged until the annealing temperature up to 800 °C, which is much higher than the Curie temperature $T_c \sim 520$ °C.

1. Introduction

Great attention has been paid to the high temperature piezoelectric materials with good piezoelectric properties due to the urgent demands for the applications in space explorations, electric aircrafts, deep oil drilling rigs and automotive smart brakes, which usually requires an operation temperature higher than 300 °C.¹⁻⁴ In recent years, $\text{Bi}(\text{Me})\text{O}_3\text{-PbTiO}_3$ solid solution, 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., $\text{Mg}_{1/2}\text{Ti}_{1/2}$ and $\text{Ni}_{2/3}\text{Nb}_{1/3}$), became a research hotspot of high temperature piezoelectric materials because of their good piezoelectric properties and high Curie temperature.^{1, 5-7} Specifically, $0.38\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-}0.62\text{PbTiO}_3$ (0.38BMT-0.62PT) single crystal, which was first grown by us,¹ exhibits promising applications in high-temperature, high-performance actuators and transducers. 0.38BMT-0.62PT single crystal is a novel high temperature ferroelectric. The Curie temperature T_c , piezoelectric coefficient d_{33} and electromechanical coupling factor k_{31} of (001) orientation are 520 °C, 208 pC/N and 0.45, respectively. Most importantly, the piezoelectric properties were almost unchanged until the temperature up to the $T_c \sim 520$ °C of the crystal¹. What's more, in the subsequent experiments the self-poling was found in

0.38BMT-0.62PT single crystals.

In most cases, the as-prepared unpoled ferroelectrics seldom show a macroscopic polarization, since there are several different polarization states or multi-domains. However, sometimes due to the self-poling, the poled state can set in in materials without application of any external electric field. Most of the self-poling phenomena were observed in thin films, such as BiFeO_3 , $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, BaTiO_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ based films.⁸⁻¹² However, in bulk materials, the self-poling phenomena only were reported in a few kinds of materials, such as BiFeO_3 ceramics which was treated by a great temperature gradient, $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ single crystals with the dimensions of $1 \times 1 \times 0.2$ mm³ and LiNbO_3 -based single crystals with strong thermoelectric effect.¹³⁻¹⁵

The reasons for self-poling in different materials are not the same. However, the internal electric field E_i and mechanical forces are the two most important factors. For instance, Chen *et al.* found an obvious self-poling phenomenon in BiFeO_3 ceramics. The high-temperature gradient and corresponding thermal strain caused during the heat treatment process can introduce defect dipoles through separating bismuth vacancies from oxygen vacancies. A mass of these dipoles introduced a macroscopic E_i which poled BiFeO_3 ceramics.¹³ Bdkin *et al.* observed a self-polarization in $\text{Pb}(\text{Zr}_{0.35}\text{Ti}_{0.65})\text{O}_3$ single crystals via piezoresponse force microscopy (PFM). It was thought that the chemical gradients of lead deficiency near the surface can form a macroscopic E_i which poled the crystals.¹⁴ Epitaxial strain can introduce self-poling in some ferroelectric films through the coupling between polarization and strain gradient, i. e. flexoelectricity. Lu *et al.* demonstrated that the strain gradient generated by the tip of an atomic force microscope can mechanically switch the polarization of a 4.8 nm thickness BaTiO_3 epitaxial film on (001) SrTiO_3 substrate.⁷ In addition, in the case of LiNbO_3 single crystals the self-poling was caused by the thermoelectric effect and the electric field can be formed by the temperature gradient (Seebeck effect) in the crystals growth process.¹⁵

^a Key Laboratory of Transparent Opto-Functional Advanced Inorganic Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 588 Heshuo Road, Shanghai 201899, China. E-mail: gshxu@mail.sic.ac.cn; Fax: +86-21-59927184; Tel: +86-21-69987753.

^b University of Chinese Academy of Sciences, Beijing 100049, China.

In this investigation, a macroscopic self-poling was observed in 0.38BMT-0.62PT single crystals. The E_i exists and the value is 4.34 kV/cm at the applied electric field of 40 kV/cm. The d_{33} of the as-prepared sample is 158 pC/N, which is as high as 75% of the magnitude produced by an external electric field. What's more, it is found that the self-poling is quite stable, and the d_{33} value nearly keeps the same under various annealing temperatures with the highest temperature up to 800 °C. Thus, due to the self-poling, 0.38BMT-0.62PT crystals may be directly used in some cases without polarization by an external electric field and the piezoelectric properties can self restore at the temperature lower than the T_c if the piezoelectric properties depolarize because of the usage temperature higher than the T_c .

2. Experiment

0.38BMT-0.62PT single crystals have been grown by flux method. The details were shown in reference 1. To measure the electrical properties, the samples were oriented along their crystallographic direction (001). Silver paste was coated on both sides of the (001) plane with thickness of 0.6 mm and fired for 30 min at 750 °C to form electrodes. The samples polarized by an external electric field were poled at 135 °C in a silicon oil bath under a DC field of 5.5 kV/mm for 30 min. The piezoelectric coefficient 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 as-prepared unpoled and poled samples with silver electrodes for 2 h at various temperatures, cooling to room temperature, measuring d_{33} , and repeating the procedure up to 800 °C. The polarization-electric field (P - E) hysteresis loops were performed simultaneously using an aixACT TF 2000 analyzer ferroelectric measuring system (aixACT Co., Germany) at a frequency of 1 Hz. The X-ray photoelectron spectroscopy (XPS) measurements were recorded on an ESCALAB 250Xi (Thermo Scientific) using AlK_{α} radiation. The dielectric properties were measured using an HP4284A LCR meter connected to a computer-controlled furnace.

3. Results

The grown single crystals are rectangular in shape and 2-10 mm in size. Fig.1 shows the image of the typical single crystals. The crystals were grown layer by layer.



Fig. 1. Image of the 0.38BMT-0.62PT single crystals.

The piezoelectric coefficient d_{33} of the as-prepared tetragonal 0.38BMT-0.62PT single crystals with (001) orientation is 158 pC/N, which means that the self-poling exists in the crystals.

The d_{33} of the sample poled by an external electric field is 208 pC/N.¹ Therefore, the self-poling is very strong and the magnitude of d_{33} is as high as 75% of the value produced by the external electric field.

The effect of thermal depoling on the values of d_{33} for the as-prepared 0.38BMT-0.62PT single crystals is demonstrated in Fig. 2(a). It is worth noting that the d_{33} at room temperature almost keep the same value in the annealing temperature range from 25 °C to 800 °C. Usually a high temperature annealing (above T_c) can result in the complete disappearance of the polarized state or piezoelectric properties in materials with self-poling¹⁶ or poled by an external electric field. However, it is surprisingly found that the value of d_{33} at room temperature doesn't change even under the heat treatment temperature up to 800 °C, which is much higher than the $T_c \sim 520$ °C of the sample. Besides d_{33} , the electromechanical coupling factor k_{31} is also quite stable as shown in reference 1. The k_{31} is about 0.45 at room temperature and it is almost unchanged until the temperature up to the $T_c \sim 520$ °C. At the temperature above 520 °C, the k_{31} of the sample is disappeared.

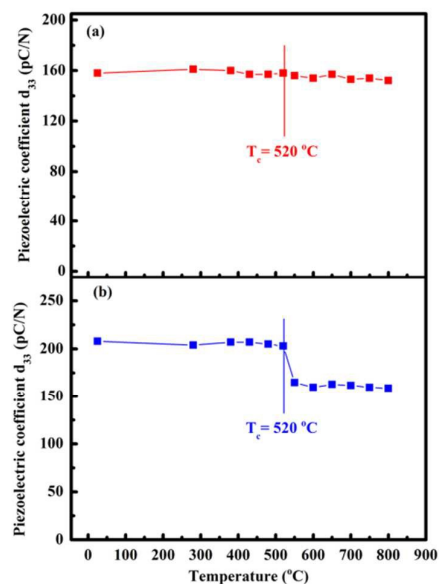


Fig. 2. Piezoelectric coefficient d_{33} at room temperature for (a) 0.38BMT-0.62PT single crystal with self-poling and (b) 0.38BMT-0.62PT single crystals poled by an external electric field as a function of annealing temperature.

Fig. 2(b) shows the annealing temperature dependences of the d_{33} of the sample poled by an external electric field. It can be seen that the value of d_{33} at room temperature is nearly unchanged with the annealing temperature increasing from 25 °C to the T_c of the sample. However, when the annealing temperature was higher than the T_c , the value of d_{33} decreases to about 160 pC/N, and then it is mainly stable up to 800 °C. By comparison the data between Fig. 1(a) and Fig. 1(b), we can conclude that the d_{33} of the sample poled by an external electric field consists of two parts. One part is induced by self-poling, and the other is induced by the external electric field. When the heat treatment temperature is higher than the T_c ,

the d_{33} induced by the external electric field vanishes, while the d_{33} induced by self-poling self-restores at the temperature below the T_c . As a result, the d_{33} values of the self-poling sample and the poled sample by an external electric field are nearly the same when the annealing temperature is higher than the T_c . Because the silver electrodes of the sample are easily damaged at the heat treatment temperature above 800 °C, the annealing temperature is not set higher than 800 °C.

4. Discussion

In order to explain the self-poling phenomenon in (001) oriented 0.38BMT-0.62PT single crystals, the P - E loops were measured as shown in Fig. 3. It is obvious that the remnant polarization increases with increasing electric field and the maximum polarization does not occur at maximum field, which is similar to the result of BiFeO₃ ceramics with self-poling.¹³ It suggested that the existence of oxygen vacancies ($V_{O''}$) increases the leakage current and then results in the counterfeiting. Large leakage current also was observed in the process of poling 0.38BMT-0.62PT single crystals. More importantly, it is noted that the P - E loops are strongly asymmetric with developing of an E_i .

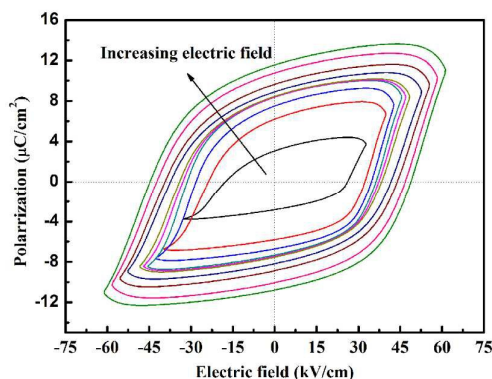


Fig. 3. P - E hysteresis loops of the 0.38BMT-0.62PT single crystals with self-poling measured at 1Hz as a function of applied electric field.

Fig. 4 displays the E_c and E_i as a function of applied electric field for the as-prepared sample with self-poling. The magnitude of E_i and coercive field E_c is determined by $E_i = (E_+ + E_-)/2$ and $E_c = (E_+ - E_-)/2$, where E_+ and E_- are the intersections of polarization loops with positive and negative field axis, respectively. The value of E_c increases with increasing the applied electric field. There is no tendency of saturation, which may originate from the existence of point defects and electric conductance. The maximum E_i is 4.34 kV/cm at the applied electric field of 40 kV/cm. As the self-polarized state mainly forms during the paraelectric-ferroelectric phase transition around T_c , the E_c of (001) oriented 0.38BMT-0.62PT single crystals at this high temperature is much smaller than that at room temperature and the polarization switching can take place in relatively weak electric field. As a result, it's possible for E_i to be larger than E_c and then to self-pole the as-prepared sample.¹³

The internal bias field E_i was usually observed in piezoelectric materials and resulted from the orientation of the defect

dipoles.^{2, 17, 18} According to the unsaturated P - E loops and large leakage current in the poling process, we can speculate that point defects also exist in 0.38BMT-0.62PT single crystals.

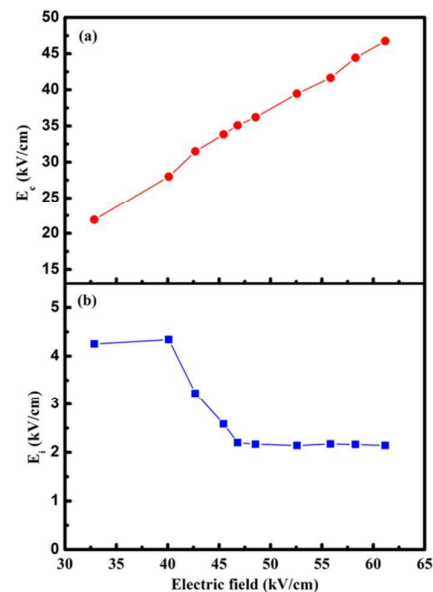


Fig. 4. Coercive field E_c and internal electric field E_i of the 0.38BMT-0.62PT single crystals with self-poling as a function of applied electric field.

Fig. 5(a) and 5(b) present the XPS spectra of O 1s of 0.38BMT-0.62PT single crystal before and after sputtering, respectively. For the sputtering sample, the surface of the single crystal was sputtering by argon ion beam about 1 min. Both of the two spectra exhibit a shoulder in the higher binding energy region. The peak at lower binding energy has been attributed to the lattice oxygen in the BMT-PT structure. The other peak at higher binding energy does not follow a regular variation with composition and can be related to the oxygen deficiency.¹⁹⁻²¹

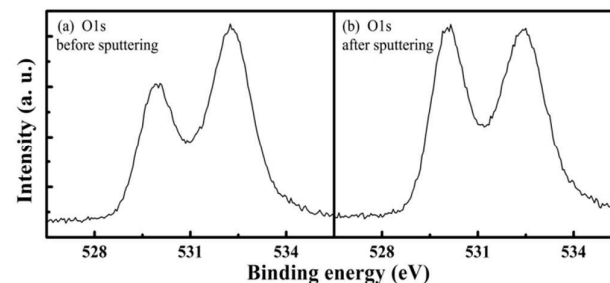


Fig. 5. The O1s spectra of 0.38BMT-0.62PT single crystal (a) before sputtering and (b) after sputtering.

Fig. 6 shows the temperature dependence of dielectric permittivity (ϵ_r) for the crystal at 100 Hz and 1000 Hz from room temperature to 710 °C. Two obvious dielectric peaks are observed. The first one at about 520 °C corresponds to the Curie temperature, which was proved by the high temperature XRD of 0.38BMT-0.62PT samples.^{1, 22} The other one is owing to the space charge polarization resulting from oxygen vacancies. The similar phenomena are frequently observed in BMT-PT ceramics.²³

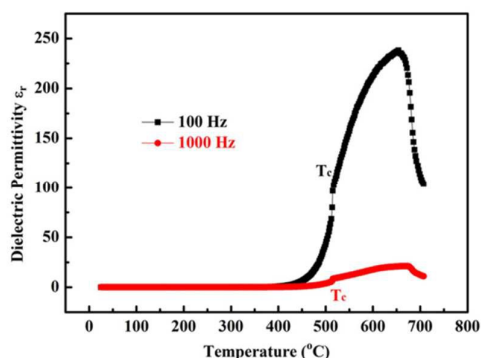


Fig. 6. Temperature dependence of the dielectric permittivity ϵ_r of the 0.38BMT-0.62PT single crystals at 100 Hz and 1000 Hz.

Due to the inevitable volatilization of Bi and Pb during the process of high-temperature single crystals growth, a corresponding amount of V_{Bi}''' and V_{Pb}'' should form. As a result, the defect dipoles in 0.38BMT-0.62PT single crystals may be $V_O''-V_{Bi}'''/V_{Pb}''$. Because V_O'' is the most mobile ionic defect in oxide perovskite, the orientation of the defect dipoles takes place via V_O'' diffusion.²⁴ However, the driving force of the diffusion of V_O'' in 0.38BMT-0.62PT single crystals is not very clear. We guess that the compositional gradient of point defects such as lead deficiency or bismuth deficiency may be one of the main reasons for the orientation of the defect dipoles in 0.38BMT-0.62PT single crystals, which is similar to the reason for the self-poling in $Pb(Zr_{0.35}Ti_{0.65})O_3$ single crystals.

With increasing electric field, the shape of $P-E$ exhibits a tendency of changing from asymmetric loops to symmetric ones and the E_i reduces gradually from 4.34 kV/cm at 40 kV/cm to 2.17 kV/cm at 48.5 kV/cm, which may be caused by the partial realignment of V_O'' and the defect dipoles relax under higher driving electric field. However, the E_i nearly remains the same value while the applied electric field increases from 48.5 kV/cm to 61 kV/cm. Maybe at the measured frequency 1Hz, only partial defect dipoles can switch by the external electric field, while the other defect dipoles remain in the original direction due to insufficient time for V_O'' to migrate.²⁵ Nevertheless, the E_i may become lower if the applied electric field is much higher or the measured frequency is much lower.

The defect dipoles also related to the good temperature-stable piezoelectric properties. The defect dipoles can pin on the ferroelectric domains, stabilize the domain configuration and reduce domain wall mobility.^{2, 17} So the piezoelectric properties of the (001) oriented 0.38BMT-0.62PT single crystals are very stable from 25 °C to T_c . At the annealing temperature above the T_c , 0.38BMT-0.62PT single crystal transforms from ferroelectric phase to paraelectric phase. However, in the successive cooling process, because the E_i caused by oriented defect dipoles still exists and repolarizes the sample when the temperature falls below the T_c and the piezoelectric performance self restores almost completely (for unpoled samples) or mostly (for poled samples) as illustrated in Fig.1. It means that the piezoelectric properties of the actuators and

transducers can recover at the temperature lower than the T_c if the piezoelectric properties depolarized because of the usage temperature higher than the T_c . This is very important for the piezoelectric devices used in high temperature environment.

Conclusions

The peculiar temperature-stable piezoelectric performance and strong self-poling effect was observed in 0.38BMT-0.62PT single crystals for the first time. The piezoelectric coefficient d_{33} of the as-prepared sample is 158 pC/N and as high as 75% of the magnitude produced by an external electric field. The hysteresis loops are strongly asymmetric with the developing of an internal electric field. The value of E_i is 4.34 kV/cm at the applied electric field of 40 kV/cm. The defect dipoles pin on the ferroelectric domains and stabilize the piezoelectric properties. The value of d_{33} at room temperature almost unchanged in the heat treatment temperature range from 25 °C to 800 °C. The unique self-poling phenomenon found in BMT-PT crystals suggests that the thermal depolarization properties of piezoelectric materials could be improved greatly by designing self-poling in ferroelectric materials.

Acknowledgements

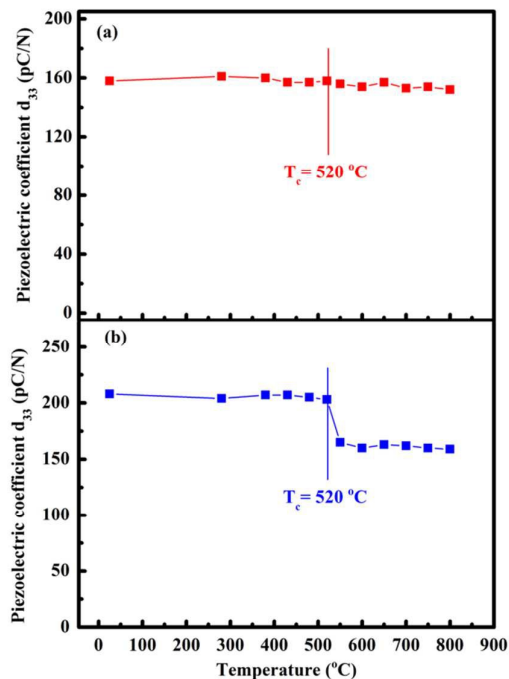
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The peculiar temperature-stable piezoelectric performance and strong self-poling effect was observed in tetragonal phase ferroelectric single crystals $0.38\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{-}0.62\text{PbTiO}_3$. The piezoelectric coefficient d_{33} of the as-prepared sample is 158 pC/N and nearly unchanged until the annealing temperature up to 800 $^{\circ}\text{C}$, which is much higher than the Curie temperature $T_c \sim 520^{\circ}\text{C}$.