Dielectric and Piezoelectric Properties of Mn-Doped Bi(Mg_{1/2}Ti_{1/2})O_3-PbTiO_3 Piezoelectric Single Crystals with MPB Composition

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Abstract: Mn-doped BMT-PT single crystals were grown using a flux method. The crystals were irregular and 4–10 mm in size. The EPMA and XRD results showed that the composition of the crystals was in the range of MPB. The room temperature dielectric permittivity $\epsilon_r$ and dielectric loss $\tan\delta$ were 806 and 3.4% at 1 kHz. As the temperature increased, the rhombohedral phase did not first transform into the tetragonal phase, but transformed into the cubic phase directly. Owing to the Mn-doping, the ferroelectric hysteresis loops of the sample were quite narrow. The Curie temperature $T_c$, piezoelectric coefficient $d_{33}$ and thickness electromechanical coupling factor $k_t$ of the single crystals along the <001> direction were 464 °C, 392 pC/N and 0.51, respectively. The piezoelectric properties are much better than the values of the ceramics and the undoped BMT-PT single crystals with a MPB composition.

Keywords: BMT-PT; single crystals; MPB; piezoelectric properties

1. Introduction

Great attention has been given to piezoelectric materials with high Curie temperatures ($T_c$) because both high piezoelectric performances and good temperature stability are required for applications in automotive, aerospace and related industries [1–4]. In recent years, Bi(Me)O_3-PbTiO_3 solid solutions, such as (1-x)BiScO_3-xPbTiO_3 (BS-PT) and (1-x)Bi(Mg_{1/2}Ti_{1/2})O_3-xPbTiO_3 (BMT-PT), have become a research hotspot in the area of high temperature piezoelectric materials, due to the good piezoelectric properties and high Curie temperature [5–7]. The $T_c$ and piezoelectric coefficient $d_{33}$ of BS-PT ceramics with a morphotropic phase boundary (MPB) ($x = 0.64$) composition are 450 °C and 460 pC/N [8]. While for BS-PT single crystals with a MPB composition, the $d_{33}$ of the (001) orientation is as high as 1150 pC/N with the $T_c$ of 402 °C [9]. However, the potential applications of BS-PT were limited by the high cost of the scandium sources as the major chemical constituent. By comparison, BMT-PT exhibits better potentials for high-temperature device applications because of its high $T_c$, relatively good piezoelectric properties and low cost.

The MPB of the BMT-PT is in the range of 0.36 ≤ $x$ ≤ 0.38. The $T_c$, $d_{33}$ and planar electromechanical coupling factor $k_p$ of BMT-PT ceramics with a MPB composition are 430 °C, 225 pC/N and 0.40, respectively [6,10,11]. The temperature stability of BMT-PT is quite good [12,13], while the values of the piezoelectric properties are not very high. Due to the anisotropy, the piezoelectric properties of the single crystals with the optimal orientation are much higher than that of the ceramics. Therefore, our group carried out the growth research of BMT-PT single crystals, and the result of the tetragonal 0.38BMT-0.62PT single crystals and the 0.63BMT-0.37PT single crystals with MPB composition has

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already been reported [3,14]. The $T_c$, $d_{33}$ and electromechanical coupling factor $k_{31}$ of the 0.38BMT-0.62PT single crystals are $520 \, ^\circ C$, $208 \, \text{pC/N}$ and $0.45$, respectively. The values of the $d_{33}$ and $k_{31}$ were almost unchanged until $T_c \approx 520 \, ^\circ C$ [3]. The $T_c$ and $d_{33}$ of the 0.63BMT-0.37PT single crystals is higher than the values of ceramics with the same composition and the tetragonal single crystals. However, the dielectric loss ($\tan \delta$) of the single crystals is very large. Therefore, in the present study, we grew Mn-doped BMT-PT single crystals with a MPB composition. The dielectric, piezoelectric and ferroelectric properties are characterized here.

2. Materials and Methods

MnO$_2$ doped BMT-PT single crystals were grown using a flux method. The high-purity powders Bi$_2$O$_3$, MgO, Pb$_3$O$_4$ and TiO$_2$ were selected as starting materials. The amount of $1.0 \, \text{mol} \%$ of MnO$_2$ was added to decrease the dielectric loss. The dielectric loss of the undoped BMT-PT single crystals was $5.6 \%$. PbO and Bi$_2$O$_3$ were 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. In the process of single crystal growth, the platinum crucibles were maintained at $1200 \, ^\circ C$ for more than $10 \, \text{h}$ and then slowly cooled down to $1000 \, ^\circ C$ at a rate of $1 \, ^\circ C/\text{h}$ and finally to room temperature at a rate of $2 \, ^\circ C/\text{min}$. After completion of the growth, the crystals were detached with the platinum crucibles and immersed in acetic acid to dissolve the flux. The composition of the crystals was detected by electron probe microanalysis (EPMA, JXA-8100). The analysis of the crystal structure was performed by powder X-ray diffraction (XRD) analysis (Cu$K\alpha$, Rigaku, D/max 2550 V). To measure the electrical properties, silver paste was coated on both sides of the (001) plane with thickness of $0.6 \, \text{mm}$ and fired for $30 \, \text{min}$ at $750 \, ^\circ C$ to form electrodes. The samples were poled at $135 \, ^\circ C$ in a silicon oil bath under a DC field of $5.5 \, \text{kV/mm}$ for $30 \, \text{min}$. The dielectric properties were measured using an HP4284A LCR meter connected with a computer-controlled furnace at various temperatures ($20–680 \, ^\circ C$) and at $500 \, \text{Hz}$, $1 \, \text{kHz}$, $10 \, \text{kHz}$ and $100 \, \text{kHz}$ frequencies. The resonance–antiresonance frequency spectrum was measured using an HP4294 impedance analyzer (Hewlett-Packard, Palo Alto, CA, USA) and the $k_t$ was calculated from the values of resonance–antiresonance frequency. The $d_{33}$ was measured by a piezoelectric $d_{33} \, \text{m}$ (ZJ-4A, institute of Acoustics, Chinese Academy of Sciences, China). The polarization electric field hysteresis loops were performed simultaneously using an aixACT TF 2000 analyzer ferroelectric measuring system (aixACT Co., Aachen, Germany) under the frequency of $1 \, \text{Hz}$ at $25 \, ^\circ C$, $125 \, ^\circ C$, $150 \, ^\circ C$ and $175 \, ^\circ C$.

3. Results and Discussion

The piezoelectric properties of the crystals in the range of MPB were much better than those of other composition. The crystals with a MPB composition were grown using a flux method. The obtained Mn-doped BMT-PT single crystals, as shown in Figure 1, are dark in color and $4–10 \, \text{mm}$ in size. The color is distinguished from the fulvous color of undoped 0.38BMT-0.62PT crystals [3]. The shape of the crystals is irregular, which is quite different from the rectangular shape of the tetragonal 0.38BMT-0.62PT single crystals [3]. A few flux inclusions can be observed in some crystals. The EPMA was used to determine quantitatively the amount of the element present in the crystals. The ratio of Bi(Mg$_{1/2}$Ti$_{1/2}$)$_2$O$_5$ to PbTiO$_3$ is $0.63\pm0.37$. Consequently, the actual composition of the single crystals is Mn-doped 0.63BMT-0.37PT and it is in the range of MPB [12].

The XRD result of the powder ground from the single crystals is shown in Figure 2. It is apparent that the specimen exhibits a pure perovskite structure and no detectable traces of impurities can be observed. According to the splitting peaks at about $2\theta = 45^\circ$, the tetragonal phase obviously exists together with the rhombohedral phase in the sample from $25 \, ^\circ C$ to $400 \, ^\circ C$. Therefore, the composition of the single crystals at room temperature
is in the range of MPB. However, the peaks at about 45° change from being clearly split to being unsplit with the increasing temperature up to 550 °C, which signifies that the crystal structure of the sample undergoes a phase transition from the mixture of the tetragonal phase and the rhombohedral phase to the cubic phase. The result is consistent with the phase fields of the BMT-PT system [10]. As the temperature increases, the rhombohedral phase does not transform into the tetragonal phase first but transforms into the cubic phase directly.

![Photograph of Mn-doped BMT-PT single crystals.](image1)

**Figure 1.** Photograph of Mn-doped BMT-PT single crystals.

![High temperature XRD patterns of Mn-doped BMT-PT powder ground from the single crystals.](image2)

**Figure 2.** High temperature XRD patterns of Mn-doped BMT-PT powder ground from the single crystals.

The piezoelectric properties of the single crystals in the <001> direction are much higher than that of other directions due to the anisotropic. Therefore, the Mn-doped 0.63BMT-0.37PT single crystals for electrical properties measurements were oriented along <001> direction. Like the undoped BMT-PT ceramics and the single crystals near the MPB, the Mn-doped BMT-PT single crystals is also hard to pole. Figure 3 shows the temperature dependence of the dielectric permittivity, $\varepsilon_r$, and dielectric loss, $\tan\delta$, of the poled sample at a different frequency. The room temperature $\varepsilon_r$ and $\tan\delta$ are about 806 and 3.4% at 1 KHz.
The \( \tan \delta \) of the Mn-doped sample is much smaller than that of the undoped sample (5.6%). Two obvious dielectric peaks are observed. The first one, at about 464 \( ^\circ \)C, corresponds to the ferroelectric to paraelectric phase transition, and the \( T_c \) of the Mn-doped 0.63BMT-0.37PT single crystals is about 464 \( ^\circ \)C. This is consistent with the result of the high temperature XRD, which shows that there is a phase transition at the temperatures between 400 \( ^\circ \)C to 550 \( ^\circ \)C. The second anomaly dielectric peak at about 643 \( ^\circ \)C is related to the oxygen vacancies. Similar phenomena are frequently observed in BMT-PT samples [12,14,15]. In fact, Bidault et al. have observed that there are similar phenomena in more than 100 oxides, and they considered that this is due to the space charge polarization, resulting from oxygen vacancies [16].

![Figure 3](image-url)  
**Figure 3.** Dielectric permittivity and dielectric loss as a function of temperature at different frequency for the poled 0.63BMT-0.37PT single crystals.

The ferroelectric P-E hysteresis loops at different temperatures for the Mn-doped 0.63BMT-0.37PT single crystals measured at 1 Hz are shown in Figure 4. Compared with the undoped BMT-PT single crystal and ceramics [10,11,14], the hysteresis loops of Mn-doped BMT-PT single crystals are quite narrow. Maybe this is caused by the dopant Mn. It has been suggested that Mn\(^{4+}\) occupies the Ti\(^{4+}\) in the B-site of the perovskite structure and can be reduced to Mn\(^{2+}\) and Mn\(^{3+}\), which leads to the creation of oxygen vacancies to keep electrical neutrality [17–19]. The ferroelectric domains are pinned by the defect dipoles caused by a non-centric distribution of oxygen vacancies and dopants Mn ions [20,21]. As a result, the switching of domains becomes harder and the hysteresis loops are very difficult to broaden.

Figure 5 presents the temperature dependent of the coercive field \( E_c \) and remnant polarization \( P_r \) of the single crystal. The \( E_c \) and \( P_r \) increase with the increasing temperature in the measured temperature range. This may be due to the fact that the pinning of the ferroelectric domains becomes weak at elevated temperatures. The \( E_c \) and \( P_r \) at 25 \( ^\circ \)C are 3.03 kV/cm and 0.26 \( \mu \)C/cm\(^2\), while the \( E_c \) and \( P_r \) increase to 9.49 kV/cm and 0.91 \( \mu \)C/cm\(^2\) at 175 \( ^\circ \)C.

Table 1 shows the piezoelectric coefficient \( d_{33} \), Curie temperature \( T_c \), room temperature dielectric permittivity \( \varepsilon_r \) and dielectric loss \( \tan \delta \) comparisons of different piezoelectric materials. Due to the anisotropy, the piezoelectric properties of the Mn-doped 0.63BMT-0.37PT single crystals along the \(<001>\) direction are much higher than those of the ceramics. The \( d_{33} \) and \( k_t \) of the single crystals in the \(<001>\) direction are 392 pC/N and 0.51, respectively. The \( d_{33} \) is about 75% higher than the value of BMT-PT ceramics with a MPB composition [10] and about 23% higher than that of the undoped 0.63BMT-0.37PT single crystals. Owing to the MPB composition, the \( d_{33} \) of Mn-doped 0.63BMT-0.37PT single crystals is about 88% higher than the value of the tetragonal 0.38BMT-0.62PT single crystals [3]. Therefore, the Mn-doped 0.63BMT-0.37PT single crystals are a kind of piezoelectric material with high \( T_c \).
and good piezoelectric properties and may be suitable for high temperature transducers and actuators applications.

![Figure 4. Polarization versus electric field P-E hysteresis loops at different temperatures for the Mn-doped 0.63BMT-0.37PT single crystals measured at 1 Hz.](image)

**Figure 4.** Polarization versus electric field P-E hysteresis loops at different temperatures for the Mn-doped 0.63BMT-0.37PT single crystals measured at 1 Hz.

![Figure 5. Temperature dependence of the coercive field $E_c$ and remnant polarization $P_r$ of Mn-doped 0.63BMT-0.37PT single crystals.](image)

**Figure 5.** Temperature dependence of the coercive field $E_c$ and remnant polarization $P_r$ of Mn-doped 0.63BMT-0.37PT single crystals.

| Material                              | $d_{33}$ (pC/N) | $T_c$ (°C) | $\varepsilon_r$ | tanδ (%) | Ref.       |
|---------------------------------------|-----------------|------------|-----------------|----------|------------|
| Mn-0.63BMT-0.37PT single crystals     | 392             | 464        | 806             | 3.4      | this work  |
| 0.63BMT-0.37PT single crystals       | 320             | 460        | 542             | 5.6      | [14]       |
| 0.38BMT-0.62PT single crystals       | 208             | 520        | 108             | 0.4      | [3]        |
| 0.63BMT-0.37PT ceramics              | 225             | 430        | 1050            | 7        | [10,12]    |
| 0.36BS-0.64PT single crystals        | 1150            | 402        | 3000            | 4        | [9]        |
| 0.70PMN-0.30PT single crystals       | 1760            | 155        | 5110            | 0.39     | [4]        |
4. Conclusions

Perovskite Mn-doped 0.63BMT-0.37PT single crystals with a MPB composition were grown using a flux method. Typical crystals obtained were irregular in shape, 4–10 mm in size and dark in color. The $\varepsilon_r$ and $\tan \delta$ at room temperature were 806 and 3.4% at 1 kHz. The rhombohedral phase did not transform into the tetragonal phase first but transformed into the cubic phase directly as the temperature increased. The ferroelectric P-E hysteresis loops of the single crystals were quite narrow due to the Mn-doping. The $T_c$, $d_{33}$ and $k_i$ of the single crystals along the <001> direction were 460 °C, 392 pC/N and 0.51, respectively. Their piezoelectric properties are much better than those of ceramics with the similar composition and the undoped 0.63BMT-0.37PT single crystals. Therefore, the Mn-doped 0.63BMT-0.37PT single crystals may be suitable for high temperature transducers and actuators applications.

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