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Dielectric and piezoelectric properties of high curie temperature $0.63Bi(Mg_{1/2}Ti_{1/2})O_3$–$0.37PbTiO_3$ single crystals with morphotropic phase boundary composition

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ABSTRACT

Novel perovskite ferroelectric $0.63Bi(Mg_{1/2}Ti_{1/2})O_3$–$0.37PbTiO_3$ (0.63BMT–0.37PT) single crystals with a composition around the morphotropic phase boundary (MPB) were successfully grown by a self-flux method. They presented Curie temperature (T_c) about 460 °C and a rhombohedral to tetragonal phase transition temperature (Tr-t) 249 °C. The piezoelectric constant d_{33} for (001) oriented 0.63BMT–0.37PT single crystals reached 320pC/N, which was higher than that (208pC/N) in the tetragonal phase 0.38BMT–0.62PT crystals. The large piezoelectric constant d_{33} and high T_c make BMT–PT single crystals promising candidates used for the next generation of high performance and high temperature actuators and transducers.

1. Introduction

Since the discovery of PZT (Lead zirconate titanate) ceramics in the 1950s, they have been widely used as piezoelectric materials in the sensors and actuators due to their excellent piezoelectric performances [1–4]. However, a great demand has been raised for piezoelectric materials for usage at high temperature, especially in the aerospace, aircraft and automotive industries [5–8]. Commercially available materials are generally limited to the usage temperature of one half of the Curie temperature (T_c), approximately 150 °C for most PZT ceramics [1,9]. Recently, the Bi-based perovskite compounds and their solid solutions with lead titanate such as $BiMeO_3$–$PbTiO_3$, in which *Me* are cations with an valence of +3 (Me: Fe^{3+}, Sc^{3+}, $Ni_{1/2}Ti_{1/2}$, $Mg_{1/2}Ti_{1/2}$, and $Zn_{1/2}Ti_{1/2}$, etc.) have attracted much attention because of their high Curie temperature [10–12]. The $BiScO_3$–$PbTiO_3$ (BS–PT) ceramics with a MPB composition exhibit a high T_c (~450 °C) and excellent piezoelectric properties (d_{33}=460pC/N) [13,14]. Meanwhile for BS-PT single crystals with the composition near MPB, the d_{33} of (001) orientation samples is about 1150pC/N with the T_c of 402 °C [5,15–17]. However, the utility of BS–PT materials is seriously limited by their too high cost of Sc_2O_3 raw materials.

Compared to BS–PT system, $Bi(Mg_{1/2}Ti_{1/2})O_3$–$PbTiO_3$ (BMT–PT) ceramics near the MPB compositions exhibit relatively high T_c (~430 °C) and excellent piezoelectric properties (d_{33}=220pC/N) [12]. More important, the BMT–PT ceramics possessed lower cost. Thus, the BMT–PT system was also believed to potential high temperature piezoelectric materials.

To date, however, almost all of the investigations related to BMT–PT focused on the ceramic materials [18–20], few papers reported on the growth and properties of BMT–PT single crystals. We presented the growth and piezoelectric properties of tetragonal 0.38BMT–0.62PT crystals in the Ref. [21], however, BMT–PT crystals near their MPB composition have not been reported. In the current work, we attempt to grow BMT–PT single crystals near MPB composition and characterise their crystal structure, dielectric, piezoelectric and ferroelectric properties.

2. Experimental procedure

The 0.63BMT–0.37PT crystals were grown via the flux method. Powders of Bi_2O_3(99.999%), MgO(99.99%), TiO_2(99.99%), Pb_3O_4(99.99%) were used as the raw materials and Pb_3O_4 and Bi_2O_3 were added as a self-flux. Sintered BMT–PT materials with various ratios of flux were loaded into a platinum crucible, which was sealed completely to minimize the evaporation of the component. Then the platinum crucible was put into a large corundum crucible, which was filled with alumina powders to maintain the stability of temperature and absorb any potential leakage. The

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growth experiments were implemented in a box furnace. The materials were heated to 1180 °C and allowed to soak for 10 h, followed by different cooling rates to 200 °C. To reduce the crystal crack and the time of crystal growth, the cooling process must be slow and could be divided into several stages. The crucible was then furnace-cooled to room temperature. Once cooled, the platinum crucible was removed and the boule was immersed in hot acetic acid to dissolve the flux which surrounds the crystals.

X-ray diffraction (XRD) analysis, ranging from 10 to 80° (2θ), was performed to confirm the structure of the achievable 0.63BMT–0.37PT single crystals. For measurement of electrical properties, crystal plates with 0.6 mm in thickness were polished with Al_2O_3 powders. Silver paste was painted on the surfaces of plates and fired at 750 °C for 30 min. The dielectric constant and loss were measured as a function of temperature (30–700 °C) and frequency (1kHz–100kHz) by an Agilent E4980A LCR meter. The samples were immersed in silicon oil at 135 °C and poled in a DC field of 60 kV/cm for 30 min. The polarization vs electric field (P–E) hysteresis loop of the crystals were recorded using a ferroelectric test system (TF Analyzer 2000), and the data were collected at a maximum electric field of 5 kV/mm and at a frequency of 1 Hz. Measurements at variable temperatures were made with the samples held at certain temperature for 5 min. The piezoelectric constant d_{33} was measured using a d_{33} meter (ZJ-4A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). A heat treatment experiment was carried out to investigate the high-temperature stability of piezoelectric properties of 0.63BMT–0.37PT single crystals. The d_{33} were measured at room temperature after dwelling for 2 h of annealing at each temperature.

3. Results and discussion

3.1. Crystal morphology and phase structure analysis

The as-grown single crystals of 0.63BMT–0.37PT are shown in Fig. 1. The obtained single crystals were light yellow and translucent with 2–10 mm in size. Different from tetragonal 0.38BMT–0.62PT crystals [21], the 0.63BMT–0.37PT crystals show irregular shape instead of cubic one, which means that the BMT–PT crystals have different growth habits with the variation of solid solution composition.

The powder X-ray diffraction pattern of 0.63BMT–0.37PT crystals measured at room temperature is shown in Fig. 2a indicating a pure perovskite structure without the formation of any secondary phase while Fig. 2b shows the XRD of (001) oriented 0.63BMT–0.37PT single crystal plates. To accurately study the crystal structure of 0.63BMT–0.37PT, the splitting of (002) peaks around 45° is shown in the inset of Fig. 2a. The widened diffraction peak of (002) revealed the coexistence of rhombohedral and tetragonal phases, confirming that the composition of the grown crystals indeed falls into the MPB region. Furthermore, to determine the amount of each element quantitatively, EDS analysis measured at four different points of the crystals is performed and shown in Fig. 2c. The content of $PbTiO_3$ is calculated by the formula:

$$PbTiO_3(mol\%) = Pb(at\%)/[Pb(at\%) + Bi(at\%)]. \quad (1)$$

The average mole percent of $PbTiO_3$ was 37 mol%, which is consistent with that of BMT–PT ceramics with MPB composition, further confirming that the composition for the as-grown crystal is in the MPB region.

3.2. Dielectric properties

The temperature dependence of dielectric properties of poled 0.63BMT–0.37PT crystals at 1 kHz, 10 kHz and 100 kHz frequences are shown in Fig. 3. The dielectric constant ε_r and dielectric loss $\tan\delta$ at room temperature are about 542 and 5.6%, respectively (@1 kHz). It can be seen that there are three dielectric peaks. The first dielectric peak appears at 249 °C, which is thought to be associated with the rhombohedral to tetragonal phase transition temperature (Tr-t). The second dielectric peaks at 460 °C, corresponds to the Curie temperature (T_c). Around T_c, the obviously diffused phase transition and frequency dispersion behavior can be observed, indicating that the 0.63BMT–0.37PT single crystals belong to relaxor ferroelectrics. The origin of the relaxor behavior could be associated with the disorder that results from the simultaneous occupation of the A and B sites by two different cations [22,23]. In addition, a high temperature dielectric anomaly presented at 637 °C is ascribed to the space charge polarization caused by oxygen vacancies. Such dielectric anomaly was also observed in BMT–PT ceramics and other oxides [12,24,25]. At low frequency (1 kHz), the dielectric constant rises sharply above 637 °C, possibly because of the result of the vast space charges, which was generated in the high temperature and lack of oxygen environment for crystal growth, involving in the polarization. However, it is found that the dielectric anomaly disappears at higher frequencies (10 kHz and 100 kHz). This is because the lower

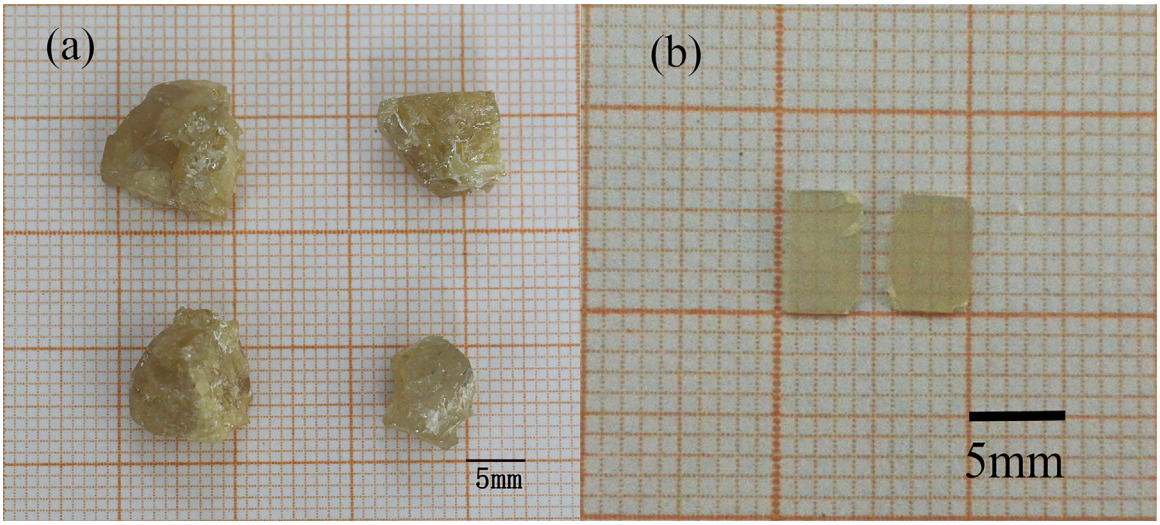

Fig. 1. (a) As-grown 0.63BMT–0.37PT single crystals and (b) (001)-cut plates.