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Quenched bismuth ferrite-barium titanate lead-free piezoelectric ceramics

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ABSTRACT

In this work, the quenched method can effectively promote the electrical properties of bismuth ferrite-barium titanate ($BiFeO_3$–$BaTiO_3$, BFO-BTO) ceramics. Here we mainly focused on the modification of the quenched methods in the $0.67Bi_{1.05}FeO_3$–$0.33BaTiO_3$ ceramics with rhombohedral-cubic phase boundary. By optimizing the preparation conditions, the ceramics possess high Curie temperature (T_C~457 °C), large piezoelectricity (d_{33}~170 pC/N), and good ferroelectricity (P_r~22 μC/cm^2). The enhanced electrical properties are mainly assigned to the quenching technique with optimized conditions. We believe that such a systematic research can point out a way for further fabricating high-performance ceramics.

1. Introduction

$BiFeO_3$ (BFO)-based ceramics were considered as one of high-temperature piezoelectric ceramics because of its good piezoelectricity (d_{33}) and a high Curie temperature (T_C) [1]. Therefore, BFO-based ceramics have recently attracted considerable attention in order to realize the enhancement of electrical properties [2–26]. Site engineering [3–7] and the addition of second members [8–15,18–21,25,26] are the main methods to promote electrical properties of BFO-based ceramics. As far as ion substitution was concerned, it is difficult to attain the saturated polarization-electric field loops and enhanced piezoelectricity (d_{33} > 50 pC/N) due to high coercive filed and large leakage current [3–7]. However, the formation of solid solutions with other ABO_3-type perovskite can greatly promote piezoelectric activity of BFO bulks, such as $BaTiO_3$ [8–15,18–20,25,26], $PbTiO_3$ [16], $SrTiO_3$ [17], and so on [28,29]. Among these material systems, $BiFeO_3$–$BaTiO_3$ has been given considerable attention due to its high T_C, relatively good d_{33}, and lead-free characteristics [8–15,18–20,25,26].

In 2000, the phase transformation of (1-x)$BiFeO_3$-$x$$BaTiO_3$ ceramics with variations of x was investigated, and a rhombohedral-cubic (R-C) phase boundary was determined at $x = 0.33$ [18]. In 2009, both high T_C (~619 °C) and large d_{33} (~116 pC/N) were reported in the Mn-modified $0.75BiFeO_3$–$0.25BaTiO_3$ ceramics [12], and however some special preparation conditions (i.e., an oxygen atmosphere, the sintering aids, etc) were required [12]. Previously, it was reported that the quenched technique can effectively promote the electrical properties of BFO-based ceramics due to the great suppression of both oxygen vacancies and Fe^{2+} [3,9,19,20]. However, there are few reports on the relationships between preparation process and electrical properties of BFO-BTO ceramics. In addition, the different preparation parameters also affect electrical properties of BFO-BTO ceramics [12,19]. Therefore, we mainly explored the influence of the quenched process on the microstructure and electrical properties of $0.67Bi_{1.05}FeO_3$–$0.33BaTiO_3$ ceramics.

In this work, the $0.67Bi_{1.05}FeO_3$–$0.33BaTiO_3$ ceramics were prepared by the quenched sintering method. Our objective is to investigate the relationships between quenched preparation parameters and electrical properties of the ceramics. The optimum electrical properties (i.e., T_C~457 °C, d_{33}~170 pC/N, and P_r~22 μC/cm^2) can be exhibited. In addition, the saturated *P-E* loops can be attained in the ceramics due to the quenching technique. The related physical mechanisms for enhanced electrical properties were also illuminated.

2. Experimental procedure

High-purity oxide powders {e.g., Bi_2O_3 (99%), Fe_2O_3 (99%), $BaCO_3$ (99%), and TiO_2 (98%)} were used to prepare $0.67Bi_{1.05}FeO_3$–$0.33BaTiO_3$ ceramics, where 5% mol of excess Bi was added to compensate for its volatility during the sintering process. All raw materials were weighted and ball milled for 24 h with

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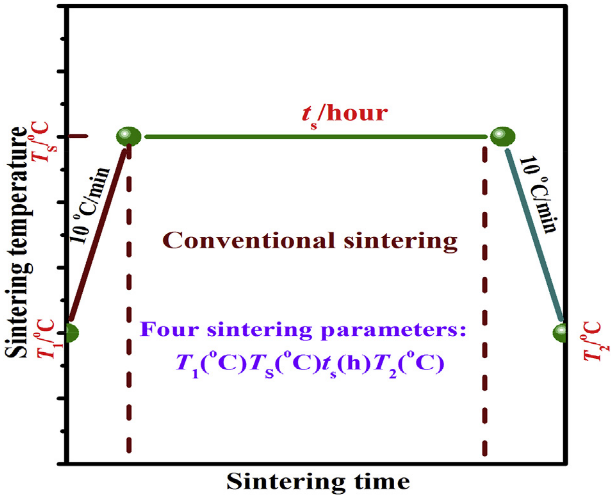

Fig. 1. The sintering sketch diagram of 0.67BFO-0.33BTO ceramics.

alcohol. After that, the mixing slurries were dried and calcined at different calcined temperatures for 2 h, and the calcined temperature is defined as T_{cal} (°C). These calcined powders were mixed with a binder of 6 wt% polyvinyl alcohol (PVA) and then were pressed into pellets with 10 mm diameter and 0.6 mm thickness under a pressure of 10 MPa. After burning off PVA at 500 °C for 3 h, the ceramics were sintered in air and then quenched in water. The sintering sketch graph is shown in Fig. 1. The initial sintering temperature, the sintering temperature, the dwell time, and the quenching temperature are defined as T_1 (°C), T_S (°C), t_S (h), and T_2 (°C), respectively. The heating and cooling rates are 10 °C/min. For characterizing electrical properties, all samples were pasted with silver plasma as electrodes and then fired at 600 °C for 10 min, and then a direct current electric field of 1–8 kV/mm was applied to the samples for 30 min in a silicon oil bath.

The phase structure of the ceramics was measured by X-ray diffraction (XRD) (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuKa). The temperature dependence of capacitance and dielectric loss were measured using an *LCR* analyzer (HP 4980, Agilent, U.S.A.) in the temperature range of 20–500 °C. The surface microstructure was characterized by the field emission-scanning electron microscopy (FE-SEM) (JSM-7500, Japan). The polarization-electric (*P*–*E*) hysteresis loops were measured by Radiant Precision Workstation (USA) at f = 100 Hz and room temperature, and d_{33} was measured by piezo-d_{33} meter (ZJ-3 A, China).

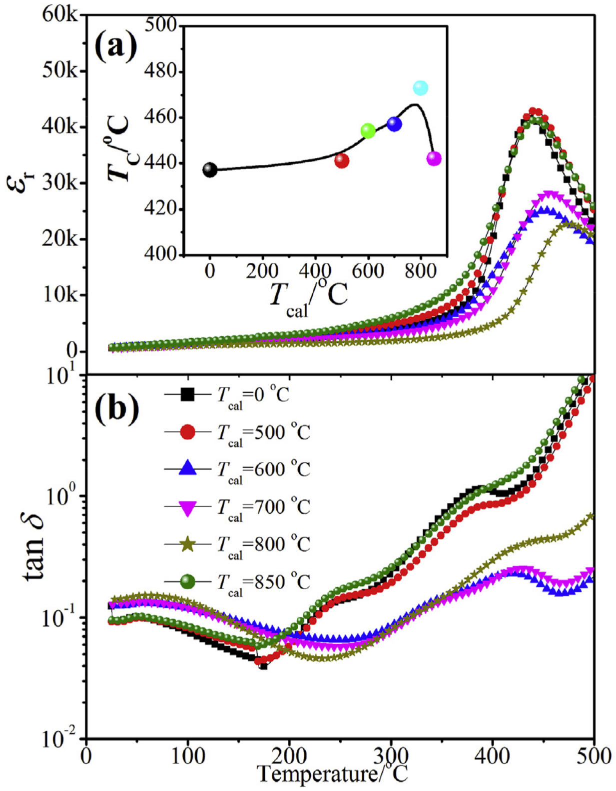

Fig. 3. Temperature dependence of (a) ε_r and (b) tan δ of the ceramics as a function of T_{cal}, and the inset in (a) is T_C against T_{cal}.

3. Results and discussion

3.1. Calcined temperature vs. properties

In this part, we mainly investigated the effects of calcined temperature (T_{cal}) on phase structure, microstructure, and electrical properties of 0.67BFO-0.33BTO ceramics, where T_1, T_S, t_s, and T_2 are respectively 700 °C, 990 °C, 3 h, and 700 °C, and the poling temperature (T_p) and poling electric field (E) are 120 °C and 2.0 kV, respectively. Fig. 2 shows the XRD patterns of the ceramics as a function of T_{cal}, measured at room temperature and 2θ = 20–70°. All samples exhibit a pure perovskite structure, indicating the formation of a stable solid solution. Previously, it was reported that the phase structure of BFO-BTO ceramics can be identified by the

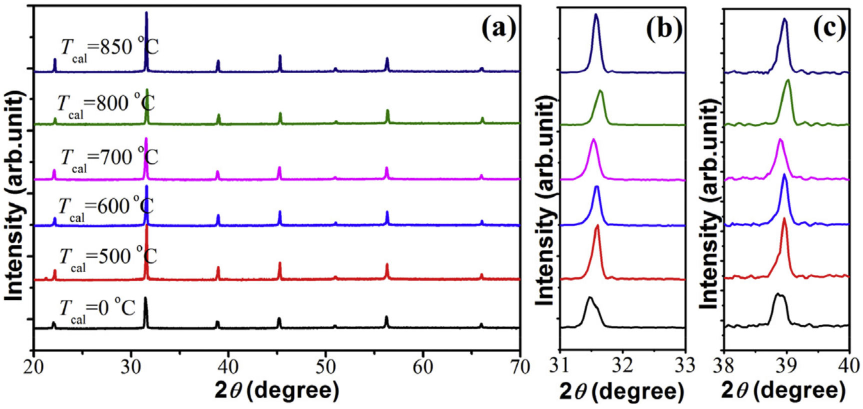

Fig. 2. XRD patterns of the ceramics with different T_{cal}, measured at (a) 2θ = 20–70°, (b) 2θ = 31–33°, and (c) 2θ = 38–40°.