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 ($\text{BiFeO}_3\text{-BaTiO}_3$, BFO-BTO) ceramics. Here we mainly focused on the modification of the quenched methods in the $0.67\text{Bi}_{1.05}\text{FeO}_3\text{-}0.33\text{BaTiO}_3$ ceramics with rhombohedral-cubic phase boundary. By optimizing the preparation conditions, the ceramics possess high Curie temperature ($T_C \sim 457^\circ\text{C}$), large piezoelectricity ($d_{33} \sim 170 \text{ pC/N}$), and good ferroelectricity ($P_r \sim 22 \mu\text{C/cm}^2$). 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.

Keywords: $\text{BiFeO}_3\text{-BaTiO}_3$; Lead-free ceramics; Quenched method; Electrical properties

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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 field 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 $(1-x)\text{BiFeO}_3$ - $x\text{BaTiO}_3$ 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 ($\sim 619^\circ\text{C}$) 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 $0.67\text{Bi}_{1.05}\text{FeO}_3\text{-}0.33\text{BaTiO}_3$ ceramics.

In this work, the $0.67\text{Bi}_{1.05}\text{FeO}_3\text{-}0.33\text{BaTiO}_3$ 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., $T_C \sim 457^\circ\text{C}$, $d_{33} \sim 170$ pC/N, and $P_r \sim 22$ $\mu\text{C}/\text{cm}^2$) 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 $0.67\text{Bi}_{1.05}\text{FeO}_3\text{-}0.33\text{BaTiO}_3$ 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 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} ($^\circ\text{C}$). 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 ($^{\circ}\text{C}$), T_s ($^{\circ}\text{C}$), t_s (h), and T_2 ($^{\circ}\text{C}$), respectively. The heating and cooling rates are $10^{\circ}\text{C}/\text{min}$. For characterizing electrical properties, all samples were pasted with silver plasma as electrodes and then fired at 600°C for 10 minutes, and then a direct current electric field of $1\sim 8\text{ kV}/\text{mm}$ 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, CuK α). 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 $20\sim 500^{\circ}\text{C}$. 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 $f=100\text{ Hz}$ and room temperature, and d_{33} was measured by piezo- d_{33} meter (ZJ-3 A, China).

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. Figure 2 shows the XRD patterns of the ceramics as a function of T_{cal} , measured at room temperature and $2\theta=20\sim 70^{\circ}$. 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

selected peaks at $2\theta=31\sim33^\circ$ and $38\sim40^\circ$ [8, 14-15, 18-19]. As shown in Fig. 2, the ceramics without calcination exhibited a rhombohedral phase due to the splitted peaks of (110) and (111). It was reported that $(1-x)\text{BFO}-x\text{BTO}$ ceramics with $x=0.33$ exhibited a morphotropic phase boundary (MPB) consisting of rhombohedral and pseudo-cubic phases [18]. As a result, the ceramics possess the R-C phase boundary as T_{cal} increases ($\geq 500^\circ\text{C}$).

Figures 3(a) and (b) show the temperature dependence of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the ceramics with different T_{cal} . As shown in Fig. 3(a), all curves have a sharp dielectric peak, which corresponds to their T_C . A higher or lower T_{cal} (0, 500, 850 $^\circ\text{C}$) can lead to a much higher $\tan \delta$ in the region of high temperatures [See Fig. 3(b)]. In addition, all samples have a similar changing trend of $\tan \delta$ with varied temperatures, that is, $\tan \delta$ decreases firstly and then increases with the increase of measurement temperatures. When the temperature reaches about 200 $^\circ\text{C}$, a lower $\tan \delta$ value can be observed in the ceramics with $T_{\text{cal}}=600\text{-}800^\circ\text{C}$. Finally, the curve of T_C against T_{cal} of the ceramics was shown in the inset of Fig. 3(a). One can find that T_C gradually increases and then decreases with rising T_{cal} , reaching a peak value for $T_{\text{cal}}=800^\circ\text{C}$. The varied T_C may be related to the composition fluctuations during calcination, especially for the loss of Bi. As a result, it is very important to choose T_{cal} for BFO-BTO ceramics.

Figure 4 shows the surface microstructure of the ceramics with $T=0, 500, 700$, and 850 $^\circ\text{C}$. We can see from Fig. 4 that a dense microstructure can be attained in all ceramics, and the grain sizes almost keep unchanged with the variations of T_{cal} , indicating that the calcined temperatures slightly affect the microstructure of the

ceramics.

Figure 5(a) shows the effect of T_{cal} on P - E loops of the ceramics, measured at room temperature and $f=100$ Hz. One can see from Fig. 5(a) that all ceramics have saturated P - E loops. Figure 5(b) shows the remnant polarization (P_r) and piezoelectricity (d_{33}) of the ceramics as a function of T_{cal} . P_r and d_{33} firstly increase and then decrease as T_{cal} rises, getting a maximum value ($P_r \sim 22 \mu\text{C}/\text{cm}^2$ and $d_{33} \sim 170 \text{ pC}/\text{N}$) for $T_{\text{cal}}=700^\circ\text{C}$. As a result, the dielectric, ferroelectric, and piezoelectric properties of BFO-BTO ceramics can be enhanced by modifying the calcined temperature.

3.2 Sintering condition vs. Electrical Properties

In this part, the effects of sintering temperature (T_s) and dwell time (t_s) on phase structure, microstructure, and electrical properties of the ceramics were systematically studied. T_{cal} , initial sintering temperature (T_1), and quenching temperature (T_2) are fixed to be 700°C , and their T_p and E are 120°C and 2.0 kV , respectively. Figure 6(a) shows the XRD patterns of the ceramics sintered for 3 h as a function of T_s , measured at room temperature and $2\theta=20\sim 70^\circ$. A pure perovskite structure can be obtained in all ceramics. As shown in Fig. 6(a), the ceramics sintered at 950°C show a splitted peak of (110) and (111), and thus the phase structure can be defined as an R phase. A mixed phases appear with the increase of T_s , as shown in the XRD patterns with $2\theta=38\sim 40^\circ$. Therefore, the R-C phase coexistence can be formed for $T_s=965\sim 1020^\circ\text{C}$. Figure 6(b) shows the XRD patterns of the ceramics sintered at 990°C under different t_s . As mentioned above, the R-C phase coexistence can be well established in the ceramics sintered at 990°C for 3 h. As shown in Fig. 6(b), t_s almost did not change the phase structure of the ceramics, indicating that a mixed phase still exists in the ceramics

with different t_s .

Figures 7(a) and (b) show the temperature dependence of ε_r and $\tan \delta$ of the ceramics sintered for 3 h under different T_s , and T_C as a function of T_s was shown in the inset of Fig. 7(a). T_C shifts to a low temperature as T_s increases up to 990 °C and then fluctuates in the vicinity of 460 °C with further increasing T_s . It was previously reported that the grain sizes of the ceramics have a close relationship with T_C , that is, the large grains can decrease T_C with respect to small grains [8, 22]. Therefore, the relationships between T_C and grain size will be discussed later. In addition, a lower $\tan \delta$ can be attained in the ceramics sintered in 965~1020 °C [See Fig. 7(b),]. Figures 7(c) and (d) show the temperature dependence of ε_r and $\tan \delta$ of the ceramics sintered at 990 °C with different t_s , and T_C as a function of t_s was shown in the inset of Fig. 7(c). A decreased T_C can be observed for $t_s=0.5-1$ h, and t_s slightly affects $\tan \delta$ [Fig. 7(d)].

Figure 8(a)-(f) shows the surface microstructure of the ceramics with different sintering temperatures and dwell time. One can observe from Fig. 8(a) that a small grain size can be observed in the ceramics with $T_s=950$ °C. It can be found that the ceramics have the larger grain sizes with the increase of T_s [Fig. 8(b)]. In this work, the decreased T_C of the ceramics with $T_s=950\sim 990$ °C should be due to the large grain sizes [8]. In addition, one can see from Figs. 8(b) and (c) that the grain sizes of the ceramics sintered at 990 °C and 1020 °C almost keep unchanged, which results in the slight changes of T_C . The ceramics show a similar changing trend of grain sizes under different sintering temperatures [See Figs. 8(a)~(f)]. A poor microstructure can be found in the ceramics sintered at 990 °C for 0.5 h, and thus a higher T_C may be due to the presence of small grains [8]. However, the grains melt together when t_s is

extended to 7 h. As a result, the denser microstructure together with a larger grain size can be attained when both T_S and t_s increase. Interestingly, all ceramics sintered at $T_S=990\sim1020$ °C and $t_s=3\sim7$ h have a bimodal grain size distribution, that is, large and small grains simultaneously appear in the ceramics. With the increase of T_S and t_s , the bimodal grain size distribution becomes more obviously. Previously, it was reported that an increase in the number of abnormal grains can be observed in the KNN-based ceramics doped with Na_2O with the increase of sintering temperatures, and the increased T_S reduces the critical driving force needed for rapid grain growth and thus increases the number of abnormal grains [23-25].

Figures 9(a) and (b) show the P - E loops of the ceramics as a function of T_S and t_s . All samples show the typical P - E loops. In order to show the variations of ferroelectricity and piezoelectricity with different T_S and t_s , their P_r and d_{33} as a function of T_S and t_s were shown in Figs. 9(c) and (d). As shown in Fig. 9(c), P_r and d_{33} have a similar trend with the increase of T_S , that is, P_r and d_{33} quickly increase as T_S increases to 980 °C and then maintain a high value with further increase of T_S . Optimum ferroelectric and piezoelectric properties ($P_r\sim22$ $\mu\text{C}/\text{cm}^2$ and $d_{33}\sim170$ pC/N) can be attained in a wide T_S range of 980~1010 °C. As shown in Fig. 9(d), both P_r and d_{33} of the ceramics sintered at 990 °C increase sharply when t_s extends from 0.5 h to 1 h. After that, P_r and d_{33} have a slight increase with further increase of t_s , indicating that appropriate increase in T_S and t_s can enhance electrical properties. The changing trend of P_r and d_{33} with T_S and t_s is almost similar to other reported results [25]. Here, we explained the phenomenon about the changing trend of the ceramics with T_S and t_s . Firstly, combined with the analysis of XRD and microstructure, the ceramics sintered at 950 °C for 3 h belong to be a R phase, and moreover a loose microstructure can be found

in the ceramics sintered at 950 °C for 3 h and 990 °C for 0.5 h. As a result, the R phase and the poor microstructure are the main reason to the poor electrical properties. In addition, the ceramics with 965~1020 °C and 1~7 h possess the R-C phase coexistence together with a dense microstructure, thus leading to the enhanced electrical properties. Secondly, it was reported that the grain sizes can greatly affect the extrinsic contributions to the piezoelectric performance [26-27]. The domain mobility and reorientation can be limited by a strong coupling between domain walls and grain boundaries in the ceramics with small grain sizes, resulting in lower degree of polarization and poorer piezoelectric response [26, 27]. As a result, these factors (phase boundary, dense microstructure, and large grain size) can totally lead to the enhancement of electrical properties of this work.

3.3 Quenching technique vs. Electrical Properties

For BFO-based ceramics, the quenching technique is used to prepare the ceramics with excellent electrical properties [3, 9, 19-20]. However, there is almost no detailed exploration about quenching technique. Therefore, we systematically investigated the effects of quenching technique on phase structure, microstructure, and electrical properties of 0.67BFO-0.33BTO ceramics. T_{cal} , T_s , and t_s are 700 °C, 700 °C, and 3 h, respectively. The ceramics were sintered at RT-990-RT with a slow heating rate of 3 °C/min (non-quenched) for comparison. The XRD patterns of the ceramics with different initial sintering temperature (T_1) and quenching temperature (T_2) were shown in Figs. 10 (a) and (b), measured at room temperature and $2\theta=20\sim70^\circ$. As shown in Fig. 10, a pure structure can be observed in all ceramics. One can find that the variations of T_1 and T_2 cannot induce the changes of phase structure, and thus all ceramics are still R-C mixed phases.

Figures 11(a) and (b) show the temperature dependence of ε_r and $\tan \delta$ with different T_1 , measured at $f=100$ kHz, and T_C as a function of T_1 was shown in the inset of Fig. 11(a). Figures 11(c) and (d) show the temperature dependence of ε_r and $\tan \delta$ with different T_2 , measured at $f=100$ kHz, and T_C as a function of T_2 can be found in the inset of Fig. 11(c). As shown in Fig. 11(b), a much worse dielectric behavior can be observed in the ceramics with $T_1=RT$ or $RT-990-RT$, showing that it is an useful way to reduce $\tan \delta$ in the high-temperature region by choosing higher T_1 and T_2 . T_C is almost dependent on T_1 and T_2 , while the dielectric peak of the ceramics with $RT-990-RT$ shifts to a low temperature, as shown in Fig. 11(a). Therefore, the conventional solid-state method results in the composition fluctuations and thus T_C reduced.

Figures 12(a)-(f) show the surface microstructure of the ceramics with different quenched processes. All samples show a dense microstructure, and a bimodal grain size distribution can be found in the ceramics processed by the quenched method [Figs. 12(a)~(e)]. However, a uniform grain size distribution can be observed in the ceramics by the normal sintering method, as shown in Fig. 12(f). As a result, the formation of bimodal grain size distribution is also partly due to the quenched process.

Figures 13(a) and (b) show the P - E loops of the ceramics with different T_1 and T_2 . All ceramics sintered by the quenched method exhibit the saturated P - E loops, while a roundish P - E loop can be observed in the ceramics with $RT-990-RT$ due to the involvement of a high leakage current, confirming that the quenched technique is an

effective method to attain the saturated P - E loops of BFO-BTO ceramics. Figures 13(c) and (d) show the effect of T_1 and T_2 on P_r and d_{33} of the ceramics. d_{33} slightly increases as both T_1 and T_2 increase, that is, higher T_1 and T_2 can slightly improve the d_{33} . In addition, the ferroelectricity treated by quenched technique can be well maintained. Some physical mechanisms have been used to unveil the improvement of piezoelectricity and ferroelectricity. The electrical properties of a piezoelectric material are related to the domain wall mobility, while the domain wall movement can be strongly prohibited by charged defects [20]. For the ceramics treated by quenched process, the disordered defect state can be freezed, and then their electrical properties can be enhanced [20]. As a result, the quenched technique is useful to promote T_C , d_{33} , and P_r of BFO-BTO ceramics.

3.4 Polarization condition vs. Electrical Properties

Poling condition (i.e., poling temperature and electric field) is very important for the improvement of piezoelectricity in a ferroelectric ceramic. In this part, we studied the effects of T_p and E on the piezoelectricity of 0.67BFO-0.33BTO ceramics, where T , T_1 , T_S , t_s , T_2 are fixed to be 700 °C, 700 °C, 990 °C, 3 h, 700 °C, respectively. Figure 14(a) shows d_{33} against T_p of the ceramics, measured at $E=2.0$ kV. We can find from Fig. 14(a) that d_{33} increases gradually with the increase of T_p , illustrating that a high T_p can benefit the polarization rotation. Figure 14(b) gives d_{33} against E of the ceramics, measured at $T_p=120$ °C. One can see from Fig. 14(b) that d_{33} increases sharply when E increases from 0.5 kV to 1.0 kV and then maintains at a relatively stable value of ~ 170 pC/N with further increase of E .

4. Conclusion

0.67Bi_{1.05}FeO₃-0.33BaTiO₃ ceramics with R-C phase boundary were fabricated by the quenched method, and the effects of preparation parameters on their phase structure, microstructure, and electrical properties were systematically investigated. High Curie temperature ($T_C \sim 457$ °C), large piezoelectricity ($d_{33} \sim 170$ pC/N), and saturated P - E loops ($P_r \sim 22$ $\mu\text{C}/\text{cm}^2$) were attained by optimizing the preparation conditions (e.g., $T_{\text{cal}} = 700$ °C, $T_s = 990$ °C, $t_s = 3$ h, $T_1 = 700$ °C, $T_2 = 700$ °C, $T_p = 120$ °C, and $E = 2.0$ kV/cm). The enhancement of electrical properties may be due to the R-C phase boundary, optimized preparation process as well as quenched technique.

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Figure captions

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

Figure 2: XRD patterns of the ceramics with different T_{cal} , measured at (a) $2\theta=20-70^\circ$, (b) $2\theta=21-23^\circ$, and (c) $2\theta=38-40^\circ$

Figure 3: Temperature dependence of (a) ϵ_r and (b) $\tan \delta$ of the ceramics as a function of T_{cal} , and the inset in (a) is T_C against T_{cal} .

Figure 4: Surface microstructure of the ceramics with different T_{cal} .

Figure 5: (a) P - E loops and (b) P_r and d_{33} of the ceramics with different T_{cal} .

Figure 6: XRD patterns of the ceramics as a function of (a) sintering temperature and (b) dwell time

Figure 7: Temperature dependence of (a) ϵ_r and (b) $\tan \delta$ of the ceramics as a function of T_s . Temperature dependence of (c) ϵ_r and (d) $\tan \delta$ of the ceramics as a function of t_s . The insets in (a) and (c) are T_C against T_s and t_s , respectively.

Figure 8: Surface microstructure of the ceramics with different T_s and t_s .

Figure 9: P - E loops of the ceramics with different (a) T_s and (b) t_s , and P_r and d_{33} of the ceramics as a function of (c) T_s and (d) t_s .

Figure 10: XRD patterns of the ceramics as a function of (a) initial sintering temperature ($T_2=700^\circ\text{C}$), and (b) quenched temperature (T_2) ($T_1=700^\circ\text{C}$).

Figure 11: Temperature dependence of (a) ϵ_r and (b) $\tan \delta$ of the ceramics as a function of initial sintering temperature (T_1) ($T_2=700^\circ\text{C}$). The temperature dependence of (c) ϵ_r and (d) $\tan \delta$ of the ceramics as a function of quenching temperature (T_2) ($T_1=700^\circ\text{C}$). The insets in (a) and (c) are T_C as a function of T_1 and T_2 , respectively.

Figure 12: Surface microstructure of the ceramics with different T_1 and T_2 .

Figure 13: P - E loops of the ceramics with different (a) T_1 and (b) T_2 , and P_r and d_{33}

of the ceramics as a function of (c) T_1 and (d) T_2 .

Figure 14: d_{33} of the ceramics as a function of (a) T_P and (b) E .

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