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Effects of grain size on domain structure and ferroelectric properties of barium zirconate titanate ceramics

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ABSTRACT

Barium zirconate titanate ($BaZr_{0.2}Ti_{0.8}O_3$, short for BZT) ceramics were prepared by conventional ceramic method, and the effect of grain size on domain structure and ferroelectric properties were studied by XRD, scanning electron microscopy (SEM) and LC material analyzer. It is found that $BaZr_{0.2}Ti_{0.8}O_3$ ceramics is of perovskite crystal structure. As the sintering time increased from 0.5 h to 2 h, 4 h and 8 h, the average grain size of BZT ceramics increased from ∼25 μm to ∼40 μm, ∼45 μm and ∼80 μm. It is shown that the grain size influences on the types of domains of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics, and 90°-domain has not been observed in large grain size sample. Moreover, domains with herribone, lamellar and "water-mark" characters are observed. The coercive electric field decreases and the remanent polarization increases as the grain size of BZT ceramics increases.

1. Introduction

Barium titanate ($BaTiO_3$) is the most common ferroelectric oxide in the perovskite ABO_3 structure. $BaTiO_3$ is widely used as a capacitor because of its high dielectric constant. In order to reduce the dielectric loss at low frequencies, SrO or ZrO_2 was used as a dopant. Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, short for BST) has high dielectric constant, low leakage current and low dielectric dispersion against frequency [1–5]. However, the leakage current often abruptly turns up in orders of magnitude as the applied field exceeds a critical value of several hundreds kV/cm, and breakdown occurs at a field around 2 MV/cm [4,5].

Barium zirconate titanate ($BaZr_xTi_{1-x}O_3$, short for BZT) has attracted immense attention for their potential applications for the microwave technology, due to their high dielectric constant, low dielectric loss, and large tunability compared with BST, because the Zr^{4+} ion (0.087 nm) is chemically more stable than the Ti^{4+} (0.068 nm) and has a larger ionic size to expand the lattice. Therefore, the conduction by electron hopping between Ti^{4+} and Ti^{3+} would be depressed by the substitution of Ti with Zr [6–13]. Ferroelectrics are characterized by ferroelectric domain. Ferroelectric properties are mainly controlled by the ferroelectric domain structures and their evolution. Therefore, study of ferroelectric domain structure is of both fundamental interest and technological importance and is expected to provide clues to modify ferroelectric properties. Many efforts, including theoretical and experimental, have been taken to study ferroelectric domain structure in the ceramics and thin films [14–16]. BZT is a new microwave ferroelectric material, its domain structures have compound effect on ferroelectric properties. But ferroelectric domain structures of BZT ceramics have not been investigated.

In this paper, the grain size effect on the domain structure and ferroelectric properties of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics were investigated.

2. Sample preparation and experimental details

$BaZr_{0.2}Ti_{0.8}O_3$ ceramics were prepared by solid-state reaction using high purity $BaCO_3$ (≥99.9%), TiO_2 (≥99.9%) and ZrO_2 (≥99.5%) powders. Stoichiometrically weighed powders were wet-milled with distilled water for 2 h, dried and calcined at 1100 °C/4 h. The calcined powders were milled and compacted into disks with a diameter of 10.0 mm and thickness of 1.0 mm disc with 20 MPa pressure and sintered at 1350 °C for 0.5–8 h.

X-ray diffraction data of BZT ceramics samples were obtained with Cu K_α radiation at 36 kV. The sintered ceramic discs were cleaned by ultrasonic cleaning to observe the ferroelectric domain and microstructure by using scanning electron microscopy (SEM, JEOL, JSM-6460LV).

In order to measure the dielectric properties, silver paste was painted on the polished samples as the electrodes and fired at

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830 °C for 15 min. The polarization–electric field (*P*–*E*) hysteresis characteristics were performed out using a Radiant Precision LC material analyzer.

3. Results and discussions

3.1. Crystal structure

Fig. 1 shows the room temperature XRD patterns of $BaZr_{0.2}Ti_{0.8}O_3$ ceramic samples sintered at 1350 °C for various sintering time. The BZT ceramic samples sintered at 1350 °C for 0.5 h, 2 h, 4 h and 8 h posses a pure perovskite structure and no secondary phase is observed. This is a clear indication that Zr^{4+} is systematically dissolved in $BaTiO_3$ lattice with homovalent substitution of Ti^{4+} (ionic radius 0.068 nm) by Zr^{4+} (ionic radius 0.079 nm) to form a homogeneous solid solution having tetragonal symmetry. (1 1 0) and (0 0 2) diffraction peak of BZT phase shifted to the lower 2θ angle region with the increase of sintering time from 0.5 h to 2 h, 4 h and 8 h. The result suggests that the larger lattice parameter of BZT is achieved in the longer sintering time. This is because that more Zr ion has diffused into the barium titanate lattice in the longer sintering time. In the XRD patterns, the reason that the (1 1 0) peak intensity diminished with the increase of the sintering time is unclear.

3.2. Domain structure

Fig. 2 shows the SEM patterns of BZT ceramics sintered for different sintering time (0.5 h, 2 h, 4 h, 8 h). By using Image Pro Plus software, the grain sizes of $BaZr_{0.2}Ti_{0.8}O_3$ ceramic samples had been determined. There was amorphous phase in BZT ceramics sintered for 0.5 h. It was too short for sintering time to crystallize. BZT ceramics sintered for 2 h, had a dense microstructure and uniform grain. The average grain size of the BZT ceramics in Fig. 2(a)–(d) were ~25 μm, ~40 μm, ~45 μm and ~80 μm, respectively. BZT ceramics sintered for 8 h had some large grains. That is to say, the grain sizes of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics increased as the sintering time increased.

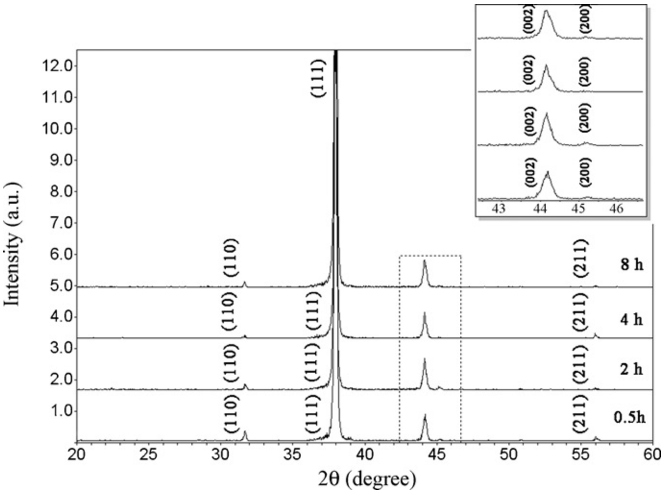

Fig. 1. XRD patterns of $BaZr_{0.2}Ti_{0.8}O_3$ ceramic sintered at 1350 °C for 0.5 h, 2 h, 4 h and 8 h, respectively.

The domain structures of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics with various grain sizes can be clearly seen from Fig. 3. 180°-Domains are observed in $BaZr_{0.2}Ti_{0.8}O_3$ ceramics samples with 25 μm, 40 μm, 45 μm and 80 μm, as indicated with circles B, E, G and I in Fig. 3(b)–(e). But 90°-domains only can be observed in samples with 25 μm, as indicated with circle C in Fig. 3(b). This means that the BZT ceramics with the large grain have no 90°-ferroelectric domains. This is because that the strain energy on the grain

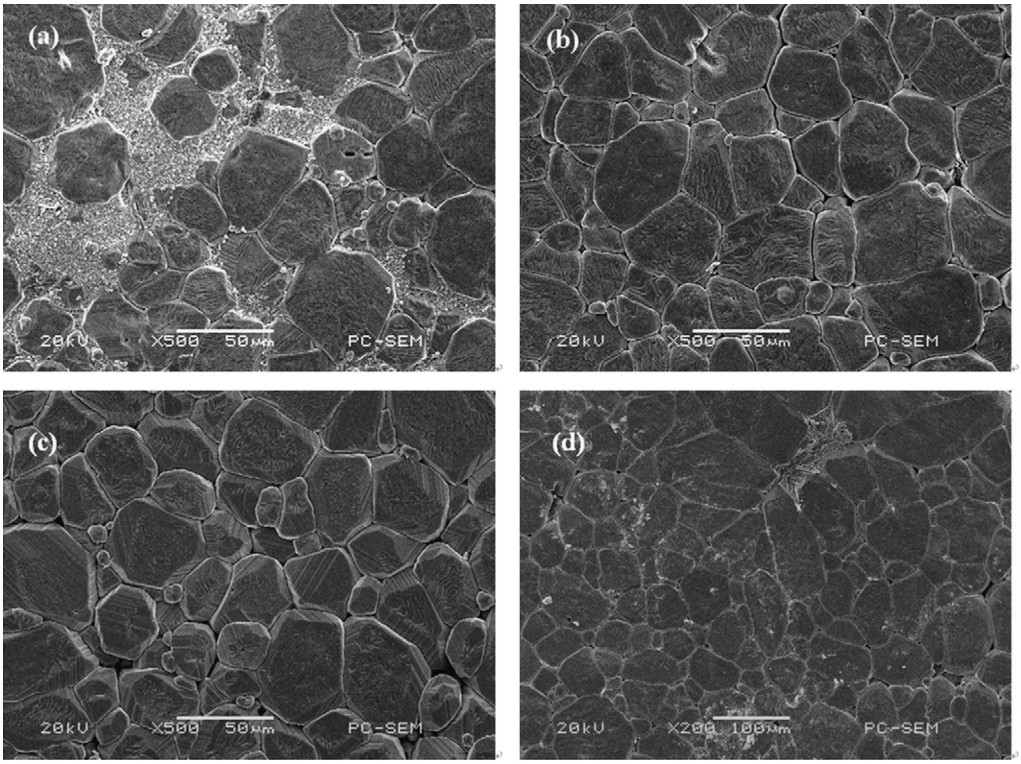

Fig. 2. Scanning electron microscopy micrographs of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics sintered at 1350 °C for: (a) 0.5 h, (b) 2 h, (c) 4 h, (d) 8 h.

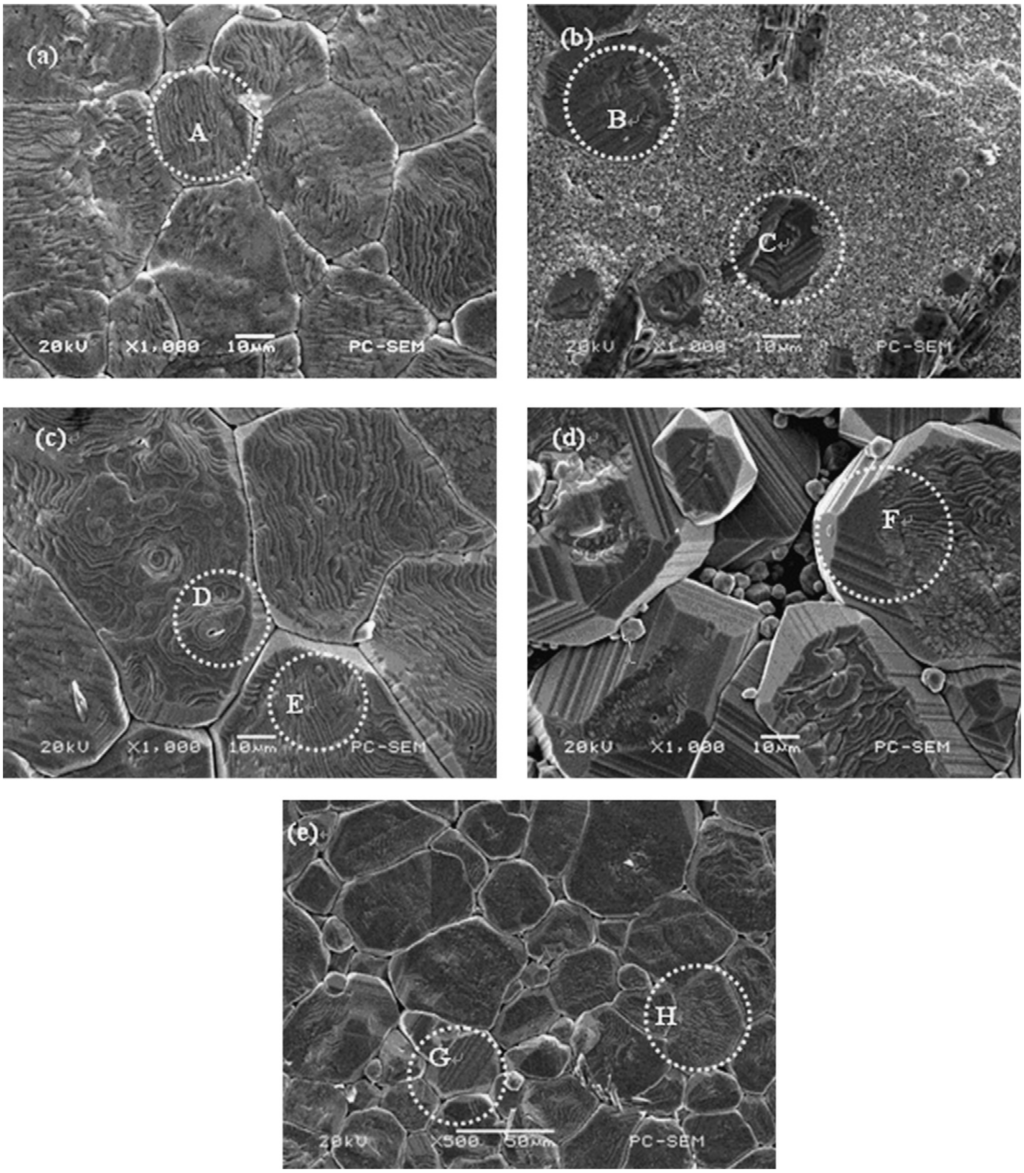

Fig. 3. Domain structures of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics with various average grain sizes: (a, b) 25 µm, (c) 40 µm, (d) 45 µm, (e) 80 µm.

boundary is higher than the grain. The strain energy of the BZT ceramics with small grain is more than that of the BZT ceramics with large grain. The depolarization energy of the BZT ceramics with large grain is primary. Therefore, the strain energy and the depolarization energy of the BZT ceramics with small grain can be reduced by forming 90°-domains and 180°-domains. However, the BZT ceramics with large grain can reduce energy by forming 180°-domains.

Domain shapes of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics include herribone, lamellar and "water-mark". Domains with herribone character are observed in $BaZr_{0.2}Ti_{0.8}O_3$ ceramics sintered for 0.5 h, as indicated with circle C in Fig. 3(b). Domains with "water-mark" character appear in $BaZr_{0.2}Ti_{0.8}O_3$ ceramics samples, as shown in circles A, E, F and H. Domains with the lamellar feature are only observed in $BaZr_{0.2}Ti_{0.8}O_3$ ceramics samples sintered for 2 h, as indicated with circle D in Fig. 3(c). It is found that sintering time (or say grain size) influence types of domain of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics, the BZT ceramics with large grain size have no 90°-domains.

3.3. *Hysteresis loop*

Fig. 4 shows the hysteresis loops of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics measured at room temperature and 1 kHz. It is found that the coercive electric (E_C) field decreases as grain size increases. Energy barrier for switching ferroelectric domain must be broken through and energy barrier decreases as grain size increases. So reversal polarization process of a ferroelectric domain is much easier inside a large grain than in a small grain[17]. Moreover, It is also found that the remanent polarization (P_r) increases with the increase of grain size of BZT ceramics. Effect of grain boundary on polarization includes two facets. On the one hand, grain boundary is a low-permittivity region. That means the grain boundary has poor ferroelectricity. Therefore, polarization of grain boundary may be little, and even none. On the other hand, space charges in grain boundary exclude polarization charge on grain surface, and depletion layer on grain surface can be formed. That results in polarization discontinuity on grain surface to form depolarization field, and polarization decreases. The number of grain boundary

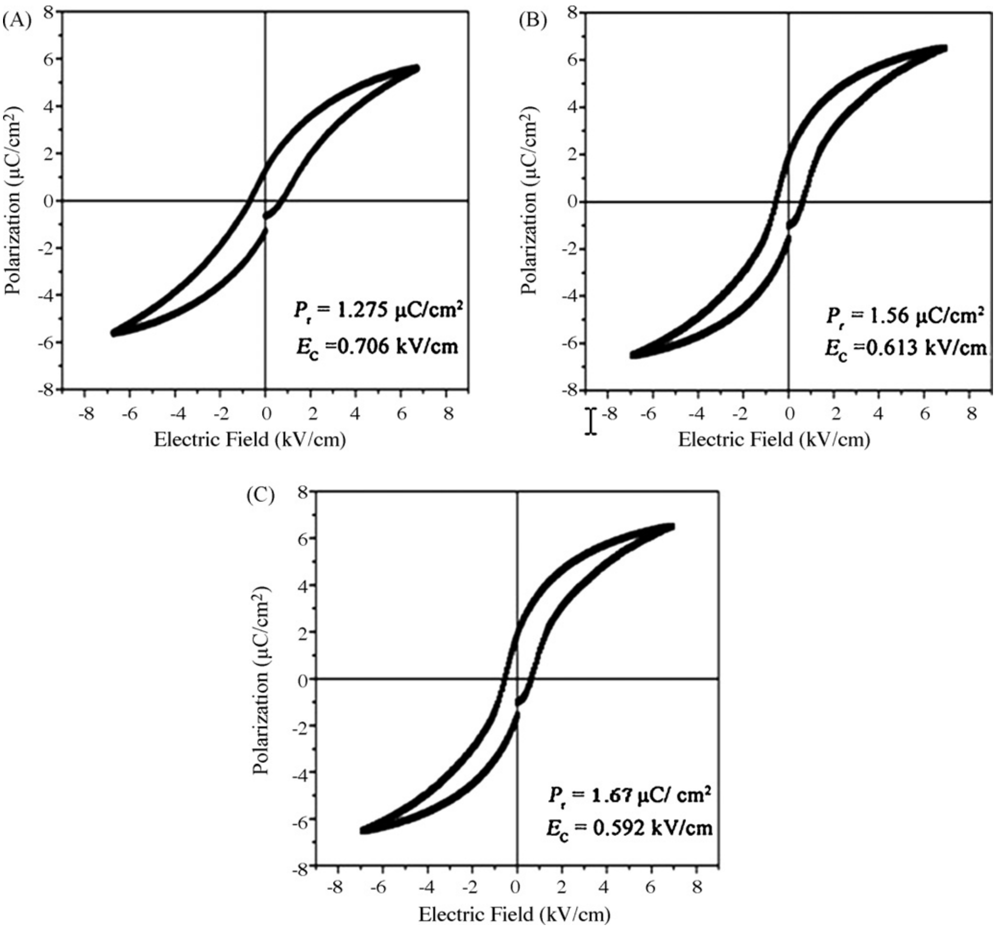

Fig. 4. Hysteresis loops of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics at room temperature and 1 kHz with grain sizes: (a) 25 μm, (b) 45 μm, (c) 80 μm.

increases as grain size decreases. Consequently, the remanent polarization increases as the grain size increases.

4. Conclusions

$BaZr_{0.2}Ti_{0.8}O_3$ ceramics with various grain sizes are fabricated via the conventional solid-state reaction method sintered at 1350 °C for various sintering time. From the results of X-ray diffraction (XRD), it is evident that BZT is of perovskite crystal structure. As the sintering time increased from 0.5 h to 2 h, 4 h and 8 h, the average grain size of BZT ceramics increased from ~25 μm to ~40 μm, ~45 μm and ~80 μm. According to SEM micrographs, it is found that sintering time (or say grain size) influence types of domain of BZT ceramics, i.e. no 90°-domains have been observed in those ceramics with large grain sizes. Domains with herribone, lamellar and “water-mark” characters are observed. From the results of hysteresis loops of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics with various grain sizes at room temperature and 1 kHz, we found that the coercive electric field decreases and the remanent polarization increases as the grain size of BZT ceramics increases.

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