

Effect of Zr⁴⁺ Content on Crystal Structure, Micromorphology and Dielectric Properties of Ba(Zr_xTi_{1-x})O₃ Ceramics

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Ba(Zr_xTi_{1-x})O₃ ceramics (X=1.5, 2.0, 2.5, 3.0) were prepared by solid-state reaction method. Effect of controlling the ratio of Zr/Ti on the crystal structure, micromorphology and dielectric properties of BZT ceramics. Their crystal structures, morphologies, and electric properties were respectively characterized using X-ray diffraction, scanning electron microscope and impedance analyzer. The X-ray diffraction patterns show that the zirconium titanate ceramic samples behave cubic phase structure and no secondary phase. The ratio of Zr/Ti has a great influence on the crystal structure, microstructure and dielectric properties. As the Zr⁴⁺ content increases, the lattice constant increases and the grain size decreases. The dielectric constant is the largest when the Zr content is 15%. As the Zr⁴⁺ content increases, the dielectric constant decreases gradually, and the Curie temperature moves toward the low temperature region.

Keywords: Barium Zirconate Titanate, Solid State Reaction, Dielectric Constant, Dielectric Loss

Introduction

Barium titanate (BTO) is a typical ferroelectric material and is widely used in multilayer ceramic capacitors (MLCC), sensors and memories due to its excellent dielectric and piezoelectric properties [1-4]. However, since the phase transition point of the cubic phase to the tetragonal phase of the material is around 120°C, the potential of the room temperature environment is limited. By modifying the BTO ceramics, the researchers have a better application prospect at room temperature. In the BTO system, most of the modification is mainly by substitution of the A site of the Ba²⁺ ion and the B site of the Ti⁴⁺ ion. Ba_{1-x}Sr_xTiO₃ (BST) material is A-site substitution of BTO ceramics, and the Curie temperature is close to room temperature when the Sr²⁺ ion content is 30%, although BST ceramics have higher dielectric constant, lower leakage current density, etc [5-8]. However, when the external electric field of the BST ceramic exceeds several hundred kilovolts per centimeter, the leakage current suddenly increases by an order of magnitude and even breaks down, thereby limiting its good application prospect. Zirconium zirconate titanate Ba (Zr_xTi_{1-x})O₃ (BZT) ceramics have larger dielectric nonlinearity and smaller dielectric loss than BST ceramics. More importantly, Zr⁴⁺ ions have larger ionic radii than Ti⁴⁺ ions. When the Ti⁴⁺ ion is replaced by Zr⁴⁺ ions, the chemical structure is more stable, so zirconium titanate (BZT) can be an ideal material to replace BST.

BZT ceramic is a solid solution of barium titanate and barium zirconate, which can be mutually dissolved in any ratio because the two are completely solid solution. In addition, as the amount of zirconium increases, the three phase transition points of -90 °C, 5 °C and 120 °C of BTO ceramics are close to each other. When the amount of zirconium reaches 15%, the three phase transition points coincide with each other, which is beneficial to dielectric [9-11]. Yan Zhang et al. prepared BZT ceramics by solid state reaction method and studied the application of BZT ceramics with Zr⁴⁺ content of 5~20% in high voltage capacitors [12]. Aditya Jain et al. reported the effect of ZnO doping on the structure, dielectric, and ferroelectric properties of BaZr_{0.1}Ti_{0.9}O₃ ceramics [13]. Zixiong sun et al. prepared BaTi_{0.95}Zr_{0.05}O₃ ceramics by hydrothermal method, and studied the effect of immersion time on grain size, dielectric and ferroelectric properties [14]. Many reports focus on the application of BZT ceramics, doping modification and improvement of preparation process. At present, there are few reports on the influence of different Zr/Ti components on the physical properties of lanthanum zirconate titanate ceramics. However, this work has the most important significance for the research and practical application of BZT ceramics.

In this paper, the effects of Zr/Ti ratio on crystal structure, grain size and dielectric properties of Ba(Zr_xTi_{1-x})O₃ (x=0.15, 2.0, 2.5, 3.0) ceramics were investigated by solid-state reaction.

Experimental procedures

Ba(Zr_xTi_{1-x})O₃ ceramics (x=0.15, 2.0, 2.5, 3.0) were prepared by a conventional solid phase reaction preparation process. The

powder raw materials for the preparation of ceramics were BaCO₃ (Alfa Aesar, 99.8%), TiO₂ (Alfa Aesar, 99.5%) and ZrO₂ (Aladdin, 99.99%). The powder raw materials were weighed according to the molar ratio, placed in a nylon ball mill jar containing agate balls, and an appropriate amount of absolute ethanol was added as a ball milling medium for planetary ball milling for 12 hours. After the ball milling, the slurry was taken out, dried at 1150°C and kept for 12 h. The calcined material was crushed in an agate mortar and ball milled again for 24 hours. After drying, 5% polyvinyl alcohol (PVA) was used as a binder for granulation. The green body having a diameter $\Phi=10$ mm and a thickness $d=1$ mm was pressed by a press under a pressure of 20 MPa. The PVA glue was discharged by heating at 600°C for 0.5 h, and the final ceramic sample was prepared by holding at 1350°C for 4 h. The prepared ceramic sample was double-sided polished and coated with silver paste, and kept at 600°C for 0.5 h to make the electrode in good contact with the sample to reduce the error in the test. The crystal structure of the BZT ceramic sample was tested by an X-ray diffractometer (Rigaku Ultima IV), and the microscopic morphology was observed by a scanning electron microscope (JSM-6390LV). The lattice constants a and c are calculated from the formula $c=(2d_{002})$ and $a = \frac{2}{\sqrt{4d_{202}^2 - d_{002}^2}}$ [15].

The density of the ceramic is determined by the Archimedes principle. Dielectric properties were measured by an impedance analyzer (Keysight E4990A), which was completed using a liquid-free physical synthesis test system (Quantum Design, PPMS). The dielectric constant is obtained by the following formula:

$$\epsilon = \frac{Cd}{\epsilon_0 A} \quad (1)$$

C is the capacitance (F), ϵ_0 is the vacuum dielectric constant (8.855×10^{-12} F/m), A is the ceramic electrode area (m²), and d is the thickness (m) of the ceramic plate capacitor.

Results and discussion

Figure 1a is an XRD pattern of a BZT ceramic sample. All the samples show a perovskite cubic phase structure with complete diffraction peaks and no second phase, indicating that Zr⁴⁺ has entered the interior of the lattice and completed the B-site substitution. Fig. 1(b) is an enlarged view of the (002) diffraction peak near 45°. It can be clearly seen from the figure that the (002) peak of the BZT-15 sample is at 44.9°, and the (002) peak position of the BZT-30 sample. At 44.6°, the position of the peak shifts to a small angle as the Zr content increases. The main reason is that the radius of the Zr⁴⁺ ion is 0.072 nm, and the radius of the Ti⁴⁺ ion is 0.0605 nm. The Zr⁴⁺ ion replaces the Ti⁴⁺ ion and causes a slight distortion of the lattice constant. As shown in Fig. 2, as the Zr content increases, the lattice constants a and c increase gradually, and the ratio of a/c remains approximately at 1, indicating that the BZT ceramics still have a cubic phase structure with increasing Zr content. Corresponding to the XRD pattern.

Fig. 3 is a SEM photograph of a BZT ceramic having different Zr/Ti compositions, and (a-d) corresponding to ceramic samples of BZT-15, BZT-20, BZT-25 and BZT-30, respectively. The microstructure of the ceramic sample can be clearly seen from the SEM photograph. The grain size is uniform and the grain boundaries are clear in the photo, indicating that the crystals of all the ceramic samples are relatively perfect. In Fig. (a), the average grain size is about 6 μm , and there are small holes in some places. First, because the BZT-15 sample grows faster in the sintering temperature zone, the grain size is larger, and the probability of defects in the grain growth process

due to grain combination and grain boundary fusion increases. Secondly, when the Zr content is low, the sinterability is poor, and small pores are formed on the surface of the crystal grains. Figure (b), along with the increase of Zr content, is conducive to the liquid phase sintering effect, the average grain distribution is more uniform and compact, the ceramic sample structure is denser, and the average grain size is 4 μm . In Figure (c), as the Zr content continues to increase, the average grain size gradually decreases. When the Zr content is 30%, the average grain size is only 2.5 μm as shown in Fig. (d). Comparing the SEM photographs of four different Zr/Ti compositions in Fig. 3(a-d), it can be clearly found that the grain size gradually decreases with the increase of Zr content. On the one hand, the Zr-O bond has higher bond energy than the Ti-O bond (Zr-O bond 776.1 kJ/mol, Ti-O bond 672.4 kJ/mol). Zr⁴⁺ replaces Ti⁴⁺ to provide higher energy with the increase of Zr⁴⁺ content. The optimum sintering temperature of BZT ceramics is increased with the Zr⁴⁺ content is increased. However, the sintering temperature of the four samples prepared in this paper is 1300 °C, so the grain size decreases with the increase of Zr content. On the other hand, grain growth mainly depends on the fusion of grain boundaries and the annexation of small grains. Zr⁴⁺ has a larger ionic radius than Ti⁴⁺, so the ion mobility decreases with the increase of Zr content, which is not conducive to the movement of grain boundaries. The grain size is reduced [16-17].

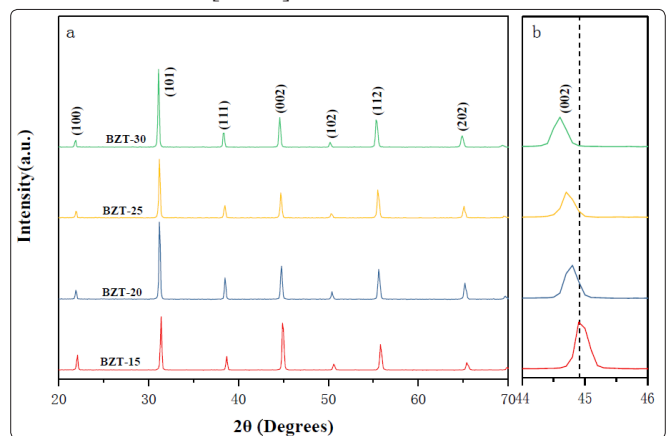


Figure 1: The XRD patterns of Ba(Zr_xTi_{1-x})₃O₃ ceramics at different Zr/Ti ratio

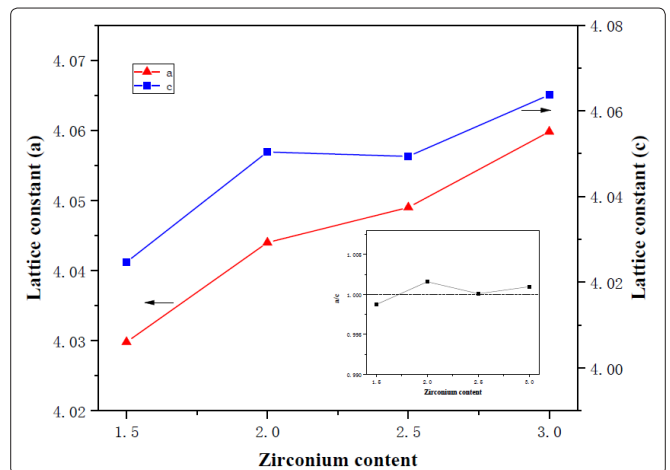


Figure 2: Lattice constant of Ba(Zr_xTi_{1-x})₃O₃ ceramics at different Zr/Ti ratios

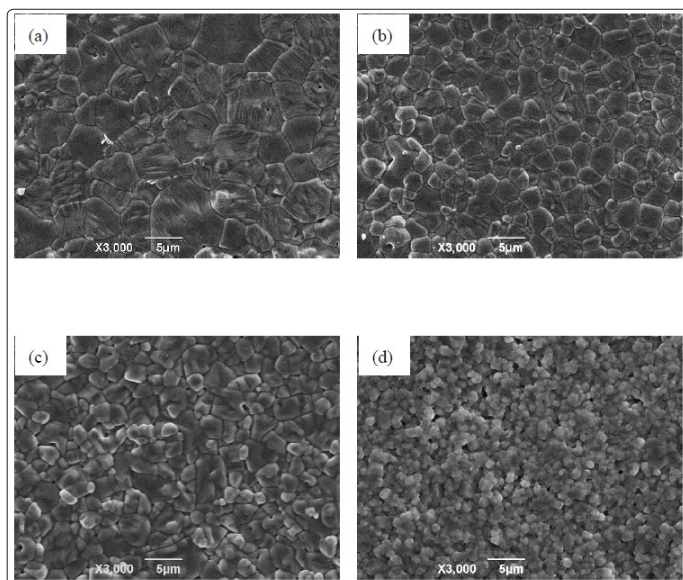


Figure 3: SEM photos of $\text{Ba}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ ceramics at different Zr/Ti ratios

Figure 4 shows the density curves of BZT ceramic samples with different zirconium contents. The densities of all BZT ceramic samples reached 97%. It can be seen from the figure that the density of the BZT-15 sample is relatively small, and the density of the BZT ceramic sample increases with increasing Zr^{4+} ion content, and decreases when the Zr content is 30%, which corresponds to the SEM photograph of Fig. 3. Due to the excessive growth of the grain during the sintering of the BZT-15 sample, the probability of defects occurring in the growth process of the grains is large, resulting in a phenomenon of low density. The decrease of the density of BZT-30 sample is due to the decrease of grain size with the increase of Zr^{4+} ion content. When the grain size is small, more grain boundaries are produced per unit volume, the grain boundary density is smaller and the defects are more, which leads to a decrease in density.

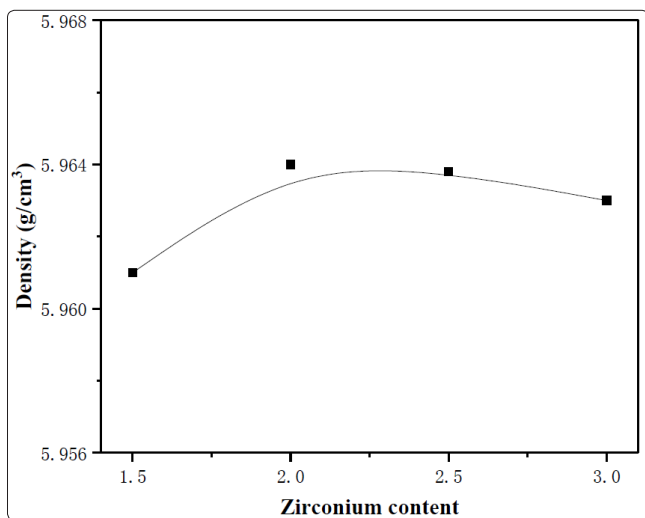


Figure 4: Density curve of $\text{Ba}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ ceramics at different Zr/Ti ratios

Figure 5 is a graph showing the dielectric constant and dielectric loss of a BZT ceramic sample with different Zr/Ti compositions

as measured by temperature at 1 kHz. The BZT-15 sample can be clearly seen in the figure. It has the best dielectric properties in all the samples. The maximum dielectric constant is 11050. It has a sharp dielectric peak. The dielectric peak gradually increases with the increase of Zr content being broadened. As shown in Fig. 6, the dielectric constant gradually decreases as the Zr content increases. On the one hand, because BZT-15 has a large grain size, the grain size decreases with the increase of Zr content, and the grain size has a large influence on the dielectric constant. Zheng Sun et al. reported that samples with larger grain sizes have better dielectric properties [18]. On the other hand, since BaZrO_3 (BZO) does not have ferroelectricity, BZT ceramics are solid solutions of BTO and BZO. As the Zr content increases, the composition of BZO gradually increases, which lowers the dielectric properties of BZT ceramics. On the other hand, there are three phase transition points in the barium titanate ceramic, which are the trigonal phase to the oblique phase, the oblique phase to the tetragonal phase, the tetragonal phase to the cubic phase, and the three phase transition points are close to each other as the Zr content increases. When the Zr content is 15%, the three phase transition points coincide with each other, and the coincident phase transition points enhance the dielectric properties.

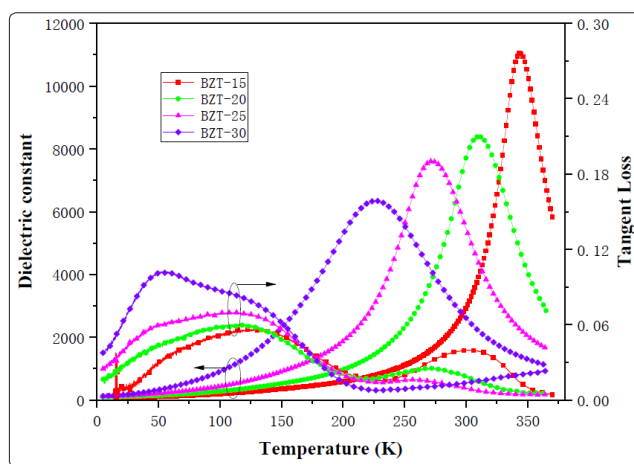


Figure 5: The dielectric constant and dielectric loss curve of $\text{Ba}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ ceramics with different Zr/Ti ratios

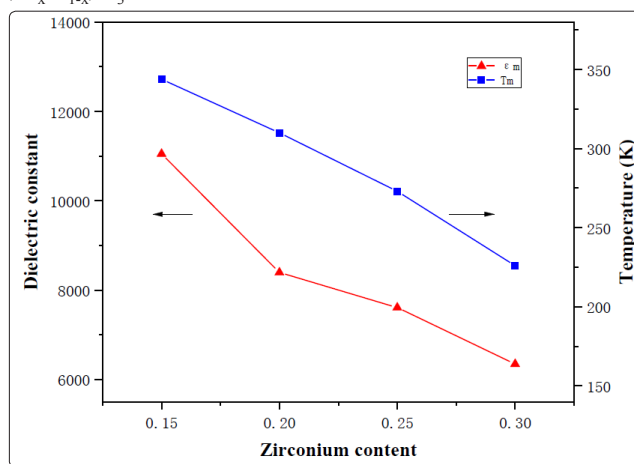


Figure 6: Maximum dielectric constant and corresponding temperature of $\text{Ba}(\text{Zr}_x \text{Ti}_{1-x})\text{O}_3$ ceramics with different Zr/Ti ratio

The Curie temperature of BZT-15 sample is 344K, and the Curie temperature of BZT-30 sample is only 226K, indicating that the Curie

temperature gradually decreases with the increase of Zr content. First, the influence of grain size on the Curie temperature decreases with the increase of Zr content. It is reported in the literature that the Curie temperature moves to the low temperature region as the grain size decreases [19]. Second, the Zr-O bond has a higher bond energy than the Ti-O bond, so there is no need to provide excessive energy during the phase transition, so the Curie temperature moves toward the low temperature region as the Zr content increases. [20] The curve of dielectric loss with temperature in Fig. 5 can be clearly seen. Two dielectric loss peaks T1 and T2 appear at 300K and 125K, and there are similar reports [21]. As the Zr content increases, both peaks move toward the low temperature zone. In addition, it can be seen that the dielectric loss T1 gradually decreases, and the dielectric loss T2 gradually increases, which may be caused by lattice distortion caused by an increase in the Zr content.

Figure 7 is a plot of dielectric constant and dielectric loss versus frequency change for BZT ceramic samples of different Zr contents at room temperature. As shown in the figure, the BZT-20 sample has the largest dielectric constant, and the dielectric constant decreases with increasing Zr content. However, in Figure 5, the BZT-15 sample has the highest dielectric constant, and the sample is only higher than the BZT-30 sample in the dielectric spectrum of Figure 7. Because the BZT-15 sample has a Curie temperature of 344K, which is much higher than room temperature, the lower polarization of the sample results in a lower dielectric constant in a room temperature environment. The Curie temperature of BZT-20 is 310K. The curve of Figure 7 is measured at room temperature, so the BZT-20 sample has the largest dielectric constant in this curve. In the curve of dielectric loss with frequency, the BZT-15 and BZT-30 samples change significantly with frequency in the low frequency region and the dielectric loss is large. The dielectric loss curve gradually stabilizes with the increase of frequency. Because in the low frequency region, the polarization of the ceramic sample is mainly composed of interfacial polarization, ion displacement polarization and electron displacement polarization. The dominant role is interfacial polarization and ion displacement polarization, and dominates in the high frequency region. The role is electronic displacement polarization and ion displacement polarization. Two samples of BZT-15 and BZT-30 were affected by frequency and high dielectric loss in the low frequency region, probably because some samples had some macro defects, but the reasons for formation were different. The sample of BZT-15 may be because the grain growth is faster and larger during the sintering process, and there may be some defects such as interlayers and bubbles in the mutual annexation of the grains and the fusion of the grain boundaries. These defects are in the polarization process. More space charge and internal energy are generated. These factors are the main reason for the large dielectric loss of BZT-15 samples in the low frequency region. The main reason why the sample of BZT-30 is affected by the low frequency is that the grain size of the sample is small, while the smaller grain size produces more grain boundaries per unit volume, and the ferroelectricity of the grain boundary is small or not. Ferroelectricity, in addition, the probability of generating macroscopic defects in the grain boundary is large, so the dielectric loss in the low frequency region is large. The dielectric loss of the four samples gradually stabilized with increasing frequency, indicating that there are fewer defects in the crystal structure and microscopic scale, and the crystallization is more complete, corresponding to the XRD pattern.

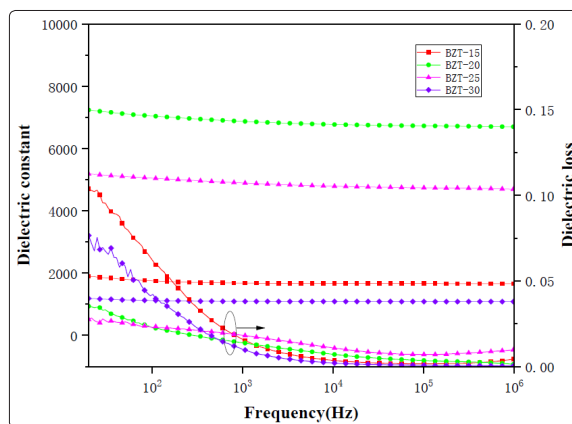


Figure 7: The dielectric constant and dielectric loss curve of $\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics with different Zr/Ti ratios measured at room temperature

Conclusions

$\text{Ba}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics ($X=1.5, 2.0, 2.5, 3.0$) were prepared by solid phase reaction at 1350°C for 4 h. The effect of the ratio of Zr/Ti on the properties of BZT ceramics was investigated by crystal structure, morphology, density and dielectric properties. The results show that when the Zr content is 15%, the dielectric constant is 11050, which is the largest in all samples, and the dielectric loss is only 0.014. With the increase of Zr content, the dielectric constant decreases and the dielectric peak is broadened, the grain size decreases, the lattice constant increases, and the Curie temperature decreases from 344K to 226K. When the amount of Zr is 20%, the Curie temperature is 310K which is closest to room temperature.

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