

EFFECT OF DOPING CaO ON DIELECTRIC PROPERTIES OF BaZr_{0.05}Ti_{0.95}O₃ CERAMICS

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CaO-doped BaZr_{0.05}Ti_{0.95}O₃ (BZT) ceramics were prepared by the conventional solid state reaction route, and the effects of CaO on phase composition, microstructure development and temperature-dependent dielectric properties were investigated. The phase composition was analyzed by XRD pattern, and the microstructures of the samples were observed by scanning electron microscopy (SEM), and their dielectric properties were measured at 1 kHz. The variation of dielectric properties at different sintering temperature was also discussed. The results of XRD test show that the main crystal phase of BZT based ceramics does not change obviously, and the perovskite structure is still present. However, with the increase of the amount of doping, some impurity phase will be produced. Microstructure analysis shows that the doping of calcium oxide to BZT can make the grain more compact and homogeneous. When BZT ceramics doped with CaO as 5 mol% and the sintering temperature is 1330 °C, the grain size is more uniform and the growth is better. With the increase of CaO contents the dielectric constant increased and reached a maximum value at 5mol%. The dielectric loss decrease with increasing CaO concentration, and the value of T_m is regularly shifted to lower temperature and broaden. Dielectric properties of doped samples were significantly modified.

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1. Introduction

In recent years, barium titanate is the most widely studied ceramic material which has excellent dielectric, piezoelectric and ferroelectric properties [1-4]. Since the perovskite lattice of barium titanate has capability to host ions of different size, it is possible to tailor the properties of this material by deliberate addition of different dopants, such as Zr⁴⁺, Sn⁴⁺ for Ti⁴⁺ and Sr²⁺ for Ba²⁺ [5]. Usually, dopant at low concentration will affect the crystal structure, grain growth and microstructural homogeneity of BaTiO₃, thereby changing the electrical properties [6]. The effects of different ions doping on dielectric relaxation and ferroelectric phase transition have been widely studied [7]. Ba (Ti_{1-x}Zr_x) O₃ (BZT) is an important system after solid solution of ferroelectric BaTiO₃ and ZrO₂. Some literatures also point out that BZT with perovskite structure can be formed by solid solution of ferroelectric BaTiO₃ (BT) with the paraelectric BaZrO₃ (BZ) [8]. Since Zr⁴⁺ has more stable chemical structure than Ti⁴⁺ in BaTiO₃ [9], it has high dielectric constant, good ferroelectricity, piezoelectricity, withstand voltage and insulation properties. It has been observed that the partial substitution of Zr⁴⁺ to Ti⁴⁺ can not only reduce the Curie temperature, but also help to stabilize the BZT lattice [7]. But the homogeneous and dense BZT ceramics is quite hard to be obtained and their sintering temperatures are usually required to be as high as 1400–1500 °C, and dielectric constant needs to be improved. These drawbacks severely restrict their practical applications [10]. Recently, several sintering aids, such as CuO, Li₂O, MnO₂, Bi₂O₃ have been used to lower the sintering temperatures of BZT ceramics [11-14]. As an additive, CaO can produce liquid phase in the sintering process, which can promote the densification and improve the dielectric properties. However, the effect of the addition of CaO on the dielectric properties of

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BZT ceramics has been seldom reported. In this article, the microstructure and dielectric properties of $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ -based ceramic materials doped with different content of CaO have been studied.

2. Experimental

$\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ samples were prepared by conventional solid state reaction route. BaCO_3 , TiO_2 and ZrO_2 powders with > 99.0% purity were used as the starting materials. The powder is weighed according to the chemical formula and ball milled for 4 hours in deionized water. Then it was dried and calcined at 1090°C for 2 hours, and obtained $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ powder. The calcined powder was broken up and mixed intimately with x mol% ($x=0, 5, 10, 15, 20, 25$) CaO. The mixture is ball milled again for 6 hours, so that the components are evenly distributed. After drying, the ceramic powders were passed through a 120-mesh sieve, mixed with 5 wt% polyvinyl alcohol (PVA) binder and then pressed into thin disks under 3 MPa pressure using an uniaxial hydraulic pressing die. The sample was sintered at the temperature of $1250\sim 1350^\circ\text{C}$, and the heating rate was $5^\circ\text{C}/\text{min}$. The two sides of the sample are coated with silver pulp and burned at 550 degrees to measure the dielectric properties of the sample.

The microstructural phase of the sample was probed by the Cu K α target X-ray diffraction (XRD, Rigaku D/ max 2500V/pc) from Japan Science and Technology. The samples were scanned by microscopic scanning electron microscopy (SEM) of Japan Hitachi S-4800 cold field emission scanning electron microscopy (SEM).

The capacitance C and the dielectric loss factor D be tested by using the Automatic LCR Meter 4225 bridge, the automatic LCR Meter 4225 bridge combined with the intelligent temperature control system was used to measure the dielectric constant of the material at 1 kHz frequency the temperature spectrum, the dielectric constant The peak temperature in the temperature spectrum is T_c [15].

Calculate the dielectric constant and dielectric loss of the sample:

$$\epsilon = \frac{14.4Ch}{\Phi^2} \quad (1)$$

$$\tan\delta = \frac{fD}{1000} \quad (2)$$

In the formula: h—the thickness of the sample (cm); Φ —the electrode diameter of the sample(cm); C—the capacitance of the sample (pF); f—test frequency; D—Dielectric loss factor.

3. Results and discussions

3.1 Effect of doping amount on crystal structure of BTZ Specimen

The results of XRD test are shown in Fig. 1 under the condition of 1330°C for 2 h sintering.

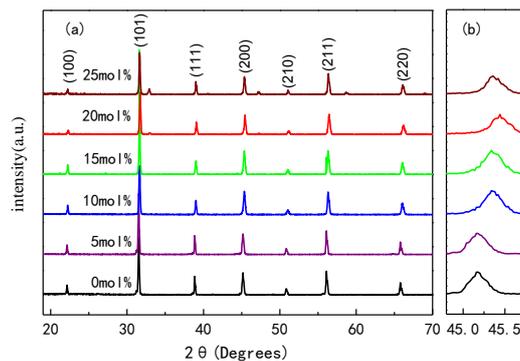


Fig. 1. XRD patterns of BZT ceramics sintered at 1330°C for 2 h.

Fig. 1(a) shows the XRD patterns in the 2θ range of $20\text{--}70^\circ$ of CaO-doped BZT ceramics sintered at 1330°C for 2 h. The XRD results demonstrate that all samples display a typical perovskite structure and the secondary phases are formed for BZT ceramics with increasing CaO content at $x=25\text{mol}\%$ within the sensitivity of XRD. Because the radius of the Ca^{2+} is smaller than the Ba^{2+} , it can enter the gap position of the crystal and form the impurity phase [16-19]. In order to make a clearer observation of the influence of the amount of doping on the diffraction peak, the (200) crystal surface in the diffraction spectrum in Fig. 1 is locally amplified. From the diagram (b), it is found that with the increase of Ca^{2+} doping amount, (200) the diffraction peak of the crystal surface moves in the direction of high angle first and then moves to the low angle. According to the Prague formula, the larger the diffraction angle, the smaller the spacing of the crystal surface is [20]. The radius of Ca^{2+} (0.1 nm) is smaller than that of Ba^{2+} (0.161 nm), and the substitution of Ca^{2+} to Ba^{2+} leads to the lattice contraction and the decrease of the space between the surfaces. Due to the limit of solid solubility of Ca^{2+} ion in the BZT matrix, with increase of the CaO concentration the Ca^{2+} gather at the grain boundary and begin to replace the ions of the B site, which leads to the expansion of the lattice and the increase of the space between the surfaces. When the doping amount of CaO is 20 mol%, the diffraction angle is the largest, and the space between the crystal surface is the smallest.

Fig. 2 (a)~(f) shows CaO doping amount of 0~25 mol% respectively. The samples were sintered at 1330°C for 2 h and doped with different amount of CaO. The image obtained by scanning with SEM is shown in Fig. 2 below:

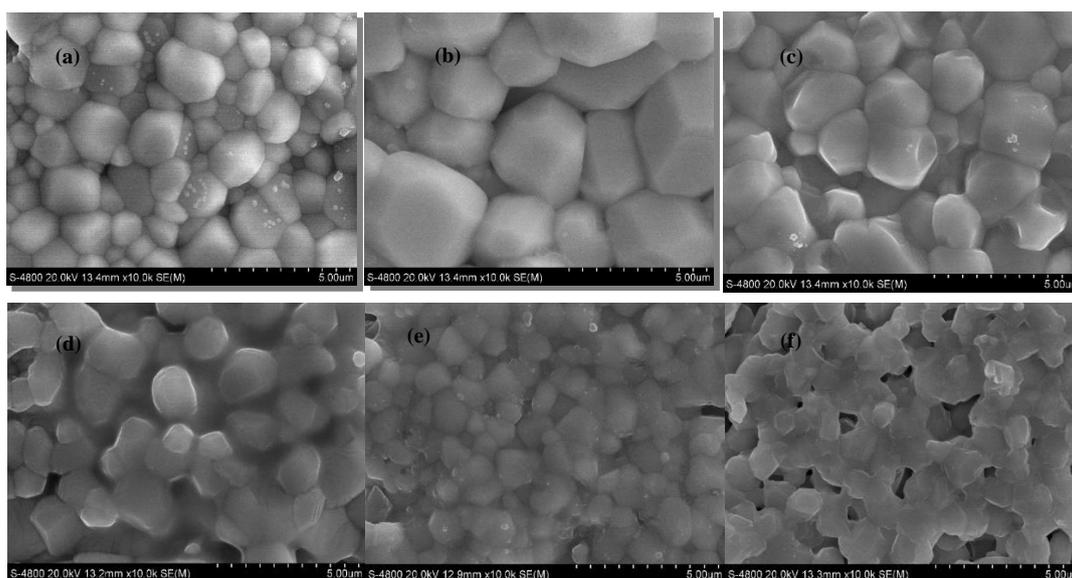


Fig. 2. SEM photomicrographs of BZT sintered at 1330°C for 2h: a-f is 0-25mol% wt CaO.

From the diagram (a) - (f), it can be seen that the grain shape of BZT ceramic specimen is clear, and the sintering density is good, and the porosity is relatively low with a clear grain boundary. Compared with (a), the grain size of (b) is larger and the shape of particles tends to be spherical, indicating that the grain growth is promoted with the addition of calcium oxide. The improvement of the microstructure of BZT ceramics is due to the liquid phase sintering of CaO. Because the grains were enclosed by liquid phase in the sintering process, the grain growth tended to be isotropic, and thus the spherical grains were developed finally and more likely to be nucleated [10]. However the excessive Ca^{2+} ion makes the pores of BZT ceramics increase and reduce the density as shown in Fig. 2(c)-(f). Because excessive Ca^{2+} ions concentrated on the grain boundary which prohibited the grain growth, and it is not easy to grow in nucleation [21,22].

3.3 Effect of CaO doping on the dielectric properties of BZT Sample

Fig. 3 shows that dielectric constant ϵ with Ca^{2+} doping and temperature changes in the situation. Fig. 4 shows that the dielectric loss of the sample at different temperatures.

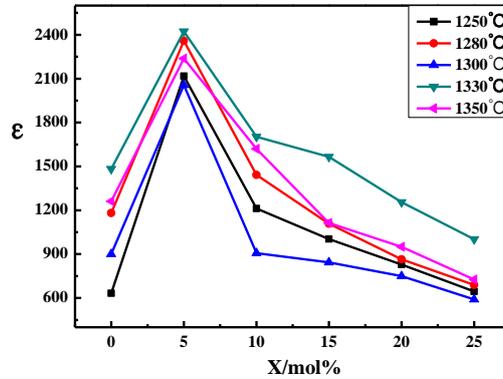


Fig. 3. Dielectric constant of CaO doped with BZT at room temperature.

As can be seen from Fig. 3, CaO can significantly reduce the sintering temperature as a sintering agent. With the addition of a small amount of CaO, the dielectric constant of the sample is increasing. When the doping amount is $x=5$ mol%, the dielectric constant of the sample reaches the maximum, and then the dielectric constant of the sample decreases. The reason is that in the initial stage, Ca^{2+} enters A position of the perovskite structure, and the radius of Ca^{2+} (0.1nm) is smaller than Ba^{2+} (0.161nm) radius, which makes lattice volume shrink as seen in the previous SEM, resulting in lattice distortion, internal stress and the increase of dielectric constant [23]. When the CaO doping amount of X exceeds 5 mol%, the Ca^{2+} limited by the solid solubility begins to enter the B position of the perovskite structure. The radius of Ca^{2+} (0.1nm) is larger than Ti^{4+} (0.065 nm) and Zr^{4+} (0.072 nm). The substitution of calcium ions for B site ions causes lattice volume expansion, so that the orientation of B ions is broken down and spontaneous polarization decline of the system, resulting in the decrease of dielectric constant. On the other hand, low valence ion substitution of high valence ions produces a part of oxygen vacancy, resulting in the effect of "pinning", which leads to the decrease of the dielectric constant of the sample.

Formula can be written as follows:

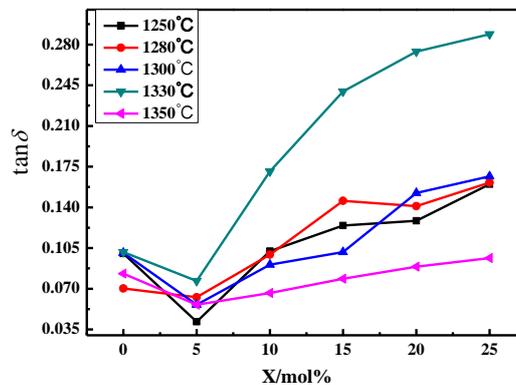


Fig. 4. Dielectric Loss of CaO doped with BZT at room temperature.

As in Fig. 4, with the increase of the amount of doping, the dielectric loss of the sample is reduced. When the doping amount is 5 mol%, the dielectric loss reaches the minimum, and then the $\tan\delta$ begins to increase. The high doping amount Ca^{2+} enters the B site to form acceptor ions, while the charge of the main ions is compensated by oxygen vacancies and suppresses the reduction of Ti^{4+} . The dielectric loss is improved. When the sintering temperature is 1330°C , the value of the dielectric constant is the highest, and the value of the dielectric loss is also low [24,25]. Therefore, when the doping amount of CaO is 5 mol% and the sintering temperature is 1330°C , the dielectric properties of the samples are the best.

The temperature of 1330°C for 2 h sintering, Fig. 5 shows that the temperature spectrum of ceramic samples. With temperature changes different Ca^{2+} content of the sample at 1 kHz have different dielectric loss.

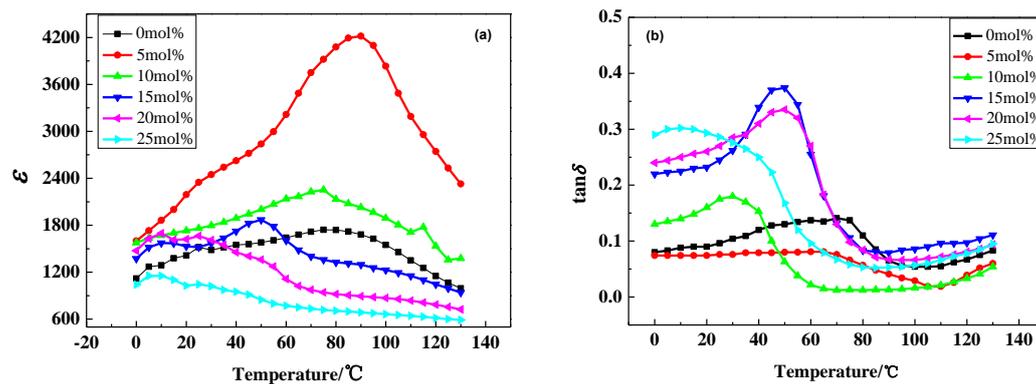


Fig. 5. Temperature dependence of the dielectric constant and tangent loss of CaO doped BZT ceramics.

The relationship between dielectric constant and temperature of BZT ceramics at the frequency of 1 kHz is shown in Fig. 5 (a) and the dielectric constant and the CaO doping at different levels. The dielectric constant of the sample increases with the increase of CaO addition, reaches the maximum at 5 mol% CaO, and then it begins to decrease. It is well known that the grain size affects the dielectric constant. Moulson and Herbert et al. reported that the increase of grain size resulted in a significant increase in the dielectric constant of barium titanate. The high grain size of 5 mol% CaO leads to high dielectric value of BZT ceramics [26]. The results are in agreement with the results of the SEM analysis in Fig. 2. On the other hand, most of the Ca^{2+} enters the A position, which enhances the ferroelectric property of the sample, and the CaO has the peak lifting effect, resulting in the increase of the dielectric peak value of the sample. When calcium ions are doped, the Curie peak has a certain movement effect in microscopic scale, moving to low temperature, and there is the role of broadening the Curie peak [16]. And the reduction of dielectric constant may be due to the formation of the impurity phase and the strengthening of calcium ions [27]. It can also be seen in Fig. 4 (b) that dielectric loss varies greatly with temperature, and too much or too little incorporation will cause thermal instability of dielectric loss. When the amount of doping is 5 mol%, the dielectric loss is relatively small and the image is gentle indicating that the dielectric loss is very stable. This is due to the formation of liquid sintering and the formation of anoxia when CaO is added. The grain boundary and various defect structures of polycrystalline ceramics are also other factors affecting the dielectric loss [28].

4. Conclusions

Barium zirconate titanate (BZT) ceramic powders were prepared by using BaCO₃, ZrO₂ and TiO₂ as raw materials and CaO as dopant material at different amounts of dopant and sintering temperature.

(1) The XRD diagram shows that the main crystalline phase of the BZT doped ceramic samples still exhibits perovskite structure, and the change of sintering temperature does not cause the structure change of the main phase. However, a small amount of impurity appears when the doping of calcium oxide exceeds the solid solubility of BZT.

(2) SEM scanning shows that the calcium doped zirconium barium titanate (BZT) ceramic pattern has clear grain profile, compact sintering and low porosity, and has a clear grain boundary. It is shown that the doping of CaO can promote the growth of grain, improve the density and uniformity of BZT ceramics. When the doping amount of Ca²⁺ ion is 5mol% and the sintering temperature is 1330 °C, the grain size is uniform and the growth is good.

(3) When the zirconium barium titanate (BZT) based ceramic samples doped with Ca²⁺, with the increase of doping amount, dielectric constant pattern increases first and then decreases; the dielectric loss decreases first and then increases, the amount of Ca²⁺ doping 5 mol%, the sintering temperature is 1330°C, the dielectric ceramic samples to achieve optimal performance. Due to the weakening of the B-O bond by adding Ca²⁺, the sintering temperature is reduced effectively, so that the Curie peak moves to a low temperature and has the role of broadening the Curie peak.

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