

Effect of different Ce_2O_3 ON the structure and properties of BZT-CT ceramics

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Barium acetate, Zirconium nitrate and Calcium nitrate, Tetrabutyl titanate and Ce_2O_3 were used as the starting materials, the $0.68 \text{ BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $0.32 \text{ Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ceramics are prepared by using sol-gel method, and effects of Ce_2O_3 content on structure, dielectric and piezoelectric properties of $0.68 \text{ BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $0.32 \text{ Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ceramics are investigated. The phase composition was detected by using X-ray diffraction characterization, and the micrographs were observed by field emission scanning electron microscopy. The results show that Ce^{3+} doped $0.68 \text{ BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $0.32 \text{ Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ceramics have perovskite structure, when the Ce^{3+} doping amount is 0.006 mol%, the density is the highest, the grain size is the most uniform, and the porosity is the smallest. With the increase of Ce^{3+} doping content, the dielectric constant and piezoelectric constant of the sample first decreases, then increases and then decreases, meanwhile the dielectric loss first decreases and then increases. Very coincidentally, when the Ce^{3+} doping amount is 0.04 mol%, the dielectric constant, piezoelectric constant and planar electromechanical coupling factor k_p are the highest. So the dielectric and piezoelectric properties of $0.68 \text{ BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $0.32 \text{ Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ceramics are optimized when the Ce^{3+} doping amount is 0.04 mol%.

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1. Introduction

$\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$ - CaTiO_3 (BZT-CT) ceramics material is a kind of lead-free piezoelectric ceramic material with excellent piezoelectric properties [1-3]. BZT-CT pseudo binary system has huge piezoelectric properties. In a narrow composition range, the structure mechanism of enhanced response can be obtained, that is, ceramics with high dielectric constant, and ceramics with flexible ferroelectric polarization and huge electromechanical properties can also be obtained [4-6]. Perovskite oxides have a variety of microstructure characteristics including high phase instability, lattice softening and microminiaturization of polar domains with low domain wall energy density.

Although BZT-CT is a good research system, it is still necessary to adjust the local or average structure, microstructure characteristics, ferroelectric phase transition type and the functional properties of BZT-CT by doping in A or B sites. It is generally believed that the variation of ferroelectric relaxor ferroelectricity (breaking the cooperative dipole long-range order formed by the off center displacement of Ti^{4+} ions in the octahedron of TiO_6) and the variation of the highest intermediate temperature of disordered $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ (BTZ) and BCTZ solid solutions are controlled by the ratio of Zr / Ti [7-10]. However, the doping of elements with different chemical valence and ionic radius on the a site may lead to structural changes at the micro and nano scale. For example, doping rare earth elements in Ba^{2+} sites (such as La^{3+} , Y^{3+} , Nd^{3+} , Eu^{3+} , Er^{3+} , Pr^{3+} , etc.) will lead to ion defects in perovskite structure and maintain electronegativity through charge compensation mechanism [11]. In addition, it is clearly proved that rare earth substituted ions with larger radius are more difficult to enter the lattice cell, and the crystal growth is more effectively inhibited than the lattice with small radius [12].

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The pseudo binary system of $(1-x) \text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 - x\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ has huge piezoelectric properties, which can be observed in the range of composition, that is, high dielectric constant, flexible ferroelectric polarization and composition are very close to the huge electromechanical coefficient of $x = 0.32$. In this paper, Ce_2O_3 is used as dopant to improve the piezoelectric properties, and the effects of Ce^{3+} content on the crystal structure, microstructure, dielectric properties and piezoelectric properties of $0.68 \text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 - 0.32\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ base ceramics were studied.

2. Experimental

Weigh raw materials according to the stoichiometric ratio. Dissolve Barium acetate, Zirconium nitrate and Calcium nitrate into 36% acetic acid, named the solution A. Tetrabutyl titanate was dissolved in ethanol and glacial acetic acid, stir evenly for 0.5 h with ice as solvent to obtain solution B; La_2O_3 was dissolved with nitric acid (water) to obtain solution C. Slowly add B and C to A, adjust the solution pH=3-4, stir evenly, mix and dissolve in the water bath, stir until the sol is formed, then gel at room temperature for 24 h. Then the gel was dried to form xerogel, and the xerogel was sintered at 920°C for 2 h, then BZT-CT powder was formed, next cooling to room temperature with the furnace. The sintering aids were added into the powder, then dried and ground, and then 5 wt% PVA was added for granulation. Under the pressure of 400 MPa, the powder was pressed into a disc with a diameter of 12 mm and a thickness of 1.4 mm. The ceramic plates were sintered at 1300°C , 1350°C , 1400°C and 1450°C , respectively. After ultrasonic cleaning, a layer of silver electrode paste was coated on both sides of the sintered ceramic sample, and the silver electrode was prepared by sintering at 550°C .

The phase composition of the samples was detected by using X-ray diffraction (XRD, RIGAKU D/MAX 2500V/PC, Japan). The micrograph of the samples was observed by field emission scanning electron microscopy (FE-SEM, Hitachi s4800). Room-temperature dielectric constant and dielectric loss were measured by using a LCR meter (Model YY 281 automatic LCR Meter 4225). The temperature dependence of the dielectric constant (ϵ) and the dielectric loss ($\tan\delta$) was measured by using a capacitance apparatus (Model YY 281 automatic LCR Meter 4225) at 1 kHz in a temperature range over 0°C to 125°C . The piezoelectric constant d_{33} of the samples was measured by a quasi-static piezo- d_{33} meter (ZJ-4 A, China) after the samples were placed for 24 h.

3. Results and discussions

The X-ray diffraction patterns of ceramic samples sintered at 1400°C for 2 h are shown in Fig. 1. As shown in Fig. 1, the characteristic peaks of (100), (110), (111) and (200), et al, for perovskite structure appear in Ce^{3+} doped BZT-CT ceramics, and no other diffraction peaks are observed, indicating that the Ce-doped ceramics are of single perovskite structure, and the doping of Ce^{3+} ions does not change the main crystal structure of the ceramics. In order to study more clearly the influence of different Ce^{3+} doping amount on diffraction peak. Fig. 2 is a local enlarged view of the X-ray diffraction pattern of the sample in the range of 44.5 - 45.5 degrees. It can be seen from the figure that with the increase of doping amount, the diffraction peak first moves to the low angle and then to the high angle. The shift of diffraction peak angle affects the distance between crystal planes, that is to say, the cell parameters of ceramic.

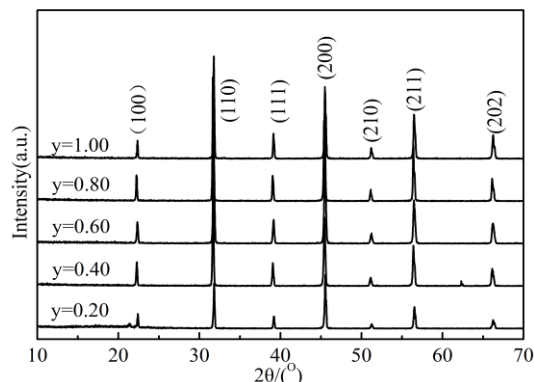


Fig. 1. XRD patterns and enlarged patterns of samples with different Ce^{3+} content.

It can also be found from Fig. 2 that the sample has a single peak at $2\theta = 45^\circ$ and a splitting peak (220) / (202) at $2\theta = 66^\circ$, respectively, which can prove that the sample is R3m rhombohedral structure. According to the principle of ion substitution, the radius of $r_{\text{Ce}^{3+}}$ is 0.114 nm (CN=12) and 0.087 nm (CN=6), $r_{\text{Ba}^{2+}} = 0.161$ nm (CN=12), $r_{\text{Ti}^{4+}} = 0.061$ nm (CN=6) [13], firstly, Ce^{3+} replaces Ba^{2+} at A site, and then replaces Ti^{4+} at B position. Because of the size difference between substituted ions, the crystal cell structure changes slightly, and the microstructure of ceramic samples changes, which eventually leads to the change of macro properties. Therefore, when Ce^{3+} occupies A or B sites, the crystal cell structure will be changed, which will affect the fine shift of diffraction peaks in different directions. It can be seen from Table 1 that the tetragonal stability of ceramic samples decreases first and then increases with the increase of Ce^{3+} content.

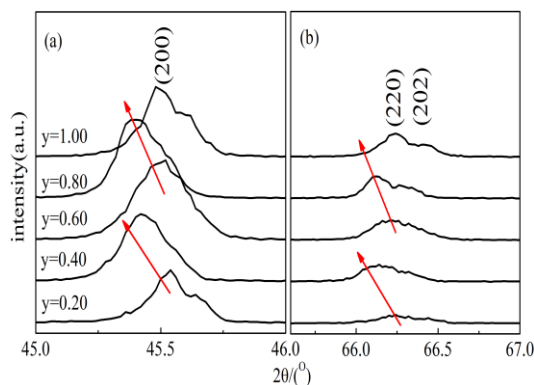


Fig. 2. Enlarged patterns of BZT-CT ceramics.

Table 1. 1 Lattice parameters of BZT-CT ceramic samples.

$x/(\text{mol}\%)$	$a/\text{\AA}$	$c/\text{\AA}$	c/a	Volume/ \AA^3
0.20	3.97327	4.01097	1.00949	63.32
0.40	3.98501	4.0089	1.00599	63.66
0.60	3.98502	3.99467	1.00242	63.44
0.80	3.98660	4.00657	1.00501	63.68
1.00	3.97778	4.00453	1.00672	63.36

Fig. 3 shows the SEM images of BZT-CT ceramics with different Ce^{3+} doping sintered at 1400°C for 2 h. As shown in the figure, with the increase of Ce^{3+} content, the grain size of the sample first increases and then decreases. The addition of a small amount of Ce^{3+} can promote the growth of grains. Ce^{3+} ions replace Ba^{2+} ions on a site, which results in lattice distortion due to the difference of radius between ions, which promotes the growth of grains. Due to the difference of ion valence among Ce^{3+} , Ba^{2+} and Ti^{4+} , in order to maintain the balance of electricity price, V_{Ba}'' and $\text{V}_{\text{O}}^{\bullet\bullet}$ will be generated, as shown in formulas (1) and (2), those defects promote the growth of grains [14]. If the doping amount is too much, small grains will be precipitated in the grains, and the cell growth will be inhibited.

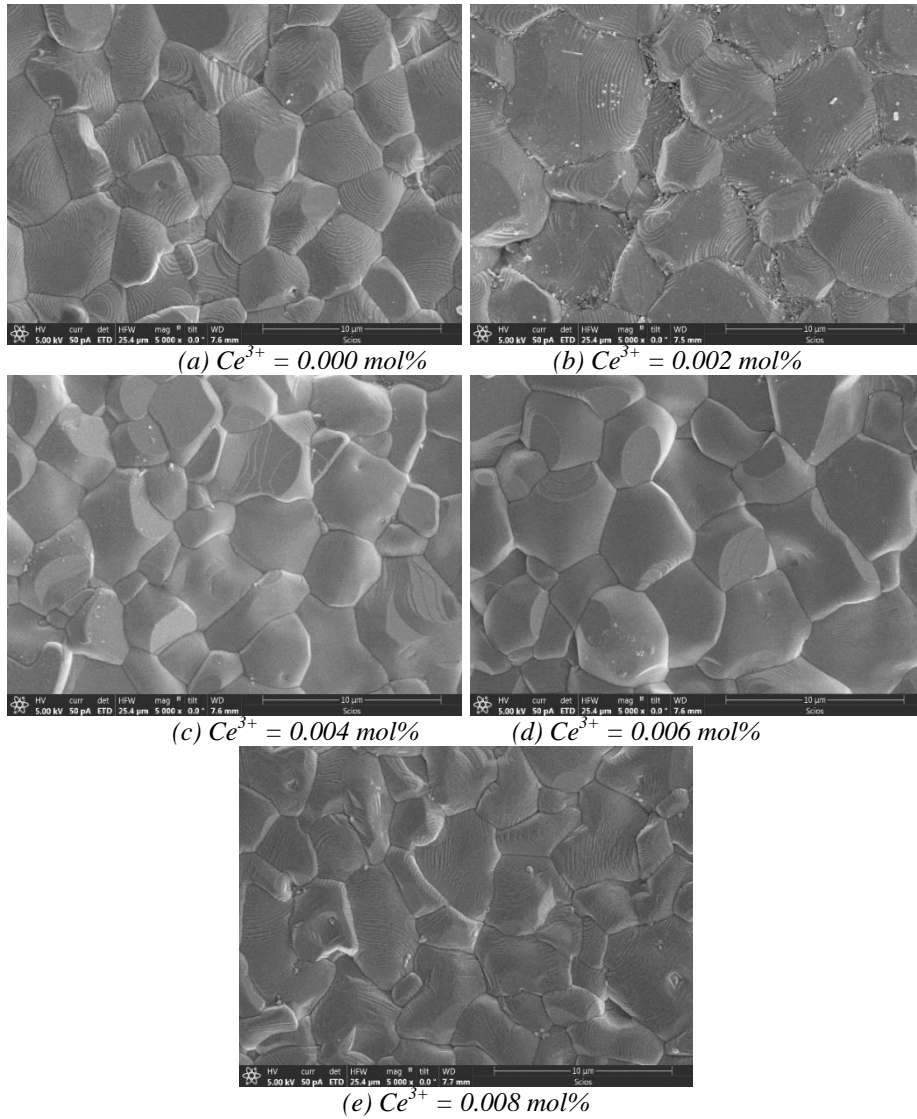
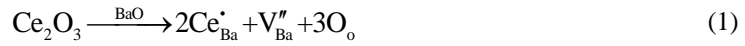


Fig. 3. SEM image of BZT-CT ceramics with different Ce^{3+} content.

The dielectric constant and dielectric loss are shown in Fig. 4 for the ceramics sintered at 1400 °C for 2 h. It can be seen from Fig. 4 that the dielectric constant of the sample is low when the doping amount of Ce^{3+} is small. When the doping amount of Ce^{3+} is increased to 0.4 mol%, the dielectric constant is 5127, meanwhile the dielectric loss is 0.01, and the dielectric loss is relatively small, afterwards, with the continuous increase of Ce^{3+} doping amount, the dielectric constant of the sample shows a downward trend. The microstructure of the sample affects the macroscopic properties of the ceramic sample, obviously, when the grain size is large, the grain boundary is relatively small, the interaction between the space fields is small, and the role of ferroelectric domain is increased, the material with good dielectric properties will be obtained, and the dielectric constant is relatively high, on the contrary, the small crystal cell, with more grain boundaries, is not conducive to the movement of ferroelectric domain, and the dielectric property is reduced.

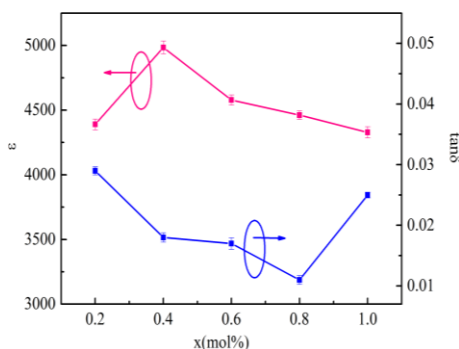


Fig. 4. Dielectric constant (ϵ) and dielectric loss ($\tan\delta$) for BZT-CT ceramics with different Ce^{3+} content.

According to the ion replacement rules, Ce^{3+} as donor element into the lattice to replace Ba^{2+} , and a small amount of Ce^{3+} can promote the growth of grains. Due to the difference of radius between ions, the lattice will be distorted, which promotes the growth of grains. Due to the difference of Ce^{3+} , Ba^{2+} and Ti^{4+} electricity prices, in order to maintain the balance of electricity prices, V_{Ba}'' and V_{O}'' will be generated, as shown in the formulas (1) and (2), thus the growth of grains is promoted and the dielectric constant is increased. When the amount of dopant exceeds the limit of solution, the growth of grains will be inhibited, resulting in the decrease of dielectric constant.

At 1 kHz test frequency, the curves of BZT-CT ceramics are shown in Fig. 5 with different Ce^{3+} doping amount sintered at 1400 °C. It can be seen from Fig. 5 that the dielectric peak of all ceramics is relatively wide, indicating that the dielectric constant is relatively stable at low temperature. With the increase of Ce^{3+} content, the dielectric peaks of the ceramic samples are gradually broadened, and the dispersion of the samples is enhanced, showing a certain dielectric relaxation property. When the doping amount is more than 0.4 mol%, the decreasing range increases, which is due to the substitution of Ce^{3+} . When the doping amount is less than 0.4 mol%, according to the ion replacement rule, Ce^{3+} replaces Ba^{2+} , and a small amount of Ce^{3+} will cause lattice distortion due to the difference of radius between ions. Due to the different electricity prices of Ce^{3+} , Ba^{2+} and Ti^{4+} , and in order to keep the balance of electricity prices, and V_{Ba}'' and V_{O}'' will be generated. Additionally, the formation of vacancy and lattice distortion promote the growth of grains, lead to the increase of dielectric constant, which has the effect of raising the peak value of dielectric. When too much Ce^{3+} is added, small grains will appear at the grain boundary, which makes the dielectric constant decrease, so the addition of cerium makes the Curie peak move and widen.

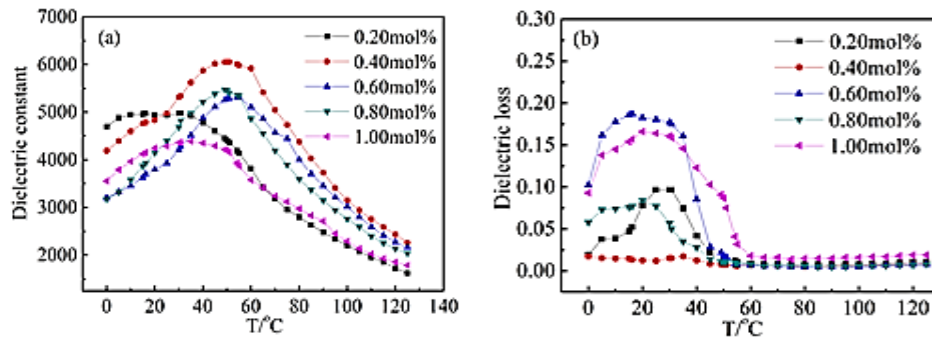


Fig. 5. Temperature dependence of the ϵ and $\tan\delta$ of BZT-CT ceramics.

The piezoelectric coefficient d_{33} and planar electromechanical coupling factor k_p are shown in Fig. 6 for the ceramics sintered at 1400 °C for 2 h at room temperature. It can be seen from Fig. 6 that the piezoelectric constant d_{33} and planar electromechanical coupling coefficient k_p of BZT-CT ceramics firstly increase and then decrease with the increase of Ce^{3+} doping amount. When $x = 0.4$ mol%, the maximum value is reached, and $d_{33} = 249$ PC / N, $k_p = 45\%$. When $x = 0.4$ mol%, the piezoelectric properties of this sample are higher than that of other samples, the grain size is larger, the grain boundary is relatively small, the interaction between space fields is relatively small, and the role of ferroelectric domain is increased, the piezoelectric properties of this sample are better than other samples. On the contrary, the smaller the cell size is, the more grain boundaries are, which is not conducive to the movement of ferroelectric domains, resulting in the reduction of piezoelectric properties. In addition, with the increase of Ce^{3+} doping amount, the size mismatch between ions will lead to the substitution deformation of oxygen octahedron, lattice distortion, local electric field and strain field, which will also improve the piezoelectric properties of the samples.

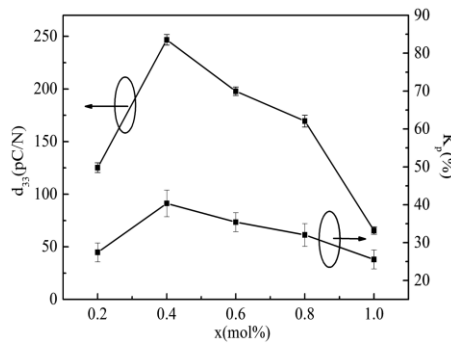


Fig. 6. d_{33} and k_p of BZT-CT ceramics with different Ce^{3+} content.

4. Conclusions

In this paper, the effects of the doping amount of Ce^{3+} on the microstructure and electrical properties of $0.68 \text{ BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ - $0.32 \text{ Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ceramics were investigated. The ternary system is still a pure perovskite structure with no impurity phase. The study determined that the optimum Ce^{3+} doping amount was 0.04 mol%. Compared with the binary system ceramics, the ceramics doped with 0.04 mol% Ce^{3+} has a denser microstructure. Thanks to the doping of Ce^{3+} ion, the dielectric constant increases from 4378 to 5127, and the piezoelectric constant 126 pC/N increased to 249 pC/N, in the same time, the planar electromechanical coupling factor k_p increased from 27% to 45%.

Acknowledgements

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