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MICROSTRUCTURE AND DIELECTRIC PROPERTIES OF Fe^{3+}-DOPED Ba(Zr, Ti)O_3 CERAMICS

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Using $BaCO_3$, ZrO_2 and TiO_2 et al as crude materials, Fe_2O_3 as dopant, $BaZr_{0.05}Ti_{0.95}O_3$ ceramics of perovskite structure were prepared by solid-state reaction method. We investigated the effects of Fe_2O_3-doping on the dielectric properties and microscope morphology Characteristics of $BaZr_{0.05}Ti_{0.95}O_3$ ceramics. The results show that: Fe_2O_3-doping have no effect on the main crystal phase of the sample, the addition of Fe_2O_3 can improve the dielectric properties and dielectric loss of $BaZr_{0.05}Ti_{0.95}O_3$ ceramics evidently, especially, when the doping amount of Fe_2O_3 is 0.5 mol%, the optimized dielectric constant is 2202 and the dielectric loss is as low as 0.013, making it a superior candidate material for applications. The curie temperature of the samples moves to room temperature with the increasing doping amount of Fe_2O_3.

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Keywords: BZT; solid state reaction; doping; dielectric properties

1. Introduction

The study of capacitor can be traced back to the 19th century, in all sorts of medium material of capacitor, ceramic capacitors occupy an important position, although other structural ceramic materials are widely used, but most of them contain lead, which is harmful to human body and the environment. Because all countries attach great importance to the control of environmental pollution, it has become an inevitable trend to develop new types of environmental friendly material. In order to meet the requirements of practical application, $BaTiO_3$ ceramics are often regulated with the purpose of improving its properties, in which the changing of formulation and preparing conditions are the main ways. [1-4] As the representative of a kind of lead-free ferroelectric materials, $BaTiO_3$ ceramics will inevitably occupy the leading position in the industry field. [5, 6]

$BaTiO_3$ ceramic materials have high dielectric constant, good piezoelectric and ferroelectric properties, it can be widely used in multilayer ceramic capacitor. [7] But the pure $BaTiO_3$ has a high Curie temperature, and the dielectric constant is low at room temperature, usually, researchers use the method of doping to change its properties. The study found that $BaZr_xTi_{1-x}O_3$ (BZT) is one of the capacitor materials with excellent performance. Because Zr^{4+} has better chemical stability than Ti^{4+}, Using Zr^{4+} to substitute Ti^{4+} (which was in B site of perovskite structure) can make BZT ceramics with high dielectric constant at room temperature. [8, 9] The radius of Zr^{4+} ion (0.072 nm) is larger than the radius of Ti^{4+} (0.061 nm), which changes the lattice constants of the material, make the phase transition temperature between tetragonal phase and

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cubic phase move to room temperature. This experiment uses conventional solid-state reaction method to prepare Fe^{3+}- doped Ba(Zr, Ti)O_3 ceramics, the results shows that: with different doping amounts of Fe^{3+}, the samples show different dielectric properties, and the dielectric properties of the ceramic samples were greatly improved.

2. Experiment

2.1. Preparation of Fe_2O_3-doped samples

The raw materials used in the experiment are: $BaCO_3$，TiO_2，ZrO_2，MgO，MnO_2，Fe_2O_3。All raw materials are analytical reagent. We use conventional solid-state reaction method to prepare Fe^{3+}-doped Ba(Zr, Ti)O_3 ceramic samples, Fe_2O_3 doping amount is 0.25mol%, 0.5mol%, 0.75mol%, 1mol%, 1.25mol% , 1.5mol%, respectively. According to the main formula, we weighed $BaCO_3$, $ZrCO_3$, TiO_2 etc as primary materials, according to primary material: ball: water = 1:1:2, mixed with deionized water ball-milling for 4 h, and then to be dried. The ball-milled raw mixture was pre-synthesised at 1100 °C for 2h, the heating rate is 5 °C / min, and then the $BaZr_{0.05}Ti_{0.95}O_3$ powers were obtained. After doping Fe_2O_3, according to regrind material: ball: water =1:1:1.5, mixed with deionized water ball-milling for 6h again, then to be dried. And then the powers of (1-x）$BaZr_{0.05}Ti_{0.95}O_3$（BZT）+xFe_2O_3（x= 0.25mol%, 0.5mol%, 0.75mol%, 1mol%, 1.25mol% , 1.5mol%）were obtained. 7%PVA solution was added into the above ball-milled material to granulate, The granulated materials were sifted on 40 mesh sieve, an then pressed into the desired form ($\Phi \times d = 13$ mm × 1.00 mm) at 150 MPa, and then sintered at different temperature from 1280℃ to 1330℃ for 2 h in the air, respectively. The heating and cooling rate is 5 °C / min, and then the ceramic samples were obtained. The samples were coated by a layer of silver at 550 °C after cleaned with ultrasonic cleaning instrument for 30min, and then to be tested.[10]

2.2. Performance Testing

In this experiment, the micrographs of the samples were observed by environmental scanning electron microscopy (SEM, Hitachi S-4800). The crystal structures of the specimens were confirmed by X-ray diffraction analysis (XRD, Rigaku D/max 2500v/pc) with Cu Kα radiation. In this experiment, we use an Automatic LCR Meter (Automatic LCR Meter 4425, Tianjin) to test the capacitance C and dielectric loss factor D. The dielectric constant - temperature spectrum of the sample was measured by LCR Meter Automatic 4225 together with the intelligent temperature control system at 1 kHz. The T_c of the sample was determined by the peak temperature of the dielectric constant - temperature spectrum. The dielectric constant and dielectric loss $tan\delta$ of the sample were calculated based on the following formulation:

$$\varepsilon_r = \frac{144Ch}{d^2} \tag{1}$$

$$\tan\delta = \frac{fD}{1000} \tag{2}$$

In the formulation : *h* - the thickness of the sample (mm); *d*- the diameter of the electrode of the sample (mm); *C* - capacitance of the sample (pF) ; *f* - test frequency; *D* - dielectric loss factor.

3. Results and discussion

3.1 XRD analysis

The X-ray diffraction (XRD) patterns of BZT ceramics sintered at 1300℃ for 2h are shown in Fig. 1. The Zr^{4+} ions can be infinitely solid dissolved in the $BaTiO_3$ crystal, the same as Ti^{4+} ions. From Fig.1 it can be seen that in the range of doping concentration, the addition of Fe_2O_3

did not result in a new phase, and the BZT ceramic samples have a perovskite structure. [11]

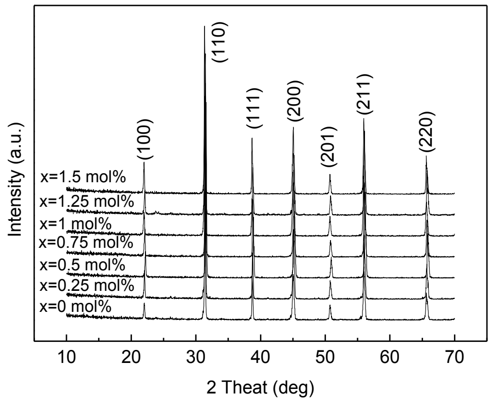


Fig.1 X-ray diffraction (XRD) patterns of BZT ceramics sintered at 1300 ℃ for 2h

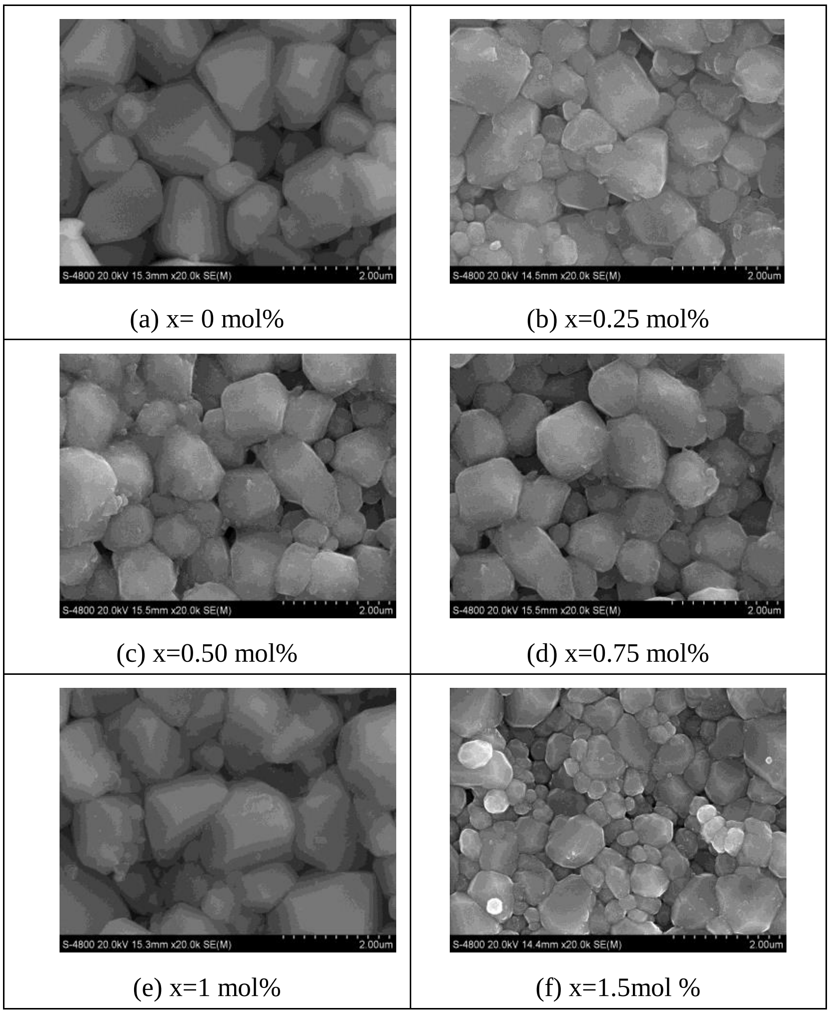
The radius of Ti^{4+}、Ba^{2+}、Fe^{3+} are 0.061nm、0.161nm、0.092nm each, Based on the calculation formula of tolerance factor: $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$, The tolerance factor *t* of Fe^{3+} doped BZT are shown in Tab.1. Tab.1 shows that Fe^{3+} enter the lattice inside, can replace A site , also can replace B site.

Table 1. Tolerance factor t of Fe^{3+}-doped BZT

Substitution position	*t*
Position A($BaTiO_3$)	0.816
Position A($BaZrO_3$)	0.774
Position B($BaTiO_3$/$BaZrO_3$)	0.917

3.2. Scanning electron microscopy (SEM) analysis

Fig.2 shows the SEM images of different amounts of Fe^{3+} doped BZT ceramics. It can be seen From Fig. 2(a) that: the grain counter of pure BZT ceramic is clear, and the grain boundaries are clear too. When a small amount of Fe^{3+} ions are doped, the grains are obviously refined, which indicates that the addition of Fe^{3+}plays a role in the refinement of the grain, which is beneficial to the improvement of the dielectric properties of the ceramics. [12] With the increase of Fe^{3+} doping amount, the porosity increases obviously, and the particle size tends to be uniform. When Fe^{3+} doping amount is further increased, as shown in Fig.2(e). At this time, Fe^{3+} doping amount is 1mol%, the grain size increases obviously, and the ceramic structure is more compact. However, when Fe^{3+} is excessively doped, the grain size decreases and the porosity increases. These phenomena can be explained as follows: due to the existence of grain boundaries, the ions preferentially accumulate at the grain boundaries, which produce pinning effect, and hinder the movement of grain boundaries, and further hinder the growth of grain. Therefore, with the addition of a small amount of Fe^{3+}, Fe^{3+} ions accumulate at the grain boundary, restrain the growth of the grain, and the grain size decreased obviously. At the same time, Fe^{3+} also reacts with the main crystal structure of BZT for substitution of Ti^{4+} at B site, leading to defect reaction, resulting in increased lattice oxygen vacancy concentration, which is conducive to sintering and grain growth. These changes in the microstructures of the crystals cause a significant change in the macroscopic dielectric properties of the ceramic crystals.



(a) x= 0 mol%

(b) x=0.25 mol%

(c) x=0.50 mol%

(d) x=0.75 mol%

(e) x=1 mol%

(f) x=1.5mol %

Fig.2 Scanning electron microscope (SEM) photographs of BZT ceramics sintered at 1300 ℃ for 2h, (a) x=0 mol%; (b) x=0.25 mol% ; (c) 0.50 mol% ; (d) 0.75 mol%; (e) 1.0 mol% ; (f) 1.50 mol%

3.3 Dielectric properties analysis of BZT ceramic samples

Fig.3 and Fig.4 show the dielectric properties of BZT ceramics sintered at different temperature versus Fe_2O_3 doping amount x. The Figs shows that: sintered at 1280℃, 1300℃ and 1330℃, the dielectric constant ε first increases and then decreases with the increase of Fe_2O_3 doping amount x , and reaches its high value when the doping amount x is 0.50 mol %, and the dielectric loss shows a decreasing trend.

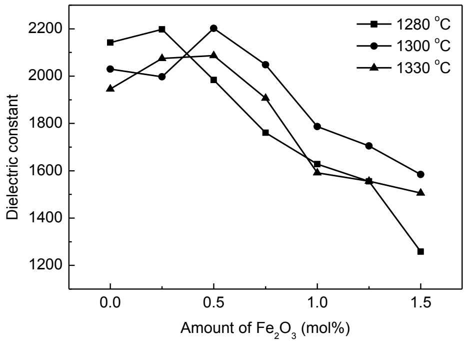


Fig.3 Dielectric constant (ε) of various Fe_2O_3 doped BZT ceramics sintered at different temperature

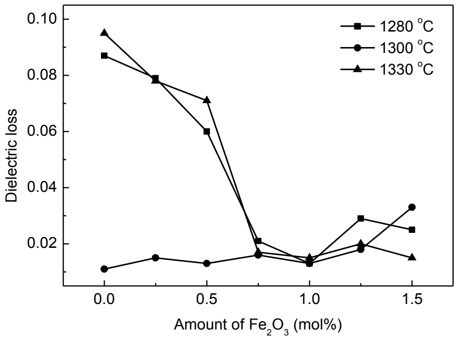


Fig.4 Dielectric loss (tanδ) of various Fe_2O_3 doped BZT ceramics sintered at different temperature

When the doping amount of Fe^{3+} is small (0 mol% ≤x≤0.5 mol%), Fe^{3+} substitute Ba^{2+} at A site, because the $r(Fe^{3+}) < r(Ba^{2+})$, high price (Fe^{3+}) replace low price (Ba^{2+}), in order to keep the price conservation, the Ba^{2+} vacancy is generated, which causes the lattice contracts, the internal stress increases and make the dielectric constant increase. With the increase of the doping amount of Fe^{3+}（0.5 mol% ≤x≤1.5 mol%）, Fe^{3+} substitute Ti^{4+} at B site, the O^{2-} vacancy is generated, and the “pinning effect” of O^{2-} vacancy occurs[13],which make ionic polarization weaken, and decrease the dielectric constant.

When the doping amount of Fe^{3+} is small, Fe^{3+} substitute Ba^{2+} at A site, because the $r(Fe^{3+}) < r(Ba^{2+})$, the unit cell shrink, cell density increases and dielectric loss decreases; with the increase of the doping amount of Fe^{3+}, Fe^{3+} substitute Ti^{4+} at B site, some Ti^{4+} become Ti^{3+} through non-stoichiometric reaction, and the O^{2-} vacancy is generated, the existence of oxygen vacancies makes the ceramic grains smaller, the density increases, and the dielectric loss decreases.

Under the condition of sintering at 1300 °C for 2h, temperature dependence of dielectric constant of samples with different doping amount of Fe^{3+} at 1 kHz is shown in Fig.5.As can be seen from Fig.5, with the increase of the doping amount of Fe^{3+}, the peak value of dielectric constant increases first increases and then decreases. When Fe^{3+} doped into BZT, Fe^{3+} entering Ba^{2+} changes the crystal axis rate (c/a), has certain effect on moving Curie peak, Curie peak shifts to low temperature, Curie temperature decreased obviously, and improve the dielectric temperature change rate, which have an effect on lowering and widening the peak. [14]

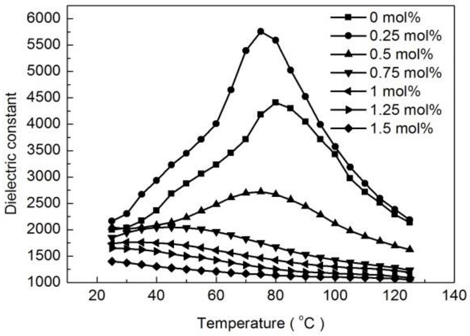


Fig.5 Temperature dependence of dielectric constant of Fe_2O_3 doped BZT ceramics

4. Conclusions

The XRD patterns show that the Fe^{3+}-doped ceramic samples have a single perovskite structure and no other new phases are formed;

The SEM images show that the grain boundaries are clear and the crystal grain is clear too. When the Fe^{3+} doping amount is small, the grains can be refined to a certain extent and the porosity is reduced, the increase of doping amount will promote the grain growth;

Fe^{3+} doping can significantly change the dielectric properties of BZT ceramics, make curie temperature shifting to low temperature, and play a role of lowering and widening the peak, when the Fe_2O_3 doping amount x = 0.5 mol%, the dielectric properties are the best.

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