EFFECT OF La$_2$O$_3$ DOPING ON DIELECTRIC PROPERTIES OF BaZr$_{0.1}$Ti$_{0.9}$O$_3$CERAMICS BY SOL-GEL METHOD

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Lanthanum doped BaZr$_{0.1}$Ti$_{0.9}$O$_3$ (BZT10) dielectric ceramics were prepared by sol-gel method using barium acetate, zirconia nitrate, butyl titanate and La$_2$O$_3$, etc, as raw materials and La$_2$O$_3$ as dopant, the effects of La$_2$O$_3$ doping on dielectric properties of BaZr$_{0.1}$Ti$_{0.9}$O$_3$ ceramics are also investigated. The XRD results show that the crystal structure for BZT10 ceramics is a single perovskite structure, and the admixture of La^{3+} does not generate new phase. With the increase of La$_2$O$_3$ content, the grain size decreases continuously when the doping amount x ≤ 0.5 mol%, when the doping amount x > 0.5 mol%, the grain size basically remains unchanged, and the grain size is uniform. With the La$_2$O$_3$ content increasing, the dielectric constant rises at first and then decreases for the samples sintered at 1280 $^{\circ}$C, 1300 $^{\circ}$C and 1330 $^{\circ}$C, when the sintering temperature is 1280 $^{\circ}$C and the La$_2$O$_3$ doping amount is x = 0.7 mol%, the dielectric constant is the largest. It can also be seen that the dielectric loss of La^{3+}-doped sample is lower than that of the blank sample in the temperature range from room temperature to 125 °C. In the terms of dielectric constant, dissipation factor and temperature stability for dielectric loss, the trace amount of La^{3+} doping could influence the dielectric properties remarkably.

1. Introduction

Due to high dielectric constant, good piezoelectric and ferroelectric properties, Barium titanate (BT) ceramics can be widely used in multi-layer ceramic capacitors [1-3]. However, pure barium titanate has high Curie temperature and low dielectric constant at room temperature, so doping is usually used to change its performance [4-6]. In recent years, the research on the preparation and properties of Ba(Zr$_x$Ti$_{1-x}$)O$_3$(BZT) ceramic materials has received more and more attention. Since

Zr^{4+} has a more stable chemical structure than Ti^{4+} in BaTiO$_3$ [7-9], then BZT ceramics can be replaced with(Ba$_{1-x}$Sr$_x$) TiO$_3$(BST) as capacitors. For BZT ceramics, when x>0.08, due to the difference between the radius of the Ti^{4+} ion (0.061 nm) and the radius of the Zr^{4+} ion (0.072 nm) besides the uneven distribution of the Zr^{4+} at the Ti site, the system can produce mechanical

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stress. Therefore, the dielectric spectrum of the system near the Curie temperature becomes flat, which is very conducive to the manufacture of temperature stabilized ceramic capacitors. When the composition of zirconium x>0.15, the three phase transitions of BZT ceramics begin to contract, and the three phase transitions all move in the direction of room temperature. when x~0.20, the three phase transition points of BZT ceramics are combined into one, only one phase exists, and the phase transition temperature is close to room temperature. x>0.25, BZT showed relaxation behavior. Recently, with the improvement of the requirements of the electronics industry, the requirements for the powder preparation of barium titanate have become more and more high, such as, granularity requirements are finer, purity requirements are higher, and uniformity is better, etc. The solid phase method can no longer meet the requirements for preparation of electronic ceramic powders in many applications [10,11]. The preparation of nanosized and uniform ultrafine powder by liquid phase method has become a hot topic in the preparation of $BaTiO_3$ based powder [12].

In this experiment, $BaZr_{0.1}Ti_{0.9}O_3$ (BZT10) ceramic powder is prepared by sol-gel method, in order to study high-quality dielectric ceramic materials with high dielectric constant, low dielectric loss and high dielectric stability, the effects of the content La_2O_3 on the crystal structure, microstructure and dielectric properties of $BaZr_{0.1}Ti_{0.9}O_3$ (BZT10) base ceramics were studied.

2. Experimental

The main raw materials for the preparation of $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramic powders are barium acetate, zirconia nitrate, butyl titanate, $NH_3 \bullet H_2O$ (ammonia), La_2O_3, $Mn(CH_3COO)_2 \bullet 4H_2O$, $C_4H_6MgO \bullet H2O$, etc. Among them, Barium acetate, zirconia nitrate, and butyl titanate are used to synthesize the main crystal phase $Ba(Zr_{0.1}Ti_{0.9})O_3$, La_2O_3 is used as capping agents, and manganese acetate and magnesium acetate are used as sintering auxiliaries, $NH_3 \bullet H_2O$ (ammonia) is used to regulate the pH of the sol. According to the formula, the quality weighing drugs of barium source, titanium source, zirconium source and doped elemental oxide were calculated and put into three beakers respectively. Using acetic acid to dissolve barium acetate, stir alone with a magnetic mixer for 0.5 h to form a sol. The tetrabutyl titanate and alcohol are arranged in a ratio of 1: 6 in the molar ratio, and they are stirred separately on the magnetic mixer for 0.5 hours to form a sol. The citric acid is added to zirconia nitrate in accordance with molar ratio 1: 3, add 5ml distilled water and stir it to dissolve under constant temperature bath heating, then add anhydrous ethanol in accordance with mass ratio 1: 1.2 and continually stir for 0.5 h to form sol. Antimony trioxide is dissolved in nitric acid. Finally, mix the above four kinds of sol, stir for 1 h at 80 ^{o}C, then add 0.5 ml acetylacetone, continually stir for 1.5 h to form sol. The sol is placed at room temperature for a day to obtain a wet gel. The wet gel is then dried and dehydrated and decolorized to give a dry gel.

The dry gel was calcined at 925°C for 2 h. The above precursor with sintering auxiliaries was weighed and mixed, granulated (with polyvinyl alcohol as binder), pressed into the desired form ($\Phi \times d$=7.00×2.00 mm^2) at 30 Mpa, and then sintered at 1250°C, 1280°C, 1300°C and 1330°C for 2 h in the air, respectively. The sintered samples were cleaned using an ultrasonic bath, then dried. Both sides of the specimens for dielectric property measurements were screened electrode paste composing mainly of AgO, some fluxes and binders, then fired at 550°C for 10 minutes.

The crystal phase of the samples was tested using X-ray diffractometer (XRD, Model RIGAKU D/MAX 2500V/PC, Japan) with a 2θ range from 10° to 70°. The surface micrographs of the samples were observed using field emission scanning electron microscopy (SEM, Hitachi s4800). The temperature dependence of the dielectric constant (ε) and the dielectric loss ($tan\delta$) was measured by a capacitance apparatus (Model YY 281 automatic LCR Meter 4225) at 1 kHz in a temperature range over 0 °C to 125 °C.

3. Results and discussions

The XRD results for BZT10 ceramics doped with different La_2O_3 content sintered at 1280 ^{o}C for 2 h were shown in Fig. 1. From the Fig.1, it can be seen that the ceramic samples all exhibit a single perovskite structure, there is no significant change for main crystal phase in the BZT10 ceramics, and the admixture of La^{3+} has no new phase generation.
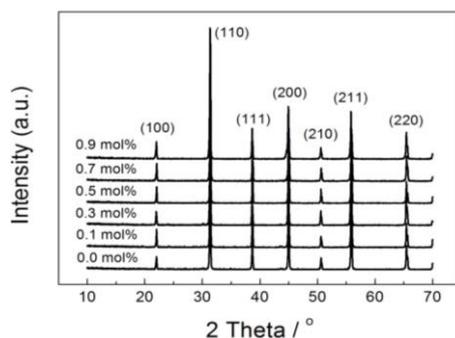

Fig. 1. XRD patterns of BZT10 ceramics doped with different La₂O₃ content.

SEM micrographs of the surface of BZT10 ceramics sintered at 1280 ^{o}C for 2 h are shown in Fig .2. As can be seen from Fig. 2, the grain boundaries for the different content La_2O_3 doped BZT10 ceramics are relatively clear. For the blank sample, the grain size is about 3 um. When a small amount La_2O_3 is doped, the size of the grain is slightly smaller. With the increase of La_2O_3 content, the grain size decreases continuously, when the doping amount x = 0.5 mol%, the grain size is about 3 um as shown in Fig. 2 (d). When the doping amount x > 0.5 mol%, the grain size basically remains unchanged, the grain size is uniform. The results are also consistent with the following analysis of dielectric properties at room temperature. With the increase of doping, the grain size becomes smaller, the particle size distribution is more uniform, the porosity decreases, and the structure is denser. La_2O_3 acts as donor doping and replaces the Ba^{2+} site in the lattice. Some La^{3+} ions accumulate at the grain boundary nailed the grain boundary movement, inhibiting the growth of the grain [13].

(a) 0 mol%

(b) 0.1 mol%

(c) 0.3 mol%

(d) 0.5 mol%

(e) 0.7 mol%

(f) 0.9 mol%
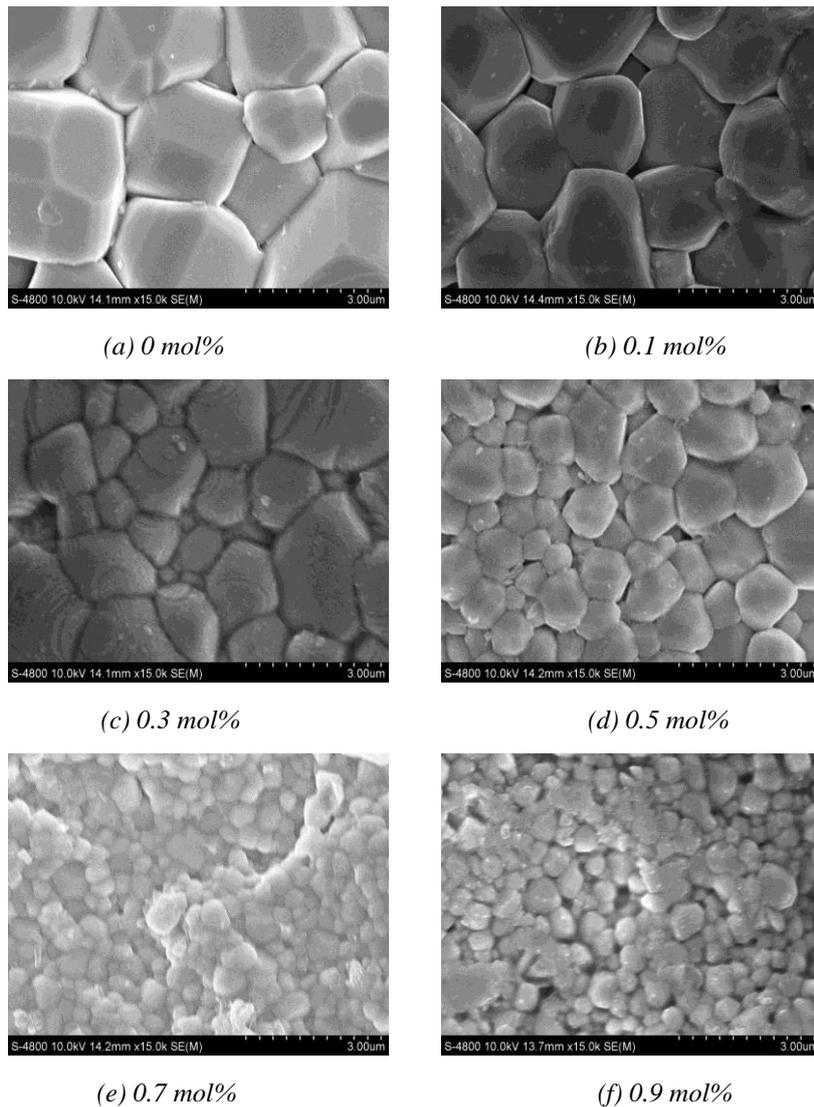
Fig. 2 SEM micrographs of the surface of BZT10 ceramics
doped different La_2O_3 content

Dielectric constants are shown in Fig. 3 for each sample with different sintering temperatures of 1250 ^{o}C, 1280 ^{o}C, 1300 ^{o}C, 1330 ^{o}C, respectively, for 2 h. From the Fig. 3, with the La_2O_3 content increasing, it can be seen that the dielectric constant rises at first and then decreases for the samples sintered at 1280 ^{o}C, 1300 ^{o}C and 1330 ^{o}C. When the sintering temperature is 1280 ^{o}C and the La_2O_3 doping amount is x = 0.7 mol%, the dielectric constant is the largest. Dielectric loss is shown in Fig. 4 for each sample with different sintering temperatures of 1250 ^{o}C, 1280 ^{o}C, 1300 ^{o}C, 1330 ^{o}C, respectively, for 2 h.
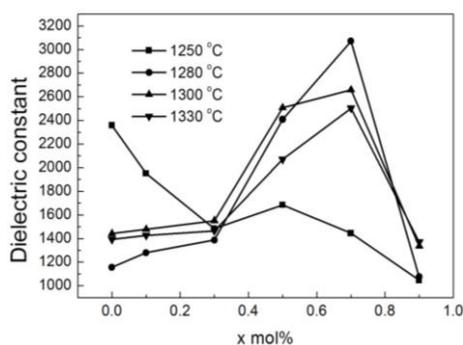
Fig. 3. Dielectric constants of BZT10 ceramics with various La$_2$O$_3$ doping content.
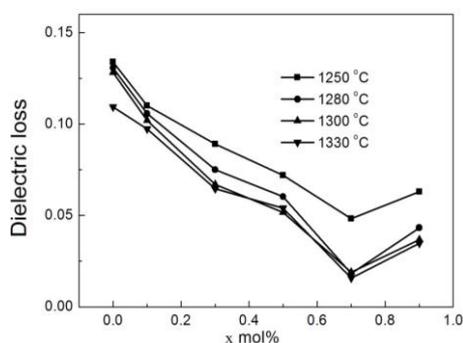

Fig. 4. Dielectric loss of BZT10 ceramics with various La$_2$O$_3$ doping content.

In the initial stage, with the increase of the La$_2$O$_3$, on one hand, the radius of La^{3+} is smaller than that of Ba^{2+}, La^{3+} ions enter the A site in the cell, as shown in the chemical reaction equation (1).
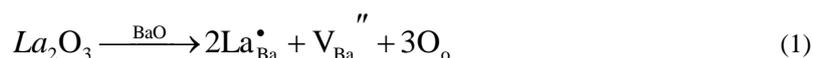
$$La_2O_3 \xrightarrow{\text{BaO}} 2La_{Ba}^{\bullet} + V_{Ba}^{''} + 3O_o \tag{1}$$

The cell parameters decreases, resulting in lattice contraction and lattice distortion, therefore the spontaneous polarization of the crystal increases, hence the dielectric constant of the samples increases [14]. On the other hand, when La^{3+} ion enters the A site, some electrons will be generated, the appearance of the electrons will increase the electron conductivity of the specimen, the weak bound electrons are easily compounded with the positive charge of the A site, thereby weakening the electron polarization and ion polarization of the crystal, then the dielectric constant is increased. When x(La$_2$O$_3$) > 0.7 mol%, La^{3+} ion will partially enter the B site, as shown in the chemical reaction equation (2), resulting in a part of the oxygen vacancy. Due to the nail action of the oxygen vacancy, the dielectric constant will be reduced [15].

$$La_2O_3 \xrightarrow{\text{TiO}_2} 2La_{Ti}^{'} + V_O^{\bullet\bullet} + 3O_o \tag{2}$$
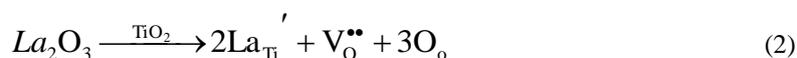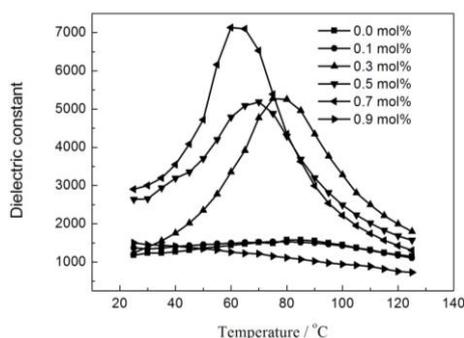
Fig. 5. Temperature dependence of dielectric constants of BZT10 ceramics.
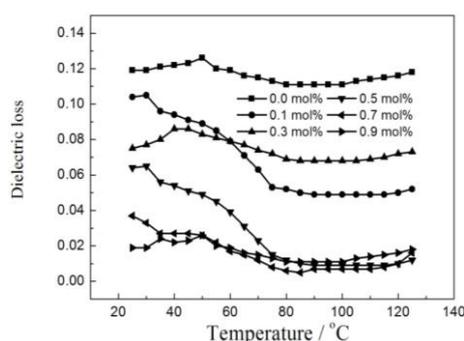

Fig. 6. Temperature dependence of dielectric loss of BZT10 ceramics.

Under 1 kHz test frequency conditions, the dielectric constant and dielectric loss changes with temperature are shown in Fig. 5 and Fig. 6, respectively. It can be seen from the fig.5 that when x(La$_2$O$_3$) = 0.7 mol%, the dielectric peak of the sample is the largest. From the previous analysis, it can be obtained that La^{3+} ion enters the A site, and the cell parameter decreases, which results in a contraction of the crystal lattice and a large lattice distortion of the sample, so the polarization ability is enhanced, and the ferroelectricity of the sample increases, therefore, the dielectric constant at the Curie point increases. When x(La$_2$O$_3$) > 0.7 mol%, the Curie dielectric peak of the specimen is suppressed, the dielectric peak becomes significantly wider, and the dielectric peak becomes relatively flat near the Curie point, which is obviously related to the electrons generated from that La^{3+} ion enters the B site. It can be seen that the dielectric loss of La^{3+}-doped sample is lower than that of the blank sample in the temperature range from room temperature to 125 °C, therefore, in the terms of dielectric constant, dissipation factor and temperature stability for dielectric loss, the trace amount of La^{3+} doping could influence the dielectric properties remarkably.

4. Conclusions

The BZT10 ceramics are prepared using sol-gel method. Effects of La$_2$O$_3$ dopant on microstructure and dielectric properties of BZT10 ceramics are investigated. When La$_2$O$_3$ is doped with BZT10 ceramics, the ceramic samples exhibit a single perovskite structure, there is no

significant change for main crystal phase, and the admixture of La^{3+} has no new phase generation. As the amount of La_2O_3 doped increases, the grain size gradually decreases, when the amount of La_2O_3 doping continues to exceed 0.5 mol%, the grain size basically remains unchanged. Owing to the La^{3+} substituting for Ba^{2+}, the cell parameters decreases, resulting in lattice contraction and lattice distortion, therefore the spontaneous polarization of the crystal increases, hence the dielectric constant of the samples increases. Afterwards, La^{3+} ion partially enter the B site, resulting in a part of the oxygen vacancy, due to the nail action of the oxygen vacancy, the dielectric constant is reduced.

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