EFFECT OF Gd_2O_3 DOPING ON DIELECTRIC PROPERTIES OF $Ba(Zr_{0.1}Ti_{0.9})O_3$ CERAMICS

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Using $BaCO_3$, TiO_2, ZrO_2 and Gd_2O_3 as the starting materials, the $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics are prepared using solid state synthesis method, and effects of Gd_2O_3 dopant on microstructure and dielectric properties of $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics are investigated. The results show that the crystal structure for $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics is a single perovskite structure, and the doping of Gd^{3+} does not generate new phase. With the Gd_2O_3 concentration increasing, the grain size increases continuously, when the doping amount x ≥ 0.5 mol %, the grain size basically remains unchanged, the grain size is uniform. With the Gd_2O_3 content increasing, the dielectric constants rose first and then decreased under different sintering conditions of 1280 °C, 1300 °C, 1330 °C, and 1350 °C. When the sintering temperature is 1350 °C and the Gd^{3+} doping amount is x = 0.5 mol %, the dielectric loss is minimal, the dielectric constant is the highest, and the dielectric performance at room temperature is optimal. Gd_2O_3 doping has little effect on the movement of the Curie point of BZT ceramics, but the doping of Gd_2O_3 can increase the peak of the dielectric peak at the Curie point.

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Keywords: Ceramics, Dielectric properties, Dope, Microstructure

1. Introduction

Barium titanate (BT) ceramics can be widely used in multi-layer ceramic capacitors for its high dielectric constant, good ferroelectric properties [1-3]. Ceramic samples based on barium titanate are among the most studied lead-free ferroelectric materials. However, barium titanate ceramics has low dielectric constant at room temperature, so doping is an effective method to tailor its performance [4-6]. Much research has proved that Zr is a very suitable substitute in BT to form $Ba(Ti_{1-x}Zr_x)O_3$ (BZT) solid solution, the substitute of Zr in barium titanate ceramics can not only to shift the T_c to lower temperature, but also to broaden the temperature dependence of dielectric constant [7-9]. Indeed, when x ≥ 0.25, $BaZr_xTi_{1-x}O_3$ (BZT) system shows a relaxor state, which has been rooted from a breakage in the correlation displacement of B-site cations caused by

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the substitution of Ti^{4+} by Zr^{4+} [10-12]. Laulhe′ et al. [12] found that the local structure around Zr differs considerably from the average cubic structure investigated by X-ray diffraction and the distance between Zr atoms and their first oxygen neighbors is equal to the distance measured in the $BaZrO_3$ compound independently of the Zr substitution rate. The authors observed that Zr atoms tended to be segregated in Zr-rich regions and the relaxor behavior in BZT could be influenced by the random elastic fields generated by the chemical arrangement of Zr atoms.

Combined with previous studies, the BZT ceramics has high dielectric properties at room temperature. The effect of various dopants such as Ce^{4+}, Y^{3+}, Ho^{3+} and Ca^{2+} on a BZT system has been studied [13–16]. In order to further improve the dielectric properties, the effects of the content and sintering temperature on the crystal structure, microstructure and dielectric properties of $BaZr_{0.1}Ti_{0.9}O_3$ (BZT10) base ceramics were studied by adding Gd_2O_3.

2. Experimental

The general formula of the materials studied was $BaZr_{0.1}Ti_{0.9}O_3$ + x Gd_2O_3, where x=0.0-0.7 mol%. The samples were prepared by the two-stage method to acquire a pure phase of perovskite. Reagent-grade oxide powders, TiO_2, $BaCO_3$, ZrO_2 and Gd_2O_3, were used as the starting materials. At first, a powder of $BaZr_{0.1}Ti_{0.9}O_3$, was prepared by calcination of $BaCO_3$, TiO_2 and ZrO_2, at 1100°C for 2 h. Secondly, the above precursor with Gd_2O_3 was weighed and mixed through use of a polyethylene jar and agate balls milling media. The mixture was then dried at 120°C, granulated (with polyvinyl alcohol as binder), pressed into the desired form ($\Phi \times d$=12.30×2.00 mm^2) at 160 Mpa, and then sintered at 1280°C, 1300°C, 1330°C and 1350°C for 2 h in the air, respectively. The obtained samples were cleaned by an ultrasonic bath, and then dried. Both sides of the obtained samples were screened electrode paste, and then fired at 610°C for 10 minutes.

The crystal feature of the samples was analyzed by X-ray diffractometer (XRD, Model RIGAKU D/MAX 2500V/PC, Japan) with a 2θ range from 10^o to 70^o. The surface micrographs of the samples were observed by field emission scanning electron microscopy (SEM, Hitachi s4800). The temperature dependence of the dielectric constant (ε) and the dielectric loss ($tan\delta$) was measured using a capacitance apparatus (Model YY 281 automatic LCR Meter 4225) at 1 kHz in a temperature range over 0 °C to 130 °C.

3. Results and discussions

The XRD patterns of the samples with different amounts of Gd_2O_3 contents sintered at 1350 ^{o}C for 2 h are shown in Fig. 1. It can be seen from Fig. 1 that after doping with different amounts of Gd_2O_3, $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics all have characteristic peaks of perovskite structure, and Gd_2O_3 with different doping quantities does not cause too many changes in the structure of BZT crystals. Therefore, it can be inferred that the $Ba(Zr_{0.1}Ti_{0.9})O_3$ + x Gd_2O_3 ceramic is a tetragonal phase at room temperature, and the amount of doping does not change the main crystal phase structure of the $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics.

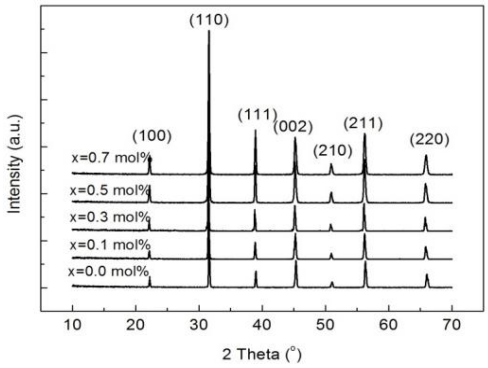
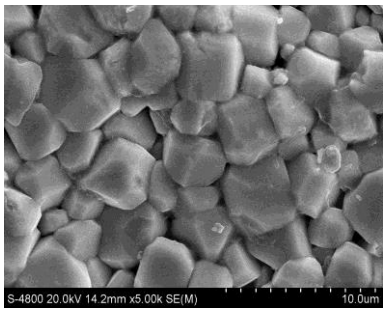
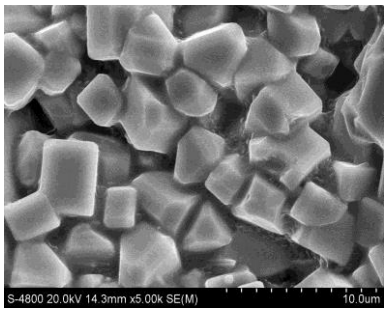


Fig. 1. XRD patterns of the Gd_2O_3 doped BZT10 ceramics.

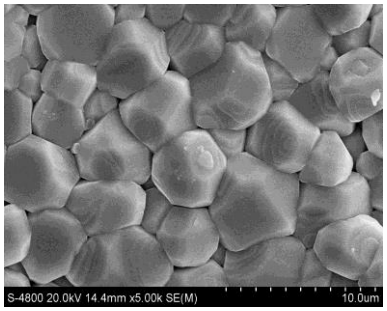
Fig. 2 shows the SEM images of Gd^{3+}-doped BZT10 ceramics. As can be seen from Fig. 2, the grain boundaries for different Gd_2O_3 doped $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramic are relatively clear. The crystal size of pure barium zirconate titanate ceramics is uneven and the density is small.



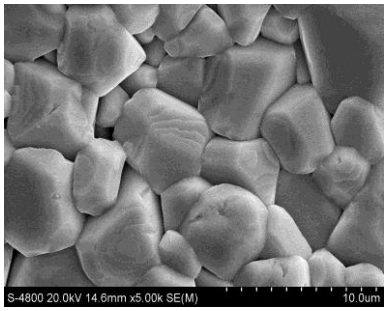
(a) x=0.0mol%



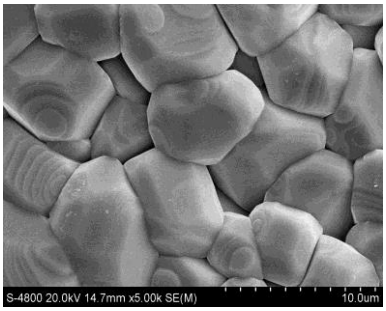
(b) x=0.1mol%



(c) x=0.3mol%



(d) x=0.5mol%



(e) x=0.7mol%

Fig. 2. Surface SEM images of the Gd2O3 doped BZT10 ceramics.

A small amount of Gd_2O_3 doped sample grain presents a regular boundary. The size of the grain is slightly smaller, and the liquid phase is produced, resulting in an increase in density. With the increase of Gd_2O_3 content, the grain size increases continuously, and its shape is ellipsoidal, and the porosity increases and the density decreases. When the doping amount $x \geq 0.5$ mol%, the grain size basically remains unchanged, the grain size is uniform, and the density increases. The result is also consistent with the following analysis of dielectric properties at room temperature because the porosity of the ceramic body has a great influence on the dielectric properties of dielectric ceramics.

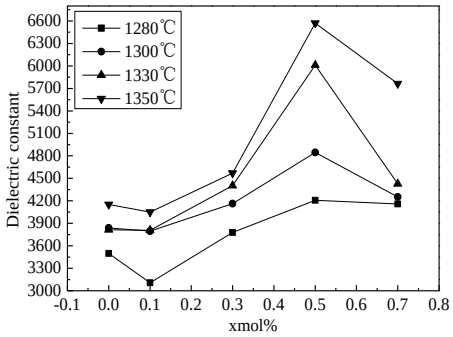


Fig. 3. Dielectric constant of BZT10 ceramics with various Gd2O3 doping concentration.

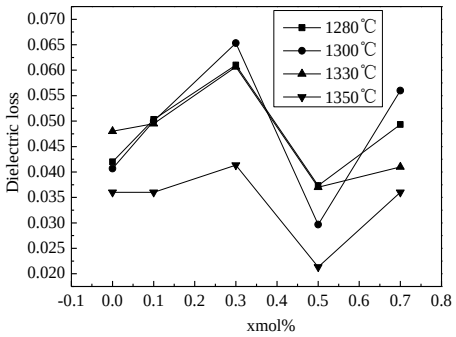


Fig. 4. Dielectric loss of BZT10 ceramics with various Gd2O3 doping concentration.

Fig. 3 and Fig. 4 show influence of Gd^{3+} content on dielectric constants and dielectric loss of the samples sintered at 1280 ^oC, 1300 ^oC, 1330 ^oC and 1350 ^oC for 2 h, respectively.

As can be seen from Fig. 3 and Fig. 4, with the Gd_2O_3 content increasing, the dielectric constants rose first and then decreased under different sintering conditions of 1280 °C, 1300 °C, 1330 °C, and 1350 °C. When the sintering temperature is 1350 °C and the Gd^{3+} doping amount is x = 0.5 mol%, the dielectric loss is minimal, the dielectric constant is the highest, and the dielectric performance at room temperature is optimal.

In the initial stage, the dielectric constant increases with the increase of the doping Gd^{3+} concentration. On the one hand, Gd^{3+} enters the A site, since the radius of Gd^{3+} is smaller than that of Ba^{2+}, the cell parameter decreases, causing the lattice to shrink, then the lattice distortion increases, accordingly the spontaneous polarization of the crystal increases, so the dielectric constant of the ceramic sample increases. On the other hand, when Gd^{3+} enters the A site, the electron can be generated, the appearance of these electrons will increase the electron conductivity

of the sample, and the weak bound electrons are easy to interact with the positive charge at A site, therefore, the electron polarization and ion polarization of the crystal are weakened, and the dielectric constant of the ceramic sample is increased. When x(Gd_2O_3) > 0.3 mol%, Gd^{3+} will partially enter the B site, resulting in a part of the oxygen vacancy. Due to the nail action of the oxygen vacancy, the sample dielectric constant will be reduced, and the oxygen vacancy can inhibit Ti^{4+} to Ti^{3+} reduction, resulting in the reduce of dielectric loss [17].

At the sintering temperature of 1350 °C for 2 h, the curves of dielectric constants and dielectric loss with temperature are shown in Fig. 5 and Fig. 6 for different Gd_2O_3 doped BZT ceramics. It can be seen from the figure that when x(Gd_2O_3) = 0.5 mol%, the maximum dielectric peak of the sample is highest. From the previous analysis, at this time, Gd^{3+} enters the A site, and the cell parameter decreases, resulting in a contraction of the lattice of the sample and a large lattice distortion, then the polarization ability is enhanced. Therefore, the ferroelectricity of the sample increases, and the dielectric constant at the Curie point increases. When x(Gd_2O_3) > 0.5 mol%, the Curie dielectric peak of the specimen is suppressed, the dielectric peak becomes significantly wider, and the specimen becomes relatively flat near the Curie dielectric peak, which is obviously related to the electrons generated by Gd^{3+} entering the B site. The dielectric loss of different Gd_2O_3 doped samples showed an overall trend of decreasing with temperature change. When the doping of Gd_2O_3 was 0.5 mol%, the dielectric loss of the sample was minimized and remained at about 0.015. Gd_2O_3 doping has little effect on the movement of the Curie point of BZT ceramics, and the Curie temperature is about 60 °C, but the doping of Gd_2O_3 can increase the peak of the dielectric peak at the Curie point.

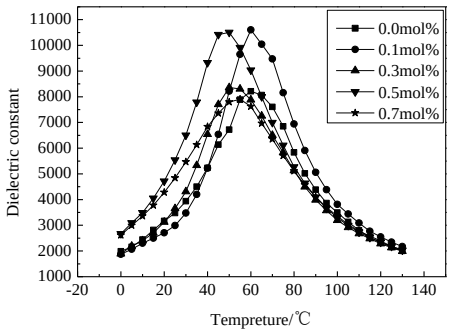


Fig. 5. Temperature dependence of dielectric constant of Gd2O3 doped BZT10 ceramics.

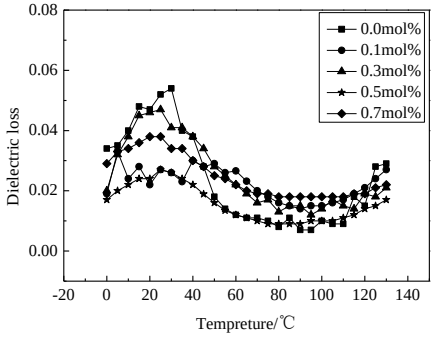


Fig. 6. Temperature dependence of dielectric loss of Gd2O3 doped BZT10 ceramics.

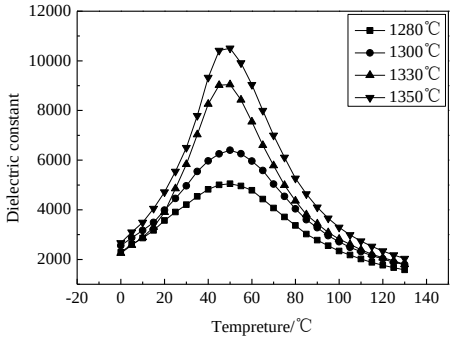


Fig. 7. Temperature dependence of dielectric constant of 0.5 mol% Gd2O3 doped BZT10 ceramics at various sintering temperature.

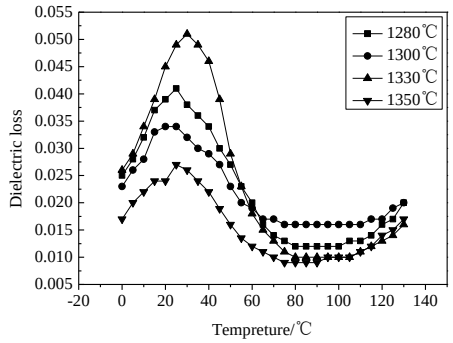


Fig. 8. Temperature dependence of dielectric loss of 0.5 mol% Gd_2O_3 doped BZT10 ceramics at various sintering temperature.

Fig. 7 and Fig. 8 show the variation of dielectric constant and dielectric loss with temperature at different sintering temperatures for 0.5 mol% Gd_2O_3 doped BZT10 ceramics. It can be seen from the figure that with the increase of sintering temperature, the dielectric constant increases and the dielectric loss decreases. The increase of sintering temperature can increase the dielectric constant at Curie temperature and reduce the dielectric loss, and this is mainly related to the fact that the grain development is more complete, the material becomes more dense, and the porosity decreases with the increase of sintering temperature.

4. Conclusions

The BZT10 ceramics are prepared using solid state reaction method. Effects of Gd_2O_3 dopant on microstructure and dielectric properties of BZT10 ceramics are investigated. The crystal structure for Gd_2O_3 doped $Ba(Zr_{0.1}Ti_{0.9})O_3$ ceramics is a single perovskite structure, and the doping of Gd^{3+} does not generate new phase. Owing to the dopant of Gd^{3+}, the grain size increases continuously at first with the Gd_2O_3 concentration increasing, when the doping amount $x \geq 0.5$ mol %, the grain size basically remains unchanged, the grain size is uniform. In the initial stage, Gd^{3+} ion enters the A site, the cell parameter decreases, accordingly the spontaneous polarization

of the crystal increases, so the dielectric constant of the ceramic sample increases. When x(Gd_2O_3) > 0.3 mol %, Gd^{3+} can partially enter the B site, generating the oxygen vacancy. Due to the nail action of the oxygen vacancy, the sample dielectric constant will be reduced, and the oxygen vacancy can inhibit Ti^{4+} to Ti^{3+} reduction, resulting in the reduce of dielectric loss. Thanks to the dopant of Gd^{3+}, the dielectric loss is minimal, the dielectric constant is the highest, and the dielectric performance at room temperature is optimal when the sintering temperature is 1350 °C and the Gd^{3+} doping amount is x = 0.5 mol %.

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