Digest Journal of Nanomaterials and Biostructures Vol. 14, No. 4, October-December 2019, p. 917-922

EFFECT OF Ta_2O_5 DOPING ON DIELECTRIC PROPERTIES OF $BaZr_{0.1}Fe_{0.05}Ti_{0.85}O_3$ CERAMICS

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Using TiO_2, $BaCO_3$, ZrO_2 and Fe_2O_3 as the starting materials, the BZFT ceramics are prepared using solid state synthesis method, and effects of Ta_2O_5 dopant on microstructure and dielectric properties of BZFT ceramics are investigated. The results show that the crystal structure for BZFT ceramics is a single perovskite structure, and the admixture of Ta^{5+} does not generate new phase. With the amount of Ta_2O_5 concentration increasing, the grains gradually grow, the porosity rate increases, when the amount of Ta_2O_5 exceeds 0.6 mol%, the grain size begins to decrease. Due to the Ta^{5+} substituting for Ti^{4+}, the dielectric constant is increased. Afterwards, with the increase of Ta_2O_5 doping concentration, the size of sample particles becomes smaller, resulting in a decrease in the dielectric constant. Owing to the Ta^{5+} substituting for Ti^{4+}, the temperature stability of dielectric loss is enhanced, and the dielectric loss maintains at a lower value.

(Received May 6, 2019; Accepted October 18, 2019)

Keywords: Ceramics, Dielectric properties, Dope, Microstructure

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. As we known that Zr is an effective substitute in BT to form $Ba(Ti_{1-x}Zr_x)O_3$ (BZT) solid solution, it can not only to shift the T_c, but also to broaden the dielectric constant-temperature dependence [4-6]. Therefore, BZT can be easily adapted to meet the Z5U specification, and the Zr^{4+} ion is chemically more stable than the Ti^{4+}. Consequently, the Zr/Ti ratio in the $BaTiO_3$–$BaZrO_3$ system can tailor the ferroelectric–paraelectric phase transition type, its characteristic temperature and the functional properties [7-9]. Many studies have shown that the dielectric loss of ceramics can be reduced, at the same time, the density and dielectric properties are increased under the modification of Fe_2O_3 doping [10,11]. The effects of Ta_2O_5 on the structure and properties of dielectric ceramics have been widely studied [12,13].

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Combined with previous studies, the BZT ceramics has high dielectric properties at room temperature when Fe^{3+} ion replaces Ti^{4+} ion. 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 $BaZr_{0.1}Fe_{0.05}Ti_{0.85}O_3$ (BZFT) base ceramics were studied by adding Ta_2O_5.

2. Experimental

The general formula of the materials studied was $BaZr_{0.1}Fe_{0.05}Ti_{0.85}O_3$ + x Ta_2O_5, where x=0.0-1.0 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, Fe_2O_3 and Ta_2O_5, were used as the starting materials. At first, a powder of $Ba_{0.95}Zr_{0.1}Fe_{0.1}Ti_{0.85}O_3$, was prepared by calcination of TiO_2, $BaCO_3$, ZrO_2 and Fe_2O_3, at 1090°C for 2 h. Secondly, the above precursor with Ta_2O_5 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 ($\Phi \times d$=12.00×2.00 mm^2) at 200 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 structure of the samples was analyzed using X-ray diffractometer (XRD, Model GIRAKU D/MAX 2500V/PC, Japan) with a 2θ range from 10^o to 70^o. The 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 25 °C to 125 °C.

3. Results and discussions

The results of the XRD test for BZFT ceramics doped with different Ta_2O_5 content sintered at 1300 ^oC for 2 h were shown in Fig. 1. It can be seen from the figure that the ceramic samples prepared by different doping quantities and different sintering temperatures all exhibit a single perovskite structure, there is no significant change in the material composition of barium titanate ceramics, and the admixture of Ta^{5+} has no new phase generation.

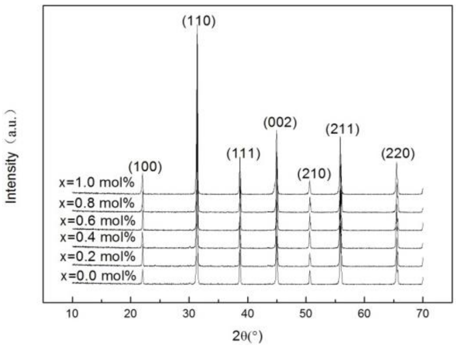


Fig. 1. XRD patterns of BZFT ceramics doped with different Ta_2O_5 content.

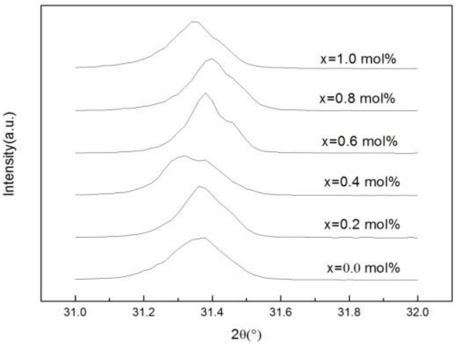
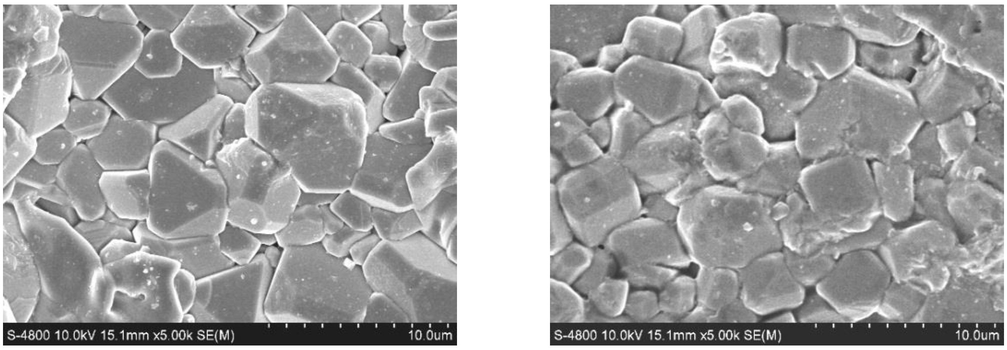


Fig. 2. Local amplification for XRD patterns of the crystal surface (110).

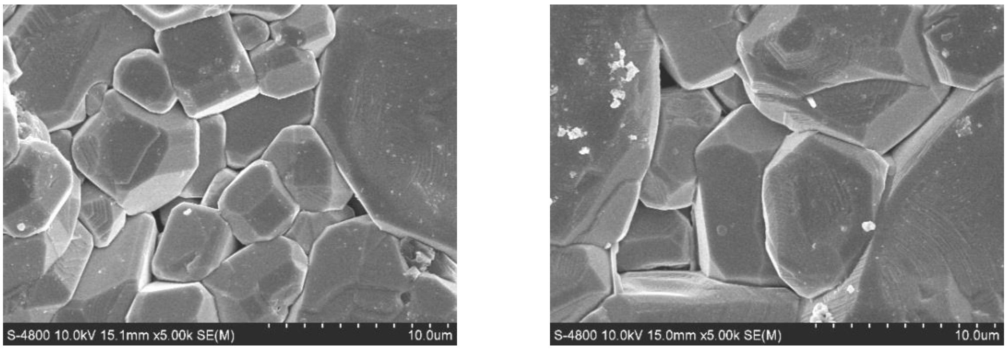
Fig. 2 is a diffraction map of the crystal surface (110) for local amplification. From the figure, there is a slight change in the gradient of the diffraction pattern of samples with different doping concentration. The ion radii of Zr^{4+}, Ti^{4+}, and Ta^{5+} are 0.079 nm, 0.069 nm, and 0.072 nm, respectively. From the perspective of ion radius, Ta^{5+} ions can replace the position of Ti^{4+} ions or Zr^{4+} ions. When the doping amount is less than 0.4 mol%, the position of the diffraction peak angle is basically unchanged. When the doping amount is greater than 0.4 mol% and less than 0.6 mol%, the diffraction peak moves toward a high angle, indicating that the doping can reduce the lattice spacing, and Ta^{5+} ions replace the Zr^{4+} ions at the B site. When the doping amount is greater than 0.6 mol%, the diffraction peak moves toward a low angle with the increase of the doping amount, indicating that the doping can increase the lattice spacing and Ta^{5+} ions replace Ti^{4+} ions at the B site [14].

The results of the SEM test for BZFT ceramics doped with different Ta_2O_5 content sintered at 1300 °C for 2 h were shown in Fig. 3. As shown in the figure, the shape of ceramic grains that are not doped with Ta_2O_5 is irregular, and the size of the grains is not uniform. As the amount of Ta_2O_5 doped increases, the grains gradually grow, the porosity rate increases, and the homogenization occurs; When the amount of Ta_2O_5 doping continues to increase, the grain size decreases, the porosity rate decreases, the grain density increases, and when x = 1.0 mol %, the grain surface appears glass phase.

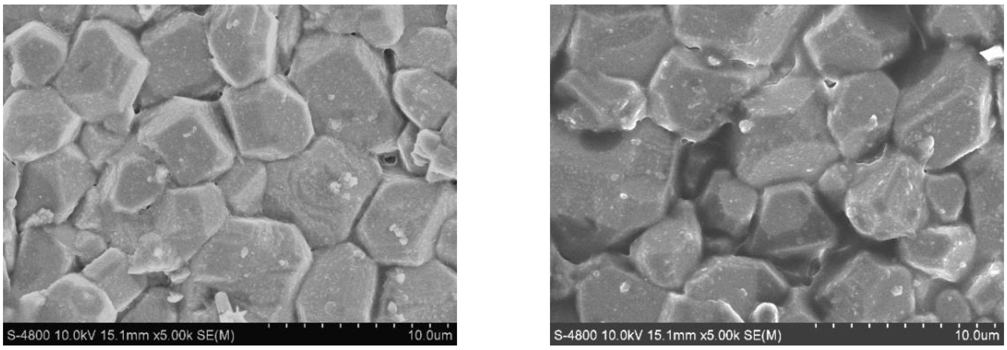


(a) x= 0.0 mol%

(b) x= 0.2 mol%



(c) x= 0.4 mol% (d) x= 0.6 mol%



(e) x= 0.8 mol% (f) x= 1.0 mol%

Fig. 3. SEM micrographs of the surface of BZFT ceramics.

The ion radii of Ba^{2+} and Ti^{4+} are 0.16 nm and 0.069 nm, respectively, while the ion radius of Ta^{5+} is 0.072 nm. Therefore, Ta^{5+}, which is a doped ion, enters the lattice and easily replaces the Ti^{4+} ion with a similar ion radius, undergoes a defect reaction, forms a weakly bound electron, and produces a weakly bound electron polarization. At the same time, the deformation of the main crystal phase structure caused by the A-site substitution also enhanced the ion polarization, which was conducive to sintering and promoted the growth of the grains. However, when the Ta^{5+} ion partially replaces the A site, the weakly bound electrons are also prone to compound with the structurally unstable A-site ion, and compound with the positive charge, thereby weaken the electron and ion polarization. Furthermore, due to the existence of the grain boundary, the doped ions at the grain boundary can produce nail action, then prevent the growth of grains.

Under different sintering temperatures and 1 kHz test frequency conditions, the dielectric constant changes with Ta_2O_5 doping content are shown in Fig. 4. It can be seen from the figure that with the increase of Ta_2O_5 doping, the dielectric constant of the sample increases first and then decreases, and the dielectric constant is the highest when the doping amount is x = 0.80 mol%. At a certain amount of Ta_2O_5 doping, with the increase of the sintering temperature, the dielectric constant increases first and then decreases, and the dielectric constant is the highest at 1300 °C.

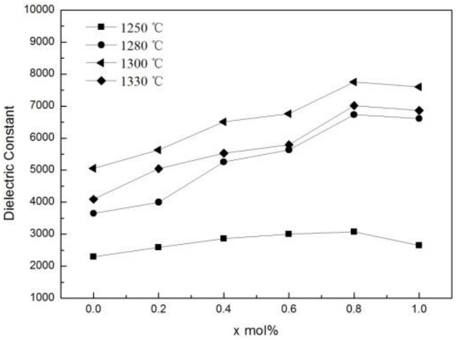


Fig. 4. Dielectric constants of BZFT ceramics with various Ta_2O_5 doping content.

The ion radii of Ba^{2+}, Ti^{4+}, and Ta^{5+} are 0.16 nm, 0.069 nm, and 0.072 nm, respectively. The ion radius of Ta^{5+} is closer to the ion radius of Ti^{4+}, when Ta^{5+} ion doping $x \leq 0.8$ mol%, Ta^{5+} ion preferentially replaces Ti^{4+}. The reaction that occurs is as follows (1),

$$Ba^{2+}Ti^{4+}O^{2-}{}_3 + xTa^{5+} \rightarrow Ba^{2+}[Ti^{4+}{}_{1-2x}Ta^{5+}{}_x(Ti^{4+}e)_x]O_3 + xTi^{4+} \tag{1}$$

Since the ion radius of Ta^{5+} is greater than the ion radius of Ti^{4+}, and the price of Ta^{5+} ion is higher than the price of Ti^{4+} ion, in order to maintain the conservation of the price of electricity, Ti^{4+} becomes Ti^{3+}, that is, Ti^{4+} ions weakly bind an e and form(Ti^{4+}•e). As the electron polarization of the weakly bound electrons increases, lattice distortion is caused and the dielectric constant is increased. Afterwards, with the increase of doping, the size of sample particles becomes smaller, resulting in a decrease in the dielectric constant [15].

Under different sintering temperatures and 1 kHz test frequency conditions, the dielectric constant changes with temperature are shown in Fig. 5. It can be seen from the figure that at different sintering temperatures, Ta^{5+} is doped to BZFT ceramics, which has a significant movement effect on the Curie temperature and moves the Curie temperature toward a low temperature. With the increase of Ta_2O_5 doping, the dielectric constant at the Curie temperature point also increases, which has the effect of increasing dielectric constant at the Curie temperature.

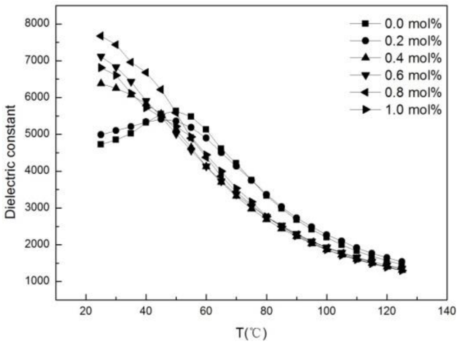


Fig. 5. Temperature dependence of dielectric constants of BZFT ceramics.

Under different sintering temperatures and 1 kHz test frequency conditions, the dielectric loss changes with temperature are shown in Fig. 6. As can be seen from the figure, with the increase of the content of Ta^{5+} ion, the dielectric loss of the sample decreases at room temperature. With the increase of ambient temperature, the temperature stability of the sample dielectric loss is enhanced and maintains at a lower value. Therefore, when preparing BZT matrix dielectric materials, adding an appropriate amount of Ta_2O_5 can produce dielectric materials with low dielectric loss and good temperature stability.

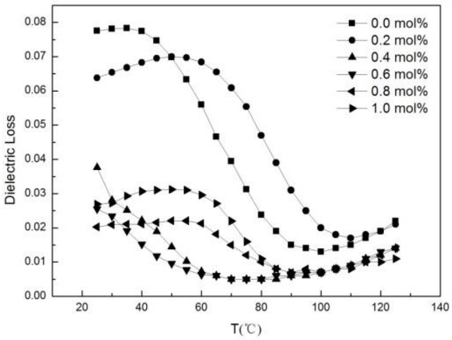


Fig. 6. Temperature dependence of dielectric loss of BZFT ceramics.

4. Conclusions

The BZFT ceramics are prepared using solid state synthesis method. Effects of Ta_2O_5 dopant on microstructure and dielectric properties of BZFT ceramics are investigated. When Ta_2O_5 is doped with BZTF ceramics, the crystal structure is a single perovskite structure, and the admixture of Ta^{5+} has no new phase generation. As the amount of Ta_2O_5 doped increases, the grains gradually grow, the porosity rate increases, when the amount of Ta_2O_5 doping continues to increase, the grain size decreases. Thanks to the Ta^{5+} substituting for Ti^{4+}, the electron polarization of the weakly bound electrons increases, then the dielectric constant is increased. Afterwards, with the increase of doping, the size of sample particles becomes smaller, resulting in a decrease in the dielectric constant. With the increase of ambient temperature, the temperature stability of dielectric loss is enhanced, and the dielectric loss maintains at a lower value. Therefore, adding an appropriate amount of Ta_2O_5 can produce BZFT ceramics with low dielectric loss and good temperature stability.

Acknowledgements

This work is partially supported by the National Natural Science Foundation of China (Grant No. 51874137) and the Natural Science Foundation of Hebei Province (Grant No. E2017209223).

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