The investigation of electrical properties and microstructure of ZnO-doped $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ ceramics

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$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ ceramics with or without ZnO have been prepared by traditional solid state reaction method. The XRD analysis showed that the doped Zn^{2+} ions diffused into the BST crystal lattice, resulting in the variation of dielectric properties. Especially the dielectric constant at Curie point decreased with doping ZnO content when it is lower than 0.5 mol%. Due to the promotion of sintering, doping ZnO can enhance the density of ceramics but increase grain size. However, ZnO is a kind of semiconductor and can lead to the decrease in electrical breakdown strength value.

Keywords: BST ceramics; ZnO doped; dielectric properties.

1. Introduction

Ferroelectric ceramics have been widely used in many areas, including sensors, actuators and capacitors, due to their high dielectric and piezoelectric responses.^{1–3} During the past decades, lead-based ferroelectric materials dominated the application, and the representative systems were lead-based ferroelectric materials, such as $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, and relaxor- PbTiO_3 systems.^{4–7} However, due to limitation of lead and other harmful elements used in electronic devices by the EU and other countries, developing lead-free ferroelectric materials becomes an urgent challenge from both fundamental and applying researches.^{8–11} Among all lead-free ferroelectric materials, $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) are frequently studied. BST is a complete solid solution of BaTiO_3 and SrTiO_3 , and has shown a large dielectric constant with an applied DC electric field and low dielectric loss.¹² Moreover, it is very convenient that the Curie temperature of BST ceramics can be controlled to meet the requirements of various applications by modifying the molar fraction x .¹³ Therefore, BST ceramics have been widely utilized in many electronic fields.

Generally, in order to promote the performances of the BST ceramics and to meet the requirements of different applications, doping different kinds of equivalence or unequivalent ions into BST ceramics have been widely adopted in many researches,^{14–16} such as Ce^{4+} ,¹⁷ Sb^{3+} ,¹⁸

Mg^{2+} ,¹⁹ etc. It has been reported that ZnO can promote ceramics to gain excellent properties,^{20–22} however, there are few reports about BST ceramic doped with ZnO. Therefore, the purpose of this investigation is to study the influence of electrical properties and microstructure when doping ZnO into BST ceramic, and figure out the doping mechanism in the BST ceramics.

2. Experimental Details

$\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ powders were prepared by the conventional solid state reaction method. BaCO_3 (99.8%), TiO_2 (99%) and SrCO_3 (99.5%) (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) powders were mixed in deionized water and ball milled with zirconia milling media in a sealable PE bottle for 24 h, followed by a drying process. After drying, the above mixture was pressed into pellets with 30 mm in diameter and calcined at 1200°C for 4 h with a heating rate of 5°C/min. The calcined pellets were crushed and ball milled in deionized water for another 24 h to obtain fine $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ powders, abbreviated as BST0. Afterwards, both the as-prepared BST powders and the commercial ZnO nanoparticles were weighed according to the formula of $\text{BST} - x\text{ZnO}$ with $x = 0.1, 0.2, 0.3, 0.4, 0.5$ (mol%). The mixed powders were abbreviated as BST1–BST5. Each mixture was ball milled again in deionized water for 24 h. After drying, the mixed

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powders and PVA were mixed well, sieved through a 300 μm -size, and pressed into small pellets with 10 mm in diameter and 1 mm in thickness under a pressure of 8 MPa. After debinding, the small pellets were sintered in air at 1320–1350°C for 0.5 h with a rapid increasing and decreasing temperature rate of 10°C/min. Silver paste was added onto both sides of the pellets and sintered at 700°C for 10 min.

The densities of studied samples were measured using Archimedes' method. Phase analyses were performed by an X-ray diffractometer (6100, Shimadzu, Japan) with a monochromatic $\text{CuK}\alpha$ radiation in a θ - 2θ scanning function from 20° to 70° with a speed of 0.02°/s. The microstructures of the fractured surfaces were observed by a scanning electron microscope (JSM 6610, JEOL, Tokyo, Japan). For electrical properties characterization, silver paste was added onto both sides of the sample pellets and sintered at 700°C for 10 min to form electrodes. The temperature-dependent dielectric properties at 1, 10 and 100 kHz, were measured from room temperature to 400°C by an LCR meter (E4980AL, Keysight, USA) with a heating rate of 2°C/min. Room temperature polarization–electric field (P–E) hysteresis loops were measured based on a Sawyer–Tower circuit (TF analyzer 2000E, aixACCT, Aachen, Germany) at a frequency of 1 Hz.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) patterns for pure BST and ZnO-doped BST ceramic samples. From the diffraction patterns, it can be seen that both pure BST and doped BST show the same peak, indicating the same perovskite structure. The peaks were analyzed incorporating PDF cards, and it is found that the major phases of all components are

Fig. 1. Room temperature XRD patterns for BST and ZnO-doped ceramic samples measured from 20° to 70° with a scanning step of 0.02°.

tetragonal according to the peak splitting occurring at 2 θ around 45°. ²³ No second phase was detected, indicating that ZnO has entered the lattice of BST and forms solid solution with BST.

Figure 2(a) shows the densities of pure BST and doped BST samples. It can be seen that by increasing the ZnO content, the average density increases first, and then continues to increase after a small fluctuation. Finally, it does not change too much. Moreover, the sample with 0.2% doping content possessed the maximum value, i.e., 5.87 g/cm³. When the ZnO content is 0.3%, the density of BST3 decreased. Generally speaking, introducing the ZnO into the BST system can generate two effects. On the one hand, it can promote the densification of BST ceramics, and finally lead to an increase in density. On the other hand, the introduction of ZnO will naturally decrease the density of BST, due to its lower theoretical density compared with that of BST ceramic. Thus, it is likely that the two effects work together, and finally result in the above phenomenon. Figure 2(b) shows the electrical breakdown strength (BDS) of the ceramic samples. It can be seen that by increasing the ZnO content, the BDS of studied samples is decreased from 40 kV/cm to 30 kV/cm level. There are many factors which can affect the BDS,

Fig. 2. Variation of the density as a function of the ZnO content for pure and doped BST ceramic samples.

such as density, grain size, etc. Because ZnO is a kind of semiconductor, the BDS of the doped ceramics will decrease compared with the pure BST ceramic. However, ZnO is also one kind of sintering aid, thus it can improve densification and enhance density. Therefore, the variations of BDS of doped ceramics are generally affected by the aforementioned two effects.

The micrographs of the fractured surface of representative BST0, BST1, BST2 and BST4 ceramics are shown in Fig. 3. Because of the rapid heating and cooling rates during sintering process, pure BST ceramics show fine grains (average grain size less than $1\ \mu\text{m}$) and compact structure. However, by increasing the ZnO doping concentration, the grain sizes increased drastically. Typical structures can be seen in Figs. 3(b)–3(d). Besides the increase of average grain size, abnormal growth in some grains has also been observed. That is mainly because Zn^{2+} can promote the sintering of matrix and decrease the sintering temperature.²²

The temperature-dependent permittivity and dielectric loss measured at 100 Hz, 1 kHz, 10 kHz and 100 kHz from 20°C to 160°C are shown in Fig. 4. It can be seen that for each composition, only one peak is observed around 90°C , which indicates a ferroelectric-to-paraelectric phase transitions.

Above this phase transition temperature (T_m), the permittivity measured at different frequency is the same, while loss shows some difference at higher temperature. The T_m for BST0 is 94.9°C . By introducing the ZnO into the BST system, it decreased to 91°C at first, and then increased to 96°C . Finally, it shows a variation from 85.9°C to 90°C . It is different to get the variation trend of the T_m with respect to the increase of the ZnO content. This might be due to the small amount of the doping content.

For all the studied ceramic samples, the permittivity above T_m shows a monotonous decrease with respect to the increase of the temperature. Such a dielectric dispersion can be fitted by a modified Curie–Weiss law as suggested in Eq. (1),^{24,25}

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C}, \quad (1)$$

where C is the Curie constant, ε_r and ε_m correspond to the dielectric permittivity and permittivity at the T_m , respectively, and γ is the degree of the diffuseness with the value varying from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric. As shown in Fig. 5, the dielectric permittivity above T_m for all studied samples can be fitted by Eq. (1). For the sample without and with low content of the ZnO, all the

Fig. 3. SEM micrographs of the fractured surface morphologies of the BST ceramic samples with various ZnO contents: (a) BST, (b) 1 mol%, (c) 2 mol% and (d) 4 mol%.

Fig. 4. Dielectric permittivity and loss tangent as a function of temperature for the pure BST and doped BST ceramic samples measured at 100 Hz, 1 kHz, 10 kHz and 100 kHz from 20 °C to 160 °C with a heating rate of 2 °C/min. (a) BST0, (b) BST1, (c) BST2, (d) BST3, (e) BST4 and (f) BST5.

data can be well fitted. But for the samples with 0.4 and 0.5 mol% ZnO, the permittivity near the T_m is out of the fitting curves, suggesting some changes in the structures. The γ values of all studied samples are between 1.15 and 1.25 as shown in Fig. 6(b), indicating a rather weak relaxor nature. For classical ferroelectric, the modified Curie–Weiss law can be applied to describe the permittivity response for the whole temperature range. However, with the interference by the ZnO, the long range order for ferroelectricity is disturbed and thus there is a deviation of the dielectric response from the modified Curie–Weiss law, especially at the temperature region close to the T_m .

Normally with the appearance of the relaxor nature, the dielectric peaks would also become wider especially at the high temperature side. This broadening effect is attributed to the diffuse phase transition (DPT) due to the inhomogeneous distribution of the A-site or B-site ions in the perovskite structure. In order to characterize the diffuseness of the DPT, we use Eq. (2) to extract the diffuseness temperature,²⁶

$$\frac{\varepsilon_m}{\varepsilon_r} = 1 + \frac{1}{2} \left(\frac{T - T_m}{\delta_g} \right)^2, \quad (2)$$

where δ_g is the Gaussian diffuseness temperature. Note that only the permittivity in the limitation of $1 < \varepsilon_m/\varepsilon_r < 1.5$ can

Fig. 5. Fitting results of the dielectric permittivity above T_m based on Eq. (1) for pure and doped BST ceramics samples measured at 1 kHz. (a) BST0, (b) BST1, (c) BST2, (d) BST3, (e) BST4 and (f) BST5.

be used for fitting. Figure 6(a) shows the fitting results by applying Eq. (2) to the data, and the diffuseness temperatures are shown in Fig. 6(b) as a function of ZnO content. The values are between 10.9°C and 13.2°C. These values are very close to value of a typical ferroelectric. It can be seen that by introducing the ZnO into the BST system, both the γ and δ_g show very little variation with respect to the ZnO content, suggesting that ZnO may enter the BST lattice partially, although this deduction cannot be verified by the XRD due to the low concentration of the ZnO.

The P-E hysteresis loops for BST and doped BST samples are shown in Fig. 7. For BST sample, the P-E hysteresis loop shows a very weak pinched feature, which might be related to the relatively high conductivity of the sample.²⁷ By increasing the ZnO content, the P-E hysteresis transfers into slim and slanted shapes, and meanwhile the pinched feature becomes weaker. All these characters suggest that ZnO promotes the sintering of the ceramics and decreases the conductivity effectively. By increasing the addition of ZnO, the remnant polarization decreased first. However, when doping content is 0.3%, the remnant polarization increased. Further increasing the doping content to 0.4% and 0.5%, the remnant polarization decreased once again. It is well known that ZnO is one kind of polar molecule, and doping it into BST ceramic can make the spontaneous polarization much easier. Moreover, BST3 has the minimum of BDS, as shown in Fig. 2(b). This indicates that the polarization of BST3 is relatively easier. Therefore, BST3 ceramic has the maximum remnant polarization. Moreover, the density of BST3 is also relatively low, so it can be deduced that there are pores and other defects in BST3 samples. Generally, the charge carriers can

Fig. 6. (a) Fitting results of the dielectric permittivity above T_m based on Eq. (2) for pure and doped BST ceramics samples measured at 1 kHz. (b) γ coefficient and diffuseness temperature for pure and doped BST ceramics samples determined from the permittivity measured at 1 kHz.

Fig. 7. Room temperature P-E hysteresis loops for BST ceramic samples with different ZnO contents measured at 1 Hz. (a) BST0, (b) BST1, (c) BST2, (d) BST3, (e) BST4 and (f) BST5.

be captured by these defects, which can cause electrostatic force, finally hindering the polarization switching.²⁸ Therefore, the coercive field increased.

4. Conclusions

ZnO has been doped into BST ceramics through the traditional electroceramic processing. Peak splitting at 2θ around 45° indicated that the major phases of all components are tetragonal, and there was no second phase formed, showing that ZnO had entered the lattice of BST ceramic. ZnO generally has two effects during doping. One is promoting densification, and the other is its lower density. It is highly likely that the aforementioned effects work together, and finally result in the variation of densities. With more addition of ZnO, the grain sizes became larger. Oxygen vacancy will be generated by Zn^{2+} , which can cause distortion of lattice and make the peaks become wider. Meanwhile, ZnO is a kind of polar molecule, and doping ZnO into BST can make the spontaneous polarization much easier, resulting in the variation of P-E loops.

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