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Effects of B_2O_3-SiO_2 doping on electrical properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics①

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Abstract: $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics doped with B_2O_3-SiO_2 glass composition were prepared by using conventional solid-state reaction method. The effects of glass dopant on the dielectric and ferroelectric properties were investigated. The results show that the dielectric constant decreases while the dielectric loss increases after doping. And as the glass content increases the dielectric constant decreases while the dielectric loss changes slightly. From the complex impedance analysis the resistance and the relaxation time of the grain and the grain boundary can be calculated. Comparing the P—E hysteresis loop of undoped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics with that of B_2O_3-SiO_2 doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics, it can be seen that the remanent polarization decreases when the B_2O_3-SiO_2 content is lower than 8% (molar fraction), and the coercive field increases with the increase of B_2O_3-SiO_2 content.

Key words: $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics; B_2O_3-SiO_2; dielectric properties; impedance; ferroelectric properties
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1 INTRODUCTION

(Ba, Sr)TiO_3 (abbreviated as BST) is a solid solution of $BaTiO_3$ and $SrTiO_3$, it exhibits excellent properties, such as high dielectric constant, low dielectric loss, low leakage current, high dielectric tunability, and huge pyroelectric coefficient. Besides, it has a remarkable characteristic that the Curie temperature of BST can be controlled by varying the molar content of the strontium to meet the requirement of various applications. Therefore BST is an attractive candidate for DRAM, phase shifter, tunable filters and infrared detectors and other fields[1, 2].

To date, much effort has been directed towards the investigation of the processing and the properties of BST ceramics[3-10]. SU et al[3] investigated the effects of processing on the properties of BST ceramics and Szymczak et al[4] investigated the sintering effects on the dielectric properties of BST ceramics. However, the sintering temperature of BST ceramics prepared by using conventional solid-state method is very high and the grains are not homogeneous in their investigation. Several studies have been carried out on the decrease of the sintering temperature and promoting the density[1, 11-18], but the results haven't been satisfied. ZHAI et al produced glass doped BST powders by sol-gel processing, and calcining and sintering with conventional solid-state reaction method, then they obtained BST ceramics with glass-like materials. By this way, the sintering temperature of BST ceramics has been decreased, but the properties are not satisfactory.

Despite intensive experimental efforts, however, an effective measurement to decrease the sintering temperature of BST ceramics has been lack. In our work, BST ceramics were prepared by using conventional solid-state reaction method, and B_2O_3-SiO_2 is added to decrease the sintering temperature. B_2O_3 has a melting point of 445 ℃, and it forms liquid during the sintering and promotes the sintering. Several reports have shown that when B_2O_3 is the only addition, it indeed decreases the sintering temperature but at the same time $BaTi(BO_3)_2$ and other materials form[13]. SiO_2 has a melting point of 1 670 ℃, and it cannot decrease the sintering temperature of BST ceramics[18]. But when B_2O_3-SiO_2 is added, the sintering temperature of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics is decreased and no second phase is detected from XRD patterns.

In this paper, the effects of B_2O_3-SiO_2 doping on the dielectric and ferroelectric properties of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics were investigated. The impedance plot was employed to estimate the resistance of the grains and the grain boundary, and the relaxation time was also estimated.

2 EXPERIMENTAL

$Ba_{0.65}Sr_{0.35}TiO_3$ ceramics and B_2O_3-SiO_2 doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics were prepared by conven-

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tional solid-state reaction method. $BaCO_3$, $SrCO_3$, TiO_2, B_2O_3 and SiO_2 were used as starting materials. The weighted stoichiometric powders were mixed by ball-milling in agate mortars for 4 h, then dried and calcined at 1 000 ℃ for 2.5 h. The calcined aggregate were again ball-milled for 4 h, then dried and pressed into d11 mm × 1.5 mm green pellets at a pressure of 200 MPa. The undoped green pellets were sintered at 1 390 ℃ for 2 h and B_2O_3-SiO_2 doped green pellets were sintered at 1 200 ℃ for 2 h. Then the sintered specimens were polished to a thickness of 0.9 mm and electroded with silver paste and dried.

The dielectric constant, the dielectric loss and the impedance were measured with HP4192A low frequency impedance analyzer. The P—E hysteresis loops were measured with a Sawyer-Tower circuit at 12 ℃.

3 RESULTS AND DISCUSSION

3.1 Dielectric properties

Fig. 1 shows the relationship between the dielectric properties and glass-doped content at room temperature. It can be seen that the dielectric constant decreases and the dielectric loss increases when B_2O_3-SiO_2 content is lower than 1% (molar fraction). However, the dielectric constant decreases sharply as the doping glass content increases while the dielectric loss changes slightly. This can be explained by that in ceramics the dielectric constant is strongly affected by the composition of $Ba_{0.65}Sr_{0.35}TiO_3$ and B_2O_3-SiO_2, while the dielectric loss is strongly affected by the distribution of these two phase[19]. As B_2O_3-SiO_2 content increases, the change of the composition is larger than that of the distribution, which causes the larger change of the dielectric constant. When B_2O_3-SiO_2 distributes homogeneously in $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics, the dielectric constant of the doped ceramics can be calculated by logarithmic mixture rule[20], which can be expressed as

$$\lg\varepsilon = y_1 \lg\varepsilon_{BST} + y_2 \lg\varepsilon_{B\text{-}Si} \quad (1)$$

where ε is the dielectric constant of doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics, ε_{BST} and $\varepsilon_{B\text{-}Si}$ are the dielectric constants of undoped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics and B_2O_3-SiO_2 glass respectively, and y_1, y_2 are the volume fractions of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics and B_2O_3-SiO_2, respectively. The dielectric constant of B_2O_3-SiO_2 is less than 4.5, which is much lower than that of undoped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics, so the dielectric constant of doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics is smaller. This is also confirmed in Fig. 1. In our work, the experimental data of the dielectric constant of doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics is smaller than the calculated data, which may be caused by the defects in the grain boundary.

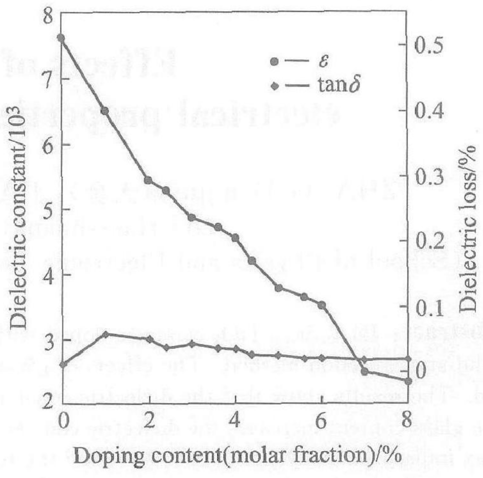

Fig. 1 Dielectric properties vs B_2O_3-SiO_2 content

3.2 Impedance analysis

Complex impedance plot of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics at 355 ℃ and its equivalent circuit are shown in Figs. 2(a) and (b), respectively. In Fig. 2(a), the experimental data can be well fitted into semicircles except at very low frequency. It is very clear that there are two semicircles for the impedance plot of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics in the frequency range from 5 Hz to 13 MHz. The semicircle in low frequency can be equalized as a parallel circuit of a resistor and a capacitor and the semicircle in high frequency can be equalized as a resistor[21, 22], as shown in Fig. 2(b). The complex impedance Z of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics can be expressed with the following formulation[23]:

$$Z = R_g + \left(\frac{1}{R_{gb}} + j\omega C_{gb}\right)^{-1} \quad (2)$$

where R_g is the resistance of grains, R_{gb} is the resistance of grain boundary and ω is the angular frequency. From the formulation above, the real part of the complex impedance can be expressed as

$$Z' = R_g + \frac{R_{gb}}{1 + (\omega R_{gb} C_{gb})^2} \quad (3)$$

It indicates that when $\omega \to \infty$, $Z' \to R_g$. Fitting the curve, on the real axis the interception can be considered as R_g. From Eqn. (2), the imaginary part of the impedance can be deduced as

$$Z'' = R_{gb} \cdot \frac{\omega C_{gb} R_{gb}}{1 + (\omega C_{gb} R_{gb})^2} \quad (4)$$

At the maximum of the imaginary part of the impedance, the relation is satisfied:

$$\omega C_{gb} R_{gb} = 1 \quad (5)$$

Then R_{gb} can be estimated. It can be seen from the impedance plot that R_g is about 5 Ω, while R_{gb} is about 20 kΩ, which indicates that the grain boundary effects play an important role in $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics.

From Fig. 2(c) the relaxation time τ can also be calculated according to the formulation $\omega_{max}\tau = 1$ at the maximum of the imaginary part of the impedance. The relaxation time of grain boundary τ_1 and that of grain τ_2 can be calculated from the frequency of the peak imaginary as 7×10^{-3} s and 3.1×10^{-6} s, respectively. This indicates that the movement of the dipole in the grain boundary is more difficult than in the grains.

3.3 Ferroelectric properties

The remanent polarization and the coercive field of BST ceramics are listed in Table 1. It can be seen that the coercive field increases with the increase of the doping glass content, while the remanent polarization decreases with the increase of the doping glass content when the doping content is lower than 8%. B_2O_3-SiO_2 has no ferroelectricity, so that the content increases, the ferroelectricity of the ceramics decreases and the remanent polarization decreases. At the same time, as B_2O_3-SiO_2 content increases the grain size decreases and the ratio of the grain boundary in the ceramics increases, so the movement of the domain becomes more difficult, which causes the increase of the coercive field. In Table 1, it's very clear that when the content of B_2O_3-SiO_2 reaches 8%, the remanent polarization increases abruptly. It may be caused by a new material formed in the ceramics. The typical P—E hysteresis loop of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics in Fig. 3(a) is slimmer than that of 8% B_2O_3-SiO_2 (molar fraction) doped ceramics in Fig. 3(b),

Table 1 Remanent polarization and coercive field of BST ceramics

Specimen	B_2O_3-SiO_2 doped (molar fraction) / %	Remanent polarization/ ($\mu C\cdot cm^{-2}$)	Coercive field/ ($kV\cdot cm^{-1}$)
BST 1	0	12.2	67
BST 2	1	9.4	142
BST 3	5	6.9	156
BST 4	8	13.9	176

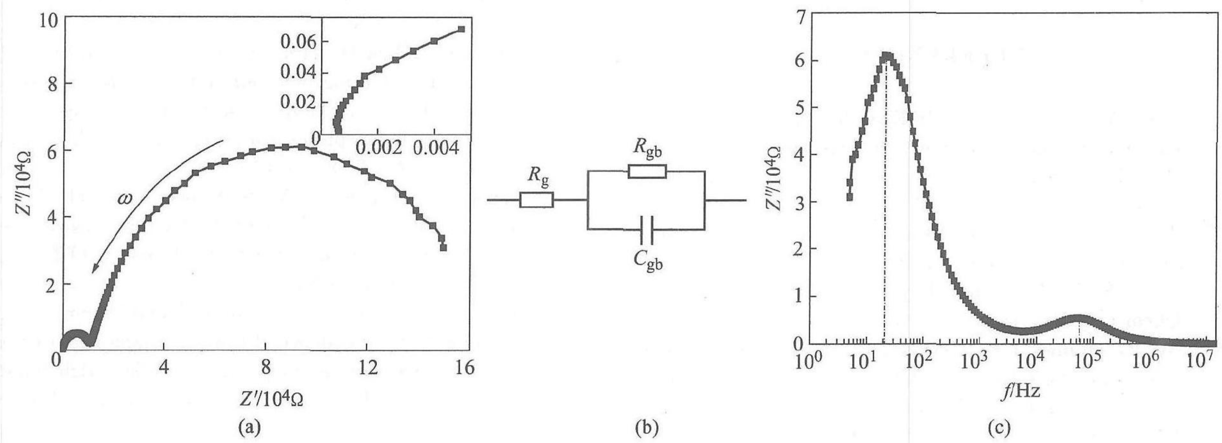

Fig. 2 Typical impedance plot and its equivalent circuit
(a) —Impedance plot; (b) —Equivalent circuit; (c) —Frequency dependence of imaginary part of impedance

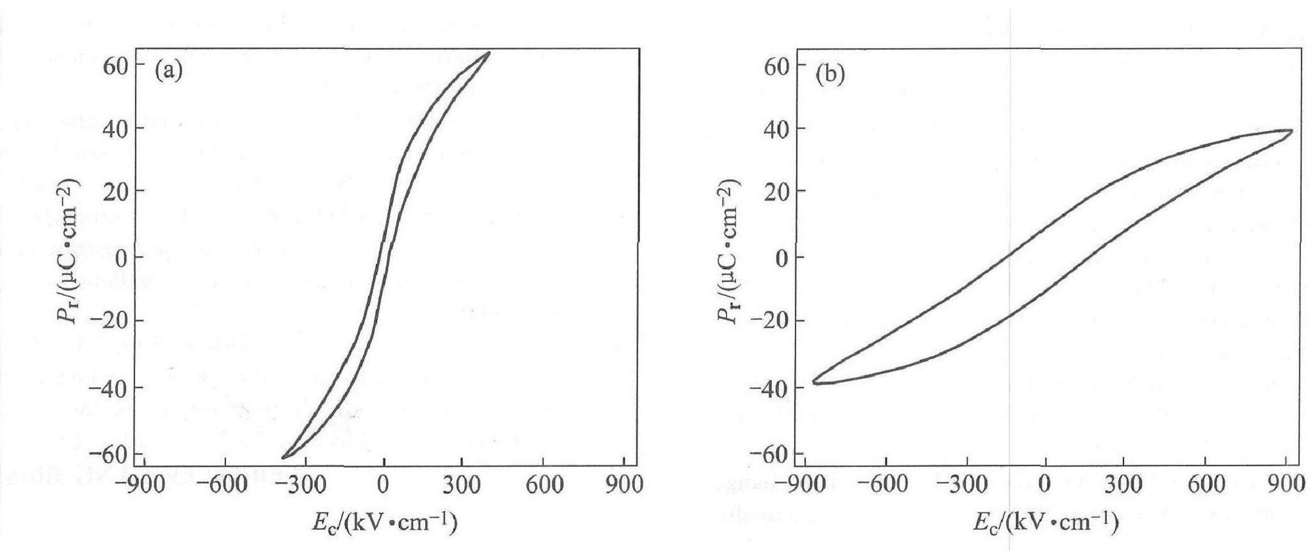

Fig. 3 Typical hysteresis loops of BST ceramics
(a) —BST ceramics; (b) —8% B_2O_3-SiO_2 (molar fraction) doped BST ceramics

which is also confirmed in Table 1.

4 CONCLUSIONS

The sintering temperature of BST ceramics prepared by conventional solid-state reaction method is decreased by adding B_2O_3-SiO_2. Investigation of the effects of glass doping shows that the dielectric constant and the dielectric loss of B_2O_3-SiO_2 doped $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics decrease as the glass content increases. From the typical impedance plot of BST ceramics at 355 ℃, the resistances of grain and grain boundary can be calculated as 5 Ω and 20 kΩ, respectively. The relaxation time of grain boundary and gain can also be calculated from the frequency dependence of imaginary part of impedance as 7×10^{-3} s and 3.1×10^{-6} s, respectively. The coercive field increases, while the remanent polarization decreases with the increase of the doping glass content, which indicates that doping B_2O_3-SiO_2 decreases the ferroelectricity of $Ba_{0.65}Sr_{0.35}TiO_3$ ceramics.

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