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Dielectric relaxation behavior and energy storage properties in $Ba_{0.4}Sr_{0.6}Zr_{0.15}Ti_{0.85}O_3$ ceramics with glass additives

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Abstract

$Ba_{0.4}Sr_{0.6}Zr_{0.15}Ti_{0.85}O_3$ ceramics with $SrO–B_2O_3–SiO_2$ glass additives were prepared via the solid state reaction route. The effects of glass contents on the sintering behavior, dielectric properties, microstructures, and energy storage properties of BSZT ceramics were investigated. Dielectric breakdown strength of 22.4 kV/mm was achieved for BSZT ceramics with 20 wt% glass addition. Dielectric relaxation behavior was observed in dielectric loss versus temperature plots. In order to investigate the mechanism of dielectric breakdown performance, the relationship between dielectric breakdown strength and grain boundary barrier was studied by the measurements of breakdown strength and activation energy. A discharged energy density of 0.45 J/cm^3 with an energy efficiency of 88.2% was achieved for BSZT ceramics with 5 wt% glass addition.

Keywords: A. Sintering; B. Grain boundaries; C. Dielectric properties; D. Glass

1. Introduction

Future technological advances in power inversion systems based on SiC modules will depend on advances in dielectric materials with high energy and power densities. One way to achieve these advances is to develop new materials for ceramic capacitor with high energy storage density [1–3]. High energy storage density capacitors with decreased volume, weight and cost are urgently needed for electric vehicles. In accordance with the energy storage density equation for nonlinear dielectrics [4,5], two key materials parameters to obtain high energy density are high dielectric constant and high breakdown strength (BDS, E_b), while high E_b makes a more pronounced contribution toward the energy density.

Recently, $Ba_xSr_{1-x}TiO_3$ (BST) ceramics have received interest in energy storage densities of the dielectric materials because of their extremely high dielectric constants [6,7]. Unfortunately, BST ceramics have a relatively low E_b due to the existence of defects (such as pores). Researches [8–11] have shown that the substitution of Ti^{4+} with Zr^{4+} ions in BST can reduce the dielectric loss or leakage current in the material, which improved the dielectric BDS obviously. In addition, it was reported that the addition of glasses to BST ceramics notably improved its BDS as well [12–14]. However, researchers mainly focused on the effect of glass additives on the sintering temperature and microstructure, rarely mentioned on the mechanism of breakdown. Huang et al. [15] found that dielectric breakdown strength strongly depends on the interface polarization in BST glass ceramics. In fact, interface polarization is also present in the glass added ceramics. The glass located at the grain boundary or surrounding the grains in glass added ceramics [12–14], impeding the transfer of free charge, and resulting in accumulation of charges or ions in intergranular area.

In this paper, $SrO–B_2O_3–SiO_2$ glass used as sintering additives for $Ba_{0.4}Sr_{0.6}Zr_{0.15}Ti_{0.85}O_3$ (BSZT) ceramics was prepared. The effect of glass contents on the dielectric properties, microstructures, and energy storage properties

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was investigated. In addition, we mainly discussed the dielectric relaxation behavior and the mechanism of breakdown of BSZT ceramics. The goal is to get new information on the dielectric relaxation behavior and mechanism of dielectric BDS of BSZT ceramics.

2. Experimental procedure

BSZT powder was prepared by the solid-state method using analytical reagent grade $BaCO_3$, $SrCO_3$, ZrO_2 and TiO_2 powders. Stoichiometrically weighed powders were wet-milled with distilled water for 4 h, dried and calcined at 1300 °C/4 h. According to the glass formation region [16], a glass with the composition of 51.62% SrO, 41.35% B_2O_3, 7.03% SiO_2 (weight fraction) was prepared from the analytical reagent grade carbonates or oxides. The appropriate constituents were well mixed and melted in corundum crucible at 1250 °C for 1 h. The molten glass was quenched in distilled water and then ball milled to fine powders. The glass powders were mixed with BSZT powder in the ratio corresponding to the following chemical composition: $(100-x)\%$ BSZT$+x\%$ glass (weight fraction), where $x=0$, 5, 10, 15 and 20. The mixed powders were pressed into pellets and then sintered at different temperatures for 2 h in air.

The sintered samples for dielectric measurement were polished to 0.5 mm in thickness and painted with silver paste and fired at 650 °C for 20 min. The frequency dependence of dielectric properties was measured using a precision LCR Meter (E4980A, Agilent Tech., CA, US) over a frequency range from 20 Hz to 2 MHz at room temperature, the temperature dependence of dielectric properties were measured over a temperature range from 40 to 450 °C, and the impedance data were measured over frequencies from 20 Hz to 2 MHz in a temperature range of 200–500 °C without bias voltage. The DC BDS measurement was performed using a withstanding voltage tester at room temperature. All samples were immersed in silicone oil to prevent surface flashover. At least 10 specimens were used for each composition during BDS testing. The polarization–electric field (P–E) hysteresis loops were measured using a ferroelectric tester (TF Analyzer 2000, aixACCT, Aachen, Germany) at room temperature.

3. Results and discussion

In order to determine the suitable sintering temperature (SST) [8], the bulk density of all samples sintered at different temperatures was measured by the Archimedes method. The measured density shows that the SSTs of the ceramics are 1450, 1240, 1220, 1180, and 1160 °C, when $x=0$, 5, 10, 15, and 20, respectively. The addition of glass largely decreases the SSTs of BSZT ceramics. In the rest of this paper, all the samples were prepared at their SSTs.

Fig. 1 presents the frequency dependence of dielectric constant and dielectric loss for BSZT ceramics with different glass contents. The dielectric constant of samples shows good frequency stability in the measured frequency range. Pure BSZT ceramic possesses a dielectric constant of about 1000, while the dielectric constant of BSZT ceramic with 20 wt% glass addition is only about 100, an order of magnitude reduction in dielectric constant was observed. The sharp decrease in the dielectric constant can be attributed to the addition of low dielectric constant component (glass). The dielectric loss of samples decreases gradually with increasing frequency, which tends to be stabilized at about 1×10^{-3} from 1 kHz to 2 MHz. According to the previous report [17], the dielectric loss at frequency range from 20 Hz to 1 kHz may induced by the leakage currents.

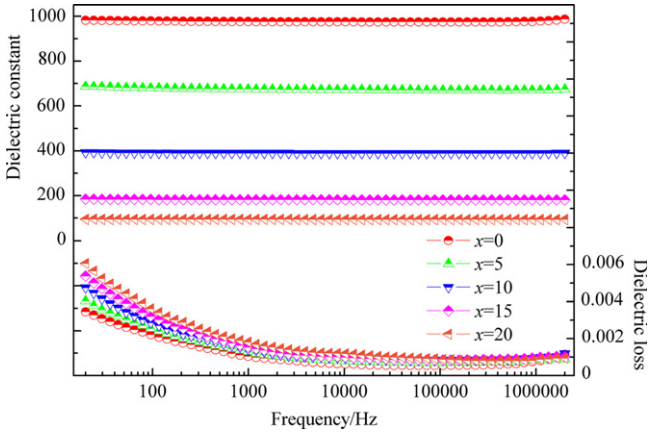

Fig. 1. Frequency dependence of dielectric constant and dielectric loss for BSZT ceramics with different glass contents.

Fig. 2 shows the variation of dielectric constant and dielectric loss with temperature at a few selected frequencies for pure BSZT ceramics and ceramics with 10 wt% glass addition. The dielectric constant and dielectric loss remain constant up to a certain temperature and thereafter, increase rapidly with increasing temperature. The temperature dependence of dielectric loss plot shows a peak. The position of the peak shifts to higher temperature with increasing frequency. Similar results were observed in other samples ($x=5$, 15, and 20). It is indicated that some relaxation polarization mechanism is existed in both pure BSZT ceramics and glass-added ceramics [18,19].

The complex impedance spectrum has been proved to be a powerful method for investigating the relaxation polarization mechanism of grain and grain boundary in ceramics [15,20]. The samples are measured at different temperatures at every 20 °C interval in order to get series of the Cole–Cole images. The complex impedance spectra measured at different temperatures for pure BSZT ceramics and ceramics with 10 wt% glass addition were presented in Fig. 3. Similar results were observed in other samples ($x=5$, 15, and 20). Two semicircles can be observed in the two diagrams, which indicate that two distinct dielectric relaxation processes exist in the sample. At low temperature (<380 °C), the first semicircle at low frequency cannot be obtained because of the high resistivity.