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Dielectric properties of Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$

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Abstract

Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ (BSYT) dielectric ceramics were prepared by conventional solid state method, and their dielectric properties were investigated with variation of Sb_2O_3 doping content and sintering temperature. The X-ray diffraction patterns indicated that all the BSYT specimens possessed the perovskite polycrystalline structure. The experimental results reveal that the introduction of Sb_2O_3 into $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ can control the grain growth, reduce the relative dielectric constant and dielectric loss, shift the Curie temperature to lower temperature and significantly improve the thermal stability of the BSYT ceramics. The samples doped with 1.6 wt.% Sb_2O_3 sintered at 1320 °C for 2 h exhibited attractive properties, including high relative dielectric constant (>1500), low dielectric loss ($<40\times10^{-4}$), low temperature coefficient of capacitor(<±35%) over a wide temperature range from −25 °C to +85 °C.

Keywords: $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$; Sb_2O_3; Perovskite; Dielectrics; Microstructure; Electrical properties

1. Introduction

Capacitors have a wide range of applications in electrical and electronic products [1]. For several decades, lead oxide based ferroelectrics have been widely used in capacitors due to their outstanding dielectric properties. However, PbO vapor volatilized during processing causes serious environmental pollution. Therefore, it is necessary to search for lead-free ferroelectric ceramics with excellent properties comparable to those of lead-based ceramics.

Since the discovery of ferroelectric $BaTiO_3$ ceramics with high permittivity in 1943, considerable efforts have been focused on development and application of $BaTiO_3$-based ceramics [2]. Among the $BaTiO_3$-based ceramics, $Ba_{1-x}Sr_xTiO_3$ (BST) ceramics have received extensive attentions because of their predominant properties, such as high dielectric constant, low dissipation factor and adjustable Curie temperature. However, poor thermal stability limits their applications. For perovskite structures (ABO_3), doping with small amounts of ions can greatly affect the dielectric properties [3]. So recently a small quantity of the rare-earth oxides or transition-metal oxides have been employed as dopants to improve dielectric performances of BST ceramics [4–7].

In this paper, Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ dielectric ceramics were prepared by conventional solid state method. The Sb ion as dopant was added to improve the dielectric properties. The microstructural and dielectric properties of all specimens were investigated for capacitor applications.

2. Experimental

The chemical compositions of the specimens were given by the formula $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3+x$ wt.% Sb_2O_3 (x=0, 0.4, 0.8, 1.2, 1.6, 2.0). High purity $BaCO_3$ (>99.0%), $SrCO_3$ (>99.0%), TiO_2 (>98.0%) and Y_2O_3 (>99.5%) powders were used as starting raw materials. All the oxides and carbonates were weighed, ball-milled, dried and calcined at 1080 °C for 2 h. The calcined powders were mixed with Sb_2O_3 according to the above formula, reground, dried and added with polyvinyl alcohol (PVA) as a binder for granulation. The granulated powders were sieved through 40-mesh screen and then pressed into pellets of 10 mm in

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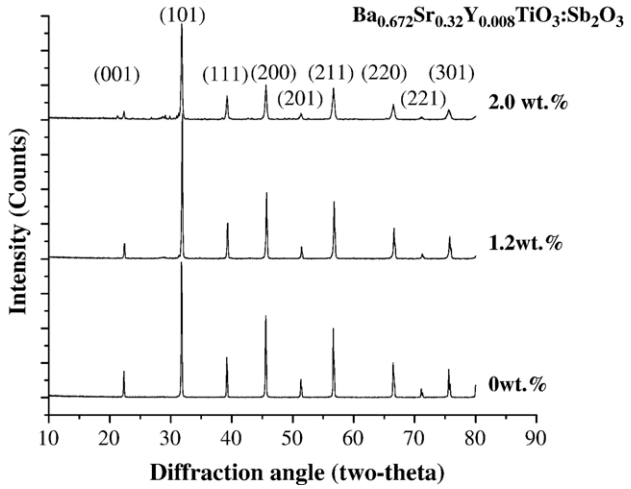

Fig. 1. XRD patterns of the Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ samples sintered at 1320 °C.

diameter and 2 mm in thickness under 250 MPa. Sintering was conducted in air at 1280–1320 °C for 2 h. The silver paste was painted on both sides as electrodes to provide ohmic contacts after the sintered samples were ultrasonically cleaned in distilled water. Finally the painted samples were fired at 530 °C for 10 min.

The phase detection and analysis were accomplished by XRD (Rigaku D/max 2500 V/pc) with Cu Kα radiation. The surface morphologies of the specimens were studied using the SEM (PhilipXL30 ESEM). The dielectric properties of ceramic bodies were measured with YY 2811 Automatic LCR Meter 4425 at 1 kHz. With the capacitance C and the dissipation factor D of the sample measured, the relative dielectric constant ε_r and the loss tangent tan δ were calculated as follows:

$$\varepsilon_r = \frac{14.4Ch}{\phi^2}$$

$$\tan\delta = \frac{fD}{1000}$$

where C is the capacitance (pF), h is the thickness (cm), ϕ is the diameter of the electrode (cm), f is the test frequency(Hz) and D is the dissipation factor. The temperature coefficient of capacitor TCC was determined using the following equation:

$$\mathrm{TCC} = \Delta C/C_0 \times 100\%$$

where C_0 is the capacitance at room temperature, and ΔC is the change in capacitance relative to C_0.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ bulk samples sintered at 1320 °C. It appears that perovskite polycrystalline structure is formed in all specimens and no secondary phase is detected even for the doping content of Sb_2O_3 up to 2.0 wt.%. Since the radii of Sb^{3+} (0.076 nm) ions are smaller than those of the Ba^{2+} (0.161 nm) and Sr^{2+}(0.144 nm) ions, the substitution for A-site with any of the Sb^{3+} ions leads to a distortion of the ABO_3 pervoskite structure. In this study, the addition of Sb_2O_3 to the BSYT ceramics results in the decrease of all the XRD peak intensity.

Fig. 2 shows the surface morphologies of $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ with various Sb_2O_3 content observed by SEM. All the samples exhibit

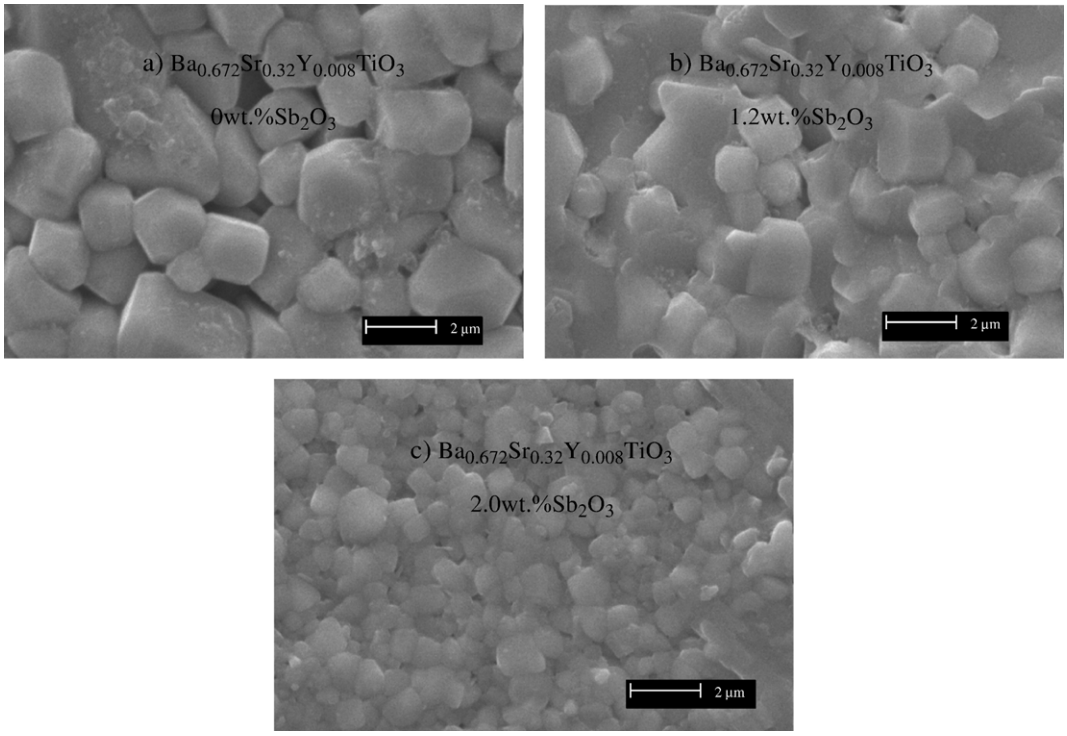

Fig. 2. Surface morphologies of the $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ bulk ceramics with various Sb_2O_3 contents.

a dense and uniform microstructure. The average grain size of BSYT ceramics doped with 2.0 wt.%Sb_2O_3 is merely about 700 nm. The grain size decreases with increasing amount of Sb_2O_3 because a large portion of the doping Sb ions precipitate out of the normal grains and stay at the grain boundaries which subsequently restricts the grain growth.

The variation of the relative dielectric constant and dielectric loss of BSYT specimens as a function of Sb_2O_3 content and sintering temperature at 1 kHz is shown in Fig. 3. It is clear that the relative dielectric constant of samples sintered at various temperatures decreases dramatically with increasing Sb_2O_3 doping content in the less than 0.8 wt.% range, and gradually saturates at around 1.6 wt.%. The replacement of Ba^{2+} ion (0.161 nm) or Sr^{2+} ion (0.144 nm) by smaller Sb^{3+} ion (0.076 nm) and Y^{3+} (0.090 nm) ion results in a shorter distance between the center ion and its nearest neighbors of the octahedron, so the movement of Ti ion is confined. This weakens the spontaneous polarization of the grain lattice, and consequently, the relative dielectric constant decreases with an increasing Sb_2O_3 content macroscopically. As shown in Fig. 3, the dielectric loss initially decreases with increasing doping content up to 1.2 wt.% and then increases. The reason for the decrease of the dielectric loss is also because of the weakening of the spontaneous polarization which results in the appearance of paraelectric tiny regions. These paraelectric regions make the hysteresis loop of the polycrystal narrow and even vanish.

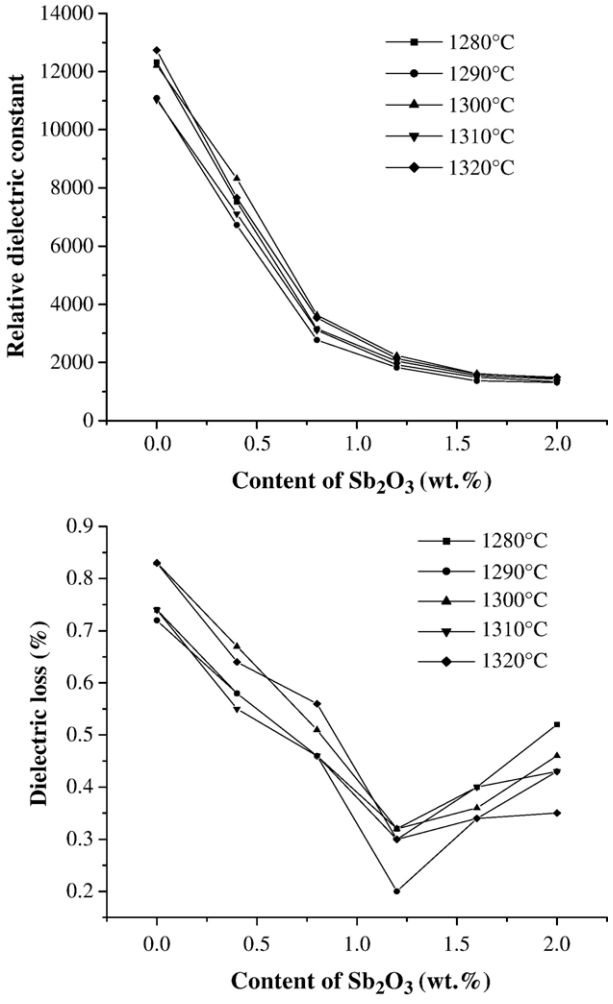

Fig. 3. Relative dielectric constant and dielectric loss of $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ as a function of Sb_2O_3 content and sintering temperature at 1 kHz.

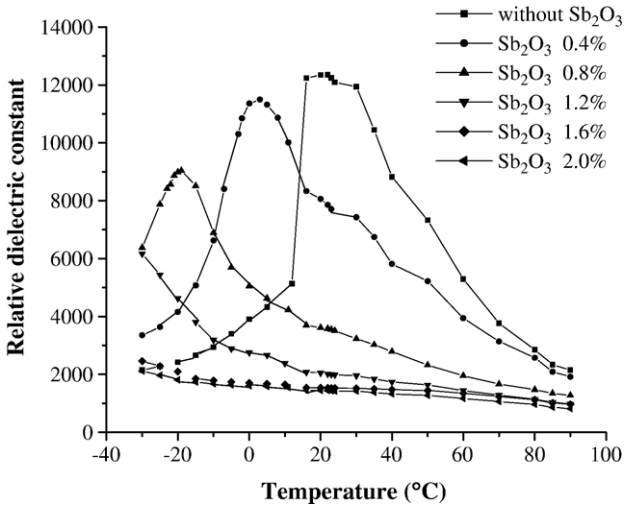

Fig. 4. Relative dielectric constant as a function of temperature for $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ with various Sb_2O_3 contents sintered at 1320 °C.

The temperature dependence of relative dielectric constant of BSYT with various Sb_2O_3 contents sintered at 1320 °C is shown in Fig. 4. It is obvious that the Curie temperature shifts to lower value with increasing doping content, from 22 °C for undoped BSYT to below −30 °C for 1.6 wt.% Sb_2O_3-doped BSYT. And the overall relative dielectric constants of the BSYT ceramics are significantly suppressed as the Sb_2O_3 content increases. In particular, the peak value decreases gradually from >12,000 to <9100 as the Sb_2O_3 content increases up to 0.8 wt.%. Furthermore, it is noteworthy that the more the doping content is, the flatter the curve becomes. At low Sb_2O_3 doping contents (<0.8 wt.%), the curves are characterized with narrow peaks which implies high values of temperature coefficient of capacitor. When the Sb_2O_3-doping content is above 1.6 wt.%, low temperature coefficient of capacitor (<±35%) over a wide temperature range from −25 °C to +85 °C is obtained.

For substitution Sb–Ba/Sr, the bonding force between the A-site ion and the oxygen ion of ABO_3 perovskite structure becomes stronger because the radius of Ba ion or Sr ion is larger than that of Sb ion. The bonding force Ti–O(Sb), therefore, becomes weaker than the Ti–O(Ba/Sr) bond. The weakening of Ti–O bond brings about a weaker distortion of the octahedron and leads to a decrease in the c/a ratio, thus inducing a drop in the Curie temperature. The other part of the doping Sb ions staying at the grain boundaries restrict the grain growth, which makes the non-ferroelectrics existing at the boundaries increase along with the augment of the grain boundaries. The increase of non-ferroelectrics makes for the weakening of ferroelectricity of the samples. Therefore, the peak value of relative dielectric constant in Fig. 4 is depressed and the curve becomes more complanate with the increasing doping content.

4. Conclusions

Sb_2O_3-doped $Ba_{0.672}Sr_{0.32}Y_{0.008}TiO_3$ ceramics were fabricated using conventional solid state method. Their structural and dielectric properties were investigated with variation of Sb_2O_3 doping content at different sintering temperatures. All BSYT specimens showed a perovskite polycrystalline structure without any secondary phase. The average grain size of samples decreased with an increase of doping content and the specimens doped with 2.0 wt.% Sb_2O_3 showed a value of 700 nm. With increasing amount of Sb_2O_3, the relative dielectric constant and Curie

temperature decreased in the whole measurement range, nevertheless the dielectric loss decreased down to minimum and then increased. The samples doped with 1.6 wt.% Sb_2O_3 sintered at 1320 °C for 2 h exhibited excellent properties, such as high relative dielectric constant (>1500), low dielectric loss($<40\times10^{-4}$), low temperature coefficient of capacitor($<\pm35\%$) over a wide temperature range from −25 °C to +85 °C.

Acknowledgements

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