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# Dielectric properties and phase transitions of La<sub>2</sub>O<sub>3</sub>- and Sb<sub>2</sub>O<sub>3</sub>-doped barium strontium titanate ceramics

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Abstract: The dielectric properties and phase transition characteristics of  $La_2O_3$ - and  $Sb_2O_3$ -doped barium strontium titanate ceramics prepared by solid state route were investigated. The microstructure was identified by X-ray diffraction method and scanning electron microscope was also employed to observe the surface morphologies. It is found that (La,Sb)-codoped barium strontium titanate ceramics exhibit typical perovskite structure and the average grain size decreases dramatically with increasing the content of  $Sb_2O_3$ . Both  $La^{3+}$  ions and  $Sb^{3+}$  ions occupy the A-sites in perovskite lattice. The dielectric constant and dielectric loss of barium strontium titanate based ceramics are obviously influenced by  $La_2O_3$  as well as  $Sb_2O_3$  addition content. The tetragonal-cubic phase transition of  $La_2O_3$  modified barium strontium titanate ceramics is of second order and the Curie temperature shifts to lower value with increasing the  $La_2O_3$  doping content. The phase transition of (La,Sb)-codoped barium strontium titanate ceramics diffuses and the deviation from Curie-Weiss law becomes more obvious with the increase in  $Sb_2O_3$  concentration. The temperature corresponding to the dielectric constant maximum of (La,Sb)-codoped barium strontium titanate ceramics decreases with increasing the  $Sb_2O_3$  content, which is attributed to the replacement of host ions by the  $Sb^{3+}$  ions.

Key words: barium strontium titanate; La<sub>2</sub>O<sub>3</sub>; Sb<sub>2</sub>O<sub>3</sub>; perovskite; ceramics; dielectric properties; phase transition

# **1** Introduction

In recent years, ceramics with high dielectric constant have attracted much attention in the development of environment friendly capacitors. Barium strontium titanate ( $Ba_{1-x}Sr_xTiO_3$ , BST), one of the most important perovskite ferroelectrics, has been widely studied because of its high dielectric constant and adjustable phase transition temperature [1–3]. The dielectric behavior of BST can be modified not only by controlling the Ba/Sr ratio but also through partial substitution of isovalent or aliovalent cations for A-sites and/ or B-sites in ABO<sub>3</sub> perovskite system [4].

The influence of rare earth oxides on the structural and dielectric properties of barium strontium titanate ceramics has been extensively researched in recent years. HUANG et al [5] reported that  $Dy_2O_3$ -doped BST capacitor ceramics showed high permittivity ( $\varepsilon$ =5245),

low dielectric loss (tan  $\delta$ =0.0026) and high DC breakdown voltage ( $E_{\rm b}$ =5.5 MV/m). According to ZHAO [6], comprehensive properties ( $\varepsilon$ =3658, et al tan  $\delta$ =0.0093,  $\Delta \varepsilon / \varepsilon = 14.1\%$ ) were obtained in Y<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub>-doped BST ceramics. Furthermore, LI et al [7] believed that there was an alternation of substitution preference of  $Y^{3+}$  ions for the host cations in perovskite lattice. When the doping concentration increased up to 0.5% (mole fraction),  $Y^{3+}$  ions tended to occupy the B-sites, causing the drop of dielectric constant. The effects of La2O3 addition on microstructure of BST ceramics were also investigated. La<sup>3+</sup> ions dissolved in the A-sites and effectively suppressed the grain growth of BST ceramics [8]. However, research effort towards the dielectric properties of La<sub>2</sub>O<sub>3</sub>-doped BST ceramics, especially the temperature dependence of dielectric parameters, is still scant.

The effects of antimony substitution on structure and electrical properties of several kinds of perovskite

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oxides have received considerable attention. BERCHMANS et al [9] envisaged the electrical and morphological features of Sb<sup>3+</sup> substituted LaFeO<sub>3</sub> using co-precipitation method. DUTTA et al [10] reported the dielectric, ferroelectric and conductive properties of (La,Sb)-modified lead zirconate titanate (PZT) ceramics. Sb-doped BaTiO<sub>3</sub> ceramics were also fabricated for applications in positive temperature coefficient of resistance (PTCR). CHIOU et al [11] reported that the lattice constant ratio c/a and Curie temperature of BaTiO<sub>3</sub> ceramics decreased with increasing the Sb concentration. It has been well documented that a small amount of impurity ions can dramatically modify the properties of BST ceramics in general, whereas the La<sub>2</sub>O<sub>3</sub>- and Sb<sub>2</sub>O<sub>3</sub>-codoped BST ceramics have never been investigated. The effects of La<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> on the structure, dielectric characteristics and phase transition behaviors of BST ceramics are yet to be further explored.

The present work aims to study the structure, dielectric properties and phase transition of (La,Sb)-modified BST ceramics prepared by solid state reaction technique. The purpose is to assess the possibility of their utilization in ceramic capacitor applications.

#### **2** Experimental

Two-stage method was employed to synthesize the x% La<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics (x=0.2, 0.4,0.6, 0.8, in mole fraction). The 0.8% La<sub>2</sub>O<sub>3</sub> and y%Sb<sub>2</sub>O<sub>3</sub> co-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics (y=0, 0.4, 0.8, 1.2, 1.6, 2.0, in mass fraction) were also prepared according to the following procedures. In the first stage, BaCO<sub>3</sub>(>99.0%), SrCO<sub>3</sub> (>99.0%), TiO<sub>2</sub>(>98.0%) and La<sub>2</sub>O<sub>3</sub>(>99.5%) powders used as starting raw materials were weighed, ball-milled, dried and calcined at 1080 °C for 2 h. In the second stage, the obtained powders were mixed with Sb<sub>2</sub>O<sub>3</sub> (>99.0%), reground, dried and added with 5% (mass fraction) polyvinyl alcohol (PVA) as the binder for granulation. The mixture was sieved through 40-mesh screen and then pressed into pellets (10 mm in diameter and 2 mm in thickness) under 250 MPa. Sintering was conducted in air at 1260–1300 °C for 2 h. To measure the dielectric properties, both sides of the specimens were coated with silver paste after ultrasonic bath cleaning and then fired at 530 °C for 10 min.

The crystal structures of the specimens were confirmed by X-ray diffraction analysis (XRD, Rigaku D/max 2500v/pc) with Cu K<sub> $\alpha$ </sub> radiation. The surface morphologies of the specimens were observed using the ESEM (PhilipXL30 ESEM). The capacitance quantity (*C*) and dissipation factor (*D*) were measured with YY 2811 Automatic LCR Meter 4425 at 1 kHz. The dielectric constant ( $\varepsilon_r$ ) and the loss tangent (tan  $\delta$ ) were calculated as follows:

$$\varepsilon_{\rm r} = \frac{14.4Ch}{\Phi^2} \tag{1}$$

$$\tan \delta = \frac{fD}{1000} \tag{2}$$

where *h* is the thickness;  $\Phi$  is the diameter of the electrode; *f* is the test frequency. The samples coated with silver electrodes were also applied to measuring the temperature dependence of dielectric constant. An automatic measuring system consisting of automatic LCR Meter and THP-F-100 temperature control unit was used to record the capacitance quantity (*C*) from -30 °C to 90 °C at 1 kHz.

### **3 Results and discussion**

#### 3.1 XRD and SEM analyses

The X-ray diffraction patterns of (La, Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  bulk ceramics sintered at 1280 °C are shown in Fig. 1. All these samples exhibit a typical perovskite structure, which implies that La<sup>3+</sup> and Sb<sup>3+</sup> ions have incorporated into the lattice and thus maintained the perovskite structure of BST solid solution. The diffraction peak intensity, especially that of the (101)



Fig. 1 XRD patterns of (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics

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or (200) peaks, decreases with increasing the doping content. It can be attributed to the distortion of ABO<sub>3</sub> unit cell caused by the replacement of A-site and /or B-site ions. The XRD profiles focusing on the (101) diffraction peaks are presented in Fig. 1(b). A slight shift of diffraction peaks to higher  $2\theta$  values with the increase of Sb<sub>2</sub>O<sub>3</sub> concentration was observed. A similar phenomenon has been previously reported for Sr substituted Ba(Zr,Ti)O<sub>3</sub> materials [12] and Ca-substituted BST ceramics [13].

The ionic radii of  $Ba^{2+}$ ,  $Sr^{2+}$  in 12 coordination and  $Ti^{4+}$  in 6 coordination are 0.161, 0.144 and 0.061 nm, respectively. The A-site radius and B-site radius of La<sup>3+</sup> ion are 0.132 nm and 0.1045 nm, respectively. In terms of size, La<sup>3+</sup> ions prefer to occupy the A-sites in BST solid solution. For further understanding of La<sup>3+</sup> substitution behavior, the average lattice constants  $(a^2c)^{1/3}$  were calculated from peak locations and Miller indices, where a and c were lattice parameters of tetragonal cell. It is found that the average lattice constant decreases from 0.3969 nm for 0.2%La2O3doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics to 0.3958 nm for 0.8%La<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics. This demonstrates that Ba<sup>2+</sup> or Sr<sup>2+</sup> ions are partially replaced by smaller La<sup>3+</sup> ions, consequently causing the decrease of  $(a^2c)^{1/3}$  value. The substitution preference of La<sup>3+</sup> ions in the present system accords with that in  $Ba_{0.6}Sr_{0.4}TiO_3$ ceramics [8]. The average lattice constants of BST based ceramics with different Sb<sub>2</sub>O<sub>3</sub> addition content were also obtained. The structural parameters  $(a^2c)^{1/3}$  decrease to 0.3947 nm for 0.8% La<sub>2</sub>O<sub>3</sub> in mole fraction and 1.2% Sb<sub>2</sub>O<sub>3</sub> in mass fraction codoped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics compared with none Sb<sub>2</sub>O<sub>3</sub>-doped ceramics and then decrease to 0.3941 nm for 0.8% La2O3 in mole fraction, and 2.0% Sb<sub>2</sub>O<sub>3</sub> in mass fraction co-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics. This means that the average lattice constants of (La,Sb)-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics decrease with increasing the Sb<sub>2</sub>O<sub>3</sub> content. The radius of  $Sb^{3+}$  ion (0.076 nm, coordination number=6) is larger than that of Ti<sup>4+</sup> ion but smaller than that of host A-site ion. So, the above shrinkage of unit cell suggests that the substitution of  $Sb^{3+}$  ions for the host A-site ions takes place in the present samples.

Figure 2 shows the surface morphologies of (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics sintered at 1280 °C. The microstructure of  $La_2O_3$ -doped BST ceramics is shown in Fig. 2(a). Figures 2(b) and (c) show the micrographs of  $La_2O_3$  and  $Sb_2O_3$  co-doped BST ceramics. All the samples exhibit a dense microstructure and no abnormal grain growth is observed. The average grain size decreases dramatically with increasing the content of  $Sb_2O_3$ . And the grain size distribution is narrowed down by  $Sb_2O_3$  doping. The substitution of

smaller Sb<sup>3+</sup> ions for the A-sites in perovskite structure as discussed above causes the lattice deformation. It is the lattice deformation that restrains the grain growth of the present BST based ceramics and thus brings about the fine grain structure. Furthermore, the grains change from spherical to irregular ones with increasing the Sb<sub>2</sub>O<sub>3</sub> addition content.



**Fig. 2** Surface morphologies of (La,Sb)-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)-TiO<sub>3</sub> ceramics: (a) y=0, x=0.8; (b) y=0.8, x=0.8; (c) y=2.0, x=0.8

#### 3.2 Dielectric characteristics

Table 1 shows the dielectric constant and dielectric loss of  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics with different La<sub>2</sub>O<sub>3</sub> contents at room temperature. All the La<sub>2</sub>O<sub>3</sub>-doped BST ceramics possess high dielectric constant (more than 4500), making these compounds potential candidate for capacitor applications. With the increase of La<sub>2</sub>O<sub>3</sub> doping content, the dielectric constant and dielectric loss of BST ceramics increase considerably. It has been reported that the substitution of rare earth ions for A-sites in BST perovskite structure causes deterioration in dielectric loss due to the generation of electrons which are trapped by

 $Ti^{4+}$  ions and thus promotes the formation of  $Ti^{3+}$  ions [4]. The increase of dielectric loss in La<sub>2</sub>O<sub>3</sub> doped BST ceramics is also due to the deoxidization of  $Ti^{4+}$  ions during the process of La<sup>3+</sup> ion occupying the A-site of crystal lattice.

Table 1 Dielectric properties of  $La_2O_3$ -doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics at room temperature

x	У	ε <sub>r</sub>	tan $\delta$
0.2	0	4910	0.005
0.4	0	6661	0.005
0.6	0	7501	0.006
0.8	0	8504	0.015

Figure 3 shows the dielectric constant of (La,Sb)doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub>ceramics sintered at different temperatures as a function of Sb<sub>2</sub>O<sub>3</sub> content. It can be noted that the dielectric constant at room temperature enhances at first and then decreases with increasing the Sb<sub>2</sub>O<sub>3</sub> addition content. The specimen modified with 0.4%Sb<sub>2</sub>O<sub>3</sub> possesses the highest permittivity which is more than 11500 (sintered at 1300 °C). When Sb<sup>3+</sup> ions substitute for Ba2+ or Sr2+ ions, the A-site vacancies resulting in the shrinkage of crystal lattice as mentioned above are produced. Consequently, the lattice deformation and inner press, which were reported to cause the rise of dielectric constant [14], come forth in the ceramics with low Sb<sub>2</sub>O<sub>3</sub> content. On the other hand, the replacement of A-site ion by smaller Sb<sup>3+</sup> ion results in a shorter distance between the center ion and its nearest neighbors of the octahedron, and thus confines the movement of Ti4+ ion. This reveals that the spontaneous polarization of the grain lattice gets weaker with increasing the Sb<sub>2</sub>O<sub>3</sub> content. Accordingly, the dielectric constant of ceramics with high Sb<sub>2</sub>O<sub>3</sub> doping content decreases macroscopically. Sintering conditions have remarkable influence on dielectric properties of barium titanate and barium strontium titanate ceramics [15,16]. For 0.4% Sb<sub>2</sub>O<sub>3</sub>-doped samples, the dielectric



Fig. 3 Dielectric constant of (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics as function of  $Sb_2O_3$  content

constant increases prominently with the increase of sintering temperature. However, the effects of sintering temperature become weaker as the Sb<sub>2</sub>O<sub>3</sub> doping level increases.

The dielectric loss of (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_{3}$ ceramics sintered at different temperatures as a function of Sb<sub>2</sub>O<sub>3</sub> content is shown in Fig. 4. The dielectric loss at room temperature initially decreases and then increases slightly with increasing the Sb<sub>2</sub>O<sub>3</sub> concentration. Due to the weakening of spontaneous polarization after Sb<sub>2</sub>O<sub>3</sub> doping, the hysteresis loop of the ferroelectric polycrystal is affirmed to be narrow or even vanish [17]. As a result, the dielectric loss at room temperature decreases with increasing Sb<sub>2</sub>O<sub>3</sub> content incipiently. The dissipation factor was related to the reduction of Ti<sup>4+</sup> ion in titanium-containing ceramics [4]. The limited reduction of Ti<sup>4+</sup> ion in perovskite structure is sufficient to cause a severe deterioration in the dissipation factor. When the Sb<sup>3+</sup> ions substitute for A-sites as donor in the present samples, the electrons will be generated and then trapped by the Ti<sup>4+</sup> ions. Hereby, the dissipation factor, in other words, the dielectric loss tends to increase with increasing the Sb<sub>2</sub>O<sub>3</sub> content. All the samples sintered at proper temperature exhibit low dielectric loss in the Sb<sub>2</sub>O<sub>3</sub> addition range of 0.8%-2.0%. And the minimal dielectric loss of 0.0028 is obtained in 0.8% Sb<sub>2</sub>O<sub>3</sub>doped ceramics when sintering is conducted at 1290 °C. The low dielectric loss coupled with high dielectric constant makes BST materials with proper La<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> doping content suitable for many device applications.



Fig. 4 Dielectric loss of (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics as function of  $Sb_2O_3$  content

#### 3.3 Phase transition behaviors

Figure 5 shows the dielectric constant and inverse dielectric constant of  $La_2O_3$ -doped ( $Ba_{0.74}Sr_{0.26}$ )TiO<sub>3</sub> ceramics sintered at 1280 °C as a function of temperature. The dielectric constant first increases, achieves a maximum value and then decreases with increasing the



**Fig. 5** Temperature dependence of dielectric constant for  $La_2O_3$ -doped ( $Ba_{0.74}Sr_{0.26}$ )TiO<sub>3</sub> ceramics: (a) x=0.2, y=0; (b) x=0.4, y=0; (c) x=0.6, y=0

temperature. The peak is an indication of ferroelectricparaelectric phase transition. Above the transition temperature, the dielectric constant  $\varepsilon_r$  of ferroelectrics as a function of temperature *T* can be described by the Curie-Weiss law:

$$\varepsilon_{\rm r} = \frac{k}{T - T_0} \tag{3}$$

where k is the Curie constant and  $T_0$  is the Curie-Weiss temperature. Therefore, the temperature dependence of

inverse dielectric constant  $1/\varepsilon_r$  can be expressed linearly:

$$1/\varepsilon_{\rm r} = \frac{1}{k} \cdot T - \frac{T_0}{k} \tag{4}$$

The ferroelectric-paraelectric phase transition is of first order under the condition that  $T_0$  is lower than the Curie temperature  $T_c(T_0 < T_c)$  and of second order when  $T_0$  is equal to  $T_c(T_0=T_c)$  [7]. It is clear that the tetragonalcubic phase transition of La<sub>2</sub>O<sub>3</sub> modified BST ceramics is of second order and the Curie temperature shifts to lower value with increasing the La<sub>2</sub>O<sub>3</sub> doping content. The substitution for A-site with any of the La<sup>3+</sup> ions leads to a deformation of the ABO<sub>3</sub> pervoskite structure, thus inducing a drop in the Curie temperature.

Figure 6 shows the dielectric constant and inverse dielectric constant of La<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> co-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics sintered at 1280 °C as a function of temperature. The temperature dependence of  $1/\varepsilon_r$  deviates from the Curie-Weiss law above the phase transition temperature in La<sub>2</sub>O<sub>3</sub>- and Sb<sub>2</sub>O<sub>3</sub>-doped specimens, as shown in Figs. 6(b)–(d). Sb<sub>2</sub>O<sub>3</sub> addition into the BST lattice results in the diffusion of ferroelectric-paraelectric phase transition. Hereby,  $\Delta T_m$  is defined to measure the degree of deviation from the Curie-Weiss law:

$$\Delta T_{\rm m} = T_{\rm cw} - T_{\rm m} \tag{5}$$

where  $T_{\rm cw}$  denotes the temperature from which the dielectric constant fails to accord with the Curie-Weiss law and  $T_{\rm m}$  represents the temperature corresponding to the maximum of permittivity. It can be seen that  $\Delta T_{\rm m}$  increases dramatically with increasing the Sb<sub>2</sub>O<sub>3</sub> content. It demonstrates that the deviation from Curie-Weiss law becomes greater with the increase in Sb<sub>2</sub>O<sub>3</sub> content.

The temperature corresponding to the maximum dielectric constant T<sub>m</sub> for (La,Sb)-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)-TiO<sub>3</sub> ceramics decreases with increasing the Sb<sub>2</sub>O<sub>3</sub> content, from 23 °C for 0.8% (mole fraction) La<sub>2</sub>O<sub>3</sub>doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics to below -25°C for 1.6% (mass fraction) Sb<sub>2</sub>O<sub>3</sub> and 0.8% (mole fraction) La<sub>2</sub>O<sub>3</sub> co-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub>, ceramics, as shown in Fig. 6(e). For A-site substitution of  $Sb^{3+}$  ion, the bonding force between the A-site ion and the O<sup>2-</sup> of ABO<sub>3</sub> perovskite structure becomes strong due to the smaller radius of Sb<sup>3+</sup> ion. The bonding force Ti-O(Sb), therefore, becomes weaker than that of the Ti-O(Ba/Sr). The weakening of Ti-O bond brings about a weaker distortion of the octahedron and thus induces a drop in the  $T_{\rm m}$ . In other words, the substitution for A-site ion with any of the Sb<sup>3+</sup> ions leads to the weakening of spontaneous polarization of the grain lattice as mentioned before. Therefore, the  $T_{\rm m}$  value decreases with increasing the Sb<sub>2</sub>O<sub>3</sub> content. The charged vacancies caused by A-site substitution give rise to the local deformation of the perovskite unit cells which also



**Fig. 6** Temperature dependence of dielectric constant for (La,Sb)-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub>ceramics: (a) *y*=0, *x*=0.8; (b) *y*=0.4, *x*=0.8; (c) *y*=0.8, *x*=0.8; (d) *y*=1.2, *x*=0.8; (e) *y*=1.6, *x*=0.8; (f) *y*=2.0, *x*=0.8

causes the reduction of  $T_{\rm m}$ .

As shown in Fig. 6, the peak value of dielectric constant for (La,Sb)-doped  $(Ba_{0.74}Sr_{0.26})TiO_3$  ceramics is suppressed dramatically as the Sb<sub>2</sub>O<sub>3</sub> content increases. When the concentration of Sb<sub>2</sub>O<sub>3</sub> dopant reaches up to 1.2%, a relatively low peak value which is less than 5500 is observed. The effect of Sb<sub>2</sub>O<sub>3</sub> addition on the maximum dielectric is caused by the weakening of ferroelectricity which is attributed to the replacement of Sb<sup>3+</sup> ions for the host ions in perovskite lattice.

## **4** Conclusions

1) The (La,Sb)-doped ( $Ba_{0.74}Sr_{0.26}$ )TiO<sub>3</sub> ceramics were prepared by the solid state reaction technique. The La<sup>3+</sup> and Sb<sup>3+</sup> ions occupy the A-sites in perovskite lattice and with increasing the content of Sb<sub>2</sub>O<sub>3</sub>, the average grain size of BST ceramics decreases dramatically.

2) The permittivity and dielectric loss at room

temperature are intensively influenced by La<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> doping concentration. The low dielectric loss (<0.003) coupled with high dielectric constant (>5000) makes the 0.8% (mass fraction) Sb<sub>2</sub>O<sub>3</sub> and 0.8% (mole fraction) La<sub>2</sub>O<sub>3</sub> co-doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics suitable for capacitor applications.

3) The tetragonal-cubic phase transition of  $La_2O_3$  modified BST ceramics is of second order and the Curie temperature  $T_c$  shifts to lower value with increasing the  $La_2O_3$  doping content.

4) The phase transition of (La,Sb)-doped BST ceramics is diffused and the deviation from Curie-Weiss law becomes more obvious with the increase in Sb<sub>2</sub>O<sub>3</sub> content. Attributed to the replacement of host ions by the Sb<sup>3+</sup> ions, the temperature corresponding to the maximum dielectric constant  $T_{\rm m}$  for (La,Sb)-doped BST ceramics decreases with increasing the Sb<sub>2</sub>O<sub>3</sub> content.

#### References

- ALEXANDRU H V, BERBECARU C, IOACHIM A, NEDELCU L, DUTU A. BST solid solutions, temperature evolution of the ferroelectric transitions [J]. Appl Surf Sci, 2006, 253(1): 354–357.
- [2] IOACHIM A, TOACSAN M I, BANCIU M G, NEDELCU L, DUTU A, ANTOHE S, BERBECARU C, GEORGESCU L, STOICA G, ALEXANDRU H V. Transitions of barium strontium titanate ferroelectric ceramics for different strontium content [J]. Thin solid Films, 2007, 515(16): 6289–6293..
- [3] IANCULESCU A, BERGER D, VIVIANI M, CIOMAGA C E, MITOSERIU L, VASILE E, DRĂGAN N, CRIŞAN D. Investigation of Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub> ceramics prepared from powders synthesized by the modified Pechini route [J]. J Eur Ceram Soc, 2007, 27(13–15): 3655–3658.
- [4] LI Y, QU Y. Dielectric properties and substitution mechanism of samarium-doped Ba<sub>0.68</sub>Sr<sub>0.32</sub>TiO<sub>3</sub> ceramics [J]. Mater Res Bull, 2009, 44(1): 82–85.

- [5] HUANG X Y, GAO C H, CHEN X C, ZHENG X L, HUANG G J, LIU H P. Dielectric properties of Dy<sub>2</sub>O<sub>3</sub>-doped (Ba,Sr)TiO<sub>3</sub> ceramics [J]. J Rare Earths, 2004, 22(z3): 226–228.
- [6] ZHAO C, HUANG X Y, GUAN H, GAO C H. Effect of Y<sub>2</sub>O<sub>3</sub> and Dy<sub>2</sub>O<sub>3</sub> on dielectric properties of Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> series capacitor ceramics [J]. J Rare Earths, 2007, 25(Sp.2): 197–200.
- [7] LI Y, QU Y. Substitution preference and dielectric properties of Y<sup>3+</sup>-doped Ba<sub>0.62</sub>Sr<sub>0.38</sub>TiO<sub>3</sub> ceramics [J]. Mater Chem Phys, 2008, 110(1): 155–159.
- [8] ZHANG J, ZHAI J, CHOU X, YAO X. Influence of rare-earth addition on microstructure and dielectric behavior of Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> ceramics [J]. Mater Chem Phys, 2008, 111(2–3): 409–413.
- [9] BERCHMANS L J, SINDHU R, ANGAPPAN S, AUGUSTIN C O. Effect of antimony substitution on structural and electrical properties of LaFeO<sub>3</sub> [J]. J Mater Process Technol, 2008, 207(1–3): 301–306.
- [10] DUTTA S, CHOUDHARY R N P, SINHA P K. Electrical properties of antimony doped PLZT ceramics prepared by mixed-oxide route [J]. J Alloys Compd, 2006, 426(1–2): 345–351.
- [11] CHIOU B S, WANG I H. Effect of MgO addition on the electrical transport properties of highly Sb-doped BaTiO<sub>3</sub> ceramics [J]. J Mater Sci: Mater Electron, 1998, 9(2): 145–150.
- [12] BHASKAR REDDY S, PRASAD RAO K, RAMACHANDRA RAO M S. Structural and dielectric characterization of Sr substituted Ba(Zr,Ti)O<sub>3</sub> based functional materials [J]. Appl Phys A, 2007, 89(4): 1011–1015.
- [13] YUN S, WANG X, LI B, XU D. Dielectric properties Ca-substituted barium strontium titanate ferroelectric ceramics [J]. Solid State Commun, 2007, 143(10): 461–465.
- [14] LI W, QI J, WANG Y, LI L, GUI Z. Doping behaviors of Nb<sub>2</sub>O<sub>5</sub> and Co<sub>2</sub>O<sub>3</sub> in temperature stable BaTiO<sub>3</sub>-based ceramics [J]. Mater Lett, 2002, 57(1): 1–5.
- [15] YING K L, HSIEH T E. Sintering behaviors and dielectric properties of nanocrystalline barium titanate [J]. Mater Sci Eng B, 2007, 138(3): 241–245.
- [16] SZYMCZAK L, UJMA Z, HANDEREK J, KAPUSTA J. Sintering effects on dielectric properties of (Ba,Sr)TiO<sub>3</sub> ceramics [J]. Ceram Int, 2004, 30(6): 1003–1008.

# La<sub>2</sub>O<sub>3</sub>与 Sb<sub>2</sub>O<sub>3</sub>掺杂钛酸锶钡陶瓷的介电性能及相变

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摘 要:采用固相法制备 La<sub>2</sub>O<sub>3</sub> 与 Sb<sub>2</sub>O<sub>3</sub> 掺杂的钛酸锶钡陶瓷,研究其介电性能及相变特性。通过 X 射线衍射法 分析体系微观结构并利用扫描电镜观察其表面微观形貌。(La,Sb)共掺杂的钛酸锶钡陶瓷具有典型的钙钛矿结构, 且随着 Sb<sub>2</sub>O<sub>3</sub> 掺杂量的增多其平均粒径显著减小。La<sup>3+</sup>离子以及 Sb<sup>3+</sup> 离子均占据钙钛矿晶格的 A 位。La<sub>2</sub>O<sub>3</sub> 与 Sb<sub>2</sub>O<sub>3</sub> 添加量的改变显著影响钛酸锶钡基陶瓷的介电常数以及介电损耗。La<sub>2</sub>O<sub>3</sub> 改性的钛酸锶钡陶瓷其四方-立方相变为 二级相变,且居里温度随着 La<sub>2</sub>O<sub>3</sub> 掺杂量的增多向低温方向移动。(La,Sb)共掺杂的钛酸锶钡陶瓷则体现为弥散相 变,随着 Sb<sub>2</sub>O<sub>3</sub> 含量的增大而偏离居里一外斯定律越显著。由于 Sb<sup>3+</sup> 离子对晶格原位离子的取代使得(La,Sb)共掺 杂的钛酸锶钡陶瓷的介电常数最大值下的温度亦随着 Sb<sub>2</sub>O<sub>3</sub> 含量的增大而降低。 关键词: 钛酸锶钡; La<sub>2</sub>O<sub>3</sub>; Sb<sub>2</sub>O<sub>3</sub>; 钙钛矿; 陶瓷; 介电性能; 相变

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