

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 27(2017) 2656–2662

# Dielectric properties and point defect behavior of antimony oxide doped Ti deficient barium strontium titanate ceramics

Chen ZHANG, Zhi-xin LING, Gang JIAN, Fang-xu CHEN

Provincial Key Lab of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, China

Received 27 September 2016; accepted 17 March 2017

Abstract: The microstructures and dielectric properties of  $Sb_2O_3$ -doped Ti deficient barium strontium titanate ceramics prepared by solid state method were investigated with non-stoichiometric level and  $Sb_2O_3$  content by SEM, XRD and LCR measure system. It is found that with the increase of  $\delta$ ,  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics transform from single phase solid solutions with typical cubic perovskite structure to multiphase compounds while  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics remain to be single-phase with the increasing  $Sb_2O_3$  content. The distortion of the ABO<sub>3</sub> perovskite lattice caused by  $V_{Ti}^{""}$  and  $V_{O}^{\bullet\bullet}$  induces the drop of Curie temperature and the rise of relative dielectric constant in  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics with increasing  $\delta$  value. The orientation of  $V_{O}^{\bullet\bullet}$  elastic dipoles results in the domain-wall pinning and thus the reduction of the dielectric loss. With increasing  $Sb_2O_3$  content, the relative dielectric constant maximum and Curie temperature of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics decrease dramatically while the dielectric loss increases.

Key words: barium strontium titanate; defects; dielectric properties; non-stoichiometric ceramics

## **1** Introduction

Barium strontium titanate (Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub>, BST) as a ferroelectric material with perovskite structure has drawn considerable attention in the microelectronic industries because of its outstanding properties such as adjustable phase transition temperature, high dielectric constant and low dielectric loss [1], which allows it to have a great potentiality for phase shifter, phased array antenna, resonator and capacitor applications. However, the conflict between the fine dielectric properties at room temperature and good dielectric temperature stability remains in the uniform BST ceramics [2]. In order to overcome the above mentioned drawback, the traditional doping method applied widely in electronic ceramics has been introduced into BST ceramics [3–5].

Due to the intermediate size and charge of trivalent ions compared with the  $Ba^{2+}$ ,  $Sr^{2+}$  and  $Ti^{4+}$  ions, the aliovalent doping mechanism and the substitution preference of trivalent ions in BST ceramics as well as in  $BaTiO_3$  ceramics have been debated for many years [6]. However, it is no doubt that the dielectric properties of perovskite BST ceramics are related to the doping mechanism and correspondingly the point defect behavior. In many cases, the doping mechanisms are not only dependent on the oxygen partial pressure  $(p_{O_2})$  and sintering temperature/time but also the overall  $n_A/n_B$ ratio [7]. Many literatures have been focused on the relationships between the point defect behavior and  $n_A/n_B$ ratio in BaTiO<sub>3</sub> ceramics [8,9]. Also, some influences of  $n_A/n_B$  ratio on the microstructures and dielectric properties in BST ceramics are gradually understood. DONG et al [2] concluded that adding excessive TiO<sub>2</sub> could remarkably inhibit grain growth, suppress and broaden the Curie peaks in compositionally BST inhomogeneous ceramics. SYAMAPRASAD et al [10] found that excess Ba led to high un-changed dielectric constant with a slight decrease of loss tangent in Ba<sub>0.71</sub>Sr<sub>0.29</sub>TiO<sub>3</sub> ceramics.

In our previous work, the dielectric properties of Sb<sub>2</sub>O<sub>3</sub>-doped stoichiometric BST ceramics such as (Ba<sub>0.992-x</sub>Sr<sub>x</sub>Y<sub>0.008</sub>)TiO<sub>3.004</sub> ceramics ( $n_A/n_B=1$ ) have been investigated and the Sb<sub>2</sub>O<sub>3</sub> dopant showed extraordinary effects on the dielectric temperature stability improvement [11,12]. So, in this work, we report a

Foundation item: Project (BK20140517) supported by the Natural Science Foundation of Jiangsu Province, China; Project (14KJB430011) supported by Jiangsu Provincial Natural Science Foundation for Colleges and Universities, China

Corresponding author: Chen ZHANG; Tel:+86-511-84401184; Fax: +86-511-84407381; E-mail: czhang1981@hotmail.com DOI: 10.1016/S1003-6326(17)60294-2

systematic study of the microstructure, point defect behavior and dielectric properties of Ti deficient (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>1- $\delta$ </sub>O<sub>3-2 $\delta$ </sub> ceramics ( $n_A/n_B>1$ ) still taking the trivalent Sb<sup>3+</sup> ions as dopant. The influences of  $\delta$  value (namely the  $n_A/n_B$  ratio) and doping content on point defect behavior and the dielectric properties in barium strontium titanate ceramics are discussed.

# 2 Experimental

The chemical compositions of the Sb<sub>2</sub>O<sub>3</sub>-doped Ti deficient barium strontium titanate specimens were given by the formula  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}+0.6\%Sb_2O_3$  ( $\delta$ = 0.002, 0.004, 0.006, 0.008) and (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub>+ xSb<sub>2</sub>O<sub>3</sub> (x=0, 0.4%, 0.8%, 1.2%). High purity BaCO<sub>3</sub> (>99.0%), SrCO<sub>3</sub> (>99.0%) and TiO<sub>2</sub> (>98.0%)powders used as starting raw materials were weighed according to the above specimens, ball-milled, dried and calcined at 1080 °C for 2 h. The calcined powders were mixed with Sb<sub>2</sub>O<sub>3</sub> (>99.0%), reground, dried and added with 5% polyvinyl alcohol (PVA) as a binder for granulation. The mixture was sieved through 250 µm screen and then pressed into pellets of 10 mm in diameter and 2 mm in thickness under 250 MPa. Sintering was conducted in air at 1300-1320 °C for 2 h. For dielectric measurement, both the flat surfaces of the specimens were coated with BQ-5311 silver paste after ultrasonic bath cleaning and then fired at 800 °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 SEM (JSM-6480 ESEM). The capacitance quantity (*C*) and dissipation factor (*D*) were measured with LCR-8101G Automatic LCR Meter at 1 kHz. The relative dielectric constant ( $\varepsilon_r$ ) and the loss tangent (tan  $\delta$ ) were calculated as follows:

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

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

where *h* is the thickness (cm), *d* is the diameter of the electrode (cm) and *f* is the test frequency (Hz). An automatic measuring system consisting of Automatic LCR Meter and THP-F-100 temperature control unit was used to record the capacitance quantity and dissipation factor from -20 °C to 50 °C at 1 kHz for measuring the temperature dependence of dielectric parameters.

# **3** Results and discussion

#### 3.1 XRD and SEM analysis

The X-ray diffraction patterns of 0.6%Sb<sub>2</sub>O<sub>3</sub>-doped

 $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  bulk ceramics are shown in Fig. 1. With the increase of  $\delta$  value,  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}+$ 0.6%Sb<sub>2</sub>O<sub>3</sub> ceramics transform from single phase solid solutions with typical cubic perovskite structure to multiphase compounds. In other words, to maintain the ABO<sub>3</sub> perovskite single phase structure, the  $\delta$  value should be restricted to a very narrow range which is no more than 0.006 in present samples. Also, a slight shift of diffraction peaks to higher  $2\theta$  values with the increasing  $\delta$  value was observed, especially for the (110), (200) and (211) peaks, which indicated that the unit cell volumes of  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics decreased as the non-stoichiometric level of Ti ions in present ABO3 perovskite structure increased. Similar phenomena have been previously reported in Ca substituted BST ceramics [13] and in our previous work for (La, Sb)doped (Ba<sub>0.74</sub>Sr<sub>0.26</sub>)TiO<sub>3</sub> ceramics [14]. Apparently, this shrinkage of unit cell volume is mainly attributed to the appearance of *B*-site vacancies  $V_{\text{Ti}}'''$  and oxygen vacancies  $V_{O}^{\bullet\bullet}$  in  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics which is revealed by the following point defect reaction equation:

$$(\operatorname{Ba}_{0.75}\operatorname{Sr}_{0.25})\operatorname{Ti}_{1-\delta}\operatorname{O}_{3-2\delta} \rightarrow 0.75\operatorname{Ba}_{\operatorname{Ba}} + 0.25\operatorname{Sr}_{\operatorname{Sr}} + (1-\delta)\operatorname{Ti}_{\operatorname{Ti}} + (3-2\delta)\operatorname{O}_{\operatorname{O}} + \delta V_{\operatorname{Ti}}^{""} + 2\delta V_{\operatorname{O}}^{\bullet\bullet}$$
(3)



Fig. 1 XRD patterns for  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}+0.6\%Sb_2O_3$ ceramics: (a)  $\delta$ =0.002; (b)  $\delta$ =0.006; (c)  $\delta$ =0.008

The X-ray diffraction patterns of sintered Sb<sub>2</sub>O<sub>3</sub>doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> bulk ceramics are shown in Fig. 2. All these polycrystals are single-phase compounds with perovskite structure, which implies that Sb<sup>3+</sup> ions have incorporated into the lattice and thus maintain the perovskite structure of non-stoichiometric barium strontium titanate solid solution. The XRD profiles focusing on the (110) diffraction peaks are presented in Fig. 2(b). It shows that the diffraction peaks move towards lower  $2\theta$  values and then shift to higher  $2\theta$  values as the Sb<sub>2</sub>O<sub>3</sub> doping content increases in



Fig. 2 XRD patterns for Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics with different Sb<sub>2</sub>O<sub>3</sub> contents (1 - 0; 2 - 0.4%; 3-1.2%)

(Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics, which reveals a variation of the unit cell volume for Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics. To be specific, with the increase of Sb<sub>2</sub>O<sub>3</sub> content, the unit cell volume increases and then decreases slightly. In terms of size, the ionic radii of Ba<sup>2+</sup>, Sr<sup>2+</sup> in 12 coordination and Ti<sup>4+</sup> in 6 coordination are 0.161, 0.144 and 0.061 nm, respectively. The radius of Sb<sup>3+</sup> ion in 6 coordination is 0.076 nm which is bigger than that of Ti<sup>4+</sup> ion but smaller than that of host A-site ion. Therefore, B-sites in the perovskite lattice are partially occupied by bigger Sb<sup>3+</sup> ions for present low Sb<sub>2</sub>O<sub>3</sub> doping content samples, consequently causing the increase of the unit cell volume. While the above shrinkage of unit cell suggests that the substitution of Sb<sup>3+</sup> ions for the host A-site ions takes place in high Sb<sub>2</sub>O<sub>3</sub> doping content samples. The substitution preference of Sb<sup>3+</sup> ions in present system is opposite to that in  $(Ba_{0.992-x}Sr_xY_{0.008})TiO_{3.004}$  ceramics [11]. This difference of Sb<sup>3+</sup> substitution preference in perovskite lattice can be explained by the existence of B-site vacancies V<sub>Ti</sub>"" in non-stoichiometric (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)- $Ti_{0.998}O_{2.996}$  ceramics as shown in Eq. (3). The incorporation of Sb<sup>3+</sup> ions into the lattice also brings about some kinds of point defects which turn out to be the main factors changing the dielectric characteristics of non-stoichiometric barium strontium titanate ceramics. In  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  samples with low Sb<sub>2</sub>O<sub>3</sub> doping concentration, Sb<sup>3+</sup> ions enter *B*-sites in the perovskite structure and serve as an acceptor dopant. The defect reaction is as follows:

$$Sb_2O_3 \rightarrow 2Sb'_{Ti} + V_0^{\bullet\bullet} + 3O_0$$
 (4)

For high  $Sb_2O_3$  doping concentration samples,  $Sb^{3+}$  ions tend to occupy the *A*-sites and serve as a donor dopant. The defect reaction is as follows:

$$\mathrm{Sb}_2\mathrm{O}_3 \to 2\mathrm{Sb}_\mathrm{A}^{\bullet} + V_\mathrm{A}^{"} + 3\mathrm{O}_\mathrm{O}$$
 (5)

Figure 3 shows the surface morphologies of 0.6%Sb<sub>2</sub>O<sub>3</sub>-doped Ti deficient  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics. And the surface morphologies of Sb<sub>2</sub>O<sub>3</sub>-doped  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics are shown in Fig. 4. It appears that all samples exhibit dense microstructure and no abnormal grain growth is observed. There is no obvious change in the average grain size of



Fig. 3 SEM images of 0.6%Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)-Ti<sub>1- $\delta$ </sub>O<sub>3-2 $\delta$ </sub> ceramics: (a)  $\delta$ =0.004; (b)  $\delta$ =0.006; (c)  $\delta$ =0.008



Fig. 4 SEM images of (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics with various Sb<sub>2</sub>O<sub>3</sub> contents: (a) 0; (b) 0.4%; (c) 0.8%; (d) 1.2%

 $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics as the  $\delta$  value increases, presenting that the non-stoichiometric level makes little contribution to refine the grain size. Distinguishingly, the average grain size of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics decreases dramatically after applying the  $Sb_2O_3$  dopant while remains almost the same when gradually increasing the  $Sb_2O_3$  content. And the grain size distribution of sintered ceramics can be refined by  $Sb_2O_3$  addition.

#### 3.2 Dielectric characteristics

Table 1 shows the relative dielectric constant and dielectric loss of 0.6%Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>1-δ</sub>- ${
m O}_{3\text{-}2\delta}$  ceramics with different  $\delta$  values at room temperature. It is obvious that all the non-stoichiometric  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics possess high relative dielectric constant (more than 4000) at room temperature. With the increase of  $\delta$  value which is in the range of 0.002-0.006, the relative dielectric constant increases notably while the dielectric loss decreases considerably. This demonstrates that a proper non-stoichiometric level in  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$ ceramics helps to improve the dielectric properties at room temperature.  $n_{\text{Ba}^{2+}}/n_{\text{Ti}^{4+}} > 1$  in BaTiO<sub>3</sub> has been demonstrated by HYATT et al [15] to reduce the loss tangent particularly in the paraelectric region above the Curie temperature. In our present  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$ ceramics satisfying the condition of  $(n_{Ba^{2+}}+n_{Sr^{2+}})/n_{Ti^{4+}}>1$ , the dielectric loss is now proved to decrease with the increasing non-stoichiometric level, which is in accord with Hyatt's results.

**Table 1** Dielectric properties of  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}+$ 0.6% Sb<sub>2</sub>O<sub>3</sub> ceramics

0.070 50203 ceramics								
δ	$arepsilon_{ m r}^{ m RT}$	$\tan \delta^{\mathrm{RT}}$	$T_{\rm C}/^{\circ}{\rm C}$	$\varepsilon_{\rm r}^{\rm max}$				
0.002	4036	0.017	6.8	6041				
0.004	4187	0.013	4.7	6504				
0.006	4420	0.012	3.8	7007				
0.008	4416	0.012	3.1	6694				

Temperature dependence of relative dielectric constant and dielectric loss for 0.6%Sb<sub>2</sub>O<sub>3</sub>-doped  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics is shown in Fig. 5. The relative dielectric constant first increases, achieves a maximum remarked as  $\varepsilon_r^{max}$  and then decreases with increasing temperature. Contrarily, the dielectric loss decreases at the beginning, achieves a minimum and then increases with increasing temperature. The temperature corresponding to the relative dielectric constant maximum is taken as the Curie temperature  $T_{\rm C}$ . It is obvious that the Curie temperature (see Table 1) decreases with increasing  $\delta$  value. The *B*-site vacancies  $V_{\text{Ti}}^{""}$  and oxygen vacancies  $V_{\text{O}}^{\bullet\bullet}$  in  $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1-\delta^{\bullet}}$  $O_{3-2\delta}$  ceramics resulting in the shrinkage of crystal lattice as mentioned above lead to a distortion of the ABO<sub>3</sub> perovskite structure thus inducing a drop in the Curie temperature. Also, the lattice deformation and inner stress were reported to cause the rise of dielectric constant [16], which exactly explains the increase of relative dielectric constant with the increasing  $\delta$  value in present  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics. It is noteworthy that in the whole temperature range the higher the  $\delta$ 

value is, the lower the dielectric loss of ceramics  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$ becomes. This phenomenon is related to the existing point defects as well. Oxygen vacancies  $V_0^{\bullet\bullet}$  residing at the corners of octahedra are well interconnected and therefore can be regarded as relatively mobile defects. The mobile defects migrate to domain boundaries. Orientation of the elastic dipoles caused by  $V_{\rm O}^{\bullet\bullet}$  results in the domain-wall pinning and thus the reduction of the dielectric loss.



**Fig. 5** Temperature dependence of relative dielectric constant (a) and dielectric loss (b) for  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}+0.6\%$  Sb<sub>2</sub>O<sub>3</sub> ceramics

The relative dielectric constant and dielectric loss of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics with different Sb<sub>2</sub>O<sub>3</sub> doping contents at room temperature are shown in Table 2. It is clear that the relative dielectric constant of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics decreases dramatically with increasing Sb<sub>2</sub>O<sub>3</sub> addition content. The substitution for *A/B*-site with any of the Sb<sup>3+</sup> ions leads to a shorter distance between the *B*-site ion and its nearest neighbors of the octahedron, so the movement of *B*-site ion is restricted, which weakens the spontaneous polarization of grain lattice, and consequently, the dielectric constant decreases with increasing Sb<sub>2</sub>O<sub>3</sub> content macroscopically. The dielectric loss of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics increases with the increase of Sb<sub>2</sub>O<sub>3</sub> content. Orientation

of the electric dipoles formed from  $Sb^{\bullet}_{A} - V''_{A}/Sb'_{Ti} - V^{\bullet}_{O}$ complexes shown in Eqs. (4) and (5) leads to domain-wall pinning and thus a reduction of the dielectric loss. In titanium-containing ceramics the dissipation factor is always related to the reduction of  $Ti^{4+}$  ion [4]. When the Sb<sup>3+</sup> ions substitute for host ions in present samples, the electrons will be generated and then trapped by the Ti<sup>4+</sup> ions. Hereby, the limited reduction of Ti<sup>4+</sup> ion in (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics is sufficient to cause a severe deterioration in dielectric loss. Therefore, the electric dipoles related to the point defect and the reduction of Ti<sup>4+</sup> ion caused by Sb<sup>3+</sup> ion substitution for host ion become two conflicting factors for the dielectric loss. Apparently, the latter is the controlling factor for Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>- $O_{2.996}$  ceramics since the dielectric loss increases with the increasing Sb<sub>2</sub>O<sub>3</sub> content.

Table2Dielectricpropertiesof $Sb_2O_3$ -doped $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics

Sb <sub>2</sub> O <sub>3</sub> content/%	$\boldsymbol{\varepsilon}_{\mathrm{r}}^{\mathrm{RT}}$	tan $\delta^{\mathrm{RT}}$	$T_{\rm C}/^{\rm o}{\rm C}$	$\mathcal{E}_{r}^{max}$	
0	6514	0.0076	24.4	6526	
0.4	5014	0.0078	16.6	5328	
0.8	3013	0.0079	2	3550	
1.2	2560	0.0082	< -20	_	

Temperature dependence of relative dielectric constant and dielectric loss for Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics is shown in Fig. 6. It is obvious that the Curie temperature of Sb<sub>2</sub>O<sub>3</sub>-doped (Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub> ceramics (see Table 2) shifts to lower value with increasing Sb<sub>2</sub>O<sub>3</sub> doping content, which is attributed to the weakening of spontaneous polarization of the grain lattice caused by the substitution for host ion with any of the Sb<sup>3+</sup> ions as mentioned before. The charged vacancies caused by A-site /B-site substitution give rise to the local deformation of the perovskite unit cells, which also causes the reduction of Curie temperature. In the whole temperature range relative dielectric of Sb<sub>2</sub>O<sub>3</sub>-doped constants ceramics are significantly  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$ suppressed as the Sb<sub>2</sub>O<sub>3</sub> content increases. At high Sb<sub>2</sub>O<sub>3</sub> doping contents (>0.8%), the curves become flat, which implies the high thermal stability of Sb<sub>2</sub>O<sub>3</sub>-doped non-stoichiometric barium strontium titanate ceramics. Particularly, the peak value remarked as  $\varepsilon_r^{max}$  decreases with the increase of Sb<sub>2</sub>O<sub>3</sub> content. The effects of Sb<sub>2</sub>O<sub>3</sub> content on dielectric maximum are caused by the weakening of ferroelectricity, which is attributed to the replacing reaction of Sb<sup>3+</sup> ions for the host ions in perovskite lattice. As shown in Fig. 6(b) the dielectric loss decreases dramatically with the increasing temperature in low temperature range and reaches the

minimum at around 35 °C. Also,  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics with high  $Sb_2O_3$  content exhibit better thermal stability of dielectric loss than that with low  $Sb_2O_3$  content.



Fig. 6 Temperature dependence of relative dielectric constant (a) and dielectric loss (b) for  $Sb_2O_3$ -doped  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}$ - $O_{2.996}$  ceramics

#### 4 Conclusions

1)  $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics transform from single phase solid solutions with typical cubic perovskite structure to multiphase compounds with the increase of  $\delta$ value while  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics remain to be single-phase solid solutions with the increasing  $Sb_2O_3$ doping content.

2) The *B*-site vacancies  $V_{\text{Ti}}^{""}$  as well as oxygen vacancies  $V_{\text{O}}^{\bullet\bullet}$  exist in  $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{1-\delta}\text{O}_{3-2\delta}$  ceramics and the  $\text{Sb}_{\text{A}}^{\bullet} - V_{\text{A}}^{"}/\text{Sb'}_{\text{Ti}} - V_{\text{O}}^{\bullet\bullet}$  complexes show in  $\text{Sb}_2\text{O}_3$ -doped  $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{0.998}\text{O}_{2.996}$  ceramics. Due to the existence of  $V_{\text{Ti}}^{""}$  in Ti deficient  $(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Ti}_{0.998}\text{O}_{2.996}$  ceramics, the substitution preference of  $\text{Sb}^{3+}$  ions is opposite to that in stoichiometric barium strontium titanate ceramics.

3) The distortion of the ABO<sub>3</sub> perovskite structure caused by  $V_{\text{Ti}}'''$  and  $V_{\text{O}}^{\bullet\bullet}$  facilitates the drop of Curie temperature and the rise of relative dielectric constant in

 $(Ba_{0.75}Sr_{0.25})Ti_{1-\delta}O_{3-2\delta}$  ceramics with increasing  $\delta$  value. The orientation of the elastic dipoles caused by  $V_{O}^{\bullet\bullet}$  leads to the domain-wall pinning and thus the reduction of the dielectric loss. With increasing Sb<sub>2</sub>O<sub>3</sub> content, the relative dielectric constant, dielectric constant maximum and Curie temperature of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics decrease dramatically. Contrarily, the dielectric loss increases with the increasing Sb<sub>2</sub>O<sub>3</sub> content because of the reduction of Ti<sup>4+</sup> ion induced by Sb<sup>3+</sup> ion substitution for host ion.

4) The average grain size and grain size distribution of  $(Ba_{0.75}Sr_{0.25})Ti_{0.998}O_{2.996}$  ceramics can be refined by  $Sb_2O_3$  addition.

## Acknowledgements

This work is supported by the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and also sponsored by Suzhou Pante Electric Ceramics Tech. Co., Ltd., China.

# References

- [1] SAEED A, RUTHRAMURTHY B, YONG W H, HOONG O B, BAN T K, KWANG Y H. Structural and dielectric properties of iron doped barium strontium titanate for storage applications [J]. Journal of Materials Science: Materials in Electronics, 2015, 26: 9859–9864.
- [2] DONG Han-ting, JIN Deng-ren, XIE Chao-jun, CHENG Jin-rong, ZHOU Li-xin, CHEN Jian-guo. Compositionally inhomogeneous Ti-excess barium strontium titanate ceramics with a robust dielectric temperature stability [J]. Materials Letters, 2014, 135: 83–86.
- [3] SU B, BUTTON T W. Microstructure and dielectric properties of Mg-doped barium strontium titanate ceramics [J]. Journal of Applied Physics, 2004, 95: 1382–1385.
- [4] LI Yuan-liang, QU Yuan-fang. Dielectric properties and substitution mechanism of samarium-doped Ba<sub>0.68</sub>Sr<sub>0.32</sub>TiO<sub>3</sub> ceramics [J]. Materials Research Bulletin, 2009, 44: 82–85.
- [5] LIU S J, ZENOU V Y, SUS I, KOTANI T, SCHILFGAARDE M, NEWMAN N. Structure-dielectric property relationship for vanadium- and scandium-doped barium strontium titanate [J]. Acta Materialia, 2007, 55: 2647–2657.
- [6] FREEMAN C L, DAWSON J A, CHEN H R, BEN L B, HARDING J H, MORRISON F D, SINCLAIR D C, WEST A R. Energetics of donor-doping, metal vacancies, and oxygen-loss in *A*-site rare-earth-doped BaTiO<sub>3</sub> [J]. Advanced Functional Materials, 2013, 23: 3925–3928.
- [7] KISHI H, MIZUNO Y, CHAZONO H. Base metal-electrodemultilayer ceramic capacitors: Past, present and future perspective [J]. Japanese Journal of Applied Physics, 2003, 42: 1–15.
- [8] LU Da-yong. Self-adjustable site occupations between Ba-site Tb<sup>3+</sup> and Ti-site Tb<sup>4+</sup> ions in terbium-doped barium titanate ceramics [J]. Solid State Ionics, 2015, 276: 98–106.
- [9] LU Da-Yong, CUI Shu-Zhen. Defects characterization of Dy-doped BaTiO<sub>3</sub> ceramics via electron paramagnetic resonance [J]. Journal of the European Ceramic Society, 2014, 34: 2217–2227.
- [10] SYAMAPRASAD U, GALGALI R K, MOHANTY B C. Capacitor ceramics in pure and doped Ba<sub>0.71</sub>Sr<sub>0.29</sub>TiO<sub>3</sub> [J]. Materials Letters, 1989, 8: 36–40.
- [11] ZHANG Chen, QU Yuan-fang, MA Shi-cai. Structural and dielectric

2662

properties of Sb<sub>2</sub>O<sub>3</sub>-doped  $(Ba_{0.992,x}Sr_xY_{0.008})TiO_{3.004}$  ceramics [J]. Materials Science and Engineering B, 2007, 136: 118–122.

- [13] YUN Si-ning, WANG Xiao-li, LI Bo, XU De-long. Dielectric properties Ca-substituted barium strontium titanate ferroelectric ceramics [J]. Solid State Communications, 2007, 143: 461–465.
- [14] ZHANG Chen, QU Yuan-fang. 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 [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: 2742–2748.

- [15] HYATT E P, LONG S A, ROSE R E. Sintering high-purity BaTiO<sub>3</sub>
   [J]. American Ceramic Society Bulletin, 1967, 46: 732–736.
- [16] LI Wen, QI Jian-quan, WANG Yong-li, LI Long-tu, GUI Zhi-lun. 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]. Materials Letters, 2002, 57: 1–5.

# 氧化锑掺杂贫 Ti 钛酸锶钡陶瓷的介电性能及缺陷行为

张 晨,凌志新,简 刚,陈方旭

江苏科技大学 江苏省先进焊接技术重点实验室,镇江 212003

**摘 要:**采用固相法制备 Sb<sub>2</sub>O<sub>3</sub> 掺杂的贫 Ti 钛酸锶钡陶瓷,通过 SEM、XRD 和 LCR 测试系统研究其显微结构及 介电性能随非化学计量比及 Sb<sub>2</sub>O<sub>3</sub> 含量的变化。结果表明:随着δ值增大,(Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>1-δ</sub>O<sub>3-2δ</sub>陶瓷由典型立方 钙钛矿结构单相固溶体转变为多相化合物,而(Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub>陶瓷随 Sb<sub>2</sub>O<sub>3</sub> 掺杂量增加始终为单相固溶体。 由 V<sub>T</sub>""及 V<sub>0</sub><sup>••</sup> 引起的 ABO<sub>3</sub>型钙钛矿晶胞畸变导致(Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>1-δ</sub>O<sub>3-2δ</sub>陶瓷随δ值增大居里温度降低且相对介电 常数增高。弹性偶极子 V<sub>0</sub><sup>••</sup> 的定向引起畴壁钉扎而导致其介电损耗降低。(Ba<sub>0.75</sub>Sr<sub>0.25</sub>)Ti<sub>0.998</sub>O<sub>2.996</sub>陶瓷的相对介电 常数、介电常数最大值及居里温度均随着 Sb<sub>2</sub>O<sub>3</sub> 掺杂量增加显著降低而其介电损耗却随 Sb<sub>2</sub>O<sub>3</sub> 掺杂量的增加而 增大。

关键词: 钛酸锶钡; 缺陷; 介电性能; 非化学计量陶瓷

(Edited by Xiang-qun LI)