

## Microstructure, dielectric properties and phase transition of Y<sub>2</sub>O<sub>3</sub>-doped barium tin titanate ceramics

F. M. Wang<sup>a,\*</sup>, Y. L. Li<sup>b</sup>, C. L. Yan<sup>b</sup>

<sup>a</sup>College of Science, North China University of Science and Technology, Tangshan 063021, Hebei Province, China

<sup>b</sup>Comprehensive Testing and Analyzing Center, North China University of Science and Technology, Tangshan 063021, Hebei Province, China

BaCO<sub>3</sub>, SnO<sub>2</sub> and TiO<sub>2</sub> et al were used as crude materials, and Y<sub>2</sub>O<sub>3</sub> was used as dopant, BaSn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (BTS) ceramics were prepared by solid-state reaction sintering technology. The results show that the doping of Y element does not change the lattice structure of barium tin titanate obviously, and there is no new phase, however, owing to the Y<sup>3+</sup> ion doping, the diffraction peak position is changed as the Y<sup>3+</sup> doping amount increasing. Interestingly, Curie temperature of the sample increased from 35 °C (blank sample) to 50 °C (0.05 mol%), and then the Curie temperature moved to low temperature as the doping amount increased continuously, which is related to the doping mechanism of Y<sup>3+</sup> ion. After doping Y<sub>2</sub>O<sub>3</sub>, the dielectric loss of the samples decreases, especially when the doping amount reaches 0.10 mol%, the specimen shows excellent temperature stability of dielectric loss, making it superior candidates for applications.

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### 1. Introduction

BaSn<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (BTS) is a kind of dielectric non-linear material with lower leakage current and higher voltage strength [1-3]. Barium tin titanate Ba(Ti, Sn)O<sub>3</sub> solid solution system is the first discovered ferroelectric material with diffusion phase transition, which is an important inorganic ferroelectric material, it has the advantages of high permittivity, strong dielectric nonlinearity, low fatigue and adjustable Curie temperature, therefore, it usually can be used to prepare pyroelectric infrared detectors, dynamic random access memory (DRAM), dielectric phase shifters, second harmonic generators and other components [4-7]. Therefore, the preparation of small particle size, good chemical uniformity of barium tin titanate powder has a very important application significance. At present, there are many methods to prepare barium tin titanate powder, such as solid phase synthesis, hydrothermal synthesis, and sol-gel synthesis, etc [8-10].

The peak permittivity can be increased when the addition amount is appropriate, and the Curie peak can be decreased and widened when the Sn<sup>4+</sup> amount is more than a certain amount. The tetragonal and trapezoidal phase transition temperatures, the trapezoidal and trigonal phase transition temperatures of BaTiO<sub>3</sub> increase significantly when the addition amount of Sn<sup>4+</sup> is less than 10wt%, respectively [11,12].

It is an effective method to modify barium titanate ceramics by adding dopant, and many research and experiments show that many kinds of dopants can obviously improve the properties of barium tin titanate ceramics [8,13]. By substituting the dopant, the phase change diffusion is produced in the system, and the expansion and displacement of Curie peak are realized. In this paper, the effect of doping concentration on the dielectric properties (dielectric constant  $\epsilon$  and dielectric loss  $\tan\delta$ ) of BTS ceramics and the rule of phase transition (Curie temperature) were studied.

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\* Corresponding author: 32458467@qq.com

## 2. Experimental

The starting raw materials used in the experiment are BaCO<sub>3</sub>(chemical purity), SnO<sub>2</sub>(chemical purity), TiO<sub>2</sub>(chemical purity) and a small amount of dopant Y<sub>2</sub>O<sub>3</sub>(analytical purity), et al. The main formula in the experiment is Ba (Ti<sub>1-x</sub>Sn<sub>x</sub>)O<sub>3</sub>, the amount of Y<sub>2</sub>O<sub>3</sub> is 0.0 mol% -0.4 mol%, and the others are a few fixed additives. According to the main formula, BaCO<sub>3</sub>, SnO<sub>2</sub> and TiO<sub>2</sub> were taken, then the mass ratio of  $\zeta$  (once material: Ball: water) = 1:1:2, and the deionized water ball was added to grind for 4h. After drying, the ball abrasive was synthesized at 1080 °C for 2h, doped with Y<sub>2</sub>O<sub>3</sub>, and then milled with deionized water for 6h according to  $\zeta$  (secondary material: Ball: water) = 1:1:1.5. After drying, 5% PVA aqueous solution was added to the ball abrasive for granulating, the granulating material was sifted, and then pressed to form a  $\Phi 20$  mm  $\times$  2 mm disc sample under 100 MPa pressure. The samples were sintered at 1300 °C for 2 h. After ultrasonic cleaning for 30 min, the samples were sintered at 470 °C with silver electrode.

The phase structure was performed by using D/Max -2500 V/PC polycrystalline X-ray diffractometer produced by Rigaku company of Japan, using CuK $\alpha$  radiation (40 kV, 100 mA). The surface morphology of the samples was observed by the field emission scanning electron microscope (FE-SEM, S4800, Hitachi, Japan). The ceramic sheets were cleaned with distilled water for 10 min, subsequently dried and cooled in an oven for SEM analysis, and the natural surface of the sample was observed. Both  $\varepsilon$  and  $\tan\delta$  were measured by Automatic LCR Meter 4225. The dielectric temperature coefficient was obtained by Automatic LCR Meter 4225 and combined with intelligent temperature control system at 1 kHz, furthermore Curie temperature is determined by the dielectric constant temperature spectrum.

## 3. Results and discussion

The diffraction results of the sample are shown in Fig. 1. It can be definitely confirmed that all the samples own a typical perovskite structure, indicating that the doping agent of yttrium does not change the lattice structure of barium tin titanate obviously, and there is no new phase. A careful comparison of X-ray diffraction pattern shows that the diffraction peaks and the corresponding diffraction angles change slightly due to the addition of Y<sub>2</sub>O<sub>3</sub>, the reason may be that the high temperature of 1300 °C makes the synthesis of BTS more fully, and the lattice structure is changed. This phenomenon also has a lot to do with Y<sup>3+</sup> doping. As we all know, the Y<sup>3+</sup> ionic radius is larger than that of Ti<sup>4+</sup> (0.061 nm) and Sn<sup>4+</sup> (0.071 nm) in the six-coordinated body, in the meantime, the Y<sup>3+</sup> ionic radius (0.090 nm) in dodecyl ligand is smaller than that of Ba<sup>2+</sup> ion (0.161 nm) [14]. Therefore, in the terms of ion radius, Y<sup>3+</sup> ions can enter position A and position B, respectively. In addition, Table 1 shows the tolerance factor  $t$  of Y<sup>3+</sup> ion entering into A position and B position in BTS ceramics, respectively. From the table, it can be seen that the tolerance factor  $t$  of Y<sup>3+</sup> ions in BTS ceramics is between 0.77 and 1.10, and it is close to the ideal perovskite structure tolerance factor  $t$  ( $t=1$ ), indicating that Y<sup>3+</sup> ions can form stable perovskite (structure) at both A and B positions in BTS ceramics. Obviously, when Y<sup>3+</sup> ions enter into the lattice, the cell parameters of the sample will change, so the diffraction peak position will change with the increase of Y<sup>3+</sup> doping amount.

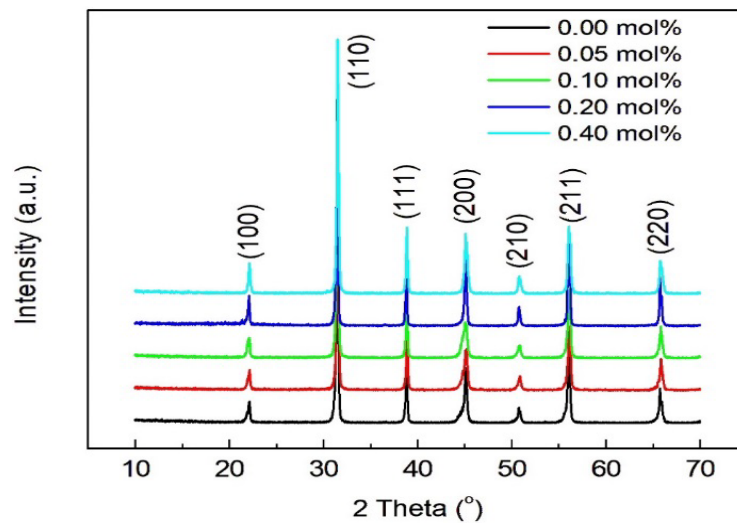


Fig. 1. XRD patterns of BTS specimens with various  $Y_2O_3$  content (a) 0.0 mol%, (b) 0.05 mol%, (c) 0.1 mol%, (d) 0.2 mol%, (e) 0.4 mol%.

Table 1. Tolerance factor  $t$  for  $Y^{3+}$  ions doping in BTS ceramics.

Substitution position	$t$
A (in $BaTiO_3$ crystal)	0.87
A (in $BaSnO_3$ crystal)	0.83
B ( $Ti^{4+}$ 或 $Sn^{4+}$ )	0.93

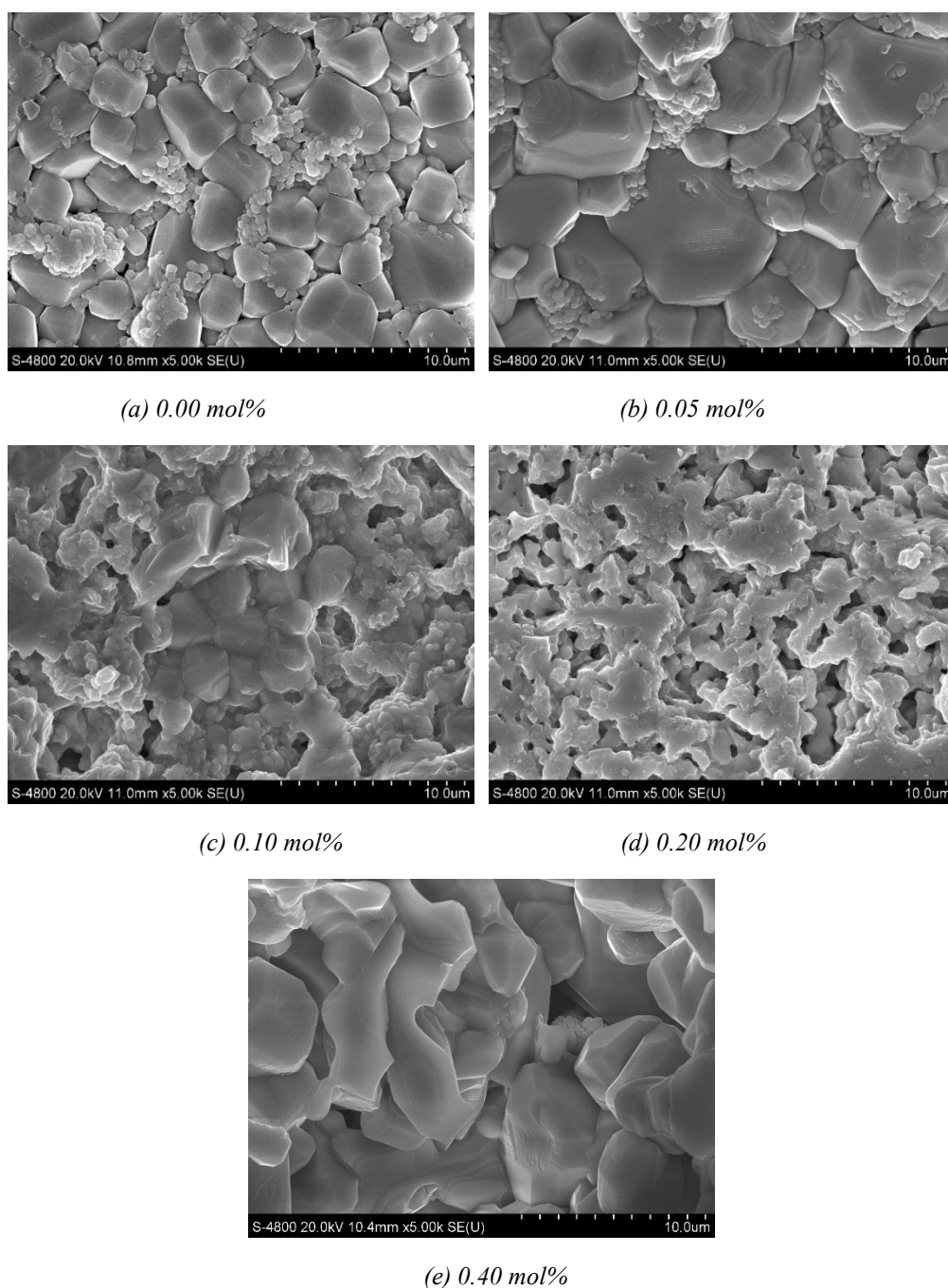


Fig. 2. The surface of various  $Y_2O_3$  content doped BTS specimens.

Fig. 2 exhibits the surface topography of the samples. From Fig. 2, it can be found that the grain size of doped  $Y_2O_3$  (0.05 mol%) increases obviously, and the grain size becomes to be more uniform and better developed than that of the blank sample, the grains are refined. Moreover, it can be deservedly noticed from Fig. 2 that the porosity of the sample increases obviously when the mole percentage is 0.1 and 0.2, and unfortunately, the increase of porosity usually plays a negative effect on the dielectric properties of the sample.

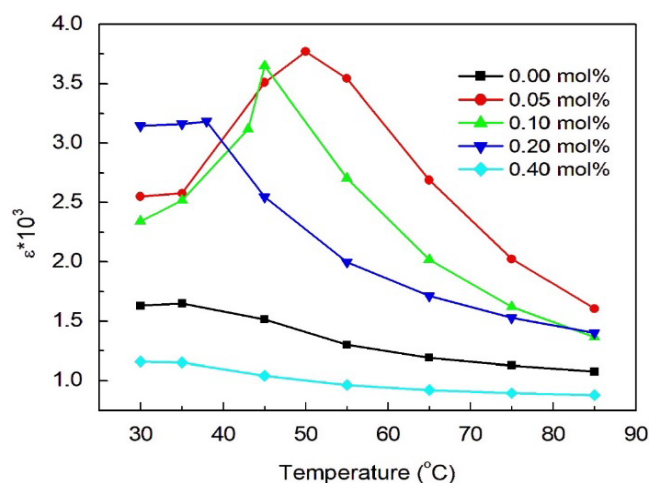


Fig. 3. Temperature dependence of  $\epsilon$  for various  $Y_2O_3$  doping in BTS ceramics.

Fig. 3 shows the dielectric temperature spectrum of the sample, from which it can be observed that the dielectric constant increases obviously when the  $Y_2O_3$  doping amount is less than 0.2 mol%, and the dielectric constant of the blank sample and the doped 0.40 mol% sample changes smoothly with the temperature. With the doping of  $Y_2O_3$ , the Curie temperature of the sample increased from 35 °C (blank sample) to 50 °C (0.05 mol%), and then the Curie temperature moved to low temperature as the doping amount increased continuously, which is related to the doping mechanism of  $Y^{3+}$  ion. According to the analysis of ion radius and tolerance factor  $t$ ,  $Y^{3+}$  ion can replace A position and B position in the system, respectively.

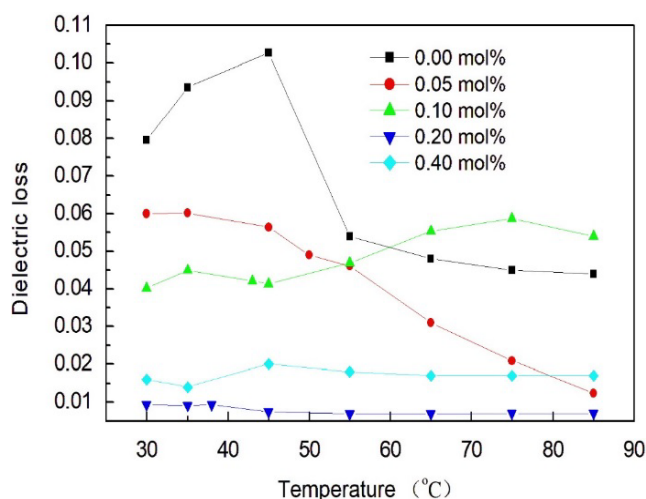


Fig. 4. Temperature dependence of  $\tan\delta$  for various  $Y_2O_3$  doping in BTS ceramics.

In this experiment, the substitution process of  $Y^{3+}$  ions in BTS ceramics is mainly divided into two stages. In the first stage, when the amount of  $Y_2O_3$  doping does not exceed 0.05 mol%,  $Y^{3+}$  mainly enters the A position, at this time, there is a large binding energy between Ti-O, and this strong coupling between Ti-O make a more stable state, definitely, higher thermal kinetic energy is required to disrupt the asymmetric equilibrium, which leads to an increase in Curie temperature; In the second stage, when the amount of  $Y_2O_3$  is more than 0.05 mol%,  $Y^{3+}$  mainly enters the B position, and the octahedral gap is relatively narrow because the radius of  $Y^{3+}$  is larger

than that of  $Ti^{4+}$ , the lower the interaction energy between the off-center B-site ion and the nearby oxygen ion, the lower the temperature, and so the Curie temperature drops. Undoubtedly, the above analysis agree with the experimental results.

Fig. 4 is the temperature spectrum of dielectric loss. From the diagram, we can see that after doping  $Y_2O_3$ , the dielectric loss of the samples decreases, especially when the doping amount reaches 0.10 mol%, the specimen shows excellent temperature stability of dielectric loss. From the previous analysis, we can know that with the increase of the amount of  $Y^{3+}$ , some  $Y^{3+}$  will enter the position B, and with the appearance of oxygen vacancy, it will make up for the electric price of the system, thus the dielectric loss of the sample was reduced [15].

#### 4. Conclusion

$BaSn_xTi_{1-x}O_3$  (BTS) ceramics owned perovskite structure were achieved by solid-state sintering reaction method. XRD results state clearly that the yttrium doping does not change the phase structure of barium tin titanate, however, it is worth noting that the diffraction peak position is changed with the increase of  $Y^{3+}$  doping amount. The doping of  $Y_2O_3$  not only has obvious effect on the dielectric properties but also has an impact on the Curie temperature, when the doping amount of  $Y_2O_3$  is below 0.2 mol%, the dielectric constant increases obviously, meanwhile, the Curie temperature of the sample increased from 35 °C (blank sample) to 50 °C (0.05 mol%), and then the Curie temperature moved to low temperature as the doping amount increased continuously. Thanks to the doping  $Y_2O_3$ , the dielectric loss of the samples decreases, especially when the doping amount reaches 0.10 mol%, the specimen shows excellent temperature stability of dielectric loss.

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