

## EFFECT OF Nb<sub>2</sub>O<sub>5</sub> DOPING ON DIELECTRIC PROPERTIES OF BaTi<sub>0.9</sub>Sn<sub>0.1</sub>O<sub>3</sub> CERAMICS

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Pure and Nb<sup>5+</sup> (0.0-0.8mol%) doped barium stannum titanate (BaTi<sub>0.9</sub>Sn<sub>0.1</sub>O<sub>3</sub>, BTS) ceramics were prepared by solid state reaction method. The XRD patterns indicate that all the samples show a pure perovskite phase and no secondary phase occurs. The microstructural investigation on the ceramics samples showed that Nb<sup>5+</sup> doping reduced the grain size of pure BTS ceramics and make structure density. The electrical properties of BTS ceramics were measured and the results indicated that the dielectric constant of samples increases first and then decreases with the increasing of Nb<sup>5+</sup> doping. The highest dielectric constant of the BTS ceramics was found at 0.6 mol% Nb<sup>5+</sup> in room temperature at 1 kHz. The Curie peak of ceramics samples moves to room temperature, and becomes wider. All samples exhibit low dielectric loss.

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### 1. Introduction

Capacitor ceramics have been widely used in various fields of life, such as electronic information, aerospace, navigation, defense, agriculture, nuclear industry, etc<sup>[1-3]</sup>. Ceramic capacitors are required to operate with high voltage, low power consumption, and stable performance. In addition, the ceramic capacitor also has the advantages of high temperature resistance and corrosion resistance, and conforms to the development trend of the miniaturization and high capacity of the integrated circuit.

Lead based perovskite ceramics exhibit excellent ferroelectric and dielectric properties, but the ceramic containing lead perovskite has great harm to human body and environment. Research and development of new environmentally friendly ceramic materials has become one of the materials developed by many countries in the world as people pay more attention to the ecological system and the awareness of environmental protection and sustainable development has gradually increased. Barium titanate ceramics, as a representative of lead-free ferroelectric materials<sup>[4-6]</sup>, will inevitably take the lead in the industrial field. Barium stannum titanate ceramics are widely used for their many advantages<sup>[7,8]</sup>. Scholars have found that doping rare earth elements in barium stannum titanate ceramics can effectively improve their dielectric properties<sup>[9-12]</sup>.

According to a large number of studies, barium stannum titanate ceramics (BaTi<sub>0.9</sub>Sn<sub>0.1</sub>O<sub>3</sub>, BTS) have the excellent performance as ceramic capacitor. By using the principle of ion substitution<sup>[13]</sup>, to make Sn<sup>4+</sup> replace Ti<sup>4+</sup>, doping metal oxide<sup>[14]</sup>, to reduce the sintering temperature, smaller grain size and improve the density of the ceramic, to increase operating temperature range<sup>[15]</sup>, barium stannum titanate ceramics are prepared into high performance ceramic capacitor materials.

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In this paper, by doping  $\text{Nb}_2\text{O}_5$ , the effects of  $\text{Nb}^{5+}$  doping on BTS ceramic microstructure and dielectric properties were studied, to find the optimal doping amount of  $\text{Nb}^{5+}$  and the optimal sintering temperature, for preparation of excellent dielectric properties of lead-free ceramic capacitors.

## 2. Experimental

Main raw materials:  $\text{BaCO}_3(\text{AR})$ ,  $\text{TiO}_2(\text{AR})$ ,  $\text{SnO}_2(\text{AR})$ ,  $\text{Nb}_2\text{O}_5(\text{AR})$ ,  $\text{Gd}_2\text{O}_3(\text{AR})$ .

The sample was prepared by conventional solid state reaction route, and the main formula was BTS. The doping amount of  $\text{Nb}_2\text{O}_5$  is  $x$  mol% ( $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ ). According to chemical formula, the powders were weighed and ball-milled for 4 h in deionized water. Then it was dried and calcined at  $1090^\circ\text{C}$  for 2 h. The calcined powder was broken up and mixed intimately with  $x$  mol%  $\text{Nb}_2\text{O}_5$ . The mixture are ball-milled again for 6 h in order to make component uniform. After drying, the ceramic powders were passed through a 40-mesh sieve mixed with 5 wt% polyvinyl alcohol (PVA) binder and then pressed into thin disks under 6 MPa pressure. The sintering of samples was carried out at  $1250\sim 1300^\circ\text{C}$  for 2 h, using a heating rate of  $5^\circ\text{C}/\text{min}$ . Silver paste was coated on both surfaces and fired at  $550^\circ\text{C}$  for the measure of the dielectric properties.

The main crystal phase of the sample was determined by D/max2500v/PC X ray diffractometer. The dielectric constant ( $\epsilon$ ) and dielectric loss ( $\tan\delta$ ) were measured using a capacitance apparatus (automatic LCR Meter 4225) at a function of temperatures under 1 kHz.

## 3. Results and discussions

The RT XRD patterns of un-doped and  $\text{Nb}^{5+}$  doped ceramics sintered at  $1300^\circ\text{C}$  are shown in Fig.1. It can be seen from the Fig.1 (a) that a pure perovskite phase was formed for all the samples and no other second phase could be observed within the sensitivity of XRD.

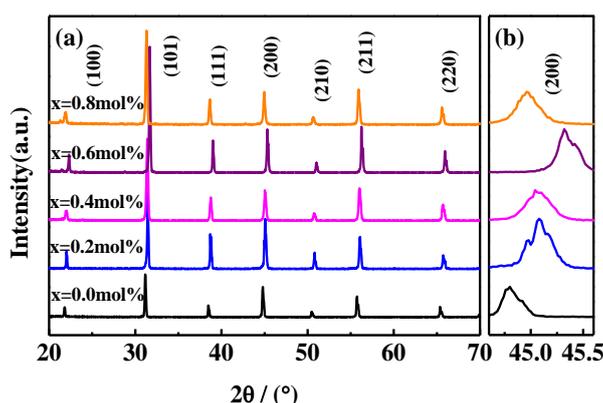


Fig. 1 XRD patterns of  $\text{Nb}_2\text{O}_5$  doped BTS ceramics sintered at  $1300^\circ\text{C}$  for 2 h

It is shown that  $\text{Nb}^{5+}$  can be dissolve into a homogeneous solid solution in BTS crystals. Fig.1 (b) is a magnification diagram of (200) crystal surface. It can be seen that the diffraction peak shifts towards a high angle when the  $\text{Nb}^{5+}$  doping amount is less than or equal to 0.6%, and when the  $\text{Nb}^{5+}$  doping amount is 0.8%, the diffraction peak shifts to a low angle. According to the Bragg's Law, the distance between crystal planes decreases first and then increases, and the minimum is at 0.6 mol%.

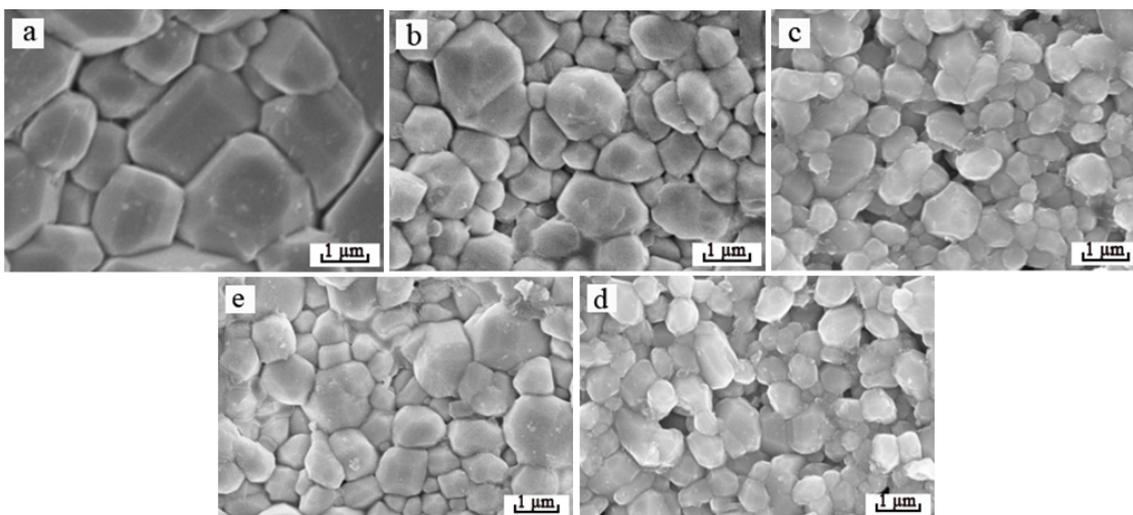


Fig. 2 SEM images of (a) BTS and  $\text{Nb}_2\text{O}_5$  doped BTS ceramics. (b) 0.2 mol% (c) 0.4 mol% (d) 0.6 mol% (e) 0.8 mol%

Fig. 2 shows the microstructure of the sample surface with different  $\text{Nb}^{5+}$  doping concentration sintered at  $1300\text{ }^\circ\text{C}$ . It can be seen from (a) that pure BTS ceramics have large grain size. When the  $\text{Nb}^{5+}$  doping concentration is 0.2 mol% (Fig.2 (b) ), the grain refine and the structure is denser. When the  $\text{Nb}^{5+}$  doped concentration increased to 0.4 mol% (Fig.2 (c) ) and 0.6 mol% (Fig.2 (d) ), the grain of the sample is further refined, but a few pores appear.  $\text{Nb}^{5+}$  ions enter into the B site to replace  $\text{Ti}^{4+}$ , the oxygen octahedra gap shrinks, the number of oxygen vacancies decreases and grain growth is inhibited, thus the grain size decreases. Another reason for the decrease in grain size is that some  $\text{Nb}^{5+}$  ions with smaller size accumulated near the grain boundaries, resulting in the inhibition of grain growth during sintering in the sintering process<sup>[16]</sup>. In general,  $\text{Nb}^{5+}$  ion is easier to enter  $\text{BaSn}_{0.1}\text{Ti}_{0.9}\text{O}_3$  structure B site due to electric balance. When  $\text{Nb}^{5+}$  enters B site of BTS ceramics<sup>[17]</sup>, it tends to substitute for  $\text{Ti}^{4+}$  to produce a positive charge<sup>[18]</sup>, which combined with  $\text{O}^{2-}$  to form oxygen removal to form pores. When the  $\text{Nb}^{5+}$  doped concentration increase to 0.8 mol% (Fig.2 (e) ), the grain size increased slightly but still smaller than pure BTS. During the sintering process the BTS ceramic in terms of lattice diffusion of vacancies from the pore to the grain boundaries which lead to grain growth. For  $\text{Nb}^{5+}$  doped BTS ceramics, it was found that the  $\text{Nb}^{5+}$  ion increased the diffusion coefficient of vacancies so  $\text{Nb}^{5+}$  doping improved mass transport in BTS ceramics<sup>[19,20]</sup>, and promoted the grain growth.

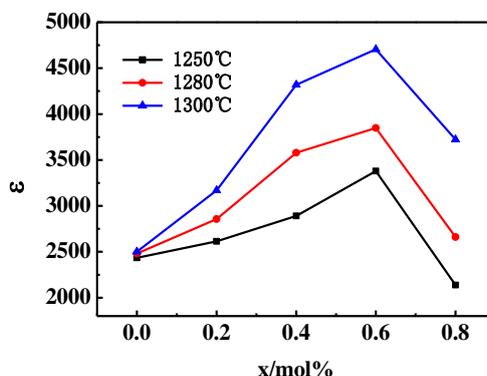
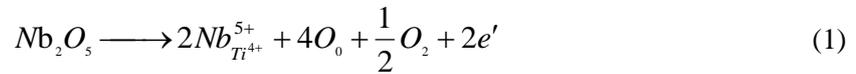
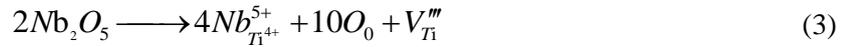
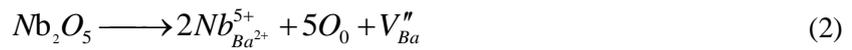


Fig. 3 Dielectric constant of  $\text{Nb}_2\text{O}_5$  doped BTS in different sintering temperature at room temperature

Fig. 3 illustrates the dielectric constant of BTS ceramics with different  $\text{Nb}^{5+}$  doped at 1 kHz, room temperature in different sintering temperatures. The dielectric constant of all samples increases first and then decreases with the increase of  $\text{Nb}^{5+}$  doping content at different sintering temperatures, and the maximum dielectric constant is reached at 0.6 mol%. The causes of this phenomenon are mainly related to the substitution mechanism of  $\text{Nb}^{5+}$  in BTS ceramics. The ionic radius of  $\text{Nb}^{5+}$  is 0.064 nm, the ionic radius of  $\text{Ti}^{4+}$  is 0.065 nm, and the ionic radius of  $\text{Ba}^{2+}$  is 0.161 nm. At low concentration ( $\leq 0.6\text{mol}\%$ ),  $\text{Nb}^{5+}$  ions enter into the B site of BTS ceramic instead of  $\text{Ti}^{4+}$ , resulting in lattice distortion and internal stress, affecting the dielectric constant. In general, the internal stress of ceramics can be released through the pores<sup>[21]</sup>. Therefore the ceramics with a smaller number of pores have a higher dielectric constant. Grain boundary slip is another way to relieve internal stresses<sup>[23]</sup>. Therefore, dense ceramic with fine grain should have higher dielectric constant than ceramic with coarse grain. When  $\text{Nb}^{5+}$  enters the B site, due to the larger valence of  $\text{Nb}^{5+}$  ions, a certain amount of electrons was produced. The new electron increased the sample's electronic conductivity, the dielectric constant of the sample increased. The substitution equation is as follows:



While the  $\text{Nb}^{5+}$  concentration exceeds 0.6 mol%, the replacement method change, the equation is as follows:



In this way,  $\text{Nb}^{5+}$  enters the sites A and B. The high valence  $\text{Nb}^{5+}$  replaces  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  to produce barium vacancies and titanium vacancies. Due to the "pinning" effect of vacancies<sup>[22]</sup>, the dielectric constant of the samples decreases.

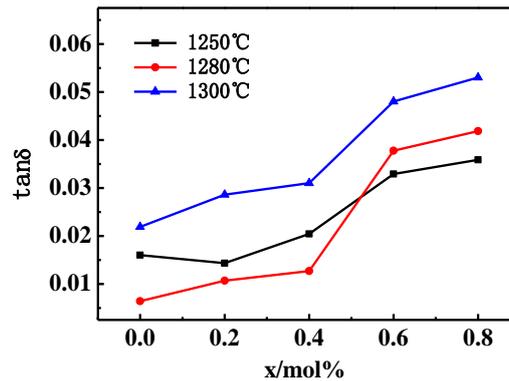


Fig.4 Dielectric Loss of  $\text{Nb}_2\text{O}_5$  doped BTS in different sintering temperature at room temperature

Fig.4 shows the dielectric loss of  $\text{Nb}^{5+}$  doped BTS ceramics in different sintering temperatures at room temperature. It can be observed clearly that the dielectric loss of BTS ceramics increases with the increase of  $\text{Nb}^{5+}$  concentration, but the dielectric loss of the samples is low overall. In Ti-containing ceramics, an important reason for the increase of dielectric constant is the reduction of  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ . BTS ceramics are sintered in high temperature in the air. Due to the deficiency of oxygen content, oxygen vacancy is produced. These oxygen vacancies can adsorb free electrons, causing relaxation polarization and increasing dielectric loss. The addition of small

amounts of  $\text{Nb}^{5+}$  to replace  $\text{Ti}^{4+}$  produces an extra positive charge, which increased electron conductance and increased dielectric loss<sup>[24]</sup>. The increase in dielectric loss at high doping levels (0.8 mol%) is due to the formation of a large number of vacancies for the substituted  $\text{Ti}^{4+}$  and  $\text{Ba}^{2+}$  with the higher valence state  $\text{Nb}^{5+}$ . The dielectric loss of the sample increases with the sintering temperature increase. This was due to an increase in ion mobility and material defects<sup>[25]</sup>. Compared with Fig.3, the peak dielectric loss and peak permittivity are not coincidence. The Kramers-Kronig relationship indicates that it was the result of the temperature relaxation near Curie temperature<sup>[25]</sup>.

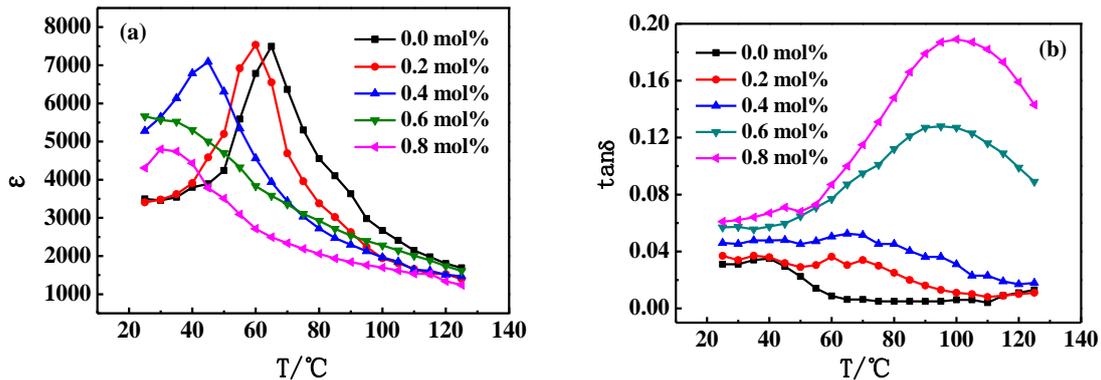


Fig.5 Temperature dependence of the dielectric constant (a) and dielectric loss (b) of  $\text{Nb}_2\text{O}_5$  doped BTS ceramics

The dielectric constant ( $\epsilon$ ) (at 1 kHz) as a function of temperature are displayed in Fig.5 (a). The two phase transition peaks can be observed in pure BTS ceramics. The rhomboidal phase is transformed into a tetragonal phase at 40 °C and the tetragonal phase is transformed into a cubic phase at 65 °C. With the increase of  $\text{Nb}^{5+}$  concentration, the maximum dielectric peak moves to low temperature and decreases. It is shown that there is a negative correlation between the maximum dielectric peak of the BTS ceramics and the  $\text{Nb}^{5+}$  content. As mentioned above,  $\text{Nb}^{5+}$  is preferred to replace  $\text{Ti}^{4+}$  in BTS ceramics.  $\text{Nb}^{5+}$  (0.064 nm) ions with small radius instead of  $\text{Ti}^{4+}$  (0.065 nm) ions with large radius. The partial substitution will lead to lattice distortion and reduction of cell volume, resulting in a decrease of the lattice parameter  $c/a$ , leading to the Curie peak moving towards low temperature.  $\text{Nb}^{5+}$  doping increases the distortion energy and promote the vibration of  $\text{Ti}^{4+}$  at relatively low temperature, which contributes to the stability of  $\text{Ti}^{4+}$  in the center of the oxygen octahedron. Therefore, the maximum dielectric constant decreases with the increasing  $\text{Nb}^{5+}$  content. With the increase of  $\text{Nb}^{5+}$  content, the peak near the maximum dielectric constant becomes wider. This phenomenon is called diffusion phase transition<sup>[26]</sup>. This may be due to lattice disorder and unbalanced cation caused by the substitution of  $\text{Ti}^{4+}$  by  $\text{Nb}^{5+}$ , which leads to inhomogeneity in the structure. In B site,  $\text{Ti}^{4+}$  leads to local polar regions, while  $\text{Nb}^{5+}$  leads to local non-polar regions, which make different diffusion rates in  $\text{Nb}^{5+}$  doped BTS ceramics. Besides lattice disorder and unbalanced cation, grain boundary is another factor that can affect the behavior of diffusion phase transition<sup>[27]</sup>. The grain boundary is nonferroelectric phase and no ferroelectric - paraelectric phase transition. The volume fraction of grain boundary increases with the decrease of grain size. Therefore, in smaller grain ceramics, the proportion of tetragonal phases and ferroelectricity is lower. The phase transition process becomes more diffuse.

Fig.5 (b) shows that when a small amount of  $\text{Nb}^{5+}$  is doped, the dielectric loss decreases with increasing temperature, and the dielectric loss changes little with the temperature. When the doping amount exceeds 0.6 mol%, the dielectric loss increases first and then decreases as the temperature with a large change range. This shows that excessive  $\text{Nb}^{5+}$  doping will cause thermal instability of the dielectric loss of the system. In summary, the dielectric properties of BTS ceramics are best when the  $\text{Nb}^{5+}$  doping amount is 0.6 mol%.

#### 4. Conclusions

Lead-free BTS-based ceramic samples with  $x$  mol% ( $x=0, 0.2, 0.4, 0.6, 0.8$ )  $\text{Nb}_2\text{O}_5$  were prepared by solid state reaction method. The dielectric properties of ceramic samples of different  $\text{Nb}^{5+}$  doping amount were studied. The XRD patterns show that the main crystal phase of all samples is the same as that of BTS ceramics, which is a single perovskite phase with no impurity phase. According to the microstructure analysis,  $\text{Nb}^{5+}$  doping can refine grains. When the doping concentration of  $\text{Nb}^{5+}$  is low ( $\leq 0.6$  mol%), the grain size becomes smaller, but a few pores appear. When the doping concentration of  $\text{Nb}^{5+}$  is higher (0.8 mol%), the grain size of the sample slightly increases, but still smaller than pure BTS ceramic. Overall, all samples are dense. The dielectric constant of BTS ceramics increases first and then decreases with the increase of  $\text{Nb}^{5+}$  doping content, and the maximum dielectric constant is reached at 0.6 mol%. Dielectric loss increases with the amount of  $\text{Nb}^{5+}$  doping. When the doping amount is 0.6 mol% and 0.8 mol%, dielectric loss is high at high temperature. The doping of  $\text{Nb}^{5+}$  moves the Curie peak to low temperature, and the Curie peak broadens. The Curie peak of  $\text{Nb}^{5+}$  doped ceramics moves in the direction of low temperature and becomes wider.

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