

INFLUENCE OF DOPING Yb_2O_3 ON DIELECTRIC PROPERTIES OF $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ CERAMICS

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$\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ (BTS) ceramics were prepared by a solid reaction method using BaCO_3 , SnO_2 and TiO_2 as raw materials, and the influence of Yb_2O_3 addition on phase composition, microstructure and dielectric properties. The variation of dielectric properties at different sintering temperature was also discussed. The phase composition was analyzed by XRD pattern, and the microstructures of the samples were observed by SEM, and their dielectric properties were measured at 1 kHz. From the XRD patterns, the results show that all samples exhibited pure perovskite phase with no impurity phase, which suggested that the Yb^{3+} ion can be dissolved in BTS to form a homogenous solid solution. Doping Yb_2O_3 can also refine grain size. When BTS ceramics doped with Yb_2O_3 as 0.5 mol% and the sintering temperature is 1300 °C, the grain size is uniform and the growth is good. With the increase of Yb_2O_3 contents the dielectric constants increased and reached a maximum value at 0.5 mol%. The tangent loss decrease with the increase of Yb_2O_3 contents, and the peak temperature T_m at the maximum dielectric constant is shifted to lower temperature and broaden. When BTS ceramics doped with Yb_2O_3 as 0.5 mol% and the sintering temperature is 1300 °C the dielectric properties of the ceramic samples are optimized.

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1. Introduction

With the development of science and technology BaTiO_3 -based ceramics play an important role in the electronic ceramic industry. Barium titanate is an important electronic ceramic materials, and it is widely used in the preparation of small size, large capacity of the micro-capacitors and the grain boundary layer capacitors of semiconductor characteristics, PTC thermistor and other components, in order to meet the practical application requirements, barium titanate ceramics are often changed the composition formula and preparation conditions as the main way to improve its performance^[1-2]. The ferroelectric ceramics, represented by BaTiO_3 -based ceramics, have a high dielectric constant and are the basic raw materials for the manufacture of ceramic capacitors^[3-4]. BaTiO_3 is a simple perovskite type compound, but its dielectric constant at the room temperature is only one of sixth of the Curie peak. Barium titanate ceramics which has high dielectric loss also needs improve its characters in some areas. Therefore, the researchers began to modify barium titanate ceramics with doping^[5-8]. The relevant researchers study found that $\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3$ system has function with diffusion phase transition, and Sn^{4+} has the same function with Zr^{4+} in modification^[9]. The dielectric constant of the Curie peak is moved to the low temperature zone. When adding the appropriate amount of Sn^{4+} , the peak dielectric constant will be increased obviously. When the amount of Sn^{4+} is more than a certain

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number, the concentration of Sn^{4+} is reduced to 10% , BaTiO_3 tetragonal and diagonal phase transition temperature and the oblique and triad phase transition temperature will increase obviously ^[10]. BTS is a small grain ferroelectric ceramics, high dielectric constant, low dielectric loss, excellent ferroelectric, piezoelectric, voltage and insulation properties make tin barium titanate-based ceramics are widely used in large capacity Of the miniature capacitors, thermistors, etc.^[11] In this paper, Yb_2O_3 was the doping component with different doping amount. The samples of the dielectric properties were studied by using $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ -based ceramic materials.

2. Experimental

BTS ceramics were prepared by conventional solid-state reaction method using BaCO_3 (analytical pure), SnO_2 (analytical pure), TiO_2 (analytical pure) and Yb_2O_3 (analytical pure) powders as raw materials, in which BaCO_3 , SnO_2 , and TiO_2 were prepared to synthesize BTS main phase. $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramic powders were prepared by solid state mixed oxide technique. A stoichiometric amount of powders was mixed and doped Yb_2O_3 with x mol% (x=0, 0.1, 0.3, 0.5, 0.7 and 0.9). According to the formula calculation results, weighed BaCO_3 , SnO_2 , and TiO_2 into Ball mill in deionized water and then dried, and powders, ball and deionized with proportion of 1 : 1 : 2. After ball milling at 4h, then the dried powders were calcined at 1090 °C for 2h. At last we can obtain $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramic powders. After that $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ceramic powders and Yb_2O_3 were added and mixed by a ball mill. Re-milled powders were dried for 8 h in an oven. After passing 40 mesh sieve pressed into disks of 13 mm in diameter and 2 mm in thickness under 60 MPa. sintering at 1250 °C ~1330 °C for 2 h. After firing the ceramic sample by ultrasonic cleaning 30 min, the two sides of the sample coated with silver electrode paste, after 550 °C burning silver electrode, the sample placed 24 h after the performance test.

The microstructural phase of the sample was probed by the $\text{CuK}\alpha$ target X-ray diffraction (XRD, Rigaku D/ max 2500V/pc) from Japan Science and Technology. The samples were scanned by microscopic scanning electron microscopy (SEM) of Japan Hitachi S-4800 cold field emission scanning electron microscopy (SEM).

The capacitance C and the dielectric loss factor D be tested by using the Automatic LCR Meter 4225 bridge, the automatic LCR Meter 4225 bridge combined with the intelligent temperature control system was used to measure the dielectric constant of the material at 1 kHz frequency the temperature spectrum, the dielectric constant The peak temperature in the temperature spectrum is T_c ^[12].

Calculate the dielectric constant and dielectric loss of the sample:

$$\varepsilon = \frac{14.4Ch}{\phi^2} \quad (1)$$

$$\tan \delta = \frac{fD}{1000} \quad (2)$$

In the formula: h —the thickness of the sample (cm); Φ —the electrode diameter of the sample (cm); C —the capacitance of the sample (pF); f —test frequency; D —Dielectric loss factor

3. Results and discussions

3.1 Effect of Doping Amount on Crystal Structure of BTS Specimen

The results of XRD test are shown in Fig. 1 under the condition of 1300 °C for 2 h sintering.

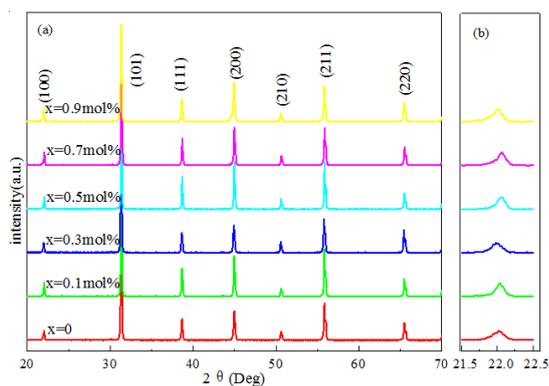


Fig.1 XRD patterns of BTS ceramics sintered at 1300 °C for 2 h

Fig.1 (a) shows the XRD patterns of various amounts of Yb_2O_3 doped BTS-based ceramics sintering at 1300 °C for 3 h. The XRD results demonstrate that all the samples display a desired perovskite structure, which indicates that the Yb_2O_3 have diffused into the BTS lattice to form a solid solution. In order to study the effect of the doping amount on the diffraction peak more clearly, the (100) crystal plane in the diffraction spectrum of Fig. 1 was partially amplified. From the graph (b), it is found that the diffraction peak of the (100) crystal plane moves in the high angle with the increase of the Yb^{3+} doping amount. When the doping amount is 0.5 mol%, the diffraction angle is the largest. According to the Bragg formula, At this time the smallest interplanar spacing.

3.2 Effect of Microstructure on Doped BTS Materials

Fig.2 (a)~(f) shows Yb_2O_3 doping amount of 0~0.9 mol% respectively. The samples were sintered at 1300 °C for 2 h and doped with different amount of Yb_2O_3 . The image obtained by scanning with SEM is shown in Figure 2 below:

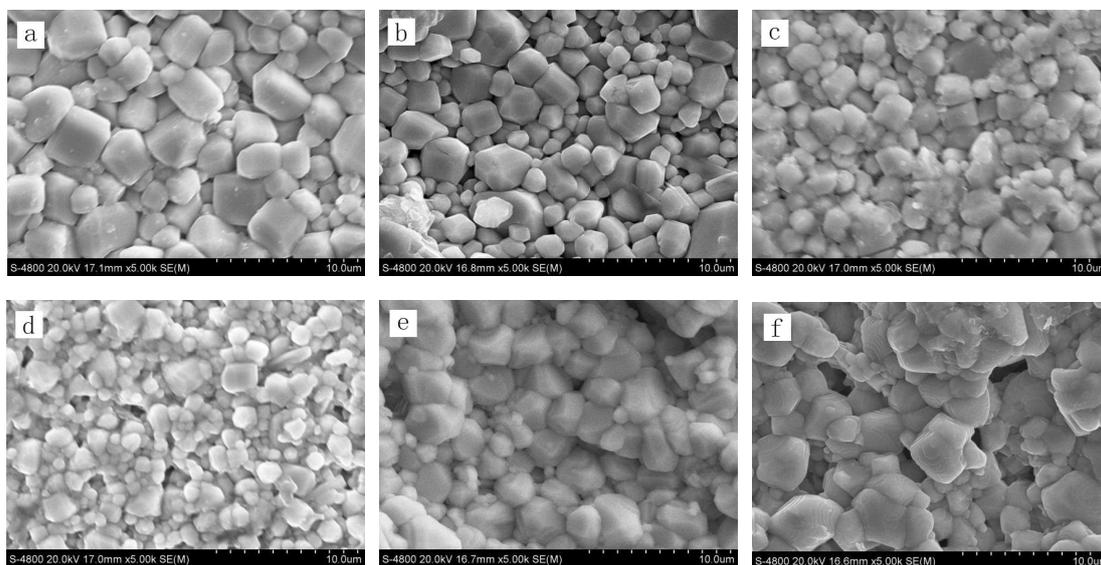
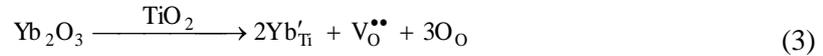


Fig. 2. SEM photomicrographs of BTS sintered at 1300°C for 2h: a 0.0% wt Yb_2O_3 , b 0.1% wt Yb_2O_3 , c 0.3% wt Yb_2O_3 , d 0.5% wt Yb_2O_3 , e 0.7% wt Yb_2O_3 , f 0.9% wt Yb_2O_3

It can be seen from the figure, (a)~(f) of the six BTS ceramic sample grain profile is clear, and have good sintered density. Porosity is relatively low and there have a clear grain boundary. Compared with (a), The insets of (d), (c) and (d) show the addition of a small amount of Yb^{3+} ions

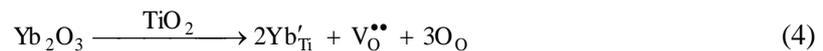
can refine grain and make grain size down, grow well. Yb^{3+} ions into the A-site lead to oxygen octahedral gap contraction, the number of oxygen vacancies decreased, grain growth was inhibited, so the grain size decreased [13].



When added a small amount of Yb_2O_3 , Yb^{3+} accumulates at grain boundaries and acts as a pinning grain boundary, result in inhibiting grain growth [14]. And when Yb_2O_3 doping amount x exceeds 0.5 mol%, Yb^{3+} mainly enters B position.

The radius of Ba^{2+} is 0.161nm. The radius of Ti^{4+} is 0.065 nm. The radius of Sn^{4+} is 0.069 nm. The radius of Yb^{3+} is 0.0868 nm. The radius of Yb^{3+} is greater than Ti^{4+} and Sn^{4+} , making the grain size increases. On the other hand, low prices instead of high prices, resulting in a large number of oxygen vacancies, promote grain diffusion and growth. As shown in the figure (e) and (f).

Formula can be written as follows:



3.3 Effect of Yb_2O_3 doping on the dielectric properties of BTS Simple

Fig.3 shows that dielectric constant ϵ with Yb^{3+} doping and temperature changes in the situation. Fig.4 shows that the dielectric loss of the sample at different temperatures.

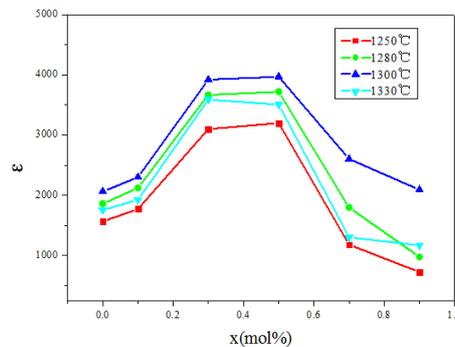


Fig. 3. Dielectric constant of Yb_2O_3 doped with BTS at room temperature

For the substitution order of rare earth ions in the perovskite structure, Watanabe [15] considered that there were three stages. The first two stages are that rare earth ions replace the A and B sites respectively, and the third stage was that the doping amount exceeded the ion of the solid solution limit, creating a second phase. Which can be introduced that when Yb^{3+} into the lattice first to enter the A-bit and then replace Ba^{2+} . Fig.3 show that with the amount of Yb_2O_3 doping increasing, the sample dielectric constant is also increasing. When the doping amount x is 0.5 mol%, the dielectric constant of the sample reaches the maximum, and then with the increase of the doping amount the dielectric constant begins to decrease. In the initial stage, the dielectric constant ϵ increases with the increase of x (Yb_2O_3) because Yb^{3+} enters the A-position and the Yb^{3+}

radius is 0.0868 nm smaller than the Ba^{2+} radius of 0.161 nm, so that the lattice volume shrinks, as seen in the previous SEM, Resulting in lattice distortion caused by internal stress, making the dielectric constant increased. [13] When Yb^{3+} into the A-bit, and it will produce a corresponding amount of electrons, the emergence of electrons will increase the sample of dielectric constant. When Yb_2O_3 doping amount x more than 0.5mol%, Yb^{3+} mainly into the B-bit, the radius of Ti^{4+} is 0.065 nm. The radius of Sn^{4+} is 0.069 nm. The radius of Yb^{3+} is 0.0868 nm. The radius of Yb^{3+} is greater than Ti^{4+} and Sn^{4+} , making Lattice volume expansion, and making the B-type ion orientation was broken ring, making the spontaneous polarization of the system led to decreased dielectric constant. While the low price to replace the high price of a part of the oxygen vacancy, resulting in "pinning" The dielectric constant decreases.

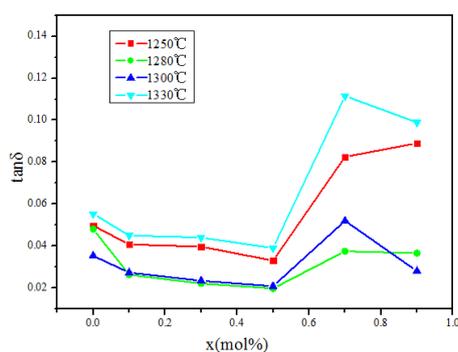


Fig. 4. Dielectric Loss of Yb_2O_3 doped with BTS at room temperature

As shown in Fig.4, the dielectric loss of the sample is decreasing as the doping amount increases. When the doping amount exceeds 0.5 mol%, the dielectric loss starts to increase. When the doping amount exceeds 0.7 mol%, the dielectric loss continues to decrease, and the high doping amount Yb^{3+} enters the B-site to form the acceptor ions, while the charge of the acceptor ions is compensated by the oxygen vacancy and suppresses the reduction of Ti^{4+} . The electrical loss is improved. When the sintering temperature is 1300 °C, the dielectric constant of the sample is the highest and the dielectric loss is also low [16-17]. Therefore, when the doping amount of Yb_2O_3 is 0.5 mol% and the sintering temperature is 1300 °C, the ceramic sample has the best dielectric properties.

The temperature of 1300 °C for 2 h sintering, Fig.5 shows that the thermograms of ceramic samples. With temperature changes different Yb^{3+} content of the sample at 1k Hz have different dielectric loss.

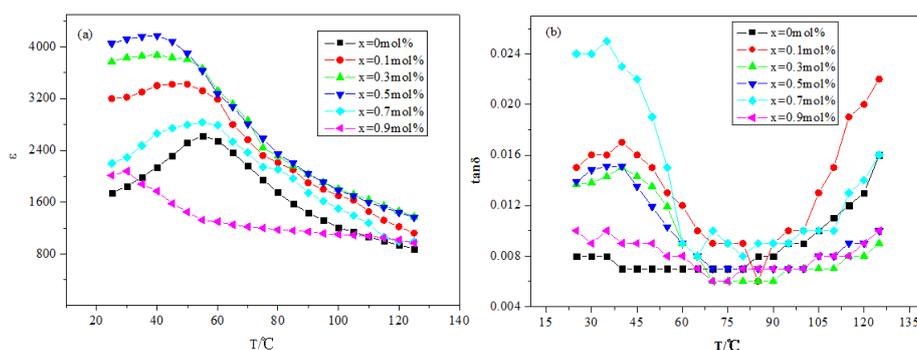


Fig.5 Temperature dependence of the dielectric constant and tangent loss of Yb_2O_3 doped BTS ceramics

From Fig.5 (a), with the increase of temperature the dielectric constant of most samples decreases. With the temperature change rate the dielectric constant of the sample decreases. And the dielectric temperature in the low temperature region and the high temperature region is becoming steady. With the increasing amount of Yb^{3+} doping, the dielectric constant of the sample increases at firstly. When the doping amount is more than 0.5 mol%, it begins to decrease obviously. This is related to the substitution mechanism of Yb^{3+} in the system. When the doping amount is 0.1~0.5 mol%, most of Yb^{3+} enters the A position and enhances ferroelectricity, Yb_2O_3 has a peak effect, resulting in increased sample dielectric peak. When doped Yb^{3+} , The Curie peak has a certain movement in macroscopic scale, moving to low temperature, there is the role of broadening Curie peak [13]. From the graph (b), it can be seen that the addition of a small amount of Yb^{3+} will increase the dielectric loss of the sample in a certain extent. The dielectric loss varies greatly with the temperature. The dielectric loss of the sample is unstable due to excessive Yb^{3+} or too little Yb^{3+} . When the doping amount exceeds 0.1 mol%, the dielectric loss of the sample is decreasing, and when the doping amount is 0.5 mol%, the dielectric loss is minimized, and the dielectric loss of the sample starts to increase. As the temperature increases, the dielectric loss of the ceramic sample decreases at firstly, and then tends to be gentle, and then begins to increase. In summary, when the added Yb^{3+} is 0.5 mol%, the sample has a high dielectric constant and a lower dielectric loss, and its Curie peak is also wide, and the temperature is also low.

4. Conclusions

$\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ (BTS) ceramics were prepared by a solid phase reaction method using BaCO_3 , SnO_2 and TiO_2 as raw materials, and the influence of Yb_2O_3 addition on phase composition, microstructure and dielectric properties. The microstructure of the samples were observed by SEM scanning electron microscopy (SEM), and the phase composition was analyzed by XRD pattern.

(1) The XRD patterns show that the main crystal phase of the doped BTS-based ceramic samples does not change significantly, showing a single perovskite structure, no other impurity phase formation, and the change of sintering temperature does not cause the main The structure of the crystal phase changes.

(2) The SEM images show that the grain size of barium titanate (BTS) is relatively clear, the sintered compactness is good, the porosity is relatively low, there is a clear grain boundary, and the doped Yb_2O_3 has fine grain When the doping amount of Yb^{3+} ions is 0.5 mol% and the sintering temperature is 1300 °C, the grain size is uniform and the growth is good.

(3) When the Yb^{3+} is doped with the barium titanate ceramic sample, with the increase of the doping amount the dielectric constant of the pattern increases and the dielectric loss decreases. When the doping amount of Yb^{3+} ions is 0.5 mol% and the sintering temperature reaches at 1300 °C, the ceramic sample of the dielectric properties to achieve the best. Add Yb^{3+} Curie peak to have a certain role in the movement, moving to low temperature, there is the role of broadening Curie peak.

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