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Effects of La_2O_3-Doping and Sintering Temperature on the Dielectric Properties of $BaSrTiO_3$ Ceramics

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Using $BaCO_3$, $SrCO_3$ and TiO_2, et al as crude materials, La_2O_3 as dopant, $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) Ceramics of perovskite structure were prepared by solid state reaction method. We investigated the effects of La_2O_3-doping and sintering temperature on the dielectric properties of $BaSrTiO_3$ ceramics. The experiment results show that: The amount of La_2O_3 can increase the dielectric constant of the sample, with the doping amount increasing, the dielectric constant increases. The sintering temperature has also significant impact on the dielectric properties. The dielectric constant of the sample reaches its highest point at 1280 °C.

Keywords: *BST, Lanthanum Oxide, Samarium Oxide, Dielectric properties, Doping*

Capacitor is one of the main components used in electronic devices on a large scale [1], whether in industry, agriculture, national defense, scientific research, or in everyday life, which has a wide range of applications [1]. Ceramic capacitors are widely used in bypass, coupling and filtering circuits. Miniaturization, high-capacity, high-quality and low-cost are long-term goals of producing ceramic capacitors [2]. Because of its high dielectric constant, low dielectric loss, excellent ferroelectric, piezoelectric and insulated properties, $Ba_xSr_{1-x}TiO_3$ (BST) ceramics are important electronic ceramic materials and widely used in small size and large-capacity mini-capacitors, thermistors, very large scale dynamic random access memory and tuning microwave devices [3].

In order to meet the requirements of producing miniaturized-high-capacity and high-quality ceramic capacitors, a lot of study has been done on the basis of BST ceramics to modify the system. It has been found that the size and type of the substituting ions in different positions have a very important influence on the dielectric properties of the capacitors.[4-7]. La^{3+} ions dissolved in the A-sites and effectively suppressed the grain growth of BST ceramics [8, 9]. However, research effort towards the dielectric properties of La_2O_3-doped BST ceramics is still scant. In this experiment, we investigated the effects of different amounts of lanthanum oxide doped and sintering temperature on the dielectric properties of BST ceramics.

1. Experiment

The raw materials used in the experiment are: $BaCO_3$ (Beijing Hongxing Chemical Factory), $SrCO_3$ (Tianjin Chemical Reagent Factory three), TiO_2 (Tianjin Chemical Reagent Factory three) and a small amount of dopant Sm_2O_3 (Shanghai Yuelong Chemical Factory), All raw materials are analytical reagent.

The main formula of this experiment is $(Ba_{0.8}Sr_{0.2})TiO_3$ (BST20), Sm_2O_3 doping amount is 0.2 mol%, La_2O_3 doping amount is 0.0mol%, 0.05mol%, 0.1mol%, 0.2mol%, 0.4mol%, 0.6mol%, respectively, denoted by A - F, The results are shown in Table 1. Reagent-grade oxide powders TiO_2 (AR, China), $SrCO_3$ (AR, China), $BaCO_3$ (AR, China), Sm_2O_3 (99.99%, China) and La_2O_3 (99.99%, China) were used as received. According to the main formula, we weighed $BaCO_3$, $SrCO_3$, TiO_2 etc as primary materials, according to primary material: ball: water = 1:1:2, mixed with deionized water ball-milling for 4 h, and then to be dried. The ball-milled raw mixture was pre-synthesised at 1080 °C for 2h, After doping Sm_2O_3, according to regrind material: ball: water =1:1:1.5, mixed with deionized water ball-milling for 6 h again, and then to be dried. 7%PVA (5at%) solution was added into the above ball-milled material to granulate, The granulated materials were sifted on 40 mesh sieve, an then pressed into the desired form ($\Phi \times d = 13$ mm × 1.00 mm) at 150 MPa, and then sintered at 1260 °C, 1270 °C, 1280 °C, 1290 °C and 1300 °C for 2 h in the air, respectively. The heating and cooling rate is 5 °C / min, and then the ceramic samples were obtained. The samples were coated by a layer of silver at 470 °C after cleaned with ultrasonic cleaning instrument for 10min, and then to be tested.

The crystal structures of the specimens were confirmed by X-ray diffraction analysis (XRD, Rigaku D/max 2500v/pc) with Cu Kα radiation. In this experiment, we use an Automatic LCR Meter (Automatic LCR Meter 4425, Tianjin) at 1 kHz to test the Capacitance C and dielectric loss factor D. The dielectric coefficient of the sample is measured by

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Table 1. Chemical composition of the samples (g)

Number	La_2O_3	Sm_2O_3	$Ba_{0.8}Sr_{0.2}TiO_3$
A	0.0000	0.1551	49.8000
B	0.0362	0.1550	49.7637
C	0.0723	0.1549	49.7274
D	0.1445	0.1546	49.6551
E	0.2881	0.1542	49.5110
F	0.4309	0.1538	49.3677

LCR Meter Automatic 4225 and the intelligent temperature control system at 1 kHz.

The dielectric constant and dielectric loss *tanδ* of the sample were calculated based on the following formulation:

$$\varepsilon_r = \frac{14.4Ch}{\varphi^2} \quad (1)$$

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

In the formulation : h - the thickness of the sample (cm); Φ- the diameter of the electrode of the sample (cm); C - capacitance of the sample (PF) ; f - test frequency; D - dielectric loss factor.

2. Results and discussion

2.1 XRD analysis

In all formulas, the dopants such as Sm_2O_3 and La_2O_3 etc were added after the raw material was pre-synthesised, the synthesis conditions of all formulas were the same, so the XRD analysis of the pre-synthesised sample A was selected. The results are shown in Figure 1. From Figure 1 it can be seen that the raw material was well pre-synthesised, the main crystal phase of the pre-synthesised material is $Ba_{0.8}Sr_{0.2}TiO_3$, without any other impurity phase. After sintered for 2h at 1280 °C, the diffraction patterns of the samples were shown in Figure 2. It can be seen From Figure 2 that: the diffraction peaks of (100), (110), (111), and (200) appeared in the sample, all of the samples have a typical perovskite structure, which indicates that the doping of La_2O_3 has not changed the structure of the main crystal phase.

2.2 Samarium oxide content unchanged to determine the effect of doping different contents of lanthanum oxide on the dielectric properties of the sample

Under the condition of sintering at 1280 °C for 2h, the dielectric constant of the sample with the different content addition of La_2O_3 was shown in Figure 3.

As can be seen from Figure 3, at a certain temperature, the dielectric constant gradually decreased with the increase of the doping amount of La_2O_3, after the doping amount reached 0.20mol%, the dielectric constant increased sharply. When the maximum amount of 0.60mol% reached, the trend was still on the rise. Under the condition of being sintered at 1280 °C for 2h, the dielectric loss of the sample with the different content addition of La_2O_3 was shown in Figure 4. As can be seen from Figure 4, at a certain temperature, With the increase of La_2O_3 doping amount, the dielectric loss first decreases and then increases, and reached its lowest point when the doping amount of La_2O_3 were 0.1 mol% and 0.2 mol%, respectively.

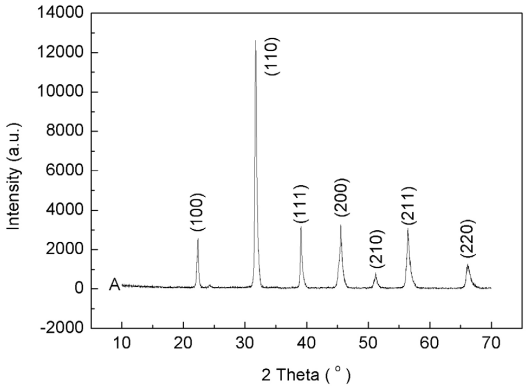

Fig. 1 The diffraction pattern of pre-synthesised sample A

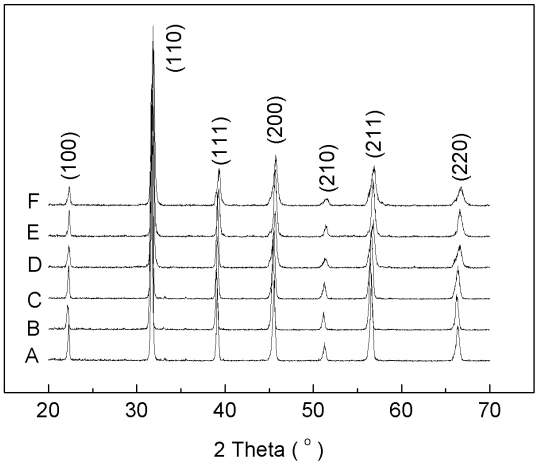

Fig. 2 The diffraction pattern of samples A-F

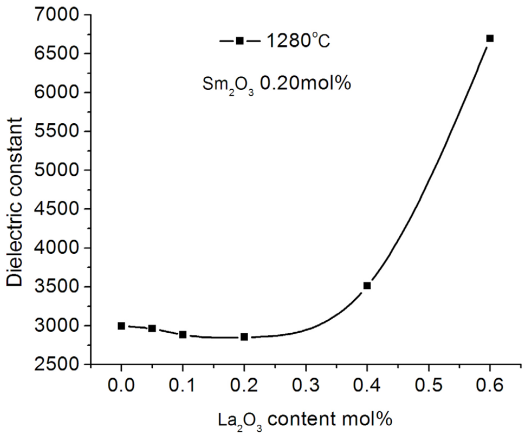

Fig. 3 The relationship curves between the dielectric constant and the content of La_2O_3 (mol%)

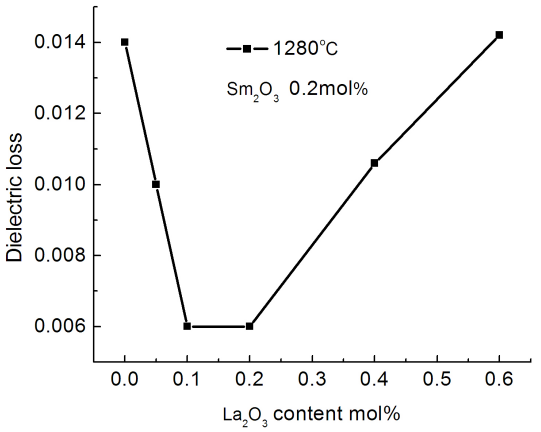

Fig. 4 The relationship curves between the dielectric loss and the content of La_2O_3 (mol%)

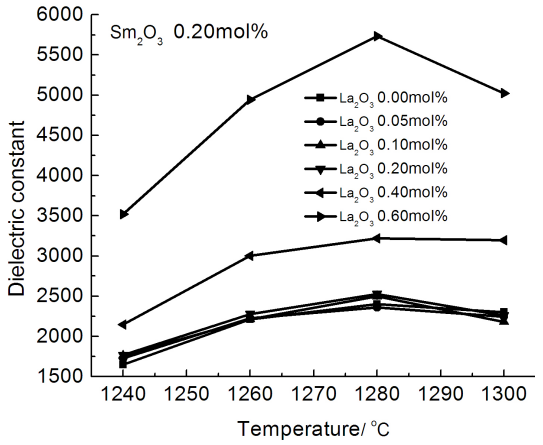

Fig. 5 The relationship curves between the dielectric constant and the sintering temperature with Sm_2O_3 doped

The trend of dielectric properties of the sample with different doping amounts of La_2O_3 is related to the substitution mechanism of La^{3+} ion in BST ceramics**.** The radius of La^{3+} ion in the six ligand (0.103 nm) is larger than the radius of Ti^{4+} (0.061 nm), while the radius of La^{3+} ion in the twelve ligand (0.136 nm) is less than that of Ba^{2+} (0.161 nm), but larger than the radius of Sr^{2+} (0.118 nm) [10]. Therefore, in terms of the ionic radius, La^{3+} ions can replace Ba^{2+} ions and Sr^{2+} ions in the A position respectively.

It can be concluded that when the La_2O_3 doping amount is less than 0.2 mol%, La^{3+} ions enter the A site to replace Sr^{2+} ions, which results in the increase of lattice and decrease of the internal stress, and both of the dielectric constant and the dielectric loss decline. When the La_2O_3 doping amount is more than 0.2 mol%, La^{3+} ions enter the A site to replace Ba^{2+} ions, the lattice contracts, the internal stress increases, so the dielectric constant increases.

After excessive La^{3+} ions entered the A site, the Ti^{4+} ions can be reduced to Ti^{3+} ions, which leads to the deterioration of the dielectric loss. This is consistent with our experimental results.

2.3 Effect of sintering temperature on dielectric properties of $BaSrTiO_3$ ceramics

Sintering is the process of densification and re-grains of the ceramic body. At high temperatures, with the exhaust gas in the body, the contact area between the Billet particles expand, a series of physical and chemical changes have occurred, and gradually formed grains and grain boundaries, the movement of grain boundary makes the grain growth. The Porosities in the body are separated from each other by the mutual connection, and gradually reduced, and finally discharged from the body by the grain boundary, so the body densification.

Figure 5 shows the relationship curves between the dielectric constant and the sintering temperature of each sample, it can be seen from Figure 5 that with the increasing sintering temperature, the dielectric constant of the sample first increased and then decreased and reached its highest point at 1280 °C.

For BST ceramics, its high dielectric constant is partly related to the lattice structure, since the special lattice structure can cause spontaneous polarization, which is the fundamental reason for the high dielectric constant of BST ceramics [11]. Meanwhile, it is also partly related to its' polycrystalline structure, and the interaction between grains and grain boundaries in polycrystalline structure have an important effect on its dielectric properties as well. In the solid state reaction, the sintering temperature is an essential parameter, the ideal structure and properties can be obtained at a temperature which is close enough to the best sintering temperature. When the sintering temperature is too low, the sample cannot be sintered completely, which will cause the point defect concentration in the sample to increase, and the lattice constant to be larger, It can lead to a smaller dielectric constant, and more frequency dielectric.

In addition, when the sintering temperature is too high, it will accelerate the grain boundary's moving speed and make some grain's growth speed significantly higher than other grains, resulted in excessive sintering phenomenon in the sample, which can lead to abnormal interactions between grain and grain boundary. Therefore, the dielectric properties of BST ceramics deteriorate and the reverse trend that the dielectric constant decreases with an increasing temperature appears. However, the effect of sintering condition on other properties of BST ceramics still needs further work.

3. Conclusions

Using $BaCO_3$, $SrCO_3$ and TiO_2 as crude materials, $Ba_{0.8}Sr_{0.2}TiO_3$ (BST) ceramics were prepared by the solid-state reaction method, the effects of La_2O_3 doping amount and sintering temperature on the dielectric properties of $BaSrTiO_3$ ceramics were investigated. At a certain temperature, the dielectric constant gradually decreases with the increasing of the doping amount of La_2O_3, After the doping amount reaches 0.20mol%, the dielectric constant increases sharply. After the maximum amount of 0.60mol% is added, the upward trend continues; At a certain temperature, with the increase

of La_2O_3 doping amount, the dielectric loss first decreases and then increases, and reaches its lowest point when the doping amount of La_2O_3 are 0.1 mol% and 0.2 mol%; With the increasing sintering temperature, the dielectric constant of the sample first increased and then decreased and reaches its highest point at a temperature of 1280 °C.

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