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# MICROWAVE DIELECTRIC PROPERTIES AND DOPING MECHANISMS OF La-DOPED $Ba_{0.8}Sr_{0.2}TiO_3$

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The microwave dielectric properties of La doped $Ba_{0.8}Sr_{0.2}TiO_3$(BST in abbreviation) and their doping mechanisms were studied. BST ceramics could be densified at a sintering temperature of 1300 °C via a sol-gel method. Different amounts of $La(NO_3)_3$ doped BST ceramics were prepared. When doped small amount of $La(NO_3)_3$, no second phase was detected, La act as a donor dopant. Meanwhile oxygen vacancy was compensated. When increasing amount of $La(NO_3)_3$ was added, a hexagonal $La_4Ba_4Ti_7O_{24}$ phase was detected, and the electronic donor-doping mechanism was replaced by an ionic compensation mechanism. For BST ceramic with 0.2mol% $La(NO_3)_3$ sintered at 1280 °C,the $\varepsilon r$, $Q\times f$ value and $\tau_f$ were 176 ,4148GHz and 63ppm/ °C,respectively.

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*Keywords*: Electronic technique, $Ba_{0.8}Sr_{0.2}TiO_3$, Microwave dielectric ceramics, La-doping

## 1 . Introduction

Barium-strontium titanate ceramics are widely used in DRAM, microwave dielectric resonators, planar antennas, etc. because of its high dielectric constant, low dielectric loss and good ferroelectric property [1-4]. Researchers have widely investigated the dielectric properties of $Ba_xSr_{1-x}TiO_3$ ceramics by changing their grain size, grain boundary and other microstructure appearance. Conventional solid-state reaction methods of $Ba_xSr_{1-x}TiO_3$ ceramics is harmful to experimental facilities and grains are apt to overgrow because of a high sintering temperature (1460 °C). Furthermore, additives could not be evenly dispersed. A sol-gel method can provide pure evenly-dispersed and nanometer level powders.

Szymczak et al. [5] reported when x is 0.8, well sintered $Ba_{0.8}Sr_{0.2}TiO_3$ ceramics have well-grown grains and good microwave dielectric properties. It is well known that La doped perovskite ceramics have satisfactory sintering behavior and good dielectric properties. The microwave dielectric properties, microstructure appearance and phase transition of different amount of La doped $Ba_{0.8}Sr_{0.2}TiO_3$(BST) ceramics were investigated in this paper.

## 2. Experimental

BST powder was prepared by a sol-gel method. The BST sample compositions are shown in Table 1.

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Table 1. sample prescriptions.

| Sample | Compositions |
|---|---|
| BST-0 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.0mol% $La(NO_3)_3$ |
| BST-1 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.1mol% $La(NO_3)_3$ |
| BST-2 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.2mol% $La(NO_3)_3$ |
| BST-3 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.3mol% $La(NO_3)_3$ |
| BST-4 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.4mol% $La(NO_3)_3$ |
| BST-5 | $BaO_{0.8}Sr_{0.2}TiO_3$+0.5mol% $La(NO_3)_3$ |

The precursors were: barium nitrate($Ba(NO_3)_2$>99.9%), strontium nitrate($Sr(NO_3)_2$>99.9%), lanthanum nitrate($La(NO_3)_3$>99.9%), tetrabutyl titanate ($(Ti(C_4H_9O)_4$ purity>98.0%), EDTA(purity>98.0%). All these reagents were, respectively, dissolved into ethanol and acetic acid glacial and then mixed to get final solution. The flow chart is shown in Fig. 1.

After aging and drying, the xerogels were calcined at 700 °C for 2h, then crushed and ground by agate ball milling with ethanol for 24 h to obtain fine powders. The powders were mixed with 4 wt% of 10% PVA solution and then pressed into disc-shaped pellets that were16mm in diameter and 3mm in thickness. The green pellets were sintered at 1220 °C ~1300 °C for 2h.

Bulk density measurements were made by the Archimedes technique, using distilled water as liquid medium. The X-ray diffraction analysis was carried out using CuKα radiation with 2 θ from 10° to 80°. The microstructure was investigated on the as-fired surfaces of the sintered specimens, using scanning electron microscopy(SEM,FEI QUANTA 200)

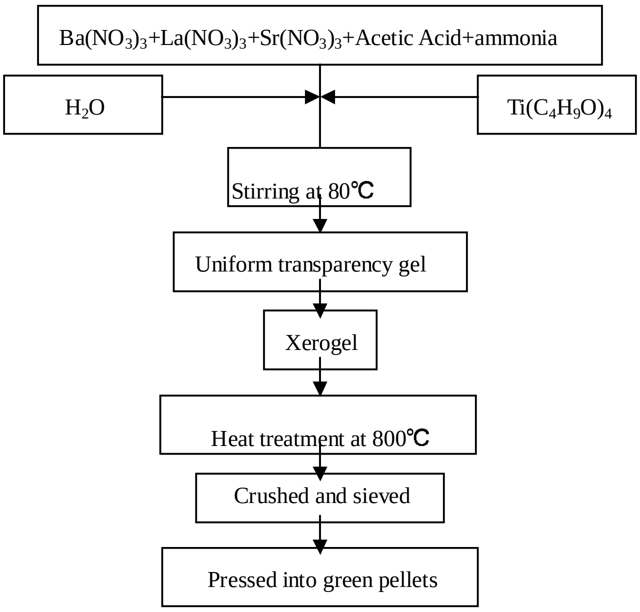

Fig. 1. Flow chart for the preparation of BST cermics.

Ag paste was painted onto the surface of the polished parallel discs as the electrode and fired at 520 °C for 20 min. The dielectric constant and dielectric loss were measured using a Hakki-Coleman method at a frequency of 9.375 GHz. The temperature coefficient of resonant frequency was carried out in the temperature ranging from -25 to 85 °C. The $\tau_f$ value can be calculated by the following relationship:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 \text{ (ppm/}^\circ\text{C)}$$

where $f_1$ and $f_2$ represent the resonant frequencies at $T_1$ and $T_2$, respectively.

## 3. Results and discussion

The effect of La content to the sintered BST ceramics is correlated with their densification, grain growth behavior and dielectric properties. Fig 1 shows the density versus sintering temperature of BST ceramics.

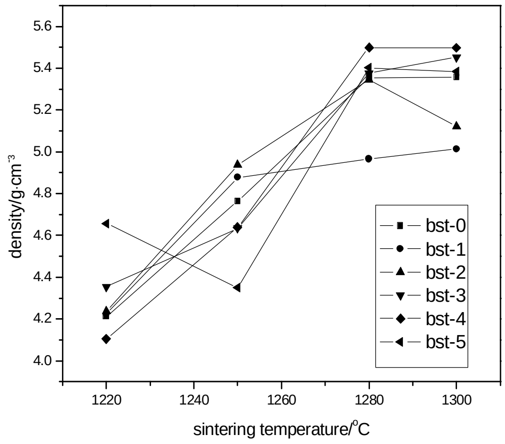

Fig. 1. BST samples' densities as a function of sintering temperature

The relative density decreased when La content is small, then increased with increasing content of La. All sample densities were above 93% of theoretical density.

BST powders produced by sol-gel method were of nanometer in dimension. Due to its surface effect and size effect, BST samples could be well sintered at a relatively low temperature, while by a conventional solid-state reaction method BST ceramics must reach 1460 °C before it can be densified. BST samples doped with different amount of $La(NO_3)_3$ could be well sintered at a much lower temperature because of parts of La congregated at the grain boundary and restrain elements separated out from grain boundary. BST-0 attained its maximum density at 1300 °C and other samples in 1280 °C.

The XRD patterns for BST-0 (sintered in 1300 °C), BST-1~BST-5(sintered in 1280 °C) are shown in Fig. 2.

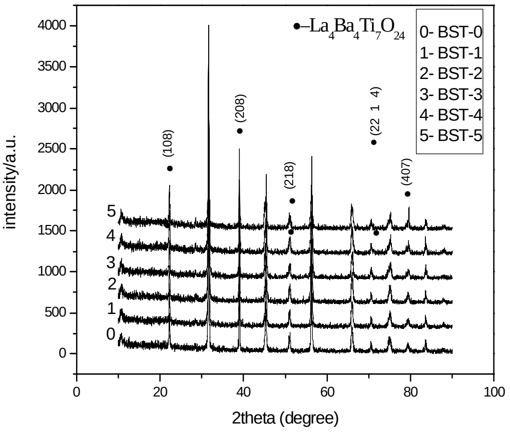

Fig. 2. BST samples XRD patterns.

Only $Ba_{0.8}Sr_{0.2}TiO_3$ phase was detected when $La(NO_3)_3$ content is less than 0.3mol%. When $La(NO_3)_3$ dopant is more than 0.3mol%. A hexagonal $La_4Ba_4Ti_7O_{24}$ phase was detected.

The microwave dielectric properties of BST ceramics are shown in *Fig 3* and *Fig 4*. When doping 0.1mol% $La(NO_3)_3$, no second phase was detected, and its dielectric property was worse than that of BST-0.It is believed that $La^{3+}$ can act as a "donor" dopant , according to the equation:

$$Ba^{2+} \Rightarrow La^{3+} + e^- \quad (1)$$

The extra free electron increases the conductivity of samples, thereby, decreases the dielectric constant and Q×f value(Q represents the reciprocal of tgδ).

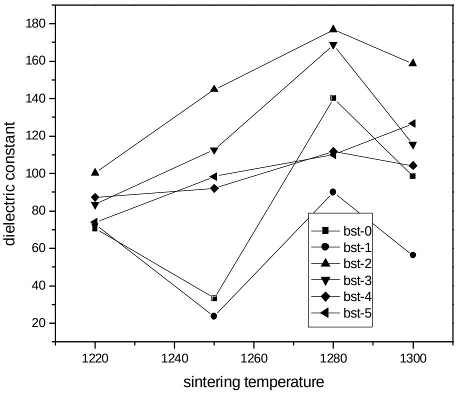

Fig. 3. Samples' dielectric constant as a function of sintering temperature.

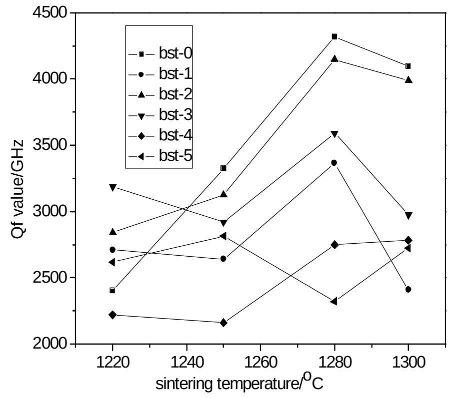

Fig. 4. Samples' Q$\times\phi$ value as a.

Although there were no second phase in BST-2 and BST-3, the dielectric properties were different from that of BST-1. The dielectric constant dramatically increased and, the Q×f value was also greater than that of BST-1.It is believed that $La^{3+}$ ion compensates the oxygen vacancy produced during sintering process:

$$O^{2-} \Rightarrow \frac{1}{2}O_2 + 2e^- \quad (2)$$

$$La_2O_3 + V_O^{\cdot\cdot} \xrightarrow{2BaO} 2La_{Ba}^{\cdot} + 3O_o \quad (3)$$

The oxygen vacancy produced by equation (2) was compensated by function of equation (3)($La_2O_3$ was decomposed from $La(NO_3)_3$). Thus the dielectric properties improved. It is noticed that BST-2 has better dielectric property than BST-3,This is probably because more $La^{3+}$ ions in BST-3 take part in equation (3) on account of more $La(NO_3)_3$ doped.

When $La(NO_3)_3$ content added up to 0.4~0.5mol%, there was a hexagonal $La_4Ba_4Ti_7O_{24}$ phase in BST-4 and BST-5. Their dielectric properties of them were similar to BST-1. This has been attributed to a switch from the electronic donor-doping mechanism to an ionic compensation mechanism,where

$$Ba^{2+} + \frac{1}{4}Ti^{4+} \Rightarrow La^{3+} \quad (4)$$

Four $Ba^{2+}$ and one $Ti^{4+}$ were replaced by a $La^{3+}$.

Table 2 shows BST ceramics' resonant frequency temperature coefficient. 1300 °C sintered BST-0 and 1280 °C sintered BST-1~5 were measured.

Table 2. samples temperature coefficient of resonant frequency

| Sample | BST-0 | BST-1 | BST-2 | BST-3 | BST-4 | BST-5 |
|---|---|---|---|---|---|---|
| $\tau_f$/ppm $^oC^{-1}$ | 88 | 85 | 63 | 51 | 74 | 55 |

From the figure below, exiguous and fine uniform structures were obtained by sol-gel method. Some coarse loaf-like grains emerge in *Fig d*. It is thought to be the hexagonal $La_4Ba_4Ti_7O_{24}$ phase.

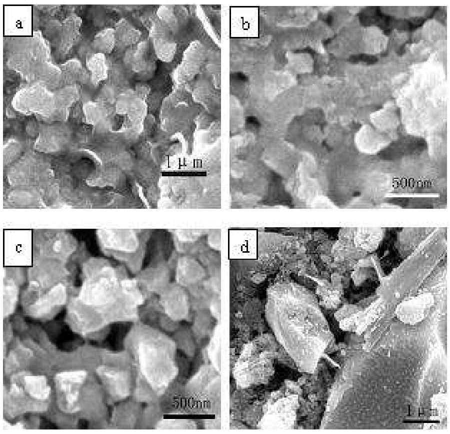

Fig. 5. SEM micrographs of BST ceramics (a-BST-0,b-BST-1,c-BST-3,d-BST-5)

## 4 . Conclusions

1. BST ceramics could be well sintered by sol-gel method in a lower sintering temperature. BST ceramics. BST ceramics with La doping could be well sintered in 1280 °C.
2. Single perovskite $Ba_{0.8}Sr_{0.2}TiO_3$ phase is detected when $La(NO_3)_3$ dopant is less than 0.3mol% and, a hexagonal $La_4Ba_4Ti_7O_{24}$ phase exists when more $La(NO_3)_3$ is doped.
3. $La^{3+}$ ions act as donor dopant when adding small amount of $La(NO_3)_3$.. The extra free electrons thus produced can impair the dielectric properties. But when adding more $La(NO_3)_3$, oxygen vacancies are compensated and therefore, better dielectric properties are obtained. A hexagonal phase emerges because donor doping mechanism is replaced by ionic compensation mechanism with further more $La(NO_3)_3$ is doped. Worse dielectric properties are obtained due to the development of the second phase.
4. When $La(NO_3)_3$ dopant is 0.2mol% and sinter in 1280 °C for 2h, the best dielectric properties are obtained: $\varepsilon = 176$, $Q \times f = 4148$ GHz, $\tau_f = 63$ ppm/ °C.

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