

Enhanced dielectric properties of low-temperature-sintered $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thick films

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Abstract $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thick films were fabricated at a lower temperature of 880°C by adding Li_2O as sintering aid. A novel pretreatment of cold isostatic pressing was introduced to enhance the quality of films. After cold isostatic pressing prior to annealing, the thick film had a more compact morphology and better dielectric properties. The permittivity and tunability were increased to 1,318 and 19.04% from 925 and 14.81% while the dielectric loss was still kept low (1 MHz, 16 kV/cm). The enhanced properties and low-temperature sintering made BST thick films a potential candidate for Low Temperature Co-fired Ceramic (LTCC) and microwave tunable devices.

Keywords BST · Low-temperature sintering · Thick films · Tunability

1 Introduction

The perovskite barium strontium titanate $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) material is a solid solution of BaTiO_3 and SrTiO_3 with excellent dielectric properties. Because of the high permittivity and tunability, it has been widely considered as a promising candidate for microwave tunable device applications, such as tunable oscillators, phase shifters, and varactors [1–3]. However, the high sintering temperature of 1350–1400°C [4] limits the applications of BST in multilayer devices. Thus, noble metals, such as Pd or Pt, must be used as the inner electrode, which increases the

manufacturing costs. A lot of work has already been done to effectively lower the sintering temperature of BST ceramics to an appropriate range. Rhim et al. reduced the sintering temperature to 1150°C by adding 0.5 wt% B_2O_3 [5]. The dielectric properties reported did not degrade. Valant et al. reported a low sintering temperature below 900°C by adding 0.4–1 wt% Li_2O [6]. The permittivity and the dielectric loss reduced, while the tunability showed no significant change. A moderate dielectric permittivity for impedance matching, a low dielectric loss tangent and a high dielectric tunability in certain electric field ranges are needed for microwave tunable devices [7]. The high permittivity of bulk ceramics increases the difficulty of design and technology of microwave device. Compared to bulk ceramic, thick films have more advantages. It can be fabricated easily by screen printing. And the moderate permittivity and relatively low operating voltages make it attractive. If thick films with a low sintering temperature (such as below the silver melting point of 960°C) can be obtained, it will be a breakthrough for the development of multilayer tunable devices. There were few works focusing on low-temperature sintering of thick films. Tick et al. reported a good work on thick films fabrication [8]. Unfortunately, previous work on thick films showed porous morphology caused by the strain shrinkage between films and bottom substrate. The films are likely to crack, and the dielectric properties and the tunability degrade.

This work mainly aimed at fabricating low-temperature sintered BST thick films and enhancing its microstructure and dielectric properties. It was achieved by a novel pretreatment consisting of cold isostatic pressing of the green films. The ceramic powders with the composition of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST6/4) were prepared by conventional solid-state method. 1 wt% Li_2O (Which was added through the corresponding molar fraction of Li_2CO_3 .) was added to

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the BST6/4 powders as sintering aids. In order to investigate the effect of isostatic pressing, the pretreatment was introduced to some screen printed BST6/4 films before sintering (Both films were doped by Li_2O , and the thick film without pretreatment was called BST-1#, the thick film with pretreatment was called BST-2#). The microstructure and dielectric properties of two kinds of BST6/4 thick films were studied in this paper. Compared with the BST-1# thick films, the permittivity and tunability of the BST-2# thick films increased while the dielectric loss was still kept low. The films also exhibit a more compact microstructure after the pretreatment.

2 Experimental procedure

BST6/4 powders were prepared by conventional solid-state method. The starting materials were barium carbonate (BaCO_3 , 99%), strontium carbonate (SrCO_3 , 99%), and titanium oxide (TiO_2 , 98%). They were all from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The powders were ball milled for 4 h and then calcined at 1100°C for 4 h. 1 wt% Li_2O was added through the corresponding molar fraction of Li_2CO_3 (98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). The mixed powders were then ball milled for 4 h and dried for the next step.

The well dispersed powders were mixed with an organic vehicle (terpineol and ethyl cellulose) to obtain the slurry for screen printing. The weight ratio of powders/organic vehicle was 7:4. The thick films were fabricated on alumina substrates with an Ag bottom electrode. In order to improve the microstructure of thick film, it was divided into two parts, and a high isostatic pressure of 140 MPa was applied on one part of the green film for 1 min. With a heating rate of $3^\circ\text{C}/\text{min}$, the films were preserved at 450°C for 2 h and then sintered at 880°C for 2 h. The upper electrode, also a screen-printed Ag paste, was calcined at 600°C for 10 min (the electrode size was 2 mm in diameter, 3.14 mm^2 in area).

Room-temperature X-ray diffraction data for the phase identification were collected on a diffractometer (Rigaku D/MAX-2400, Tokyo, Japan) using $\text{CuK}\alpha$ radiation. The microstructural characterization was performed by a scanning electron microscope (SEM) (Jeol/EO, Tokyo, Japan). The frequency dependence of permittivity and dielectric loss was measured by an impedance analyzer (Agilent 4294A, Palo Alto, CA, USA). It was also used to measure the tunability under the DC bias of 40 V at 1 MHz. The temperature dependence of the permittivity and dielectric loss was measured from -50°C to 85°C by Agilent 4284A (Agilent 4284A, Palo Alto, CA, USA). The tunability under high voltage was measured up to the maximum DC bias of 300 V at 10 kHz by TH 2816 LCR (TH 2816 LCR, Changzhou, China).

3 Result and discussion

After isostatic pressing on the BST-2# green film for about 1 min, both BST-1# and BST-2# films were sintered at 880°C for 2 h. The phase structures of the films were investigated from films prepared on alumina substrates. As seen in Fig. 1, the perfect pure perovskite phase of BST formed in both films, and no obvious secondary phase was detected. It indicated that the sintering aids of Li_2O did not react with BST and the microstructure of BST6/4 did not change.

The morphology of thick films was presented in Fig. 2. The green films were printed 3 times, and both samples had an average thickness of $25\ \mu\text{m}$ after sintering. The surface morphology comparison showed that the BST-2# thick films had a more compact microstructure than BST-1# films had. This was owed to the pretreatment of isostatic pressing to the green films before sintering. When the green films printed were dry, a part of organic vehicle volatilized leaving a volume of pores. If the bulk ceramics were sintered, it would shrink to get a dense microstructure during the sintering process, and the volume of pores would decrease. That was the model for materials in the free space. However, when sintering the thick films, the model should be like this. The tight contact between film and bottom electrode or substrate would limit the shrinkage of the film. The growth of grains resulted in the partial shrinkage of ceramic particles and formed the pores and cracks in films. This model could also explain why the thick films were always easy to be broken down under the DC bias. The pretreatment of isostatic pressing can solve this problem to a certain extent. The obvious cracks decreased in Fig. 2(d). The particles could join each other

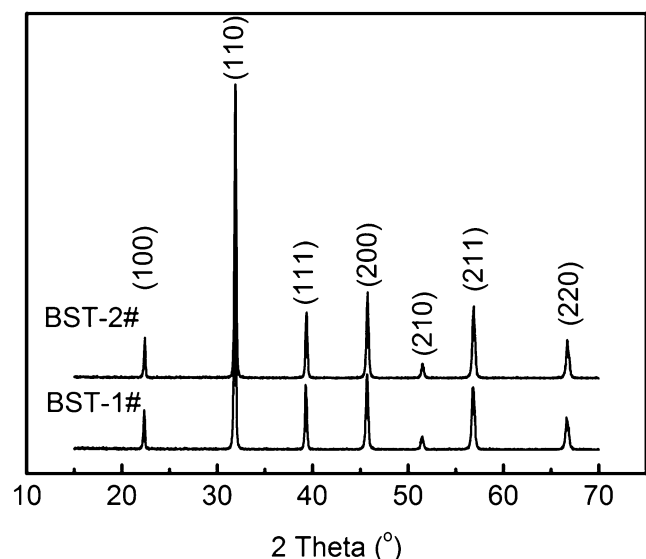


Fig. 1 XRD pattern of BST-1# and BST-2# films sintered at 880°C , no obvious secondary phase appears

Fig. 2 (a) Macro surface morphology, (b) micro surface morphology and (c) cross section morphology of BST-1# thick film. (d) macro surface morphology, (e) micro surface morphology and (f) section morphology of BST-2# thick film

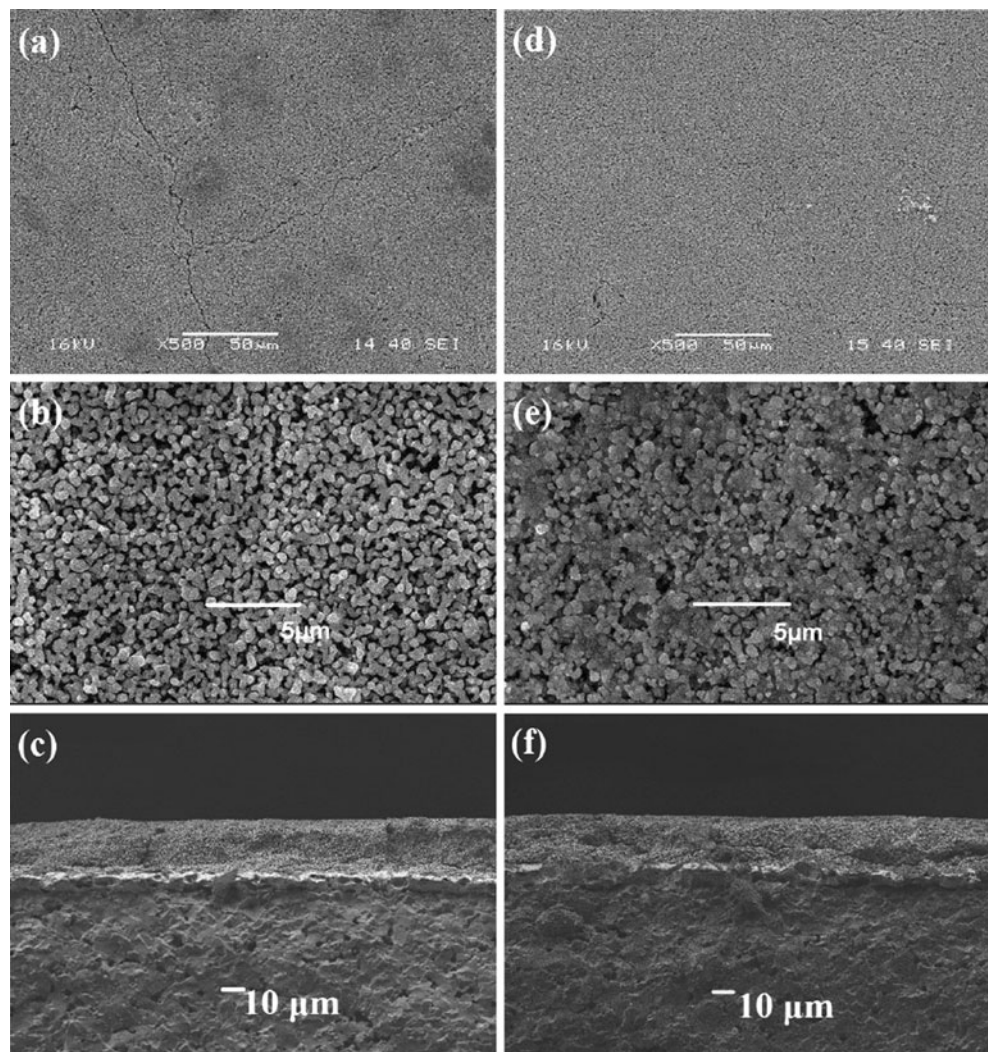


Fig. 3 The frequency dependence of permittivity and loss of BST thick films

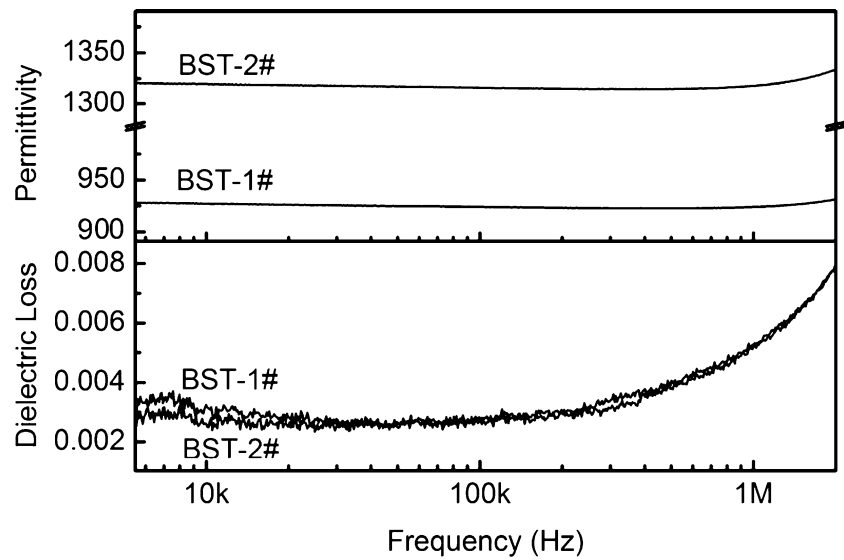


Table 1 Dielectric properties of the BST thick films

Samples	ϵ (0 V/cm)	$\tan\delta$ (0 V/cm)	ϵ (16 kV/cm)	$\tan\delta$ (16 kV/cm)	Tunability (16 kV/cm)
BST-1#	925	0.006	788	0.005	14.81%
BST-2#	1,318	0.006	1,067	0.005	19.04%

The data were measured at 1 MHz by Agilent 4294A

more tightly then decrease the volume of pores in films so as to avoid cracking greatly. It would get a more compact morphology and larger grain size after sintering which could be seen in Fig. 2(e).

Frequency dependence of permittivity and loss of the samples was investigated from 1 kHz to 2 MHz. Good morphology and growth of grains led to excellent properties. As seen in Fig. 3, the BST-2# thick films had a high permittivity of 1,318 and low dielectric loss of 0.006 at 1 MHz. Compared with the BST-1# samples, the permittivity of BST-2# increased by 42.48% and the losses of the two samples were kept at a low level. The permittivity, loss tangent and relative tunability of the both samples were listed in Table 1. All the data listed were measured at 1 MHz. The dielectric properties at 0 bias and 16 kV/cm were measured and the tunability was calculated. Sengupta found that the BST/MgO ceramic tapes and the bulk materials with 60 wt% MgO content exhibited a high relative tunability of 12–15% (measured at 20 kV/cm) (The sintering temperature is 1250°C.) [9]. The Li-doped BST ceramics reported by Valant et al. had the tunability of 13.5% to 16.5% (measured at 1 MHz, 30 kV/cm) [6]. The BST-2# thick films in this work had a high relative tunability of 19.04% under 16 kV/cm, which was comparable with that of ceramic samples in the literatures mentioned. Compared with the BST-1# thick films, it was about 28.56% increased. It was indicated that the pretreatment of isostatic pressing did improve the dielectric properties.

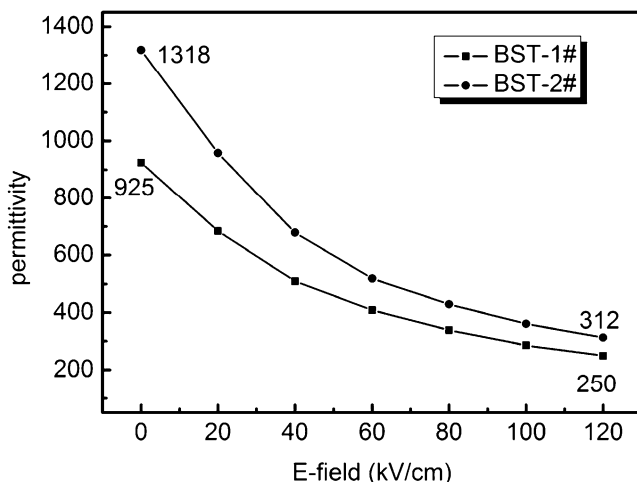


Fig. 4 The bias dependence of permittivity of two BST samples under high voltage

Tagantsev et al. studied the mechanism of the tunable ferroelectric materials. He pointed out there were some situation where the tunable material can be treated as a ferroelectric/dielectric composite. Due to the strain shrinkage discussed above, the films with pores could be treated by spherical inclusion model [10]. In this model, holes or pores in the thick film could be regarded as dielectric spheres. Tagantsev also gave an expression for the permittivity of this model as [10]

$$\epsilon_{mix} \approx \epsilon \left(1 - \frac{3}{2} q \right) \quad (1)$$

and loss as

$$\tan \delta_{mix} \approx \tan \delta \quad (2)$$

Where q , ϵ_{mix} and $\tan \delta_{mix}$ is the volume fraction of pores, the permittivity and the dielectric loss tested, respectively. The relationship between porosity and permittivity could be seen from (1). The permittivity of this composite was strongly controlled by the porosity in films. The little change in porosity could result in big difference of permittivity. Further investigation on quantitative porosity of the film is needed by efficient and precise method, which could give direct relationship between porosity and dielectric properties.

The tunability can be represented as

$$n = \frac{\epsilon(0)}{\epsilon(E)}, \quad (3)$$

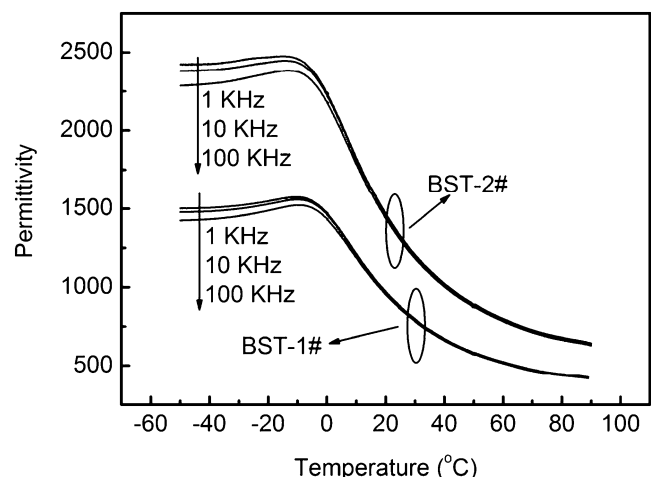


Fig. 5 The temperature dependence of permittivity and loss of BST thick films from -50°C to 85°C

and relative tunability

$$n_r = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} = \frac{n - 1}{n} \quad (4)$$

Where $\varepsilon(0)$ and $\varepsilon(E)$ are the permittivity under 0 DC field and under E DC field. The permittivity decreased nonlinearly with the increasing of applied DC field. This trend was really strong in the limit of weak nonlinearity, i.e. at $n_r \ll 1$. According to their work, the tunability n can be represented as [10]

$$n = \frac{\varepsilon(0)}{\varepsilon(E)} = 1 + 3\beta\varepsilon(0)\varepsilon_0 P_{DC}^2 \approx 1 + 3\beta(\varepsilon(0)\varepsilon_0)^3 E^2 \quad (5)$$

This equation shows that the relative tunability increases strongly with $\varepsilon(0)$. Thus the microstructure determined permittivity and tunability of films. As seen in Fig. 4, the permittivity under high DC bias showed great improvement on BST-2# films with the pretreatment of isostatic pressing. The highest relative tunability was 76% with $n=4.22$ at 120 kV/cm. It also illustrated the advantage that thick films only needed relatively low driving voltage to obtain the wanted tunability.

Tagantsev figured $n_r \propto \varepsilon(0)^3$, when $n_r \ll 1$. In the limit of ultrahigh fields where $n \gg 1$, $n \propto \varepsilon(0)$ [10]. Seen in Fig. 4, the tested data showed the conformity with this trend. The dielectric loss as a function of the bias field showed similar behavior to that of the permittivity. More studies were needed to fully understand the factors affecting the tunability of porous films. And in another hand, one could also obtain moderate permittivity with proper tunability by carefully controlling porosity in films, which could satisfy different microwave tunable applications.

The behavior of the dielectric properties of the film with respect to temperature was shown in Fig. 5. Both films showed a peak in the permittivity versus temperature, which represented the ferroelectric to paraelectric transition. Both samples had a same Curie temperature at about -12°C , which was almost same as reported in bulk ceramic [10]. BST-2# had higher permittivity than BST-1#, which could also be explained by the morphology improvement. Compared with BST ceramics, both peaks were diffusive, which could be explained by the growth of the grains. According to Liou et al., the grain size is an important factor that decided the permittivity. When the grain size increased, the permittivity increased and the ferroelectric to paraelectric transition became more narrow [11]. Because the permittivities of both films were much less than that of ceramics, the peaks of two films diffused. And, the particles of BST-2# were easier to grow larger than that of BST-1# in the sintering process after the pretreatment. The higher permittivity made the peak of BST-2# a bit narrower. It suggested that the dielectric properties promotion by

isostatic pretreatment didn't contribute to any composition change but from the morphology improvement of the films.

4 Conclusion

$\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thick films doped by 1 wt% Li_2O were prepared. The BST ceramic powders were prepared by conventional solid-state methods. Compared with the conventional high-temperature sintering at more than 1300°C , the BST thick film doped by Li_2CO_3 could be sintered below 900°C without any detected secondary phase. A restricted sintering process and spherical inclusion model could explain the porous microstructure of the films. Both dielectric properties and microstructure of the films were improved by a pretreatment of cold isostatic pressing to the green films prior to annealing. The permittivity was 1,318 and dielectric loss was below 0.006 at 1 MHz. The relative tunability was as high as 19.04% under a DC bias of 16 kV/cm. The highest tunability measured in this work was 76% at 10 kHz under 120 kV/cm. It provided a simple and efficient way to obtain high quality thick films. By further careful study of controlling permittivity and tunability, the low temperature sintered BST thick films will suggest their suitability for application in microwave tunable devices compatible for hybrid integration and LTCC technology.

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