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Research Article

The Effect of Isostatic Pressing on the Dielectric Properties of Screen Printed $Ba_{0.5}Sr_{0.5}TiO_3$ Thick Films

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$Ba_{0.5}Sr_{0.5}TiO_3$ thick films with B_2O_3–Li_2O glass sintering aid were prepared by the screen printing method on Al_2O_3 substrates. A 200 MPa isostatic pressure was applied to the films before sintering. After being sintered at 950 °C, lower porosity and denser microstructure was obtained compared with the films without isostatic pressing. The dielectric constant and dielectric loss were 238 and 0.0028, respectively. A tunability of 61.7% was obtained for the isostatic pressed films, a 27.8% enhancement compared to unpressurized films. These results suggest that isostatic pressing is an effective way to prepare dielectric thick films with dense microstructure, low dielectric loss, and high tunability.

1. Introduction

Barium strontium titanate solid solutions ($(Ba_{1-x}Sr_x)TiO_3$, denote as BST) are well-known dielectric materials and have been widely investigated and applied in many areas such as multilayer ceramic capacitors, ferroelectric random access memories, and optical modulators [1–4]. Of note, their characteristic of high dielectric nonlinearity (i.e., exhibiting a large dielectric constant change under DC bias electric field) enables BST materials to be one of the most promising materials to realize the applications of tunable ceramic capacitors, dielectric filters, phase shifters, and other tunable microwave devices [5, 6]. On approach to fabricating these devices, however, people find that BST bulk ceramics are not suitable for the field applications due to their size encumbrance, and also their relatively high dielectric constants (above 1500) are difficult to satisfy the impedance matching and high power requirement in microwave device designs which prefer lower dielectric constant values ($30 < \varepsilon_r < 1000$) [7]. BST thin films (normally with thickness less than 1 μm) can have lower dielectric constant but still cannot be applied properly in electric functional devices because of their relatively inferior dielectric properties and long term stability issues. Compared with thin film technologies, thick film fabrications, with membrane thickness in microns ranges, such as tape casting and screen printing techniques are mature techniques and have been applied in the industry applications for many years [8, 9]. BST thick films have steadily superior dielectric performances, bigger driving force, and higher compression strength. Further, compared with bulk ceramics, BST thick films not only have the appropriate lower dielectric constant, but also take the incomparable advantage in the use of low biasing voltages due to its relatively low film thickness. Taking one with another, BST thick films are believed to fill out the gap between bulk materials and thin films.

Many methods and techniques have been applied to prepare BST thick films, such as sol-gel, electrophoretic deposition, tape casting, and screen printing [8–11]. Of all the options, screen printing is a flexible, versatile, and simple technology. Owing to its several advantages such as readily obtained and cost effective apparatus, screen printing technology has now been widely adopted in the preparation of thick films in industry. In this paper, we adopted the screen printing method to prepare BST thick films. Since BST bulk ceramics need a high sintering temperature (over 1200°C) for densification, for the preparation of BST thick films, usually high temperature substrates not reacting with BST materials are needed to support the thick films for

the cosintering process. An alternative is to prepare low temperature-fired BST materials and thus can be screen printed on readily accessible low temperature substrates. Herein we prepared 5 wt% B-Li glass added $Ba_{0.5}Sr_{0.5}TiO_3$ powders to prepare BST thick films on Al_2O_3 substrates since the B-Li glass doped BST dense bulk ceramics can be sintered at 950°C [12]. To assist the densification process, we applied isostatic pressing treatment on the BST-Al_2O_3 substrates before sintering. Although the isostatic pressing may improve densification for materials [13], its effect on the properties of Al_2O_3 supported BST thick film is unknown. The effect of isostatic pressing treatment on the structural and dielectric properties and capacitance-voltage characteristics of the BST thick films were thus investigated.

2. Experimental

The $Ba_{0.5}Sr_{0.5}TiO_3$ powder was first prepared stoichiometrically with starting $BaTiO_3$ and $SrTiO_3$ powders (99.9%, both hydrothermally synthesized by Shandong Guoteng Materials Co. Ltd.). $BaTiO_3$ and $SrTiO_3$ were mixed homogeneously using alcohol and zirconia milling media for 24 h. After drying, the mixture was calcined at 1100°C for 4 h in air and then grinded and sieved to obtain BST powder. H_3BO_3 and Li_2CO_3 were weighted stoichiometrically as sintering aid via the following reaction:

$$4H_3BO_3 + 3Li_2CO_3 = (2B_2O_3 + 3Li_2O) + 3CO_2 \uparrow + 6H_2O \uparrow \quad (1)$$

H_3BO_3 and Li_2CO_3 were mixed and sintered at 1100°C for 30 min and then quenched to form B-Li glass. The glass was grinded and sieved to form glass powders. In consideration of our previous results [12], 5 wt% content B-Li glass powder was added to the BST powder as sintering aid. The screen printing paste was prepared with the glass-added BST powder and organic slurry. The composition of the slurry is m(ethyl cellulose) : m(terpineol) = 1 : 10 and the weight proportion of the powders to the slurry is 1 : 1. Al_2O_3 ceramic plates (purity 99%) with $30 \times 30 \times 0.5\,mm^3$ were used as the substrates. A commercial silver-palladium paste (Guangdong Fenghua Co. Ltd.) was screen printed and fired as the bottom electrode. Thick film paste was then screen printed on the bottom electrode and dried. Figure 1 shows the schematic of the thick film configuration. Some of the green films were pressed under an isostatic pressure of 200 MPa for 5 min before sintering. All of the thick films were then sintered at a temperature of 950°C for 2 h. The film thicknesses are measured by a thickness gauge (CH-1-ST, Shanghai Liuling, China). X-ray diffraction (XRD) (Rigaku, Japan) with Cu Kα radiation was employed to characterize the phase structures. Scanning electron microscope (SEM) (JSM EMP-800) was utilized to characterize the microstructures of the thick films. The temperature dependence of the dielectric constant and loss tangent were measured using an LCR meter (HP 4284A, Agilent, Palo Alto, CA, USA). The tunability of thick film was measured at 10 kHz and room temperature using a Keithley model 2410 electrometer coupled with a TH2613A LCR meter.

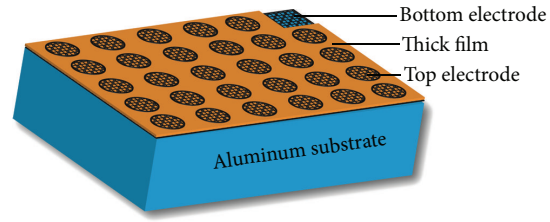

Figure 1: Schematic of the thick film configuration.

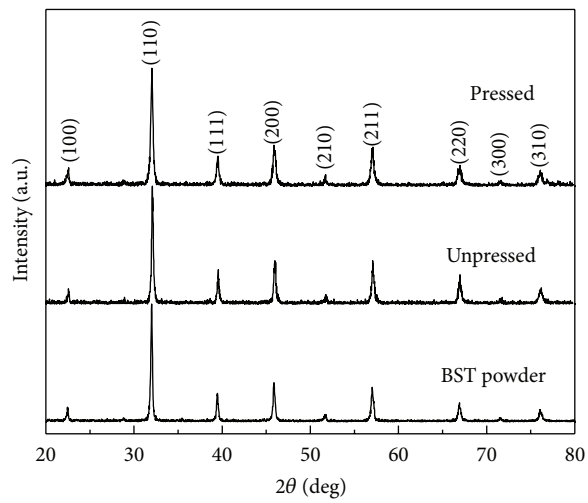

Figure 2: XRD patterns of $Ba_{0.5}Sr_{0.5}TiO_3$ powder and B-Li glass doped $Ba_{0.5}Sr_{0.5}TiO_3$ thick films with isostatic pressing (denoted as pressed) and without isostatic pressing (denoted as unpressed).

3. Results and Discussion

Figure 2 shows the XRD patterns of the B-Li glass doped $Ba_{0.5}Sr_{0.5}TiO_3$ calcined powder and thick films without isostatic pressing (unpressed) and with isostatic pressing (pressed) after being sintered at 950°C for 2 h. All the diffraction peaks can be indexed to perovskite structured cubic phased $Ba_{0.5}Sr_{0.5}TiO_3$ (space group $Pm\text{-}3\,m$, PDF no. 39-1395) [14]. Both the powder and thick films are well crystallized with no preferred orientation and second phase. It can be seen that the addition of B-Li glass as well as the isostatic pressing treatment has no obvious impact on the crystallization of the thick films.

Figure 3 shows the microstructures of BST thick films after sintered at 950°C for 2 h, with and without the isostatic pressing treatment. The SEM analysis reveals that the surface morphology of the thick film with the isostatic pressing treatment is notably different from the one without treatment. The thick film without isostatic pressing (shown in Figures 3(a1) and 3(a2)) shows a coarse surface, a porous and inhomogeneous microstructure. In contrast, the thick film with the isostatic pressing step (shown in Figures 3(b1) and 3(b2)) exhibits a smoother surface, more uniform and denser microstructure. Furthermore, for the isostatic pressed sample, larger grains are formed compared with the unpressed thick film where sphered small grains are

Table 1: Thickness of the films in different steps with and without isostatic pressing.

Thick film sample	Thickness of green film	Thickness after pressing	Thickness after sintering
Unpressed	25.5 μm	—	21 μm
Pressed	26 μm	21.5 μm	19.5 μm

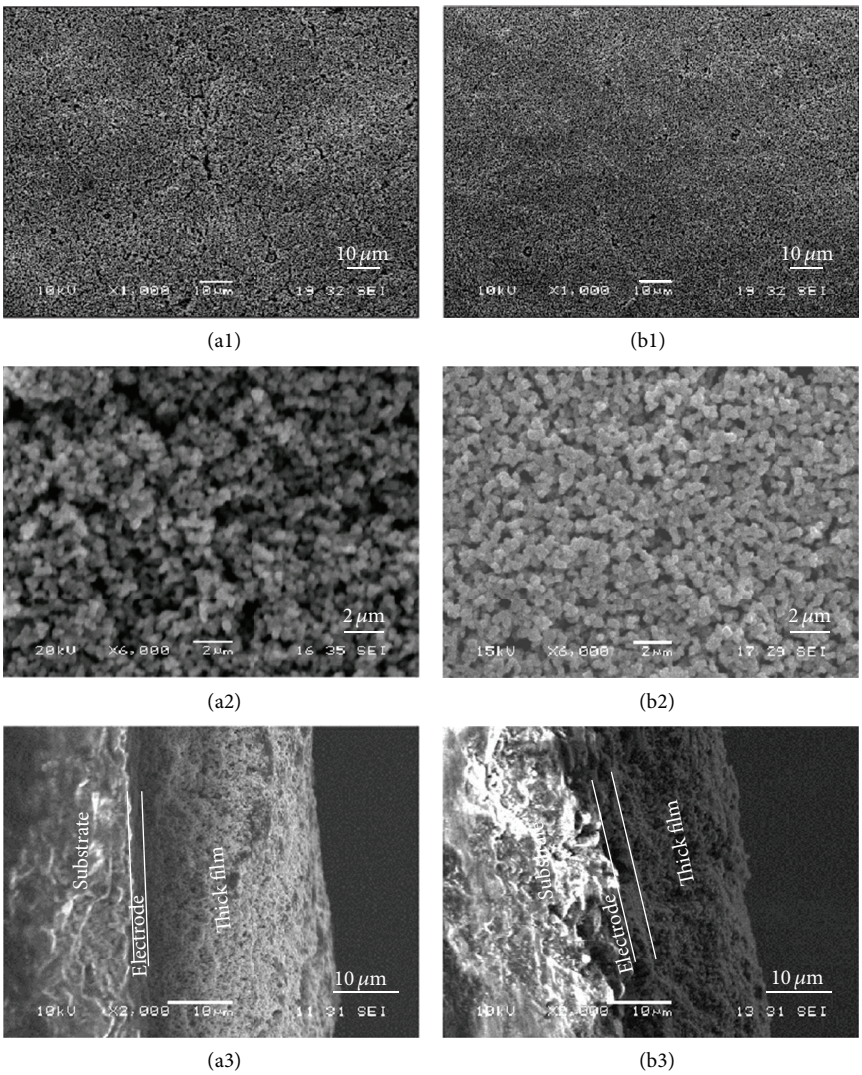

Figure 3: SEM photographs of $Ba_{0.5}Sr_{0.5}TiO_3$ thick films. (a1–a3) without isostatic pressing treatment, (b1–b3) with isostatic pressing treatment, (a1, b1) surface morphologies, (a2, b2) expanded view of surface morphologies, and (a3, b3) cross-sectional images.

loosely distributed, which is an indication that the thick film with isostatic pressure shows better sinterability. The cross-sectional SEM pictures of the thick films are shown in Figures 3(a3) and 3(b3). Since the thick films are sintered at 950°C, a temperature significantly lower than the diffusion temperature of barium into Al_2O_3 (above 1200°C [15, 16]), there is no reaction between the substrate and BST. Table 1 measures the thickness of thick films in different steps with and without the application of isostatic pressing treatment. It can be seen that the thick film after isostatic pressing shows thinner film thickness. The reduction of the thickness of the film with isostatic pressing from green film state to sintered state is about 25%, compared to 17.6% for the film without treatment. This difference may be expected with the reason that with the application of isostatic pressing treatment, powders are more compactly contacted with each other and the effect of sintering aid is thus functioning better for the pressurized samples. The sintered film thus shows lower porosity and denser microstructure and the thickness was reduced at a large scale [13]. It is noted that due to the difference of thermal expansion coefficient between BST and Al_2O_3, the BST thick films we prepared are not fully

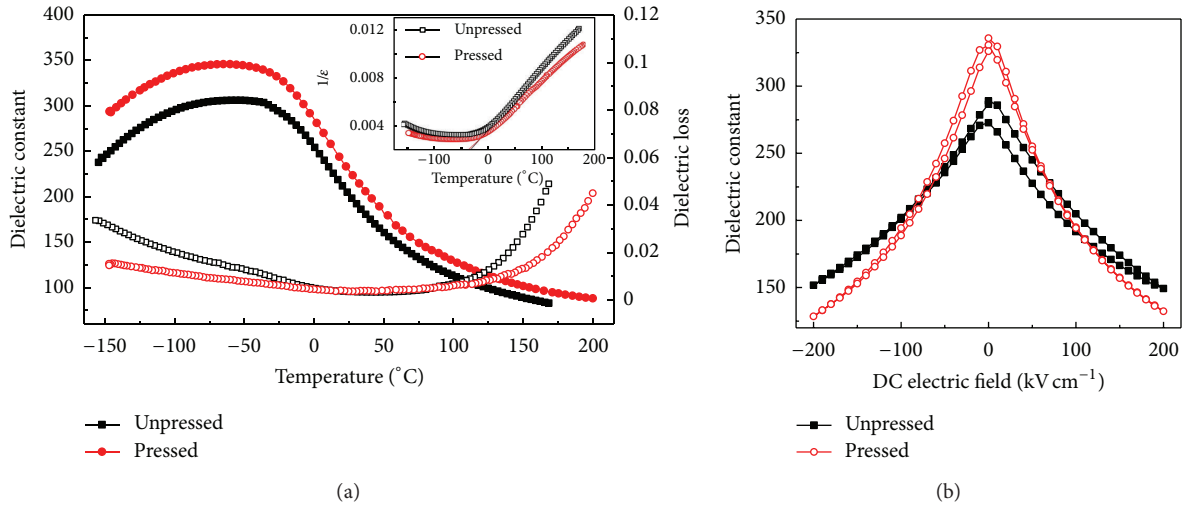

Figure 4: (a) Temperature dependence of dielectric constant and dielectric loss of $Ba_{0.5}Sr_{0.5}TiO_3$ thick films with and without isostatic pressing; inset: the inverse dielectric constant ($1/\varepsilon$) as a function of temperature. The symbols: experimental data; the solid line: fitting to the Curie-Weiss law. (b) DC electric field dependence of thick films with and without isostatic pressing.

dense compared with bulk ceramics [12]. Although porous dielectric materials are hot research topics, it is out of our scope, and for a better sinterability of the BST thick films, besides the isostatic pressure, a proper substrate as well as an optimum sintering temperature is needed. It is also possible that the electrode may affect the properties of the thick film, while in our study, on the one hand, we use Pd-Ag electrode, with low sintering temperature of the electrodes, the diffusion of electrodes to the ceramic is suppressed and cannot be observed, and on the other hand, since the Unpressed and Pressed thick films both use the same electrode and share the same structure; the influence of electrodes should be similar; thus in our study, the influence of electrode on the ceramics is not considered.

The temperature dependence of dielectric constant and loss of the thick film with and without the application of isostatic pressing are presented in Figure 4(a). The dielectric peaks are suppressed and broadened compared with bulk BST [17]. The inverse dielectric constant ($1/\varepsilon$) as a function of temperature by using the Curie-Weiss equation has been plotted. Figure 4(a) inset shows the plots of inverse dielectric constant as a function of temperature. The solid lines are plotted by fitting the Curie-Weiss law [18]

$$\frac{1}{1/\varepsilon} = (T - T_c), \quad (T > T_c). \tag{2}$$

The Curie temperature is thus estimated from the intercept of the fitted line with the temperature axis. The Curie temperatures are −36.4°C and −30.5°C for the films with and without isostatic pressing, respectively. The decrease of Curie temperature of the thick film with isostatic pressing treatment can be attributed to the strains introduced into the lattice at the onset of spontaneous polarization. The decreasing trend is in agreement with the results reported by Samara [19]. At 10 kHz and room temperature, the dielectric constants of the films with and without treatment are 238 and 210, respectively, both of which are suitable for microwave device designs in quest of impedance matching and high power requirement [7]. The increase of the dielectric constant is also a reflection of more densified microstructure. A porous ceramic can be considered dual-phase system composed of bulk ceramic and air pores. Considering that the dielectric constant of air is around 1, less air pores will lead to higher dielectric constant [20]. The dielectric losses in the sample with isostatic pressing treatment are generally lower than unpressed one. At temperature ranging from room temperature to 100°C, the dielectric losses are within the same lower scale for both unpressed and pressed samples. When the testing temperature goes higher (>100°C) or lower (< −50°C), the dielectric loss increases, which is not beneficial for applications. It is noted that the dielectric loss of the pressed sample has lower degree of increment. The dielectric loss is affected by many factors such as external frequency and temperature, internal structure and lattice defects such as grain boundaries, void and defects [21]. The dielectric properties of thick films are closely related to the microstructure of the dielectric layer and the grain size effect [8]. Denser microstructure with less external porosity is beneficial for lower dielectric loss. For the unpressed thick film, its porous microstructure and rough surface deteriorate the dielectric properties. At room temperature, the dielectric loss at 10 kHz in the film after pressing is 0.0028, compared with 0.0037 without pressing. Compared with a bulk BST material sintered at 1350°C, with the dielectric constant above 1500 and dielectric loss in the range of 0.002 [20], the isostatic-pressure-treated screen printed BST thick films show prominent modification on dielectric constant while maintaining the low dielectric loss, which is suitable for microwave device designs.

The DC electric field dependence of the dielectric constant of the film with and without applying of isostatic pressing are presented in Figure 4(b). Considering the thickness

Table 2: Comparison of dielectric properties for BST materials prepared by different methods.

BST systems	Sintering temperature	Dielectric constant	Dielectric loss	Tunability	References
Thick film (screen printed, isostatic pressed, B-Li sintering aid, 19.5 μm)	950°C	238	0.0028	61.7% (200 kV cm^{-1})	Current work
Thick film (screen printed, 20 μm)	1200–1300°C	200	0.0027	9% (20 kV cm^{-1})	Su et al. [22]
Thick film (nanosized, screen printed)	1250°C	180	0.02	—	Ditum and Button [23]
Thick film (screen printed, PbO sintering aid)	850°C	—	—	10% (20 kV cm^{-1})	Zhang et al. [24]
Bulk material (solid state reaction)	1350°C	2500	0.0008	22.7% (30 kV cm^{-1})	Wang et al. [25]
Porous bulk material (solid state reaction)	1350°C	990	0.002	19.6% (26 kV cm^{-1})	Zhang et al. [20]
Thin film (sol-gel, (100) oriented)	1100°C	2714	0.0215	51.9% (25.3 kV cm^{-1})	Jain et al. [26]

of the films (about 20 μm), a relatively low bias voltage (400 V) can reach a relatively high electric field applied to the film (200 kV cm^{-1}), which is a big advantage of thick films if considering normally applied electric field of less than 30 kV cm^{-1} for bulk ceramics. When the electric field is set to 200 kV cm^{-1}, the tunability ($n = (\varepsilon_r(0) - \varepsilon_r(E))/\varepsilon_r(0)$) with the isostatic pressing treatment reaches 61.7%, compared to 48.3% of the film without isostatic pressing. If we consider the thick films as composites of air and BST bulk materials, more pores would dilute the tunability of BST ceramics [20]. It is noted that the tunability for the thick film is more than 3 times larger than their peer bulk ceramics [17, 20]. Table 2 compares in detail the tunability and the dielectric properties of the current work with reported publications. It can be seen that the isostatic pressed thick films obtained in this work possess combined properties of suitable low dielectric constant, low dielectric loss, and high tunability endured under high voltages, showing good enough film quality potentially applicable for the fabrication of tunable microwave thick film devices.

4. Conclusions

In summary, low-temperature-fired $Ba_{0.5}Sr_{0.5}TiO_3$ thick films were prepared by screen printing method. Isostatic pressing treatment was introduced to the thick film preparation process before sintering. A thick film with more densified microstructure and uniform surface was obtained by the isostatic pressing treatment. Increased dielectric constant and lower dielectric loss can be obtained for the pressurized thick film. The tunability of the thick film after pressing reached 61.7%, more advantageous for the fabrication of tunable advices. These results reveal that isostatic pressing treatment is an effective way to prepare denser screen printed thick films with lower dielectric loss and higher tunability for tunable dielectric and microwave devices.

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