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Letter

Dielectric properties of low-temperature sintered $Ba_{0.6}Sr_{0.4}TiO_3$ thick films prepared by reactive sintering method

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ABSTRACT

Screen printed $Ba_{0.6}Sr_{0.4}TiO_3$ (BST6/4) thick films were fabricated by reactive sintering at a low temperature below 900 °C. The dielectric properties in radio frequency range were measured on samples of sandwich structure MIM capacitors by impedance analyzer, while that in microwave frequency range were measured on samples of thick films without top and bottom electrodes by split-post dielectric resonator method. The thick films exhibited a low permittivity, while at the same time, maintained a high tunability. The permittivity and dielectric loss at 1 MHz were 228.8 and 0.007, respectively. The corresponding values measured at 9.9 GHz were 82.24 and 0.109, respectively. The tunability was as high as 72.4% (150 kV/cm, 10 kHz). This method provides a simple and effective route to obtain thick films with great potential in applications in Low Temperature Co-fired Ceramic (LTCC) and microwave tunable devices.

1. Introduction

The perovskite Barium Strontium Titanate $Ba_xSr_{1-x}TiO_3$ (BST) materials attract much attention because their permittivities can be tuned by applying the DC bias. They have been regarded as promising candidates for applications in microwave tunable devices, such as phase shifters, filters and varactors [1–3]. Barium Strontium Titanate materials have a paraelectric–ferroelectric phase transition temperature (Curie temperature) which is different with different Ba/Sr ratio. By varying the Ba/Sr ratio, this Curie temperature can be tuned over a broad range. For microwave applications, it is better to choose BST materials in paraelectric phase, because the dielectric loss of ferroelectric phase is higher than that of paraelectric phase [4]. $Ba_{0.6}Sr_{0.4}TiO_3$ (BST6/4) ceramic is one of suitable candidates since it has the Curie temperature of 272 K. It has good dielectric properties at room temperature. The tunability is 44.4%, which is measured under the applied DC bias of 20 kV/cm, 1 MHz [5].

The high sintering temperature (>1300 °C) and the high driving voltages of bulk ceramics have limited their applications in miniaturized microwave components. Quite a lot of efficient sintering aids are found to lower the sintering temperatures. Valant and Suvorov reported a low sintering temperature of BST ceramic below 900 °C by adding 0.4–1 wt% Li_2O, the tunability showed no significant difference [6]. Thick films show lower tuning voltages comparing with bulk ceramics, thus more researchers have expressed interest on low-temperature sintering BST thick films. Tick et al. reported a good work on BST thick films fabrication [7]. The sintering aids were added to BST powders to form slurry for screen printing. However, the relative high permittivity by this method made it difficult for practical device design and a high temperature around 1100 °C for phase formation is also needed to calcine the raw materials ($BaCO_3$, $SrCO_3$, TiO_2), which is highly energy-consuming.

In this paper, the reactive sintering method was adopted to fabricate BST thick films. Reactive sintering method is a simple and effective route to obtain thick films [8]. The mixture of the raw materials is directly sintered without going through calcination step. The process of the reactive sintering was carefully studied. By adding sintering aids, a low-temperature sintered BST thick film was fabricated. The dielectric properties of the BST6/4 thick films prepared by reactive sintering method were characterized from radio frequency range to microwave frequency range, which were less mentioned in other reported literatures.

2. Experimental procedure

Barium carbonate ($BaCO_3$, 99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), strontium carbonate ($SrCO_3$, 99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), titanium oxide powders (TiO_2, 98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were mixed according to the stoichiometric ratio of $Ba_{0.6}Sr_{0.4}TiO_3$. In order to lower the sintering temperature, a small amount of 1 wt% Li_2O was added by using Li_2CO_3 (98%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) as start material. The powders were ball milled for 4 h and dried. Then the powders were dispersed in an organic vehicle (terpineol and ethyl cellulose) to obtain the slurry for screen printing. The weight ratio of powders to organic

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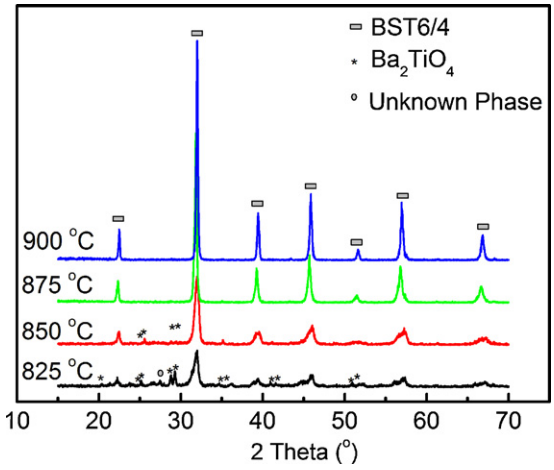

Fig. 1. XRD pattern of reactive sintered BST thick films sintered at 825, 850, 875, and 900 °C.

vehicle was 7:4. The thick films were prepared on alumina substrates with Ag as bottom electrode by screen printing. A high isostatic pressure of 140 MPa was applied on the green films before sintering. With a heating rate of 3 °C/min, the films were preserved at 550 °C for 2 h and then sintered at 825, 850, 875 and 900 °C for 2 h, respectively. The upper electrode, also a screen-printed Ag paste, was calcined at 600 °C for 10 min. For microwave frequency range measurement, the BST films were printed directly on alumina substrates.

Room-temperature X-ray diffraction data for phase identification were collected on a diffractometer (Rigaku D/MAX-2400, Tokyo, Japan) using CuKα radiation. The microstructural characterization was performed by a scanning electron microscope (SEM) (JEOL/EO, Tokyo, Japan). Dielectric measurements were conducted in the frequency range from 1 kHz to 5 MHz by an impedance analyzer (4294A, Agilent, Palo Alto, CA). The tunability under the DC bias of 40 V at 1 MHz has been measured.

$$\text{Tunability} = \frac{\varepsilon(0) - \varepsilon(v)}{\varepsilon(0)} \times 100\% \quad (1)$$

where $\varepsilon(0)$ and $\varepsilon(v)$ are the permittivities without and under a certain DC bias, respectively. The temperature dependences of permittivity and dielectric loss were measured from −50 °C to 85 °C by a LCR meter (4284A, Agilent, Palo Alto, CA) with a temperature controlled chamber (Delta 9023, Artisan Scientific, Poway, CA). The tunabilities under high electric fields were measured up to a maximum DC bias of 300 V at 10 kHz by a LCR meter (TH 2816, Tonghui Changzhou Electronic, Changzhou, China).

The dielectric properties in microwave frequency range were measured at 5, 9.9, 14.5 and 19 GHz by the split-post dielectric resonator technique. The resonators were connected to the HP8720ES network analyzer. The permittivity and dielectric loss were calculated from the resonance frequency f_0 and quality factor Q, respectively [9]. The temperature dependences of the dielectric properties from −50 to 80 °C were measured at 9.9 GHz in the temperature controlled chamber (Delta 9023).

3. Results and discussions

The phase structure and detailed formation of reactive sintering process are shown in Fig. 1. The perovskite phase of BST6/4 accompanied with secondary phase of Ba_2TiO_4 form in the film, when the films are sintered at 825 °C and 850 °C. The intensity indicates that the raw materials start to react below 825 °C. When the sintering temperature reaches 850 °C, the diffraction peaks become higher and narrower, and the secondary phase gradually decomposes with increasing of sintering temperature. No obvious secondary phase is detected in the films sintered above 875 °C.

The formation and decomposition of Ba_2TiO_4 might be explained by a series of reactions [10]. Along with the synthesis of BST, few $BaTiO_3$ also occurs at the beginning of heating by the reaction between $BaCO_3$ and TiO_2 according to Eq. (2) below 825 °C. After the amount of $BaTiO_3$ reaches some content, Ba_2TiO_4 forms according to Eq. (3). When all the $BaCO_3$ in the raw materials has been consumed above 875 °C, Ba_2TiO_4 reaches its highest fraction and then forms $BaTiO_3$ with TiO_2 according to Eq. (4). The formation enthalpies of $BaTiO_3$ and Ba_2TiO_4 at 800 °C are 97.44 kJ/mol and 234.702 kJ/mol, respectively. The Ba_2TiO_4 completely disappears above 900 °C, so the formation enthalpy of $BaTiO_3$ from Ba_2TiO_4 and TiO_2 is −139 kJ/mol at 900 °C.

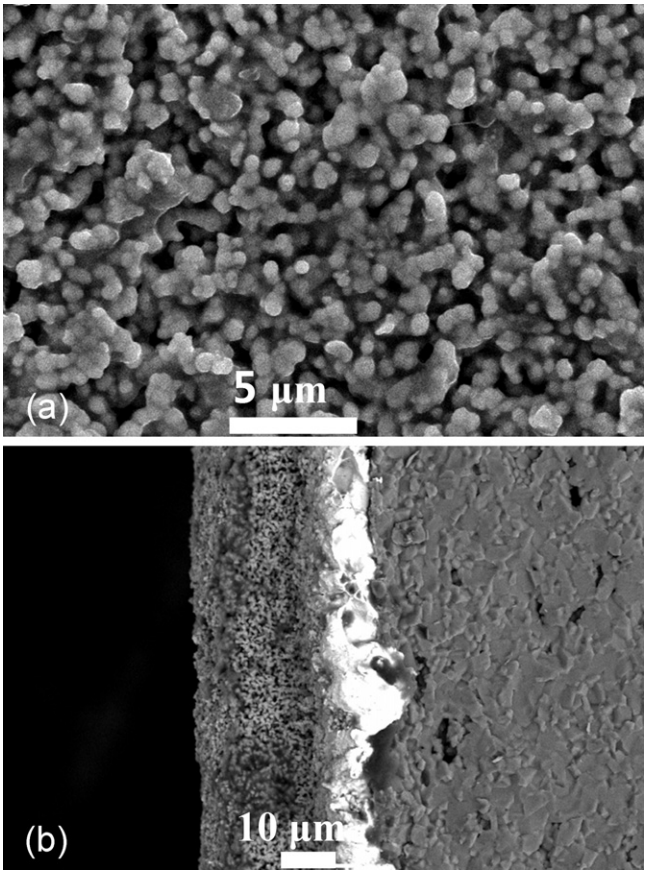

Fig. 2. Morphology of BST thick film sintered at 900 °C.

$$BaCO_3 + TiO_2 \rightarrow BaTiO_3 + CO_2 \quad (2)$$

$$BaTiO_3 + BaCO_3 \rightarrow Ba_2TiO_4 + CO_2 \quad (3)$$

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \quad (4)$$

Eutectic melt of $BaCO_3$ and Li_2O could form after 811 °C. It could provide some liquid phase to accelerate the mass transport in the sintering process [6]. The intensity changes of BST6/4 phase show excellent effect of the reactive sintering by doping Li_2CO_3. The temperature for phase formation is evidently decreased. Compared to the high sintering temperature (>1000 °C) of conventional solid-state reaction synthesis [11], the sintering in this work starts very early (<825 °C). It indicates that the liquid-phase aid and chemical reaction promote the sintering of BST6/4 thick films at lower temperature. The morphology of the film sintered at 900 °C is shown in Fig. 2. The average grains size is about 0.7 μm. Owing to isostatic pressing applied to the green films before sintering, the thick film has a relative compact microstructure. The film has an average thickness of 20 μm after sintering.

Frequency dependences of permittivity and dielectric loss of the samples from 1 kHz to 5 MHz are shown in Fig. 3(a). Because of the porous structure by reactive sintering method, the permittivities are quite low. When measured at 1 MHz, the permittivities are 35.3, 72.3 and 228.8 for the films sintered at 850, 875 and 900 °C, respectively. The corresponding dielectric losses are 0.002, 0.004 and 0.007, respectively. With the increasing of sintering temperature, the permittivity increases gradually. The permittivity and dielectric loss at microwave frequency range are measured at 5,

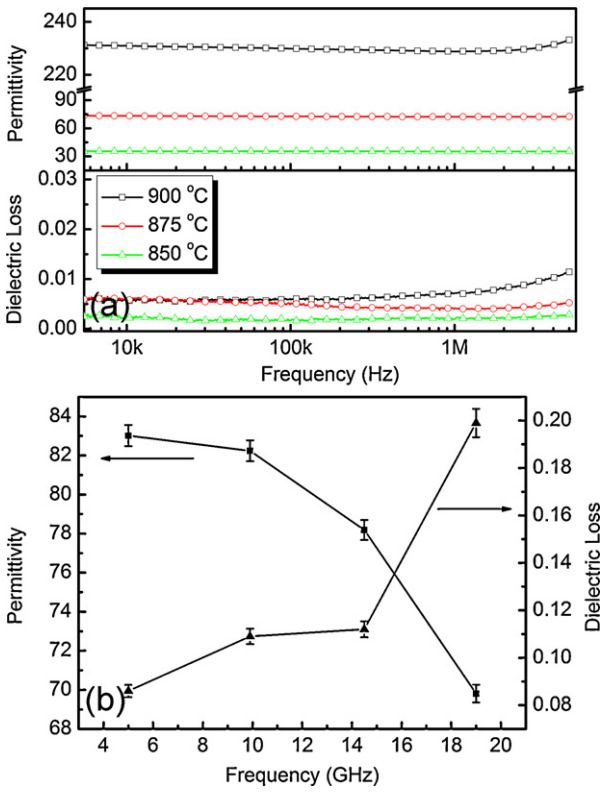

Fig. 3. Frequency dependence of permittivity and loss of BST thick films (a) sintered at 850, 875, and 900 °C from 1 kHz to 5 MHz, and (b) sintered at 900 °C at 5, 9.9, 15 and 19 GHz.

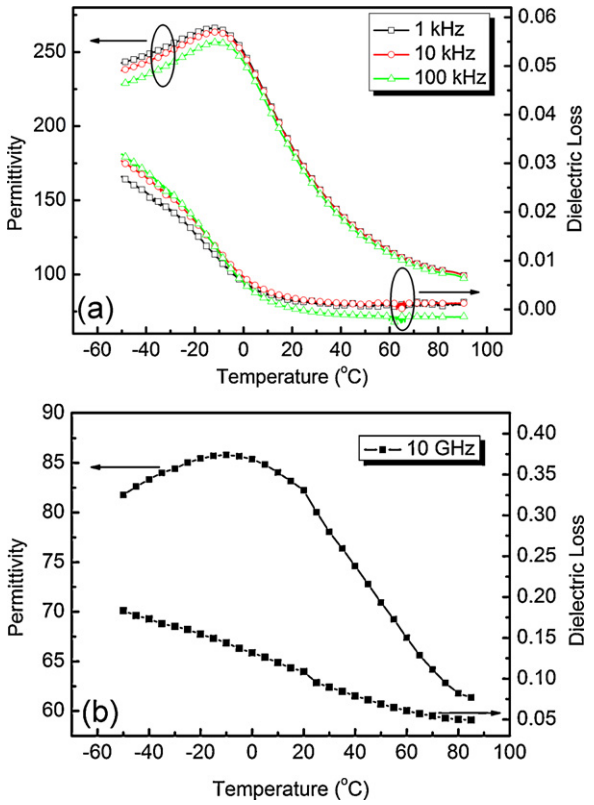

Fig. 5. Temperature dependence from −50 °C to 85 °C of BST thick films sintered at 900 °C measured at (a) 1, 10 and 100 kHz, and (b) 9.9 GHz.

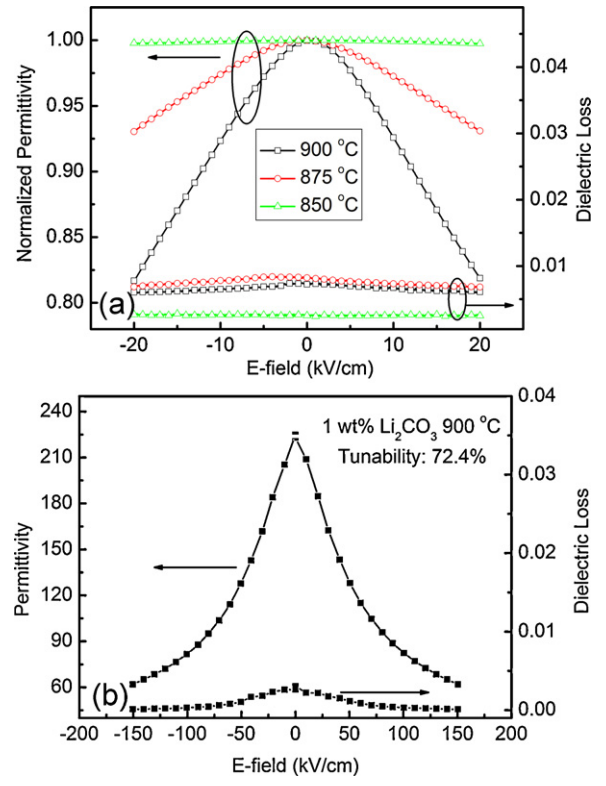

Fig. 4. Tunability of BST thick films (a) sintered at 850, 875, and 900 °C under 20 kV/cm, 1 MHz, and (b) sintered at 900 °C under 150 kV/cm, 10 kHz.

9.9, 14.5 and 19 GHz by the split-post dielectric resonator technique. The frequency dependence is shown in Fig. 3(b). For each frequency point, the measurement is repeated for three times. The average permittivity of films sintered at 900 °C is 83.01, 82.24, 78.18 and 69.81, respectively. The corresponding average dielectric loss is 0.086, 0.109, 0.112 and 0.199, respectively. Seen in Fig. 3, the permittivity and dielectric loss are almost flat with increasing of frequency at radio frequency range. While the frequency reaches to microwave frequency range, the permittivity decreases and the dielectric loss increase remarkably. As reported by Tsurumi et al., the dipole and ionic polarization contributions overlap in BST material, and the relaxation frequency of the ionic polarization occurs in terahertz region [12]. The influence of the relaxation should be taken into account, when the test frequency is high enough. It could be used to explain why the permittivity decreases and dielectric loss increases at the microwave frequency range.

Tunability is an important parameter for tunable device. According to Tagantsev et al., in the limit of weak nonlinearity, tunability is a very fast function of permittivity [4], seen in Eq. (5).

$$\frac{\varepsilon(0)}{\varepsilon(E_0)} \approx 1 + 3\beta(\varepsilon(0)\varepsilon_0)^3 E_0^2 \tag{5}$$

In most cases, the tunability is related to permittivity, and high permittivity relates to high tunability [4]. However, the high permittivity will increase the difficulty for impedance matching when designing and manufacturing microwave components. Results of tunability measurement indicate another advantage of reactive sintering method. As shown in Fig. 4(a), the film sintered at 900 °C has a high tunability of 18% under applied field of 20 kV/cm at 1 MHz. The tunability of the film is comparable with that of ceramic samples in the literature. The Li-doped BST ceramics reported by Valant and Suvorov have the tunability of 13.5–16.5%, while the permittivity is higher than 1000 (measured at 1 MHz, under 30 kV/cm) [6]. The thick films made by reactive sintering method have the advantages

of relative low permittivity as well as high tunability, which make it has great potential for the microwave device application. The highest tunability of 72.4% at 10 kHz is obtained under the applied field of 150 kV/cm, which could be seen in Fig. 4(b).

The temperature dependences of dielectric properties are measured at radio frequency and microwave frequency range respectively. The film sintered at 900 °C is chosen for the measurement. Seen from Fig. 5(a), Curie temperature of the film from 1 kHz to 100 kHz is at about −12 °C, which is lower than the reported value of bulk ceramics [5]. It might be caused by the smaller grain size due to doping of Li_2O sintering aids. The measured highest permittivity is 266 at 1 kHz. Compared with that of radio frequency measurement, the peak is diffusive and becomes much broader at 9.9 GHz. Almost the same Curie temperature point is measured, the highest permittivity is 85.8. It indicates that the temperature dependence is stable that the paraelectric–ferroelectric phase transition temperature does not change with frequency. It is also an advantage for the device design at microwave frequency range.

4. Conclusions

In summary, BST thick films by reactive sintering method are successfully fabricated below 900 °C, and the dielectric properties are investigated in detail from radio frequency range to microwave frequency range. Compared with the thick films prepared by other technology, reactive sintered films show a series of advantages. It has the low temperature for phase formation. The relatively low permittivity and high tunability make it an attractive candidate for applications in microwave tunable devices. The film sintered at 900 °C has permittivity of 231 at 1 kHz and 69.81 at 19 GHz. The corresponding dielectric loss is from 0.006 up to 0.199 when measurement frequency is from 1 kHz to 19 GHz. A high tunability of 72.4% is also reached at 10 kHz. The temperature dependence of dielectric behavior measured at radio frequency and 10 GHz indicates a stable ferroelectric to paraelectric transition.

Acknowledgments

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