J Electroceram (2008) 21:503–507
DOI 10.1007/s10832-007-9229-9

Fabrication and electrical properties of barium strontium titanate thick films by modified sol–gel method

Hongfang Zhang · Liangying Zhang · Xi Yao

Published online: 19 August 2007
© Springer Science + Business Media, LLC 2007

Abstract A modified sol–gel method has been developed to prepare for the barium strontium titanate ($Ba_{0.6}Sr_{0.4}TiO_3$, BST) thick films. The films were deposited on either Pd–Ag electroded alumina substrates (Pd–Ag/Al_2O_3) or silver electroded alumina (Ag/Al_2O_3) substrates by spin coating technique or screen printing technique. The thickness of the film was in the range of 2–10 μm. The key point of the process is to disperse fine-grained BST ceramic powders prepared by high energy ball mill into BST sol solution to form a slurry for spin coating and screen printing. In order to enhance the stability of the slurry and to avoid crack formation of the thick film, organic macromolecular poly-vinylpyrrolidone (PVP) was added to the sol solution. The structure and surface morphology of the films were studied by X-ray diffraction and Scanning Electron Microscope (SEM) techniques. It is revealed that the thick films exhibit pure perovskite phase and are crack-free, dense and homogeneous. The dielectric constant and loss tangent of the thick films are about 1200 and 0.01, at 10 °C and 1 KHz, respectively.

Keywords Barium strontium titanate (BST) · Thick film · Sol–gel

1 Introduction

The $Ba_xSr_{1-x}TiO_3$ (BST) ceramic is of considerable interest in the field of electroceramics and microelectronics [1, 2]. Barium strontium titanate (BST) can be considered as a solid solution of barium titanate and strontium titanate. $SrTiO_3$ is a cubic perovskite while $BaTiO_3$ exhibits a tetragonal perovskite structure at room temperature. The Curie temperature of $Ba_xSr_{1-x}TiO_3$ ceramic decreases linearly with the increasing amount of Sr in the $BaTiO_3$ lattice. This enables the ferroelectric–paraelectric transition temperature to be tailored by varying the Sr content for specific applications. Recent research in high frequency and microwave materials has shown good potential for BST materials to be used as tunable phase shifters, resonators, filters, wave guides and etc. [3]. Due to the high dielectric constant and low loss tangent, BST films are very effective in size reduction of microwave devices and RF-MEMS. In such applications, preparing of dense and crack-free thick films is of great importance.

Screen-printing is a conventional thick film technology suitable for fabricating films with thickness higher than 15 μm. By screen-printing process, the reduction of sintering temperature is achieved by mixing the ceramic powder with a glass powder with low melting temperature. Using such mixed ceramic-glass powder, the sintering temperature of the thick film can be effectively reduced below 1100 °C depending on the amount and melting point of the glass. However, the homogeneity of such mechanically mixed ceramic-glass powder is rather poor, which deteriorates the dielectric behavior of the film. An alternative way is highly desirable.

In the paper, a modified sol–gel method has been developed to prepare barium strontium titanate based thick films with lower sintering temperatures, better homogeneity and better performance. In this method, well calcined ceramic was prepared by conventional solid state reaction. Fine-grained ceramic powders were prepared by ball milling. Then the powders were dispersed into a sol precursor solution. Again, ball mill was used to disperse

H. Zhang (✉) · L. Zhang · X. Yao
Functional Material Research Laboratory, Tongji University, Shanghai 200092, People's Republic of China
e-mail: sansan_ss@126.com

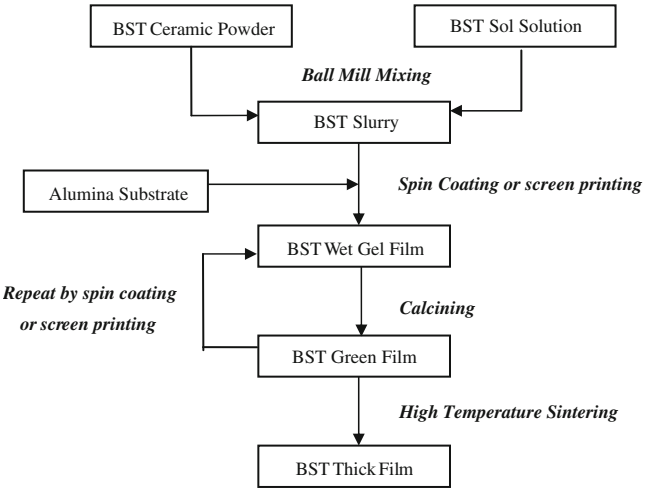

Fig. 1 Processing flow chart of BST thick films

the ceramic powder in the sol solution to form ceramic slurry. The viscosity of the ceramic slurry can be adjusted by the powder/sol ratio and the amount of solvent. Then, thick films were deposited on to substrates by spin coating or screen printing technology. Dense and crack-free ceramic films can be obtained after high temperature calcination. In this paper, processing, dielectric behaviors of $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thick films will be presented.

2 Experiments

2.1 Preparation of BST sol solution

The BST solution precursor was prepared by using polymer-assistant method. The starting materials for the preparation of BST precursor solution were barium acetate ($Ba(CH_3COOH)_2$), strontium acetate ($Sr(CH_3COOH)_2$), and titanium-tetrabutoxide ($Ti(OC_4H_9)_4$), acetic acid (CH_3COOH), isopropyl alcohol ($C_3H_7^iOH$) and PVP with average molecular weight of 10,000. The molar composition of the BST precursor solution are $Ti(OC_4H_9)_4/Ba(CH_3COO)_2/Sr(CH_3COO)_2/PVP/CH_3COOH/C_3H^i{}_7OH$= 1:0.6:0.4:1:9.08:20.

In preparing the BST sol solution, PVP was firstly dissolved in $C_3H_7^iOH$, and then CH_3COOH and $Ti(OC_4H_9)_4$ were added to the solution successively under stirring. $Ba(CH_3COOH)_2$ and $Sr(CH_3COOH)_2$ powders in proper molar ratio were dissolved in hot acetic acid. Then, the $Ba(CH_3COOH)_2$–$Sr(CH_3COOH)_2$ solution was added in drop wise to the $Ti(OC_4H_9)_4$–PVP–CH_3COOH–$C_3H_7^iOH$ solution under stirring. A light yellowish and transparent solution were then obtained.

2.2 Slurry fabrication

The barium strontium titanate BST (Ba/Sr:60/40) bulk ceramics was produced by conventional ceramic processing from barium titanate $BaTiO_3$ and strontium titanate $SrTiO_3$ at 1350 °C for 7 h. To obtain nano-sized BST powders, a high-energy ball mill machine with tungsten carbide vials and balls (Fresch Pulverisette 5 planetary ball mill) was employed. The weight ratio of powder to balls was 1:20. To avoid overheat during the ball milling, there is a 10 min break after each 25 min running, and the total milling time is 20 h. To avoid agglomeration of the powder and increase the milling efficiency, a small amount of dispersant was added and mixed with the powder. The average particle size of the powder after high energy ball mill was in the range of 20–60 nm.

The ceramic slurry for BST thick film deposition was prepared by dispersing the surface modified BST nano-sized powders into BST sol solution. After mixed by conventional ball mill for 12~18 h, very homogeneous and paint-like slurry could be obtained, which was able to be used for spin-coating or screen printing process.

2.3 Thick films deposition

The BST thick film was deposited with spin-coating process on the substrate at 2,000–4,000 rpm for 20 s. Substrates used were Ag electroded alumina substrates and Pd–Ag electroded alumina substrates. Each layer of film was preheated at 110 °C, 350 °C and 550 °C for 5 min subsequently. The spin coating process was repeated until desired thickness was reached. The resultant films were then annealed at 700–1200 °C for 2 h in furnace to crystallize the films. The overall procedure for thick film deposition is summarized in Fig. 1.

The above process is quite flexible. Changing the process parameters of the ball milling, such as revolution speed, ball milling time can easily control the particle size. The thickness of the film can be increased by repeating the spin coating or screen printing process. The viscosity of the

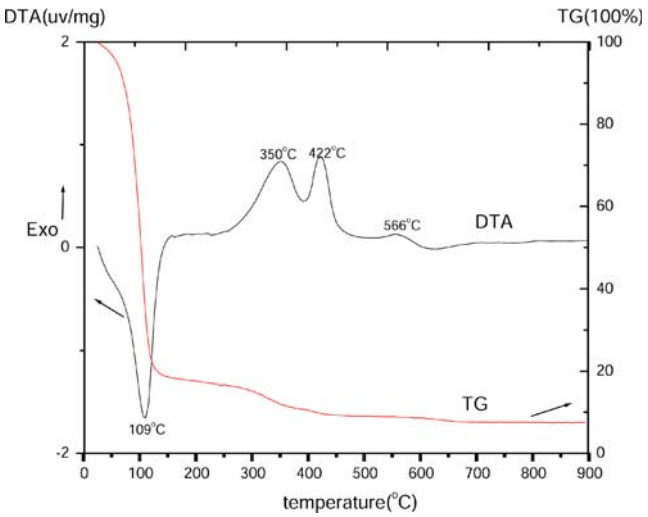

Fig. 2 DTA and TG curves of BST xero gel (heating rate: 10 °C/min in air)

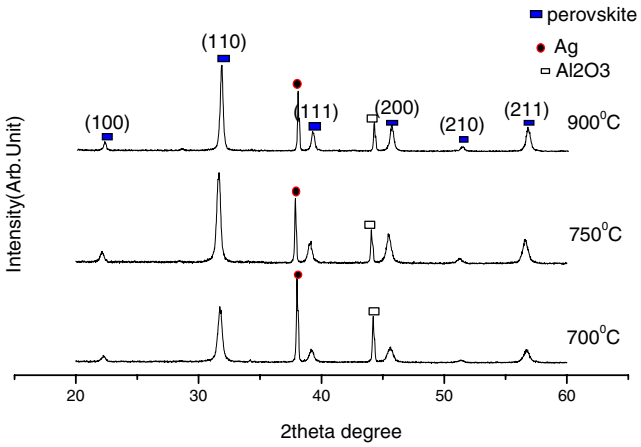

Fig. 3 X-Ray diffraction pattern of BST thick film

ceramic slurry can be adjusted by the powder/sol ratio and the amount of solvent. Depending on the viscosity of the slurry, thick films can be deposited on to substrates by either spin coating or screen printing technology.

2.4 Film characterization

Thermal property of the xero gel is analyzed by DTA-TGA (NETSCHSTA 449C). The phase structure and microstructure of the films were examined by XRD (D8 ADVANCE X-ray Diffractometer, CuKα1 radiation) and scanning electron microscopy (SEM). The particle size of the powder is studied by transmission electron microscopy (TEM); Dielectric constant and loss were examined with Hewlett-Packard 4284 LCR meter.

3 Results and discussion

3.1 Decomposition of xero gel

In order to decide suitable heat-treatment schedules for eliminating organic components from the film deposited with organic dispersants, dried xero gel precursor $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) was characterized by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) techniques at a heating rate of 10 °C/min. Figure 2 shows the typical DTA and TGA results for the formulated xero gel. There were two main stages in the decomposition reaction.

It can be seen from the figure, the large weight loss and sharp endothermic peak at 109 °C can be recognized as evaporation of solvents and other volatile species. The exothermic peak at 350 °C accompanied by mild weight loss can be attributed to the decomposition and combustion of bound organics. According to this result, a preheating temperature at 110 °C and 350 °C was chosen to eliminate organic components from the film. In DTA curve, the exothermic peak at 422 °C has not yet been recognized. In reference [4], this peak was attributed to the crystallization of intermediate phase $BaTi_2CO_3$. The weak exothermic peak at 566 °C can be recognized as the crystallization peak of perovskite. Hence, 550 °C was selected as another pre-annealing temperature to promote the formation of crystal phase in the films.

3.2 Microstructure of BST thick films

Figure 3 is a X-ray diffraction pattern of a BST thick film. It is quite evident that the crystal structure of the film is typical cubic perovskite structure. Besides the diffraction peaks of silver electrode and alumina substrates, no other stray phases can be seen.

For thick film deposition, the weight ratio of powder to precursor solution of the slurry is a critical parameter. The BST oxide powder content of the slurry is defined as follow:

$$\mathrm{BST(wt\%)} = \frac{P}{P+S}$$

Where P is the weight of BST powders added, S is the residue oxide weight of the sol solution after thermal annealing. According to our experiments, the BST (wt%) from 70 to 80% is most optimum for thick film deposition.

Figure 4 is the SEM pictures of the cross-section and surface morphology of the BST thick film annealed at 750 °C

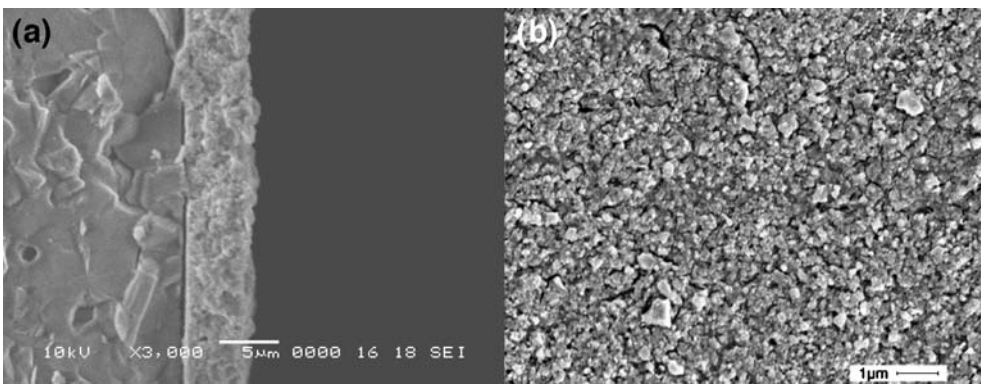

Fig. 4 Cross section (**a**) and Surface morphology (**b**) of BST thick film deposited on alumina substrate by spin coating technology at 750 °C for 30 min

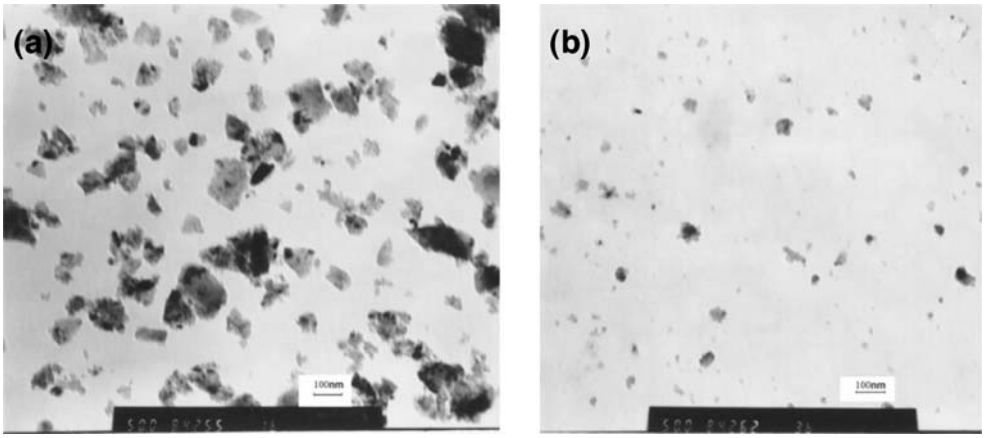

Fig. 5 TEM photographers of BST ceramic powders (*asterisk*, 50,000, 1 cm=200 nm) (**a**) a conventional ball mill for 24 h (**b**) high energy ball mill for 20 h

for 30 min. The powder content of the slurry is 72%. The film was prepared by successive spin coating for five times, the average thickness for each coating is estimated to be about 1 μm. It can be seen that the film is very dense and crack-free. The microstructure morphology of the film is quite homogeneous and the grain size is less than 1 μm.

We believe that the use of high energy ball milled BST fine powders and the use of PVP are the major factors ensuring such very high uniform microstructures.

Firstly, the high-energy ball mill method was applied to reduce the particle size of the powder. Figure 5 is TEM photographers of the particle size of the powder, in which (a) is conventional ball mill for 24 h, the particle size is in the range of 300–600 nm, and (b) is high energy ball mill for 20 h, the particle size is in the range of 20–60 nm. In the high energy planetary ball milling process, very high mechanical energy is transferred from flying balls to the powders by collision. Thereby the grain size of BST particle can be much reduced into nanometer regime. Compared with other methods, such as chemical coprecipitation, sol–gel, hydrothermal reaction and reactive calcinations, high-energy ball mill method is the simplest one to prepare fine-sized BST ceramic powders.

Secondly, When PVP is added into to the precursors, it can hybridize with metalloxane polymer in molecular scale through strong hydrogen bond between the C=O groups of the PVP and the OH groups of the metalloxane polymers [6]. Such C=O groups can be regarded as the capping agent for the OH groups of the metalloxane polymers suppressing the condensation reaction and promoting the structural relaxation. The thermal decomposition of organic polymers is completed at temperatures much higher than monomeric agents, which enables the polymers to retard condensation and promote structural relaxation at high temperatures.

3.3 Dielectric behaviors of BST thick films

In order to study the dielectric behaviors of the BST thick films, electrodes should be applied on both sides of the films. Silver (Ag), palladium–silver (Pd–Ag) can be used as bottom electrode, which can be applied on the substrates by screen printing using corresponding paste. Since the bottom electrode will be co-fired with the BST films, Ag is good for films with sintering temperatures below 900 °C. For sintering temperature higher than 1000 °C and lower than 1200 °C, Pd–Ag electrode should be used. Screen printed silver or sputtered gold can be used as top electrodes.

The temperature dependences of dielectric constants of BST thick film at 1200 °C for 2 h are given in Fig. 6, which was studied by an impedance analyzer of HP 4284 LCR meter. It can be seen from Fig. 6, the dielectric constant and loss tangent of the thick film are about 1,200 and 0.01, at 10 °C and 1 KHz, respectively. But the dielectric loss at high frequencies is higher than that in low frequency. This is due to the macro defects of the films such as porosity etc. It is well known that thick films with higher dielectric constants always have higher tunability of dielectric constant but poorer temperature stability. Reducing the dielectric constant of the film will reduce its tunability but improve its temperature stability.

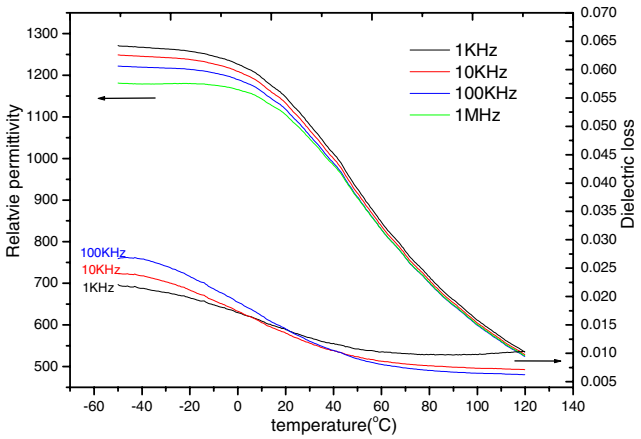

Fig. 6 Temperature dependence of dielectric constant and dielectric loss of BST thick film with Pd-Ag electrode fired at 1200 °C for 2 h

4 Conclusion

A modified sol–gel method has been successfully developed to prepare barium titanate based thick films. Thickness of the films can be prepared in the range of 2–10 μm. Alumina substrates, which are widely used in microwave devices, can also be used as the substrates of the thick films. Due to the high loading of well-crystallized micro-sized and nano-sized ceramic powders, the dielectric behaviors of the thick film are close to those of the bulk ceramics without apparent deterioration. While the low sintering temperature of the sol derived substance is able to ensure the films to be sintered at much lower temperature and co-fired with electrode. The dielectric constant and loss tangent of the BST thick film are about 1,200 and 0.01, at 10 °C and 1 KHz, respectively. The barium titanate based thick films are quite perspective in the application of tunable microwave devices.

Acknowledgement This work was supported by the Ministry of Sciences and Technology of china through 973 project under grant 2002CB613302.

References

1. J.F. Scott, Integr. Ferroelectr. **20**(1–4), 15 (1998)
2. R.E. Jones, P. Zurcher, P. Chu, D.J. Taylor et al., Microelectr. Engng. **3**, 229 (1995)
3. D. Damjanovic, Rep. Prog. Phys. **61**, 1267 (1998)
4. H. Zeng et al., J. Inorg. Mater., **14**(1), 101–106 (1999)
5. T.R. Ren, X.N. Wang, J.S. Liu et al., Appl. Phys. **35**, 923–926 (2002)
6. H. Kozuka, M. Kajimura, J. Am. Ceram. Soc. **83**(5), 1056–1062 (2002)