Journal of the European Ceramic Society 21 (2001) 2641–2645

www.elsevier.com/locate/jeurceramsoc

The processing and properties of barium strontium titanate thick films for use in frequency agile microwave circuit applications

B. Su, T.W. Button*

IRC in Materials for High Performance Applications, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Abstract

Barium strontium titanate (BST) thick films for use in frequency agile microwave circuit applications have been investigated. A potentially cost-effective processing route has been used to make BST thick films from mixed-oxide powders. BST thick films have been press-formed in a single step onto alumina substrates from a viscous polymer tape. Films with thicknesses ranging from 10 to 140 μm have been obtained. The microstructure and dielectric properties of the BST thick films have been characterised. The results show that $Ba_{0.7}Sr_{0.3}TiO_3$ thick films exhibit ~20% tunability at room temperature under a DC bias field of 5.5 kV/cm. Possibilities for further improvements are discussed in terms of reducing the interactions between the BST films and alumina substrates.

Keywords: BST; Dielectric properties; Processing; Thick films

1. Introduction

Ferroelectric materials are potential candidates for application as the phase shifting element in phased array antennas and as tuning elements in devices operating at microwave frequencies.[1] Whilst much work in the past has been focused on antennas for military systems, one of the largest civilian applications is for adaptive, or steerable, antennas for mobile communication basestation applications and is thus of enormous current interest. Barium strontium titanate (BST) has recently been shown to have lower dielectric losses at room temperature and its realisation in thick film form means the applied voltages required for tunability can be dramatically reduced from kilovolts to 10–100 V.

This paper describes the processing and characterisation of thick film BST materials for microwave circuit applications. Thick film fabrication routes have the potential for cost effective mass production of planar electronic circuits and components. The effect of powder characteristics, composition and processing and sintering conditions on the microstructure and dielectric properties of the films are discussed and compared to equivalent materials produced in bulk form. The influence of the supporting substrate is also considered.

2. Experimental

$Ba_{1-x}Sr_xTiO_3$ ($x = 0.3-0.6$) powders were synthesised via a conventional solid-state reaction method from barium carbonate (Fluka, >99%), strontium carbonate (Fluka, >99%) and titania powders (Toho Titanium Company, >99.9%). After mixing and ball milling in acetone with zirconia media, the powders were calcined at a range of temperatures from 900–1150 °C. A Viscous Polymer Processing (VPP) method[2] was used to make BST ceramics and thick films using an aqueous polyvinyl alcohol (PVA) binder system. The detailed procedure for press forming the thick films was as follows: a VPP BST/PVA tape was first obtained using twin roll milling. BST green films were then formed by pressing the BST/PVA tape onto alumina or Pt-coated alumina substrates at pressures ranging from 40 to 100 MPa. Comparative bulk samples were cut from the tape. The green pellets and thick films were burnt out at 550 °C for 1 h and sintered at temperatures ranging from 1200 to 1450 °C for 2 h. The BST powders, ceramics and films were characterised using TG-DTA (Stanton Redcroft STA-780), particle size analysis (Coulter LS 130), X-ray diffraction (XRD, Philips

* Corresponding author. Tel.: +44-121-414-5237; fax: +44-121-414-7639.

E-mail address: t.w.button@bham.ac.uk (T.W. Button).

0955-2219/01/$ - see front matter
PII: S0955-2219(01)00330-2

X'pert) and scanning electron microscopy (SEM, Jeol 5410). Dielectric properties of BST ceramics and films were calculated from the capacitance measured at 1 kHz using an impedance analyser (Hewlett-Packard HP 4194A). An internal DC bias of up to 40 V was used to change the electric field during the measurement.

3. Results and discussion

3.1. Synthesis and characterisation of BST powders

Fig. 1 shows the typical TG–DTA data for the carbonate and oxide precursors used for BST synthesis and indicates that the temperature for complete decomposition of the carbonates is ~1050 °C. However, the XRD results shown in Fig. 2 indicate that the calcining temperature should be at least 1150 °C for the formation of phase-pure BST when calcining for 2 h. Even at 1100 °C, a small amount of impurity phase is still visible (see arrows in Fig. 2).

The morphology and particle size distribution of a typical BST powder are shown in Figs. 3 and 4 respectively. It can be seen that the particle size distribution of the BST powder derived from the solid-state reaction is bimodal with the mean particle size of 1 μm, which is in agreement with the SEM results.

3.2. Microstructure and dielectric properties of BST thick films

Fig. 5 shows the relationship between the forming pressure and film thickness for pressed formed BST films. Adherent, crack-free BST films with thicknesses between 10 and 140 μm have been obtained on alumina substrates via this novel processing route. The film thickness is much larger when films are press formed on Pt-coated alumina substrates compared to films on alumina substrates. This is due to the larger roughness of the Pt coating. It has been reported that the squeeze flow of films is dependent not only on the rheology of the paste but also on the roughness of the substrates.[3] The larger roughness requires a higher pressure to facilitate the film flow.

XRD patterns of $Ba_{1-x}Sr_xTiO_3$ thick films sintered at 1300°C for $x = 0.3-0.6$ are shown in Fig. 6. The crystal

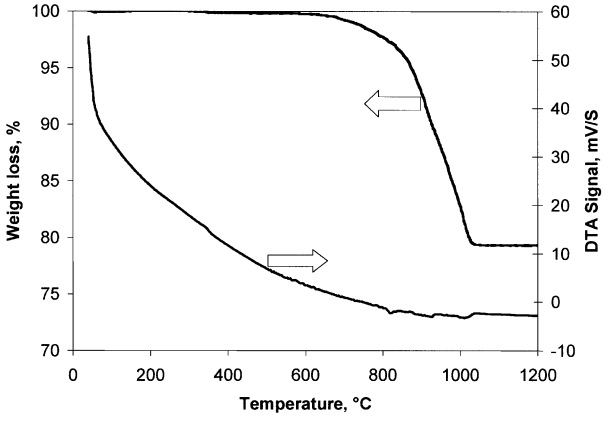


Fig. 1. A typical TG–DTA curve for BST precursors.

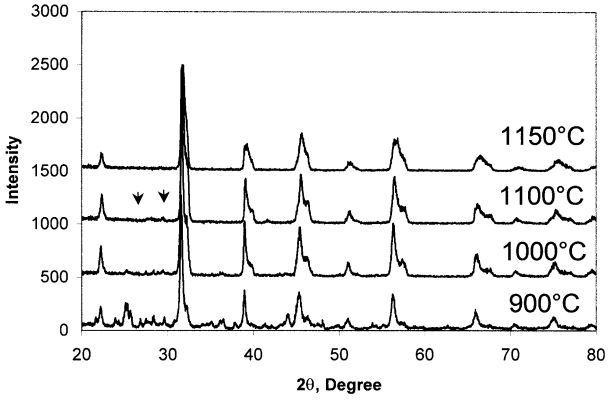


Fig. 2. XRD patterns for $Ba_{0.6}Sr_{0.4}TiO_3$ powders after calcining at temperatures from 900–1150 °C.

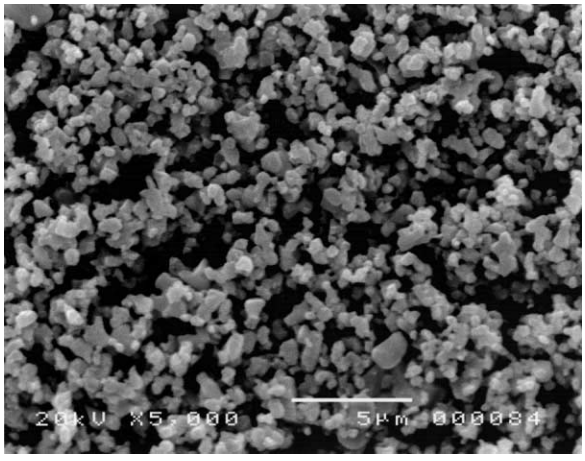


Fig. 3. SEM micrograph of a typical BST powder calcined at 1150 °C for 2 h.

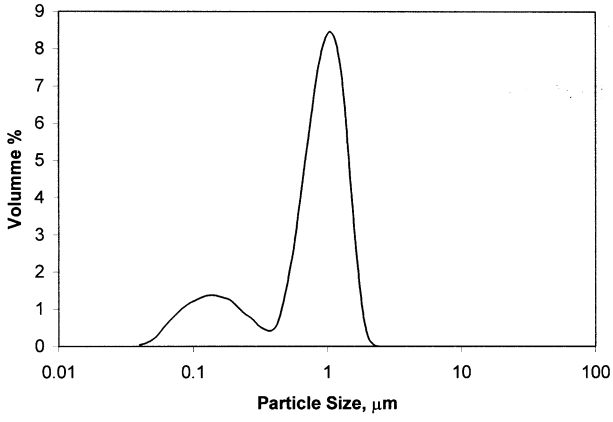


Fig. 4. Particle size distribution of a calcined BST powder.

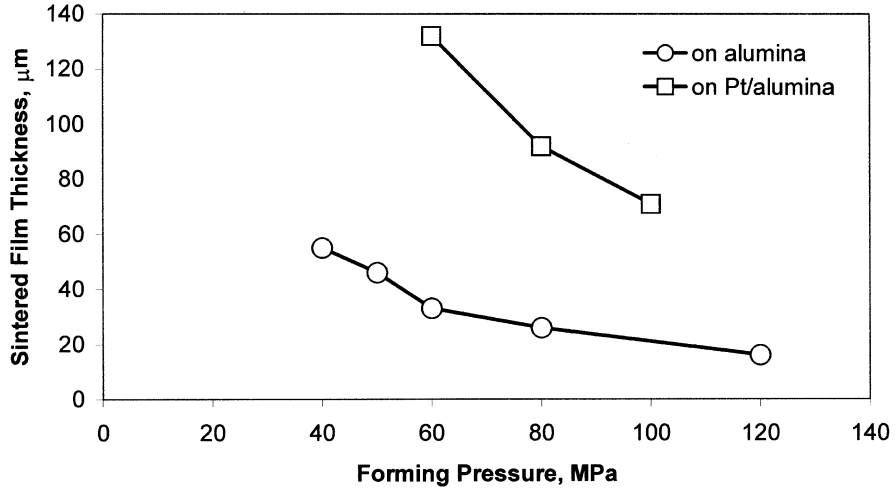


Fig. 5. Typical relationship between forming pressure and film thickness for BST films on alumina and Pt-coated alumina substrates.

structures are cubic for the investigated composition range. The unit cell parameters have been calculated and plotted in Fig. 7. It can be seen that the unit cell volume increased linearly with the Ba content, which is attributed to the larger ionic radius of Ba compared to that of Sr. At sintering temperatures above 1250 °C, interactions between the BST films and alumina substrates were observed. The inter-diffusion of Ba, Sr and Al ions will lead to the disruption of the BST solid solution and the formation of secondary phases and this has been discussed in more detail elsewhere.[4]

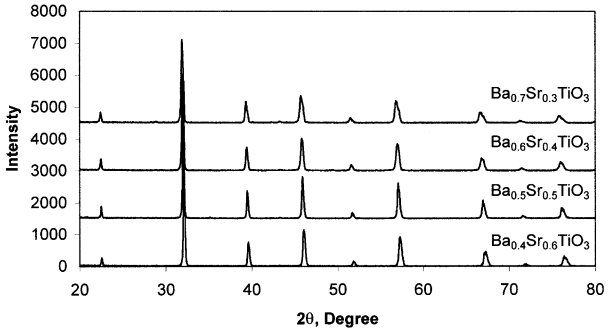


Fig. 6. XRD patterns for $Ba_{1-x}Sr_xTiO_3$ thick films sintered at 1300 °C for 2 h with $x = 0.3-0.6$.

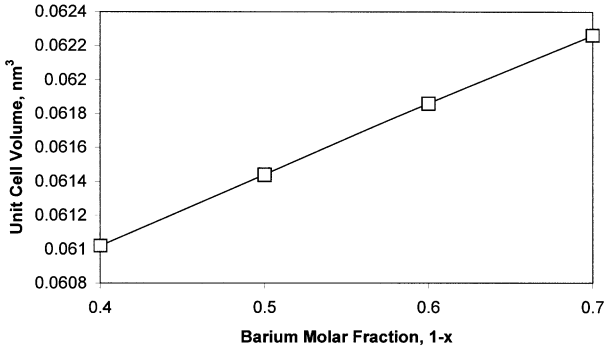
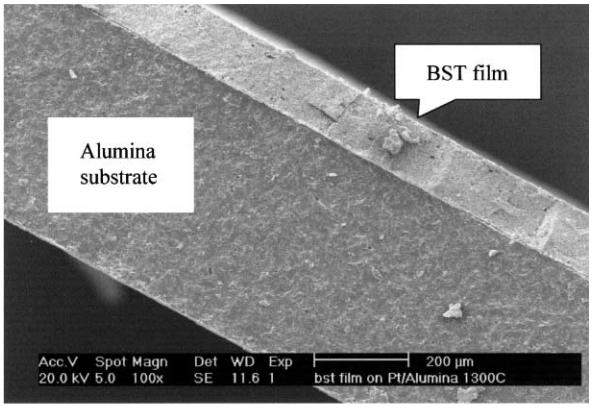
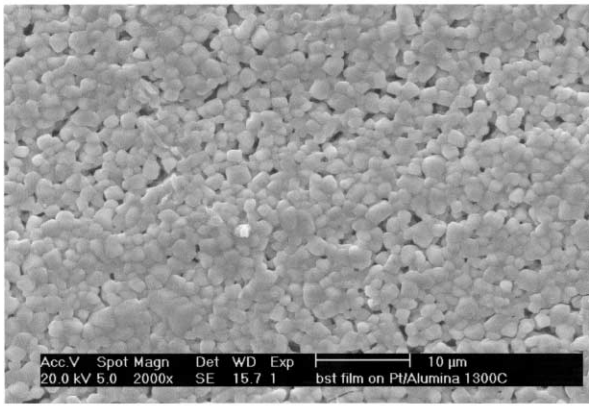


Fig. 7. The unit cell volume (a3) versus Ba content in $Ba_{1-x}Sr_xTiO_3$.

Fig. 8 shows the microstructure of BST films sintered at 1300 °C for 2 h. At this temperature, no visible interactions were observed between the BST films and alumina substrates with a Pt coating. However, the film is not fully dense and the grain size is ~1–2 μm.



(a) Cross section



(b) Film surface

Fig. 8. SEM micrographs of $Ba_{0.6}Sr_{0.4}TiO_3$ thick films sintered at 1300 °C for 2 h, (a) cross-section, (b) film surface.

The dependence of the dielectric properties on DC bias field of the BST thick films is shown in Fig. 9(a). The response of permittivity (P) with DC bias field is different at room temperature for different Ba/Sr ratios. The tunability calculated using $(P_{\text{zero bias}} - P_{\text{DC bias}})/P_{\text{zero bias}} \times 100\%$ for BST thick films ranges from 3.2 to 20.6% under a DC bias of 550 V/mm at room temperature, increasing with the increase of Ba molar fraction [see Fig. 9(b)]. It is well known that the dielectric properties of ferroelectric ceramics are temperature dependent with the permittivity reaching a maximum at the Curie temperature. Liou and Chiou reported a linear relationship between Curie temperature and Sr molar fraction in BST ceramics and maximum changes in permittivity with DC bias field also occurring at Curie temperature.[5] From their results, the Curie temperature for BST ($x = 0.3$) was ~20 °C, which is in agreement with the results shown in Fig. 8, where the tunability at room temperature is highest for the $Ba_{0.7}Sr_{0.3}TiO_3$ composition. Further improvement should still be possible as we found that the dielectric properties of the BST thick films were inferior to their ceramic counterparts, especially for BST ceramics with higher Ba content (e.g. $x = 0.3$) as shown in Fig. 10. This is mostly attributed to the constraining effect of the substrates during sintering, resulting in a less dense structure as shown in Fig. 8(b). However, severe interactions between BST films and alumina substrates took place when the sintering temperature was increased above 1250 °C unless a buffer layer was applied. Another possible solution was to increase the sintering density of the films at low temperatures by using a sintering aid. Preliminary results showed that improved dielectric properties were obtained when BST films were sintered at lower temperatures using B_2O_3 as a sintering aid.[4]

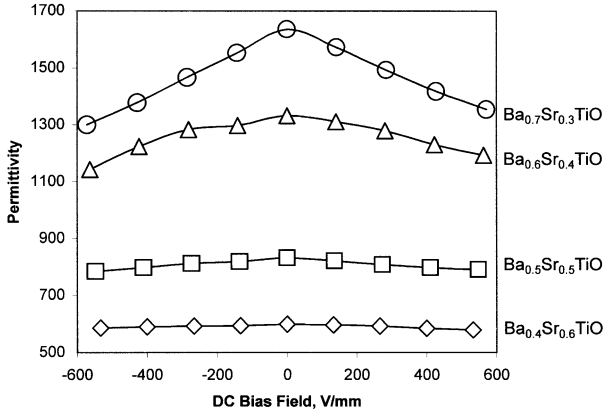


Fig. 9. Permittivity versus DC bias field (a) and room temperature tunability (b) for $Ba_{1-x}Sr_xTiO_3$ thick films sintered at 1300 °C for compositions $x = 0.3-0.6$).

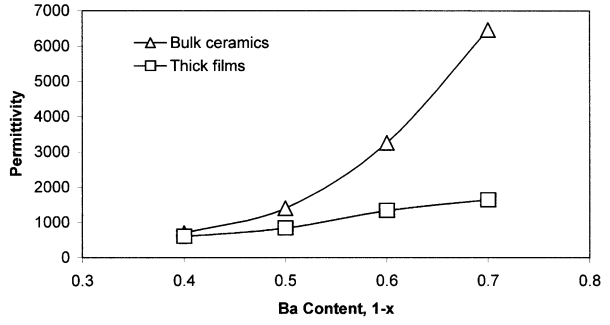


Fig. 10. Comparison of permittivity of $Ba_{0.7}Sr_{0.3}TiO_3$ thick films and bulk ceramics sintered at 1300 °C for 2 h.

4. Conclusions

A potentially cost-effective processing route has been used to make BST thick films with thicknesses ranging from 10–140 μm. The processing involves press forming a plastic BST/polymer tape onto an alumina substrate. About 20% tunability has been achieved for the $Ba_{0.7}Sr_{0.3}TiO_3$ thick films sintered at 1300 °C for 2 h under a DC bias field of 5.5 kV/cm. The room temperature tunability of the BST films increases with the Ba content in BST composition. However, when the sintering temperature is above 1250 °C, interaction between BST films and alumina substrates has been found. Possible improvements include lowering the sintering temperature by using a sintering aid or applying a buffer layer between the BST films and alumina substrates to minimise inter-diffusion.

Acknowledgements

The financial support from EPSRC and technical assistance from C. Meggs and other members of Functional Materials Group are gratefully acknowledged.

References

1. Sengupta, L. C. and Sengupta, S., Novel ferroelectric materials for phased array antennas. *IEEE Trans. Ultrasonics, Ferroelectrics, and Frequency Control,* 1997, **44**(1), 792–797.

2. Pearce, D. H., Dolman, G., Smith, P. A. and Button, T. W., Colloidal processing of lead zirconate titanate (PZT). In *Proceedings of the International Conference on Electronic Ceramics and Applications, Electroceramics* V, 2–4 September Aveiro, Portugal. Fundação João Jacinto de Magalhães, Aveiro, 1996, Book 2, pp. 385–388.
3. Oliver, D. R. and Huang, X., Squeeze film testing of ceramic pastes. *Br. Ceram. Trans.*, in press.
4. Su, B. and Button, T. W., Interactions between barum strontium titanate (BST) thick films and alumina substrates. *J. Eur. Ceram. Soc.*, 2001, **21**(15), 2777–2781.
5. Liou, J. W. and Chiou, B. S., Effect of direct-current biasing on the dielectric properties of barium strontium titanate. *J. Am. Ceram. Soc.,* 1997, **80**(12), 3093–3099.