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Journal of the European Ceramic Society 23 (2003) 2699–2703

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Dielectric and microwave properties of barium strontium titanate (BST) thick films on alumina substrates

B. Su*, J.E. Holmes, C. Meggs, T.W. Button

IRC in Materials Processing, School of Engineering, University of Birmingham, B15 2TT, UK

Abstract

The dielectric and microwave properties of barium strontium titanate (BST) thick films on alumina substrates have been investigated. The BST films were screen printed and sintered at temperatures below 1300 °C. At temperatures below the Curie point the BST films exhibit tunability in the range 15–35% under a DC bias field of 2 kV/mm. The dielectric loss is critically dependent on film thickness with lower losses ($<10^{-2}$) for the thicker films (>100 μm). A relaxation process appears to take place for the BST films in the MHz to GHz frequency regime. The variation of permittivity with bias field exhibits hysteretic behaviour in both the ferroelectric and paraelectric regions. This is believed to arise due to the non-uniform composition and existence of micro/nano-polar phases in the films.

Keywords: Films; Dielectric properties; Hysteresis; Microwave; Relaxation; Tunability; (Ba,Sr)TiO_3

1. Introduction

Ferroelectric materials have shown great promise for microwave applications as tunable devices.[1] Barium strontium titanate, $Ba_xSr_{1-x}TiO_3$, (BST) are the most extensively investigated materials to date because of their high tunability and low dielectric losses at room temperature.[2] BST thick films have recently been investigated as candidates for such applications because of the potential benefits of lower fabrication costs compared to thin film forms.[3–5] Thick films are also expected to possess similar dielectric properties to their bulk analogues while only needing relatively small DC bias voltages to achieve large tunability. Alumina is a commonly used substrate in microwave devices because of its low permittivity and low cost. However, our early studies showed that BST films are very reactive with alumina substrates at sintering temperatures above 1300 °C.[6] Therefore, for the BST films deposited on alumina substrates, the sintering temperature is limited to below that required to achieve full density. Nevertheless, the initial results show that the films, even though not fully densified, still possess good tunability, and therefore are potentially useful for tunable applications. This paper reports the dielectric and microwave properties of these 'porous' BST films. The possible origins of the tunability and relaxation behaviour with temperature and frequency are discussed.

2. Experimental

BST thick films with composition of Ba/Sr = 50/50, 60/40 and 70/30 ($x = 0.5$, 0.6 and 0.7, respectively) have been fabricated on 96% alumina substrates using a conventional screen printing method. The ink was prepared by combining BST powders produced via a solid state route together with a commercial vehicle (Blythe 6321 Medium) at a solids loading of 40 vol.%. When required, bottom electrodes (between the substrate and BST film) and top electrodes (on the top surface of the BST film) were also screen printed using platinum and silver pastes respectively, using sintering conditions of 1400 °C/2 h for the platinum and 850 °C/10 min for the silver. The BST films were sintered at temperatures from 1200 to 1300 °C for 2 h at a ramp of 2 °C/min.

The dielectric properties of the films were characterised using an impedance analyser (HP 4914A) with a metal-ferroelectric-metal (MFM) capacitor configuration at

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* Corresponding author. Tel.: +44-121-414-7840; fax: +44-121-414-7890.

E-mail address: b.su@bham.ac.uk (B. Su).

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doi:10.1016/S0955-2219(03)00171-7

frequencies from 100 Hz to 1 MHz and over the temperature range from −70 to 70 °C. The tunability of the films were measured at 10 kHz with an internal bias up to 40 V and calculated from $1-\varepsilon(V)/\varepsilon(0)$, where $\varepsilon(V)$ and $\varepsilon(0)$ is the permittivity with bias V and without bias respectively. The microwave properties of films without electrodes were characterised at room temperature using the split post method[7] and a network analyser (HP 8720A) at frequencies from 1 to 3 GHz. As these films had no electrodes the tunability was unable to be measured at microwave frequencies.

3. Results and discussion

3.1. DC bias effect

The variation of permittivity with temperature and DC bias voltage for films of the three BST compositions is shown in Fig. 1. Two distinct stages are observed for all the films. In the paraelectric (PE) region, both the permittivity and tunability increase as the temperature approaches the Curie point (T_c) of the ceramics; both become flatter in the ferroelectric (FE) region. Tunability in the FE region ranges from 15 to 35%, depending on the film composition, which is useful for most of the applications. It is believed that dielectric tuning can be achieved in two principal ways. In the PE region, dielectric tuning is achieved via a field-induced hardening of the soft phonon whereas in the FE region, tuning is achieved through polar reorientation.[8]

Good temperature stability in the FE region is believed to result from the low temperature sintering of the films which causes compositional inhomogeneity and thus a diffuse Curie transition. Previous work using differential scanning calorimetry (DSC)[9] showed that no latent heat associated with phase transition was detected for the BST films sintered below 1300 °C. This indicates that the films do not contain any regions with a sharply defined phase transition temperature. The compositions are presumed to be inhomogeneous.[10] This is also confirmed in the dielectric results where diffuse transitions are observed for both BST bulk ceramics and thick films sintered below 1300 °C. However, large differences between the ceramics and films are observed in terms of the increase of permittivity with the sintering temperature. For the BST films, the measured permittivity is significantly lower than bulk ceramics sintered at the same temperature and also does not show a large dependence on the sintering temperature. This could indicate a strong clamping effect in thick films due to the substrate constraint during sintering which may result in a lower sintered density and higher residual stress.

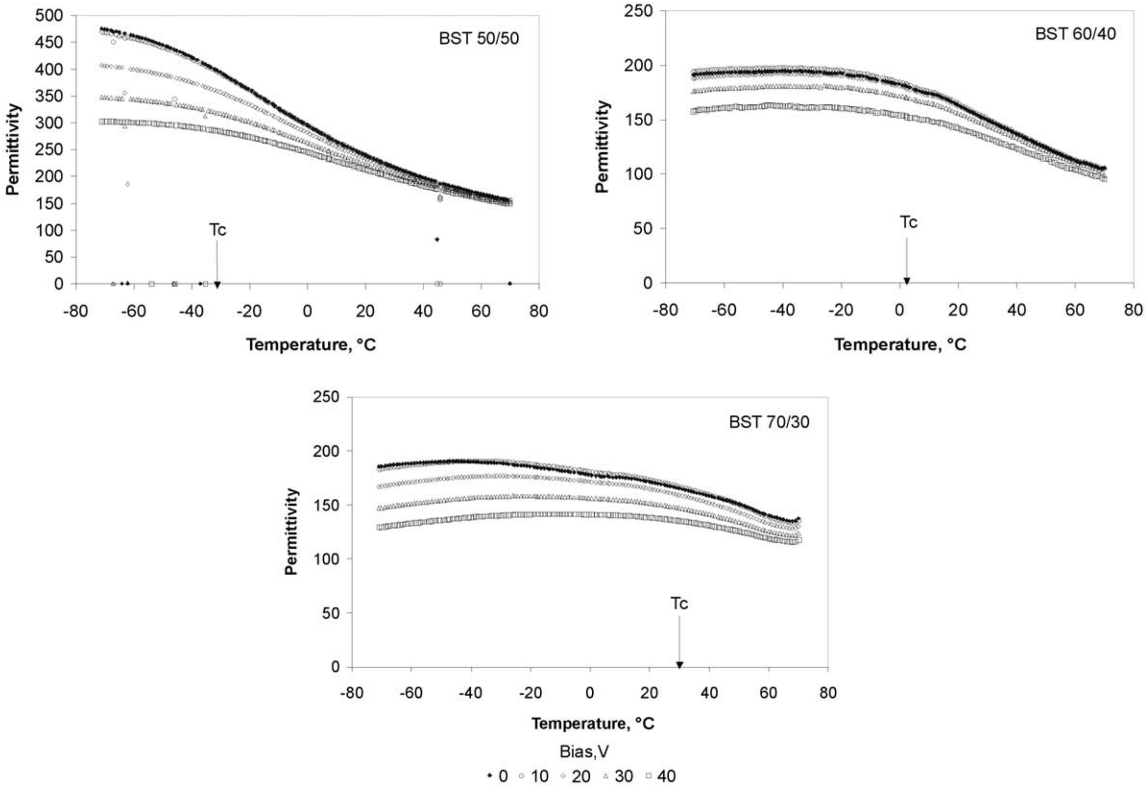

Fig. 1. Permittivity of the BST films with different compositions under DC bias voltages over temperature ranging from −70 to 70 °C.

3.2. Film thickness effect

Film thickness has a dramatic effect on the low frequency permittivity and losses of the BST films as shown in Fig. 2. For the thicker films (>100 µm), the permittivity is >1000 and the dielectric loss is generally <0.01, but for films with thickness of 20 µm, the permittivity is much lower (<300) and the dielectric loss is generally >0.01. This may indicate that the substrate constraint and/or interfacial losses predominate in the overall losses for the thinner films, which is similar to that reported in thin films.[11]

3.3. Frequency effect

The frequency dependence of the permittivity at room temperature for the BST films measured using the impedance analyser and split post methods is shown in Fig. 3. There is a significant decrease in permittivity from megahertz to gigahertz frequencies. This may indicate a relaxation process which has been observed in most ferroelectric ceramics and thin films.[12] The dielectric loss (not shown in the figure) is of the order of 10^{-2} in both the MHz and GHz ranges. Kazaoui et al have measured a relaxation frequency (f_r) for the BST 70/30 ceramic to be 450 MHz.[13] The origins of such high frequency relaxations are still not completely clear. Relaxation was first believed to be attributed to the piezoelectric resonance of the domains resulting from piezoelectric deformations of the polarised domains in an alternating electric field.[14] In a polydomain ferroelectric single crystal or ceramic, the dielectric response between MHz and GHz frequencies was suggested to be dominated by the piezoelectric resonance of the individual domains.[15] The domain width for perovskite ferroelectric single domain particles is of the order of 0.2 µm.[16] A typical microstructure of the BST films is shown in Fig. 4. The grain sizes range from 0.5 to 3 µm. Therefore, a relaxation process related to domain walls is considered likely to occur at microwave frequencies, especially for BST 70/30 composition whose T_c is around room temperature. However, a similar relaxation phenomenon has also been observed for the BST 50/50 composition whose T_c is around -30 °C. At room temperature this material is in the paraelectric phase and thus any relaxation originated from the domain wall contribution should be minimal. Only dielectric relaxation should remain above the T_c. An alternative theory based on the effect of the hopping of off-centred ferroelectric ions has also been proposed.[17] The relaxing dipoles were

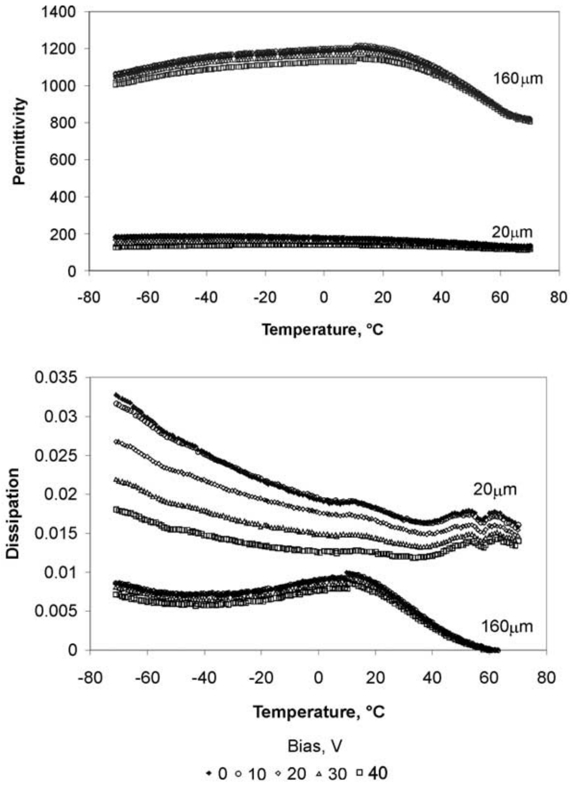

Fig. 2. Permittivity of two BST 70/30 films with different thickness (20 and 160 µm) under DC bias voltages over temperature ranging from −70 to 70 °C.

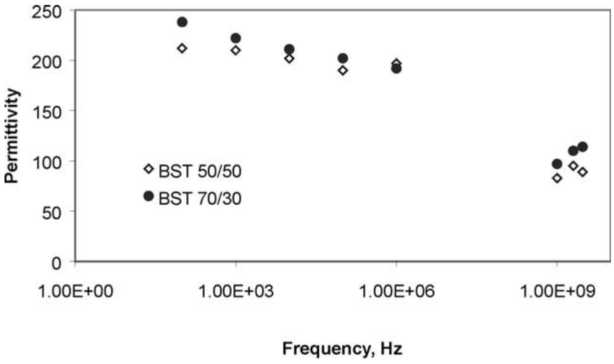

Fig. 3. Dependence of the permittivity of BST 50/50 and BST 70/30 films on frequency.

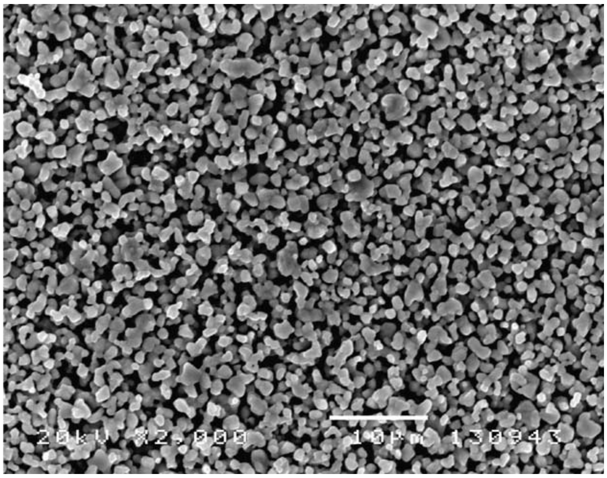

Fig. 4. SEM micrograph of a BST film sintered <1300 °C.

ascribed to chains of active ferroelectric ions (Ti^{4+} in BST) which are displaced from the centre of the oxygen octahedra. The microscopic dipolar moments which appear may lead to a dielectric relaxation when an external electromagnetic field is applied to induce a macroscopic microwave frequency dispersion. Contributions from defects, cationic and anionic vacancies, heterogeneities and residual stresses in the films may also be significant. This may be the case for BST films sintered at low temperatures.

3.4. Hysteresis effect

Fig. 5 shows the dependence of permittivity and dielectric loss of a BST 50/50 film (the T_c of the film is ca. −30 °C) on DC bias voltage measured in different temperature regions. In the FE region (−40 °C), both the permittivity and dissipation are decreased as the DC bias field is increased. A 'butterfly' hysteresis loop is observed, which is typical for ferroelectrics owing to the domain wall motion during the switching of polarisation. The dissipation is also suppressed due to the 'fixing' of the polarisation upon application of an external electric field. In the PE region (25 and 60 °C), it is surprising to note that the permittivity still shows a hysteresis loop though the magnitude becomes smaller as the temperature shifts from the FE region to the PE region. However, the dissipations are very low (10^{-3}) because of the absence of domain wall contributions to the overall loss. These results clearly indicate that micro- or nano-polar phases may be present in both the FE and PE regions. The dielectric tuning of the BST films in the PE region is not solely achieved via a field induced hardening of the soft phonon, contributions from the reorientation of micro/

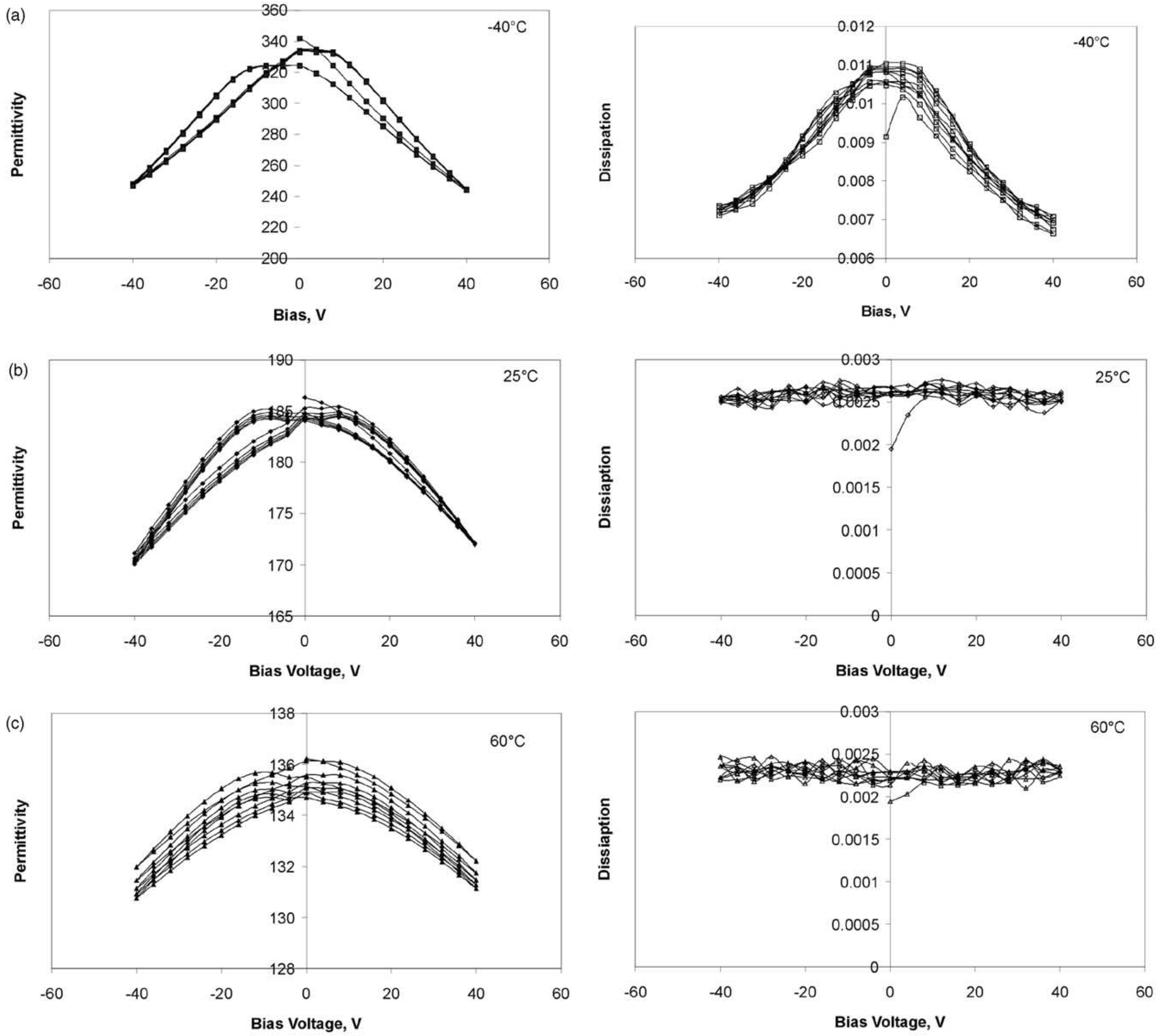

Fig. 5. Permittivity and dissipation of the BST 50/50 film with DC bias cycles measured at (a) −40 °C; (b) 25 °C and (c) 60 °C.

nano-polar phases are also possible. There have been some reports from recent studies that ordered micro-domains or nano-polar phases exist in the BST thin films.[8,18] Whether this has been the case for the BST thick films is the subject for further investigation.

4. Conclusions

The BST films on alumina substrates sintered at temperatures <1300 °C exhibit stable tunability behaviour (15–35%) under a DC bias field of 2 kV/mm below the Curie point. The permittivity and dielectric loss is critically dependent on film thickness with lower losses ($<10^{-2}$) for the thicker films (>100 μm). A relaxation process appears to take place in the MHz to GHz frequency range and the BST films exhibit hysteresis under the DC bias field in both PE and FE regions, which may be attributed to the nano/micro-polar phases present in the films.

Acknowledgements

The authors wish to acknowledge the financial support from EPSRC (GR/M88952) and European Commission (IST-2000-30162).

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