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Interactions between barium strontium titanate (BST) thick films and alumina substrates

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Abstract

Barium strontium titanate (BST) thick films have been prepared on alumina substrates using a novel press forming route. The effect of the sintering temperature on the microstructure and dielectric properties of the films has been investigated. Severe interactions between the BST films and alumina substrates has been observed for sintering temperatures $>1250\ ^{\circ}C$, with Ba and Sr ions diffusing into the substrates. The counter-diffusion of Al ions into the films resulted in the formation of strontium aluminate and the destabilisation of the BST solid solution. The use of B_2O_3 as a sintering aid and MgO as a buffer layer is also reported and discussed. MgO is shown to be effective in preventing inter-diffusion between the films and substrates and, although B_2O_3 is effective in reducing the sintering temperature and improving the dielectric properties of the films, it is not compatible with the current thick film processing route.

Keywords: Alumina substrates; BST films; Inter-diffusion

1. Introduction

Barium strontium titanate (BST) ferroelectric materials are considered good candidates to make frequency or phase agile microwave devices such as resonators and phase shifters due to their tuneable dielectric properties under a DC bias field and low dielectric loss over a wide frequency range. Polycrystalline alumina is a universal substrate material for electronic circuits as it possesses low microwave loss, good thermal conductivity and high mechanical strength and is readily available at low cost. For commercial applications, BST thick films on low-cost substrates are the preferred choice because this can overcome the problems of the large dielectric loss observed in thin films and the high voltages required to bias bulk substrates. Several techniques have been used to make thick films such as screen printing, tape casting and modified sol-gel spin coating.[1] However, the fabrication of films with thickness $>10\ \mu m$ remains problematical. A simple plastic forming technique has been developed recently for the fabrication of thick films with thicknesses in the range 10–150 μm.[2] Only a single step is needed to make films by the press forming of a viscous polymer processed ceramic tape. In this paper, the interactions between BST films and alumina substrates are reported. Possible routes to improve the film-substrate compatibility are discussed.

2. Experimental

A conventional solid-state reaction route was used to synthesis $Ba_{0.6}Sr_{0.4}TiO_3$ powders from barium carbonate (Fluka, 99%), strontium carbonate (Fluka, 99%) and titanium oxide (Toho Titanium Company, 99.9%). After mixing and ball milling, BST powders were obtained by calcining at 1150 °C for 2 h. BST tapes were prepared by twin-roll milling an aqueous viscous polymer processing (VPP)[3] formulation and these were then press-formed onto a 96% alumina or Pt-coated alumina substrate. The film thickness was controlled by the pressure and the VPP formulation. After debinding, the green films were sintered at different temperatures from 1200 to 1400 °C for 2 h. In an attempt to improve the properties of the films sintered at low temperatures, 0.5 wt.% B_2O_3 was added to the BST powder to act as a sintering aid. Conventional dry pressing and screen printing were used to make B_2O_3-doped BST ceramics and thick films because of the instant crosslinking experienced between the B_2O_3 and the PVA polymer binder used in the VPP formulation. MgO buffer layers were also applied to some alumina substrate by screen

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printing in an attempt to minimise any substrate-film interactions. The microstructure and the interfacial reaction of the films were investigated using scanning electron microscopy with an EDS attachment (Jeol 6300) and X-ray diffraction (Philips X'pert). Dielectric properties of the BST ceramics and films were calculated from the capacitance measurements using an impedance analyser (Hewlett-Packard HP 4194A).

3. Results and discussion

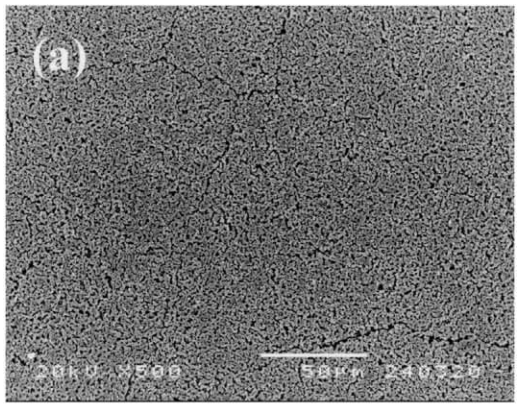
3.1. Interactions between BST films and alumina

Fig. 1 shows the SEM micrographs of the BST films sintered at temperatures from 1200 to 1400 °C. The corresponding XRD patterns are shown in Fig. 2. At a sintering temperature of 1200 °C, the film has low sintered density with small grain size (~1 μm). As the temperature was increased to 1300 °C, the grain size increased to 2–5 μm and some needle-like grains appeared. The XRD data indicate that the main phase of the film was still cubic BST (see Fig. 2). When the sintering temperature was increased to 1400 °C, however, the film morphology changed to a plate-like grain structure and a mixture of strontium aluminate, barium titanate and strontium titanate phases were observed by XRD (Fig. 2), implying that severe interactions have taken place between the films and the substrates.

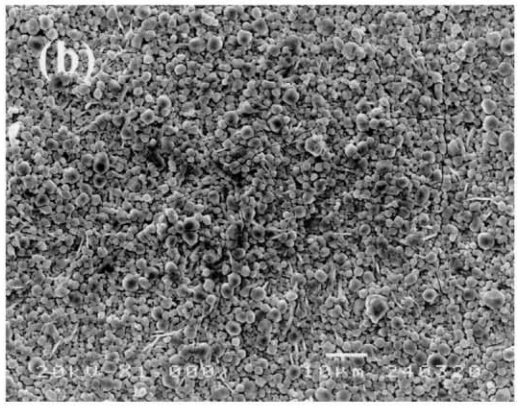
EDS analysis was performed on polished cross-sections of the films. It has been found that the highly electropositive Ba^{2+} and Sr^{2+} ions start to diffuse into the alumina substrates at a sintering temperature of 1250 °C. As the sintering temperature increases, the Ba and Sr diffusion distance in the alumina substrates, as estimated by the EDS analysis, increases rapidly (Fig. 3). In addition, EDS analysis also confirmed that Al^{3+} ions diffused into BST films as the sintering temperature was increased to 1400 °C, in agreement with the XRD results where strontium aluminate was found (see Fig. 2). Similar results have been reported in YBCO thick films on alumina substrates.[4] In the alumina substrates, both Sr and Ba peaks were detected. The inter-diffusion between BST films and alumina substrates when sintered at higher temperatures will lead to the disruption of the BST solid solution and, in turn, result in the degradation of dielectric properties of BST films.

3.2. Effect of sintering aid

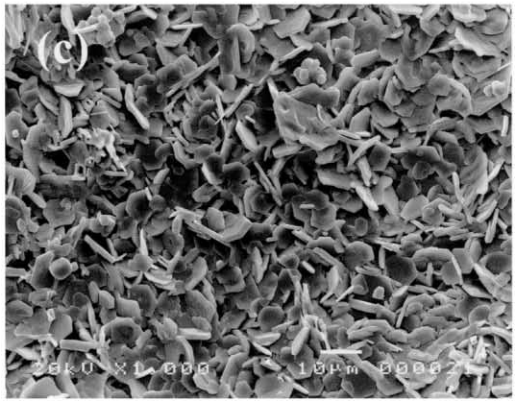
One way to reduce the inter-diffusion between BST films and alumina substrates is to lower the sintering temperature of the BST films. Rhim et al. recently reported that the addition of B_2O_3 could effectively reduce the sintering temperature of BST ceramics without significantly decreasing the dielectric properties of BST ceramics.[5] Fig. 4 shows the sintered density at various sintering temperatures for BST ceramics with and without B_2O_3 as a sintering aid. B_2O_3 seems an effective sintering aid for BST ceramics. At 1200 °C, over 90% of theoretical density could be achieved for the BST ceramic with the sintering aid. In comparison, the sintered density of the BST ceramic without the sintering aid is only ~65% of the theoretical. The comparison of the dielectric properties of the BST ceramics is shown in



(a) 1200°C



(b) 1300°C



(c) 1400°C

Fig. 1. SEM micrographs of BST films on alumina substrates sintered at temperatures of (a) 1200, (b) 1300 and (c) 1400 °C.

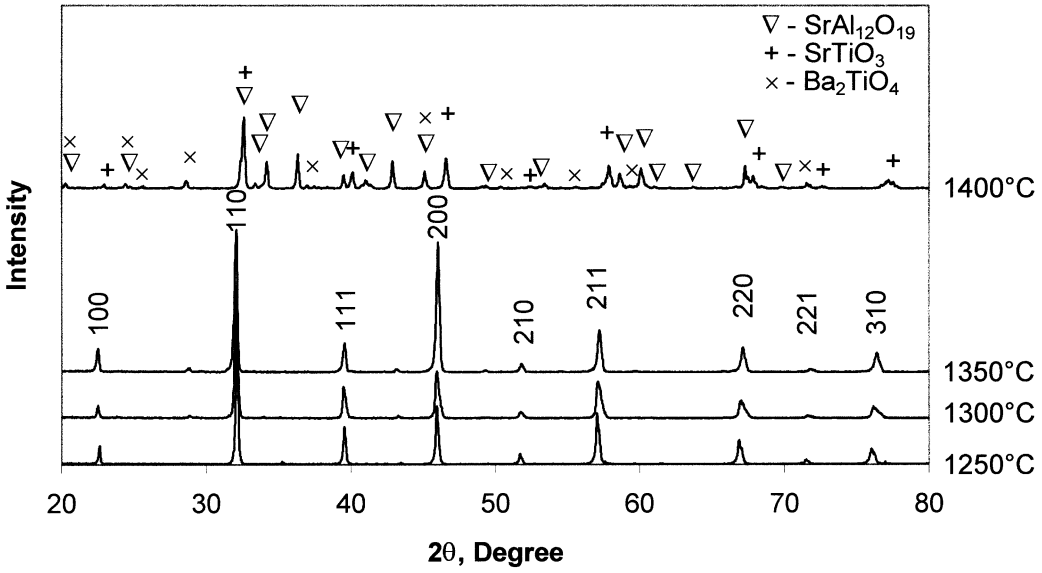


Fig. 2. XRD patterns of BST films sintered at temperatures from 1250–1400 °C.

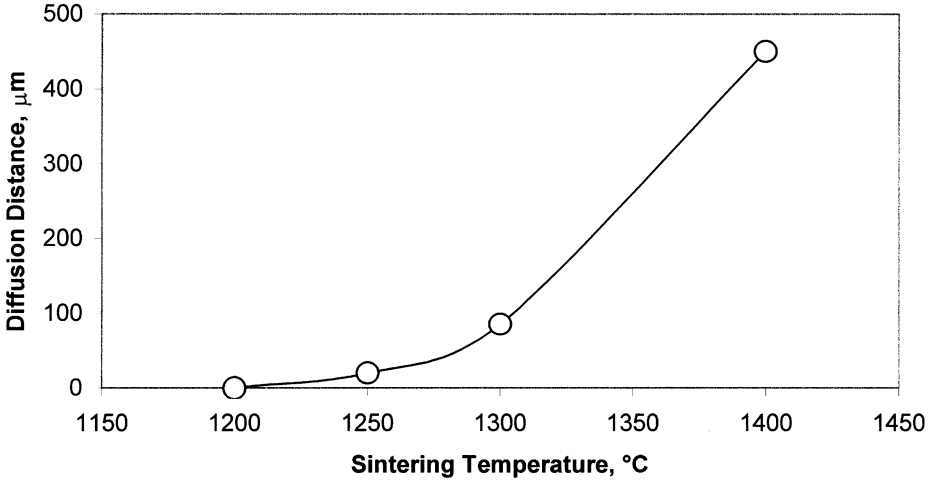


Fig. 3. Ba and Sr ions diffusion distance in the alumina substrates (estimated from EDS analysis) versus sintering temperature of the BST films.

Fig. 5. It can be seen that at temperatures <1300 °C, the presence of the sintering aid results in improved dielectric properties (lower dissipation and higher permittivity). At temperatures >1300 °C, the ceramics without the sintering aid exhibit better properties. However, it was found that the VPP technique cannot be employed to make BST thick films with the addition of B_2O_3. Hydrolysed B_2O_3, which produces H_3BO_3, is a strong crosslinking agent for PVA,[6] and instant crosslinking occurred during the VPP fabrication route resulting in gelling of the

Table 1
Dielectric properties (25 °C, 1 kHz) of BST ceramics and films produced using dry pressing and screen printing technique sintered at 1200 °C for 2 and 7 h

	Permittivity		Dissipation	
	1200 °C/2 h	1200 °C/7 h	1200 °C/2 h	1200 °C/7 h
BST ceramics without B_2O_3	950	2126	0.115	0.425
BST ceramics with B_2O_3	1272	3412	0.081	0.205
BST films without B_2O_3	559	613	0.603	0.534
BST films with B_2O_3	764	736	0.627	0.615

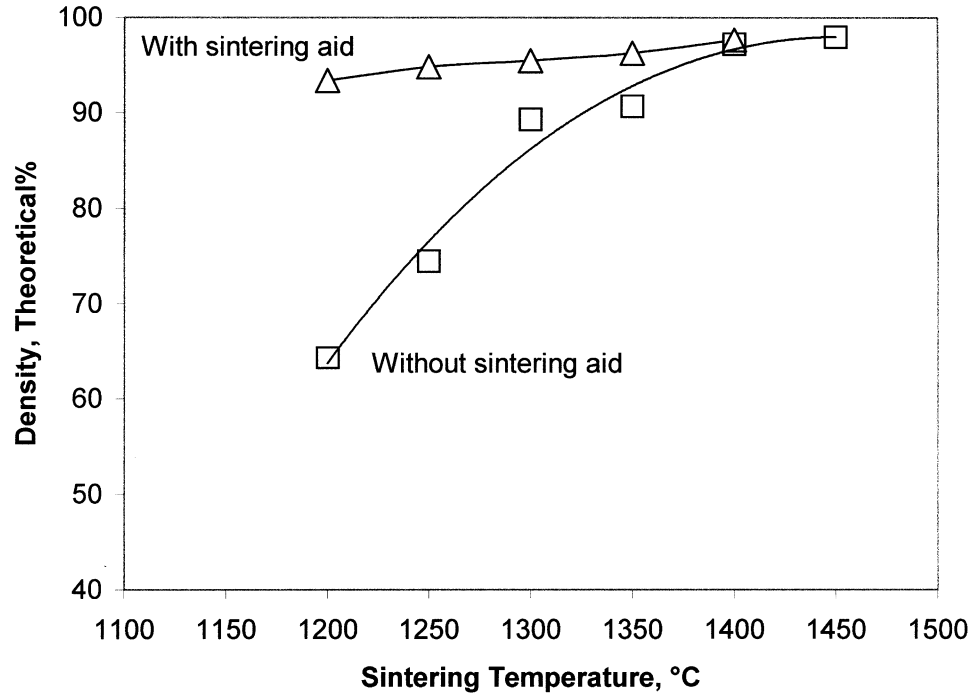


Fig. 4. Sintering density of BST ceramics sintered at temperatures from 1200 to 1400 °C with and without 0.5 wt.% B_2O_3 as a sintering aid.

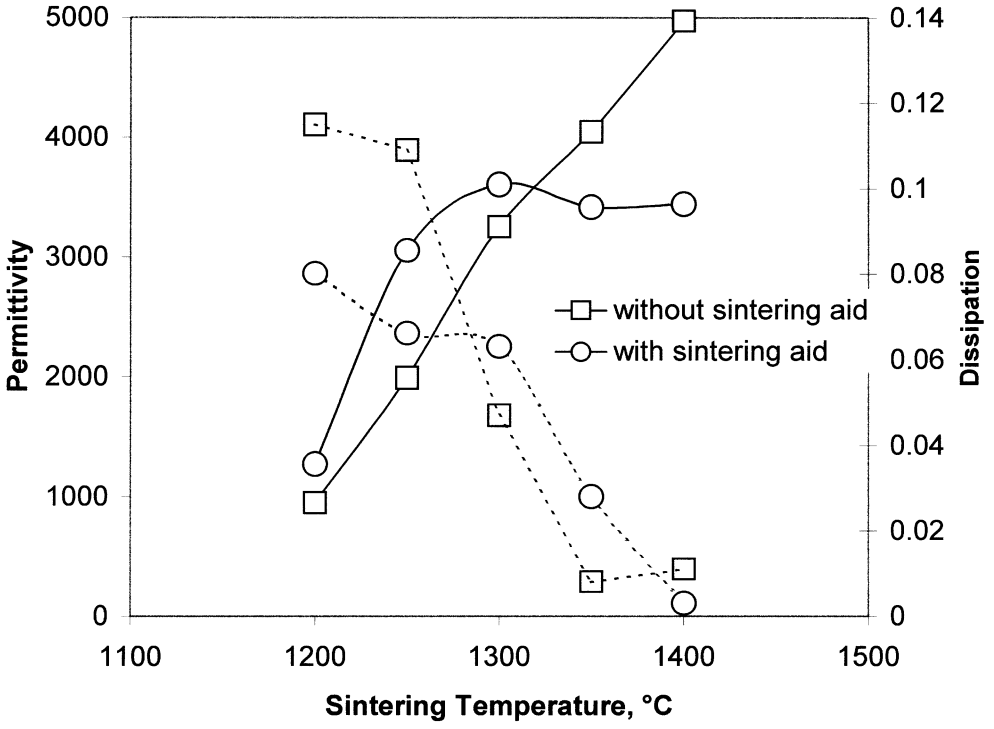


Fig. 5. Permittivity (solid line) and dissipation (dashed line) for BST ceramics with and without B_2O_3 sintering aid sintered at temperatures from 1200 to 1400 °C for 2 h.

ceramic paste. Therefore, polymer-free processing has to be used to make BST films with B_2O_3 addition. Table 1 lists the dielectric properties of the BST films and ceramics with and without B_2O_3 sintered at 1200 °C for times of 2 and 7 h. A 35% increase of permittivity was observed for BST films sintered at 1200 °C for 2 h, probably due to the improved densification of the films with B_2O_3 addition. No significant improvement was found when the sintering time was increased to 7 h for films in contrast to that observed for the bulk ceramics.

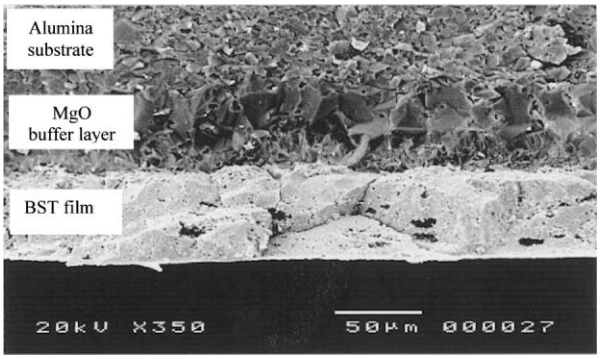


Fig. 6. SEM micrograph of cross-section of a BST film sintered at 1300 °C on an alumina substrate with MgO as a buffer layer.

The densification process of the films is thought to be retarded by the constraint of the substrates.

3.3. *Effect of buffer layer*

Another way to reduce the interactions between BST films and alumina substrates is to incorporate some form of buffer layer between them. MgO has been reported to be an effective buffer layer on alumina substrates for the deposition of thick films containing alkaline earth elements owing to its refractory character and compatibility with alumina.[7] Fig. 6 shows the SEM micrographs of cross-section of films with a screen-printed MgO buffer layer. No inter-diffusion was detected from EDS analysis. However, MgO layers produced by screen printing need to be sintered at very high temperature (e.g. 1600 °C), which can cause the alumina substrates to distort, thus making subsequent film deposition more difficult.

4. Conclusions

Barium strontium titanate (BST) thick films have been prepared on alumina substrates. Severe interactions between the BST films and alumina substrates have been observed for sintering temperatures >1250 °C, with Ba and Sr ions diffusing into the substrates. The counter-diffusion of Al ions into the films resulted in the formation of strontium aluminate and the destabilisation of the BST solid solution. The use of B_2O_3 as a sintering aid and MgO as a buffer layer has been investigated to reduce these detrimental effects. MgO is shown to be effective in preventing inter-diffusion between the films and substrates, but a low temperature deposition method is needed. Although B_2O_3 is effective in reducing the sintering temperature and improving the dielectric properties of the films, it is not compatible with the current thick film processing route where the PVA polymer binder undergoes crosslinking instantly in the presence of B_2O_3.

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