

The effect of Mn on the microstructure and properties of BaSrTiO₃ with B₂O₃–Li₂CO₃

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Abstract

Integration of ferroelectric tunable components into dielectric layers of low temperature co-fired ceramic (LTCC) systems enables the realization of more functional multilayer ceramic modules (MCMs) for telecommunication applications. A composition designed for the low temperature sintering of ferroelectric BST material has been developed based upon previous work. Small amount of manganese is introduced to modify the properties of ferroelectric BaSrTiO₃ LTCC compositions. The effects of manganese on sintering behaviour, microstructure, relative permittivity, dissipation factor and tunability are studied. Manganese enhances the sintering of the BST due to an increase in the amount of oxygen vacancies and which yields an improvement in the electrical properties of BST.

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1. Introduction

In recent years, barium strontium titanate (BST) has been extensively studied for use as an electrically tunable material in microwave devices for telecommunication/consumer application.^{1–4} BST thin films for tunable devices are commonly fabricated by physical vapour deposition (sputtering and pulsed laser deposition), chemical vapour deposition/MOCVD, sol–gel or screen printing technology. Currently, BST thick films fabricated by tape casting and low temperature co-fired ceramic (LTCC) technology are receiving a lot of attention. LTCC compositions are sought because of the process route cost effectiveness, high reliability, high integration and miniaturization. LTCC technology is widely used for multilayer ceramic modules (MCMs) and is typically co-fired with silver electrodes at temperatures between 850 and 900 °C. LTCC technology is analogous to tape casting in that it involves slurry preparation and tape casting to obtain the green tape. The green tape is subsequently punched

to form vias, and metal patterns are printed onto the single layer. Single layers are stacked, laminated and co-fired to form the multilayer structure. The sintering temperature of pure BST is relatively high, >1350 °C, and not suitable for silver electrodes. Therefore, BST films have to be doped to enable compatibility with LTCC technology which is an attractive challenge.

In previous work,^{5,6} BST-based LTCC materials were developed having sintering temperatures in the vicinity of 900 °C through the use of various sintering aids. However, the addition of sintering aids degraded the dielectric properties of BST. One demonstrated component in the previous work⁵ was based on Ba_{0.7}Sr_{0.3}TiO₃ with a 3 wt.% addition of B₂O₃–Li₂CO₃. When sintered at 890 °C, this ceramic reached the same density as pure Ba_{0.7}Sr_{0.3}TiO₃ sintered at 1360 °C. The relative permittivity and dissipation factor of this LTCC material at room temperature were 4290 and 0.005 at 1 kHz. For application at higher frequencies (GHz), lower relative permittivity (ϵ_r) and dissipation factor ($\tan \delta$) values are required.

In our current work, manganese (Mn) is added into the BST-based LTCC material to optimise the composition for

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better microstructure and dielectric properties. Manganese is known to improve the properties of capacitor materials by pinning holes and preventing oxygen vacancy migration. Oxygen vacancies are filled by substitution of Mn onto the Ti site where it acts as an acceptor.⁷

2. Experimental procedure

Powders were batched according to the formula $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ and different compositions were prepared with 0.05, 0.1, 0.2, 0.5 wt.% MnO_2 . The weighed BST powders were ball milled for 16 h under water and calcined at 1200 °C. The calcined samples were ball milled again and sieved. Pelleted samples were pressed and sintered at 1350 °C for 4 h. The pellets were then tested for density, dielectric properties and microstructure (SEM). Scanning electron microscope (SEM) imaging was made using JEOL JSM-6400, Tokyo, Japan. ϵ_r and $\tan \delta$ at 0.1 MHz were measured using a HP 4284A LCR meter at different temperatures. Tunability was measured by the group at Ecole Polytechnique Fédérale de Lausanne (EPFL) using electric fields of 2 kV mm⁻¹.

After selecting the optimum Mn-doped composition, experiments were made to reduce the sintering temperature to that suitable for LTCC processes through the use of further additives to the mix. The follow on doping trials used B and Li as the additives. $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 + 0.2$ wt.% MnO_2 powders (BST-Mn) were pre-made according to the experimental details previously outlined. B_2O_3 – Li_2CO_3 additions in varying amounts (2.0, 2.5, 3.0, 3.5, 4.0 wt.%) were made to the already prepared BST-Mn powder and mixed for 2 h. The ratio of B_2O_3 : Li_2CO_3 was maintained at 27.2:72.8 according to our previous work.⁵ After drying, the powders were die-pressed into pellets and fired at different temperatures. The sintering behaviour and microstructure were studied using pellet samples of 8.5 by 1.5 mm size. The thermal etching sample was made by polishing the sintered pellet, heating to 800 °C and holding for 1 h, and then put out the oven. The microstructures were revealed by field emission scanning electron microscope (FESEM, JEOL JSM-6300F, Tokyo, Japan). The crystal phase composition was studied by X-ray diffraction (XRD, Siemens D5000, Karlsruhe, Germany) utilizing the JCPDS data file (International Center for Diffraction Data 1992, Swarthmore, PA, USA). ϵ_r and $\tan \delta$ at different temperatures in the frequency range 1 kHz to 0.1 MHz were measured using a HP 4284A LCR meter.

3. Results and discussions

3.1. BST doped with MnO_2

The measured densities and dielectric properties at 0.1 MHz for different MnO_2 additions are listed in Table 1. Relative densities were calculated as percentages of measured density compared to theoretical density (theoretical density values used in these calculations were for BaTiO_3 6.039, for SrTiO_3 5.12 and for MnO_2 doped $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ 5.763 g cm⁻³).

From Table 1, it is obvious that MnO_2 enhances the density of BST. All doped samples were denser than pure BST. When increasing the amount of the MnO_2 from 0.05 to 0.5 wt.%, the density of the ceramics first increases from 5.52 to 5.68 and then decreases to 5.56 g cm⁻³. The tunability of doped samples also initially increased before decreasing. This decrease in density and tunability is linked to the formation of a second phase within the microstructure as can be seen in Fig. 1. The optimum MnO_2 addition to BST was 0.2 wt.%.

The dielectric properties measured as a function of temperature at 0.1 MHz are shown in Fig. 2. Addition of MnO_2 increases the relative permittivity of the ceramics and decreased the dissipation factor, compared to pure BST sintered at the same temperature. These changes in electrical properties are believed to be associated with both improving microstructure and fired density.

With excess addition of MnO_2 , the relative permittivity values decrease and the Curie temperature is shifted to lower temperatures. The maximum relative permittivity of BST with 0.05, 0.1, 0.2 and 0.5 wt.% MnO_2 additive were 20,000; 19,450; 12,400; and 9150, the corresponding T_c values were 28.1, 27.1, 26.7 and 22.6 °C. The change in T_c value may be caused by both a replacement of Ti by Mn but also the formation of second phase. It is noticeable from Fig. 2 that the transition curve becomes more diffuse with increasing Mn suggesting a composite behaviour.

In Fig. 2b, the dissipation factor of the samples are clearly improved by the addition of MnO_2 , this should be beneficial in the microwave application of BST components. At their Curie temperatures, BST with 0, 0.05, 0.1, 0.2 and 0.5 wt.% MnO_2 had dissipation factor of 0.018, 0.004, 0.004, 0.002 and 0.008, respectively. Small amounts of Mn decreased the dissipation factor due to the pinning of oxygen vacancies at the grain boundaries and lower porosity in the structure caused by Mn addition. The phenomena behind this behaviour has been discussed in literature.^{8,9} At dopant addi-

Table 1
Properties of BST with different amount of MnO_2

| MnO_2 (wt.%) | T/t sintering (°C/h) | Density (g cm ⁻³) | Relative density (%) | ϵ_r (20 °C) | $\tan \delta$ (20 °C) | Tunability (n) |
|-----------------------|------------------------|-------------------------------|----------------------|----------------------|-----------------------|--------------------|
| 0 | 1350/4 | 5.50 | 95.4 | 4540 | 0.028 | 2.6 |
| 0.05 | 1350/4 | 5.52 | 95.7 | 5910 | 0.008 | – |
| 0.1 | 1350/4 | 5.61 | 97.3 | 5410 | 0.009 | 1.6 |
| 0.2 | 1350/4 | 5.68 | 98.5 | 6710 | 0.003 | 2.0 |
| 0.5 | 1350/4 | 5.56 | 96.5 | 8670 | 0.008 | 1.8 |

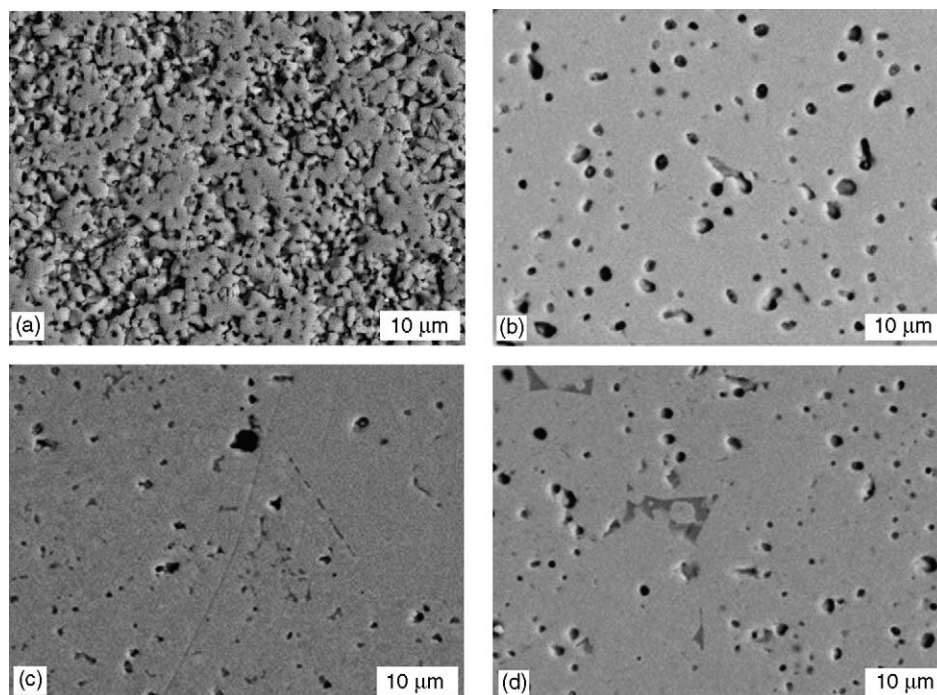
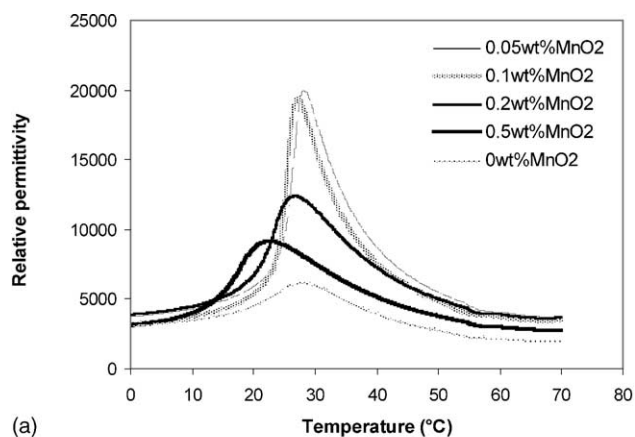
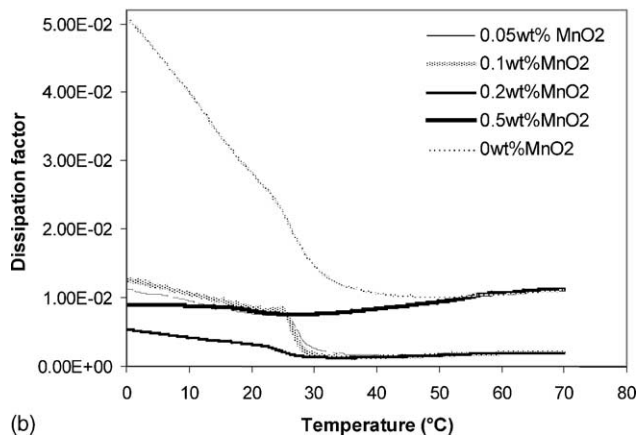


Fig. 1. SEM images of BST doped with: (a) 0 wt.% MnO₂; (b) 0.05 wt.% MnO₂; (c) 0.2 wt.% MnO₂; and (d) 0.5 wt.% MnO₂ sintered at 1350 °C for 4 h.



(a)



(b)

Fig. 2. (a) Relative permittivity and (b) dissipation factor of BST doped with different MnO₂.

tions of 0.5 wt.% MnO₂, second phase accumulates at the grain boundary, presumably MnTiO₃, which causes an increase in the dielectric loss. The dissipation factor data for 0.5 wt.% doped material was a lot flatter than for all other dopant additions. Consequently, one would expect to see a reduced dependence on $\tan \delta$ with the ferroelectric transition. However, if one examines the data carefully we still have a minimum around 22 °C in the 0.5 wt.% data curve. After 22 °C, the dissipation factor increased with temperature. Therefore, manganese can be introduced into the BST structure in limited amounts to promote improved density and $\tan \delta$ values.

3.2. BST-Mn added with B₂O₃–Li₂CO₃

According to the results of the study reported above, BST with 0.2 wt.% MnO₂ was chosen as the basic powder for the research on reduced firing temperature ceramics, the target being full density at 890 °C. The densities of the samples doped with B and Li at different firing temperatures are shown in Table 2.

BST-Mn without B₂O₃–Li₂CO₃ addition sintered at 1350 °C has a density of 5.4 g cm⁻³ and does not begin to densify at temperatures below 1050 °C. When the sintering aids B₂O₃–Li₂CO₃ were added, component densification commences at 750 °C. When sintered at 900 °C, the densities of the BST-MnBL samples were in the range of 4.9–5.2 g cm⁻³. B₂O₃ and Li₂CO₃ form liquid phases which enhance the densification of BST at lower sintering temperature through a liquid phase sintering mechanism.^{5,6,10} The BST-MnBL with 3.5 wt.% B₂O₃–Li₂CO₃ gave the highest density (Table 2),

Table 2
Densities of the sample at different temperature

| B ₂ O ₃ –Li ₂ CO ₃ (wt.%) | 750 (°C/4h) | 800 (°C/4h) | 900 (°C/4h) | 1050 (°C/4h) | 1350 (°C/4h) |
|---|-------------|-------------|-------------|--------------|--------------|
| 0 | – | – | 3.39 | 3.40 | 5.39 |
| 2.0 | 3.66 | 3.99 | 4.92 | – | – |
| 2.5 | 3.54 | 3.92 | 4.94 | – | – |
| 3.0 | 3.29 | 3.51 | 4.86 | – | – |
| 3.5 | 3.72 | 4.00 | 5.20 | – | – |
| 4.0 | 3.18 | 3.81 | 5.13 | – | – |

which led to a density of 96.5% of theoretical compared to the BST-Mn sintered at 1350 °C.

FESEM images of the BST-MnBL sintered at 900 °C (Fig. 3b–f) show that all the BST-MnBL samples have dense structures and low porosities. Please notice that the sample in Fig. 3e was thermal etched and the grain size can clearly be seen to be 1–5 μm.

XRD measurement for samples with 3.5 wt.% addition of B₂O₃–Li₂CO₃ (Fig. 4) show the main phase in BST-MnBL to be Ba_{0.7}Sr_{0.3}TiO₃ and no secondary peaks can be found.

Analysis of the dielectric properties as a function of temperature (Fig. 5), demonstrates that the addition of sintering aids B₂O₃–Li₂CO₃ decreases the relative permittivity of BST-Mn but does not change the Curie temperature. The Curie temperatures of all samples were around 30 °C. When 2.0 and 2.5 wt.% B₂O₃–Li₂CO₃ were added, the relative permittivity of BST-MnBL at 30 °C decreased to 4050 and 3280 due to relative higher porosity (Fig. 3). Larger amounts of B₂O₃–Li₂CO₃ (3.0 and 3.5 wt.%) caused the relative permittivity to increase a little (4020 and 5010) because of better densification. Too large amount of B₂O₃–Li₂CO₃ led to

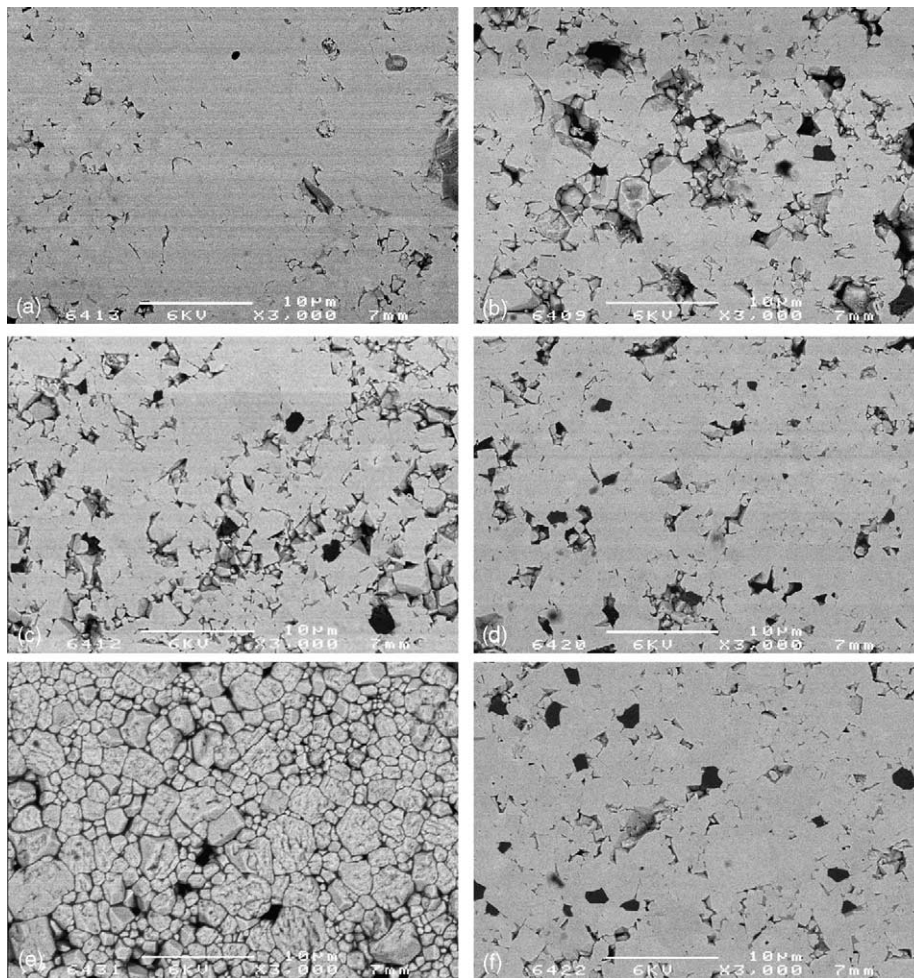


Fig. 3. FESEM images of BST-MnBL samples with: (a) 0 wt.% B₂O₃–Li₂CO₃ fired at 1350 °C; (b) 2.0 wt.%; (c) 2.5 wt.%; (d) 3.0 wt.%; (e) 3.5 wt.% (thermal etching); and (f) 4.0 wt.% B₂O₃–Li₂CO₃ fired at 900 °C 4h.

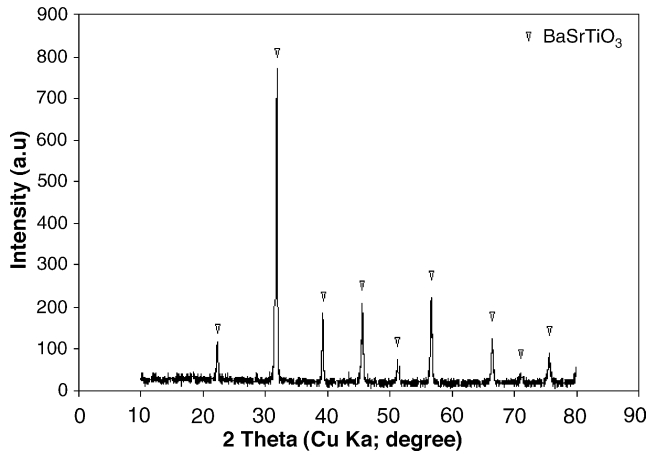
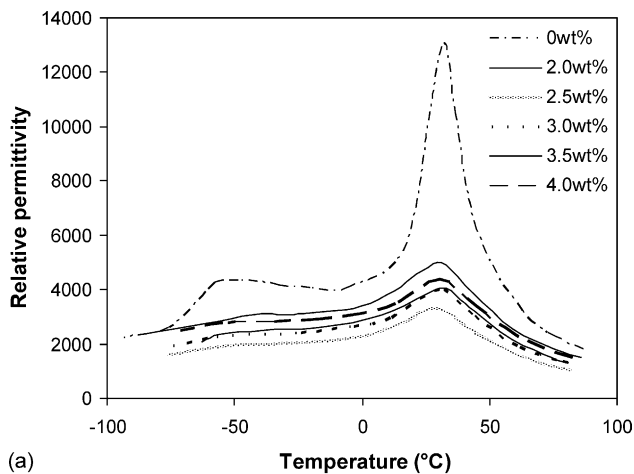
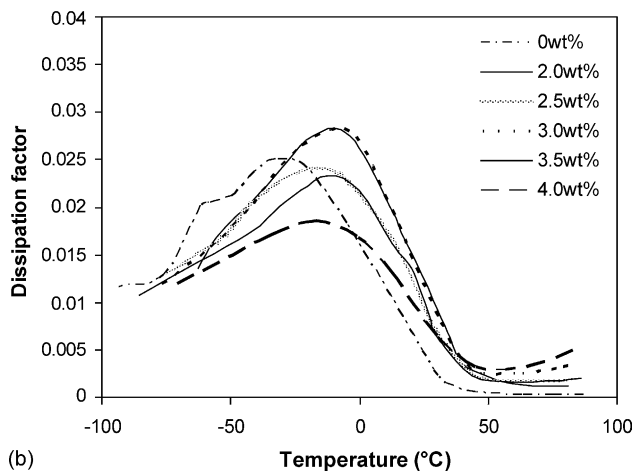


Fig. 4. XRD pattern of BST-MnBL with 3.5 wt.% $B_2O_3-Li_2CO_3$.

lower relative permittivity again due to the secondary phase. The dissipation factor of samples varied little with the different amounts of $B_2O_3-Li_2CO_3$. The optimum composition from both a microstructural and dielectric property stand-



(a)



(b)

Fig. 5. (a) Relative permittivity and (b) dissipation factor of BST-MnBL samples with different amounts of $B_2O_3-Li_2CO_3$.

point was $Ba_{0.7}Sr_{0.3}TiO_3$ with 0.2 wt.% MnO_2 and 3.5 wt.% $B_2O_3-Li_2CO_3$.

4. Conclusion

Mn-doped BST based LTCC materials were investigated for applications as tunable microwave components. The Mn significantly enhanced the density and decreased the dissipation factor of the BST. Sintering aids $B_2O_3-Li_2CO_3$ are effective in decreasing the sintering temperatures of Mn-doped BST materials. The optimised composition was BST with 0.2 wt.% MnO_2 and 3.5 wt.% of $B_2O_3-Li_2CO_3$, which sintered at 900 °C.

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