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Co-sintering of barium strontium titanate (BST) thick films inside a LTCC substrate with pressure-assisted sintering

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Abstract

Screen-printed ferroelectric BST thick films were co-fired inside a LTCC substrate by employing pressure-assisted sintering (PAS). Sintering pressure and time were varied and their effect on the microstructure and dielectric properties of the film was studied. Sintering conditions for the fabrication of buried BST thick films were experimentally defined and parallel plate capacitors were successfully fabricated inside a LTCC substrate. The relative permittivity (ε_r) of the films at 10 kHz varied from 188 to 220 depending on the sintering conditions, and the maximum tunability of the films was 44% (5.7 V/μm). The measured loss tangent (tan δ) at zero bias was 0.005.

Keywords: $BaTiO_3$ and titanates; Films; Capacitors; Dielectric properties; Pressure-assisted sintering; LTCC

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1. Introduction

Multilayer low-temperature co-fired ceramic (LTCC) is an established technology employed in the creation of highly integrated components and modules for electronics and mobile communication applications. In addition to its excellent integration capacity, LTCC technology also has great potential in the manufacture of multi-material modules, where materials with different electric and magnetic properties are combined within one substrate.[1] Materials with high permittivity, used for capacitive components, as well as materials with magnetic permeability, used for inductive components, have been presented and also integrated with commercial LTCC materials.[2–5] The main challenges in the integration of different ceramic materials in a LTCC substrate is the required low sintering temperature (~900 °C) and matching the sintering shrinkage and thermal expansion of the different materials.

Along with high permittivity and magnetic materials, ferroelectric materials have drawn the attention of microwave material researchers. Ferroelectric materials possess voltage-tunable dielectric characteristics and thus they can be used to create tunable/adaptable microwave components. Barium strontium titanate (BST) is a well researched ferroelectric material whose sintering temperature can be lowered to be compatible with LTCC process temperatures by adding small amounts of sintering aids.[6,7] Co-sintering of tape-cast-derived ferroelectric BST films inside a LTCC substrate has been achieved with the aid of pressure-assisted sintering,[8] but tape-cast layers covering the whole area of the substrate are not an ideal solution for manufacturing embedded tunable components. A more flexible and cost-effective fabrication method, such as screen printing of thick films would allow very low film thickness and localized coverage of the film, hence offering more freedom in the design.

We have recently developed a screen-printable BST thick film paste with a low sintering temperature that can be co-sintered with silver conductors.[9] The low sintering temperature also allows the use of BST thick films with commercial LTCC products. The developed paste has been used as a via fill material to integrate very small-sized variable capacitors (varactors) inside a LTCC.[10] However, the free co-sintering of large-area BST thick films inside a LTCC substrate would require both of the materials to have matched sintering shrinkage and sintering rate. This is very difficult to achieve, since very fast sintering kinetics are favoured for production reasons in a majority of commercial

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LTCC tapes. LTCC materials typically are glass–ceramic composites, in which rapid sintering kinetics are achieved through the presence of a liquid phase during sintering. The sintering mechanism of the developed BST paste is substantially different and much slower, which excludes the possibility of integrating the materials with free sintering. In the multi-material experiments reported in the literature,[3–5] warping and cracking of the substrate is avoided by keeping solely to symmetrical designs or by using pressureless-assisted sintering (PLAS), where non-shrinking layers of tape are laminated on both sides of a LTCC substrate to restrict *X* and *Y* directional shrinkage.

A pressure-assisted sintering (PAS) technique, where constraining layers of Al_2O_3 green tapes are laminated on both sides of a LTCC laminate and uniaxial pressure is continuously applied during co-firing to restrict shrinkage in the *X* and *Y* directions, has also been used to achieve zero-shrinkage sintering.[11,12] This way practically zero *X* and *Y* directional shrinkage is achieved and more importantly, shrinkage tolerance is significantly reduced compared with the free sintering process. Similar pressure-assisted sintering (hot pressing) is also used to co-sinter mixed-material ceramic–ceramic structural composites where the materials have mismatching sintering behaviours.[13]

This paper presents co-sintering of BST thick films inside LTCC substrates for the first time by using the PAS technique. The sintering conditions were varied and their influence on the microstructure and dielectric properties of the films are reported and discussed. Parallel plate variable capacitors (varactors) were fabricated inside a LTCC substrate and their electrical performance was measured.

2. Experimental

A commercial $0.99Ba_{0.55}Sr_{0.45}TiO_3 + 0.01TiO_2$ (BST-TIO) powder (Praxair Specialty Ceramics, Woodinville, WA, USA) and Li_2CO_3 (Alfa Aesar GmbH & Co., Karlsruhe, Germany) as a sintering aid were used to fabricate the ceramic powder for the paste. During the pre-reaction Li_2CO_3 decomposes to Li_2O and CO_2, thus the desired doping level of 0.8 wt.% Li_2O was achieved by adding the corresponding molar fraction of Li_2CO_3. The materials were mixed in a planetary ball mill for 24 h with a ZrO_2 grinding medium and acetone as a mixing vehicle. After drying, the powders were allowed to pre-react at 500 °C for 10 h. The powders were then hand ground and dry-milled for 1 h. The thick film pastes were prepared by adding 80 wt.% of BST powders, 16 wt.% of an organic medium (CV-6, Electro science labs, Pennsylvania, USA) and 4 wt.% of a dispersant (809, Electro science labs, Pennsylvania, USA), and then mixing them in a triple roll mill for 30 min.

A DuPont 951 LTCC tape system was used with DuPont 6142D silver pastes. The LTCC tapes were cut into 88 mm × 88 mm sheets and 200 μm via holes were drilled with a laser (Siemens Microbeam 3200, Siemens, Germany). The vias were filled with DuPont 6141 silver via fill paste. The electrodes and the BST films as well as probe contacts on the top layer were sequentially printed on the LTCC tapes using a screen printer (Ami Presco MSP-9155PC, USA). Screens with a mesh of 230 wires/in. and a 17 μm emulsion thickness were used to print the BST films. The printed LTCC tapes (DuPont 951PX) were aligned and stacked and finally laminated together with restrictive alumina tapes (DuPont 951RT). The laminated panel consisted of five 256 μm thick layers. Sintering time and pressure were varied during pressure-assisted sintering (PEO 603, ATV Technologies). Sintering times of 30 and 60 min were used with pressures of 0.5, 1 and 2 MPa.

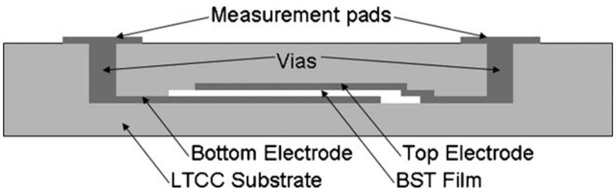

Fig. 1. Cross-section of the parallel plate capacitor.

The microstructure of the films was examined with scanning electron microscopy (SEM; JSM-6400, JEOL, Tokyo, Japan). The density of the sintered films was estimated from the SEM images by calculating the ratio of the BST and void areas in the images and then transforming the area ratio into the corresponding volumetric ratio ($R_{\text{area}}^{3/2} = R_{\text{volume}}$). The area of the voids in the SEM image was differentiated from the area of the BST phase by the difference in their tonal values. The thickness of the sintered films was measured from the cross-sections with an optical microscope measurement system (BX51, Olympus, Tokyo, Japan). The relative permittivity and loss tangent of the films as a function of bias field were measured from the parallel plate capacitor samples with a precision LCR meter (4284A, Agilent Technologies Inc., California, USA) at 10 kHz, using an external voltage source (Agilent 6675A, Agilent Technologies Inc., California, USA).

3. Results and discussion

Thick film parallel plate capacitors were prepared inside a LTCC substrate. The sample structure is presented in Fig. 1. The effective electrode area of the capacitor structure was 2.5 mm × 2 mm (5 mm^2). The samples were first visually inspected and it was found that the samples sintered under a pressure of 0.5 MPa had severe cracks, whereas the samples sintered under pressures of 1 or 2 MPa were found to be undamaged. LTCC samples of the same thickness which do not include buried BST films have been successfully sintered by using a PLAS-constrained sintering technique, and thus it can be noted that introduction of a material with unmatched sintering shrinkage and sintering rate places restrictions on the sintering conditions. Sufficient pressure is needed during sintering to overcome the stresses inflicted on the LTCC substrate by the different shrinkage behaviour of the BST film.

The microstructures of the sintered BST films are presented in Fig. 2. The estimated density values are presented in Table 1 and they show that the films that were sintered for 60 min had approximately 5% higher density than the films sintered for 30 min. The influence of the applied pressure on density during sintering could not be detected. The thickness of all the films, measured

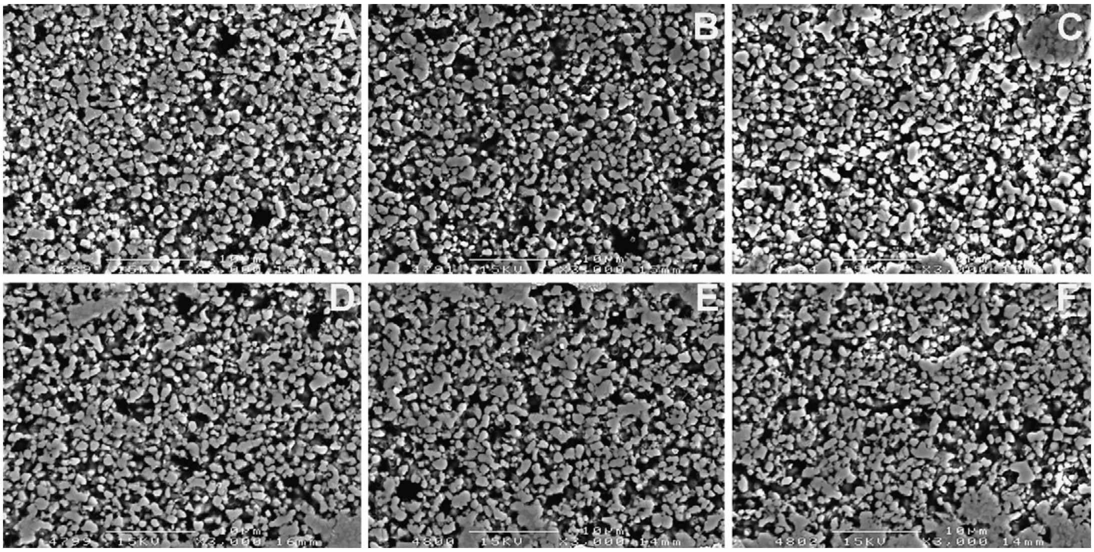

Fig. 2. SEM micrographs of the films sintered under different conditions. A: 30 min 0.5 MPa, B: 30 min 1 MPa, C: 30 min 2 MPa, D: 60 min 0.5 MPa, E: 60 min 1 MPa, F: 60 min 2 MPa.

Table 1
Densities of the sintered films analyzed from SEM images presented in Fig. 2

Density (%)	Sintering time	
Sintering pressure (MPa)	30 min	60 min
0.5	(S305) 58%	(S605) 62%
1	(S301) 57%	(S601) 60%
2	(S302) 55%	(S602) 60%

from the microscopic images, was approximately 35 μm (Fig. 3). However, the accuracy of the measurement method did not allow the film thickness to be defined with enough precision to find a correlation between the sintering conditions and film thickness.

The dielectric properties of the sintered films were measured from the parallel plate capacitor samples (Fig. 1). The films were evaluated in terms of relative permittivity and dielectric loss as a function of applied bias field. As mentioned above, the samples sintered using 0.5 MPa pressure cracked very easily due to the low pressure, which could not overcome the mismatches in the sintering behaviours of the DP951 LTCC material and the BST ceramics we used. Due to the internal cracks in the sintered samples, a proper electrical contact with the electrodes was not established and measurement of the dielectric properties of the films was impossible. In addition, it was found that the samples sintered under a pressure of 2 MPa were all short-circuited. The high sintering pressure overloaded the samples, which forced the silver electrodes to penetrate the BST film, resulting in defects and short circuits (Fig. 4). The sintering pressure of 1 MPa produced structurally and electronically functional samples.

The fabricated parallel plate capacitors were composed of two ~10 μm thick electrodes and a ~35 μm thick BST film, thus having a total thickness of ~55 μm. After isostatic lamination the buried capacitors were clearly visible as bumps on the LTCC panel surface. Therefore, it can be assumed that the actual pressure formed at the bump locations when the LTCC panel is pressed with a constant force between the flat sintering plates is significantly higher than in the bump surroundings. The size of

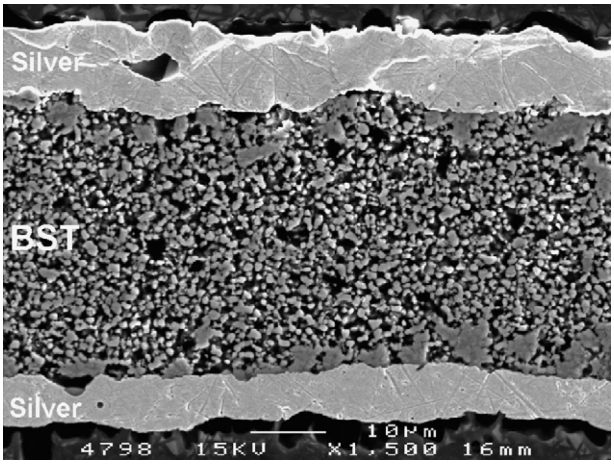

Fig. 3. Embedded BST film and silver electrodes.

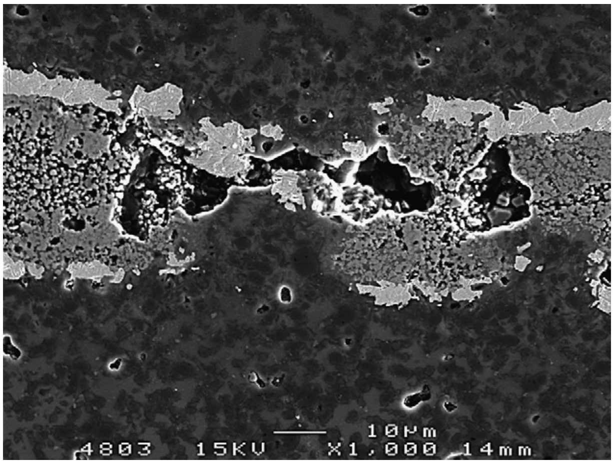

Fig. 4. Collapsed BST film.

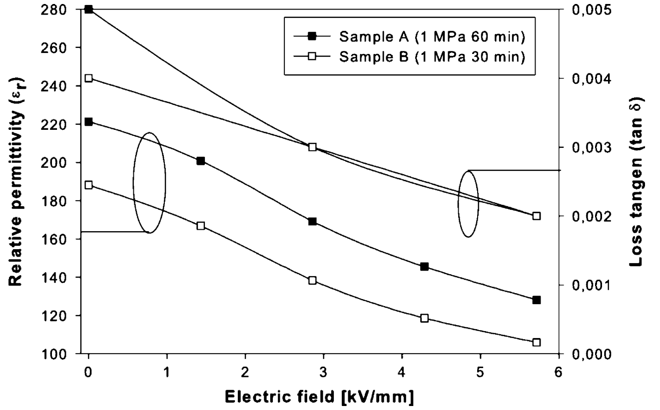

Fig. 5. Measured relative permittivities (ε_r) and loss tangents (tan δ) as a function of bias field (E) at 10 kHz.

the sintered LTCC panels was 44 mm × 44 mm (1936 mm^2) and they contained nine 2 mm × 2.5 mm (5 mm^2) capacitors. This means the pressure was focused at the bump locations and it would be approximately 40 times the sintering pressure. Such high pressures are enough to push the bumps into the LTCC substrate. Naturally, once the bumps have been pushed in, the pressure would be distributed evenly over the whole LTCC panel. As a conclusion, possible reasons for the film defects under high and low sintering pressures might be the unequal sintering pressure due to the unevenness of the laminated LTCC panel surface and the extremely high pressure at the component locations. The pressure used during sintering of a multi-material LTCC module should be carefully adjusted and further research is needed to define the optimal sintering conditions.

The measured dielectric data of the LTCC-embedded BST films are presented in Fig. 5. The unbiased relative permittivity (ε_r) of the samples sintered under a pressure of 1 MPa for 60 min (Sample S601) and 30 min (Sample S301) was 220 and 188, respectively. This agrees well with the presented porosity estimations and indicates that sintering time has a significant effect on sintered density and furthermore on relative permittivity. The electric field dependence of relative permittivity shows well-known behaviour described by Johnson.[14] The ε_r of samples S601 and S301 decreased from 220 and 188 to 128 and 105 at 10 kHz when the biasing field (E) was increased from 0 to 5.7 V/μm. Thus, the tunability $n = (\varepsilon_r(0) - \varepsilon_r(E))/\varepsilon_r(0))$ of samples S601 and S301 was 42% and 44%. The dielectric loss (tan δ) of the films at zero bias field losses was 0.005 and 0.004 at 10 kHz for samples S601 and S301, respectively. Tan δ of a thick film BST decreases as the DC bias field increases, as illustrated in Fig. 5. Loss levels are similar to those in our previous work,[9] in spite of the greater amount of Li_2CO_3 sintering aid and the use of pressure-assisted sintering.

The relative permittivity of films printed with the same BST paste on an Al_2O_3 (alumina) substrate was 552, and tunability of 41% under a bias field of 4.5 kV/mm was observed. The permittivity of the embedded films was significantly lower compared with films on the surface, whereas the tunability of the embedded films remained almost the same regardless of the lower permittivity. However, it has to be noted that the films printed on the surface of the alumina substrate were sintered for 2 h, so the results are not fully comparable. More studies are needed to identify the reasons for the lower measured relative permittivity in the embedded films.

Based on these first experiments, it seems that while pressure-assisted sintering does enable co-firing of two materials by eliminating warping of the substrate caused by mismatched sintering shrinkages, it does not enhance material densification of the embedded film. Increasing the sintering time, on the other hand, seems to directly affect the final density.

4. Conclusion

Screen-printed ferroelectric BST thick films were fabricated inside a LTCC substrate by using pressure-assisted sintering (PAS). Sintering pressure and time were varied and it was found that sintering pressure had a significant effect on the integrity of the samples. Sintering conditions were experimentally defined and parallel plate capacitors were successfully fabricated inside a LTCC substrate. The buried films were measured and they exhibited tunability and loss characteristics similar to those previously reported for non-buried films. The relative permittivity of the films was decreased significantly compared with non-buried films.

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