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Properties of compositionally graded $Ba_{(1-x)}Sr_xTiO_3$ self-standing thick films

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Abstract

Compositionally graded self-standing thick films (0.4 mm) have been fabricated using the airflow deposition method. Films were made of five layers with different composition $Ba_{(1-x)}Sr_xTiO_3$ (BST, x = 0, 0.1, 0.2, 0.3 and 0.4). The layers of different thicknesses, ranging from 80 to 30 μm, presented similar Vickers microhardness of about 0.25 GPa. The average particle size of deposited layers was finer than 500 nm and the density of as-deposited films was about 80% of theoretical. After sintering at 1350 °C samples presented increased-density (>90%) and maintained a compositional gradient. When compared to single-composition BST ceramics, permittivity of graded films was much less dependent on temperature over a wide range, from −50 to 250 °C. In addition, the films displayed polarization offset when driven by an alternating field and heated above 50 °C.

Keywords: Films; Airflow deposition; Ferroelectric properties; $BaTiO_3$ and titanates

1. Introduction

$Ba_{1-x}Sr_xTiO_3$ (BST) is a promising candidate for a wide range of applications as tunable microwave dielectric, dynamic random access memory devices and infrared sensors.[1] In addition to its many advantages like having a high dielectric permittivity and low conductivity, its lead free composition respects the environment. What's more, BST compositionally graded thin films like other graded ferroelectric devices (GFDs) have been reported in several works to show polarization offset and enhanced pyroelectric coefficient, such anomalies being a function of the applied alternating field, the temperature and the strain. Many investigators assume that these phenomena, which were first reported by Mantese and co-workers,[2] are due to the gradient of spontaneous polarization (P_s) across the ferroelectric film.[3] Both the charge offset and the permittivity dispersion have been numerically derived by introducing spatial dependence in the coefficients of Landau–Ginzburg free energy. This theory was supported by several studies and since P_s also depends on temperature and stress, polarization offset can be observed by imposing either a temperature gradient[4] or a stress gradient[5] to a homogenous bulk material. A different possible origin of the polarization offset has been proposed by Poullain et al.,[6] who suggested that the P shift is developed by asymmetrical leakage currents originated by point defects (e.g. oxygen vacancies) and concentration-dependent band structure. In the present work, BST thick films with graded composition were fabricated at room temperature using the airflow deposition method. This low energy process allows a high-density film deposition with excellent green strength and relatively low sintering temperature. It has been already applied to the realization of Bi_3TiNbO_9,[7] PZT-PMN[8] and $BaTiO_3$[9] nanostructured films and was used for the first time to fabricate GFDs.

The microstructural, dielectric and ferroelectric properties of graded thick films realised using this method are presented and compared with $Ba_{1-x}Sr_xTiO_3$ bulk ceramics prepared using the traditional method from powder recycled after each layer deposition.

2. Experimental procedure

Five $Ba_{1-x}Sr_xTiO_3$ (x = 0, 0.1, 0.2, 0.3 and 0.4) precursor powders were prepared by a conventional mixed oxide route.

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Reactant grade $BaCO_3$ (Solvay), $SrCO_3$ (Solvay) and TiO_2 (Toho) were weighed out in stoichiometric proportion, ball milled with zirconia balls in isopropanol solution for 24 h, dried and calcined at 1150 °C for 5 h.

The technique of deposition of thick film from airflow has been described in detail elsewhere.[8] The airflow was generated by a commercial jet-mill (Micron Master 02–506) fed from a compressed air line at a pressure of 700 kPa. The graded thick films were created by sequentially depositing five layers with different compositions on nickel substrate at room temperature. After deposition thick films were detached from the substrate obtaining self-standing structures with a total thickness ranging from 250 to 400 μm. Thick films were sintered at different temperatures from 900 to 1350 °C for 3 h. In addition, powders recycled after each layer deposition were pressed into 10 mm diameter and 2 mm thick green pellets, isostatically pressed under 200 MPa and fired at 1350 °C for 3 h. The density of green and sintered materials was measured by the Archimedean displacement technique. Due to the graded composition of films, sintering at one single temperature is likely to give a non-uniform residual porosity. This aspect was not investigated here and only average density values are reported.

The microstructure of samples was observed by optical microscopy (OM, Leica LM) and scanning electron microscopy (SEM, LEO 440). Energy dispersive spectroscopy (EDS, JED-2300T) was performed on graded thick films to measure the chemical composition across layers. Vickers microhardness was evaluated (Buehler Micromet 2100) on each layer of as deposited films after indentation under a load of 1 N for a period of 10 s.

For electrical characterization, samples were electroded with a silver paste using the screen-printing method. Polarization ver-

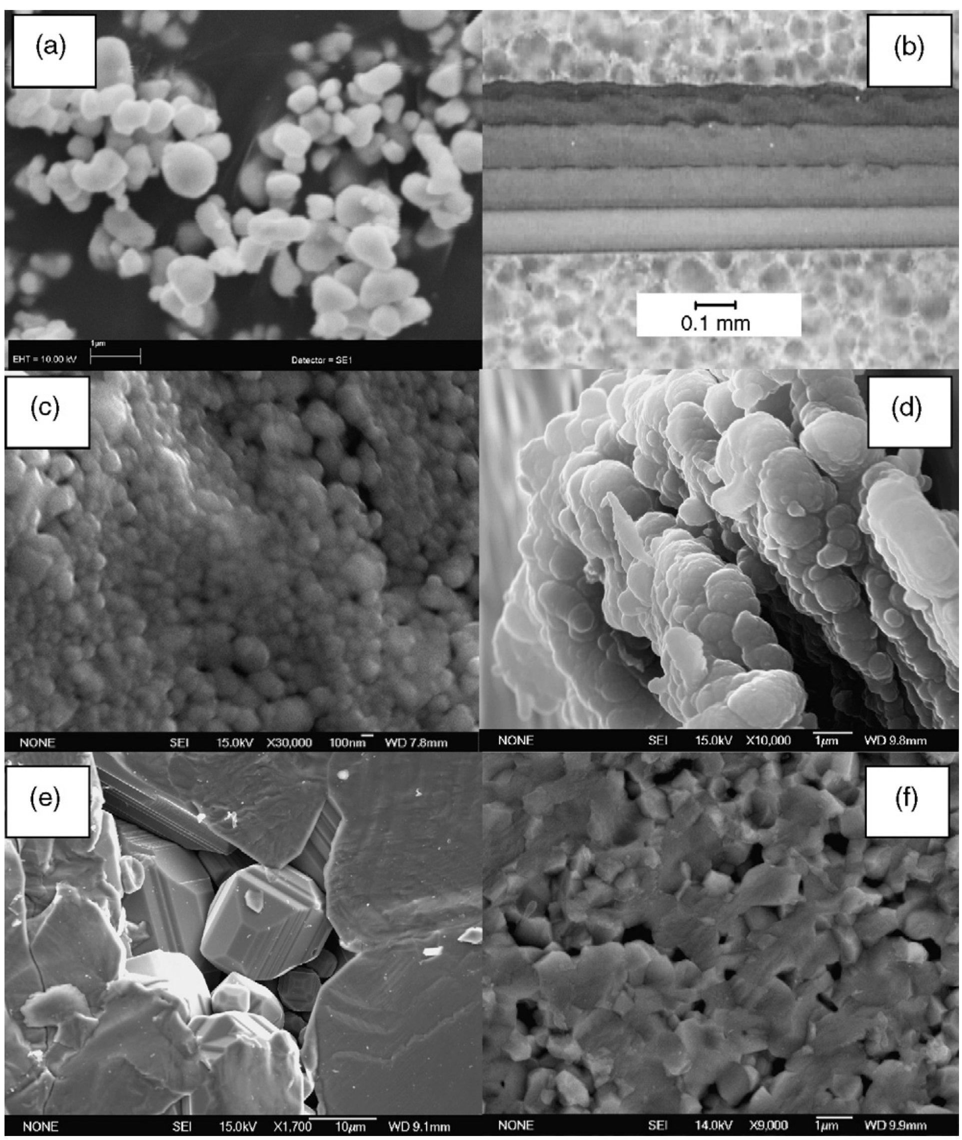

Fig. 1. $Ba_{0.6}Sr_{0.4}TiO_3$ powder used for the deposition, SEM (a); cross-section of the as-deposited film, OM (b); fracture of graded film sintered at 900 °C for 3 h, SEM (c); fracture of graded film sintered at 1100 °C for 3 h, SEM (d); fracture of graded film sintered at 1350 °C for 3 h, SEM (e); fracture of bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics sintered at 1350 °C for 3 h (f).

sus electric field hysteresis loop measurement was carried out in silicon oil using a modified Sawyer–Tower circuit at frequency of 50 Hz. The permittivity and loss tangent values were measured over the range of frequency 1 kHz–1 MHz from −50 to 300 °C with an Agilent 4294A impedance analyzer.

3. Results and discussion

Graded thick films of $Ba_{1-x}Sr_xTiO_3$ with a total thickness from 250 to 400 μm were deposited and then detached from the nickel substrate used for deposition. Fig. 1b shows OM micrograph of a green thick film. It is composed of five layers with different thicknesses, ranging from 30 μm of the top layer ($x = 0.4$) to 80 μm of the bottom one ($x = 0$).

The density of as-deposited films was estimated about 80% of the theoretical of pure $BaTiO_3$, which is very high compared to the green density of 200 MPa isostatically pressed bulk ceramics which did not exceed 70% theoretical.

The mechanical strength of the samples allowed manipulation without special care. The microhardness was about 0.25 GPa, i.e. one order less than $BaTiO_3$ ceramics in commercial MLCCs.[10]

The airflow deposition process involves particles selection by size taking place at the moment of particle bonding to the substrate or growing layer. Large particles or particles with poor bonding to the surface are removed by the incoming flux. As the result of this process the green body is composed of densely packed fine particles. The average particle size in the green films was significantly lower than that of the precursor powder. This also explains the fact that the powder recycled after deposition contained only a small amount of fine particles. Fig. 1a and c shows the $Ba_{0.6}Sr_{0.4}TiO_3$ precursor powder recycled after deposition and a deposited layer sintered at 900 °C, respectively. In the first image, the average size is about 1 μm, while in the film only particles finer than 200 nm are visible.

During the sintering stage at 1100 and 1350 °C (Fig. 1d–e), grains of thick films coarsened up to the μm range and the average density increased to about 90% theoretical. Similarly, bulk ceramics sintered at 1350 °C show grains of few microns and density about 93% of theoretical (Fig. 1f).

The Sr^{2+} ion concentration profiles across the films indicate that some interdiffusion between adjacent layers took place. According to Fig. 2, the step graded structure of unsintered films was maintained after firing only at lower Sr concentrations, while boundaries between layers containing more Sr are less evident. This result agrees with the random alloy model introduced by Manning[11] where the diffusion coefficient depends on concentration of atomic species.

Fig. 3 illustrates the temperature behaviour of the dielectric permittivity at 1 kHz, for BST bulk ceramics and graded thick film sintered at 1350 °C. Bulk ceramics show the conventional lambda-shaped curves with maxima at T_c corresponding to the tetragonal-cubic transition and shifted to lower temperature with the increase of Sr/Ba ratio.

For thick film a broad dispersion over the whole temperature range centred at 85 °C made of five smooth peaks is observed. These peaks do not correspond exactly to maxima of bulk ceramics and the dielectric permittivity is generally depressed although still above 1000 and much higher than values reported for graded thin films. The partial interdiffusion of ionic species and the presence of charged defects and pores could account for such results. The defects were also active with regard to dissipation, as indicated by 1 kHz tan δ values (3–5%) that are one order of magnitude greater than in bulk ceramics (0.1%).

Ferroelectric hysteresis loop measurements of graded structures fired at two different temperatures are shown in Fig. 4. Films sintered below 1350 °C showed very poor hysteresis as a consequence of both reduced grain size and density. Same measurements were carried out for BST solid solution (not reported) and P_r was found to decrease with increasing Sr/Ba ratio. The hysteresis loop of graded thick films sintered at 1350 °C had a similar shape to any BST bulk ceramics, P_r was about 5 μC/cm^2, which places it between $Ba_{0.9}Sr_{0.1}TiO_3$ and $Ba_{0.8}Sr_{0.2}TiO_3$ remnant polarizations. At room temperature, no polarization offset was noticeable. The application of ac field to the graded thick film samples at the temperatures above 50 °C caused the hysteresis translation along the polarization axis by two to three times the maximum P_r of the graded material. Fig. 5 shows

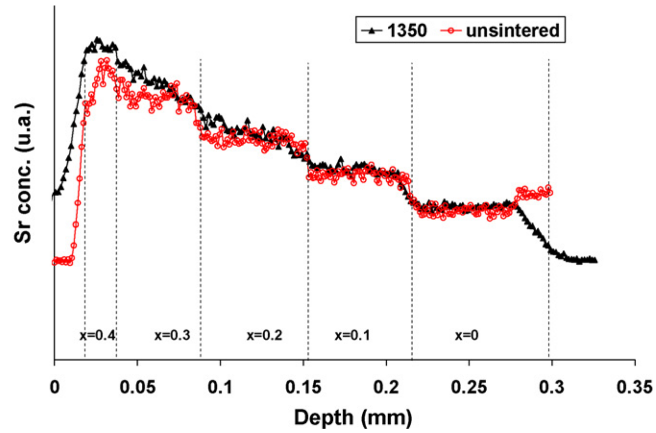

Fig. 2. Concentration profile of Sr^{2+} in as-deposited and sintered film. Dashed vertical lines mark the boundaries between layers with different composition.

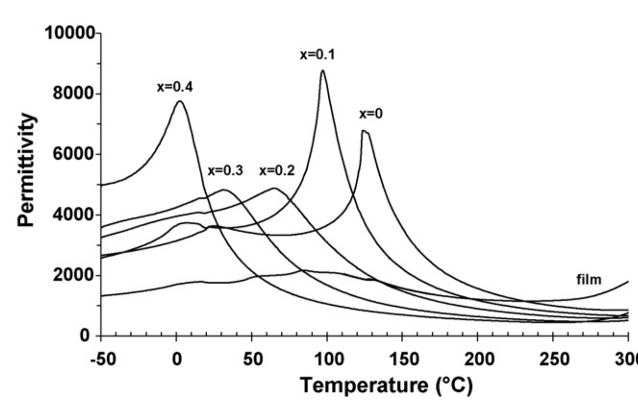

Fig. 3. Permittivity vs. temperature measured at 1 kHz in bulk BST ceramics and in graded film. All samples were sintered at 1350 °C for 3 h.

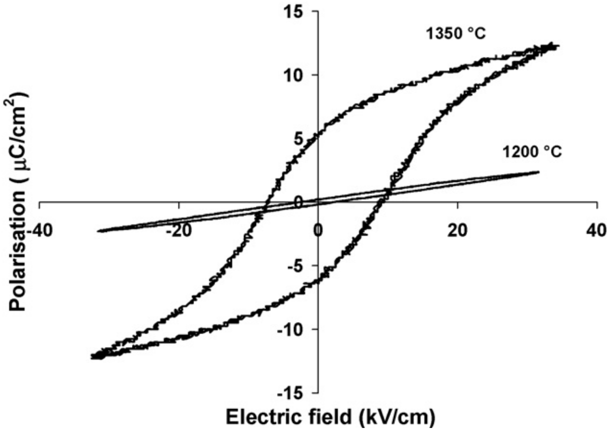

Fig. 4. Hysteresis loop in graded BST film sintered at 1200 and 1350 °C for 2 h.

unsaturated hysteresis loops collected at 70 °C for various amplitudes of the applied ac electric field. The (a and b) series were recorded after flipping the sample over with respect to the applied field.

The offset was stable in time and increased with the increase of the driving field and/or temperature in the range 25–70 °C. After flipping the thick film, the polarization offset occurred in the opposite direction of the polarization axis. The appearance of such a shift in the polarization signal can

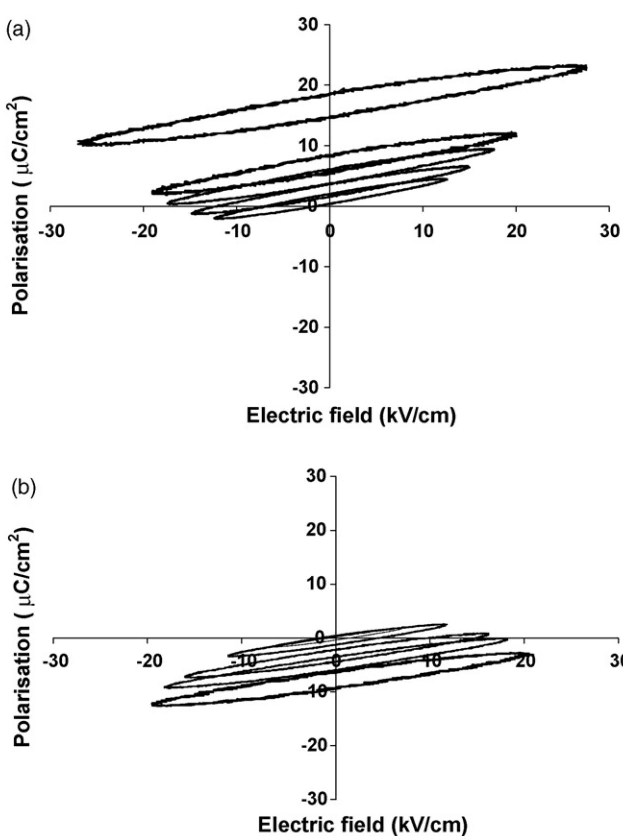

Fig. 5. Unsaturated *P–E* loops at 70 °C of graded film sintered at 1350 °C for 3 h: (a and b) series were recorded after flipping the sample with respect to applied field.

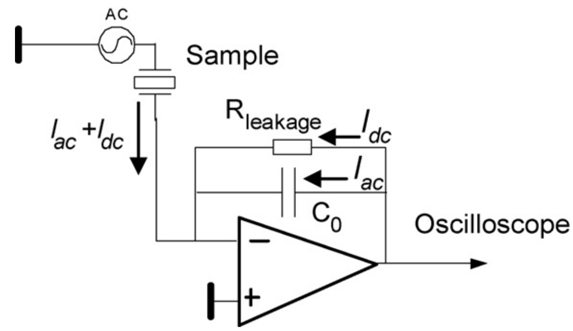

Fig. 6. Detail of the circuit used for hysteresis loops measurement.

be explained by two mechanisms: (i) a static polarization charge appearing at the surface of the sample and establishing a voltage across the measurement capacitor (C_0) in the Sawyer–Tower circuit; (ii) a current flowing through the sample and discharging through the leakage resistor shunting C_0 (Fig. 6).

No offset was observed when a sufficiently low leakage resistor was connected, suggesting that in this material an asymmetrical leakage dc current establishes under the application of the alternating field. Such an asymmetry can be related to the compositional asymmetry of the graded layered structure.

4. Conclusions

Compositionally graded self-standing thick films of $Ba_{1-x}Sr_xTiO_3$ were successfully deposited from airflow. The study showed that ferroelectric and dielectric properties of thick films fabricated by airflow deposition could be deeply modified by gradient composition. To authors' knowledge, hysteresis offset was demonstrated for the first time in such a thick (0.4 mm) compositionally graded structure.

Acknowledgement

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