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3D mapping of anisotropic ferroelectric/dielectric composites

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Abstract

Macroscopic anisotropy in polycrystalline materials is of key interest since it may help filling the gap between randomly oriented polycrystals like ceramics and single crystals. Non-destructive X-ray Computed Micro Tomography (XCMT) is a necessary step towards the full control and modelling of such anisotropy, beyond the standard scheme of interfaces. To ascertain this progress, XCMT is applied to 3D mixtures of ferroelectric and dielectric oxides processed by Spark Plasma Sintering (SPS). In such conditions, not only is this anisotropy seen in the overall dielectric parameters but it also shows up in ferroelectric properties. Experimental macroscopic parameters are linked to the 3D morphological anisotropy of individual MgO inclusions induced during SPS.

Keywords: Ceramics; Ferroelectric; Composite materials; 3Dimensional imaging; X-ray computed micro tomography

1. Introduction

Three-dimensional composites are finding an increasing numbers of uses since they provide improved functionalities as compared to the simple addition of their individual constituents. Interfaces are usually thought to be involved for such composite effects to appear and their analysis is taken as the first step towards modelling 3D materials. On the other hand, we cannot currently find out the actual shape of the composite phases with the required resolution, with the necessary large-scale extension and in 3-dimensions without destroying the samples. X-ray Computed Micro Tomography (XCMT) meets all these requirements provided that the required resolution is reached. In the field of functional materials, XCMT has been mainly used for fluid flow in porous media,[1] for the in situ control of sintering[2] and for mechanical properties.[3] In the first two cases, the resulting 3D map is the starting point for the implementation of fluid dynamics equations.[4] In the third, large-scale elastic excitations are usually considered.[5] This approach is less frequent when materials properties are sensitive to more local fluctuations like dielectrics and this is our main goal here. For this purpose, we processed composites made of a $Ba_{0.6}Sr_{0.4}TiO_3$ (BST) ferroelectric matrix in which MgO inclusions were spread.[6–8] While the former provides unique dielectric flexibility, the latter drives dielectric losses towards the levels required by the electronic industry.[9,10] In the present study, we go beyond this accumulation of properties and show a real composite effect. Thanks to the specific conditions of Spark Plasma Sintering (SPS), we are able to produce inclusions with a large aspect ratio (ellipsoid) while preserving the chemical integrity of both phases. As a result of such anisotropic microstructure, overall anisotropy of the dielectric and ferroelectric properties of the BST/MgO composites is induced. We checked that BST alone processed using the same route did not show any such anisotropy. While piezoelectric ceramics with graded porosity have already been reported to show dielectric anisotropy,[11,12] to the best of our knowledge no ferroelectric anisotropy has been reported. In addition, we propose to link our experimental parameters at low electric field to the 3D morphological anisotropy of the individual MgO

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inclusions and to the sharp inclusion edges facing each other. This is the first step towards realistic mapping of a possible electric field focusing that would fit with the available empirical models.[12–16]

2. Experimental

2.1. BST and MgO powder mixing

$Ba_{0.6}Sr_{0.4}TiO_3$ nanopowders (50 nm) were purchased from Pi-Kem (Tilley, UK) (Sections 3.1 and 3.2) and processed by solid-state route at ICMCB (grain size 200 nm) (Section 3.3). MgO (97%) supplied by Merck (Darmstadt, Germany) is made of spherical spray-dried granules with an average diameter in the range 10–100 μm. Each granule is composed of packed elementary crystallites of nanometer size. The dry powders were mixed by hand in an agate mortar. To investigate the initial state – i.e. powder bed prior to the sintering step – BST-MgO powder mixtures were introduced inside an SPS tool and consolidated using PMMA as binder.

2.2. Sintering

The Spark Plasma Sintering apparatus used was a Dr Sinter SPS-2080 SPS Syntex INC Japan from the *Plateforme Nationale CNRS de Frittage Flash (PNF2/CNRS)* located in Toulouse (France). Powders (without any sintering aids) were loaded onto a cylindrical die of 8 mm inner diameter. The temperature was raised to 600 °C over a period of 3 min, and was then monitored and regulated by an optical pyrometer focussed on a small hole located at the surface of the die. A heating rate of 100 °C min^{-1} was used to reach the final temperature of 1200 °C. All the SPS cycles were performed under vacuum and a uniaxial pressure of either 50 MPa or 100 MPa was applied immediately before and until completion of the temperature rising step. The as-obtained SPS ceramics were re-oxidized during a post-annealing performed step at 800 °C for 12 h in air.

2.3. Microstructural and dielectric study

The microstructure of the sintered compacts was studied using a scanning electron microscope JEOL JSM 6360A and a high-resolution scanning electron microscope JEOL 6700F.

Dielectric measurements were performed using a Wayne–Kerr component analyser 6425 for temperatures between 200 K and 500 K and in the frequency range: 100 Hz–100 kHz. The real part of the permittivity derived from the capacitance and dielectric losses ($\tan\delta = \varepsilon''_r/\varepsilon'_r$) was directly measured. The piezoelectric resonance was recorded using a HP4194 impedance analyser and the pyroelectric currents were measured with a Keithley 6517B electrometer. The experimental conditions are such that the error bars are estimated smaller than the symbols used in the corresponding figures.

The tunability ($A(\%) = |\varepsilon(T,E) - \varepsilon(T,E=0)|/\varepsilon(T,E=0) \times 100$, where E is the electric field and T the temperature) was measured by applying a static field of 1 kV/mm to the sample using a high voltage supply (Bertan Series 225). A homemade decoupling device ensured protection of the impedance meter from the bias. To avoid breakdown in air (~1000 V), the sample was placed in a silicone oil bath.

2.4. 3D imaging

XCMT consists in: first acquiring, for different angular positions, a large number of radiographs of a sample rotating around a fixed axis, and second, in reconstructing from this data set a 3D map of μ, the linear attenuation coefficient of the different components present within the sample.[17] The coefficient μ varies with the energy of the X-ray beam and, for each component, it depends on the average atomic number and the density. When the μ values of the different components are different, 3D μ mapping can be transformed, using image-processing tools, into a 3D image of the internal micro-geometry of the scanned sample.

Different X-ray sources can be used for XCMT. In the present work, we used synchrotron radiation from ID19 the 3D X-ray imaging beamline of the ESRF (European Synchrotron Radiation Facility, Grenoble, France) and from TOMCAT the 3D X-ray imaging beamline of the SLS (Swiss Light Source, Villigen, Switzerland). A typical experiment consisted in recording 2000 radiographs (2048 × 2048 pixels) and about 100 references during a continuous rotation through 180°. The energy was equal to 40 keV and the effective voxel size of the reconstructed 3D images equal to 0.52 μm (ESRF) or 0.37 μm (SLS).

3. Results and discussion

Different parameters can alter the effective properties of multi-materials composed of BST and MgO: the volume fraction of the dielectric phase, the shape of the dielectric inclusions, and the level of chemical inter-diffusion between the two phases. We have already shown that, in ceramics obtained from a mixture of BST and MgO powders, increasing the MgO content up to 10 wt% within the BST matrix efficiently decreases the dielectric losses but leads to a loss of tunability. The optimal value in order to decrease the low frequency dielectric losses while keeping sufficiently high permittivity tunability is around 4 wt% MgO.[8]

3.1. Tuning inclusion shape by pressure

3.1.1. Initial microstructure

First, using SEM we examined the MgO granules before mixing. They appear as spheroidal particles with a large dispersion in size (Fig. 1a). The mixing process is mild enough to maintain this shape as shown in Fig. 1b where SEM was used to scan a polished section through a sample of the initial mixture consolidated by PMMA impregnation. The section reveals the internal structure of two MgO particles that appear to be highly heterogeneous, being composed of a several spherical shells. Within the BST matrix some heterogeneities are also visible such as large zones of lower porosity. The cracks that are visible around the MgO particle and through the matrix are mainly due to the