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Electric Current as a Driving Force for Interphase Growth in Spark Plasma Sintered Dielectric Composites

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All-oxide composites are increasingly investigated in the field of microelectronics and telecommunications because of their multifunctionalities. Advanced control of interfaces is required to fully tune the macroscopic properties of the composites. Processing ferroelectric $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST65/35)- TiO_2 composites by Spark Plasma Sintering (SPS), we show that the SPS electric current promotes an interphase growth whose thickness depends on the BST/ TiO_2 stacking and on the current direction. In all cases, the interface is composed of $\text{Ba}_{1.14(2)}\text{Ti}_{8}\text{O}_{16-\delta}$ a highly defective, but stable phase which can be used to tune the overall dielectric properties of the composites.

I. Introduction

DIELECTRIC properties can be tuned in ferroelectric based composites controlling charged defects at interfaces. Focusing on BaTiO_3 ceramics, giant effective dielectric parameters can be obtained by appropriate substitutions, by assembling different phases, or decreasing grain size using fast sintering such as SPS.¹⁻³ The charges, at the origin of huge permittivity values, can arise from the reduced state of titanium due to high density of oxygen vacancies. Recently, colossal permittivity was also reported in (Nb+In) co doped TiO_2 ceramics and defects engineering at the grain boundaries was explored using the specific features of SPS to reach in depth understanding of the resulting dielectric properties.⁴ In all cases, giant effective dielectric properties are related to the localization of free electronic charges at interfaces whatever their 3D extension and their density in the materials. However, in composites, both a control and a detailed investigation of the chemistry and structure at the interface are required to tune dielectric properties. SPS is widely used for the assembly of composites, but the current and/or temperature effects on the rate of growth of interphases was mainly studied for multilayers intermetallic systems.⁵⁻⁷ The electric current is mostly assumed to enhance sintering by activating mass transport mechanisms, but its influence on the charge defects concentration and mobility was demonstrated. The impact of both the current density and direction on the formation of interphases was recently reported.⁸ It was shown that the current direction did not influence the direction of the atomic diffusion in most intermetallics.⁹⁻¹¹

We show here that such studies can be extended to dielectric materials by adjusting the composite architecture (bilayer, multilayer or random 3D mixing) and the SPS conditions. We

used SPS on ceramic composites made of ferroelectric $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ (BST65/35) and dielectric TiO_2 phases to probe the reactivity at the interfaces. Our main result is that the electrical current direction can tune the interphase growth. We ascribe this to the preferential titanium reduction in TiO_2 . As a consequence, we observe strong variations in the dielectric properties depending on the composite architecture and on the direction of the current during SPS. The specific SPS conditions thus enable the control of both the interface between the two components and the reduction level leading to interface driven dielectric properties.

II. Experimental Procedure

Bilayers and multilayer stacks were prepared using BST65/35 powders, synthesized by solid state reaction, and commercial TiO_2 . For the BST65/35 4% TiO_2 random 3D mixing ceramics, TiO_2 microspheres were prepared by spray drying (B 290 Buchi[®] device, Büchi Labortechnik AG, Flawil, Switzerland) from a suspension of nanocrystalline rutile TiO_2 powder (98% purity, Dupont[®], Wilmington, DE. The as obtained spherical microsized particles (size about 40 μm) were first consolidated individually at 1400°C during 2 h. SPS (SYNTEX, Dr. Sinter 515S, Kanagawa, Japan) was carried out in vacuum using a uniaxial pressure of 90 MPa. The sintering temperatures and the holding time were 1200°C and 1300°C, and 10 min, respectively. A pulse configuration of 12 pulses followed by two periods of zero current was used. Postannealing at 800°C during 10 h under air were performed to reoxidize the ceramics. Microstructure and chemical analysis of the composites were conducted using Scanning Electron Microscope (SEM, JSM 6330A; JEOL, Tokyo, Japan) and Electron Probe Micro Analysis (EPMA, CAMECA SX100, Gennevilliers, France).

III. Results and Discussion

(1) Control of Interdiffusion in BST/ TiO_2 Bilayers Through SPS Conditions

An interphase between the BST and TiO_2 phases was observed in SPS bilayers. EPMA analysis revealed a preferential diffusion of barium into the TiO_2 layer leading to the formation of barium titanate hollandite phase $\text{Ba}_x\text{Ti}_{2x}^{3+}\text{Ti}_{8-2x}^{4+}\text{O}_{16-\delta}$. This is in good agreement with the higher mobility of Ba^{2+} cations.^{12,13} The existence of a solid solution with a single phase region corresponding to a barium concentration in the range $1.143 < x < 1.333$ was reported in literature.¹⁴ Furthermore, the structure can adopt oxygen deficient stoichiometry (up to $\delta = 0.4$) according to the temperature and the atmosphere conditions.¹⁵ In the present work, the low oxygen partial pressure during sintering favors the creation of oxygen vacancies and associated Ti^{4+} reduction into Ti^{3+} that are preferentially localized within TiO_2 layer. This

is confirmed by the dark color of the TiO_2 layer whereas BST layer remains white. The hollandite type interphase obtained is thus assumed to be oxygen deficient with a barium concentration close to 1.14 according to EPMA analysis. However, a gradient of compositions within the hollandite phase region can be expected depending upon the thickness of interface. Further chemical and TEM analyses are required to accurately determine the composition. Here, we focused on two specific parameters to understand how the interphase is formed: the sintering temperature and the direction of the current with regard to the order of layers within the stack. The sintering temperature window was selected to enhance the defects mobility and the holding time was maintained short enough to rise the role of the electrical current with respect to thermodynamic equilibria and transport kinetics. At a sintering temperature of 1300°C , changing the layers sequence versus the direction of the electric current clearly highlighted a modification of the interface thickness: when

the TiO_2 layer was in contact with the positive electrode, the interphase thickness is $200\ \mu\text{m}$ [Fig. 1(a)], whereas the value decreases down to $100\ \mu\text{m}$ [Fig. 1(b)] when reversing the BST65/35 TiO_2 stacking. A decrease in the sintering temperature from 1300°C to 1200°C led to a decrease in interphase thickness whatever the order of the layers within the stacks [Figs. 1(c d)]. Combining a lower sintering temperature with the current direction effect allows reducing the interphase thickness down to $10\ \mu\text{m}$. This result is fully reproducible confirming thus the direct effect of the current flow on the defects mobility through the interface.

(2) Dielectric Properties of Bilayers

Dielectric measurements were performed on postannealed SPS bilayers. Permittivity values are in the range 4000 5000 [Fig. 2 (a d)] whatever the interphase thickness. However, an increase in the dielectric losses peak at low temperature is

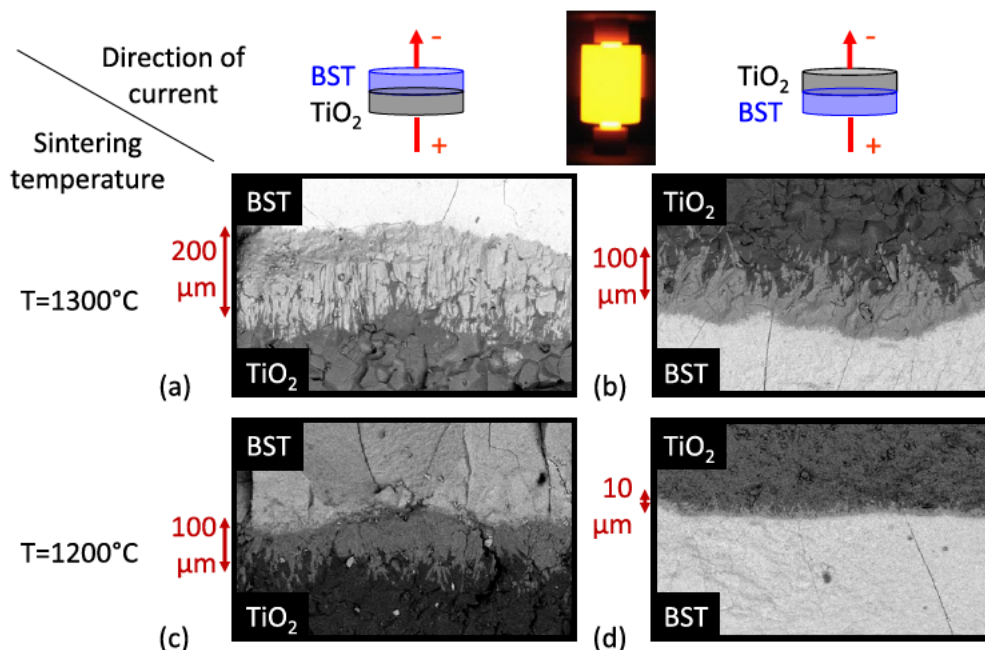


Fig. 1. (a d) SEM micrographs of the fracture surface of BST65/35 TiO_2 bilayers. The thickness of the $\text{Ba}_{1.14(2)}\text{Ti}_8\text{O}_{16-\delta}$ interphase depends on the sintering temperature and on the electric current direction.

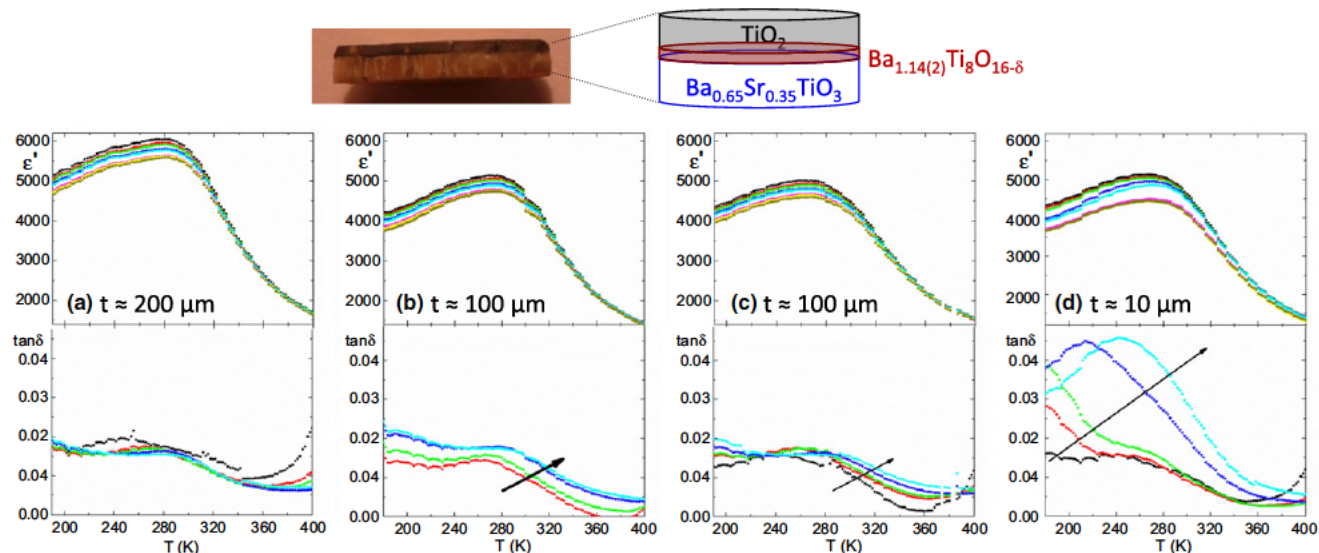


Fig. 2. Picture and schematic representation of the BST65/35 TiO_2 bilayer. Temperature and frequency dependences of the permittivity and losses of bilayers with different interphase thicknesses: (a) $t \approx 200\ \mu\text{m}$, (b c) $t \approx 100\ \mu\text{m}$ (sintered at 1300°C and 1200°C , respectively), and (d) $t \approx 10\ \mu\text{m}$. Black arrow indicates increased frequency from 100 Hz to 10 kHz.

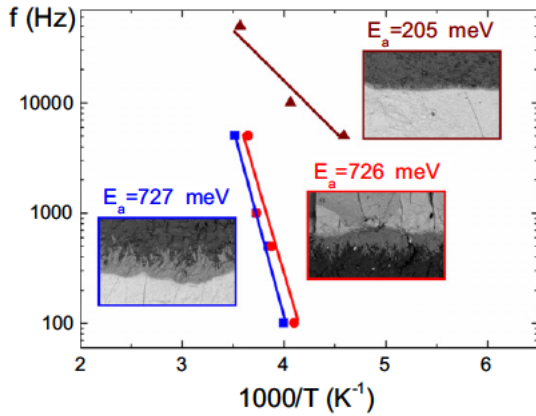


Fig. 3. Arrhenius plot for the BST65/35 TiO₂ bilayers ($t_{\text{interphase}} \approx 100$ and $10 \mu\text{m}$). Activation energies of the dielectric relaxations are reported.

observed for the composite with the $10 \mu\text{m}$ thin interphase [Fig. 2(d)].

Plotting the operating frequency at which the loss peak occurs versus the temperature on an Arrhenius scale (Fig. 3), the activation energy, which is the slope of these lines, can be linked to the thickness of the interphase in the bilayers. The activation energy is large ($E_a > 600$ meV) for $t \approx 100 \mu\text{m}$ (whatever the sintering temperature) while it is reduced in thinner interphase ($E_a \approx 205$ meV for $t \approx 10 \mu\text{m}$). Such an effect is quite unexpected since the dielectric activation energy should be related to intrinsic parameters and not to interface microstructure. Ti³⁺ impurity levels linked to oxygen vacancies can be excluded since such defects lead to

low activation energies ($E_a < 100$ meV) resulting from the vicinity of these levels to the bottom of the conduction band. The changes in activation energies may be due to the composition of the interphases. Indeed, for thin interphases the composition, mainly Ba²⁺ concentration that can vary over more than $10 \mu\text{m}$, never reaches the stable one that may favor the charges mobility (including the ionic one) thus reducing the activation energy. On the other hand, for interphases much thicker than the zone of composition variation, stable and well compensated interphase is to arise far from the BST TiO₂ interface. As a result, conductivity barrier maybe built in such interphases and the activation energy is larger. Beyond the qualitative link between the interphase thickness and the activation energy, more investigations are needed to clarify this link.

(3) Dielectric Properties of Multilayer and 3D Composite

The number of interfaces was increased in multilayers and 3D composite (Fig. 4). Whatever the architectures, TiO₂ is preferentially reduced and an interphase is formed with a composition similar to the one detected in bilayers. A dielectric relaxation is measured in both cases [Fig. 4(a)]. In the 3D composite, giant permittivity ($\epsilon'_{\text{max}}(10 \text{ kHz}) = 53400$) and high dielectric losses ($\tan\delta > 1$) are obtained even after postannealing [Fig. 4(b)]. The reoxidation of the TiO₂ inclusions can be tuned by successive calcinations in air as shown by the strong decrease in both the dielectric permittivity and losses.

IV. Conclusion

BST65/35 TiO₂ composites with 2D and 3D architectures sintered by SPS led to the formation of Ba_{1.14(2)}Ti₈O_{16-δ} interphase. This interphase, originating in the TiO₂ phase, is

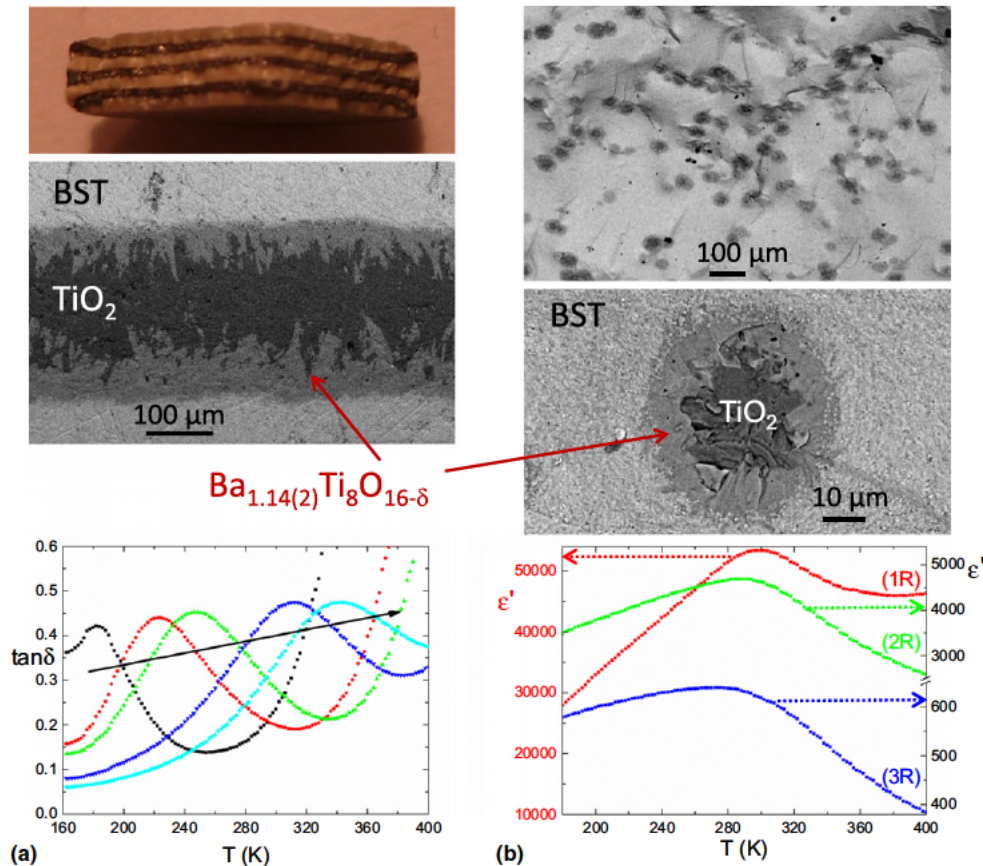


Fig. 4. SEM micrographs of the fracture surfaces of (a) the multilayer and (b) the 3D ceramics. (a) Dielectric relaxation is represented by a black arrow with increasing frequency from 100 Hz to 10 kHz. (b) Temperature dependences of the dielectric permittivity at 10 kHz after three successive reoxidation steps (1R, 2R and 3R).

oxygen depleted as compared to TiO_2 , and Ba^{2+} ions diffuse from BST to compensate the oxygen deficiency. The interphase growth rate can be tuned by the sintering temperature and the direction of the electric current during SPS. We suggest that such interphase control, which was never observed in dielectric multilayers, can be extended to other interphases between oxides of different reduction ability. We also found that the activation energy of a dielectric relaxation that appears close to room temperature depends strongly on the interphase thickness. Such a tuning is rather seldom because dielectric relaxations that originate from charged impurities mostly rely on their induced energy level within the band gap, but not on the extent of the interphases. Increasing the number of interfaces in 3D composite may result in giant permittivity and the permittivity can be tuned through reoxidation cycles. Further work is in progress to understand such interface driven dielectric properties when increasing the density of interfaces while remaining below the percolation threshold.

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