Controlling internal barrier in low loss BaTiO$_3$ supercapacitors

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Supercapacitor behavior has been reported in a number of oxides including reduced BaTiO$_3$ ferroelectric ceramics. These so-called giant properties are however not easily controlled. We show here that the continuous coating of individual BaTiO$_3$ grains by a silica shell in combination with spark plasma sintering is a way to process bulk composites having supercapacitor features with low dielectric losses and temperature stability. The silica shell acts both as an oxidation barrier during the processing and as a dielectric barrier in the final composite.

Commercial supercapacitors are using polycrystalline materials in which metallic grains or foils (such as tantalum) with extended specific surface are covered by their respective oxides (such as tantalum oxide). The resulting barrier layers locate electronic and ionic space charges, increasing the capacitance density. While such barrier layer supercapacitors are of everyday use,[1,2] an improved control of the interfaces barrier in such advanced materials would lead to increased functionalities: higher charge storage ability, lower losses, and increased cutoff frequency. We show here that individual coating of ferroelectric BaTiO$_3$ grains by a silica shell followed by a fast sintering in reducing conditions leads to such stable supercapacitor behavior in electroceramics. The tuning of a dielectric shell at the grain scale, as compared with standard routes, offers several opportunities for electroceramics.

Actually, there is an intense wave of research on materials displaying extreme dielectric parameters. Many compounds such as CaCu$_3$Ti$_4$O$_{12}$ and LuFe$_2$O$_4$ have been quoted as "giant" permittivity materials. Well known and widely used ceramics such as BaTiO$_3$ show huge effective dielectric parameters when appropriately substituted or when decreasing the grain size under fast sintering conditions.[3–6] In all cases, the apparent dielectric permittivity is high at room temperature ($\varepsilon > 10^5$ in some cases) and is temperature independent in a broad range before falling down at low temperatures. While these features are very appealing for applications, some parameters are still not controlled; the dielectric losses are high and low frequency contributions to the dielectric permittivity are ascribed to dc conductivity. In CaCu$_3$Ti$_4$O$_{12}$ ceramics, this dielectric behavior was ascribed to an internal barrier layer (IBLC) at the grain boundaries.[7] Within this model, the measured huge capacitances are not increased by intrinsic dielectric parameters but by geometrical confinement of the dielectric at the grain boundaries. All the abovementioned materials can be described using this IBLC model, each of them having different free charges able to increase the inner grain conductivity.[8] However, the key parameter, which is the grain boundary interface, is still not well understood and controlled. This is a strong drawback in order to reproduce the dielectric performances and to reduce

the dielectric losses of IBLC ceramics. We propose here to solve this issue by using advanced processing of core@shell particles sintered using spark plasma sintering (SPS).[9,10] By means of homogeneously coated BaTiO$_3$ grains with an amorphous silica shell, we were able to obtain composite ceramics of apparent permittivity of 2×10^5 and losses of only a few percent at 10^4 Hz, which are stable against temperature.

The two main conditions for the IBLC to increase the overall dielectric permittivity of oxides are the inner grain conductivity and the insulating grain boundary. The former is related to the amount of charged defects, which are intentionally introduced prior to the precursor reaction or during the sintering step under reducing conditions.[6,11] The stabilization of such charged lattice defects in a reproducible way in BaTiO$_3$ ceramics is still a challenge. Even the way to compensate for heterovalent substitution such as La^{3+} on the Ba^{2+} site of BaTiO$_3$ is still a matter of debate.[11,12]

The control of the grain boundaries (i.e., tuning their morphologies and electrical properties) is also not an easy task. Indeed, depending on the size and the chemical state of the starting grains, the sintering step of the bulk ceramics can strongly alter shape, charges, and electronic state of the grain boundaries. For BaTiO$_3$, many discrepancies have been quoted in the literature depending on the processing route.[13–15] This is even more true when fast sintering processes under reducing atmosphere such as SPS are used.

This is why we decided to coat each BaTiO$_3$ grain prior to the sintering step in order to improve the reproducibility of the grain boundaries in dense ceramics. The first step is to
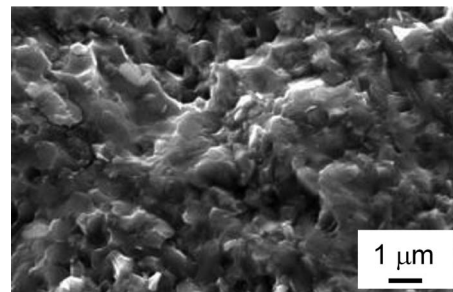

FIG. 1. HRSEM micrograph of the fracture of [BT500@Si5] sintered by SPS at 1100 °C under vacuum.

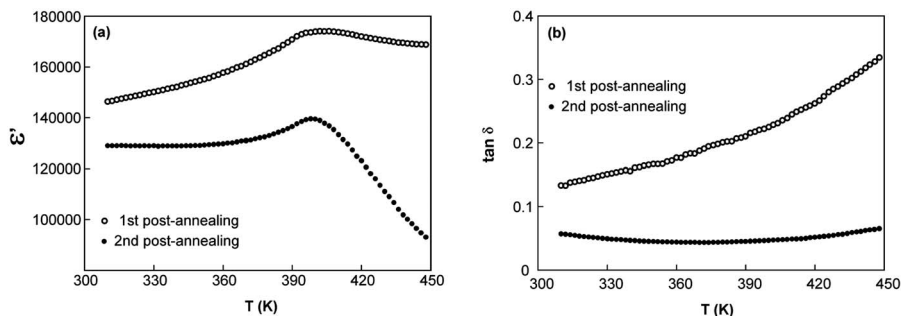a)Electronic mail: maglione@icmcb-bordeaux.cnrs.fr.

FIG. 2. (a) Thermal evolution of the real part of the permittivity at 10 kHz after first and second postannealing. (b) Thermal evolution of loss tangent at 10 kHz after first and second postannealing.

produce core@shell powders made of $BaTiO_3$ cores surrounded by a continuous and homogeneous shell of amorphous silica (SiO_2). We previously showed that the thickness of the shell can be tuned continuously from few nanometers up to tenths of microns. This core@shell architecture was efficient to decrease the dielectric losses of the final ceramics and also to achieve multifunctionality on including nanoparticles in the coating.[9,16] For the present purpose of achieving extremely high and reproducible dielectric permittivity ceramics, we started from standard $BaTiO_3$ particles of 500 nm diameter purchased from Sakai Chemical Co. (Japan). All the particles have been individually coated with a homogeneous amorphous silica shell of 5 nm thickness using a method derived from the Stöber process, as described in detail elsewhere.[9] Core@shell $BaTiO_3$(500 nm)@SiO_2(5 nm) particles are denoted as [BT500@Si5].

Once the starting core@shell particles are available, the sintering step should also be optimized since any porosity is detrimental for getting large capacitance density. Improved two-step sintering has been used but long dwelling times are required (950 °C, 12 h) and the resulting density does not reach 85%.[17] As to build an IBLC ceramic, we then need to induce charged point defects in the ceramics. It has been previously shown that SPS, which is operated under reducing atmosphere, is able to create such defects as Ti^{3+} associated to oxygen vacancies.[6] The SPS experiments were performed in a Dr Sinter SPS-2080 Syntex Inc., Japan. A heating rate of 100 °C min^{-1} was used to reach the final temperature of 1100 °C under vacuum. A uniaxial pressure of 50 MPa was applied immediately before and until completion of the temperature rising step. The as obtained ceramics have a surface layer contaminated by carbon coming from the graphite die in which the pellets are pressed. A postannealing step at 800 °C for 12 h in air is performed for decarbonation of the samples; the density reached 97% for all of them. After this first postannealing treatment, the pellet remains navy blue

stemming from the reduction state of titanium (this color being usually ascribed to Ti^{3+}-VO centers).

A second identical thermal treatment did not allow reoxidizing the sample, highlighting the efficiency of silica as a barrier against reoxidation. Considering the extreme SPS sintering conditions, the silica in the final pellet can be viewed as a glassy matrix in which the BT grains are embedded as evidenced by high resolution scanning electron microscopy (HRSEM). The grain size remains close to the initial one (i.e., 500 nm), and the fused aspect on the grains surface is attributed to the glassy silica matrix (Fig. 1).

Having confirmed that charged defects are indeed stable in the ceramics, we next need to check the silica shell at the grain boundaries. In a separate paper, we used *in situ* transmission electron microscopy (TEM), high resolution TEM, and x-ray photoelectron spectroscopy (XPS), showing the preservation of the silica coating under the mentioned SPS conditions [submitted]. We point out that cross diffusion between silica and $BaTiO_3$ is moderate and that amorphous silica is still surrounding the grains in the ceramics. The capacitance and dielectric losses of the samples were recorded as a function of temperature (4–450 K) and frequency (100 Hz–10 MHz). In Fig. 2, we report the real part of the dielectric permittivity (ε') and the dielectric losses (tan δ) in the temperature range 300–450 K for several spot frequencies. These parameters are only apparent ones, and even if they should be considered with some care because of the IBLC model, we will, however, discuss them for sake of comparison with the existing literature. First, the room temperature dielectric permittivity is in the range of the so-called giant dielectric materials ($\varepsilon \sim 2.10^5$ at $f = 10^4$ Hz), meaning that our core@shell particles are indeed leading to IBLC ceramics [Fig. 2(a)]. The main achievement here is that the dielectric losses are much smaller than the ones previously reported, i.e., tan $\delta \sim 5\%$ at $f = 10^4$ Hz instead of 100% in the existing literature [Fig. 2(b)]. Moreover, the absence of
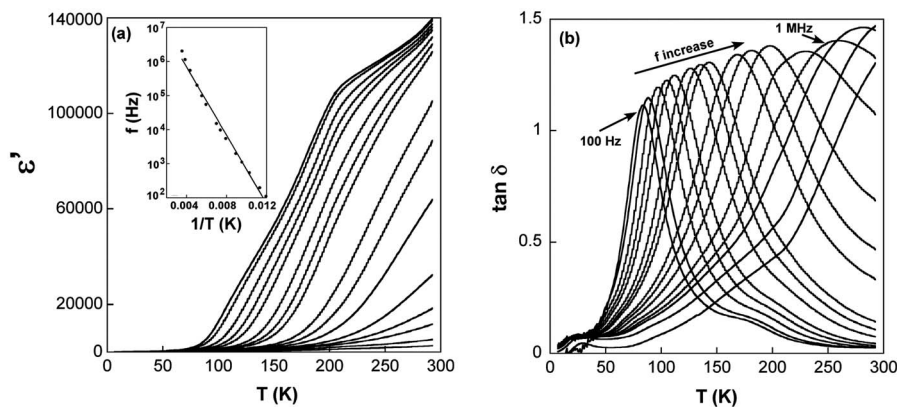

FIG. 3. (a) Dielectric permittivity at low temperature ($T < 300$ K) for several frequencies in the range of 100 Hz–1 MHz. (Inset) The activation energy of this relaxation is 0.15 eV, which is consistent with what reported in many different materials. (b) Dielectric losses at low temperature ($T < 300$ K) for several frequencies in the range of 100 Hz–1 MHz. The shift in the loss maximum stems from a dielectric relaxation whose Arrhenius behavior is evidenced.

apparent conductivity contribution at low frequencies shows a small conductivity across the whole ceramic even at $T > 100\ ^{\circ}\text{C}$. These two main features, lower dielectric losses and the absence of a conductivity contribution, may be ascribed to the silica coating. Another interesting feature is the small maximum in the dielectric permittivity at the ferroelectric/paraelectric transition temperature $T = 400$ K [Fig. 2(a)]. This means that the bulk ferroelectric properties of the material are not totally cancelled by the IBLC effect.

To get a more quantitative insight into this IBLC contribution to the increased dielectric parameters, one should follow the dielectric relaxation, which inevitably occurs for all of similar materials.[8] Such relaxation clearly appears on Fig. 3(a) where the real part of the dielectric permittivity bends down sharply at low temperatures. As for every supercapacitor, the high frequency permittivity is thus much lower than the low frequency one. The relaxation is better seen on the losses that undergo a strong maximum and whose temperature is shifted with the operating frequency [Fig. 3(b)]. Both the shape and the shift in this maximum stem from a dielectric relaxation, which is nothing but the relaxation of the space charges located at the grain boundaries. The activation energy of this space charge may be mapped out on plotting the characteristic frequencies and temperatures in an Arrhenius plot [Fig. 3(a) inset]. The linear evolution evidences the exponential behavior of the relaxation frequency $f = f_0 \exp -(E/kT)$, where f_0 is the high temperature extrapolation of the relaxation frequency and E is its activation energy; $E = 0.15$ eV, which agrees with similar relaxations observed in many other materials.[8] This supports space charge relaxation at the IBLC as a probable mechanism. Indeed, 0.15 eV is in the range of the Ti^{3+} level position below the conduction band of $BaTiO_3$. Electron hopping between such defects and their localization at the interface is thus a way to artificially increase the dielectric properties.[18,19]

Compared with IBLC ceramics referred in literature, our core@shell composites exhibit unprecedented behavior as they combine both giant permittivity and stable dielectric losses as low as 5% at 10 kHz. In a similar way, our structures can be called ISBLC (S for *silica*). The occurrence of the Curie temperature maximum indicates that the bulk properties of the composite are not cancelled by the silica barrier layer. Microstructural investigations allowed to describe the final composite structure as ferroelectric grains embedded in a glassy matrix. SPS does not only help for densification but allows quenching the amorphous silica in a glassy state,

thanks to the extremely fast sintering and cooling rates. In turn, this glassy silica cage allows an irreversible reduction in the BT core (induced by the reducing SPS sintering conditions). As a result, the SPS allows acting on both the core and the shell. The silica is both a dielectric barrier and a reoxidation barrier leading to low loss supercapacitor. In addition, its thickness can be easily controlled leading to reproducibility and reliability of our composite properties. The supercapacitor behavior has been ascribed to space charge relaxation associated to Ti^{4+} reduction.

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