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The properties of a commercial grain boundary barrier layer (GBBL) $SrTiO_3$-based capacitor are analyzed in terms of capacitance C and resistivity R of two RC elements, one for grains and one for grain boundaries. Results are compared with those of $CaCu_3Ti_4O_{12}$ (CCTO) samples showing giant permittivity, measured in the same conditions and analyzed with the same method. All CCTO samples investigated here show higher permittivity than GBBL. This is shown to be related to a higher capacitance of the grain boundaries. However, the electric losses of CCTO measured via conventional tan(δ) are found significantly higher. They are related to a resistivity of the grain boundaries lower than in GBBL capacitor. A better control of the grain boundaries in CCTO possibly via a core-shell synthesis described here, followed by thermal post treatments under a controlled atmosphere as it is performed for GBBL capacitors, is suggested to improve the resistance of CCTO dielectrics.

Keywords: Colossal permittivity, core-shell, Internal Barrier Layer Capacitance (IBLC), Grain Boundary Barrier Layer (GBBL), CCTO

1. Introduction

Class III ceramic capacitors are based on the phenomenon of barrier layers associated with grain boundaries. They offer higher volumetric efficiency than Class II capacitors. Class III ceramic capacitors are used for filtering, buffer, by-pass and coupling applications in electronic circuits. The constraints of miniaturization require increasing the permittivity of ceramic capacitors. Provided that grains are sufficiently conducting, the permittivity of Class III capacitors may be approximated by [1] [2] :

$$\varepsilon_r = \varepsilon_{gb} A/t \qquad (1)$$

ε_r is the relative permittivity of the sample, ε_{gb} the permittivity of the grain boundary, A the average grain size and t the average thickness of grain boundaries. The dielectric properties of GBBL ceramics may be properly described with two RC elements, one for grains and one for grain boundaries [3]. Since the beginning of this century, the Internal Barrier Layer Capacitance (IBLC) model has been shown to apply to $CaCu_3Ti_4O_{12}$ (CCTO) samples showing colossal permittivity [4] [5] [6] [7]. According to Eq. (1), ε_r has been shown to scale with the average grain size of CCTO [8]. ε_r/A has been shown to scale with the capacitance of grain boundaries C_{gb} which is related with ε_{gb}/t in Eq. (1) (see e.g. Fig. 2 of [9]). The resistivity of the sample has been shown to scale with the resistivity of the grain boundary [10].

In order to evaluate the potential of CCTO-based dielectrics to make competitive Class III ceramic capacitors, the characteristics of several samples of CCTO synthetized in various conditions, core-shell or organic gel-assisted citrate process [9] are compared with those of a commercial GBBL capacitor provided by Johanson Technology. The dielectric of the GBBL capacitor studied here is $SrTiO_3$-based. Since this perovskite material is an insulator, a first thermal treatment under a reducing atmosphere is applied to make the grains sufficiently conducting [11]. A second treatment under oxidizing atmosphere is applied to recover the insulating character of the grain boundaries. This second treatment should be soft enough to avoid changing the conductivity of the grains obtained in the first step.

2. Experimental

The CCTO grains were synthesized by mixing stoichiometric amount of $CaCO_3$, CuO and TiO_2 powders via ball-milling media in ethanol during 24 h. The resulted mixing was calcined at 950 °C for 24 h. The average size of CCTO particles was evaluated to 1.5 µm by a Malvern zetasizer using dynamic light scattering. Using a hielscher sonotrode, ultrasonic sol-gel reaction promote the synthesis of CCTO@Al_2O_3 core–shell [12]. The amount of aluminium isopropoxide precursor solution (0.15 g of aluminum isopropoxide dissolved in 45 mL of ethanol) was calculated from the average size CCTO particles to obtain an alumina nanocoating of 10 nm. Secondly, 5 g of CCTO powder dispersed in 420 mL of ethanol was added in the precursor solution and sonificated during 20 minutes. Then, 50 mL of H_2O/ethanol mixture (1:5 (v/v)) was added. The final mixture was ultrasonicated during 2 h. The as-formed CCTO@Al_2O_3 core-shell powder was collected by centrifugation (305 RCF-5min). After, the nanocoating powder was washed several times with ethanol and dried overnight at 60°C. Pellets of about 13 mm of diameter and 2 mm of thickness for undoped CCTO and CCTO@Al_2O_3 powders were pressed and sintered at 1050°C during 5 h. Another sample of undoped CCTO sintered at 1050°C during 24 h has also been investigated for comparison. Data of a copper-deficient sample labelled Cu2.91 studied previously [13] are also used for further comparison.

The microstructural analysis of the ceramics was performed by scanning electron microscopy (SEM, Hitachi 4160-F). For electrical measurements, the pellets was polished and sputtered with silver on each surface. The samples were characterized by complex impedance in a frequency range from 100 Hz to 10 MHz at room temperature by using an Agilent 4294A impedance analyzer. XRD analyses of the sintered pellets show no peak that does not match those of cubic CCTO.

3. Results and discussion

SEM images of undoped CCTO and core-shell CCTO@Al_2O_3, sintered during 5 hours at 1050°C, are shown in Figure 1. Figure 2 shows SEM images of the dielectric of a commercial $SrTiO_3$-based GBBL capacitor. Figure 3 compares permittivity and dielectric losses of CCTO and CCTO@Al_2O_3 samples sintered 5 hours at 1050°C, together with the data for the GBBL capacitor. The permittivity of CCTO samples appears well above that of GBBL capacitor, at least in the range from 100 Hz up to 500 kHz. Figure 4 shows a fit with two RC elements of the dielectric of the GBBL capacitor. The same kind of fitting has been performed for CCTO samples. Results are shown in Table 1. Four CCTO samples investigated here show higher permittivity at 1 kHz than that of the GBBL capacitor. According to Eq. (1), the higher permittivity is related to a higher capacitance of the grain boundaries of all CCTO samples by two or three orders of magnitude compared to that of the GBBL sample. A level 45 times higher than that of GBBL samples is even reached in the sample Cu2.91 which is copper-deficient. However this is reached at the expense of the dielectric losses. They are much too high to fulfill the criteria for a capacitor. Although remaining compatible with the requirements for Class III capacitors, it is seen that tan(δ) at 1 kHz of other CCTO samples are 5 to 8 times higher than that of the GBBL capacitor. This disadvantage is related to the lower resistivity of grain boundaries of CCTO and CCTO@Al_2O_3 samples that are at least two orders of magnitude lower than that of the GBBL capacitor. Another consequence is a sample resistivity that is at least two orders of magnitude lower in CCTO samples compared to GBBL capacitor. Another disadvantage is that the breakdown voltage of CCTO is limited to 240 V/cm. It is increased up to 410 V/cm in CCTO@Al_2O_3 but it remains lower than the breakdown voltage of the GBBL capacitor that exceeds 1300 V/cm. One CCTO sample doped by Sr and Cr nevertheless show a resistivity of 10^{10} Ω.cm. This is equivalent to that reported for the GBBL capacitor. This high level was favored by insulating TiO_2 anatase in grain boundaries as characterized by Raman scattering (De Almeida-Didry *et al* 2016). The permittivity of the doped sample reached 13,000, thus comparable to that, 15,000, of the GBBL capacitor. The lower permittivity of this sample compared to higher values of four other CCTO samples is related to a lower capacitance of grain boundaries as shown in Table 1.

4. Conclusion and perspectives

Compared to commercial GBBL capacitors, CCTO samples appear promising in terms of generally higher permittivity. However, a progress would be welcome in terms of electric losses. The key factor of progress is the properties of the grain boundary. Both capacitance and resistivity of grain boundaries would be advantageously increased. In $SrTiO_3$-based GBBL capacitors, if the grain boundary is supposed to be composed of $SrTiO_3$, two advantages are obvious: the stoichiometric composition is intrinsically insulator and its permittivity measured in bulk sample is rather elevated, ~ 100 at 1 THz. Bulk CCTO shows a similar permittivity of ~ 100 at 1 THz. CCTO is a semiconductor. This is an advantage since the thermal treatment under reducing atmosphere performed in GBBL capacitors is not needed in CCTO. However, if the composition of grain boundaries is CCTO itself, a thermal post-treatment under controlled atmosphere would be needed to make it insulating. Another method investigated here is to try by core-shell method to force the grain boundaries to be made of an insulating material, here Al_2O_3. Results of Figure 3 and of Table 1 show that this approach seems promising. For this test, the permittivity of Al_2O_3 is only ~ 6. It leaves a wide choice of materials with higher permittivity to improve ε_r via ε_{gb} in Eq. (1).

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Table caption

Table 1 – Characteristics of five CCTO samples compared to that of a GBBL commercial $SrTiO_3$ capacitor. In terms of low electric losses, characterized by high sample resistivity and high R_{gb}, the GBBL capacitor appears the best. One CCTO sample doped with Sr and Cr which has been shown by Raman scattering to have insulating anatase grain boundaries, shows similar sample resistivity et similar permittivity. Conversely, four CCTO samples show higher ε_r related to higher C_{gb} by one or even two orders of magnitude at 1 kHz. When the grains are the most conducting, they give a net signature in the Cole-Cole plot and they are well deduced from the fit to experimental data. Conversely, when the resistivity of the grains exceeds ~ 10000, their signature is too small in experimental data to be determined precisely, hence the wording “undefined” in the Table.

Sample label	ε_r at 1 kHz	tan(δ) at 1 kHz	Sample resistivity (Ω.cm)	R_{gb} (Ω.cm)	C_{gb} ($F.cm^{-1}$)	R_g (Ω.cm)
CCTO–24 h	62000	0.05	$1.3\ 10^{7}$	$8.5\ 10^{6}$	$4.5\ 10^{-7}$	~ 10000
CCTO–5 h	58000	0.08	$3.5\ 10^{6}$	$2.3\ 10^{5}$	$6.3\ 10^{-8}$	Undefined
CCTO@Al_2O_3	81000	0.08	$8.7\ 10^{7}$	10^{6}	$7.7\ 10^{-8}$	Undefined
Cu2.91	684000	7.78	$4.5\ 10^{2}$	190	$7.7\ 10^{-7}$	128
CCTO-10 % Sr^{2+}- 4 % Cr^{3+}	13000	0.06	10^{10}	$4\ 10^{6}$	$1.1\ 10^{-8}$	60
GBBL	15000	0.01	10^{10}	10^{10}	10^{-10}	53

Table 1

Figure captions

1 – SEM images of (a) CCTO and (b) CCTO@Al_2O_3 pellets sintered at 1050°C during 5 hours.

2 – SEM images of the $SrTiO_3$-based dielectric of the commercial GBBL capacitor.

3 – Frequency dependence of the relative permittivity and tan(δ) of CCTO and CCTO@Al_2O_3 samples sintered at 1050°C during 5 hours, compared to those of $SrTiO_3$-based GBBL capacitor.

4 – A fit with two RC elements and the parameters given in Table 1 to the complex impedance data measured in the $SrTiO_3$-based GBBL capacitor.

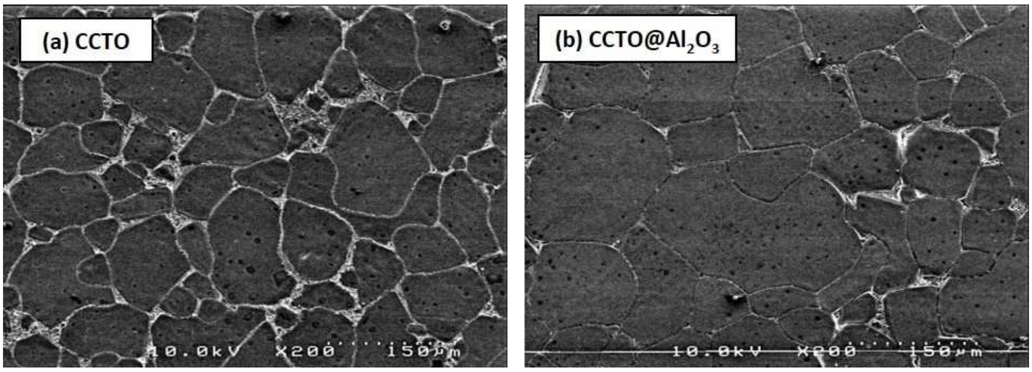
(a) CCTO
10.0kV X200 150μm
(b) CCTO@Al_2O_3
10.0kV X200 150μm

Fig. 1

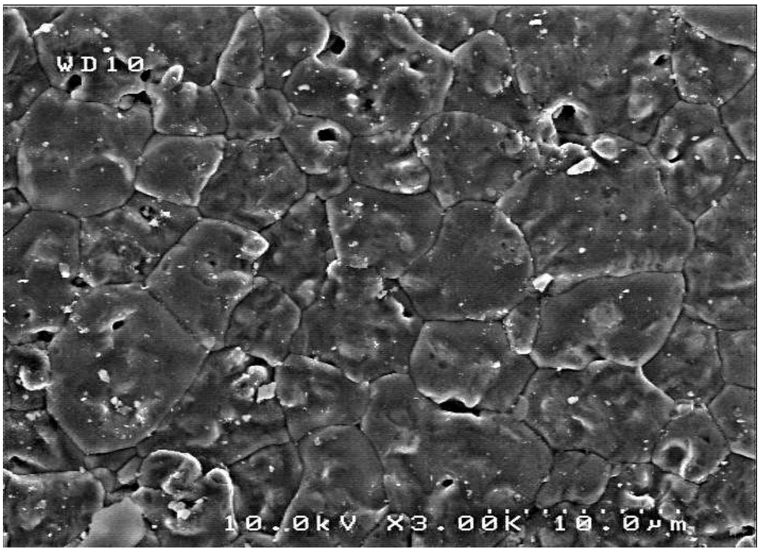
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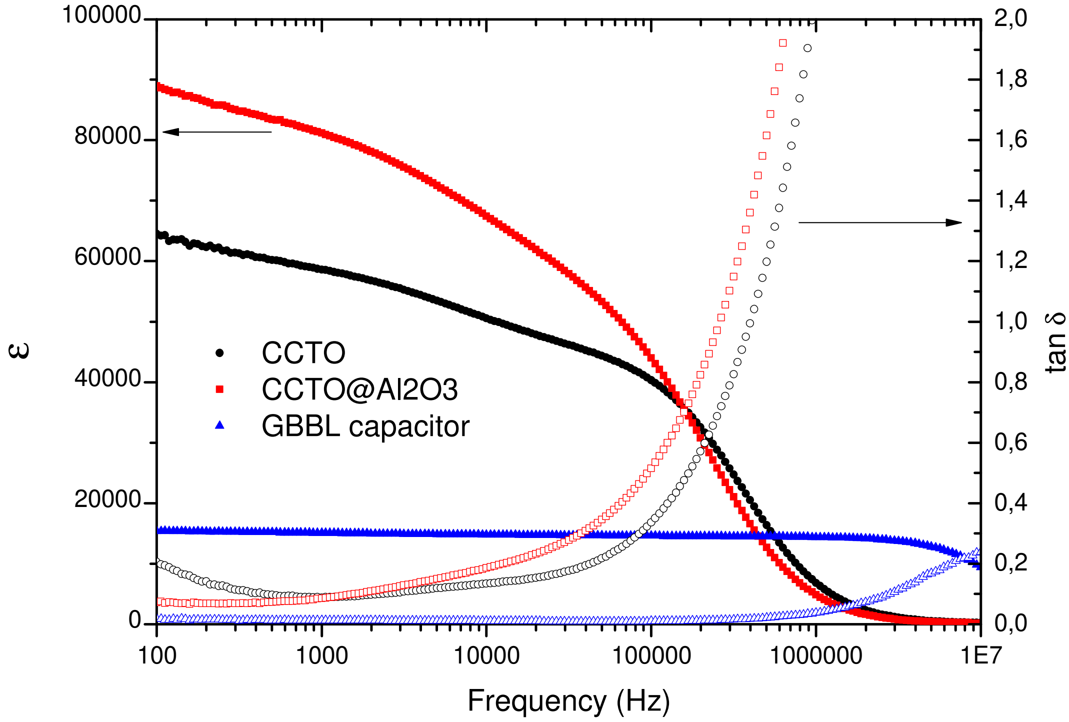
Fig. 2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GBBL capacitor
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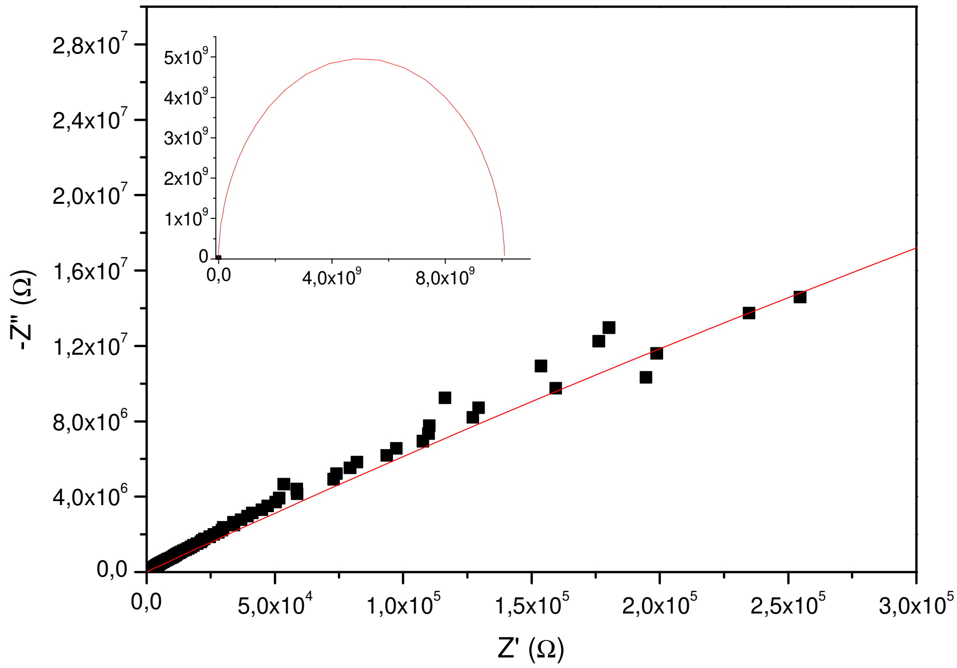
Frequency (Hz)

Fig. 3



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-Z'' (Ω)
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5,0x10^4
1,0x10^5
1,5x10^5
2,0x10^5
2,5x10^5
3,0x10^5
Z' (Ω)
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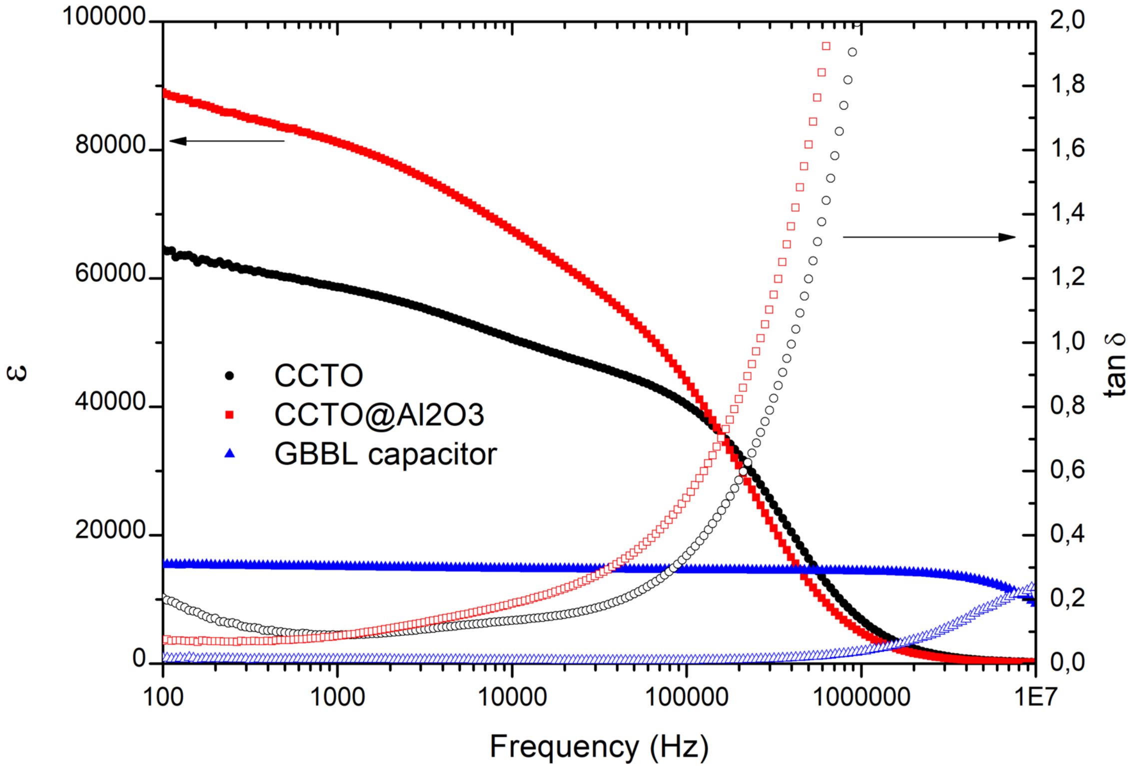
4,0x10^9
8,0x10^9

Fig. 4



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Frequency (Hz)