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$CaCu_3Ti_4O_{12}$ ceramics from co-precipitation method: Dielectric properties of pellets and thick films

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Abstract

Dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO)-based ceramics and thick films (e ~50 μm) prepared from powders synthesized by a soft chemistry method (co-precipitation) are presented and discussed. The characteristics of pellets and thick films are compared.

The pellets exhibit high values of the dielectric permittivity ($\varepsilon_r \sim 1.4 \times 10^5$) and relatively small dielectric losses ($\tan\delta \sim 0.16$) at 1 kHz and room temperature. These properties are independent of the nature of the metallization of the electrodes. In addition, the dielectric permittivity decreases when the diameter of the electrodes of the pellets increases, while the losses remain constant. This result, which is strongly related to the nature of the dielectric material in between the electrodes, constitutes a strong indication that the high dielectric permittivity values observed in this material are not related to an interfacial (electrode material) related mechanism but is an internal barrier layer capacitor (IBLC) type.

Very high values of the dielectric permittivity of CCTO thick films are measured ($\varepsilon_r \sim 5 \times 10^4$). The differences in dielectric permittivity between thick films and dense pellets may be attributed to the difference in grain size due to different CuO contents, and to the different reactivity of the materials.

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Keywords: $CaCu_3Ti_4O_{12}$; Powders-chemical preparation; Tape casting; Films; Dielectric properties

1. Introduction

A great challenge in microelectronic is to decrease the size of passive components and particularly the capacitors' one. For these reasons, there has been a considerable interest in the study of the giant dielectric permittivity of the cubic ABO_3 perovskite-type $CaCu_3Ti_4O_{12}$ (CCTO) in the last decade.[1–15]

This material presents a so-called giant dielectric permittivity value that is mostly temperature-independent.[2,3] Many studies have been performed in order to understand the origin of this colossal dielectric permittivity, generally associated with an internal barrier layer capacitor (IBLC) effect.[4–6] According to this model, CCTO ceramics are constituted of semi-conducting grains (pure CCTO phase), and insulating grain boundary layers. Previous studies[7] have shown that high values of the dielectric permittivity are obtained for $CaCu_3Ti_4O_{12}$-based multiphased pellets ($CCTO + CuO + CaTiO_3$). The raw powders are prepared by the co-precipitation route followed by calcination, a single step process under air described elsewhere.[8] The colossal dielectric permittivity is obtained after optimizing the amount of the different phases in the material. The grain growth during sintering is controlled by the amount of excess CuO in the calcined powder, thanks to the formation of a $CuO–TiO_2$ eutectic. The colossal dielectric permittivities are obtained for an appropriate ratio between the grain size and the thickness of the intergranular CuO phase.[9]

The effect of metallization on the properties of CCTO is still a point of discussion within the scientific community. Yang et al.[10] have studied the electrode/sample contact effect and have shown that, without post-annealing the sample in N_2, the dielectric

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permittivity of CCTO does not depend on the nature of the metal electrodes. As a contrast, Lunkenheimer et al.[11] Krohns et al.[12] announced that high values of the dielectric permittivity in CCTO are due to non-intrinsic phenomena (i.e. electrode polarisation effects).

In this work, the co-precipitation of oxalate precursors followed by the calcination treatment leads to the multiphased powders (CCTO + CuO + $CaTiO_3$ + TiO_2). The corresponding massive ceramics and thick films are obtained after shaping and sintering. The dielectric permittivity and the losses of CCTO-based multiphased pellets were determined for various metal electrodes. Finally, the influence of pellets geometry and the effect of different powder shaping (pellets, thick films) on the electrical properties of the sintered material are presented and discussed.

2. Experimental

The CCTO precursor powders were obtained using the well-known soft chemistry method of co-precipitation. The metal chlorides ($CaCl_2$, $TiCl_3$ and $CuCl_2{\cdot}2H_2O$) were dissolved in water, and then poured in ethanol-containing oxalic acid used as the precipitation agent. These precursors were calcined in air at 950 °C for 10 h, in order to obtain the oxide powders.[8]

The crystal structure of the oxide powders was confirmed by powder XRD recorded on a Seiffert XRD 3003TT (40 kV and 40 mA) using the Cu Kα radiation over the 25–65° 2θ range. XRD analyses were also performed on sintered pellets. The Rietveld method and Fullprof program were used for quantitative analysis. For massive ceramics, an organic binder was added to the powder, and the mixture was pressed into pellets of 6 mm in diameter and 1.5 mm thick, at a pressure of 620 MPa. Pellets were sintered in air at 1100 °C for 24 h. The CCTO thick films were realized by tape casting. The tape casting slurries were prepared by mixing the oxide powder with methyl ethyl ketone and ethanol (40/60) as solvent ($V_{\mathrm{CCTO}}/V_{(\mathrm{CCTO+solvent})} = 0.4$), alkyl ether phosphate acid as dispersant ($m_{\mathrm{dispersant}}/m_{\mathrm{CCTO}} = 0.005$), dibutyl phthalate as plasticizer ($m_{\mathrm{plasticizer}}/m_{\mathrm{CCTO}} = 0.05$) and methyl methacrylate-based polymer as binder ($m_{\mathrm{binder}}/m_{\mathrm{CCTO}} = 0.05$). After casting, the CCTO film thickness is about 100 μm. In order to sinter the films without deformation, 10 films are pressed at 50 MPa/50 °C, to reach a thickness of 1 mm. The as-prepared thick films were sintered in air at 1100 °C for 24 h, with a slow temperature rise until 450 °C in order to avoid cracking when the binder goes away from the films. The cooling rate is fixed at 150 °C/h. The thickness of the sintered film is about 500 μm. The density of the samples is measured by the Archimedes method. In order to perform the electrical measurements, metal electrodes were deposited on both sides of the samples. For the pellets, different metal electrodes were used: silver paint (fired at 700 °C for 20 min), evaporated silver, gold, aluminium and copper using an Edwards Sputter coater S150B whereas only silver paste was used for thick films' samples. The evaporated metal thicknesses are around 100 nm. Impedance spectroscopy and dielectric measurements were performed at room temperature in the 100-Hz to 1-MHz frequency range thanks to a HP4194A.

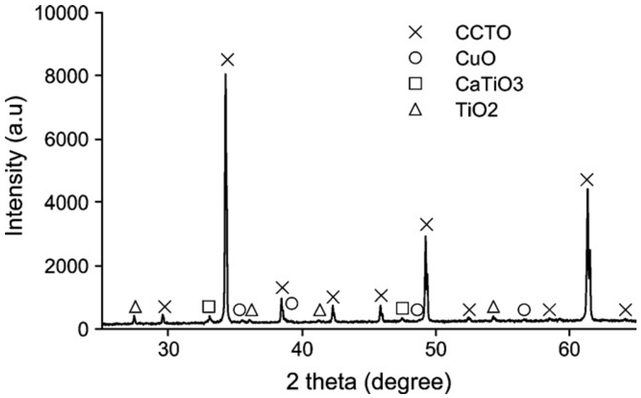

Fig. 1. XRD patterns of the multiphased powder prepared by co-precipitation and calcined at 950 °C for 10 h.

3. Results and discussion

The co-precipitation process followed by the calcination treatment leads to CCTO-based multiphased powders, made up of CCTO (92.5%), CuO (1.7%), TiO_2 (2.9%) and $CaTiO_3$ (2.9%) phases, as shown on powder X-ray diffraction patterns (Fig. 1). The amount of each phase of the analysed powder was determined from Rietveld analysis and resulted from the initial amounts of metal cations introduced during the precipitation.

3.1. Properties of CCTO dense pellets

Fig. 2 shows the XRD patterns of the corresponding pellets after sintering at 1100 °C for 24 h. A phase composition change is observed between 950 °C (calcination temperature) and 1100 °C, with an increase in CCTO proportion. CCTO still appears as the major phase (97.5%) in the dense ceramics, but in higher quantity. $CaTiO_3$ and CuO (1.2% and 1.3%, respectively) are also detected, but TiO_2 is not present anymore.

The density of the samples is approximately 4.8 g cm^{-3}. The pellets exhibit a bimodal grain size distribution (Fig. 3), with small grains of about 20 μm and large grains of size comprised between 50 and 200 μm.

Figs. 4 and 5 show the effect of different metal electrodes on the electrical properties (ε_r, tg δ) of CCTO-based multiphased

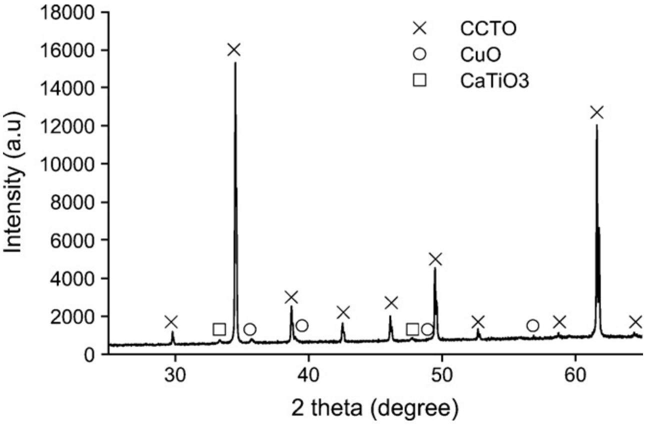

Fig. 2. XRD patterns of the CCTO-based pellets sintered at 1100 °C for 24 h.

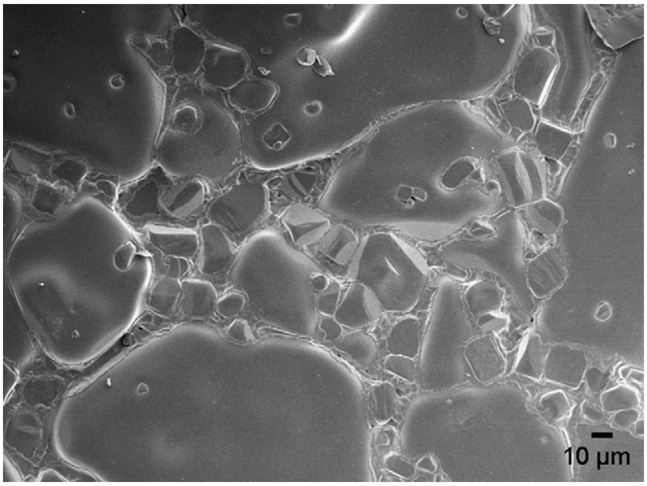

Fig. 3. FEG-SEM micrograph of a 6 mm diameter CCTO pellet sintered at 1100 °C for 24 h.

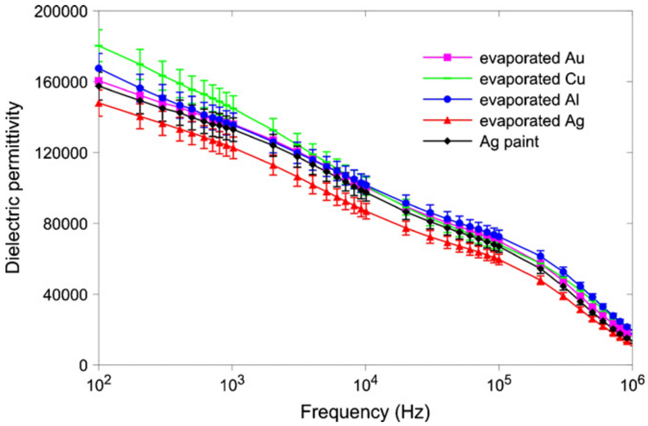

Fig. 4. Frequency dependence of the dielectric permittivity for CCTO-based pellets with evaporated Au, Cu, Al, Ag and coated Ag electrodes.

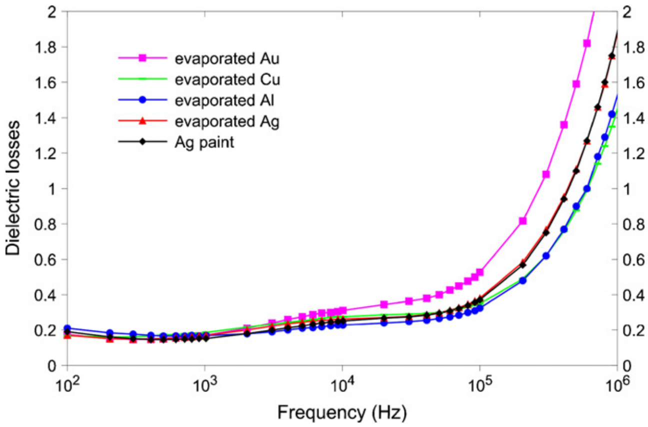

Fig. 5. Frequency dependence of the dielectric losses for CCTO-based pellets with evaporated Au, Cu, Al, Ag and coated Ag electrodes.

pellets. High values of dielectric permittivity and low losses were observed whatever the metal electrode ($\varepsilon_r \sim 1.4 \times 10^5$ and tg $\delta \sim 0.16$ at 1 kHz). The differences observed between the different samples are of the order of the uncertainty of the measurement (estimated to be ±5%) and may thus be neglected. Hence, the nature of the electrode contact has no influence on the dielectric permittivity and the losses values of CCTO pellets. Then, pellets presenting various diameters (5.9–23.2 mm) and same thickness (1.5 mm) have been prepared. The values of the dielectric permittivity and losses measured at 1 kHz and room temperature are reported in Table 1.

Since different samples were used to study the impact of the electrode diameter, we first wanted to check that the manufacturing process was not responsible for the observed differences (particularly for large sample size). Therefore, the last sample presenting the largest diameter was first characterized with an electrode diameter of 23 mm (last row in Table 1), and then the electrode diameter was reduced to about 6 mm by polishing. For this sample the permittivity measured (144 000) is very close to the one determined for the smallest pellet (147 000), and shows that the process is not questionable. The dielectric permittivity strongly depends on the sample diameter. It decreases with increasing the diameter, ranging from 147 000 for 5.9 mm diameter to 108 000 for 23.2 mm diameter. The dielectric losses remain constant whatever the diameter value. Density measurements have been performed on each sample and values are nearly the same for each of these pellets of different diameters, showing that sample densification is not responsible for the observed differences. If the formation of a Schottky diode is supposed, consequently to a depletion layer at the sample–metal interface, to explain the origin of the high dielectric permittivity as suggested by Lunkenheimer et al.,[11] Krohns et al.[12] then an increase in the electrode diameter should be accompanied by an increase in the dielectric permittivity, thanks to the formation of a larger depletion layer. But as it can be seen in Table 1, it is just the contrary that is observed: the dielectric permittivity decreases with diameter.

One obvious factor that may influence the changes in the material permittivity with the electrode diameter is a different grain size. However, SEM observations conducted on a 23-mm diameter sample (Fig. 6) did not show significant differences in grain size compared to a 6-mm diameter pellet. The bimodal distribution observed for the small diameter sample is still observed. So the grain size, since identical in the various cases, does not contribute to a permittivity change.

Moreover, the permittivity value does not depend on the nature of the metallization and decreases when the sample diameter increases. It means that it probably only depends on the nature of the dielectric material between the electrodes. As

Table 1
Dielectric properties of 1.5 mm thick CCTO-based pellets for different diameters of electrodes

Pellet diameter (mm)	Metallization diameter (mm)	ε_r (1 kHz)	tg δ (1 kHz)	Density (g cm^{-3})
5.9	5.9	147,000	0.2	4.61
8.9	8.9	123,000	0.2	4.67
12.4	12.4	116,000	0.2	4.66
23.2	23.2	108,000	0.2	4.69
	8.9	122,000	0.2	
	5.9	144,000	0.2	

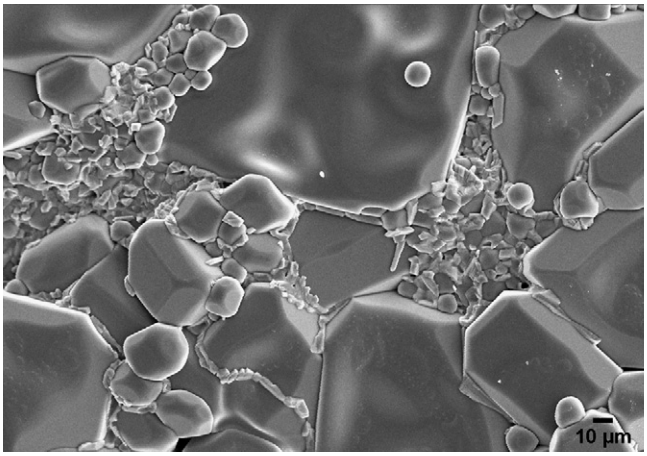

Fig. 6. SEM micrograph of a 23-mm diameter CCTO pellet sintered at 1100 °C for 24 h.

already shown,[7] an IBLC phenomenon is the most likelihood to explain the CCTO behaviours. The observed changes with the electrode diameter would be related to the number of grains and of grain boundaries.

3.2. Properties of CCTO thick films

The morphology of the sintered samples has been examined by FEG-SEM (Fig. 7). The thick films exhibit an average grain size of about 30 μm, instead of the bi-modal grain size distribution of 20 μm and 50–100 μm for the pellets. The density of the films is 4.8 g cm^{-3}, which is the same as the one of pellets. The dielectric permittivity and losses of the CCTO thick films as a function of frequency and at room temperature are shown in Fig. 8.

First of all, it is important to note that high values of the dielectric permittivity (5×10^4 at 1 kHz and room temperature) are obtained for CCTO thick films prepared by tape casting. Even if these values are lower than the ones obtained for the pellets (1.4×10^5), the losses are the same. To the author knowledge, such high values have never been reported before for thick films samples (whatever the material). It is a positive result paving the way to the use of CCTO for multilayer capacitors manufacturing.

In order to explain the difference in the dielectric permittivity of CCTO pellets and thick films, we observed the XRD patterns of sintered pellets (Fig. 2) and the one of sintered thick films (Fig. 9). We remind here the role played by the amount of additional CuO phase. An optimal dielectric constant (5.4×10^5) has been achieved by tuning the content of CuO phase to 2.4 wt%.[9] One can note the presence of TiO_2 in the case of the films, but our previous works showed that TiO_2 has no influence on the dielectric permittivity. The amount of CuO in the sintered films (0.9%) is smaller than the one of the pellets (1.3%) and could contribute to the difference in permittivity. Moreover, EDS analysis have been realised on sintered and crushed samples, and the ratio between the surfaces of the peaks has been calculated. The Ti/Ca ratio is equal to 3.64 and 3.66 for pellets and films respectively, which is nearly the same. The Ca/Cu ratio is equal to 1.00 and 1.12 for pellets and films respectively, which indicates that copper content is slightly lower in thick films, due to a possible volatilization during sintering. On the other hand, the XRD patterns of the sintered films did not show any pollution due to the casting support (siliconised Mylar). So the higher surface of thick films (300 mm^2 instead of 36 mm^2 for the pellets) exposed

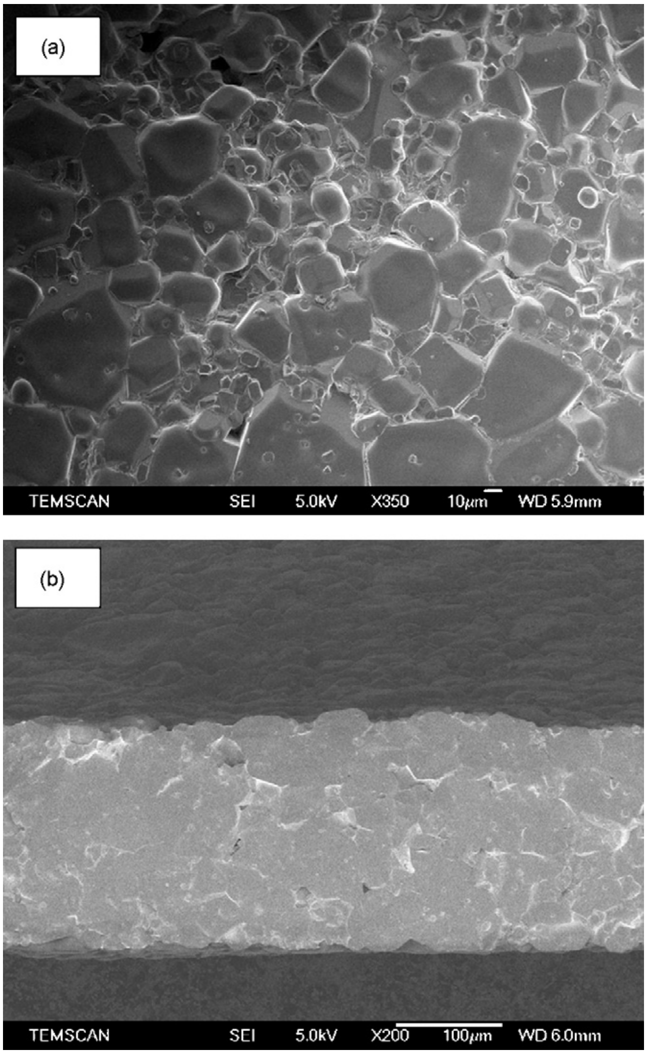

Fig. 7. FEG-SEM micrograph of CCTO thick films sintered at 1100 °C for 24 h: surface (a) and fracture (b).

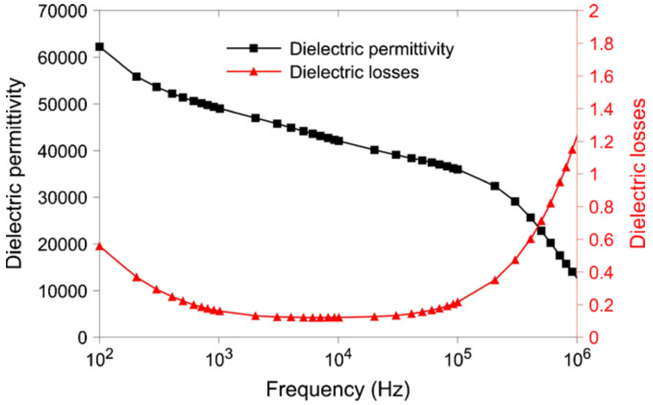

Fig. 8. Frequency dependence of the dielectric permittivity and losses for CCTO thick films with coated Ag electrode.

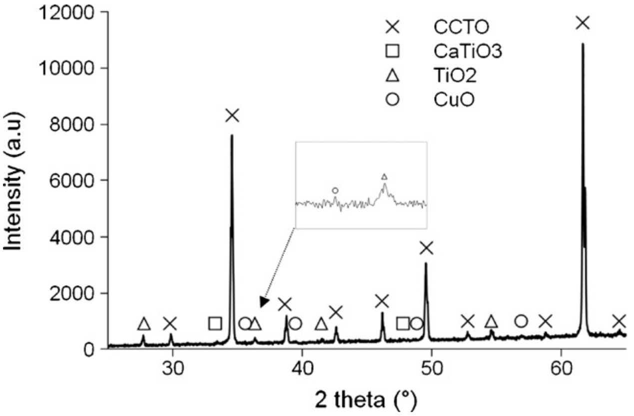

Fig. 9. XRD patterns of the CCTO-based thick films sintered at 1100 °C for 24 h.

to the sintering atmosphere and support interactions should not be responsible for the observed differences in the dielectric permittivity values. In fact, if a reduction reaction occurs during sintering, it may lead to different oxygen content in the films, due to higher "surface" (i.e. higher reactivity). However, it is very difficult to quantify the oxidation state of the cations at such level.

Then, according to the IBLC approach, the dielectric permittivity difference between pellets and thick films can be mainly explained by the difference in the grain size distribution. The grain size of the pellets is higher than the one of the thick films. The dielectric permittivity in CCTO strongly depends on the grain size, and an increase of the grain size leads to an increase of the dielectric permittivity.[2,13–15]

For IBLC ceramics

$$\varepsilon_{r_{\mathrm{eff}}} = \varepsilon_{\mathrm{gb}} \frac{d_{\mathrm{g}}}{e_{\mathrm{i}}}$$

where dg is the grain size and ei the thickness of the grain.

Hence, assuming a constant size of the grain boundary (ei), the grain size difference between thick films and pellets (dg) can at least partly explain the large discrepancy observed for the dielectric permittivity. As the CuO phase in the oxide powder allows a liquid phase sintering and facilitates the grains growth, a direct correlation between the difference in grain size and the difference in copper content between pellets and films can easily be made.

4. Conclusion

The electrical properties of $CaCu_3Ti_4O_{12}$-based pellets and thick films obtained from the same raw powders prepared by the co-precipitation method have been explored.

CCTO pellets exhibit high values of the dielectric permittivity ($\varepsilon_r \sim 14 \times 10^4$) and relatively small values of the dielectric losses ($\tan\delta \sim 0.16$) at 1 kHz and room temperature. No influence of the nature of metal electrode on the dielectric permittivity and losses has been observed. Moreover, the dielectric permittivity decreases when the diameter of the sample increases. These results are in contradiction with a metal ceramic interface related origin of the high dielectric permittivity, and in agreement with an IBLC effect origin. CCTO thick films present very high values of their dielectric permittivity ($\varepsilon_r \sim 5 \times 10^4$) even if they are lower than the one of CCTO pellets. Such high values have never been reported before for thick films. From a physical point of view the difference in copper content, the difference in grain size, and possibly various oxidation states may explain the changes in the dielectric permittivity between films and pellets. Finally, from a technological point of view, the presented results pave the way to the use of CCTO for multilayer capacitors manufacturing.

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