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Chapter

On Recent Progress on Core Shell Nanostructures of Colossal Permittivity Materials for Capacitors: Synthesis and Dielectric Properties

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Abstract

Dielectric materials with colossal permittivity show promise for the development and miniaturization of high-performance capacitors. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) improvement for multilayer ceramic capacitors (MLCCs) has been achieved. CCTO shows a large ϵ' of $\sim 10^4$ over a temperature range. This behavior is due to a potential barrier at the grain boundaries (GBs). CCTO ceramics have an electrically heterogeneous microstructure with semi-conducting grains and more insulating GBs, analyzed by an internal barrier layer capacitor (IBLC) structure model. Therefore, the dielectric properties of these materials can be improved by changing the electrical properties of the grains and GBs. In this context, core-shell approaches to control the GBs have been developed. This chapter presents advanced synthesis techniques (by chemistry way but also by cold plasma) to design the dielectric grains of CCTO by shells of different nature, morphology and crystallinity and shows the impact on the macroscopic properties.

Keywords: core-shell particles, CCTO, dielectric properties, IBLC, pulsed cold plasma

1. Introduction

Mobile electronic devices connected to the broadband network and with high transmission capacity are widespread. The trend today is toward miniaturization, better quality and lower power consumption. Capacitors, filters, resistors are among the passive components widely used. Conventional capacitors, i.e. monolayer capacitors have been primarily used. However, the MLCC component has taken the lead due to its high capacity properties even with smaller sizes, high reliability and excellent frequency characteristics [1–5]. Recently, the worldwide shortage of electronic components such as MLCC capacitors has become a major problem. In recent years,

electric vehicles, which require a large number of capacitors because of their electronic control and automation systems, have a great need of them. Many dielectric layers that are stacked alternately by internal electrodes connected in parallel constitute the MLCC device. This configuration allows increasing the capacitance of the components [6, 7]. However, the capacitance can be enhanced with thin dielectric layers and with the number of stacked layers but also by using high- k dielectrics. The BaTiO_3 -based dielectric material is used as the reference material in the multilayer ceramic capacitor (MLCC) industry with noble metals such as palladium or nickel as internal electrode. MLCCs suffer from various disadvantages. Due to the different materials (dielectric material and electrodes) with different sintering temperatures and coefficients of expansion, cracking or delamination occurs at the interfaces of the layers. This residual stress has an unfavorable effect on the mechanical and electrical properties. To overcome these problems, another promising solution has been developed, the ceramic-metal composite materials (CMC), in which metal particles are dispersed in the ceramic matrix without interacting with the network structure. In these materials, ceramic acts as an insulating phase while metal particles are used as conductors. The enhancement of the permittivity in these systems (MLCC and CMC) is due to the ceramic/metal interface [8, 9].

However, modern technologies require new materials to develop new technologies. Indeed, the nanotechnology industry continues to grow rapidly in order to expand the field of applications but also to improve the devices used today. Thus two ways are possible, the fabrication of nanomaterials or so-called “core-shell” materials. With regard to nanomaterials, a great effort has been made toward the synthesis and application of nanoparticles because of their unusual physical and chemical properties due to their very different specific surface compared to the bulk properties [10, 11].

More recently, research has focused on nano-structured “core-shell” nanoparticles to adapt structural, magnetic, electrical properties but also to change surface properties. The purpose of the “core-shell” is to coat particles with another type of material. The presence of the shell can modify the surface, to increase the core material functionality or stability. For example, the temperature stability of the dielectric properties in the capacitor is always asked to extend the field of applications. One possibility is to use these core-shell nanostructures which have a different chemical composition between bulk grain and grain boundary (GB) [12, 13]. In the literature, many different materials such as metal oxides, noble metals or polymers are used as shells to coat the BaTiO_3 particles [14, 15]. In the field of high permittivity dielectrics, such as BaTiO_3 , it is interesting to coat with a stable insulating material such as SiO_2 , which also has the advantage of being stable, chemically inert and non-toxic [16, 17]. Moreover, the preparation of the SiO_2 shell is well-known. And a homogeneous distribution of SiO_2 layer coating is very important to prevent the exaggerated grain growth and the segregation of SiO_2 which can alter the dielectric properties [18, 19]. In 2008, Wei et al. proposed a method, in their patent, for elaborating core@shell structured dielectric particles consisting of a conductor core and one or more layers of thinly-coated dielectric material for use in multilayer ceramic capacitors (MLCC) applications [20]. This new configuration was considered to replace conventional BaTiO_3 dielectric materials as capacitor active layers.

From a general point, the permittivity results from both intrinsic or extrinsic properties, the latter been associated with possible existence of domains, defects, doping, internal strains ... [21–23]. In some cases, a strong increase in permittivity, slightly constant on a large range of temperatures can be observed depending on the doped BaTiO_3 substitution [24] or on the synthesis atmosphere which can create

vacancies or doping on the grain surface but not penetrate the interior of the grains [25]. Permittivity values as high as 10^5 have been reported for nanostructured materials, such as core-shell structures with a BaTiO_3 core and a shell made of another material like SiO_2 , Al_2O_3 ... [26]. These good properties are used in industrial capacitors of type III or X7R4-5, where high permittivity and capacitance are needed. However, these capacitors come with the drawback of low breakdown voltage, high frequency sensitivity and temperature-related performance variation. For example, the high permittivity of BaTiO_3 originates from FE-PE phase transition and it means that the properties vary strongly with temperature. In this work, we will focus on the perovskite-like oxide $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) proved to be one of the best candidates due to its interesting dielectric constant $\epsilon \approx 10^4$ – 10^5 in a large temperature and frequency range [27, 28]. Despite its colossal dielectric constant, CCTO material exhibits a strong loss tangent and a low breakdown voltage that limits its use in industrial application [29]. On the other hand, numerous studies have been conducted and many mechanisms have been proposed to explain the origin of the colossal dielectric constant [21, 30]. The most widely accepted mechanism, known as the Internal Barrier Layer capacitance (IBLC), consists of semi-conducting grains and insulating GB. The grains would behave as the electrodes of a capacitor and GBs act like the dielectric. This configuration consists of many capacitors in series that could explain the high dielectric constant. Some authors attempt to approximate the permittivity as a function of the grain boundary permittivity using this formula:

$$\epsilon = \epsilon_{gb} A/t \quad (1)$$

where ϵ_{gb} is the permittivity of the grain boundary, A is the size of the grain (μm) and t is the thickness of the grain boundary (μm) [31–33].

Thus the idea of the existence of semi-conductor grains and insulating GBs leads us to the idea of making this configuration by developing nanostructured “core-shell” materials. For that, we envisaged to optimize the synthesis methods for the production of CCTO-based core-shell nanostructures. The main problem when coating the high- k material (CCTO) is achieving control over homogeneity and the shell thickness. This control is crucial not only for regulating the properties of the GBs but also for limiting the diffusion of chemical elements between the core and the shell, which can potentially alter the material’s properties. Through an overview of recent results, we will highlight the advantages and disadvantages of synthesis for different coatings. We will also show a new way of synthesizing “core-shell” which is promising for shell quality.

2. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ particles

2.1 Structure

The crystal structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was discovered at the first time by Bochu et al. and confirmed by Subramanian et al. [30, 34]. CCTO crystallizes in a cubic structure that is derived from the ideal cubic perovskite structure (ABO_3). In this structure, there is an arrangement of Cu^{2+} and Ca^{2+} cations constituting the A-site, resulting in the chemical formula $\text{AA}'_3\text{B}_4\text{O}_{12}$ formula. The Jahn-Teller effect causes the Cu^{2+} cation site to occupy a square-planar environment instead of a 12-coordination site as the ideal perovskite, which induces a strong tilting of TiO_6 octahedra.

The unit-cell body-centered cubic CCTO with the Im-3 space group consists of two formula units with cell parameters $a \approx 7.39 \text{ \AA}$. The structural analysis as a function of temperature showed no structural transition, indicating the absence of a ferroelectric transition [35].

The dielectric permittivity of CCTO has been reported in a large range from 100 to 10^5 in films, single crystals or bulk [30, 36–38] and in certain cases, the permittivity remains constant in a large domain of temperature. Even if today an explanation is not convincing, the community agrees that there is no ferroelectric transition and that the behavior is not intrinsic [39]. Then it was assumed that the colossal permittivity could find its origin from extrinsic properties of the material. In 2002, Sinclair et al. have proposed a theory to explain this behavior, based on their impedance spectroscopy results [40]. Indeed, by association of semi-conducting grains and insulating grain-boundaries, there would be an internal barriers phenomenon named “Internal Barrier Layer Capacitance” effect (IBLC). However, the strong ϵ value observed in single crystals indicates that the insulating barriers exist within the crystals themselves rather than between them, indicating the presence of twin boundaries that act like barriers [30]. Even if the structure has a decisive role, it seems that the good properties are enhanced by the microstructure of the compounds and specifically by the GBs.

2.2 Parameters influencing the CCTO properties

The CCTO dielectric properties may be affected by many factors, including the synthesis method, sintering temperature and time, doping ions and electrode materials [36, 41–44].

2.2.1 Sintering temperature and time effect

Brize et al. worked on the effects of the synthesis conditions by using various conditions such as the powder mixing, the time, the calcination temperature [45]. Although the development of oxide materials by solid-state reaction remains a widely used method of synthesis, they preferred to use the modified citrate process [46]. Nanometric powder can be obtained with this synthesis method depending on the time and the calcination temperature. They choose the temperature from 500°C up to 750°C and the time from 8 h up to 20. All pellets were sintered at the same temperature, which was maintained at 1050°C for 24 h. They showed that the best properties were observed for the powder calcined at 500°C for 20 h with dielectric constant close to 10^5 . This strong dielectric constant was related to the large grain size and density. The grain size effect was already reported by Bender et al. as early as 2005 [47]. Later, Sonia et al. confirmed that the grain size favors high permittivity (**Figure 1**) [48]. These observations validate the proportionality of ϵ_r with the size A of the grains of the IBLC model (Eq. (1)).

2.2.2 Doping effect

The cationic substitution on the A, A' and B sites can change the dielectric and electric properties. Numerous papers in the literature relate the CCTO doping by one element and more recently by two elements, i.e. the co-doping [49]. Clearly, the substitution and co-substitution have a strong influence on dielectric (ϵ_r and $\tan \delta$) and electric properties as summarized by Ahmadipour et al. [50] and S. De Almeida-Didry et al. [51]. The list is not exhaustive, but taking into account the results, the best

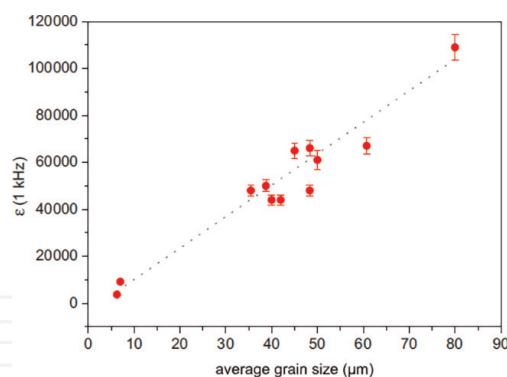


Figure 1.
 Increase of permittivity of undoped CCTO with the average size of the grains [1–5].

dielectric constant was given for the CCTO containing less copper but at the expense of the loss tangent. It was also demonstrated that the colossal dielectric properties were collapsed by Mn and Fe doping even with a slight substitution equal to 0.5% or 1% [38, 52–54]. The permittivity for further materials with doping or co-doping is between these two extremes. However, none of them satisfies the properties required for use in the industry. To understand the mechanism, Sinclair et al. did some complex impedance spectroscopy measurements [40]. They showed that the dielectric properties originate from the electric grain behavior and GBs. Indeed, the grains have a semi-conducting character and the grains boundaries are insulating. This difference between insulating GBs and semi-conducting bulk can be schematized by IBLC structure, which effectively explains the properties of these ceramics. Numerous studies have shown that copper comes out of CCTO grains during the sintering process and this causes a difference in electrical behavior in grains and GBs. Grains have copper vacancies and become conductive while GBs are insulating, leading to the formation of the IBLC structure [55–59]. Concerning the Mn and Fe doping, Krohns et al. put forward the reduction of grain conductivity that implies that the phenomenal IBLC is suppressed. They argued that the permittivity is related to the polar character of phonons without amplification by barrier layers [38]. Finally, the cations, which seem to be good candidates, are Cr^{3+} , La^{3+} , Al^{3+} , however, resistivity is still too far from the values required for industrialization [49, 60, 61].

Sinclair et al. have shown the existence of Schottky barriers at the interfaces, and they insist on the role of the GBs between semi-conducting grains. The Schottky barriers likely are at the origin of the non-linear behavior of J-E characteristics, where E is the electric field and J the current density that is a drawback in a charge storage device. Sinclair et al. have concluded their paper by the fact that CCTO ceramics with grain size of few micrometers do not present this non-linearity and could be good candidates for applications due to their permittivity resulting from a “core-shell” structure of insulating GBs and conducting grains [40].

2.3 The nature of grain boundaries understanding

To summarize, the studies conducted in the literature revealed that the GBs play a key role since the relative permittivity could be estimated according to the Eq. (1). In this purpose, the precise study of the structure, grain boundaries composition could be crucial. From a sintered ceramic of CCTO with large grains and small GBs, a cross-section sample was prepared using a dual-beam focused ion beam (FIB) based on a focused Ga^+ ion beam and transferred to a Cu-grid using a micromanipulator. The

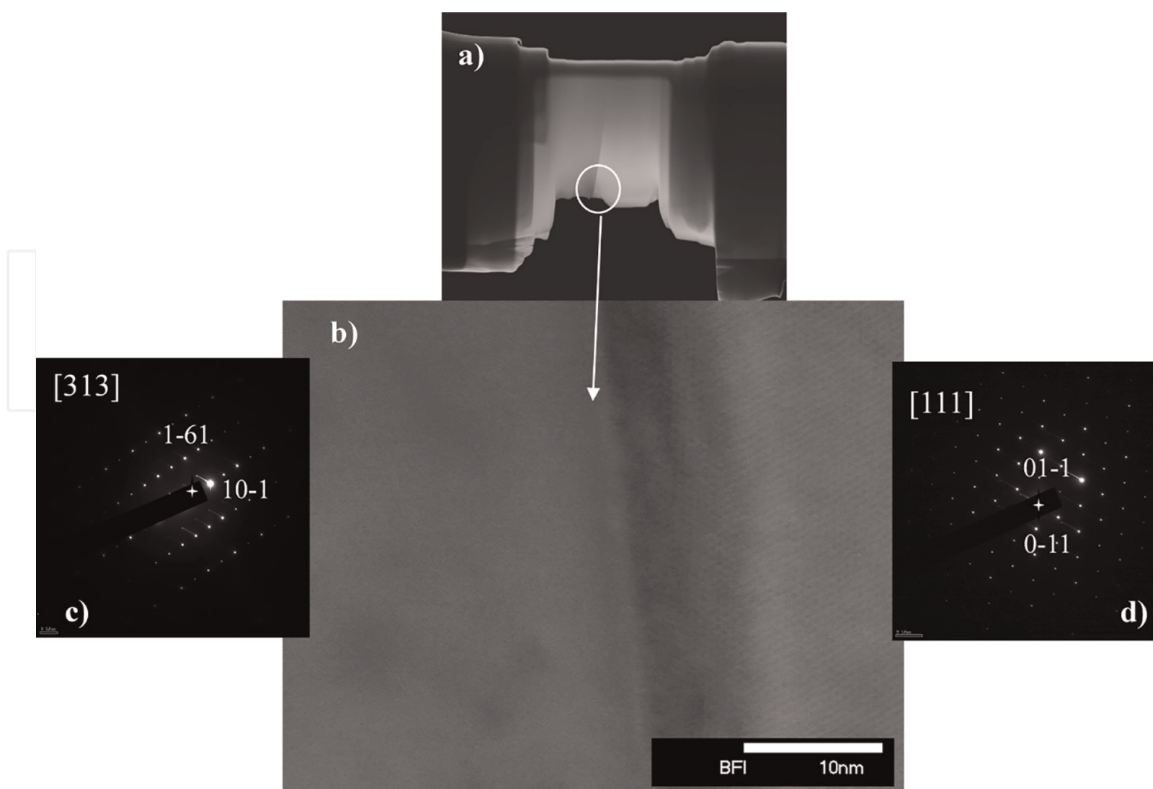


Figure 2.

(a) TEM lamella preparation by FIB, (b) STEM images showing the two grains separated by a dark line (grain boundary) and (c) and (d) SAED patterns of orientated grains.

lamella was located on a GB surrounded by two grains. **Figure 2** illustrates a SEM image of the TEM lamella with two grains separated by a GB, which appears with a darker line. SAED studies permit to obtain ED patterns for each well-crystallized grain. There is no correlation between the orientations of the grains, the main dots are indexed and the zone axes are different (**Figure 2**).

The HRTEM image (**Figure 3**) shows a view of the crystal with a uniform background contrast consisting of a very regular array of bright dots spaced by about 5.2 Å for the $\langle 011 \rangle$. No defect is evidenced. The GB cannot be aligned; its width is of a few nanometers about 5 nm (insert **Figure 3**). The observed contrast is confused and could correspond to amorphous phase or to the superimposition of two crystallized domains. HRTEM cannot bring any more information on the GB, so elementary cartography by STEM was done allowing analysis at nanometric scale. EDX line profile was performed across both grains. No change of the element ratio was observed at the interface. This study at nanometric scale was also studied by B. Domengès et al. on two different lamellar. They showed an identical result to ours on one cross-section and the other showed the existence of Cu-rich phase that can answer the question of what type of phase is constituted GB explaining the IBLC mechanism [62].

3. Strategies of design of core-shell CCTO@MO

3.1 Synthesis of the core (CCTO)

Solid-state reaction is the predominant method used to prepare the core composed of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. This method is simple and allows the preparation of the materials

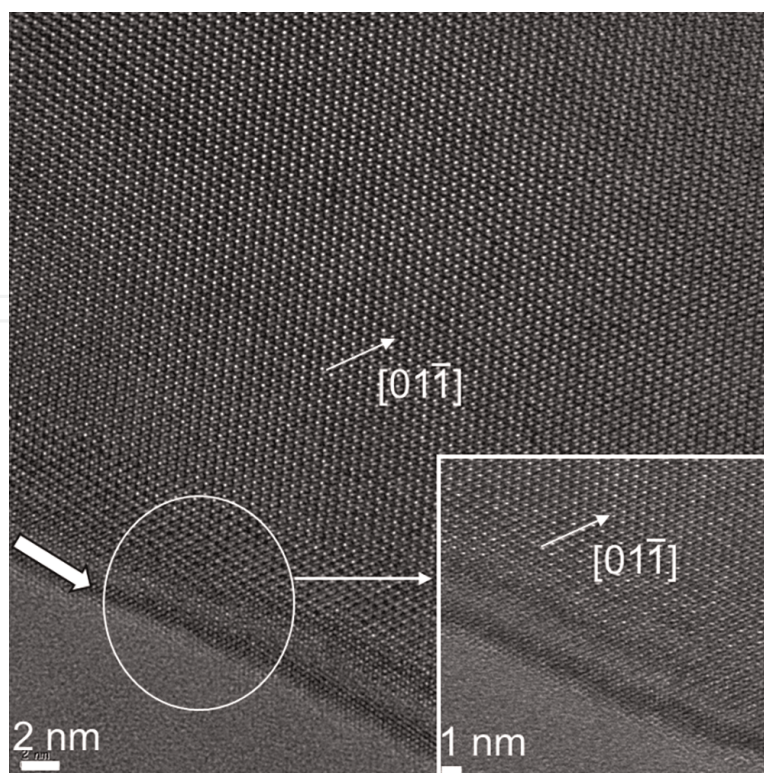


Figure 3.
 High resolution TEM images taken with $[111]$ zone axis. In inset, zoom on the GB.

from a mixture of solid starting materials. The reagents CaCO_3 , CuO and TiO_2 were weighted in stoichiometric proportions. The precursors are then mixed and ground in isopropanol using zirconia balls for 6 h to homogenize the powder. Finally, the resulting powder is put in a muffle oven for a heat treatment of 950°C for 24 h. This synthesis process was chosen for the reproducibility of the structure and microstructure of the powder, more particularly, the size of the grains remains constant and close to $1\ \mu\text{m}$ and the IBLC mechanism requires large grains (Eq. (1)). The quality of the powder was checked by XRD diffraction and the average size of the grains was analyzed using laser granulometry and SEM (**Figure 4**).

3.2 Surface charge of the CCTO particles

The dispersion of CCTO powder is a key point for the coating. This is very critical for nanopowders with size particles inferior to $100\ \text{nm}$. This is not the case of the CCTO used in this study, since the particle size is close to $1\ \mu\text{m}$. However, it is very important to be able to disperse homogeneously the particles in a solvent. For this, the particle surface charge needs to be known in an aqueous or non-aqueous medium. The particle surface properties are related to the potential of the particles in different environment. The surface charge is a property that all materials possess or acquire when they are suspended in a solution. The charge was evaluated by zeta potential measurements in relation to pH value. The started solutions contain CCTO sample mixed in a KOH solution, which is titrated with an HCl solution to decrease pH until 2. As the solution is titrated versus pH, the intercept is called iso-electric point (IEP) and corresponds at the maximum of instability of the particle dispersion. On the other hand, the maximum stability is obtained at high absolute potential values. So taking into account the **Figure 5**, the stability of the CCTO is found for a basic pH.

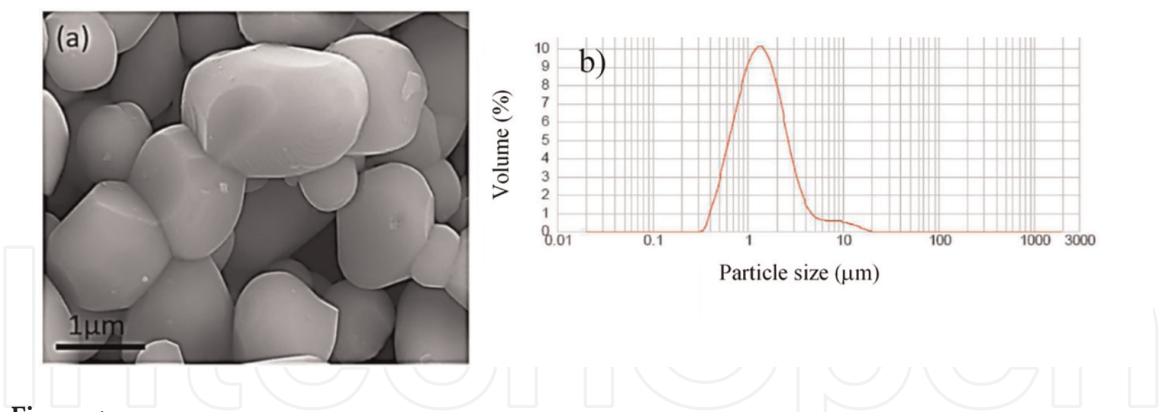


Figure 4.
(a) SEM images of CCTO particles synthesized by solid state reaction and (b) particle size distribution by granulometry.

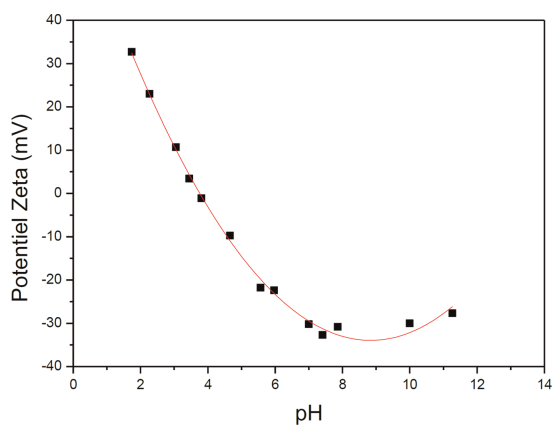


Figure 5.
Zeta potential of CCTO versus pH.

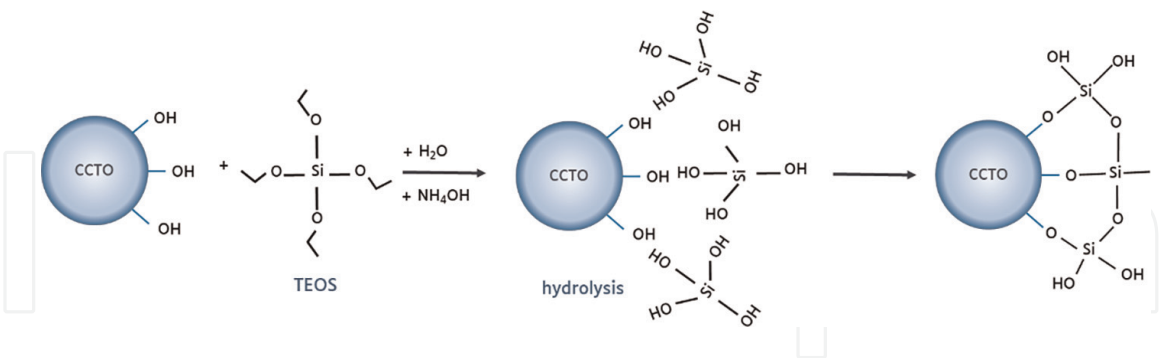


Figure 6.
Mechanism of silica shell formation on the CCTO particles.

3.3 Silica-based core-shell CCTO

The schematic illustration of the core-shell structured process is depicted in **Figure 6**. The method is based on the Stöber process [63] in which silica shell is formed around a core via the hydrolysis followed by a condensation reaction of a silicate precursor—in this work, we used TEOS. The Stöber method takes place at a basic pH close to 10. The negative zeta potential of CCTO (**Figure 5**) means that OH groups are on the surface, and then the silicate group from the TEOS precursor attaches to the -OH groups. After this first layer, additional layers are formed by hydrolysis and condensation of TEOS.

The process of CCTO core@silica-shell was as follows. At first, CCTO powder was added in a mixed solution of ethanol/H₂O/ammonia (75/23.5/1.5%vol) and the solutions were adjusted to a pH value of 10. Several concentrations of CCTO in the solution were tested (2 g/l, 5 g/l, 10 g/l). No influence on the coating and dielectric properties was identified. For industrial applications, the powder amount must be important, so the concentration of 10 g/L was chosen. The solution was stirred at room temperature during 1 h. Afterwards, tetraethyl orthosilicate (TEOS) was slowly added in the first solution under magnetic stirring. The final solution was mixed for 12 h. Finally, the mixed solutions were centrifuged and washed with ethanol several times and then the powders were dried at 80°C for 12 h to obtain core-shell structured CCTO@SiO₂ particles. This process and the volume of ammonium make it possible to obtain a homogeneous and uniform SiO₂ shell surrounding the CCTO particles [64]. The thickness of the silica shell can be calculated by changing the amount of TEOS used in the following reaction:

$$V_{TEOS} = \frac{M_{TEOS} \times \rho_{SiO_2} \times \pi}{\rho_{TEOS} \times M_{SiO_2} \times 6} \times N_p(CCTO)(D^3 - d^3) \quad (2)$$

with

$$N_p = \frac{m_{(CCTO)} \times 6}{(\rho_{(CCTO)} \pi d^3)} \quad (3)$$

Where (d) is the CCTO particle diameter (μm), (D) is the core-shell particle diameter (μm). The CCTO particles are assumed to be spherical with 1 μm as diameter (d), as observed on the as-synthesized CCTO particles. The eq. (2) is as a function of the molecular weights of SiO₂ formula unit and TEOS (g.mol⁻¹), the densities of silica and TEOS (2 g.cm⁻³ and 0.934 g.cm⁻³, respectively). The amount of TEOS was calculated from the average size CCTO particles (~1 μm) to obtain a silica nanocoating from 1 to 125 nm.

3.4 Shell thickness and uniformity

To confirm the shell, transmission electronic microscopy was used. HR-TEM images demonstrated that the particles have a core-shell structure with different contrast for both phases, light contrast for the silica shell and dark contrast for the core of CCTO (**Figure 7**). To confirm these contrasts, STEM-EDS mapping of CCTO@SiO₂ particles was conducted for a thickness close to 10 nm (**Figure 8a**). The CCTO particles were successfully coated by silica shell. As shown in **Figure 7**, we found that the shells were uniform and homogeneous. The experimental shell thickness was found to be consistent with the calculated thickness, at least up to 20 nm. Thereafter, it is observed that the thickness remains constant for a thickness slightly above 20 nm (**Figure 8c**). Thus, for a high concentration of TEOS, the appearance of spherical SiO₂ particles is observed (**Figure 8** (a thickness of 65 nm image)). The formation of spherical SiO₂ particles in addition to the particles coating is always a side effect in the coating process. Therefore, it is crucial to control the proportion not only of TEOS but also of ammonium that serves as a catalyst. In the literature, it has been shown that for an optimized ammonium concentration, there is a minimum concentration of TEOS needed to guarantee full coating of the particles, and then the shell thickness can be adjusted with the concentration of TEOS [64–66].

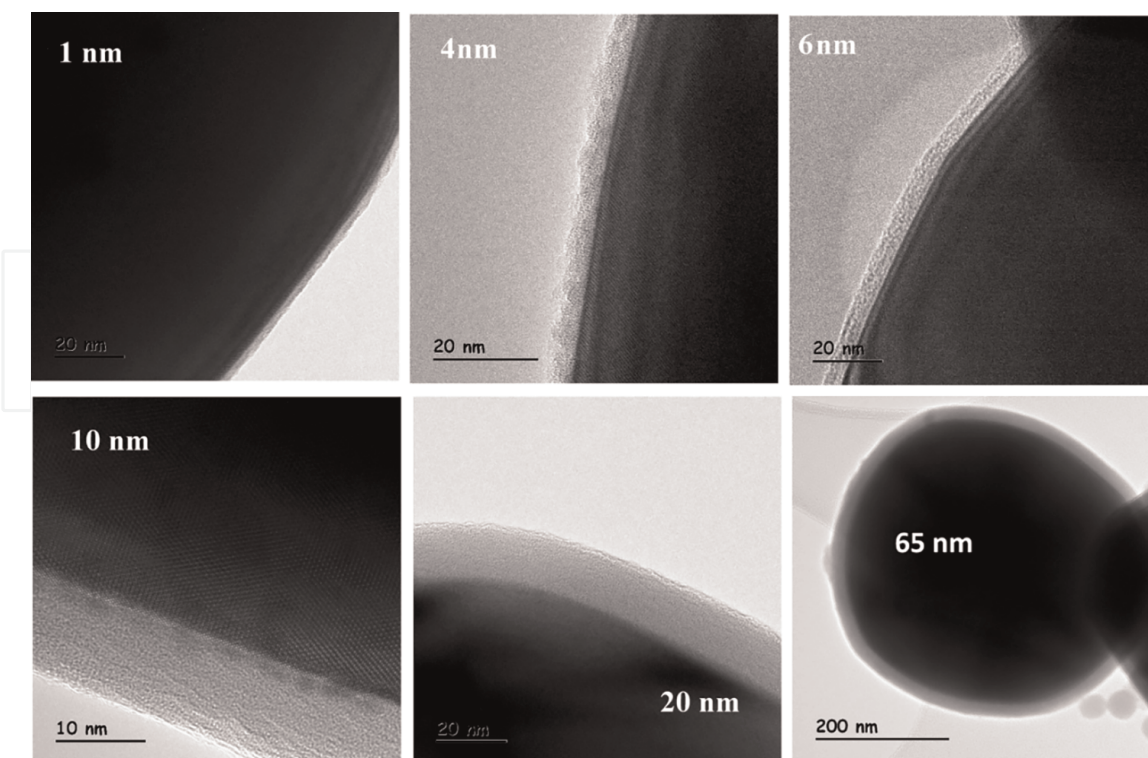


Figure 7. TEM images of CCTO@SiO₂ for thickness shell from 1 nm up to 65 nm. The light contrast corresponds to the amorphous shell.

3.5 Surfactants effects on core-shell particles

The coating by chemical process to obtain a homogeneous shell is sometimes difficult due to the nature of surface (charge, hydrophobic, ...) and mutual chemical interactions. To improve the shell, several agents can functionalize the core particles. Moreover, the surface modification is demonstrated to improve the dispersibility of particles in a solvent. Researchers have also demonstrated that the surface modification has an influence on grain growth [67, 68]. PEG, Brj58, F127 agents are used as in-situ surfactants. CCTO particles with the modified surface were then used in the Stöber process to coat them with a silica shell. Jana et al. described different mechanisms for the functionalization of core particles with the Stöber method [69]. Brij58/F127 agents are surfactants characterized by CMC (Critical Micellar Concentration). CMC is the concentration of surfactant in an environment from which micelles form spontaneously. Below this, the surfactant forms a layer on the surface of the liquid and the rest is dispersed in the solution. We tested the concentration below and above the CMC of each surfactant. Surfactants have a crucial role in improving stability of colloidal system. To investigate the stability of these systems, zeta potentials were measured at pH = 10 (**Figure 9**).

As shown in **Figure 9**, the effect of surfactant on CCTO particles is not the one expected for a pH equal to 10, which is the value of solutions in the Stöber process. However, regardless of the surfactant used, coating up to 20 nm (by step of 5 nm) was possible. For each system, the pellets from materials coated with a 20 nm thick SiO₂ shell, were sintered at 1050°C for 24 h and the dielectric properties were

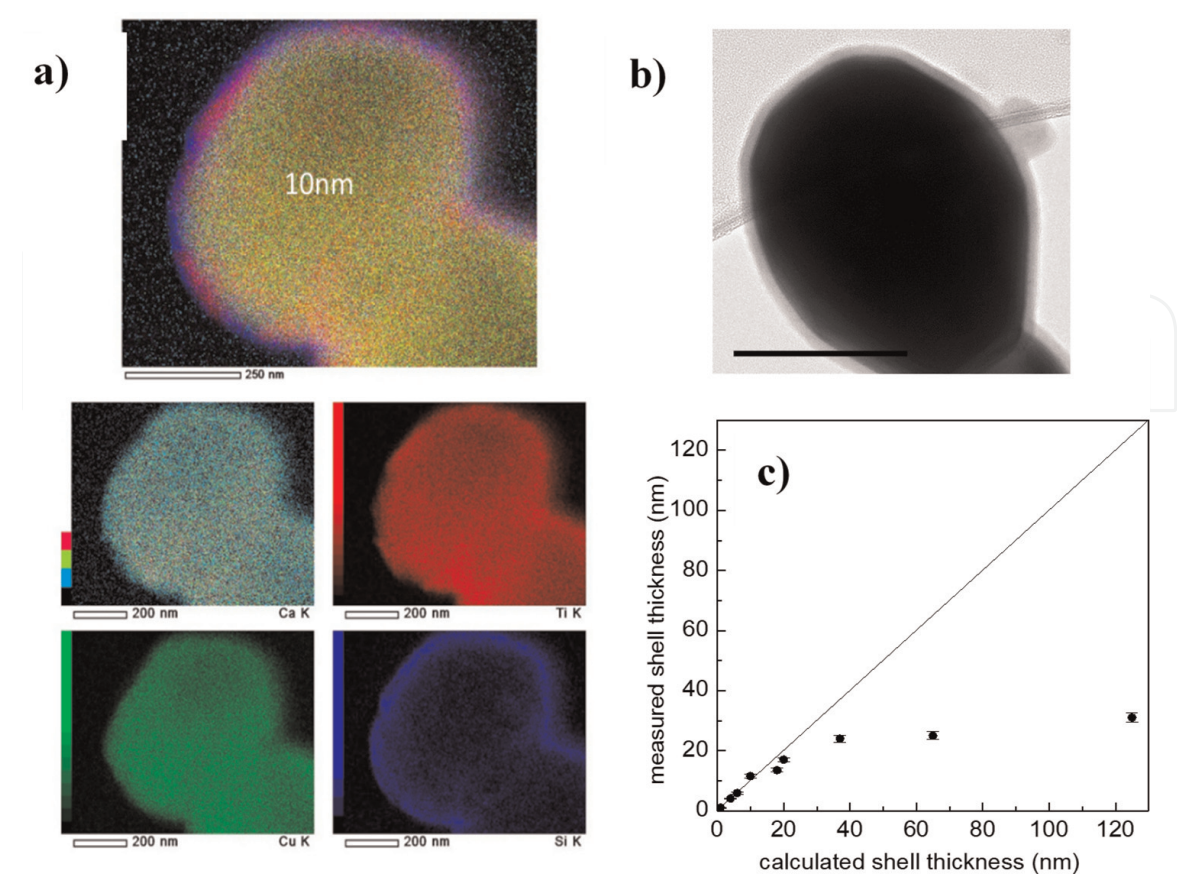


Figure 8.
 (a) Compositional elemental mapping of a core-shell nanoparticle using STEM-EDX, (b) bright-field transmission electron microscopy (TEM) image of a core-shell nanoparticle and (c) real shell thickness for all samples as function as shell thickness calculated with Eq. (2).

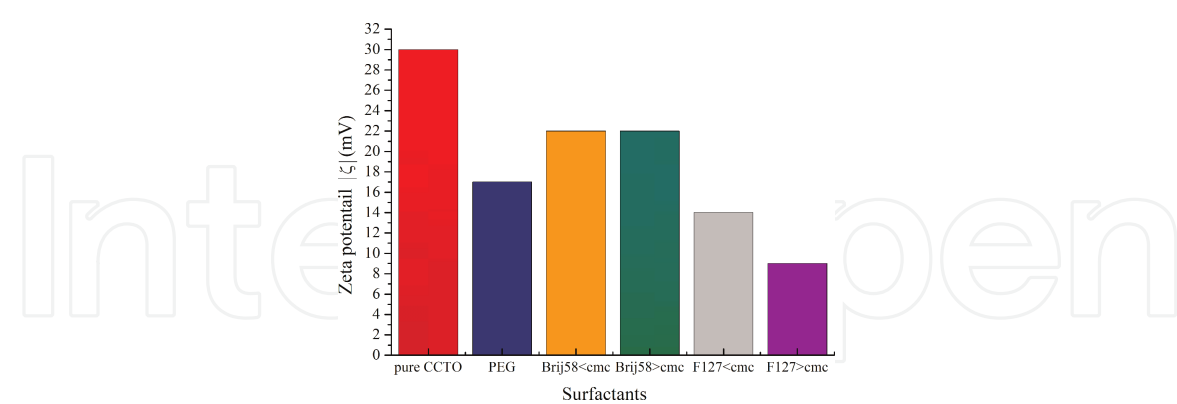


Figure 9.
 Zeta potential measured for CCTO without and with surfactants (PEG, Brij and F127).

measured (**Figure 10**). The good properties obtained in the table are linked with the high average grain size. The benefit of the surfactant in the case of SiO₂ shell is unclear and their exact role in preventing agglomeration is still under discussion. This fact was already noted in the work of Hai et al. on BaTiO₃ particles [70]. However, for other shells like Al₂O₃, the surfactant helped us to coat uniformly the particles.

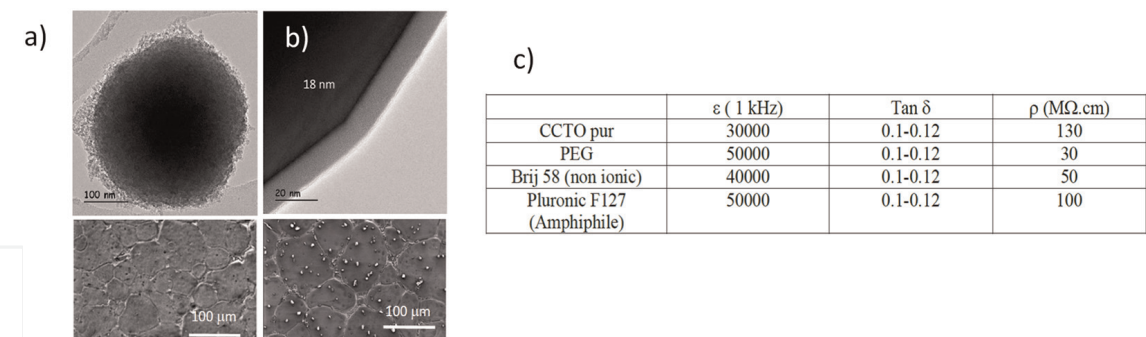


Figure 10.
(a) CCTO@SiO₂ (20 nm) with PEG (b) CCTO@SiO₂ (20 nm) with Brij58 and below for both SEM image of the corresponding pellets showing the grain and GBs. (c) table: dielectric properties for each pellets of CCTO without and with surfactant coated by 20 nm.

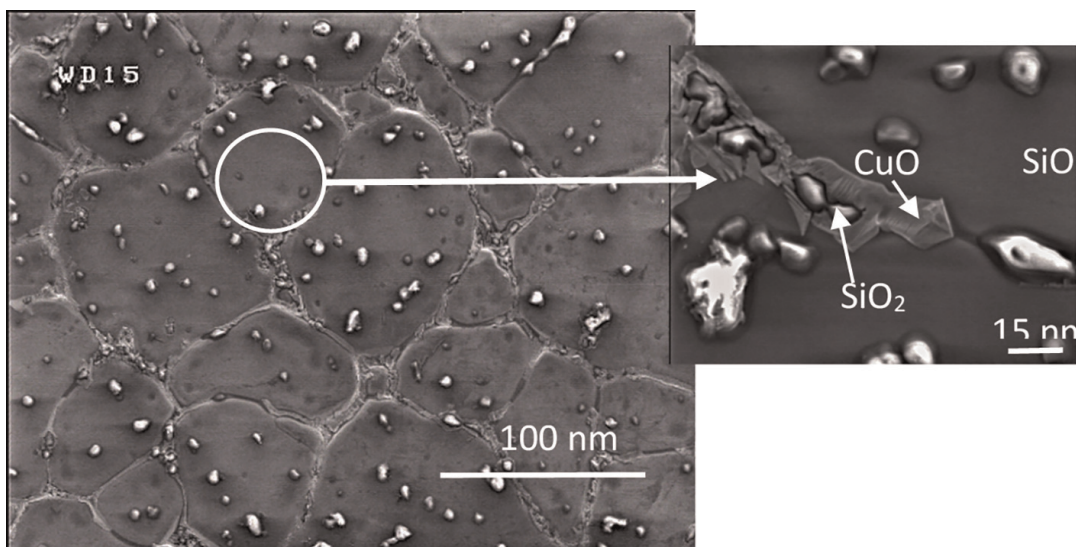


Figure 11.
SEM image of the microstructure showing the grain and GBs with some SiO₂ particles on the grains. In enlarged zone, the GBs showing the presence of CuO and SiO₂ phases.

3.6 The thickness shell effect on the properties

In order to investigate the impact of silica shell on the dielectric properties, pellets were made at 1050°C for 24 h. The average grain size of CCTO@SiO₂, about 80 μm is similar to un-doped CCTO. For this one, previous reports have shown that during sintering, a liquid copper phase appeared and led to an enhancement of the grain size [40, 71]. It seems that the same mechanisms are responsible for the grains growth of SiO₂-coated samples and that this dopant does not play a role in growth (**Figure 11**). It was also noted that the ceramic density is between 91 and 96% and no correlation with SiO₂ is observed. In addition, the initial core-shell structure is lost after thermal treatment. However, as shown in **Figure 11**, it can be noted that SiO₂ grains are located on the grains and also between the grains, i.e. constituting the GBs. CuO existence at the GBs also occurs, as attempted in the CCTO ceramics.

Dielectric measurements on the core-shell materials indicated that the dielectric constant (ϵ_r) slightly decreased with shell thickness values less than 20 nm, but then the drop is drastic and follows an exponential function (**Figure 12**). This fact could be

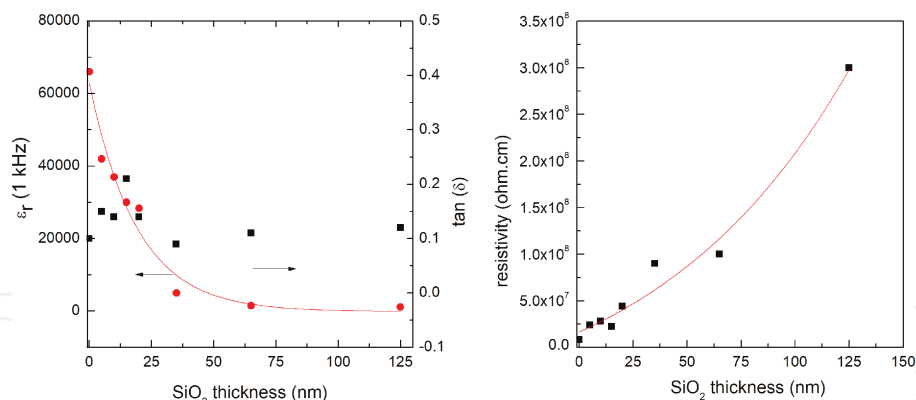


Figure 12.
 At left, evolution of dielectric constant and loss tangent and at right resistivity as function as SiO_2 shell thickness.

explained by the appearance during the synthesis of SiO_2 spherical particles, the higher the TEOS concentration is, the higher the amount of SiO_2 is (for example, the TEM image of particles coated with 65 nm in **Figure 7**). When the samples are sintered at high temperature, SiO_2 particles crystallize into SiO_2 quartz and cristobalite. SiO_2 has a very low dielectric constant and, therefore, reduces ϵ_r of the ceramic. Nevertheless, the presence of the SiO_2 phase at the GB limits the loss tangents, which remain around 0.1 regardless of the composition. Moreover, in accordance with the drop of the dielectric constant, the resistivity increases to very high values.

Although the SiO_2 shell does not improve the dielectric properties as desired, the effect is positive. Control of the GB thickness is possible with an accuracy of 1 nm and the properties for shell values <20 nm are slightly better. Beyond the amorphous silica coating, it was interesting to investigate other insulating shells that might exhibit better properties. In the literature, significant effects of the Al_2O_3 and TiO_2 shells on the resulting dielectric behaviors of the ceramics were observed. A large dielectric constant was obtained for $\text{BaTiO}_3@ \text{TiO}_2$ due to the interfaces created by the introduction of the intermediate TiO_2 layer [72]. $\text{BaTiO}_3@ \text{Al}_2\text{O}_3$ showed an enhanced dielectric breakdown strength and decreased energy loss without degradation of the dielectric constant [73].

3.7 Aluminum oxide-based core-shell nanocomposites

The process used to synthesize $\text{CCTO}@ \text{Al}_2\text{O}_3$ core-shell particles is slightly different from the one used for SiO_2 coating, but it is derived from Stöber and Peng methods [63, 74]. It is well-known that the growth of a uniform Al_2O_3 shell outside the surface is very challenging due to the large lattice mismatch between the core and Al_2O_3 , along with their relatively weak chemical interaction [75]. Aluminum propoxide was dissolved in an ethanol solution, and the precursor amount was calculated using the same Eq. (2) as was used for SiO_2 , based on the calculated average size of the CCTO particles. CCTO powder was identical for all coated samples, and as a result, the average grain size remained at 1 μm . After the dissolution of the precursor, a CCTO powder mixture with a concentration of 10 g/l with ethanol was dropped into the suspension, and then dispersed by sonification for 20 min. In parallel, a 1:5 (v/v) mixture of water and ethanol (50 mL) was added slowly drop by drop, and the mixture reaction was ultrasonicated for 2 h. The particles were collected by

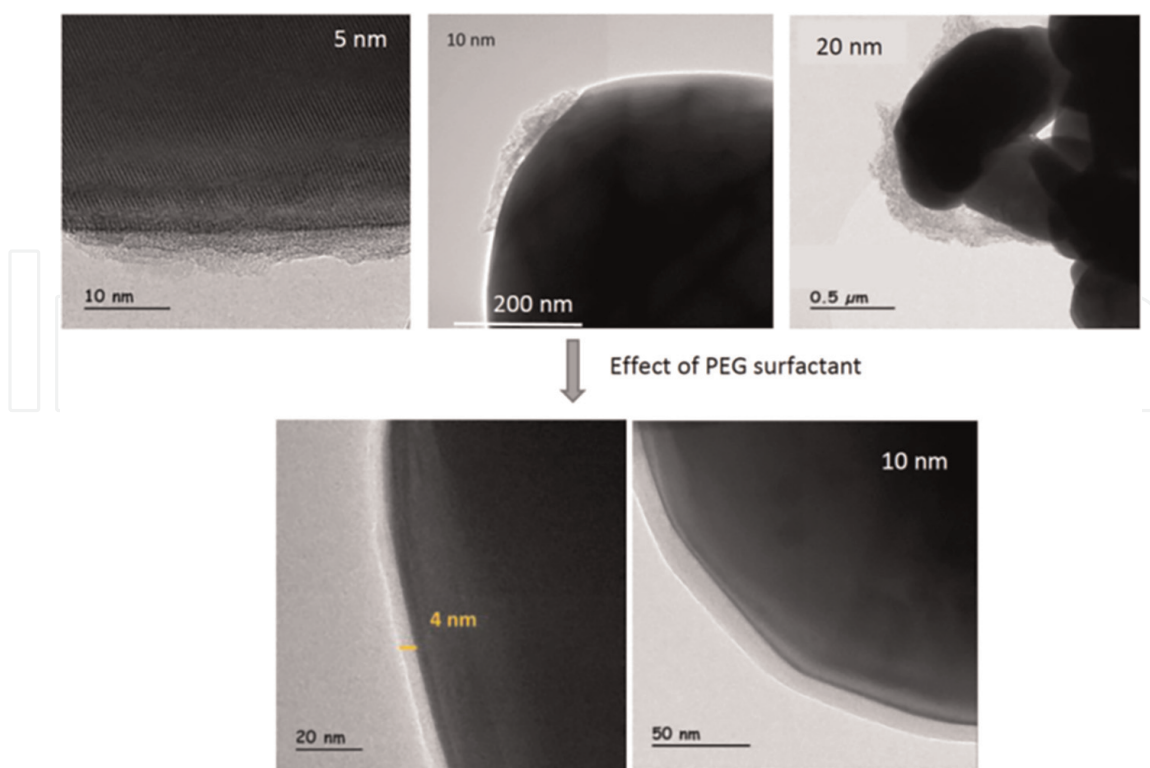


Figure 13.

TEM images of CCTO@Al₂O₃ for thickness shell from 1 nm up to 20 nm, at the top the CCTO is not functionalized, at the bottom the CCTO is worked with PEG. The light contrast corresponds to the amorphous shell.

centrifugation and washed with ethanol and ultrapure water. From this power, pellets were pressed and sintered at 1050°C during 24 h.

Figure 13 depicts the TEM images of CCT@Al₂O₃ for several thicknesses. These images clearly show that the coating is not homogeneous and uniform. Its thickness varies along the grain surface, and sometimes no coating is visible at all. This observation led us to modify the solution containing the CCTO particles. To avoid particle agglomeration, the surfactant polyethylene glycol (PEG) was used, which has been reported to be the efficient protecting agents to stabilize a solution. A series of samples were realized with CCTO functionalized by PEG and subsequently coated with aluminum propoxide using the same process (precursors, proportion of solvent, time sintered temperature ...). The TEM images confirmed a better coating for all the samples with a clear core-shell nanostructure of CCTO@Al₂O₃ with homogeneous and compact shell layer. CCTO grains were well crystallized and the shell was amorphous. EDS analysis was used to check the composition of the core-shell with Ca, Cu, Ti and Al elements.

SEM investigation of the compounds after sintering has exhibited that the average size grain for coated samples (120 μm) is bigger than CCTO (70 μm) (**Figure 14a**). At the same time, the density is found better for CCT@Al₂O₃. Then, Al₂O₃ phase acts as a sintering aid. The appearance of a liquid phase, thanks to the CuO–Al₂O₃ interaction during the ceramic sintering heating stage, results in enhanced growth of ceramics grains and density. The presence of Al element and CuO phase in the GB has been attested by EDS analysis in CCTO@Al₂O₃ sample (**Figure 14b**). However, there is no significant observation of the Al element within the grains (area 1).

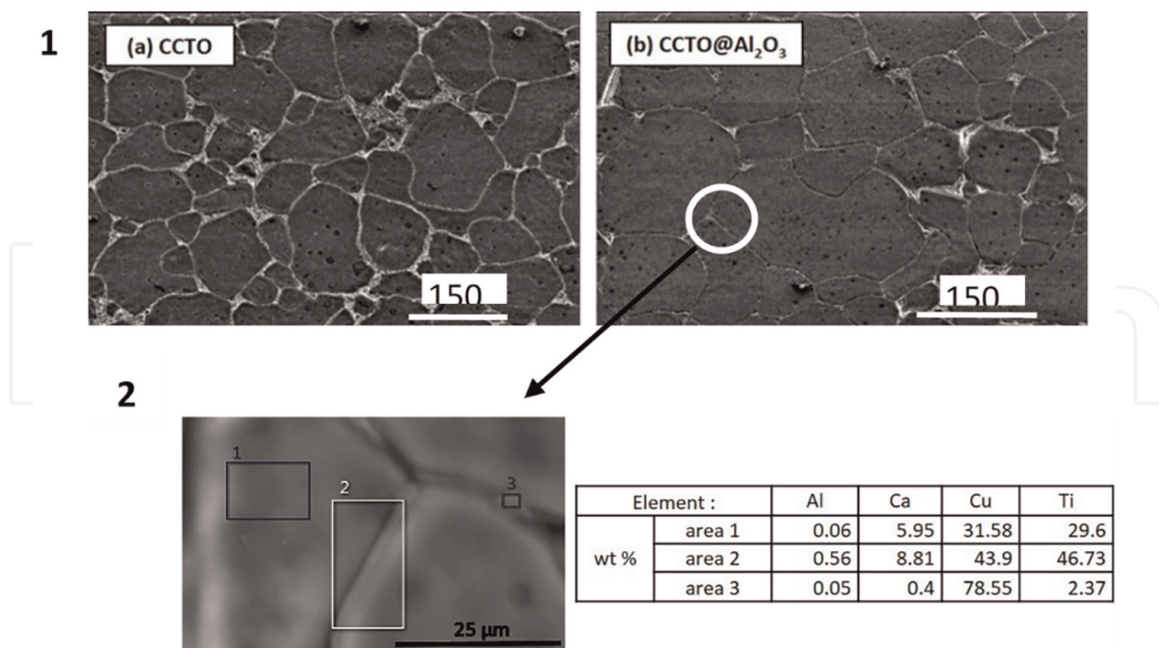


Figure 14.
(1) SEM images of (a) CCTO and (b) CCTO@Al₂O₃ pellets (2) EDS analysis in different areas: grain (1), grain boundary (2) and copper-rich phase (3) [61].

Dielectric measurements on the synthesized nanocomposites indicated that the dielectric constant (ϵ_r) at 1 kHz is higher with a value close to 91,000 than CCTO (68000). This increase can be correlated with the IBLC model describing the mechanisms leading to colossal permittivity of CCTO [48]. An interesting point of these results is that the loss tangent is slightly lower but the resistivity is slightly increased. However, the functionalization of CCTO by PEG or PVP further improves the dielectric properties and, in particular, the bulk resistivity which increases by an order to achieve $2 \cdot 10^8 \Omega \text{ cm}$. Dielectric losses are linked to the modification of the interfacial polarization between the grains, which results from the accumulation and movement of charges at the interfaces. The presence of the compact insulating Al₂O₃ phase reduces the concentration and mobility of these carriers, leading to a reduction in dielectric losses and an increase in resistivity.

3.8 Titanium oxide-based core-shell nanocomposites

The coating of CCTO particles with a titanium shell and different thicknesses has also been applied with the same process used for Al₂O₃ with the appropriate precursor tetrabutoxyde de titane -TBOT (sigma Aldrich, 97%). The scanning and transmission electron microscopy clearly indicate the shell around CCTO grains. The SEM images show a shell around a grain agglomerate. TEM and STEM clearly indicate that the obtained samples are composed of well-crystallized CCTO and amorphous TiO₂. Dielectric measurements were realized on pellets sintered at 1050°C for 24 h, as previously done, to compare the impact of the shell's composition. The permittivity found for this series is very high, with a value of 870,000 at 1 kHz for CCT@TiO₂ (10 nm), at the expense of losses and bulk resistivity. The evolution and thermal stability of CCT@TiO₂ (10 nm) compound using in situ variable temperature chamber (HT-XRD) has been determined from ambient to 1000°C. Regarding the composition evolution of the phases, the crystallization of TiO₂ phase starts to form anatase structure for T = 600°C. As temperature rises, transformation to the rutile phase takes

place at 850°C due to the isotropic thermal parameters change for oxygen. In addition, the rutile phase amount starts to rise continually. The existence of rutile phase in the CCTO@TiO₂ pellets was confirmed by Raman scattering in GBs. Baumard et al. have shown that under the experimental conditions of TiO₂ synthesis, it becomes conductive [76]. Thus it is possible that the rutile GB has become slightly conductive, which would explain the low GBs resistivity and the high $\tan(\delta)$ found. Therefore, the overall resistivity of the sample that depends on the GB resistivity is also very low. If the GB is slightly conductive, the resistivity is reduced but if the GB is not sufficiently insulating, the electrical losses increase. Thus to improve the ceramic properties, one way would be to make insulator the GBs. It could be shown that the TiO₂ phase in anatase form is insulating and, therefore, improves the properties of grain joints [59]. However, the anatase form is metastable regardless of temperature and pressure, whereas rutile is an equilibrium polymorph, in agreement with CCTO@TiO₂.

4. Toward new compositions and core-shell design

The coating of CCTO grains with single composition shells (SiO₂, TiO₂, Al₂O₃) has been successfully achieved and the shell thickness obtained can be controlled. Permittivity decreased slightly for CCTO@SiO₂ and CCTO@Al₂O₃ but remains high ($\sim 10^4$), this means that the shell does not destroy the properties. Dielectric losses are improved for these both compounds. It has also been found that resistivities are improved and more specifically for Al₂O₃ coating with a bulk resistivity that increases from 10^6 to 10^9 Ω cm. While the dielectric constant is greatly improved by CCTO@TiO₂ linked to the GB capacitance, the bulk resistivity is low [77]. The coating of CCTO compared to additives or conventional doping leads to a decrease in dielectric losses while maintaining a high permittivity [78–80]. Taking into account the best properties of each compound for a shell thickness close to 10 nm, shell mix was considered, CCT@SiO₂@TiO₂, CCTO@SiO₂@Al₂O₃, CCT@TiO₂@Al₂O₃ and CCT@SiO₂@Al₂O₃@TiO₂. The objectives were (i) to keep the high dielectric constant by improving the bulk resistivity (ii) to observe the impact of several compositions on the dielectric properties (iii) to correlate the ϵ and the capacitance of GBs and the bulk resistivity and the GB resistivity to confirm the IBLC model. The process of synthesis of these powders remained the same as before by mixing the precursors TEOS, TBOT and Aluminum propoxide depending on the desired shell. The structural and microstructural characterizations (HRTEM-SEM) showed the good conformity of the shells around the grains and the amorphous character of the shell. The question arises as to whether the 3 shells form a solid solution when the ceramics are sintered. According to the phase diagrams of the 3 binary oxides, the mutual solubility of the oxides is negligible. In the ternary Al₂O₃-TiO₂-SiO₂ system, only the aluminosilicate compound Al₆Si₂O₁₃ could be formed at identical ratios [81]. However, for $T < 1600^\circ\text{K}$, phase formation is negligible. The sintering temperature of 1050°C we used is too low, and no such phase has been demonstrated, only TiO₂ which crystallizes. From impedance spectroscopy, by fitting the data with two RC elements in series consisting of a resistor and capacitor connected in parallel, one for the grains and the second for GBs, the capacitance and resistivity of the grains and GBs were analyzed for all samples. As indicated by the IBLC model, the permittivity plotted as a function of the capacitance of the GBs follows a linear dependence in agreement with the Eq. (1) (**Figure 15a**). Moreover, GB resistivity is significantly more insulating than grain resistivity and as GB resistivity decreases, so does the overall sample resistivity is. In these figures, it

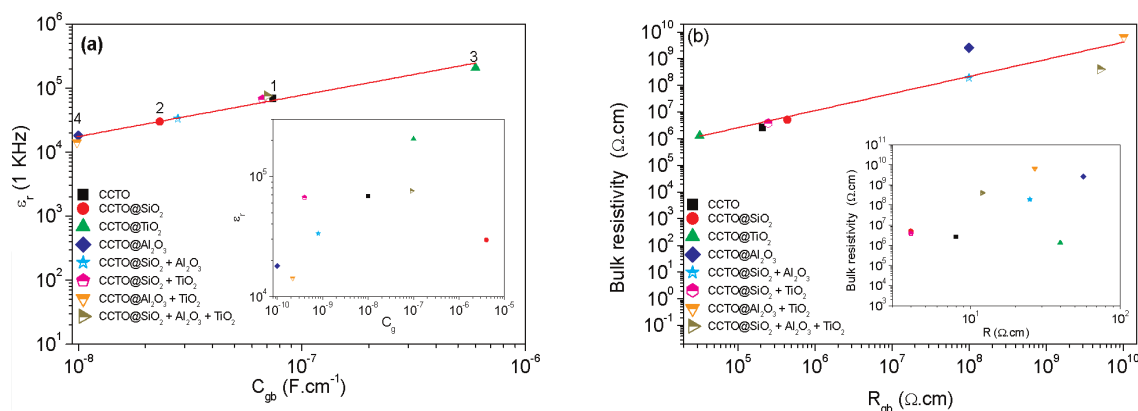


Figure 15.
(a) Correlation of ϵ_r and C_{gb} for undoped CCTO (black dot) and “core-shell” CCTO samples. No correlation of ϵ and C_b for the same samples is found in the inset (b) Correlation of sample resistivity with R_{gb} and its absence with R_b shown in the inset.

can be seen that a very high permittivity also shows the lowest resistivity, which becomes incompatible with the characteristics expected for a ceramic capacitor.

5. Toward an innovative cold plasma technology to coat dielectric particles

Cold plasmas, also named non-thermal plasmas, have shown their high efficiency in many industrial applications, including abatement of gaseous and liquid hazardous species [82–85], inactivation of micro-organisms in biomedical applications, food industry [86–91], and surface interactions [92–95]. In this type of plasma, chemical processes are initiated by collisions between energetic electrons (hot electrons) accelerated by the electric field and heavy species (atoms, molecules). Consequently, the gas temperature remains close to ambient, while the electronic temperature is much higher (some 10,000 K).

During the last 20 years, new promising processes based on various micro-plasma configurations were investigated [96–99]. Micro-plasmas are characterized by a reduced size. One of the discharge dimensions must be sub-millimeter, corresponding to a value of $p \times d$ (pressure $\times$ discharge gap) between 1 and 13 Pa m close to those of low-pressure plasmas, but with pressures that can reach atmospheric pressure. Consequently, current and energy densities are much higher than for conventional low-pressure plasmas. This leads to greater efficiency in the production of chemically active species in such plasmas [98]. These processes with small reaction volumes translate directly into short processing times.

Plasma Enhanced Chemical Vapor Deposition (PECVD) technique was successfully used for many years for plasma deposition processes. Classically, the plasma was generated by an RF-excitation (at 13.56 MHz) [100–102]. However, the coupling of a micro-plasma reactor with a nanosecond-pulsed electric generator can present many advantages: on the one hand, this allows to benefit from the intrinsic micro-plasmas properties and on the other hand, the nanosecond-pulsed plasmas results in a very efficient energy transfer, i.e. input electric energy is mainly used to produce hot electrons leading to chemical reactions but not to gas heating.

This is why it is important to estimate excitation temperatures, i.e. rotational, vibrational and electronic temperatures (T_{rot} , T_{vib} , T_e) in order to characterize the

plasma reactivity. These parameters provide information especially on the input energy distribution, and, contribute to identify the main mechanisms responsible for chemical transformations into the plasma.

For all these reasons, it seems interesting to explore a new approach to coat CCTO grains with silicon oxides by cold plasma treatments.

5.1 Experimental procedures

CCTO powder was prepared by standard solid-state reaction starting from a stoichiometric mixture of CaCO_3 , CuO and TiO_2 , described in detail above. Next, CCTO powder was mixed with an Ink Vehicle (Fuel Cells Materials) and deposited by screen-printing on a glass substrate, and finally ink.

was evaporated by heat treatment.

SiO_2 is obtained from the decomposition of hexamethyldisiloxane (HMDSO, $\text{C}_6\text{H}_{18}\text{OSi}_2$) vapor by an argon/oxygen cold plasma. A low HMDSO proportion in the Ar/O_2 /HMDSO mixture is required to obtain a higher quality SiO_2 film, typically a few 100 ppm of HMDSO [103]. In addition, in order to have a complete oxidation of HMDSO to SiO_2 , CO_2 and water vapor, a stoichiometric molecular ratio of O_2 /HMDSO must be kept at a value of 13 [104]. Plasma treatments were performed into a 21 L vacuum chamber, the Ar/O_2 /HMDSO mixture was introduced in the micro-torch by means of controlled gas and liquid mass flow meters at a working pressure of 2.9×10^{-3} Pa. A compromise was found between thickness, layer homogeneity and processing time for the gas mixture composition and the time treatment: Ar/O_2 /HMDSO = $2028 \text{ Ncm}^3 \text{ mn}^{-1}/7.84 \text{ Ncm}^3 \text{ mn}^{-1}/523 \text{ mg h}^{-1}$, respectively, and 30 min treatment in this study, the shell thickness being mainly controlled by the processing time.

The experimental setup used to realize the plasma treatments is illustrated in **Figure 16**. Optical emission measurements were performed with a 750 mm imaging

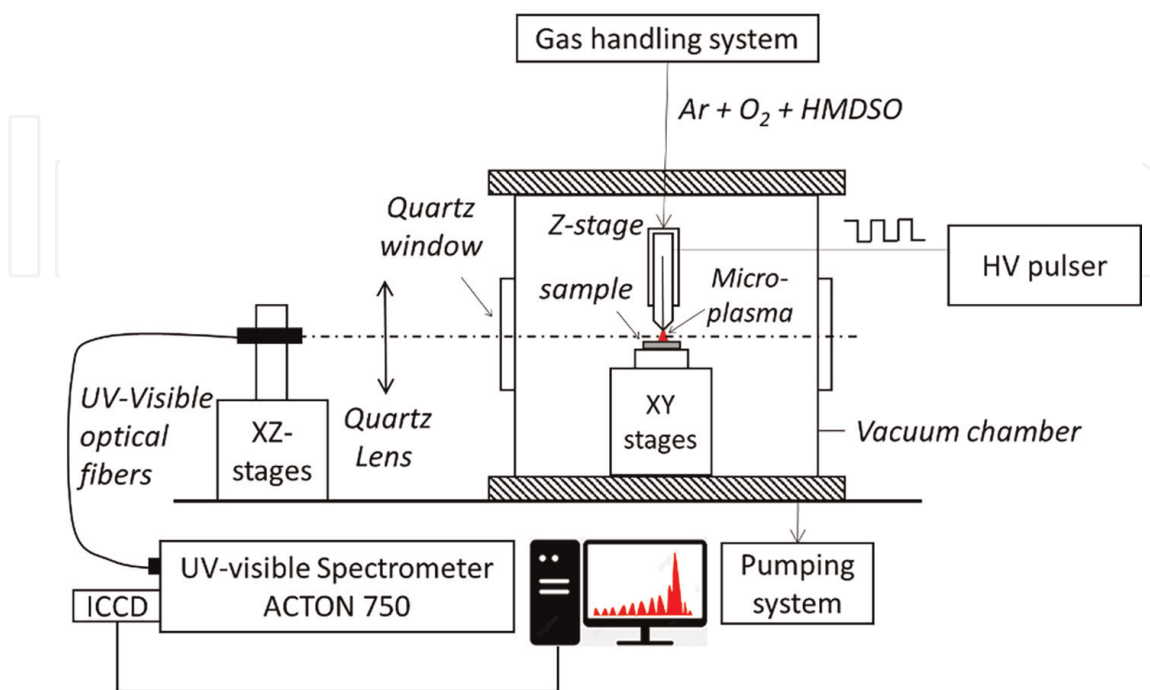


Figure 16.
Experimental setup of the plasma generator system and spectroscopic acquisition.

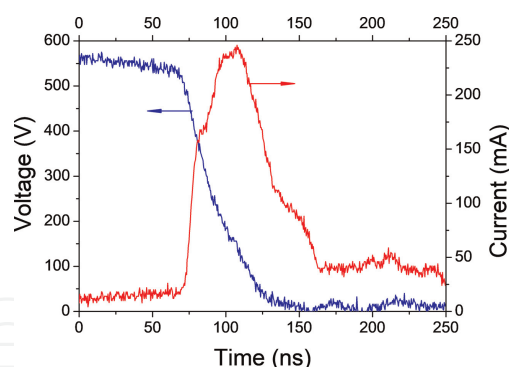


Figure 17.
 Time evolution of voltage and current of a single pulsed discharge (630 V applied voltage).

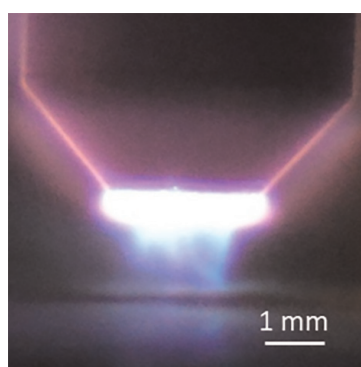


Figure 18.
 Profile of the micro-torch plasma.

spectrometer equipped with an ICCD camera. The micro-torch was driven by a high voltage pulsed generator controlled by an arbitrary function generator set in pulse mode. The maximum of current was achieved in a very short time of about 30 ns, as it can be seen on example of voltage and current record of a single discharge displayed in **Figure 17**.

The micro-torch was a wire/cylinder configuration with an annular discharge gap of 250 μm and an outer diameter of 2 mm. The gas mixture flowed on the axis of the reactor and the plasma appeared as a needle going out of the reactor. The CCTO support was placed on a translational motorized XY stage, which allows to treat a surface of $15 \times 15 \text{ mm}^2$, an example of the micro-torch plasma behavior is given in **Figure 18**.

6. Results and discussion

6.1 Spectroscopic investigations

Optical emission spectroscopy (OES) is a powerful, non-intrusive plasma diagnostic tool. It allows the identification of the species present in the plasma phase. In addition, a comparison between experimental and simulated molecular spectra provides access to the different plasma excitation temperatures. Emission of plasma was investigated in the UV-visible range. The main atomic species observed were Si I, C I, Ar I, Ar II, O I. The identified molecular species were the ro-vibrational bands of SiO

($A^1\Pi-X^1\Sigma^+$) at 234–250 nm, OH° ($A^2\Sigma^+-X^2\Pi_i$) (0,0) at 309 nm, CH ($B^2\Sigma-X^2\Pi$) (0,0) at 390 nm and CH ($A^2\Delta-X^2\Pi$) (0,0) at 430 nm, and the C_2 Swan band ($d^3\Pi_g-a^3\Pi_u$) (0,0) at 516.5 nm. An example is shown in **Figure 19**. The presence of atomic and diatomic species derived from the HMDSO molecules demonstrates the strong dissociation power of this type of plasma.

Several molecular spectral simulation software are available on the market. In this study, we have used *SPECAIR* and *LIFBASE* codes [105, 106]. Among other functions, they can be used to easily estimate plasma excitation temperatures by adjusting plasma parameters in order to obtain the best fit between simulated and experimental spectra.

An example of such processing is shown in **Figure 20** for estimating rotational temperature. The three ro-vibrational bands OH° ($A^2\Sigma^+-X^2\Pi_i$) (0,0) at 309 nm, CH ($B^2\Sigma-X^2\Pi$) (0,0) at 390 nm and CH ($A^2\Delta-X^2\Pi$) (0,0) at 430 nm were used as

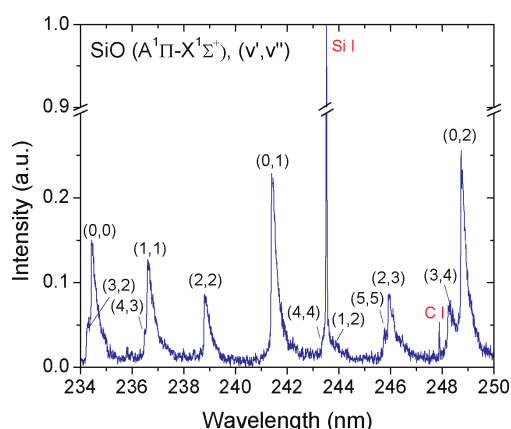


Figure 19.

Experimental spectrum in the range of 234 nm to 250 nm, mainly composed of SiO emissions, with the presence of C I and Si I lines (1000 V applied voltage).

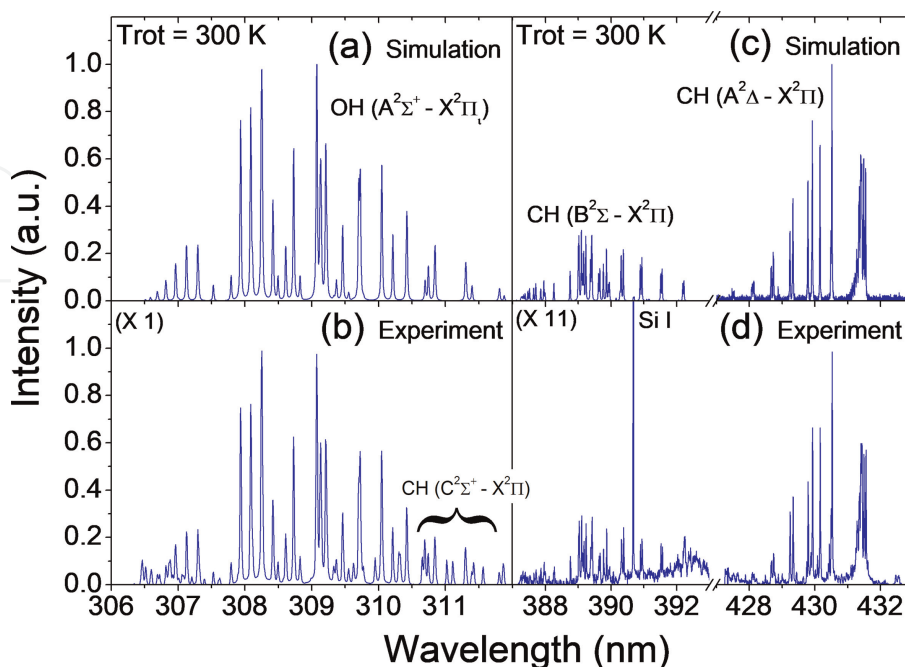


Figure 20.

Spectra of OH° ($A^2\Sigma^+-X^2\Pi_i$), CH ($B^2\Sigma-X^2\Pi$) and CH ($A^2\Delta-X^2\Pi$). (a) and (c) LIFBASE simulated spectra, and (b) and (d) experimental spectra (1000 V applied voltage).

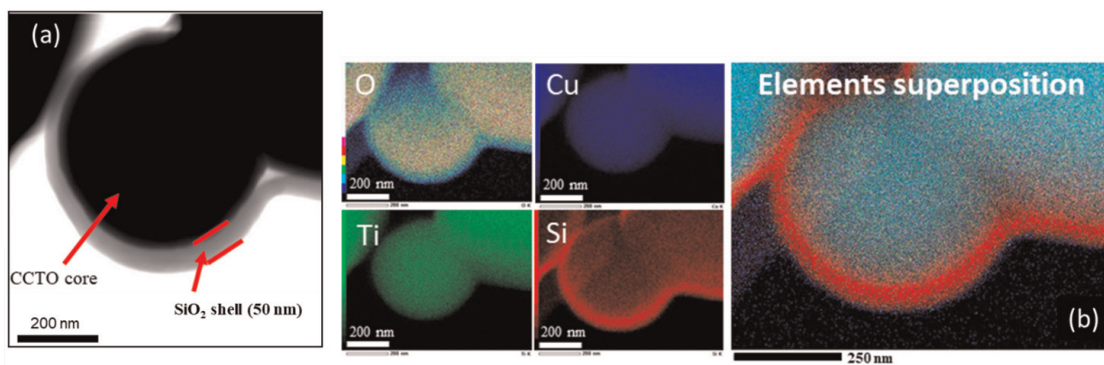


Figure 21.
(a) TEM picture of a core-shell obtained with $Ar/O_2/HMDSO = 2028 \text{ N cm}^3 \text{ mn}^{-1}/7.84 \text{ N cm}^3 \text{ mn}^{-1}/523 \text{ mg h}^{-1}$, respectively, 30 min treatment and 1000 V applied voltage and (b) EDS-STEM mapping pictures of elements and their superposition O, Cu, Ti, Si.

thermometer species. The rotational temperature T_{rot} , usually assimilated to the gas temperature T_g [107], was estimated individually for the three thermometers by simulated spectra adjustments, built from the *LIFBASE* code. The best adjustment was $T_{rot} = 300 \pm 10 \text{ K}$.

The same technique can be used to estimate the vibrational temperature of molecules T_{vib} , as well as electron temperature T_e . These values have been estimated under our experimental conditions at $T_{vib} = 2400 \text{ K}$ to 3700 K ($\pm 100 \text{ K}$) (depending on the applied voltage) and $T_e = 5.3 \text{ eV} \pm 0.2 \text{ eV}$.

These results show that this micro-plasma produces highly non-Local Thermodynamic Equilibrium (non-LTE) or cold plasmas, and respects the characteristic inequality of cold plasmas:

$$T_{rot} = T_g < T_{vib} \ll T_e \quad (4)$$

6.2 Microstructure analysis

TEM analysis revealed the presence of a particularly homogeneous shell around the CCTO grains with a constant thickness, as shown in **Figure 21a**, where the thickness is $50 \text{ nm} \pm 2 \text{ nm}$ for this sample. In addition, any orientation of SiO₂ shell was observed, which confers an amorphous character to the shell. X-ray analysis confirmed the shell's amorphous structure.

The mapping data of principal elements present in the shell zone have been analyzed by EDS-STEM and shown in **Figure 21b**. The mapping of O, Cu, Ti, Si and their superposition confirmed that CCTO grains are coated with Si. This means that there is an association between Si and O to obtain SiO (SiO₂) which confirms the core-shell structure.

7. Conclusion

Nanocomposites depicted in this review are composed of a calcium copper titanate (CCTO) core embedded in SiO₂, Al₂O₃ or TiO₂ shells. This strategy was used in order to meet the specifications in the industry, i.e. materials with a strong dielectric constant, low losses and a strong bulk resistivity. Two methods to achieve core-shell nanostructured materials have been described i) the chemical pathway and ii) the cold plasma pathway. For the chemical way, we focused on coating with different shell

compositions by modifying the surface of CCTO grains, by modulating the shell thickness at the nanoscale. Thus the modification of ceramics could make an important contribution to the control of properties through the engineering of interfaces. The main objective of this study was to control grain boundaries which are essential for obtaining good dielectric and electrical properties. While “core-shell” materials have already proved their interest in controlling properties, there are still points to be improved to understand the phenomena. In particular, in-depth studies of grain boundaries structure at the atomic scale should be carried out to better understand chemical segregation, interdiffusion but also the investigation of the semi-conductor character of grains. The reduction of the sintering temperature would be a plus to limit the deterioration of shells and preserve this microstructure.

The cold plasma coating described in this work is advantageous over other methods reported in the recent literature like: sol-gel, Stöber, hétéro-coagulation [105–107] due to its homogeneous shell and controlled thickness, its process rapidness (max 1 h vs. 1–3 days resp.) and its dry character (no by-products). Another important advantage is being able to work on all surfaces and particles with different chemical composition of the deposition, compared to the layer-by-layer deposition method [74, 108]. The metalorganic precursor (HMDSO) is totally dissociated in the plasma, leading to the nucleation of SiO₂ on the surface of CCTO particles. This system facilitated the generation of uniform core-shell grains with nanometric-controlled shell thickness. The results of temperature measurements described in this study i.e. $T_{\text{rot}} < T_{\text{vib}} \ll T_{\text{e}}$, confirm the non-thermic character of this micro-plasma. This type of plasma is therefore well adapted to chemical treatments, by efficiently generating chemically active species by electronic collisions, without overheating the whole gas.

Acknowledgements

Authors would like to thank J. Wolfman from GREMAN laboratory (France) for the TEM lamella preparation by FIB (Focus Ion Beam) and S. Magrex for final proofreading.

This work was funded in part by Région Centre-Val de Loire within the projects, Concerto (2012) and Coconut (2016).

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