

## Dielectric Properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ Synthesized by Different Routes

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**Abstract.** The perovskite  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ , with giant electric permittivity, was prepared by a soft chemistry route and by the solid state synthesis technique. The main purpose of this work is to verify the effects of the synthesis techniques on the powder characteristics, and the microstructure and dielectric properties of the sintered materials. The synthesized nanopowders were calcined, pressed into pellets and sintered using the same procedures as for the materials prepared by the conventional method. Phase analysis was performed by X-ray diffraction, microstructure observations were carried out by scanning electron microscopy, and the dielectric properties were studied by impedance spectroscopy. The electric permittivity ranged from 11,600 to 27,000 and from 5,000 to 9,000 for specimens prepared by the conventional and the soft chemistry techniques, respectively, and the dielectric losses varied between 0.1 and 1.3 (conventional) and 0.095 and 0.3 (soft chemistry) depending on the sintering temperature.

### Introduction

The complex oxide  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) has a body-centered cubic perovskite-type structure and has received great attention due to its unusual dielectric properties. This material combines a relatively low dielectric loss with giant electric permittivity. Moreover, these properties are fairly constant over a relatively wide range of temperature [1]. Owing to these characteristics, CCTO is considered as a promising material for application in microelectronics, such as microwave devices, capacitors and dielectric planar antennas [2,3]

Several works report the effects of the processing steps on the microstructure and dielectric properties of this complex oxide prepared by the conventional method of mixing the starting materials followed by the solid state reaction at high temperatures [3-6]. Relatively few works may be found in the literature with this compound prepared by a solution method, such as sol-gel [7], combustion [8] and coprecipitation [9,10].

It is generally known that the synthesis technique has large influences on the crystalline structure and final microstructure of sintered materials. Then, microstructure-dependent properties are expected to change according to the technique of synthesis.

In this work, the  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  polycrystalline ceramic was synthesized by a soft chemistry route, known as cation complexation [11], and its structure, microstructure and dielectric properties were investigated and compared to those of the same composition prepared by the conventional technique of solid state synthesis.

### Experimental

The  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  compound was prepared by the conventional and by the cation complexation techniques. In the conventional technique, stoichiometric amounts of  $\text{TiO}_2$  (99.5%, Alfa Aesar),  $\text{CaCO}_3$  (P.A., Vetec) and  $\text{CuO}$  (99.7%, Alfa Aesar) were weighted and wet-milled in a homemade attrition mill for 30 min. After drying, the mixture was deagglomerated and calcined at 900 °C for 10 h. Polyvinyl alcohol, PVA, (2 wt.%) was added to the mixture before pressing into discs and sintering in the 1070-1100 °C for 12 h.

For powders prepared by the cation complexation technique, calcium nitrate (P.A., Vetec), and copper nitrate (P.A., Vetec) solutions were mixed together in the desired proportion and homogenized by continuous stirring. Titanium isopropoxide (Aldrich) was added dropwise to an aqueous solution (1:1) of citric acid to form titanium citrate. The solution containing the other cations was slowly added to the titanium citrate solution to avoid precipitation. The ratio

metal: citric acid was fixed to 1:1.25. The temperature of the resulting solution was raised to 70 °C. Under continuous heating and stirring the solution becomes gradually more viscous, due to evaporation of water and NO<sub>x</sub> vapor, giving rise to a porous resin. The resin was thermally treated at 250 °C for 1 h, deagglomerated and calcined at 900 °C for 10 h. The calcined powder was pressed and sintered using the same procedures as for specimens prepared by solid state reaction.

The apparent density of sintered discs was determined by the immersion method using distilled water. Structural characterization was performed by room temperature X-ray diffraction (Bruker-AXS, D8 Advance) with Cu K<sub>α</sub> radiation in the 20-80° 2θ range. Identification of the crystalline phases was accomplished by comparison of the experimental profiles with JCPDS files. The morphology of the sintered pellet was observed by field emission scanning electron microscopy, FE-SEM (FEI, Inspect F50) after polishing and thermal etching. Dielectric properties of specimens were determined by impedance spectroscopy (Hewlett Packard, 4192A) in the 5 Hz to 13 MHz frequency range using ac signal of 500 mV.

## Results and Discussion

Fig. 1 shows X-ray diffraction patterns of powders (A) and sintered specimens (B) prepared by the conventional and the cation complexation techniques. In this case, the pressed specimens were sintered at 1080°C. After calcination, the powder mixture prepared by the conventional technique exhibits CuO and CaTiO<sub>3</sub> secondary phases along with the cubic perovskite-type phase characteristic of this compound. The calcium titanate secondary phase remains after sintering. In contrast, the X-ray diffraction pattern of the material prepared by the cation complexation technique seems to be single-phase.

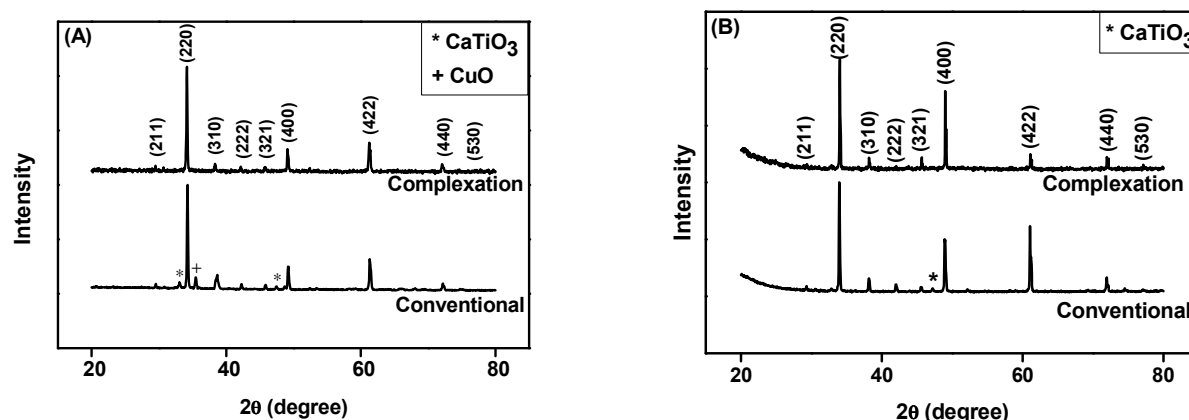


Figure 1 - X-ray diffraction patterns of (A) powders calcined at 900 °C for 10 h and (B) after sintering at 1080°C for 12 h, prepared by the conventional and the cation complexation techniques.

The apparent density increased with increasing sintering temperature, and ranged from 95 to 98% and 88 to 98% of the theoretical value (4.90 g.cm<sup>-3</sup> [12]) for specimens prepared by the conventional and the cation complexation techniques, respectively.

Fig. 2 shows representative scanning electron microscopy micrographs of pellets sintered at 1080 °C for 12 h.

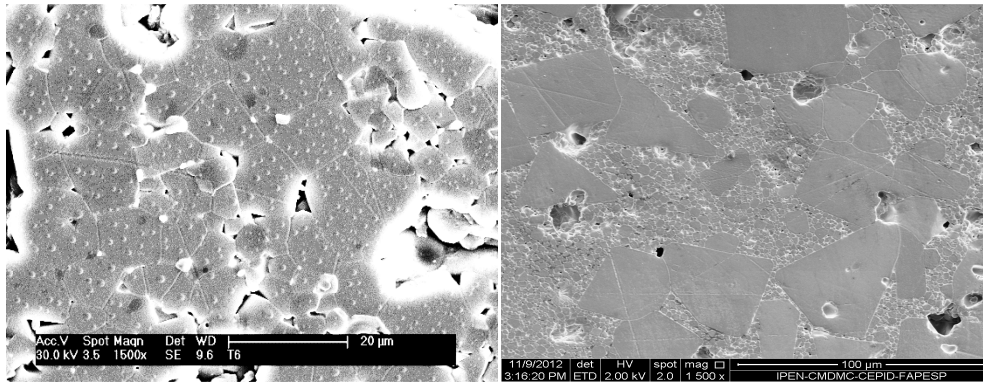


Figure 2 - FE-SEM micrographs of pellets sintered at 1080 °C for 12 h and prepared with powder synthesized by the conventional (left) and the cation complexation (right) methods.

The microstructure of the sample prepared by the conventional method (Fig. 2, left) exhibits a wide distribution of grain sizes and grain pullout along with surface defects. The microstructure of the sample prepared by the cation complexation method (Fig. 2, right) consists of a bimodal distribution of grain sizes. The larger grains are angular and contain very low intragrain porosity. The smallest grains are preferentially of spheroidal shape.

Fig. 3 shows the frequency ( $f$ ) dependence of the electric permittivity,  $\epsilon'$ , obtained at room temperatures of specimens prepared by the conventional (A) and the cation complexation (B) techniques, after sintering at several temperatures.

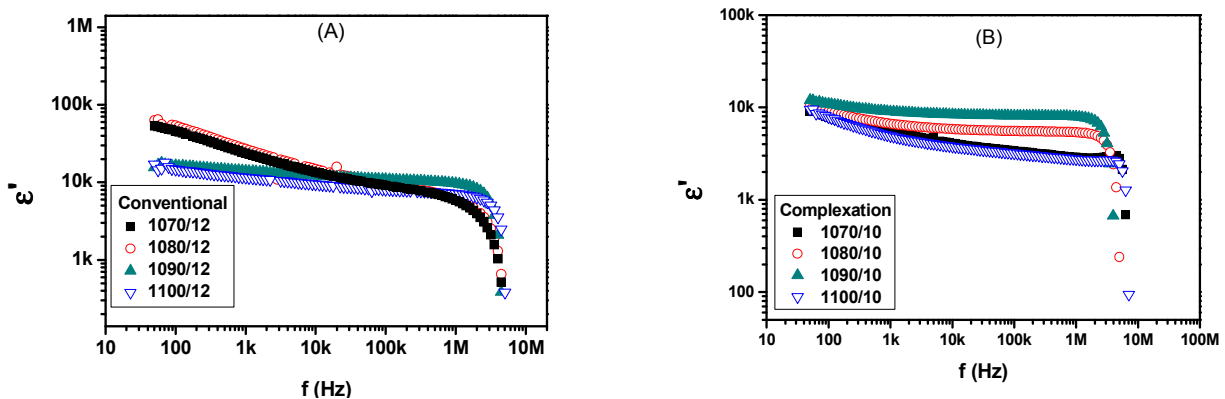


Figure 3 - Room temperature electric permittivity plots of specimens prepared by the (A) conventional and the (B) cation complexation techniques and sintered at several temperatures.

All prepared specimens reached relatively high values ( $> 1000$ ) of electric permittivity. Specimens prepared by the conventional method (Fig. 3A) show electric permittivity values at 1 kHz ranging from 11,600 to 27,000 depending on the sintering temperature. For these specimens, a wide frequency-independent behavior is observed after sintering at 1090 and 1100 °C. Decrease of the sintering temperature resulted in increase of the electric permittivity in the low-frequency range. Similar effect has been reported and attributed to deviation of Cu stoichiometry [13-15]. Specimens prepared with chemically synthesized powder (Fig. 3B) show lower values of electric permittivity (5,000 to 9,000), probably related to the large fraction of grains with relatively small sizes (Fig. 2 right). For both types of specimens a decrease in the electric permittivity occurs for frequencies above 1 MHz, which may indicate the presence of conductive grains [16].

The evolution of the dielectric loss,  $\tan \delta$ , with frequency is shown in Fig. 4 for specimens prepared by different routes and sintered at several temperatures.

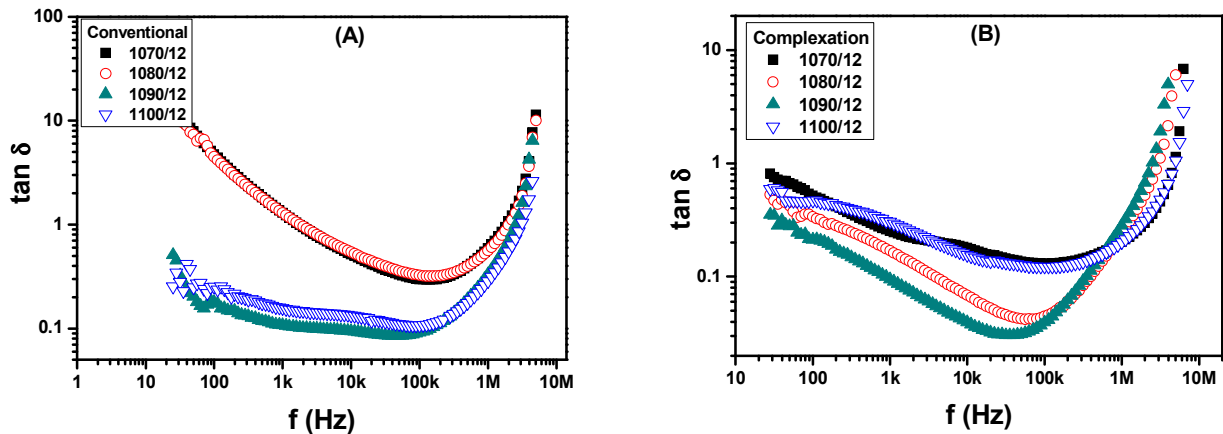


Figure 4 - Frequency dependence of dielectric loss measured at room temperature for specimens prepared by the conventional (A) and the cation complexation (B) techniques after sintering at several temperatures.

The dielectric loss decreases with increasing frequency up to approximately 100 kHz for all prepared specimens. For higher values of frequency the dielectric loss increases. Moreover,  $\tan \delta$  decreases with increasing the sintering temperature up to 1090 °C. At 1 kHz the dielectric loss varies from 0.1 to 1.3 and 0.095 to 0.3 for specimens prepared by the conventional and the cation complexation techniques, respectively.

The overall results show that independent on the synthesis technique, the final microstructure of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  is heterogeneous. Loss of stoichiometry readily occurs for specimens prepared by solid state reactions and sintered at high temperatures. The calcium titanate secondary phase seems to have a minor influence on the electric permittivity of sintered pellets. Specimens prepared with chemically synthesized powder exhibit lower dielectric loss than that prepared by the conventional technique.

## Conclusions

Sintered  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  prepared by the cation complexation technique is single-phase and exhibits lower dielectric loss than the same composition prepared by the conventional technique. Higher values of the electric permittivity were obtained for specimens prepared by the conventional technique. Small amounts of secondary phases do not influence the electric permittivity of CCTO.

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