

# Sol–gel derived $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics: Synthesis, characterization and electrical properties

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## Abstract

The giant dielectric constant material  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$  (CCTO) has been synthesized by sol–gel method, for the first time, using nitrate and alkoxide precursor. The electrical properties of CCTO ceramics, showing an enormously large dielectric constant  $\epsilon \sim 60,000$  (100 Hz at RT), were investigated in the temperature range from 298 to 358 K at 0, 5, 10, 20, and 40 V dc. The phases, microstructures, and impedance properties of final samples were characterized by X-ray diffraction, scanning electron microscopy, and precision impedance analyzer. The dielectric permittivity of CCTO synthesized by sol–gel method is at least three times of magnitude larger than that synthesized by other low-temperature method and solid-state reaction method. Furthermore, the results support the internal barrier layer capacitor (IBLC) model of Schottky barriers at grain boundaries between semiconducting grains. © 2007 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Materials with high dielectric constants are widely used in technological applications such as capacitors, resonators, and filters. High dielectric constants allow smaller capacitive components, thus offering the opportunity to decrease the size of electronic devices [1]. Recently, the discovery of giant dielectric constants in CCTO was reported [2–4]. This material exhibits a giant dielectric constant response with highly unusual temperature dependence. It has a high and relatively temperature independent low-frequency dielectric constant over a wide temperature range between 100 and 600 K. However, below 100 K its value drops abruptly by almost three orders of magnitude, an effect that is not accompanied by a long-range structural phase transition [2,3]. Its structure (s.g.  $Im\bar{3}$ ) can be derived from the ideal cubic perovskite structure by superimposing a body centered ordering of Ca and Cu ions and a pronounced tilting of the titanium centered octahedral [5,6]. The tilting dramatically alters the coordination environments of the A-site cations, leading to a 4-coordinate square-planar environment for Cu and a 12-coordinate icosahedral environment for Ca. It is the mismatch in size and bonding preferences of these two ions and the titanium that drives the large octahedral tilting distortion.

Normally, high dielectric constants are found in ferroelectric materials. CCTO was not found to be a ferroelectric material and has therefore been a material, which needed more studies. It is considered that the electrical properties

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depend greatly on the ceramic microstructure (such as average grain size and pellet density) and processing conditions (such as oxygen partial pressure, sintering temperature, and cooling rate) [7–16]. Homes et al. [4] considered that the origin of the high permittivity has therefore been attributed to the presence of thin, insulating grain boundaries in CCTO ceramics as opposed to an “intrinsic” or bulk effect associated with the rather unusual perovskite-type  $\text{ABO}_3$  crystal structure.

Generally, CCTO is usually made by traditional solid-state reactions from the metal oxides at high temperatures. This method needs tedious work, relatively long reaction times, and high calcined temperatures. In addition, some secondary phases may appear in ceramics. In contrast, synthesis from a solution affords intimate and homogeneous mixing of the metal ions at the atomic scale, thus reducing the diffusion path length required. Shorter diffusion lengths lead to shorter reaction times and lower temperatures [17]. Therefore we attempted to synthesize the CCTO by an alternate route, sol–gel method. In this route, the mixing process is performed in a sol state; therefore, metallic ions are well dispersed and separated by colloidal particle in the mixing system. Each component is uniformly even in the resulting mixture after removing organic substance by combustion.

In this article, we uncover the experimental method for synthesizing CCTO powder at low temperatures and short reaction times. The electrical properties of sintered samples prepared by sol–gel route are characterized by precision impedance analyzer at different temperatures and dc biases. It confirms the Schottky-type nature of the electrostatic barriers at the grain boundaries.

## 2. Experimental

Fine CCTO powders were prepared by the sol–gel method using calcium nitrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), copper(II) nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), tetrabutyl titanate(IV) ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ ) and ethanol as raw materials. First, an appropriate amount of tetrabutyl titanate, calcium nitrate and copper nitrate were dissolved stoichiometrically in ethanol, respectively, according to the formula of  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ . Secondly, these solutions were mixed into beaker and stirred continually to obtain sol. After that, ethanol diluted by water was added in sol drop by drop to obtain a transparent gel. The gel was then aged for 2 h at room temperature. Finally, the gel precursor was dried at  $120^\circ\text{C}$  and decomposed at a temperature  $900^\circ\text{C}$  in air. Black CCTO powder was obtained. The obtained powder was cold-pressed into pellets of 15 mm diameter and  $\sim 1$  mm thickness. The pellets were sintered at  $1040^\circ\text{C}$  in air for 3 and 30 h, respectively.

X-ray diffraction patterns were obtained using an automated diffractometer (XRD; X’Pert PRO MPD, Philips, Eindhoven, Netherlands) with  $\text{Cu K}\alpha_1$  radiation. The surface morphologies of CCTO ceramics were observed by a scanning electron microscope (SEM; JSM-5610, JEOL, Tokyo, Japan). InGa alloy tends to give ohmic contacts to n-type semiconducting titanates [18]. Therefore, InGa (60:40 mol ratios) alloy was prepared and daubed on each sample face.

Electrical properties measurements were taken with an applied voltage of 500 mV using an Agilent 4294A impedance analyzer over the frequency range of 100 Hz–100 MHz at selected temperatures between 298 and 358 K at 0, 5, 10, 20, and 40 V dc.

We obtained the complex impedance  $Z^*$  in the usual way, i.e.,  $Z^* = V^*/I^*$ , where  $V^*$  and  $I^*$  are the applied voltage and measuring current, respectively. The complex permittivity  $\epsilon^*$  was calculated as follows

$$\epsilon^* = \epsilon' - i\epsilon'' = \frac{1}{i\omega C_0 Z^*} \quad (1)$$

where  $\omega$  is the angular frequency  $\omega = 2\pi\nu$  and  $i = \sqrt{-1}$ .  $C_0 = \epsilon_0 S/d$  is the empty cell capacitance, where  $S$  is the sample area and  $d$  is the sample thickness.

## 3. Results and discussion

### 3.1. XRD measurements

X-ray diffraction patterns of CCTO powder prepared by sol–gel route; after calcined at  $900^\circ\text{C}$ , and pellets sintered at  $1040^\circ\text{C}$  for 3 and 30 h, are shown in Fig. 1. We refer to the powder sample as powder A. The sample A was cold-pressed into a pellet and sintered it at  $1040^\circ\text{C}$  for 3 h. We refer to this as sample B. Sintered a pellet at  $1040^\circ\text{C}$  for 30 h we refer to this as sample C. Samples B and C are single-phase CCTO, with all peaks attributable to its cubic crystal

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