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Grain size effects on the dielectric constant of $CaCu_3Ti_4O_{12}$ ceramics

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Abstract

The $CaCu_3Ti_4O_{12}$ (CCTO) compound shows an unusually high and almost temperature independent dielectric constant at low frequencies. CCTO powders have been synthesized by an organic gel-assisted citrate process. The ceramic microstructure was optimized for a given sintering process. Both the grain size and density are shown to be maximum when PVA is introduced in powder before the complete formation of CCTO. A correlated increase of the dielectric constant is evidenced by impedance spectroscopy measurements. Results support the IBLC model proposed to explain the high dielectric constant of CCTO.

Keywords: High dielectric constant; $CaCu_3Ti_4O_{12}$; Sintering; Organic gel-assisted; PVA

1. Introduction

Recently, the insulating $CaCu_3Ti_4O_{12}$ (CCTO) compound has attracted much interest due to its unusually high dielectric constant $\varepsilon \sim 10^4$ at low frequencies which remains almost constant between 100 and 600 K [1,2]. Therefore, this material seems promising for low frequency microelectronic applications like decoupling capacitors.

CCTO was first synthesized by Bochu et al. [3]. This titanate oxide crystallizes in a cubic structure with *Im*3 space group with a lattice parameter of 7.391 Å. The TiO_6 octaedra are tilted, resulting in the doubling of the perovskite-like lattice parameter and involves a square planar arrangement of the oxygen around the Cu^{2+} cations. Like in the perovskite, the Cu^{2+} cations have 12 nearest-neighbour oxygen atoms but the isocahedron is slightly distorted [4,5].

Very high values of the dielectric constant have been measured on single crystals, ceramics and films as well [1,4,6–8] and they appear as an inherent property of the material.

The origin of the peculiar dielectric phenomena in CCTO is not fully understood. Combined first principles calculations [9,10] and experimental research using X-ray and neutron diffraction [4,11], optical conductivity measurements [2], impedance spectroscopy [12] concluded to the absence of direct evidence for intrinsic lattice or electronic origins and led to suggest an extrinsic mechanism related to crystalline deficiencies such as domain boundaries, based on a barrier-layer mechanism. The idea is that the conductivity of the sample is prevented to percolate by the presence of insulating blocking layers at the surfaces or at internal domain boundaries. The insulating layers are thought to cause internal boundary layer capacitance (IBLC). Based on these possibilities, different morphological models were proposed to explain the unusual dielectric behaviour [13].

The IBLC model was recently supported by different observations of defects inside both single crystals [14] and grains of polycrystalline CCTO [15,16] and by complex impedance spectroscopy measurements on a CCTO crystal [17].

The dielectric properties of CCTO ceramics are very sensitive to processing. Values between 500 and 20 000 are usually reported [4,12,18,19]. Values close to 10^5, which are in the same range reported for single crystals are obtained for attrition-milled powders [20] or for three-phased ceramics (CCTO + $CaTiO_3$ + copper oxide) [21]. The highest dielectric constant (3×10^5) has been measured from powder mixed via ball milling and sintered at 1000 °C for 24 h [22].

This paper reports on the microstructure and dielectric properties of CCTO ceramics prepared through an organic

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gel-assisted citrate route [23] by using an organic binder polyvinyl alcohol (PVA) in the process of shaping the samples. The effect of the grain size will be discussed.

2. Experiment

2.1. Synthesis

In the first step, calcium carbonate and copper acetate were reacted with nitric acid to form nitrate solution. This solution and titanium citrate were mixed in a stoichiometric ratio and homogenized by magnetic stirring. A triammonium citrate solution was added to chelate all the cations into solutions. The gelation was obtained by dissolution of acrylamide and *N*,*N*′-methylene-bis-acrylamide monomers, by heating up to about 150 °C. As a radical polymerization initiator, a solution of azoisobutyronitrile (AIBN) diluted in acetone was added and a blue translucent gel was obtained. Calcination of the gels were performed using three different temperatures (500, 650 and 750 °C) and durations (2, 5 and 20 h). Conditions are listed in Table 1. Powders were ground by ball milling in iso-propanol for 2 h. PVA previously dissolved in water was then added. After elimination of water, powders were first uniaxially pressed into disc (10 mm × 1 mm) and then isostatically pressed at 4000 bar. Sintering was performed at 1000 °C for 20 h.

2.2. Characterizations

The X-ray diffraction (XRD) measurements were performed on a BRUKER D8 Bragg-Brentano diffractometer with a Cu Kα radiation. The Rietveld method using FULLPROF [24] program was used for the structural refinement. Microstructural characterization of the ceramics was carried out in a scanning electron microscope (SEM) at 15 kV, with the samples coated by a Pd–Au film.

Table 1
Thermal treatment, PVA content, density ratio, grain size

Sample #	Calcination	Binder ratio (%)	Density (%)	Grain size (μm)
1	750 °C/2 h[a]		71	1.2 ± 0.4
2	(b) 650 °C/5 h	5	68	1.4 ± 0.5
3	(d) 500 °C/5 h	5	62	1.4 ± 0.4
4	(a) 650 °C/20 h	5	81	1.3 ± 0.4
5	(c) 500 °C/20 h	5	76	4.1 ± 1.8
6	(c) 500 °C/20 h	2.5	79	3.4 ± 1.4

[a] Annealing: 900 °C/1 h.

The electrical properties were studied by impedance spectroscopy using a Schlumberger Solartron S11260 frequency response analyser. Measurements were performed under a dry nitrogen flow, with 0.1 V amplitude signal between 0.1 and 10^7 Hz. Thin gold electrode films were deposited by magnetron sputtering on both flat and polished faces of the pellets.

3. Results

The same sintering conditions were applied for all the samples studied. XRD patterns of ceramics show the presence of CCTO as a single phase. The refined lattice parameters are close to 7.393(3) Å, which is in agreement with the literature [3].

In a first study, CCTO powders was prepared with a 2-h calcination at 750 °C and annealed at 900 °C during 1 h [25]. SEM image shows however that the sintering was not optimal, with some residual porosity observed among micron-sized loosely connected grains (Fig. 1 #1). The density of those pellets was only 71% of the theoretical one (Table 1). It is well known that the thermal treatment of the gel obtained by organic gel-assisted citrate process is a key factor to control the ceramics density. To optimise the densification, new thermal treatments were performed on gels at 650 and 500 °C with different duration(s) and contents in PVA (Table 1). Calcinations at 650 or 500 °C for

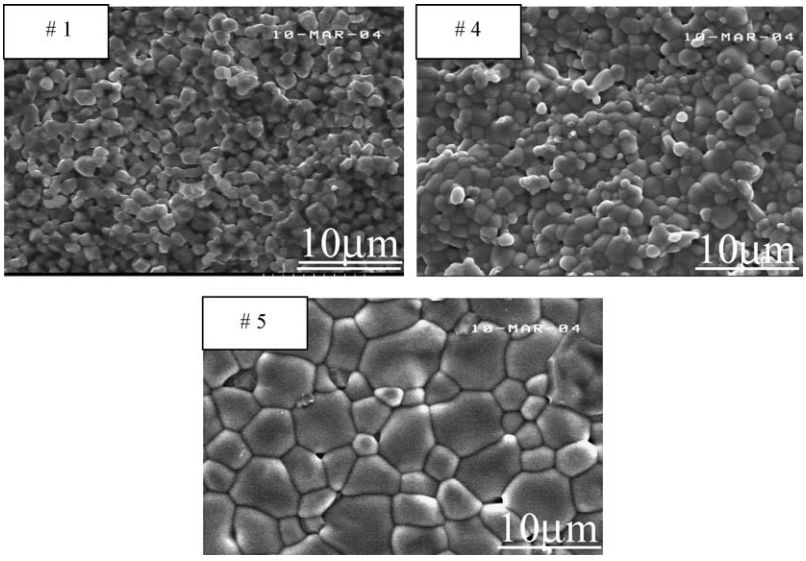

Fig. 1. SEM pictures of the surface of pellets pressed at 4000 bar and sintering at 1000 °C for 20 h. Samples # are indicated according to Table 1.