

Effect of the dwell temperature on spark plasma sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

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Abstract. Polycrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics were prepared by solid state reactions by spark plasma sintering (SPS) technique. In this study, the effects of the dwell temperature on structural, microstructural and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics have been investigated. Powder mixtures were calcined at 900°C for 18 h before SPS consolidation. The dwell temperatures were 850, 900, 915 and 930°C. Sintered pellets were characterized by X-ray diffraction, scanning electron microscopy and impedance spectroscopy. X-ray diffraction patterns show evidences of a single-phase perovskite-type structure. The calculated lattice parameter is 7.40 Å. The hydrostatic density increases slightly with increasing dwell temperature. Scanning electron microscopy observations revealed a heterogeneous microstructure for all samples. The dielectric loss remains constant over a wide temperature range. The obtained permittivity is approximately 10^3 at 1 kHz. The increase of the dwell temperature is found to produce a brittle ceramic.

Introduction

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramic material exhibits a giant permittivity, approximately 10^4 at room temperature, which is almost temperature-independent. The small variation of the dielectric constant at frequencies below 10^6 Hz is responsible for its potential application in microelectronics [1]. This giant permittivity is due to the unusual microstructure consisting of semiconductor grains with internal domains and insulator grain boundaries [2, 3]. According to previous works, the first is a low resistivity region, but the second and third ones are high resistivity regions [4].

The dielectric properties of CCTO are very sensitive to the preparation method and processing conditions including sintering, due to the extrinsic origin of the giant permittivity. Then, the processing steps and specific parameters involved in each step should be carefully selected, as they influence the sintered density, phase purity, final microstructure and, consequently, the dielectric properties [5].

In this work, the spark plasma sintering technique was used to prepare sintered pellets of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The main purpose of this work is to understand the effects of this one-step consolidation technique on the microstructure and permittivity of CCTO polycrystalline ceramics.

Experimental

Stoichiometric amounts of CaCO_3 (Vetec, 99%), CuO (Alfa Aesar, 99.7%) and TiO_2 (anatase) reagents were mixed together in acetone using a mechanical mixer (Turbula model T2C) with zirconia milling media for 1 h 15 min. After drying, the powder mixture was calcined in air at

900 °C for 18 h. Conformation and sintering were accomplished simultaneously by spark plasma sintering (SPS 1050 Dr. Sinter Syntex, Inc., Sumitomo Coal Mining Co., Japan). In a typical processing cycle, the powder mixture (~ 3 g) was loaded into a graphite die recovered with graphite sheets, as shown in Figure 1. The die containing powder was heated with simultaneous application of pressure up to 750, 850, 900, 915 and 930 °C, by a pre-set program. The maximum applied pressure was 60 MPa, which was released after a dwell time of 2 min

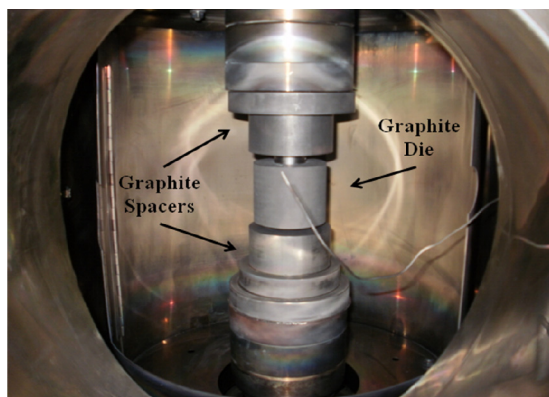


Fig. 1: Picture of the SPS camera.

Phase identification was performed by X-ray diffraction (Bruker-AXS, D8 Advance) in the 20-80° 2 θ range with 0.05° step size and 3 s of counting time, using Cu k_{α} radiation. The sintered density was determined by the immersion method using distilled water. Microstructure observation was carried out on fractured as well as polished and thermally etched surfaces of pellets by scanning electron microscopy, SEM (Philips, XL30). Electric measurements were performed by impedance spectroscopy (HP 4192A) in the frequency range swept from 5 Hz to 13 MHz, with AC signal of 500 mV, from room temperature to 200 °C. Silver was used as electrode material.

Results and discussion

Fig. 2 shows X-ray diffraction patterns of consolidated CCTO pellets with several dwell temperatures. The identification of crystalline phases was carried out by comparison of the experimental patterns with JCPDF files.

The X-ray diffraction patterns of pellets consolidated at 850 and 900 °C exhibit minor secondary phases of TiO₂ (JCPDS No. 89-6975) and CaTiO₃ (JCPDS No. 82-230), indicating that these dwell temperatures are not enough to produce a single phase material. At 915 °C a single phase body-centred cubic perovskite structure was detected. The X-ray diffraction peaks were indexed according to JCPDS No. 75-1149, with $Im\bar{3}$ space group, and the calculated lattice parameter, 0.740 nm, is in general agreement with previous works [1-3]. For the dwell temperature of 930 °C, the X-ray diffraction pattern shows several peaks attributed to CaTiO₃ and TiO₂ secondary phases. This effect is assigned to the loss of copper due to the relatively high dwell temperature. The Cu stoichiometry is considered a decisive factor for attainment of a giant value for the permittivity of CCTO. In particular, for CCTO polycrystalline ceramics, any deviation of stoichiometry leads to a dramatic decrease of the permittivity [6].

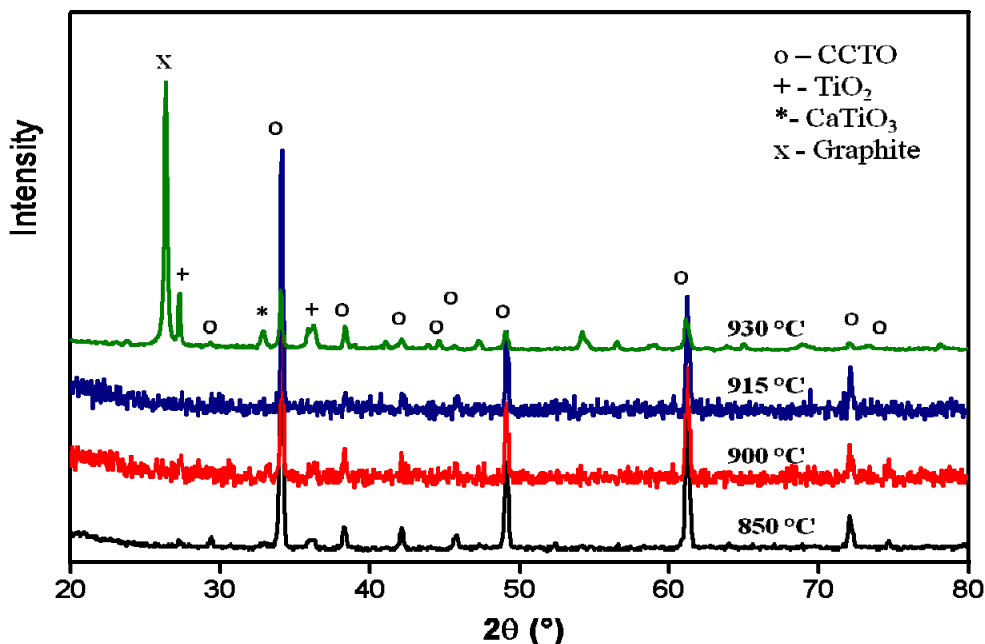


Fig. 2: X-ray diffraction patterns of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellets consolidated at 850, 900, 915 and 930 °C, for 2 minutes.

In what follows, results of pellets consolidated at 850, 900 and 915 °C will be shown. The specimen consolidated at 930 °C was brittle and did not possess enough mechanical strength for the subsequent characterizations.

Fig. 3 shows representative scanning electron microscopy micrographs of polished and thermally etched surfaces of pellets consolidated at (a) 850, (b) 900 and (c) 915 °C for 2 min.

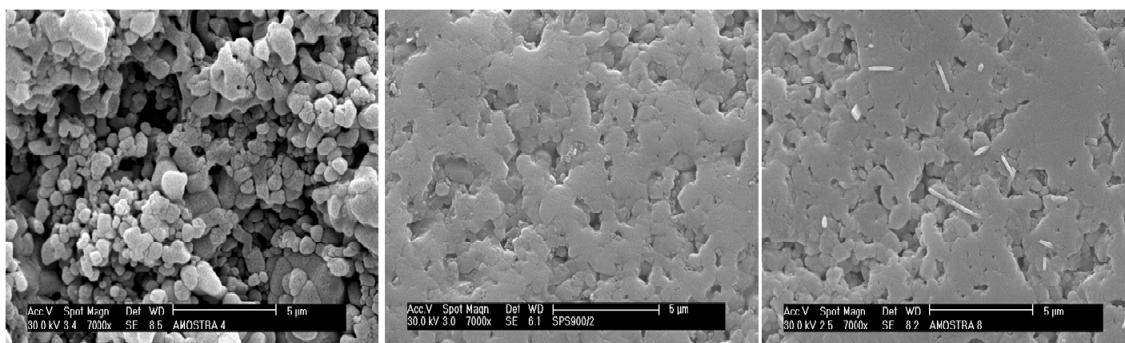


Fig. 3: Scanning electron microscopy micrographs of polished and thermally etched surfaces of CCTO samples sintered at (a) 850, (b) 900 and (c) 915 °C for 2 min.

The SEM micrographs (Fig. 3) show that in consolidated pellets the microstructural features are clearly distinct. The microstructure after consolidation at 850 °C is quite porous and the sintering process is in the first stage with still individualized particles. Densification of pellets occurred for dwell temperatures of 900 and 915 °C. It is worth to note that no sintering aid was added to the powder mixture, as usual in the preparation of CCTO ceramics, to avoid contamination.

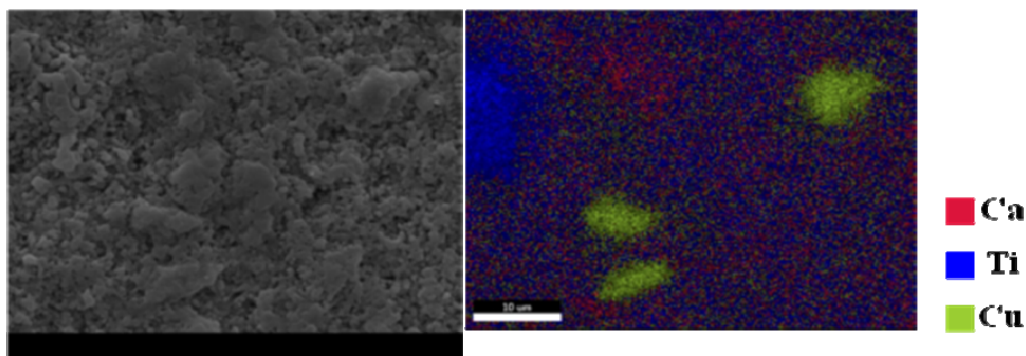


Fig.4: Scanning electron microscopy micrograph and EDS pattern for sample sintered at 900 °C during 2 min.

In Fig.4 the EDS pattern the material sintered at 900 °C during 2 min shows heterogeneous regions from the different elements. These heterogeneous regions are possibly formed during powder calcination, as the powder X-ray diffraction present secondary phases of CaTiO_3 and CuO . These secondary phases are also present on pellets sintered by SPS.

The apparent density and mean grain size of the pellets are listed in Table 1.

Table 1: Relative density and mean grain size values for CCTO samples, sintered at 850, 900, 915 °C, for 2 minutes.

Temperature (°C)	Relative density (%)	Mean grain size (μm)
850	74	1.25
900	74	1.29
915	84	1.35

For temperatures below 915 °C density values are low and do not vary significantly, this behaviour could be the result of the calcination temperature, 900 °C. There is an increase in the mean grain size when sintering temperature increases.

Fig. 5 shows the temperature-dependence of the (a) permittivity and (b) dielectric loss. All samples exhibit a high value of dielectric permittivity (~ 1500) below 1 kHz, and the permittivity versus frequency plots show a plateau in a broad frequency range. Permittivity values at 1 kHz, at room temperature, are 1.41×10^3 (850 °C), 1.43×10^3 (900 °C) and 1.68×10^3 (915 °C). These figures are in general agreement with those obtained for samples prepared by wet chemistry route and/or by conventional mixing of oxides and sintered for short times [7], i.e., for samples with relatively small grain sizes. These results evidence the effect of grain size on the giant permittivity of CCTO.

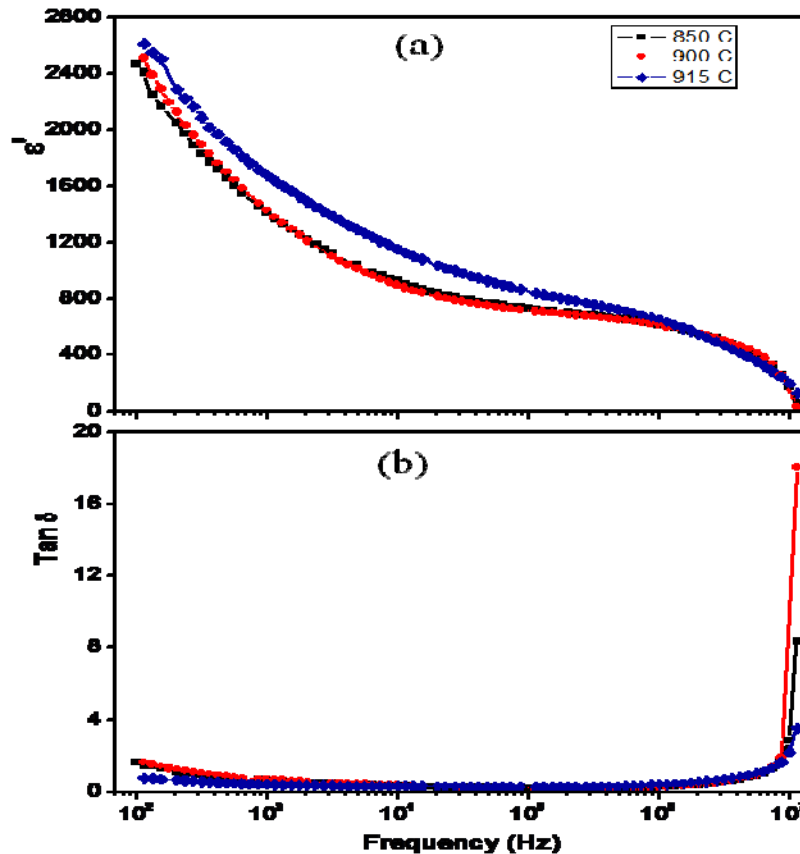


Fig. 5: (a) Real part of the complex permittivity and (b) dielectric loss at room temperature for samples sintered at 850, 900 and 915 °C, for 2 minutes.

In the frequency region below 10^4 Hz, there is an increase in the permittivity due to electrode polarization effect. The electrode and grain boundaries behave as two depletion layers inducing the low frequency relaxation [8]. In the very high frequency range, above 10^6 Hz, a dielectric dispersion is observed, which corresponds to the intrinsic electric response of the material

At 105 °C, Z^* plot of sintered pellet (Fig. 6) shows two overlapped semicircular arcs with a non-zero intercept on the Z' axis at high frequencies for all x values. These semicircles are attributed to the grain boundary and electrode, respectively. The grain component is relatively high at this temperature and lies below the x -axis, as shown in the inset. Similar impedance spectra were obtained for all studied samples, with minor differences in the relative resistivity. These differences are assigned to the grain size. The lower is the grain size the lower is the dielectric permittivity.

These results evidence that decrease of the grain size resulted in decrease of the dielectric permittivity of CCTO ceramics, although the observed values for spark plasma sintered samples are still in the range found for samples prepared by chemical methods. Therefore, the grain size has an important effect on the dielectric permittivity of CCTO. Additional experiments varying the sintering time are under way aiming to clarify the nature of the conduction mechanism with respect to the microstructure.

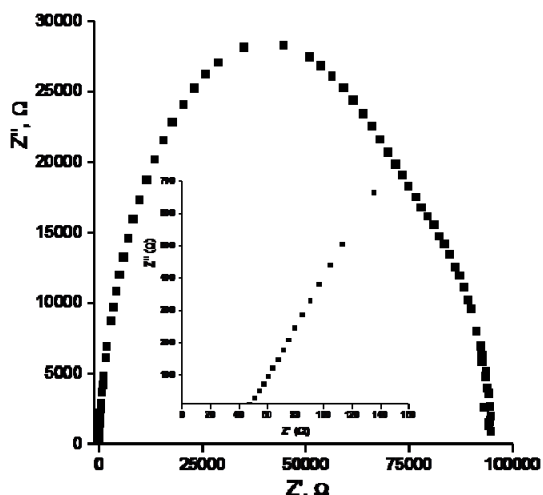


Fig.6: Complex impedance plane plot for the specimens sintered at 900 °C during 2 min. Data acquisition temperature was 105 °C. The insets show an enlarged view of the high frequency close to the origin.

Summary

CaCu₃Ti₄O₁₂ ceramics were consolidated by spark plasma sintering. The sintering temperatures varied between 850 and 930°C and sintering time was 2 min. The lowest dwell temperature resulted in samples with very low densities, whereas samples consolidated at 930°C were brittle due to heavy carbon contamination. At a dwell temperature of 915°C, the consolidated samples exhibited a pure perovskite-type structure without any trace of secondary phases. The spark plasma sintered samples show a giant dielectric permittivity of about 10³ at 1 kHz.

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