Journal of Alloys and Compounds 650 (2015) 59–64

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Influence of sintering conditions on microstructure and electrical properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics

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ARTICLE INFO

Article history:
Received 25 February 2015
Received in revised form
20 July 2015
Accepted 27 July 2015
Available online 29 July 2015

Keywords:
CCTO
Microstructure
Dielectric properties
I–V characteristic

ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) ceramic was prepared by the solid-state method. The microstructure, dielectric properties, complex impedance and nonlinear I–V characteristic were studied. The results show that increasing the sintering temperature, most grains grow up firstly, and then some diminish, resulting in depravation of the comprehensive properties in varying degrees. While prolonging sintering time promotes grain growth, microstructural densification, and improves the dielectric and nonlinear I–V properties. It should be noted that the CCTO ceramics sintered at 1050 °C for 12 h exhibit giant dielectric constant of 10^5 and low dielectric loss <0.1 with weak frequency dependence below 1 MHz, as well as a nonlinear I–V coefficient of 5.27.

1. Introduction

In recent years, $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much interest due to the unusual perovskite structure and remarkable electric properties. CCTO is a 1: 3 A-site ordered perovskite ($A'A''_3B_4O_{12}$) compound with space group Im-3, containing square-planar Cu atoms on A sites that cause tilting of TiO_6 octahedra [1]. CCTO presents an extraordinarily high dielectric constant of ~10^5, which is almost frequency-independent up to 10^6 Hz and shows good temperature stability from 100 K to 600 K. Furthermore, CCTO does not also undergo any structural phase transitions from 20 K–600 K [2]. In addition, CCTO also exhibits unusual nonlinear current–voltage (I–V) characteristic [3,4]. Therefore, CCTO has been considered as a promising material for capacitor-based applications, microwave communication devices, switching, gas sensing devices and energy storage devices [4–6].

However, the fact that giant permittivity of CCTO accompanied by high dielectric loss and sensitivity of dielectric performance to the preparation technology [7,8], seriously hinders the application of CCTO. So, lowering dielectric loss and developing stable processing technology has been becoming an urgent issue. Till now, some theoretical models have been proposed to explain the origin of giant permittivity and high loss, and finally help to develop applicable CCTO materials, such as internal domain [9], electrode polarization effect [10], bimodal grain size model [11], internal barrier layer capacitance (IBLC) [7] and nanoscale barrier layer capacitance model (NBLC) [12]. Where, the IBLC model has been widely accepted as the most approbatory explanation for the abnormal dielectric response in CCTO ceramics [8,13,14], which proposes that semiconducting grains are separated by insulating grain boundaries, producing many small capacitances and resulting in high apparent permittivity values. Afterward, the NBLC model, based on the existence of stacking faults [12], was proposed to reconcile the opposing views of intrinsic versus extrinsic debate about the origin of high dielectric constant. At the same time, the dielectric loss and nonlinear I–V properties were also discussed based on different models and most results indicated that they were closely related to the microstructure in CCTO [15–18], which can be markedly influenced by element doping [19–21] and sintering conditions [7,22].

In this work, CCTO ceramics were prepared by the conventional solid-state route at different sintering temperature and for different sintering time, in order to study the evolution of microstructure and properties with the sintering conditions. The microstructure, dielectric and impedance performance, current–voltage behaviors of obtained CCTO ceramics were characterized, in order to discuss

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http://dx.doi.org/10.1016/j.jallcom.2015.07.247

the influence of sintering time and temperature on CCTO ceramics systematically. The results offer some useful information for study and developing available high-performance CCTO materials in future.

2. Experimental section

Ceramic samples of $CaCu_3Ti_4O_{12}$ were prepared by solid state reaction and conventional sintering route, using analytical-grade (≥99.5%) powders of $CaCO_3$, CuO and TiO_2 as starting materials. The reagents were weighted according to the stoichiometric rations 1: 3: 4 and mixed thoroughly in a planetary ball mill for 4 h with zirconia balls, using deionized water as dispersant. The mixed powder was calcined at 950 °C in air for 4 h to synthesize CCTO powder. The calcined powder was ball-milled for a further 4 h to obtain fine powder ($D_{50} \approx 1.5$ μm), and then pressed into disks with 12.7 mm in diameter and 2 mm in thickness under pressure of 120 MPa by using polyvinyl alcohol as organic binders. The pellets were sintered in air at 1000 °C, 1050 °C, 1100 °C for 12 h and at 1050 °C for 4 h, 8 h and 12 h, with the heating rate of 5 °C/min, then furnace-cooled to room temperature.

The samples were characterized by different analytic techniques. Powder X-Ray diffraction (XRD) patterns were performed on a diffractometer Panalytica X'Pert PRO with Cu Kα radiation ($\lambda = 1.5406$ Å) to check the phase. The 2θ angles were scanned from 10° to 80° with step of 0.03°. Microstructure and the grain size distribution in different samples were characterized by field emission scanning electron micrograph (FESEM, TM-1000, Hitachi, Japan), the SEM micrographs were performed at an accelerating voltage of 15 kV. Pellet densities of samples were measured by the Archimedes method, $\rho = m_1/(m_1 - m_2)$, where ρ is density, m_1 is the dry mass and m_2 is the mass in deionized water.

In order to characterize electrical properties, the sintered pellet were polished and printed with silver paste on both sides and then heated at 850 °C for 15 min to form electrodes. Dielectric and impedance properties were measured from 40 Hz to 100 MHz using the impedance analyzer (Agilent 4294A, Agilent, USA) with an oscillation voltage of 0.5 V at room temperature. The I–V behaviors of the obtained CCTO ceramics were measured using Digital Source Meters (Model 2400 and 6487, Ketthley, USA) at room temperature.

3. Results and discussion

The XRD patterns for CCTO ceramics sintered under different conditions are shown in Fig. 1. All the diffraction peaks in the patterns can be perfectly indexed to the perovskite CCTO phase (JCPDS No.075-2188), and no impure peaks can be observed from possible secondary phases such as CuO, Cu_2O, TiO_2, $CaTiO_3$, especially the CuO, Cu_2O, which appeared by sintering at 1115 °C for different time [23]. The results indicate that the sintering conditions in this work have not caused observable decompositions of CCTO structure, and could be used as references for production of CCTO materials in future.

The morphology and grain size of the as-prepared ceramics are shown in Fig. 2 (different sintering temperature) and Fig. 3 (different sintering time). Fig. 2 shows SEM micrographs and relative densities of the CCTO ceramics sintered for 12 h at 1000 °C, 1050 °C and 1100 °C. As can be seen, when sintered at 1000 °C, most of the particles in ceramics are very small, about 0.3–1 μm with narrow size distribution (Fig. 2a). When sintered at 1050 °C, many particles can grow up to about 20–30 μm in size, and the number of small particles is fewer than sintered at 1000 °C (Fig. 2b). Interestingly, when sintered at 1100 °C, the grain size distributes in disorder and many particles present regular shape (Fig. 2c). The densities of ceramics are 4.71 g/cm^3 (standard deviations $\sigma = 0.014$) at 1000 °C, 4.87 g/cm^3 ($\sigma = 0.016$) at 1050 °C and 4.76 g/cm^3 ($\sigma = 0.009$) at 1100 °C, respectively, corresponding to 93.2%, 96.4% and 94.2% of theoretical density of 5.05 g/cm^3. Fig. 2d presents the change of relative density with the different sintering temperature. Obviously, the relative density of CCTO ceramics increases firstly and then decreases with increasing sintering temperature. It reveals that, the CCTO particles can grow up at suitable temperature and result in high density, low temperature will result in insufficient sintering, overheating will promote crystallization but reduce the amount of large grains and then lower densification.

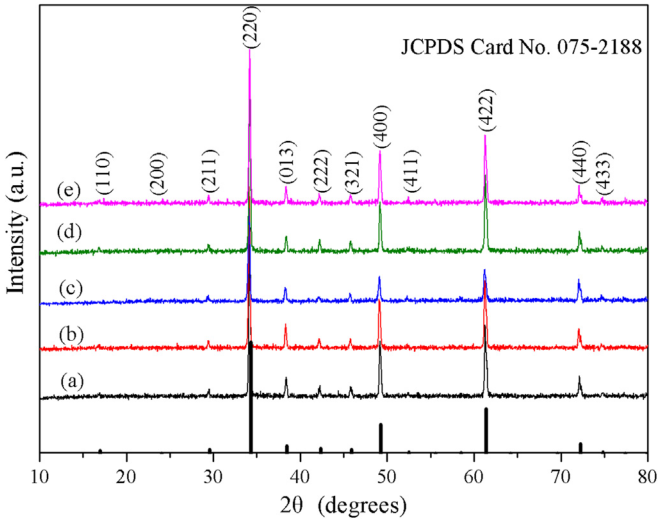

Fig. 1. XRD patterns of CCTO ceramics sintered at 1050 °C for (a) 4 h, (b) 8 h, (c) 12 h and for 12 h at (d) 1000 °C, (e) 1100 °C.

Fig. 3 shows SEM micrographs of the surface morphologies and relative densities of the CCTO ceramics sintered at 1050 °C for 4 h, 8 h and 12 h. Remarkable changes in microstructure with sintering time are clearly observed. When sintering for 4 h, almost all particles are still small, about 0.5–1.5 μm with narrow size distribution (Fig. 3a) in ceramics. With increasing to 8 h, some particles grow rapidly to large grains (about 10–20 μm) (Fig. 3b), and the microstructure shows a bimodal distribution of particles with small ones (about 1–3 μm) surrounding the large ones. When increasing to 12 h (Fig. 3c), the small particles are further swallowed by large ones to grow. As shown in micrography, the grain size and number of large grains increase with prolonging sintering time, which significantly promotes the grain growth. Fig. 3d shows the relative density changes with the sintering time. The densities of CCTO ceramics are 4.71 g/cm^3 ($\sigma = 0.025$) for 4 h, 4.83 g/cm^3 ($\sigma = 0.036$) for 8 h and 4.87 g/cm^3 for 12 h, respectively, corresponding to 93.2%, 95.7% and 96.4% of theoretical density. The microstructural densification of CCTO ceramics increases with sintering time, revealing that sufficient time allow more matter transport from ultra-fine particles for grain growth under the driving force from surface energy difference, and finally forming the bimodal distribution of particles, which will reduce the porosity effectively and increase the density.

The frequency dependence of the dielectric constant of the CCTO ceramics at room temperature is shown Fig. 4. It can be observed that the permittivity of ceramics sintered at 1050 °C for 8 h and 12 h maintain almost constant from 10^2 Hz to 10^6 Hz, presenting good frequency-stability, while the others decrease with frequency increasing in different degrees. When the frequency exceeds 10^6 Hz, the behaviors of permittivity vs. frequency for all samples are linearly declined in semi-logarithmic coordinates, corresponding to the well-known Debye-like relaxation