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Grain size effects on the dielectric properties of $CaCu_3Ti_4O_{12}$ ceramics for supercapacitor applications

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Abstract

$CaCu_3Ti_4O_{12}$ ceramic specimens for supercapacitor applications were prepared by the conventional mixed oxide method. The specimens were prepared under different sintering conditions at 1125 °C. The SEM results indicated that the mean grain size of $CaCu_3Ti_4O_{12}$ increased with increasing sintering time (30 min–12 h). Using SEM analysis, it was observed that at a sintering time of 2 h, $CaCu_3Ti_4O_{12}$ ceramic specimens had large-sized grains and the agglomerated parts consisted of small-sized grains and grain boundaries. The X-ray diffraction patterns showed single-phase ceramics with a cubic structure. Increasing sintering times led to substantial improvements in permittivity. The different spectra of frequency dependent impedance spectroscopy for large grains and small grains were compared and analyzed using Cole–Cole plots. AC conductivity as a function of the as a function of sintering times of $CaCu_3Ti_4O_{12}$ ceramics was investigated.

Keywords: B. Grain size; $CaCu_3Ti_4O_{12}$; Supercapacitor; Impedance spectroscopy

1. Introduction

In the past decade, considerable effort has been made to improve energy-storage devices with high energy-density capacities, which are classified as supercapacitors. A supercapacitor is superior to other capacitors because of its higher power capability and a longer life cycle [1,2]. Representative commercial electro-chemical supercapacitors consist of a separator sandwiched between two electrodes sealed in a liquid electrolyte, which is commonly packaged into a cylindrical container or stacked into a button cell [3,4]. Unfortunately, these device configurations can possibly leak harmful electrolytes and they use a highly complicated and expensive encapsulation technique. It is also difficult to make small, thin, and flexible devices. Hence, solid-state supercapacitors have been attracted great attentions owing to a number of desirable advantages, such as easy handling and good reliability without electrolyte leakage, a wide operating temperature range, and no need for special encapsulation devices [5,6].

The solid-state supercapacitor has been attracting attention in recent years owing to the development of advanced materials with high relative permittivity. In the future, colossal relative permittivity materials will play an important role in the advancement of supercapacitors. Colossal relative permittivity materials, such as $BaTiO_3$ [7], $BaFe_{0.5}Nb_{0.5}O_3$ [8], and $LuFe_2O_4$ [9], have been introduced in order to improve dielectric properties of supercapacitors. In the case of $BaTiO_3$-coated amorphous silica shell, relative permittivity was 2×10^5 at 10 kHz and room temperature [7]. The relative permittivity of $BaFe_{0.5}Nb_{0.5}O_3$ material was 2×10^4 at 10 kHz [8]. Moreover, $LuFe_2O_4$ had a relative permittivity of 4.2×10^3 at 10 kHz and 260 K [9]. However, the results were undesirable when the dielectric constants were increased. The dielectric losses were too high. In the early 2000's, calcium–copper–titanate ($CaCu_3Ti_4O_{12}$, hereafter CCTO) was reported to have a colossal relative permittivity. [10]. The CCTO ceramic is considered a promising material for microelectronics applications, especially in capacitive components and varistors, owing to its colossal relative dielectric permittivity of 10,000 and a very low loss tangent of 0.1. Therefore, CCTO based capacitors have garnered attention for electronic device applications that require large

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relative dielectric permittivity and a wide operating temperature range, such as large scale energy storage systems and advanced microelectronics.

The dielectric properties of CCTO ceramics are found to be very sensitive to processing conditions, such as sintering temperature and time [11,12]. However, there have been no experimental studies on the relationship between the grain size and dielectric permittivity of CCTO supercapacitors. In this study, CCTO ceramics with different grain sizes were prepared using different sintering times. The effect of sintering time on the grain size, relative permittivity, impedance, and morphology of the CCTO ceramic were investigated.

2. Experimental

$CaCu_3Ti_4O_{12}$ powders were synthesized by the conventional mixed oxide method using $Ca(OH)_2$ (Sigma-Aldrich, 95% purity), CuO (Cerac, 99.99% purity), and TiO_2 (Sigma-Aldrich, 99.9% purity from rutile) powders. These powders were ball-milled with ZrO_2 balls and alcohol for 24 h. After drying, the reagents were calcined at 900 °C for 12 h at a rate of 5 °C/min and then slowly cooled down to room temperature. The CCTO powder was pressed (1 t) into cylindrical pellets of 12 mm diameter and 1.5 mm thickness. The pellets were then sintered at 1125 °C for 30 min, 2 h, and 12 h. In order to measure the dielectric properties, the polished specimens were coated with a conducting silver paste for making electrical contacts. The dielectric properties of each sample were measured as a function of temperature (30 to 120 °C) and frequency (1 kHz to 1 MHz).

Microstructural characterization of the specimen was carried out using a field emission-scanning electron microscope (FE-SEM) (Carl Zeiss, SIGMA) at 15 kV. Energy dispersive spectroscopy (EDS) (JEOL 5410, UK) was used to investigate the chemical compositions of the CCTO ceramic specimens. X-ray diffraction (XRD) (Bruker-AXS, New D8-Advance) patterns with Cu $K\alpha$ radiation (λ=0.154 nm) was performed to examine the crystalline properties of specimens at room temperature. The relative dielectric permittivity (ε_r), the dielectric loss ($\tan\delta$), and the complex impedance of the specimens were determined using an Agilent 4294 A Precision Impedance Analyzer (40 Hz–110 MHz).

The complex impedance (Z^*) was calculated using the expression,

$$Z^* = Z' - jZ'' \tag{1}$$

where Z^* is complex impedance; Z' and Z'' are the real and imaginary parts of the complex impedance, respectively.

3. Results and discussion

Grain sizes were examined by FE-SEM. Fig. 1(a)–(c) show the FE-SEM surface microstructure of CCTO ceramic specimens that were sintered at 1125 °C for various sintering times. It is understood that the increase in sintering time promotes grain growth and microstructure densification. An image of CCTO sintered for 30 min is shown in Fig. 1(a), indicating grain sizes in the 1–2 μm range. For comparison, we also looked at SEM images of CCTO after 2 h and 12 h sintering, as seen in Fig. 1(b) and (c), respectively. The mean grain size of CCTO increased significantly with increasing sintering time. Also, abnormal grain growth was observed in the CCTO ceramic sample, shown in Fig. 1(b). Two different grain sizes, large and small, were observed in CCTO ceramic specimens sintered for 2 h. Large grains grew rapidly to ~100 μm, while small grains grew to 1–2 μm. The surface image of CCTO sintered for 2 h suggests an unstable structure. The CCTO ceramic specimens sintered for 12 h showed an enlarged grain size and high densification. As seen in Fig. 1(c), the large-sized grains in the CCTO showed a wide grain size distribution (20–100 μm). The SEM results

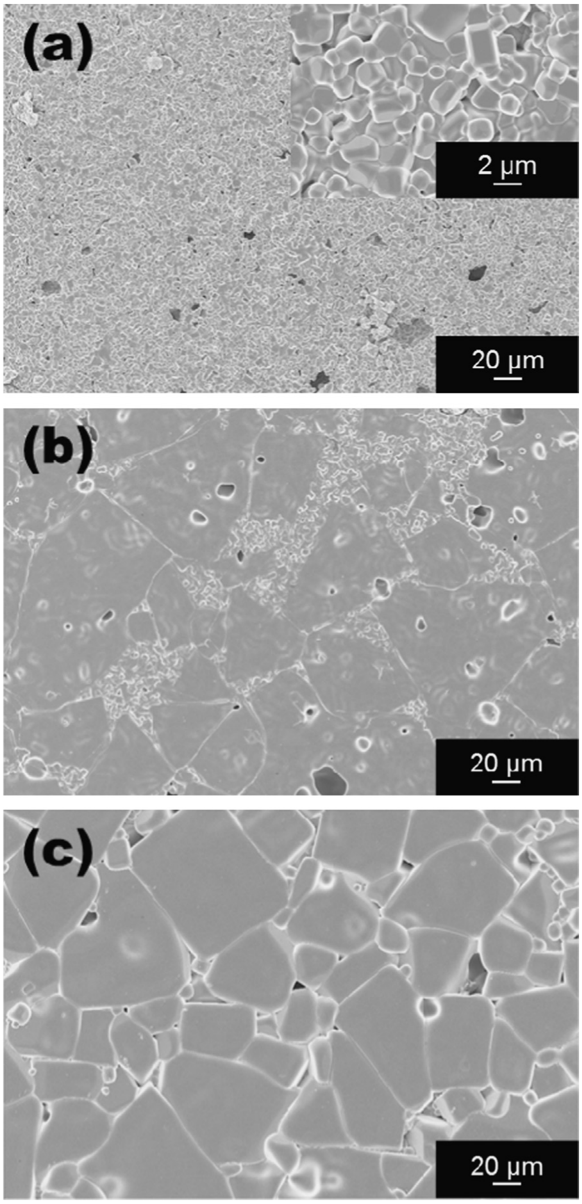

Fig. 1. Plane-view FE-SEM micrographs of $CaCu_3Ti_4O_{12}$ sintered at 1125 °C for (a) 30 min, (b) 2 h, and (c) 12 h.