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Low-toxic gelcasting of giant dielectric-constant $CaCu_3Ti_4O_{12}$ ceramics from the molten salt powder

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ABSTRACT

$CaCu_3Ti_4O_{12}$ (CCTO) nano powder was synthesized using a molten salt synthesis method in NaCl flux. Synthesis temperature and holding time were investigated. The suitable synthesis condition is 800 °C for 2 h. Aqueous CCTO slurry with high solid loading and low viscosity was prepared by using acrylic acid-2-acrylamido-2-methypropane sulfonic acid copolymer (AA/AMPS) as the dispersant. AA/AMPS dosage and pH condition have been optimized as AA/AMPS dosage of 3 wt% and pH about 9.08. A low-toxicity and water-soluble monomer, *N,N*-dimethylacrylamide (DMAA) was used as the gelling agent. CCTO green body fabricated by the gelcasting method has the homogeneous microstructure and relatively high mechanical strength of 9.27 MPa. CCTO ceramics obtained by the gelcasting method have higher dielectric constant than those prepared by the cold isostatic pressing method and show relatively low dielectric loss of below 0.2 in the wide frequency range of 10^2–10^5 Hz.

1. Introduction

Recently, the perovskite-type ternary oxide compound $CaCu_3Ti_4O_{12}$ (CCTO) has drawn much interest for its potential microelectronic applications including capacitors and memory devices due to its giant dielectric constant of ~10^5 over the wide frequency and temperature ranges [1–7].

CCTO powder is usually prepared by the traditional solid-state reaction from metal oxides with a few intermediate grinding/heating cycles [8,9]. However, this method is tedious with relatively long reaction time and high temperature (typically at 1000 °C for 10–20 h), and might still generate unwanted phases owing to the limited atomic diffusion. Other synthesis techniques such as mechanochemical synthesis, sol–gel, wet chemical method, microwave heating, mechanical alloying and polymer pyrolysis have also been reported recently, which are found to have considerable influence on dielectric properties of CCTO ceramics [10–15]. In this work, CCTO powder was synthesized by a molten salt synthesis (MSS) method using NaCl as the flux. As a low-temperature synthesis technique, MSS has been applied to synthesize many different kinds of powders, such as $LaAlO_3$, $MgAl_2O_4$, $SrBi_4Ti_4O_{15}$, $Na_2Ti_6O_{13}$, CCTO, and so on [16–19]. CCTO powder has been synthesized in the molten salt systems of KCl, NaCl–KCl or Na_2SO_4–K_2SO_4 [20–22]. However, single NaCl salt system has not been tried yet. So we will try to synthesize CCTO powders in NaCl flux in this experiment.

CCTO ceramics are conventionally prepared by the cold isostatic pressing method followed by pressureless sintering. Recently, hot-press sintering has also been used in preparing CCTO ceramics [23,24]. Gelcasting, an advanced ceramic process, is developed by Janney et al. at Oak Ridge National Laboratory (ORNL, USA) to make complex-shaped parts. Gelcasting is a colloidal processing method, and has established itself for its simplicity and its ability to produce a high degree of homogeneity as well as green body strength, resulting in good machinability [25,26]. It has been successfully used to prepare many kinds of ceramics, such as Al_2O_3, SiC, AlN, Si_3N_4, ZrO_2, SiO_2, ZrB_2–SiC and so on [27–34]. However, to our knowledge, gelcasing has never been used to prepare CCTO ceramics. So it is meaningful to try using gelcasting to prepare CCTO ceramics. Acrylamide (AM) is the first and most widely used gel monomer in gelcasting. Unfortunately, industries have been reluctant to use gelcasting in this way, because AM is a neurotoxin. In this study, we will try using a low-toxicity and water-soluble

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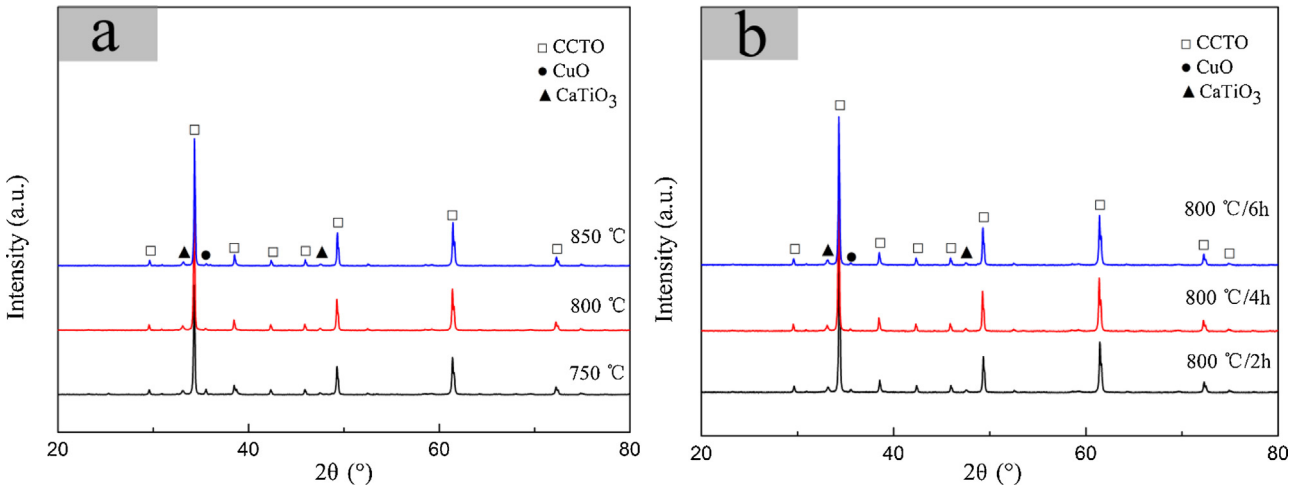

Fig. 1. XRD patterns of CCTO powders synthesized at (a) different temperatures for 2 h and (b) 800 °C for different holding times.

monomer, *N,N*-dimethylacrylamide (DMAA), as the binder to gel-cast CCTO ceramics. In the previous works of our lab, it has been proved that the DMAA gel system shows excellent performance same as even superior to the AM system [35–37].

2. Experimental

2.1. CCTO powder synthesis

First, a stoichiometric mixture of $CaCO_3$ (≥99.0%), CuO (≥99.0%) and TiO_2 (≥99.0%) was ball-milled in ethanol for 2 h. Then NaCl (≥99.5%) was added into the mixture with a 3:1 salt/oxides mass ratio and continued further ball-milling for 2 h. The final obtained mixture was divided into several parts. Some were heated in an alumina crucible for 2 h in the temperature range of 750–850 °C, the others at 800 °C for 2–6 h. The heating rate for all samples was 5 °C/min. Next, after furnace cooling to room temperature, the reacted powers were washed in 80 °C distilled water to remove NaCl salt. The washing process was repeated about 15 times until the filtrate gave no reaction with silver nitrate solution. At last, the resultant powders were oven-dried at 100 °C.

2.2. CCTO slurry, green body and ceramics preparation

N,N-dimethylacrylamide (DMAA, Kowa, Japan), *N,N*-methylenebisacrylamide (MBAM, Tianjing Chemical Reagent Research Institute, China), acrylic acid-2-acrylamido-2-methypropane sulfonic acid copolymer (AA/AMPS, Taihe Water Treatment Co., Ltd., China) and ammonium persulfate (APS) were used as the gel monomer, crosslinker, dispersant and initiator for the gel-casting process, respectively. CCTO powder used below was synthesized at 800 °C for 2 h. First, a pre-mix solution was prepared by dissolving DMAA (10 wt%) and MBAM (1 wt%) in distilled water. Next, the pre-mix solution, CCTO powder, dispersant (0.1–3.5 wt% of CCTO powder), pH regulator (ammonia water) and zirconia mill balls were added to a nylon jar, and then ball-milled for 1 h in a planetary mill at a speed of 200 rpm to obtain CCTO slurry. The studied solid volume loading was the percentage of CCTO powders volume to the total slurry volume. After adding a small amount of APS (dosage: 1 wt% of DMAA) aqueous solution (5 wt%), the slurry was degassed in a vacuum deaeration mix and then cast into stainless steel molds (with lids) and soaked in a water bath at 75 °C for an hour. APS decomposes to create free radicals ($(NH_4)_2S_2O_8 \rightharpoonup 2NH_4SO_4^{-\bullet}$) at this temperature, which initiates the polymerization reaction of the DMAA monomer and create the macromolecular gel network to solidify the ceramic suspension in situ. Then the solidified wet green bodies were carefully de-molded and dried in an oven at constant humidity and temperature of 100% and 40 °C. For comparison, the other CCTO powders were mixed with little PVA solution, and pressed into pellets. These pellets were further densified using a cold isostatic pressing method (300 MPa). Sintering of the gelcasting green bodies and these pellets was carried out in an ordinary electric furnace at 1080 °C for 4 h, assisted by heating at a rate of 1 °C/min, from 400 to 600 °C to decompose the organics.

2.3. Characterization and measurements

R/S Rheometer (R/S CC25, Brookfield Corporation, American) was used to characterize rheological behaviors of slurries. The measuring shear rate was from 0 to 400 s^{-1} and the values of viscosity and shear stress under each shear rate were automatically recorded by the computer. Zeta potential was determined by the Zeta Potential Analyzer Ver. 3.54 (Brookhaven Instruments Corp, PALS). The phases of the specimens were identified by an X-ray diffractometer (RIGAKU, CuKα, Japan). Microstructures of the as-synthesized powder and sintered ceramics were observed under a field emission scanning electron microscope (FE-SEM, HITACHI, SU8010, Japan). Mechanical strength of the green body was measured using an universal testing machine (WT-6002, Shenzhen Reger instrument Co., Ltd., China), by the three-point flexural method with a sample dimension of 3 mm × 4 mm × 40 mm and a crosshead speed of 0.5 mm/min. For dielectric measurements, both sides of ceramic pellets (thickness: 1 mm, diameter: 9.5 mm) were polished, coated with silver conductive paste, and then heated at 650 °C for 30 min. Dielectric properties were performed using an impedance analyzer (Agilent 4294A, America) over the frequency range of 100 Hz–10 MHz with the applied voltage of 500 mV at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns of the resultant powders synthesized at different temperature and holding time. All the synthesized powders contain CCTO phase. Fig. 1(a) indicates XRD patterns of powders synthesized at 750, 800, and 850 °C for 2 h, which show CCTO has been successfully synthesized at the temperature as low as 750 °C by using NaCl salt as the flux. There are little secondary phases of CuO and $CaTiO_3$ in all powders, which is the same as other MSS systems for preparing CCTO powders [17–19]. The CuO amount