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Effect of synthesizing temperatures on the microstructure and electrical property of $CaCu_3Ti_4O_{12}$ceramics prepared by sol-gel process

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ABSTRACT

A sol-gel process was used to synthesize gel precursors of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics. The XRD patterns show that a considerable amount of CCTO phase has been formed after the gels were calcined at 800 °C and 900 °C and after the sintering process for the samples all the second phases have disappeared. The SEM images display that the microstructure morphology is obviously affected by synthesizing temperatures. The grain size increases with the increasing sintering temperature and some melt Cu-rich phase appears at grain boundaries of the sample sintered at 1100 °C. Positron annihilation lifetime and Doppler broadening spectra results indicate that the concentration of Cu^{2+} vacancies increases with the increase of sintering temperature and the defect species remains the same. High defect concentration of samples sintered at1070 °C and 1100 °C leads to poor stability of permittivity and large dielectric loss values at low frequencies and poor nonlinear behavior. The results of impedance spectroscopy support well the views.

1. Introduction

In the past several years, the research on high dielectric constant materials mainly focuses on $BaTiO_3$-based ceramics because of their potential applications in a variety of devices. However, the dependence of their permittivity on temperatures will limit their applications in certain fields. So for a long time, scientists have been looking for a high dielectric constant material with good thermal stability. Recently, $CaCu_3Ti_4O_{12}$(CCTO) has drawn considerable publicity thanks to its giant permittivity and its weak dependence on the temperature and frequency over a wide range 100–600 K and 10^2–10^6 Hz respectively [1–3]. Apart from the intriguing dielectric properties, the nonlinear behaviors of CCTO are also interesting and attractive. In 2004, Chung et al. [4] found that the nonlinear coefficient (α) of CCTO ceramics rises up to the value of 912 when measured in the range of 5–100 mA and Atomic force microscopy revealed that the presence of electrostatic potential barrier at the grain boundaries is considered to be responsible for the nonlinear behaviors. Therefore, CCTO has quite promising potential applications in capacitors, varistors and their composites.

Though much research work has been done to investigate the dielectric properties, the mechanism of giant permittivity of CCTO ceramics still remains controversial and waits to be answered up to date. By now a plausible explanation recognized widely is an internal barrier layer capacitance (IBLC) model. In this model, the ceramics are assumed to be comprised of *n*-type semi-conductive grains and insulating grain or domain boundaries [5,6]. According to IBLC model, giant permittivity highly relies on the microstructures such as grain size and width of grain boundaries [7–10]. In fact, besides the effect of grain size and grain boundary width, the influence of defects on the dielectric properties and nonlinear behavior also cannot be ignored. In 2013, Yu Tang et al. reported the effect of defects on the dielectric constant of microwave ceramics [11], and they considered that more charged defects mean larger polarizability and dielectric constant. However, to our knowledge, defect is not usually studied in dielectric ceramics due to lack of an appropriate method to detect and characterize the vacancy-type defects.

Positron annihilation spectroscopy (PAS) technique has been proven to be a superb method for the study of vacancy defects in solids [12,13]. The annihilation characteristics of positrons such as

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lifetime and Doppler broadening (DB) of the annihilation radiation at vacancy-type defects will be different from that in the defect-free bulk state. Therefore, PALS and DB provide the annihilation information in defective region which presents the characteristics of defect. It has been successfully applied to detect defects in metal [14–16] and semiconductor [17,18] materials.

In this paper, the gel precursors prepared by a sol-gel processing were synthesized into CCTO ceramics at different calcining and sintering temperatures. The dielectric properties, nonlinear behaviors and impedance of CCTO are measured. The effects of defects on the dielectric properties and nonlinear behaviors of the ceramics are investigated using PALS and DB technique.

2. Experimental procedure

A sol-gel process was used to synthesize CCTO powder. $Ca(CH_3COO)_2{\cdot}H_2O$ (≥99%), $Cu(NO_3)_2{\cdot}3H_2O$ (≥99%), and $Ti(OC_4H_9)_4$ (≥99%) were weighed accurately according to the stoichiometric composition. Firstly, Cu $(NO_3)_2{\cdot}3H_2O$ and Ca $(CH_3COO)_2{\cdot}H_2O$ were dissolved in ethanol and homogenized by magnetic stirring for 30 min forming into "A" solution. $Ti(OC_4H_9)_4$ was dissolved in ethanol and fully homogenized, then acetic acid was dropped into the mixed liquid forming into "B" solution. Secondly, "A" solution was dropped into magnetic stirring "B" solution and the pH value was adjusted to about 3 using distilled water. The above mixed Ca2+, Cu2+ and Ti4+ solution was homogenized fully by magnetic stirring for 3 h and heated on a hot plate at 70 °C to yield a blue gel. Then, the gel precursors were dried at 120 °C for 10 h and then calcined in air at 800 °C, 900 °C respectively for 10 h. The calcined powder was remilled for 2 h and granulated by adding PVA, then pressed into pellets (150 MPa) with diameter of 12.0 mm and thickness of about 2.0 mm. Finally the pellets were sintered into CCTO ceramics in air at1050 °C, 1070 °C and 1100 °C for 12 h.They are named sample C800 °C S1050 °C, sample C900 °C S1050 °C, sample C900 °C S1070°Cand sample C900 °C S1100 °C, corresponding to Sample 1, Sample 2, Sample 3and Sample 4 respectively in the following discussion.

X-ray diffraction (XRD) with Cu K alpha radiation ($\lambda = 0.1541$ nm) was performed to examine the phase constitution of the calcined powder and the sintered specimens at room temperature. The dielectric properties and impedance spectrum of the ceramic pellets were determined using an Agilent 4294A Precision Impedance Analyzer from 40 Hz to 110 MHz.The current–voltage (I–V or J–E) characteristic at room temperature was measured by a commercial electrometer (Keithley 2410, Cleveland, OH). The nonlinear coefficient α values were calculated in terms of the formula:$\alpha = \frac{\lg(I_2/I_1)}{\lg(V_2/V_1)}$. Where V_1 and V_2 are, respectively, the voltage at current I_1 and I_2.α is calculated when $I_1 = 1$ mA, $I_2 = 10$ mA respectively. It is worth noting that the breakdown voltage (threshold) voltage (V_b) is measured when a current of 1 mA flows through the samples.

Positron annihilation lifetime spectra were measured using a conventional fast–fast coincidence system with time resolution of about 210ps. The ^{22}Na positron source with the activity of ~5 μCi was sandwiched between two identical sample pellets for measurements and each spectrum contains more than 10^6 counts. Doppler broadening of the annihilation radiation was measured in coincidence mode using two high purity Ge detectors. The Doppler broadening spectrum was characterized by S and W parameters, which are defined as the ratio of low momentum (511 ± 0.68 keV) region and high momentum (511 ± 2.86–511 ± 5.73 keV) region to the total area of the annihilation peak, respectively. The positron lifetime and Doppler broadening spectra were measured simultaneously.

3. Results and discussion

3.1. TG/DTA analysis

Fig. 1 shows the representative TG/DTA curves of powder precursors of CCTO. An endothermic peak is presented in the DTA curve near 110 °C and there is a weight loss of about 20% by the corresponding TG curve which is mainly attributed to the volatilization of ethanol and water. With the rise of temperature to 248 °C, a very high exothermic peak is observed in the DTA curve and there is a weight loss of about 50% in the TG curve correspondingly, which is mainly caused by the decomposition of nitrate and burning of the organic matter. During the subsequent heating process in the temperature range 400–800 °C, no obvious exothermic or endothermic peak is observed, but the minor weight loss in the amplified inset is found in the DTA curve, which is due to formation of intermediate compounds. And then, almost no weight loss and no thermal effect are noted above 800 °C, which indicates that no decomposition occurs above this temperature. Therefore, 800 °C and 900 °C are selected as calcining temperatures for the gels to synthesize CCTO ceramics in the paper.

3.2. X-ray diffraction and SEM analysis

Fig. 2 exhibits the XRD patterns for the powder calcined at 800°C/10 h and 900°C/10 h.The XRD patterns indicate that a considerable amount of CCTO phase has been formed after the gels are calcined at 800 °C and 900 °C. In addition, the latter manifests stronger CCTO but weaker second phases ($CaTiO_3$, TiO_2 and CuO) diffraction peaks than the former. Fig. 3 presents the XRD patterns for the CCTO ceramic pellets sintered at different temperatures for 6 h. It is interesting to find that all the second phases have disappeared after the sintering process for the samples, and all the major diffraction peaks are matched with those of the standard PDF (PDF card No.75-2188) database, which suggests that all the second phases in the powder have been synthesized into CCTO phase.

Fig. 4 presents the SEM images of the morphology of fracture surface of the samples, which suggests that the microstructure is influenced by synthesizing temperature. Firstly, there are significant differences in grain size and grain morphology between sample 1 (2 ± 0.5 μm) and sample 2 (5 ± 1 μm) due to the different calcining temperatures. Compared with that of sample 1, the grains of sample 2 have not only larger and rounder shape, but also contact more closely. Combined with XRD results, it can be concluded that calcining at 900° C can lower the content of the second phases,

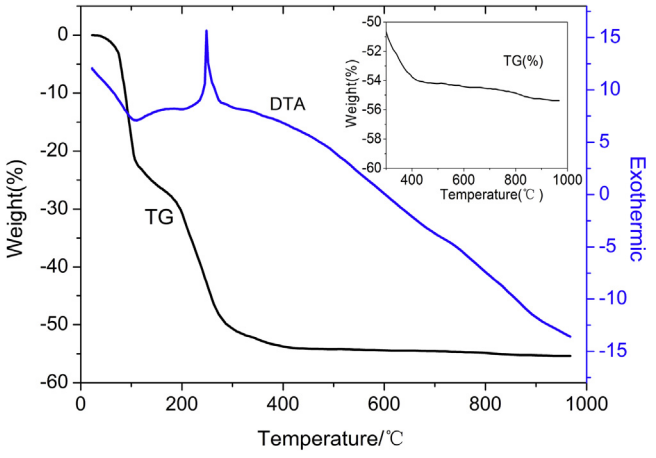

Fig. 1. The representative TG/DTA curves of the powder precursor of CCTO.