

SOL-GEL COMBUSTION SYNTHESIS OF GIANT DIELECTRIC $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANO POWDER

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ABSTRACT

Nano-sized powders of Calcium Copper Titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) were synthesized by a sol-gel combustion method without using any external fuels. The powder was calcined at 500, 650 and 800 °C in air for 3 hr. The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powders were characterized by TG-DTA, XRD, FTIR and AFM. The XRD results for the powders calcined at 650°C, 800°C and sintered at 950°C indicated the formation and confirmation of $[(\text{CaCu}_3)\text{Ti}_4\text{O}_{12}]$ CCTO phase. AFM studies showed that average particle size of the CCTO powder ranges from 60 to 80nm. HR-SEM micrographs of the sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics showed the grain size ranges from 1 to 2.8 μm . Dielectric constant (ϵ) about 9919 at room temperature for 10 kHz. It reaches as high as 1, 06,175 at 500 °C. The present material shows the dielectric relaxation at 300 °C. CCTO Nano powder prepared by the sol-gel combustion process with ideal electric properties is expected to find applications in microelectronic devices.

Keywords: *Sol-gel combustion, Giant Dielectric Constant, Nano Powder, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$.*

1. Introduction

The needs for extremely small devices in modern electronic applications are becoming a critical requirement. One area which has constantly drawn the attention of researchers is the need for very high dielectric material in applications demanding high value micro capacitors and in high energy storing capacitors used for replacement of batteries. Since 1967 the family of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ compounds has been intensively studied [1]. The $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was found to remain Centro symmetric body center cubic over a wide range of temperatures.

CCTO has attracted considerable attention recently due to its unusually giant dielectric constant ($\sim 10^4$ – 10^5), which is nearly independent of frequency (100Hz to 10 MHz) and low thermal coefficient of permittivity over a wider range of temperature (100–600 K) [1-5]. CCTO was generally prepared by the conventional solid-state method [6, 7, 8, and 9]. But it suffers from the disadvantages of inhomogeneity and other limitations [10]. It is well known that the electrical properties can be considerably improved when the ceramic is of a homogeneous microstructure [11]. Sol-gel combustion method has the advantage of preparing multi component system with high homogeneity. Since the mixing is carried out in the molecular level.

Sol-gel Combustion synthesis [12] has emerged as an important technique for the synthesis and processing of advanced ceramics (structural and functional), composites, catalysts, alloys, intermetallics

and nanomaterials. In Combustion synthesis, the exothermicity of the reduction–oxidation or electron transfer chemical reaction is used to produce useful materials [13]. Combustion synthesis processes are characterized by high-temperatures, fast heating rates and short reaction times. Recent innovations in the combustion and processing parameters have resulted in a better understanding of combustion phenomena and control of microstructure and property of the products. A wide range of technologically useful oxides were prepared with interesting magnetic, dielectric, electrical, mechanical, catalytic, luminescent and optical properties.

In this paper, we report a successful, shorter reaction time oxide material for synthesis to create $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, using sol-gel combustion method. The biggest advantage is that the single phase CCTO forms started at 650°C for 1 hr without using any external Organic fuel.

2. Experimental Setup

Calcium copper titanate (CCTO) powder was prepared by the sol–gel combustion method using $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$ as raw materials. At first, an appropriate amount of calcium nitrate and copper nitrate were dissolved stoichiometrically in ethanol, secondly the titanium tetra isopropoxide stabilized by acetetylacetone dissolved in isopropyl alcohol, according to the formula of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. These two solutions were mixed in a

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beaker and stirred continuously using a magnetic stirrer at room temperature. 10ml of dilute nitric acid (1:1) was added slowly into this solution and the temperature is slowly raised to 90°C to form gel. After stirred 45 minutes sudden self-combustion, resulting in the evolution of large amount of gases and the formation of fluffy foam is shown in Fig.1. This product was dried in oven for 24 hours at 110°C. The dried powder was calcined at 500, 650, and 800°C for three hours for complete crystallization and then the milling process was carried out in order to get a Nano powder.



Fig. 1 Sol-Gel Combustion Reaction and Product

The crystalline structures of the prepared samples were analyzed by X-ray powder diffraction (XRD) (PANalytical X'pert pro) using CuK α radiation at 45kV and 40 mA ($\lambda=0.15406$ nm) in a wide range of 2θ ($20^\circ < 2\theta < 90^\circ$). The synthesized CCTO powders were characterized by Thermo gravimetric analysis and Differential thermal analysis (TG-DTA) (NETZSCH STA 409), then functional group analyzed by Fourier transformed infrared spectrometer (PerkinElmer –RX1) and particle size measured by Atomic Force Microscopy (AFM) (Agilent 5050/5060). The calcined powders were uniaxially pressed into pellets of 10mm in diameter and 2mm in thickness with an applied load of 3.5 tons for 2 minutes, using poly vinyl alcohol (PVA) as the binders. The green pellets were then sintered at 950°C for 3hr in air in a box furnace. The microstructures of the sintered pellets were measured by HR-SEM (FEI Quanta 200FEG). Silver paste was coated on the parallel faces of the sample. The dielectric constants were measured by using LCR meter (Hioki 3532-50) over the frequency range 100 Hz–1 MHz at selected temperatures from room temperature to 500°C.

3. Results and Discussion

Fig. 2 shows the thermal analysis, TG-DTA curves of precursor powder of CCTO from room temperature to 1200°C in air with a heating rate of 10°C per minute. The TG curve showed a weight loss

of about 50% in the temperature range from room temperature to 950°C, and no considerable loss was observed above 500°C. The DTA curve also showed exothermic peaks at 126.2°C and 256.5°C indicating that the thermal events was associated with the burnout of organic species involved in the precursor powders[14]. Although the reaction mechanism is not known, the XRD pattern shows the formation of homogeneous single phase CCTO. When the sintered temperature was raised to 1000°C the material melted. Liu et al [6] have reported that the CCTO samples prepared by solid state method, melted completely when sintered at 1200°C. They proposed a mechanism that at 1000°C, CCTO undergoes a partial phase transition with the formation of Cu₂O phase.

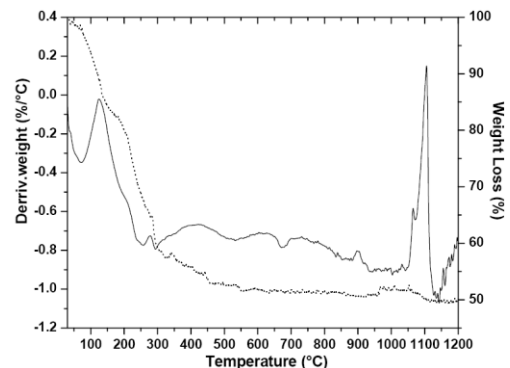


Fig. 2 Thermal Analysis TG-DTA

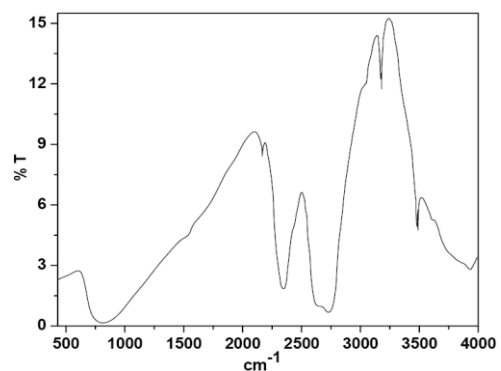


Fig. 3 FTIR Spectrum of CCTO Precursor

FTIR spectrum of precursor is shown in Fig. 3. The absorption peaks corresponding to (3475, 3200 and 2700 cm^{-1}) were related to O-H stretching. The sharp absorption peak corresponding to C \equiv N stretch was observed at 2345.61 cm^{-1} . The small sharp absorption peak at 2250 cm^{-1} due –C \equiv C– stretch. The Phase formation of CCTO was further confirmed by FTIR, calcined powder at 800°C is shown in Fig. 4.

Vibrational mode of ν Ti-O-Ti appeared at 450cm^{-1} [15]. The Cu-O bending was observed at 512cm^{-1} . The ν Ca-O was observed at 562.68cm^{-1} .

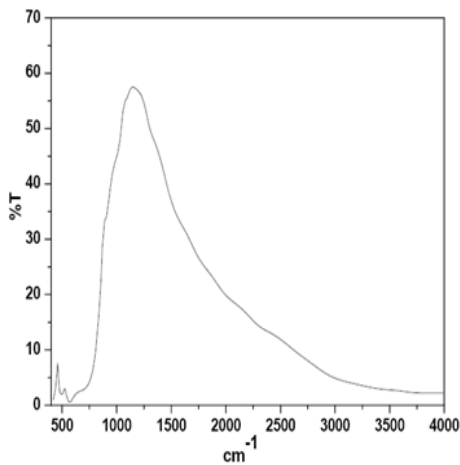


Fig. 4 FTIR Spectrum of CCTO Powder Calcined at 800°C

Fig. 5 shows X-ray diffraction patterns of powders prepared by the sol-gel combustion process at various calcined temperatures with the phase development of CCTO. In the precursor no peak of CCTO appeared, calcined powder at 500 °C a few broad peak reflections of TiO_2 and CuO and CaO phases started to be detected, indicating that the calcinations process was necessary. While at 650°C the CCTO's main peaks are very clear. With the increase of the temperature, the peaks of CCTO increased in intensity or amplitude. Thus, it was obvious that the single phase CCTO with perovskite structure formed at 650 °C, which was in good conformity with thermal analysis process. The temperature is lower than that of any other report [2, 16, 17, 18–21]. The main peaks of calcined CCTO powders 650°C, 800°C and sintered at 950 °C are compared with the standard powder diffraction pattern (JCPDS card No: 75-2188). The crystallite sizes of the calcined powder at 650°C can be estimated from ~25-55nm and ~40-75 nm for 800°C respectively, from the X-ray peak broadening using Scherer's formula [15].

$$D = K \lambda / (\beta \cos \theta) \quad (1)$$

In which, where K is a constant taken as 0.9, θ is the diffraction angle; λ is the wavelength of the X-ray radiation. β is the full width at half maximum (FWHM) of each phase and θ is the diffraction angle.

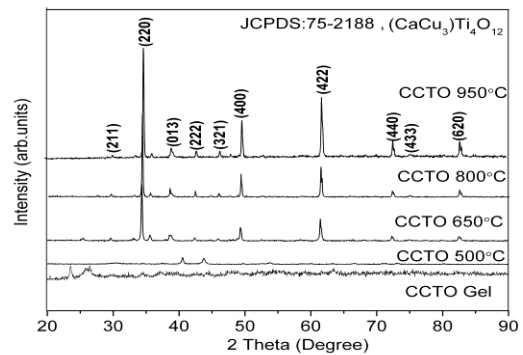


Fig. 5 XRD Patterns of CCTO Powders After Calcinations in Air at (a) Precursor (b) 500°C, (c) 650 °C (d) 800 °C and (e) Sintered at 950°C for 3 hr

The major planes correspond to (211), (220), (013), (222), (321), (400), (422), (440), (433), (620) were found to be matched which confirmed the presence of Cubic $(\text{CaCu}_3)\text{Ti}_4\text{O}_{12}$. The calcined powder at 650 °C for 3 hr, XRD result indicated the formation of CCTO single phase, which indicated that sol-gel combustion process reaction, was molecular level, shorter time, homogeneity high and temperature low.

Fig. 6 shows the AFM images. The crystalline powder was dispersed in acetone and dip coated on glass plate. The dispersed particles were analyzed by AFM. The particles shape were spherical and measurement of particle size was 60-80 nm range and of uniform size. After global fitting, line profile was taken; the size of the particle was 74 nm is shown in Fig. 7.

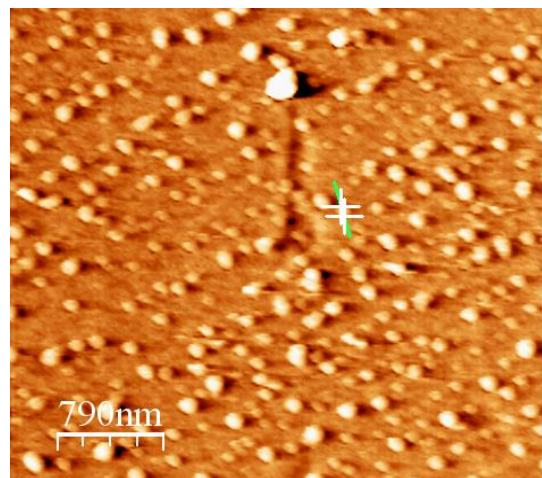


Fig. 6 AFM Image of Calcined Powder at 800°C

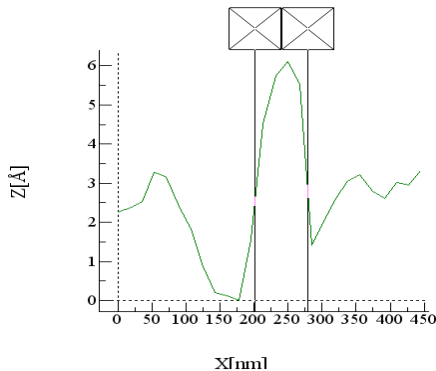


Fig. 7 Line Profile of Nano Particle

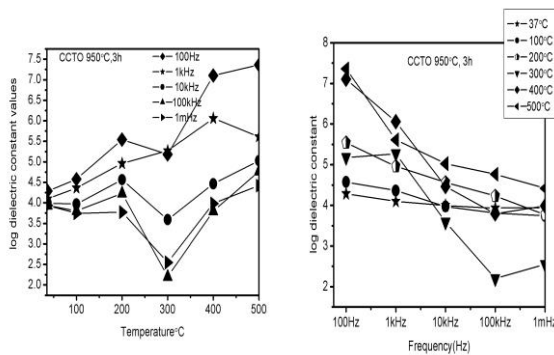


Fig. 8 HR-SEM Microstructure of the CCTO Ceramics Sintered at 950°C for 3 hr

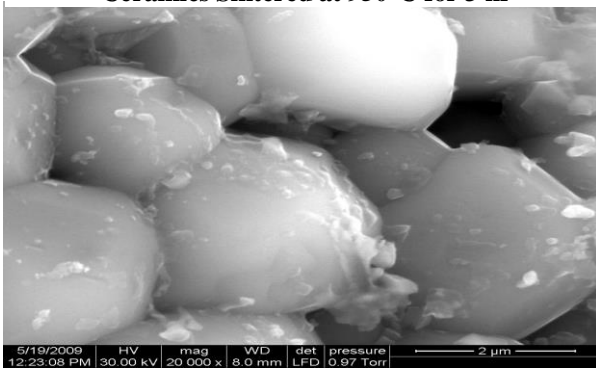


Fig. 9 Variation of Log Dielectric Constant with Temperature and Frequency

Fig. 8 shows HR-SEM microstructure of CCTO ceramics sintered at 950°C for 3 hr using a conventional furnace. The equiaxed shape grain size range was from 1 μm to 2.8 μm. It can be seen that the grain size was significantly increased with an increase of sintering time. The microstructure of 95% sintered density CCTO ceramic bulk. The sample obtained is

extremely fine and dense, which means that it has huge electrical properties; assumption that could be further supported by the measurement of relative dielectric constant and low loss tangent.

The sample was sintered at 950°C for 3hr. Fig. 9 shows the variation of log dielectric constant with temperature and frequency. Dielectric constant (ϵ) about 9919 at room temperature for 10 kHz. It reaches as high as 1, 06,175 at 500 °C. The present material shows the dielectric relaxation at 300 °C. General dielectric relaxation theory applies in this case: the lower the frequency, the higher its dielectric constant.

4. Conclusion

The single phase calcium copper titanate colossal dielectric Nanopowder was successfully prepared by the sol-gel combustion method at 650°C for 1 hr. The phase formation was confirmed by X-ray diffraction pattern. After calcined at 800°C with fine homogenous spherical shape Nano particles could be obtained. The average particle size from AFM is about 60-80 nm. CCTO ceramic with the extremely dense microstructure was obtained after being sintered at 950°C for 3 hr. The grain size 1 μm-2.8 μm measured by HR-SEM. Dielectric constant (ϵ) about 9919 at room temperature for 10 kHz. It reaches as high as 1, 06,175 at 500 °C. The present material shows the dielectric relaxation at 300 °C. CCTO Nanopowder prepared by the sol-gel combustion process with ideal electric properties is expected to find applications in electric devices.

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