

A novel technique for the synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics

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A novel, low temperature synthesis technique is developed for fabrication of nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic powders, using inexpensive and easily available reagents. Structural and microstructural characterization was undertaken by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The confirmation regarding the phase formation was done using the Reitveld analysis. The compound belongs to the cubic system with the lattice parameter $a = 7.3985 \text{ \AA}$, which agrees well with the values reported in the literature. The particles formed were spherical in shape, with the average size of 70 nm.

Keywords: *nanocrystalline materials; XRD; Reitveld analysis; SEM*

1. Introduction

Dielectric materials have many technological applications such as capacitors, resonators and filters. It is commonly accepted that high dielectric ceramic capacitors with Ba/Pb based perovskite oxides are indispensable for modern electronic devices and are found to be suitable for a wide range of applications. In general, these compounds belong to the perovskite structure where high electric permittivities are always associated with ferroelectric or relaxor properties, with a maximum depending on temperature, due to phase transition. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has the cubic perovskite crystal structure and unusual dielectric properties [1–3]. It exhibits an enormously large, low-frequency electric permittivity ϵ' (ca. 10^4), for both single crystal and ceramics at room temperature, and remains constant over 100–380 K at low frequencies. According to some researchers, this stunning dielectric behaviour is intrinsic [5], while others claim that it arises from external effects such as spatial inhomogene-

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ity [6], contact effect [7] or internal barrier-layer capacitors (IBLC). While the still exist controversies with respect to the mechanism, the IBLC explanation is rather widely accepted. Most of the reports were done on bulk materials, which were prepared by solid state reaction from metal oxides at higher temperature with several intermediate grindings. This method requires tedious work, relatively long reaction times and high temperature conditions, and still may result in unwanted phase because of limited atomic diffusion through micrometer sized grains. On the other hand, chemical methods provide atomic level mixing of individual components, and result in the formation of nanocrystalline materials at much lower temperatures compared with solid state reactions. There are many chemical methods, such as sol-gel, co-precipitation, precursor solution technique and hydrothermal process [8–13], which have already been reported for the synthesis of CCTO ceramics.

Here, we made a first time attempt to synthesize CCTO ceramics by precursor solution technique using easily available and inexpensive reagents at low temperature, and further characterize the compound by several different techniques.

2. Experimental

Nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder was prepared by a metal ion–ligand complex based precursor solution evaporation method using high purity raw materials. Calcium carbonate (CaCO_3) (Merck), copper(II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$) (Merck), ethylenediaminetetraacetic acid (EDTA) (SRL, 99%), triethanolamine (TEA) (Merck, >97%) and titanium tartarate were used. The required amount of calcium carbonate was first dissolved in a minimum amount of dilute (6 M) nitric acid to make a clear solution. The solution was then boiled for 10 min to remove CO_2 . The required amount of copper(II) acetate dissolved in water was then added, and finally EDTA was added to the solution and stirred. In order to get a clear solution, dilute ammonia solution [(2 M) was further added ($\text{pH} \approx 8$). Titanium tartarate was obtained in the laboratory in the following way. Titanium oxide (Aldrich, 98%) was dissolved in HF (M/s Merck, 40% solution, 1:7 mole ratio) by heating on a water bath for 72 h. A clear solution of titanium fluoro complex was produced. The addition of dilute ammonia to that clear solution resulted in insoluble hydrous titanium hydroxide ($\text{TiO}_2 \cdot n\text{H}_2\text{O}$) which was then separated from its solutions by filtration and was repeatedly washed with 5% ammonia to yield hydrous titanium oxide free from chloride ions. After estimating the amount of TiO_2 present in $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ by heating its small part at 1000°C for 2 h, the hydrous TiO_2 was dissolved in tartaric acid (Quest, 99%) (1:4 mol) solution to obtain titanium tartarate through constant stirring at 60°C for 8 h. Then a required amount of titanium tartarate and TEA was mixed. The final pH of this mixture was fixed at pH ca. 8 using dilute ammonia solution (2 M). Finally, both the solutions were mixed thoroughly and heated over a hot plate (ca. 200°C) for complete evaporation under constant stirring. Continuous heating of the solution led to foaming and puffing. During evaporation, the nitrate ion provides an in situ oxidizing environment for TEA, which partially converts the hydroxyl groups

of TEA into carboxylic acids. On complete dehydration of the precursor solution, the metal complexes, TEA and EDTA, decomposed with the evolution of dense fumes and resulted in a voluminous, fluffy, black carbonaceous mass, which was calcined at 700 °C to get the precursor powder.

The crystal structure of the pellet was confirmed by powder X-ray diffraction (XRD) using $\text{CuK}\alpha$ radiation from a high resolution PANalytical X'Pert PRO diffractometer equipped with a secondary beam graphite monochromator and operating with the Bragg–Brentano geometry. For determination of the instrumental broadening function, a specially prepared Si sample was used [14]. The microstructural characterization was done using a JEOL-JSM 5800 microscope and JEOL-JSM-2010. In order to study the electrical properties, pellets were formed and sintered at 800 °C. The impedance properties were measured with an HIOKI 3532 LCR METER with a high temperature attachment.

3. Results and discussion

The phase formation of the compound was confirmed by XRD, which matched well with the results reported in the literature. It was further confirmed by the Reitveld analysis using the MAUD program (Version 2.044). The XRD pattern of CCTO was simulated with the cubic space group $Im\bar{3}$ and atoms at the following Wyckoff positions: Ca (0,0,0), Cu (0,1/2, 1/2), Ti (1/4,1/4,1/4), O (0, 1/4, 1/4) (ICDD PDF Card # 21-0140). The Rietveld analysis of the XRD pattern also confirmed the formation of the CCTO phase with the lattice parameter $a = 7.3985 \text{ \AA}$, which agreed well with the values reported in the literature. With regard to the microstructure analysis for the extraction of particle size and r.m.s. microstrain values using the Rietveld method from the ‘size-strain’ broadening, we considered the model proposed by Popa involving the expansions of spherical harmonics for the prediction of the particle shapes [154]. This model accounts for the anisotropic X-ray peak broadening, i.e. the model is capable of reproducing the case where in addition to the regular diffracting angle (2θ) dependent broadening, the broadening becomes a function of the diffracting planes (hkl) as well. From the ‘size-strain’ analysis, it turned out that the particle size values are nearly isotropic along all major $[hkl]$ directions. In other words, it can be said that the particles are nearly spherical with average diameter ca. 70 nm having negligible r.m.s. strain (10^{-4}).

SEM micrographs of the calcined powders and sintered pellets are shown in Fig. 1. Due to the fineness of the particle, agglomeration took place, which resulted in the formation of a network resembling foam. The equation for grain growth at fixed temperature is:

$$G^m - (G(0))^m = Kt$$

where G is the average size, $G(0)$ is the average size at $t = 0$, K is a constant and m is taken as 3. In nanomaterials, grain growth is inhibited by open porosity, growth inhibitors and grain boundary segregation. Thus the size of the grains does not increase much.

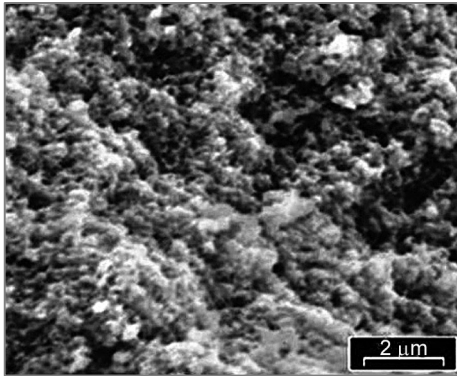


Fig. 1. SEM micrographs of calcined CCTO powders

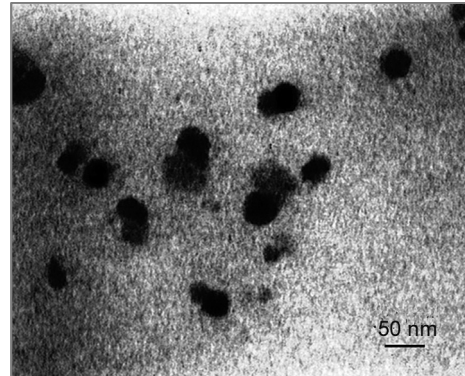


Fig. 2. TEM micrographs of calcined CCTO powders

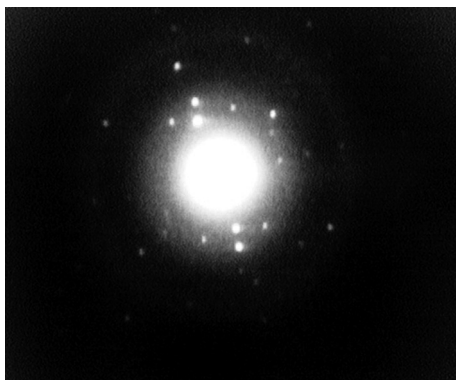


Fig. 3. Selected area electron diffraction (SAED) pattern of CCTO powders

The uniform distribution of the particles obtained from TEM is observed (Fig. 2) and the shapes of the particles are spherical. The particle size was calculated with the help of UTHSCA IMAGE TOOL considering 50 particles. After statistical analysis, the average particle size was found to be ca. 65 nm. This is in agreement with the particle size obtained from the Reitveld analysis. The corresponding selected area electron diffraction pattern (Fig. 3) shows a symmetrically dotted pattern, implying that the nanoparticles are well crystallized.

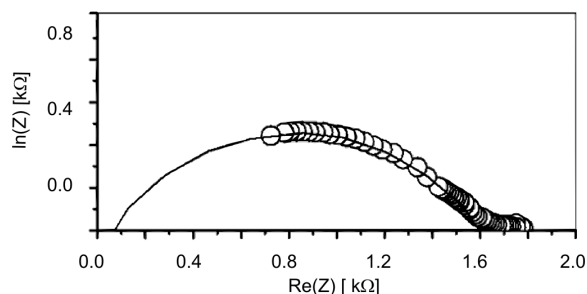


Fig. 4. Plot of the real and imaginary parts of impedance of CCTO powders

The electrical behaviour of the compound was studied using the ac technique of CIS. Figure 4 shows the plot of the real and imaginary parts of impedance at higher temperatures. The impedance spectrum is characterized by the appearance of semicircular arcs whose profile changes as the temperature increases. Also at higher temperatures only one semicircular arc was present, which clearly showed that only the bulk effect was prominent. The centre of the arcs lies below the real axis (Z'), which suggests that the relaxation is of polydispersive non-Debye type.

The complex impedance ($Z^*(\omega)$) can be expressed as:

$$Z^*(\omega) = \frac{R}{1 + \left(\frac{j\omega}{\omega_0} \right)^{1-n}}$$

where the exponent n represents the magnitude of the departure of the electrical response from the ideal condition, and is greater than zero for non-Debye type phenomena.

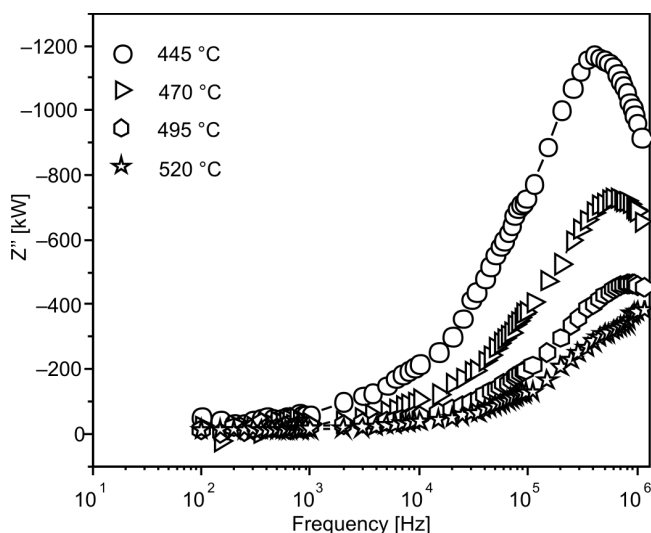


Fig. 5. Dependence of the imaginary part of impedance on frequency

The dependence of the imaginary part of impedance (Z'') on frequency at higher temperatures is shown in Fig 5. A typical peak broadening, which is slightly asymmetrical in nature, was observed at higher temperatures. This asymmetric broadening of the peaks suggests the presence of electrical processes in the material with a spread of the relaxation time. The relaxation species can be defect $\tan\delta$ complexes. In the case of dielectric materials, the localized relaxation dominates [15, 16] (i.e., defect relaxation) because of the low dielectric ratio r , ($r = \epsilon_s/\epsilon_\infty$, ϵ_s and ϵ_∞ , electric permittivity at low and high frequencies, respectively).

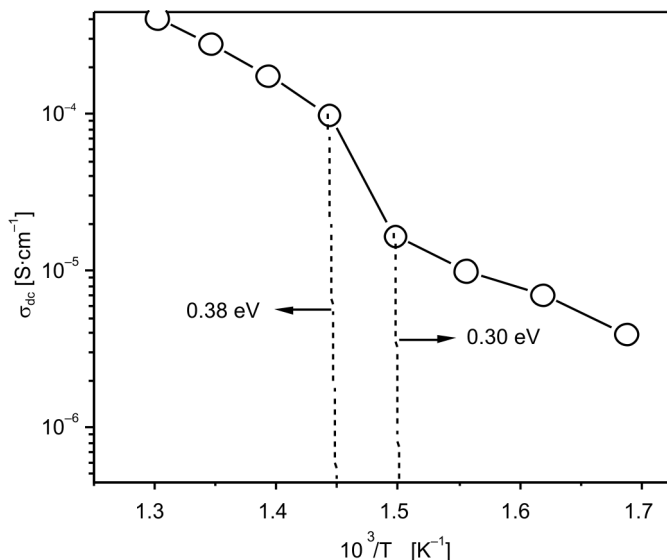


Fig. 6. Dependence of the dc conductivity on the reciprocal temperature

The bulk conductivity of the CCTO compound at higher temperatures was evaluated from the impedance data using the equation:

$$\sigma_{dc} = \frac{t}{R_b A}$$

where R_b is the bulk resistance, t the thickness and A the area of the electrode deposited on the sample. The value R_b is obtained from the low frequency intercept of the semicircle on the real axis Z' axis in the complex impedance plot. The value of the apparent bulk conductivity $(\sigma_b)_a$ determined from the complex impedance plots can be treated approximately as the true value σ_b because of the negligibly small thickness of the grain boundary layer in the sample. The dc conductivity also follows the Arrhenius law, and the activation energy was calculated from the slope of the linear portion of the plot of σ vs. $10^3/T$ (Fig. 6) [17]. It was found to be 0.3 eV at higher temperatures and 0.38 eV at lower temperatures. This value is close to the single crystal value of 0.24 eV, which again supports the existence of the internal barrier layers inside the grains [18, 19].

4. Conclusions

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics were fabricated by the precursor solution technique. Keeping in mind the importance of this compound, this process provides a novel and reproducible route for preparation using two complexing agents (EDTA and TEA). XRD analysis confirmed the formation of cubic phase, with a lattice parameter value of

7.3985 Å. Spherical particles of average 65 nm size were observed from TEM micrographs after calcination at 700 °C. The presence of single semicircular arcs obtained from the impedance plots depicted the bulk effect only. The conductivity plot follows the Arrhenius law. The obtained activation energy was close to that of a single crystal.

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