

Preparation of CCTO Powder by Solid State reaction

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by
Kshitij C Prasad
ROLL 10508002



To the
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NATIONAL INSTITUTE OF TECHNOLOGY ROURKELA

CERTIFICATE

This is certified that the work contained in the project entitled “Preparation of CCTO powder by solid state synthesis” by Kshitij C Prasad (Roll 10508002), has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

S.K.PRATIHAR
PROFESSOR
Department of Ceramic Engineering
National Institute of Technology
Rourkela-769008

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Kshit C Prasad
10508002

ABSTRACT

A stoichiometric amount of $\text{CaCO}_3, \text{CuO}, \text{TiO}_2$ was taken. The mixture was ground by agate mortar. On the ground mixture XRD analysis was performed. After confirming of the CCTO powder, pellets were formed. They were fired at 1000°C for different time periods. Density was measured of the fired samples.

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1. Introduction

1.1 Copper Calcium Titanate (CCTO)

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is a perovskite-like compound exhibiting a high dielectric constant value of $\sim 10\,000$ over a wide temperature range from 100 to 400 K.

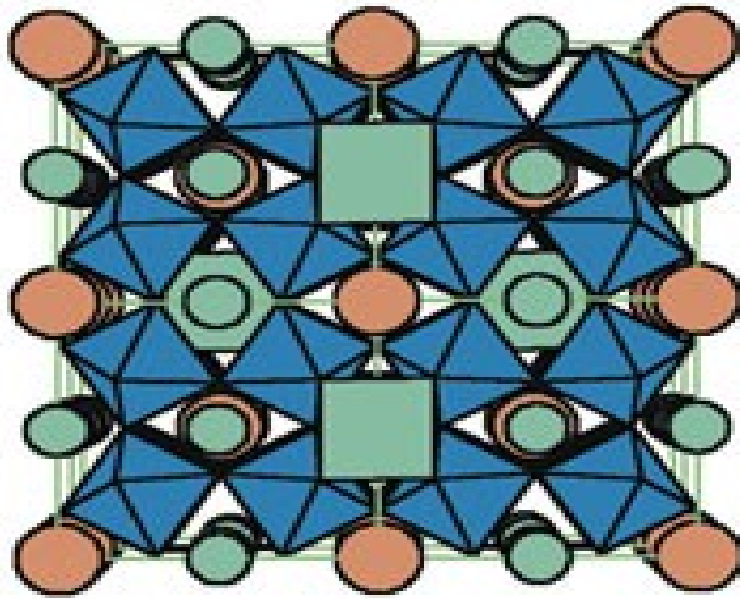


Fig 1.1 Crystal Structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

Brown spheres= Ca

Green spheres = Cu

Blue= TiO_6 units

Green squares= CuO_4 planar units

Ca^{2+} and Cu^{2+} share the A-site . The size difference between Ca^{2+} and Cu^{2+} causes the TiO_6 octahedra to undergo substantial tilting, leading to a body centred cubic supercell of space group $Im\bar{3}$ in which the Ti^{4+} ions occupy centrosymmetric position in the octahedral sites. The angle of tilt is sufficiently large that the Cu^{2+} ions occupy an essentially square-planer environment

1.2 Importance of CCTO powder

The dielectric properties make CCTO a desirable material for micro-electric applications such as static and dynamic random access memories, high dielectric capacitors, and thin film devices. Ordinarily, dielectric constants higher than 1000 are related to ferroelectric or relaxor properties.

However, this material exhibits no crystallographic structural phase transition, associated with spontaneous polarization. The drive for ultra-miniaturization of electronic devices in automobiles and aircraft requires the development of high dielectric materials that are stable over a wide range of temperatures. The typical high dielectric materials used today are normal ferroelectric oxides such as BaTiO₃ or relaxor ferroelectrics like Pb(Mg^{1/3}Nb^{2/3})O₃. However, these dielectric oxides lack either temperature and/or high voltage stability, or do not possess giant dielectric permittivity. Recently, the dielectric properties of various ACu₃Ti₄O₁₂ and ACu₃Ti₃FeO₁₂ oxides (A = metal ions) were measured. Of the 13 oxides tested, CaCu₃Ti₄O₁₂ showed exceptional properties. The room temperature dielectric constant of CCTO measured at 1 kHz was 12,000. However, unlike most undoped ferroelectrics or relaxors its dielectric constant showed very little temperature dependence between room temperature and 200 °C. As a result, this material has sparked great interest because of its potential use in microelectronics. Research indicates that CaCu₃Ti₄O₁₂ may be part of a new class of oxide perovskites whose high dielectric properties are different than classic ferroelectrics or relaxors. Unlike ferroelectrics, which show a great enhancement in permittivity near its Curie point (which is typically associated with a change in crystal structure), the dielectric constant of CCTO has been measured to be relatively stable from 100 to 600 K. Below 100K the dielectric constant drops off dramatically to around 100. However, neutron powder diffraction detects no change in crystal structure in the measured temperature range of 35–1273K or higher. Diffraction experiments detect no presence of superstructure peaks or diffuse scattering or broadening in Bragg intensities which are often indicative of nanodomains or disorder effects that are associated with relaxors.

3. Origin of Electrical Properties

The origin of giant static dielectric constant is not fully understood, though explanations in terms of atomic structure, microstructure, and extrinsic interface structure have been proposed. Based on the micro-structural evidence including domain boundaries in polycrystalline CCTO and twin boundaries in single crystal CCTO, it has been generally understood that a purely intrinsic model cannot be used to explain the origin of the high dielectric constant. Rather, it has been proposed that the reason for the abnormally large dielectric constant is due to Maxwell–Wagner relaxation,

which was supported by a first-principles study . Here, the electrical heterogeneity originating from the mobile charged species and the internal interfaces in polycrystalline CCTO gives rise to the polarization in semiconducting grains and insulating grain boundaries . The grain boundary inhomogeneity was confirmed by the existence of electrical potential barriers via current–voltage measurements. So far, the internal barrier layer capacitor (IBLC) model has been widely accepted as the most likely mechanism to elucidate the high dielectric constant in CCTO.

In order to account for the semi-conductivity in CCTO, two models have been proposed so far. First, it is known that TiO₂-based perovskite ceramics such as BaTiO₃ and SrTiO₃ become more conductive during sintering under reducing conditions due to a small amount of oxygen loss occurring at high temperatures. On the other hand, a cation non-stoichiometry model was suggested . From studies on ACu₃ Ti₄ O₁₂ (A = Ca, Sr) , Cu²⁺ reduces to Cu¹⁺ upon heating along with a charge balanced substitution of Ti⁴⁺ on the Cu site. These reduced monovalent Cu ions are re-oxidized into divalent Cu ions during the cooling stage along with the reduction of Ti⁴⁺ to Ti³⁺ where the electrons move into the 3d conduction band ,which in turn contribute to the rise in conductivity. With the recent report that a Cu₂O phase was observed inside a decomposition zone with a negligible change in bulk resistivity during a nitrogen or oxygen annealing, the cation non-stoichiometry model is likely to be the reasonable explanation for semiconducting behavior in CCTO.

1.4 Different Modes of Synthesis of CCTO

There are different modes of preparation of CCTO

- By solid state synthesis
- By Sol-gel method
- By pulsed laser deposition
- By chemical layer deposition
- By precursor oxalate route

2. Literature Review

X. H. Zheng et al prepared CCTO ceramics by the conventional

solid-state reaction method using starting materials of CaCO_3 (>99%), CuO (>99%), TiO_2 (>99%). Stoichiometric amounts of powders were mixed in distilled water by ball milling with Zirconia media for 12 h. After drying, the mixed powder was calcined in air at $950\text{ }^\circ\text{C}$ for 2 h. The calcined powder was milled again, added about 5 wt% PVA as binder and pressed into disks of 13 mm in diameter and 1–2 mm in thickness. These disks were sintered at temperatures range from $1100\text{ }^\circ\text{C}$ to $1150\text{ }^\circ\text{C}$ for different times and then cooled to room temperature in the furnace. The densities of samples were measured by Archimedes method. The crystalline phases were identified by powder X-ray diffraction analysis with Cu K α radiation (XRD, D/max-IIIIC). Microstructure of the ceramics was carried out in a scanning electron microscope (SEM, Philips XL30 ESEM-TMP). The dielectric properties and impedance analyses of the present ceramics were determined using the precision LCR meter (Agilent 4284A) in the frequency range from 20 Hz to 1 MHz over the temperature range of $25\text{--}120^\circ\text{C}$. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) ceramics were sintered with different temperatures or durations. Strong sintering effect on microstructure was found in CCTO ceramics. To appropriately extend sintering time would benefit the densification and formation of bigger and uniform grain of CCTO ceramics. The samples sintered at $1120\text{ }^\circ\text{C}$ for 3 h showed the lowest permittivity of about 514 at 1 kHz, and the ones sintered at $1120\text{ }^\circ\text{C}$ for 6 h gave the highest value large than 12,400. Furthermore, larger grains resulted in higher permittivity. According to the impedance spectroscopy of CCTO ceramics, the high permittivity could be associated Maxwell–Wagner model, which results from semiconducting grains and insulating grain boundaries.

Z.A.Ahmad et al prepared CCTO samples by solid state method. CaCO_3 ($15.52\text{ }\mu\text{m}$) (Aldrich, 99%), TiO_2 ($0.68\text{ }\mu\text{m}$) (Merck, 99%) and CuO ($6.85\text{ }\mu\text{m}$) (Aldrich, 99%) were used as starting materials. Stoichiometric ratios of the reagents were mechanically ball milled for 1h. The powder was calcined in air at $900\text{ }^\circ\text{C}$ for 12 h, then subjected to X-ray diffraction (XRD, Bruker D8) phase analysis to ensure the perovskite structure of CCTO had formed. Cylindrical specimens of 5 mm diameter and approximately 0.5–1 mm thick were pressed, then sintered in air at $1050\text{ }^\circ\text{C}$ for 24 h, followed by XRD analysis and scanning electron microscopy (SEM, Zeiss SUPRA 35VP). Based on this analysis and observation, the sintering parameters then were modified using the temperature range of $950\text{--}1050\text{ }^\circ\text{C}$ for 3–12 h with a heating rate of $5\text{ }^\circ\text{C}/\text{min}$. The microstructures were investigated on the fracture surface of the sintered specimens using SEM. The samples for measuring ϵ_r were polished to ensure surface flatness and then painted with

silver paste on both surfaces as electrodes. The measurement was done at room temperature by Hewlett–Packard 4912 Impedance Spectroscopy at the frequency range of 1 Hz to 10 GHz. They concluded It is crucial to adequately control sintering temperature and times to obtain the desired microstructure and dielectric properties. The sample sintered at 1050 °C for 24 h shows melting and abnormal grain growth. The effects of different sintering conditions on density, phase formation, microstructure and dielectric properties were discussed. Increasing sintering temperature enhances density. A clear grain and dense microstructure were observed for the samples sintered at 1000 and 1030 °C for 12 h, and for the samples sintered at 1040 °C for 3, 6 and 10 h. The melting grains in the sample sintered at 1050 °C for 12 h show the existence of a new phase, Cu₂O. The highest ϵ_r with clear uniform grain was obtained by the sample sintered at 1040 °C for 10 h.

B.A.Bender et al prepared CaCu₃Ti₄O₁₂ using conventional ceramic solid state reaction processing techniques. Stoichiometric amounts of CaCO₃ (99.98%), CuO (99.5%) and TiO₂ (99.5%) were mixed either by attrition milling (AM1 and AM2) or mortar and pestle (MP1). The MP1 powders were mixed in acetone and mortar and pestled until they could be sieved through an 180 μ m mesh. The powder was then calcined at 960 °C for 8 h. This process was repeated two more times to improve the phase purity of the CCTO powder. AM1 and AM2 powders were mixed by blending the precursor powders into a purified water solution containing a dispersant (Tamol 901) and a surfactant (Triton CF-10). The resultant slurries were then attrition-milled for one h and dried at 90 °C. AM1 was calcined for 8 h at 1000 °C then 930 °C for 4 h and 970 °C for 4 h. AM2 was calcined for 970 °C for 8 h and then 940 °C for 4 h. (The reasons for the calcination schedule are detailed in the following sections.) All calcined powders were mortar and pestled after each calcination to improve their reactivity. After the final calcination the AM1 and AM2 were attrition-milled again for 1 h to produce finer powders. X-ray diffraction (XRD) was done on the dried powders before compaction. A 2% PVA binder solution was mixed with the powder and the powder was sieved to eliminate any large agglomerates. The dried powder was uniaxially pressed into discs typically 13mm in diameter and 1.5mm in thickness. The discs were then placed on platinum foil and sintered in air at different temperatures (990–1100 °C) for various dwell times (3–16 h). The standard sintering conditions were considered to be 1100 °C

for 3 h. Multiple discs were sintered at the same time and used for subsequent characterization and thermal annealing. Thermal annealing was carried out in flowing argon at 1000 °C for 6 h. Material characterization was done on the disc and powders after each processing step. XRD was used to monitor phase evolution for the various mixed powders and resultant discs. Microstructural characterization was done on the fracture surfaces using scanning electron microscopy (SEM). To measure the dielectric properties, sintered pellets were ground and polished to achieve flat and parallel surfaces onto which palladium-gold electrodes were sputtered. The capacitance and dielectric loss of each sample were measured as a function of temperature (−50 to 100 °C) and frequency (100 Hz to 100 kHz) using an integrated, computer-controlled system. The dielectric properties of a standard processed sample (AM2) was also measured as a function of dc bias using a high voltage power supply in combination with a blocking circuit to protect the LCR meter (Hewlett-Packard 4284A) from the dc bias voltage.

The CCTO thin films were fabricated Wen Lu et al by the CSD method in the following way. The starting materials were the toluene solution of calcium and copper naphthenates, and tetrabutyl titanate with A.R. purity. They were first weighed and mixed stoichiometrically based on the chemical formula $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and then diluted with toluene in a ratio of 1:1, obtaining the so-called CCTO precursor solution. The thermal decomposition behavior of the precursor solution was investigated by thermal analysis to determine the appropriate temperature of pyrolysis. The mixed solution was spin-coated at a speed of 2000 rpm for 10 s onto the LaAlO_3 (001) substrates. Then the coated films were directly put into a tubular furnace pre-heated to 500 °C holding for 15 min. This procedure of coating and pyrolysis was repeated two or three times so as to obtain the desired films of approximately 100-nm thickness. Finally, the sample was fired at 790 °C for 2 hr and then furnace-cooled to room temperature. All the preparations were preformed in air. The thermogravimetric and differential thermal analysis (TG–DTA) were carried out from room temperature to 1000 °C at a heating rate of 15 °C/min on a WCT-2 Thermal Analyzer made by Beijing Optical Equipment Company. X-ray diffraction (XRD) was performed on a Philips X’Pert X-ray diffractometer using $\text{Cu K}\alpha$ radiations. Samples’ surface morphology was examined by an atomic force microscope (AFMII) made by Zhejiang University.

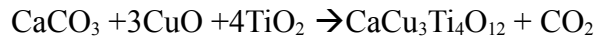
3. Objective

The objective of the project is:

- Preparation of CCTO powder
- Characterization of the obtained powder
- Characterization of the CCTO pellets.

4. Experimental Procedure

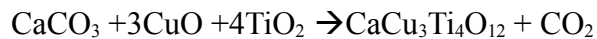
CCTO was prepared using conventional solid state reaction .



The starting powders used were CaCO_3 (99.98%) , CuO (99.5%) and TiO_2 (99.55).They were mixed in stoichiometric amounts using agate mortar. Total weight of the mixture was 10 gm. They were grinded for 3-4 hours. Initial grinding did not give the desired result. The mixture was again grinded for 3-4 hours. After grinding was completed the mixture was calcined at 1000°C for 8 hours. After calcination the mixture was again grinded for 3-4 hours. 3.096 gm of the calcined powder was taken. Phase evaluation was done using XRD. XRD was done for $20-80^\circ$ for 22 minutes. After the XRD pattern matched with the CCTO structure ,the mixture divided in to 4 parts of equal weight~0.75 gm.About 2 %PVA binder was added from 3% PVA solution . Disks were pressed out of the powders. The pressure applied was 2.5 Mpa. The four disks obtained were fired at $1000^\circ\text{c}/8$ hours, $1000^\circ\text{c}/6$ hours, $1000^\circ\text{c}/4$ hours and $1000^\circ\text{c}/2$ hours. After firing was done density measurement was carried out using Archimedes' principle.

4.1 Calculations

1) For starting powders



Weight of CaCO_3 = 100.1 g

Weight of CuO = 79.55 g

Weight of TiO_2 = 79.88 g

Weight of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ =614.27g

For 1 mol of CCTO ,1 mol of CaCO_3 ,3 mol of CuO and 4 mol of TiO_2 required.

→ for 614.27 g of CCTO ,658.27 g of mixture was required

→ For 10 g of CCTO ,10.71 g of mixture was required

Weight of CaCO_3 required= 1.62 g

Weight of CuO required = 3.88 g

Weight of TiO_2 required = 5.2 g

2) For PVA

3% PVA solution is there

2% PVA is to be added.

→ weight of PVA = 0.06192

100 ml of PVA solution → 3 g

→ 3 g → 100ml

→ 1g → 100/3ml

→ 0.06192 → 2.06 ml ~ 2 ml

→ Volume of PVA to added=2 ml

5. Results and discussion

5.1 Preparation of powder

The starting powders were mixed in stoichiometric amounts. The observed loss in weight is attributed to the formation of CO_2 . The mixture was finely ground for a total of 8-9 hours to obtain a uniform distribution of particle size. Acetone was added in required amounts to bring about the mixing of the powders properly. The powder obtained after grinding was greyish in appearance. The colour changed to dark brown after calcination of the powder. Impurity from the working surroundings must be prevented from contaminating the powder of the mixture.

5.2 XRD analysis

XRD patterns were obtained using an automated diffractometer. It was diffracted for 22 min at $20-70^\circ$. The XRD pattern obtained were compared with the available XRD pattern of CCTO. The XRD pattern obtained was in accordance with the available CCTO XRD pattern.

5.3 Firing at high temperature

After the powder were confirmed to be CCTO by XRD evaluation, the powder was made into disc using a pressure of 2.5 Mpa and the binder used was 3% PVA. 4 discs of about 0.75 g were prepared. They were fired at 1000°C at 2 hours, 4 hours, 6 hours and 8 hours. Proper precaution whilst placing the discs in furnace is required. The crucible used should be checked for impurities.

5.4 Density measurement

The density of the fired samples was measured using the Archimedes' method

Table 5.1 Density of discs

Sample	Dry weight(g)	Suspended weight(g)	Soaked weight(g)	Density(g/cc)
1000/8 hr	0.7071	0.5724	0.6807	4.10

1000/6 hr	0.7340	0.6179	0.7611	4.15
1000/4hr	0.7046	0.5932	0.7351	4.02
1000/2 hr	N.A.	N.A.	N.A.	N.A.

The data for the density of the sample fired for 2 hours is incomplete due to technical difficulties.

6. Conclusion

The CCTO powder was prepared using the conventional solid state reaction method. Single phase CCTO was identified in calcined powders. Firing was done at different time durations. Different time durations resulted in varying density for the CCTO.

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