

PRODUCING CALCIUM CUPRUM TITANIUM OXIDE
($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) VIA WET-CHEMISTRY TECHNIQUES

NORZIANA BINTI LANI

UNIVERSITI TEKNIKAL MALAYSIA MELAKA



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($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) VIA WET-CHEMISTRY TECHNIQUES**

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Engineering Materials) with Honours.

by

NORZIANA BINTI LANI

FACULTY OF MANUFACTURING ENGINEERING

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TIDAK TERHAD

Disahkan oleh:

(NORZIANA BINTI LANI)

(DR MOHD WARIKH B ABD RASHID)

Alamat Tetap:

No, 59 Jalan Cuepacs 5,

Taman Koperasi Cuepacs, 43000

Kajang, Selangor.

Cop Rasmi:

DR. MOHD WARIKH BIN ABD RASHID
Pensyarah Kanan
Fakulti Kejuruteraan Pembuatan
Universiti Teknikal Malaysia Melaka


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Signature : 
Author's Name : NORZIANA BINTI LANI
Date : 22 MAY 2009

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material) with Honours. The member of the supervisory committee is as follow:



.....
(DR. MOHD WARIKH BIN ABD RASHID)

DR. MOHD WARIKH BIN ABD RASHID
Pensyarah Kanan
Fakulti Kejuruteraan Pembuatan
Universiti Teknikal Malaysia Melaka

ABSTRACT

The Calcium Cuprum Titanium Oxide ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) was prepared via wet-chemistry techniques which are sol-gel method and co-precipitation method. The wet chemical processing technique was selected because it could give a uniform mixing in metal ions, shorter reaction time and lower production temperatures. Both methods begin with mixing the raw material followed by drying, heating, pressing and sintering process. The identification of phase formation was determine by X-ray Diffraction (XRD), microstructure was studied under Scanning Electron Microscopy (SEM), the element phase present in sample was determine by Energy Dispersive X-Ray Spectroscopy (EDS) and the electrical properties are determined by Impedance Analyzer. It was found that sample produce from sol-gel method produced smaller particle size, higher grain boundaries, higher density and higher porosity compared to the sample produce through co-precipitation method. Four elements which are calcium, cuprum, titanium and oxygen are detected in the sample for both methods. Sintered sample showed highest conductivity is sample through sol-gel method.

ABSTRAK

Calcium Cuprum Titanium Oxide ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) telah dihasilkan melalui teknik kimia basah iaitu kaedah sol-gel dan kaedah pemendakan. Teknik penghasilan kimia basah telah dipilih kerana ia boleh memberikan pencampuran ion-ion logam yang seragam, masa tindakbalas yang lebih pendek dan suhu penghasilan yang lebih rendah. Kedua-dua kaedah dimulakan dengan process mencampurkan bahan-bahan mentah diikuti dengan proses pengeringan, pemanasan, pemadatan dan pensiteran. Pengenalpastian pembentukan fasa yang terhasil dicirikan dengan XRD, morfologi diselidiki dengan menggunakan SEM, kehadiran unsur dalam sampel dilakukan menggunakan EDS dan pencirian elektrik ditentukan menggunakan penganalisis impedance. Didapati bahawa, sampel yang dihasilkan melalui kaedah sol-gel menghasilkan saiz partikel lebih kecil, sempadan-sempadan butir lebih tinggi, berketumpatan lebih tinggi dan keliangan lebih tinggi berbanding sampel yang dihasilkan melalui kaedah pemendakan. Empat jenis unsur iaitu kalsium, kuprum, titanium dan oksigen dikesan di dalam sampel bagi kedua-dua kaedah. Sampel yang disinter menunjukkan nilai kekonduksian yang tinggi dihasilkan melalui kaedah sol-gel.

DEDICATION

For my beloved mother, father, family and all my friends

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LIST OF ABBREVIATIONS

AC	-	Alternative Current
BaTiO ₃	-	Barium Titanate
BCC	-	Body-centered Cubic
Ca	-	Calcium
CaCO ₃	-	Calcium carbonate
CaCu ₃ Ti ₄ O ₁₂	-	Calcium Cuprum Titanium Oxide
CaTiO ₃	-	Calcium Titanate
CCTO	-	Calcium Cuprum Titanium Oxide
Cu	-	Copper
CuO	-	Copper (II) Oxide
DC	-	Direct Current
EDS	-	Energy Dispersive X-ray Spectroscopy
IBLC	-	Internal Barrier Layer Capacitance
SEM	-	Scanning Electron Microscopic
TiO ₂	-	Titanium (IV) Oxide
XRD	-	X-ray Diffraction

LIST OF SYMBOLS

A	-	Cross Sectional Area
C	-	Capacitance
D	-	Diameter
d	-	Thickness
m	-	Mass
Q	-	Electrical Charge
R	-	Resistance
t	-	Thickness
$\tan \delta$	-	Dissipation factor
V	-	Voltage
ϵ''	-	Loss factor
ϵ'	-	Dielectric constant
ϵ_0	-	Permittivity
κ'	-	Relative permittivity or relative dielectric constant
π	-	Pai constant = 3.142
ρ	-	Density
σ	-	Conductivity

CHAPTER 1

INTRODUCTION

1.1 Research Background

With the development of capacitor application in microelectronics, many new materials with high relative dielectric constant ($\sim 10^4$) are significant interest. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (commonly called CCTO) is a novel material with high relative dielectric constant up to 10^5 at room temperature and low loss tangent, which has potential applications in microelectronics devices. The unusual high dielectric constant ($\sim 10,000$) at 1 kHz of the perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has been reported first by Subramaniam *et al.* (2000). They first reported that large dielectric constant were found in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (A= trivalent rare earth or Bi) type material. Moreover, between -170 and 100°C , a quasi-independent behavior of the permittivity with temperature is observed. These properties are great important for the world of electronics. Indeed, there is an increasing demand on dielectrics to surpass their properties to be used as capacitors, in particular in the field of microelectronics and power electronics (Marchin *et al.*, 2007).

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has been investigated recently because of its giant dielectric constant that does not change over a wide temperature range. The large dielectric constant is very unusual because $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is not ferroelectric. Because its dielectric properties depend primary on the ceramic microstructure (such as the average grain size and pellet density) and processing conditions (such as the oxygen partial pressure, sintering temperature, and cooling rate), an intrinsic mechanism for the giant dielectric constant seems to be excluded (Liu *et al.*, 2007a).

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ are isostructural representing an $\text{AA}'_3\text{B}_4\text{O}_{12}$ ($\text{A} = \text{Ca}$, $\text{A}' = \text{Cu}$, $\text{B} = \text{Ti}$) perovskite-like phase. The crystal symmetry is cubic (space group $\text{Im}\bar{3}$) with a quadrupling of the ideal ABO_3 perovskite cell. The quadrupling of the unit cell is due to the ordering of A and A' ions and the distortion of the oxygen sublattice, which leads to a tilted three-dimensional network of BO_6 octahedra sharing corners. Two types of polyhedra are presented at A position: a slightly distorted O icosahedron around the Ca site and a roughly square planar O⁻ coordinated Cu site with a Cu⁻O distance of 1.94Å (Chen *et al.*, 2007).

The typical high dielectric materials used today are normal ferroelectric oxides such as BaTiO_3 or relaxor ferroelectrics like $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. 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 $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ oxides ($\text{A} = \text{metal ions}$) were measured of the 13 oxides tested, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ showed exceptional properties. 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 (Bender *et al.*, 2005).

1.2 Problem Statement

From the previous research, generally the conventional ceramic (solid-state) processing is used as synthesis the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. However, this synthesis technique usually needs long reaction time at elevated temperature. There are some cases reported after heating for several days at temperatures up to 1000°C with some intermittent regrinding stages for obtaining single phase $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder. Other than solid state reaction, it has been only a few reports on the solution methods to synthesize $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using a wet-chemical technique.

It has three reasons why the wet-chemistry technique is choose to produce the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Firstly, is important to show and improve the quality of the sample, by

using wet-chemistry techniques, such as the sol–gel method and co-precipitation technique, have been developed to achieve better mixing of the initial products. This is because most researchers more interested to produce the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using solid state reaction as compared with wet chemistry technique.

Second reason, if we analyze the previous reports which have been carried out using the solid state reaction to generate the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, they use high calcinations temperature and the particles produced would be coarse and also inhomogeneous particle size. Besides, the powders prepared by this method usually feature a high agglomeration (Liu *et al.*, 2007b). As compared with wet-chemistry technique, this method use lower crystallization temperature due to the mixing of liquid precursors on the molecular level. Synthesis $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ from wet-chemistry technique affords the reaction with a homogeneous mixing.

For the third reason, the period taken to produce $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ during calcination process and sintering process is an important factor that would be considered. Through solid state reaction, the mixtures are calcined at high temperature for long durations (typically 1000–1050 °C for 24 – 48 h) with repeated intermediate grindings. This method of preparation is very cumbersome, often requiring temperatures approaching the melting point of CuO (Thomas *et al.*, 2008). Compare with wet-chemistry technique, the time taken for the sintering process is about 3 – 30 hour at temperatures 900 – 1040°C. Therefore, producing the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ using wet-chemistry is chosen because of shorter diffusion lengths lead to shorter reaction times.

1.3 Objective

- (a) To produce the Calcium Cuprum Titanium Oxide ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) via wet-chemistry technique.
- (b) To investigate and analyze the characteristic of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ such as, microstructure, phase and electrical properties.

1.4 Scope of study

This research will focus to producing Calcium Cuprum Titanium Oxide via wet-chemistry techniques. In this project, there are two synthesise methods that will be applied to produce $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ which are sol-gel method and co-precipitation method. Besides, three types of sample analyses will be carried out in these studies which are phase analysis, microstructure analysis and electrical properties analysis.

For the sol-gel method, the raw materials which are Calcium nitrate tetrahydrate, Copper (II) nitrate hemipentahydrate and Titanium (IV) butoxide were dissolved together in ethanol and the mixture was stirring using magnetic stirring. The mixtures were aged for one day at room temperature until the solution is changes to gel form. Then, solutions were filter by using the filter paper to gets the powder form. After that, the powders were dried and continued steps by heating, forming and sintering process.

For the co-precipitation method, the raw materials which are Calcium chloride dihydrate, Copper (II) chloride dehydrate and Titanium (IV) butoxide were dissolved into the deionized water. Then, the oxalic acid was dissolved into the ethanol were added to the solution and the solution were aged for one day until the precipitation obtained in the sample. The process was continued by heating, forming and sintering process.

For sample testing analysis, the samples produced through both methods will be tested and analyzed to study the phase identification, morphology analysis and electrical properties analysis. Here, the phase identification is characterized by X-Ray Diffraction (XRD), the morphology analysis is studied under Scanning Electron Microscope (SEM) observation, and the electrical properties characterization is done by using impedance analyzer.

CHAPTER 2

LITERATURE REVIEW

2.1 Overview of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

The dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ material was first reported by Subramanian et.al in 2000. They first reported that large dielectric constants were found in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ (A= trivalent rare earth or Bi) type material. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, displaying the most special behavior, shows a dielectric constant about 12,000 at 1 KHz, remaining steady in a large temperature range, from 100K to 400K (Yang, 2006). These properties are of great importance for the world of electronic devices. Indeed, there is increasing demand on dielectrics to surpass their properties to be used as capacitors, in particular in the field of microelectronics and power electronics (Marchin *et al.*, 2007).

Materials with dielectric constants higher than 1,000 are associated with ferroelectric properties and the dielectric constant changes greatly during the ferroelectric phase transition (Yang, 2006). The high electric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is found in ferroelectric material, however; no evidence of phase transition (paraelectric to ferroelectric) in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has so far been found. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ was not found to be a ferroelectric material and has therefore been a material, which needed more studies (Deepam Maurya *et al.*, 2007).

Other special features of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ were discovered by Ramirez *et al.* (2004). The crystal structure of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is shown in Figure. 2.1. They reported that below 100 K the dielectric constant drops abruptly from around 12,000 to as low as 100, in addition to the fact that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ holds a large dielectric constant that barely varies in the temperature range from 100 K to 400 K as shown in Figure 2.2.

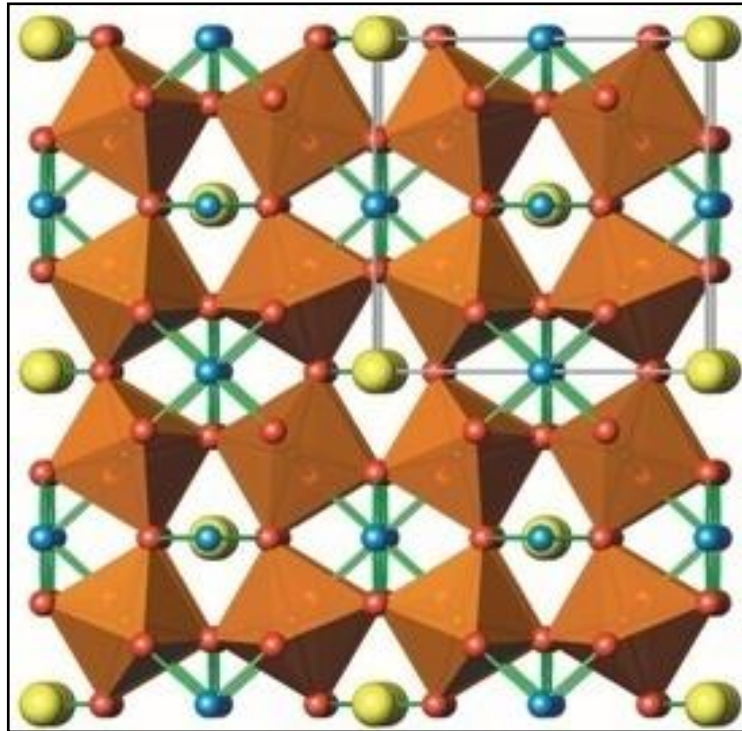


Figure 2.1: Several unit cells of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, shown as TiO_6 octahedra, This molecular model shows the arrangement of atoms of calcium (yellow), oxygen (red), copper (blue), and titanium (black, at center of double-sided brown pyramids, or octahedra) (Homes *et al.*, 2001a).

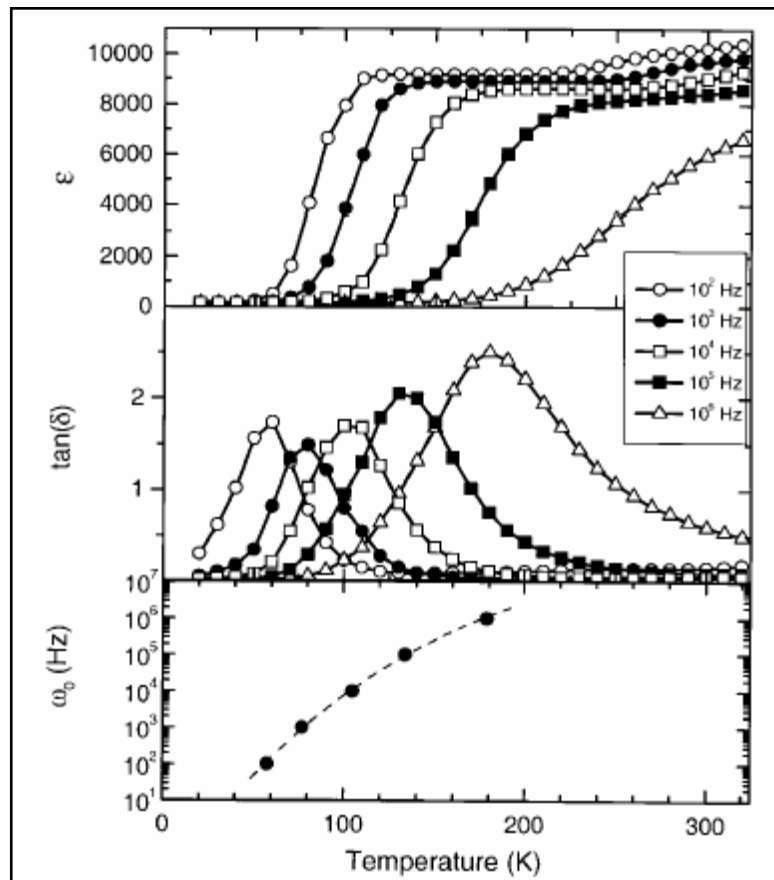


Figure 2.2: Temperature-dependence of ϵ (a), $\tan \delta$ (b), and angular relaxation rate (c) at 10^2 , 10^3 , 10^4 , 10^5 , and 10^6 Hz (Yang, 2006).