PRODUCING $CaCu_3Ti_4O_{12}$ DOPED LANTHANUM (III) ACETATE HYDRATE VIA SOLID STATE REACTIONS

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

by

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Signature	:	....
Author's Name	:	HARIS FAHAZA BIN GHAZALI
Date	:	MAY 19th ,2011

APPROVAL

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

....

Supervisor

ABSTRAK

Matlamat penyelidikan ini adalah untuk mengkaji dan memahami cara penghasilan bahan feroelektrik electro-seramik dari $CaCu_3Ti_40_{12}$ (CCTO) dengan penambahan bahan asas melalui teknik tindakbalas pepejal. Pengaruh keadaan sepuhlindap (suhu pengkalsinan, suhu pensinteran dan masa) dan konsentrasi gantian untuk fasa pembentukan, struktur mikro dan sifat elektrik (dielektrik malar, lesapan dan ketahanan dielektrik) dari $La_{2/3}CaCu_3Ti_4O_{12}$ (LCCTO) akan dipelajari secara intensif dalam penyelidikan ini. Teknik konvensional yang digunakan dalam kajian ini meliputi persiapan bahan asas, pencampuran dan pengisaran bebola, pengkalsinan, pembentukkan palet dan proses pensinteran. Teknik ini dipilih bagi penyelidikan ini untuk membolehkan proses pengkalsinan dan pensinteran di masa depan dilakukan dalam jangkamasa pendek dan pada suhu yang rendah, sehingga dapat menjimatkan masa dan tenaga. Parameter yang optimum untuk LCCTO dihasilkan melalui teknik tindakbalas pepejal adalah pengisaran bebola masa 12 jam, kalsinasi pada 1200°C selama 10 jam, dan pengsinteran pada > 1100°C selama 12 jam untuk memanjangkan tempoh masa bagi pemisahan fasa Cu. Walau bagaimanapun, tumpuan kesan pengantian Lantanum (La) pada pemalar dielektrik CCTO dijangka dapat meningkatkan sifat dielektrik pada CCTO. Selain itu, kajian ini adalah untuk menentukan samaada perlu untuk menjalankan kajian lebih lanjut menggunakan bahan gantian La. Oleh itu, dapat disimpulkan bahawa dengan pengantian jumlah tertentu La, sifat elektrik dan lesapan dielektrik CCTO dapat ditingkatkan atau berkurangan bergantung kepada parameter yang digunakan. Keputusan yang dijangka dari penghasilan LCCTO ialah ianya dapat menghasilkan saiz butiran yang seragam dengan nilai tertinggi pemalar dielektrik ε_r 33,210.

ABSTRACT

The aim of the study and investigate the electroceramic ferroelectric material of $CaCu_3Ti_40_{12}$ (CCTO) was prepared by doping the based material via solid state reaction techniques. The effect of thermal treatment (calcinations temperature, sintering temperature and time) doping concentrations in phase formation, microstructures and electrical (dielectric constant, dielectric loss and resistance) properties of $La_{2/3}CaCu_3Ti_4O_{12}$ (LCCTO) has been intensively study in this research. The conventional technique used in this experiment is covers preparation of raw material, mixing and ball milling, calcinations, pellet forming and sintering processes. This technique was chosen for this work to enable the calcinations and sintering processes in future carried out in shorter time and lower temperature, therefore it can be save time and energy. The optimum parameter to synthesized LCCTO via solid state technique are milling time for 12 hours, calcinations at 1200°C for 10 hour, and sintering at > 1100°C for 12 hours to prolonged the durations resulted in the segregation of Cu-rich phase. However, the effect doping with the Lanthanum (La) concentration on the dielectric constant CCTO simple simultaneous can exactly improved the dielectric properties of CCTO. Besides that, this sample is to determine the find out for the further study in La doping. Therefore, it can be concluded that by doping with certain amount of La, the electrical and dielectric properties of CCTO can be improved or maybe not depending on the parameters choose. The result expected get from the LCCTO produce is to have clearly uniform grain size with the highest dielectric constant value of ε_r 33,210.

DEDICATION

This dedication goes to my beloved mom's and my late father's,
Fauziah Bt. Saad and Ghazali B. Ismail
a very supportive siblings,
Hafiz Fahaza B. Ghazali, Nadzirah Fahaza B. Ghazali,
Hasyraf Fahaza B. Ghazali, Hezry Fahaza B. Ghazali
and especially Norshafiza Bt. Abu Bakar
and not forget to all my dearest friends,
Thank you.

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God bless you all.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CRT	-	Cathode Ray Tube
EDX	-	Energy-dispersive X-ray Spectroscopy
EIS	-	Electrochemical Impedance Spectroscopy
FCC	-	Face Centred Cubic
ILBC	-	Internal Barrier Layer Capacitors
IS	-	Impedance Spectroscopy
LCR	-	(Inductance (L), Capacitance (C), and Resistance (R))
PLZT	-	Lead Lanthanum Zircornate Titanate
PMN	-	Lead Magnesium Niobate
PZC	-	Point Zero Charge
PZT	-	Lead Zirconate Titanate
RS	-	Rochelle salt
SEM	-	Scanning Electron Microscope
XRD	-	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Introduction

The introduction will slightly brief the purpose of produce Lanthanum (La) doped $CaCu_3Ti_4O_{12}$ (CCTO) powders. Methods, process and also research study in doping materials developed for La doped CCTO will also covered. In the previous research done the other researchers in produce CCTO, Calcium (Ca) is used as base material. This purpose of research studies will try to doping the base materials alternatively use La and to get a result whether dielectric materials can be produce, in other hands to get a better dielectric material than CCTO. The properties in this compound will have a differential then others doped CCTO produce with other researchers, because it depending on the parameters or doping materials state by the researcher.

Recently, the interest in produce Calcium Copper Titanium Oxide ($CaCu_3Ti_4O_{12}$) as new generation of ultrahigh dielectric materials was choose because of its good dielectric properties. These materials have been demonstrated to have a dielectric constants as high as ε = 80,000 for single crystal structure at room temperature and remains constant over 100 - 600K at low frequencies (Fadhlina, 2007) (Bozin *et al.*, 2004). Dielectric materials have many technological applications in electronic devices such as capacitors, resonators, and filters.

1.2 Problem Statement

Lanthanum (La) doping was introduced into $CaCu_3Ti_4O_{12}$ (CCTO) in order to improve the dielectric properties. Some methods in generating La doped CCTO such as wet chemistry and sol-gel has identified and studied based on microstructure development. The solid state reaction method was choose in producing La doped CCTO ceramics after agree with some researchers. Most of the reports are done on this material said, it were prepared by solid state reaction from metal oxide at higher temperature with several intermediate grinding such as by using ball milling. The reason for studying this doping is to prove that with the correct parameters, La doped CCTO can be produce and resulted in the desired formation of the nanocrystalline and eliminate the factors that may influence the unwanted phase and impurities. Solid state reaction requires tedious work, relatively long reaction times for sintering such as 1000°C overnight, 1000°C for 20 hours, 1000°C for 24 hours (Liu *et. al.,* 2007) and high temperature conditions and still may result in unwanted phase because of limited atomic diffusion through micrometer sized grain (Sen *et al.,* 2010). The observation on the different samples with different parameters need to be analyze by using the XRD to determine the effect of parameters using and microstructure patterns of the La doped CCTO ceramics.

The reason Lanthanum (La) use in this experiment is to have high dielectric properties similar to CCTO or could be greater. X-ray powder diffraction analysis confirmed the formation of the monophasic compound and indicated the structure to be remaining cubic with a small increase in lattice parameter with increase in La doping. A remarkable decrease in grain size from 50µm to 3-5 µm was observed on La doping. The conducting properties of grain decreased while that of the grain boundary increased on La doping, resulting in a decrease of the layer internal barrier layer effect. The doping mechanisms and the conditions under which the ceramics are processed would influence the physical properties of, particular perovskite related electroceramics (Prakash *et. al.,* 2006). Lanthanum (La) site resulted in an increase in the resistance of the grain and a decrease in grain boundary resistance, consequently a decrease in the grain boundary internal barrier layer effect (Prakash *et. al.,* 2006); Manganese (Mn) doping can suppress the dielectric permitivity in $CaCu_3Ti_4O_{12}$ by up to two orders of magnitude (from 10^4 to 10^2), and the nonlinear varistor characteristics disappear completely, which should be mainly ascribed to the decrease of potential barrier height at the grain boundary and charge compensation for the conduction electrons caused by the doping (Cai *et. al.,* 2007), Eu_2O_3 doping can reduce the mean grain size and can also deter the formation of Cu-rich phases at the grain boundaries (Li *et. al.,* 2009), Zircornium (Zr) substituting experimental results indicated that there is no obvious effect on microstructure characteristic (Cai *et. al.*) and several more materials such as; tin oxide (SnO_2), Nickel (Ni), Sodium (Na), Iron (Fe), Cobalt (Co).

Doping of higher charge, like a La ions, enhance domain wall mobility and result in improved remaining polarization, coupling factors, dielectric constants, dielectric loss tangent and increased of optical transparency of electrically material. The measurement and characterization results of stoichiometric CCTO clearly indicated that the dielectric properties, evolution of secondary phases, and microstructures were strongly dependent upon the processing parameters (Kwon, 2008). Characterization of the Lanthanum (La) doped ceramics with XRD and SEM showed average grain sizes 1-2µm, indicating La amount to have little impact on grain size. Compared with CCTO, La doped CCTO showed a flatter dielectric constant curve related to frequency, it was found that the loss tangent of the ceramics composition of $La_{(2/3)x}Ca_{1-x}Cu_3Ti_4O_{12}$ (LCCTO) less than 0.20 in $600x10^5$ Hz region, which rapidly decreased to a minimum value of 0.03 by La doping with 0.05wt%. The $\mathcal{E}_{max}$ value became considerably high, which was almost higher than that of sample with 0.00wt%. The curves about Ɛ values of samples with 0.05 - 0.15wt% were fairly flat while the curves of 0.20wt% and 0.00wt% were much steeper (Patra, 2009).

1.3 Objective

The focus in this research is in producing $La_{2/3}CaCu_3Ti_4O_{12}$ (LCCTO) powder via solid state reaction technique and the effect of doping materials. The study of this research covered the parameters involves, microstructure and optimizing the phases and composition develop. Therefore the main objectives in this research are;

i. To determine the suitable composition (wt%) for La doped in A'$CaCu_3Ti_4O_{12}$.

ii. To analyze the effect of calcinations temperature for La doped A'$CaCu_3Ti_4O_{12}$ phases.

iii. To optimize the sintering temperature and soaking time for optimum parameter La doped A'$CaCu_3Ti_4O_{12}$.

1.4 Scopes of the Study

The scopes of the study will divide into three major difficulties that are;

Part A (To determine the suitable composition (wt%) for La doped in A'$CaCu_3Ti_4O_{12}$),

Part B (To analyze the effect of calcinations temperature for La doped A'$CaCu_3Ti_4O_{12}$ phases),

Part C (To optimize the sintering temperature and soaking time for optimum parameter La doped A'$CaCu_3Ti_4O_{12}$).

1.5 Research Methodology

In part A, different weight percentage; 0.03 wt%, 0.05 wt%, 0.07 wt% of doping material in mixed powders were determine the properties present in the specimen in a goal to have a dielectric behaviour as CCTO ceramics. The stoichiometric amount of powder will be well-mixed by using ball mill for 12 hours in stainless steel ball as medium to have nanocrystalline powder with expected size ranges from 82 µm - 101 µm with an average grain size of 5 µm for 12 hours (Ismayadi *et. al.,* 2009) of milling to obtain the single phase of CCTO, the grain size can be determine by using particle analyzer. The theoretical combinations of doping have been investigated to modify the composition.

For part B, the mixed powder then calcine at temperature determine at 1200°C for 12 hours to produce single phase CCTO (Patra, 2009). The temperature of calcination was chosen high enough to cause complete reaction. The objective of choosing calcinations temperature and suitable soaking time is to develop perovskite structure without any additional element. The composition represent in the powder is observed using X-ray diffraction (XRD) to determine the compositions develop, while scanning electron microscope (SEM) is use to inspecting micrographics and phases of samples.

In part C, the calcinations powders were press manually with hydraulic press at 214.5kN/m^2 equally to 2 ton/$inch^2$ to the pallet type specimen with the determine thickness as 0.4mm to 0.5mm. The pallet will be sinter at various temperatures 1100°C and 1200°C for 12 hours; an adequate temperature for sintering and times obtain the desire microstructure and dielectric properties. The increasing of the sintering temperature enhances the density of the specimen. The necessary soaking time between 6 hours to 12 hours are done for each specimen. At the final process, the entire specimen will undergo the X-ray diffraction (XRD) and scanning electron microscope (SEM) analysis to determine and analyze the changes happen to the heat treatment applied to the specimens. Linear Scan Volummetry will be use to measure the resistivity and conductivity for each specimen to improve that the specimen are conductive and able to hold charge as from early study of its dielectric properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter reviews related study done the researcher in producing electroceramics through solid state reaction method. This literature reviews are mainly focused in the material selection for the doping and its parameters significant to achieved perovskite structure and high electric permittivity. The effect of suitable composition will be further reviewed based on the doped material. Electroceramics can now broadly describe that ceramic material have been specially formulated for specific electrical, magnetic or optical properties. A new generation in electroceramics can be used to obtain composite with the better performance indispensable dielectric properties for modern electronic devices. In general, these compounds belong to perovskite structure where high electric permittivity is always associated with ferroelectric or relaxor properties (Sen *et al*., 2010). Ceramic materials and single crystals showing ferroelectric behaviour are being used in many applications in electronics and optics. A large number of applications of ferroelectric ceramics also exploit properties that are an indirect consequence of ferroelectricity, such as dielectric, piezoelectric, pyroelectric and electro-optic properties (Ahmad *et al.*, 2000).

2.1.1 Structure of $CaCu_3Ti_4O_{12}$ (CCTO)

A great challenge in produce microelectronic is to decrease the size of the component and yet gain its potential than the components or materials discovered before turns it into the highly suitable materials to use widely in technological applications. The

CCTO ceramics considerable as ferroelectric perovskite oxide ceramics has the isometric structure with cubic space group *lm3* (Fadhlina, 2007).

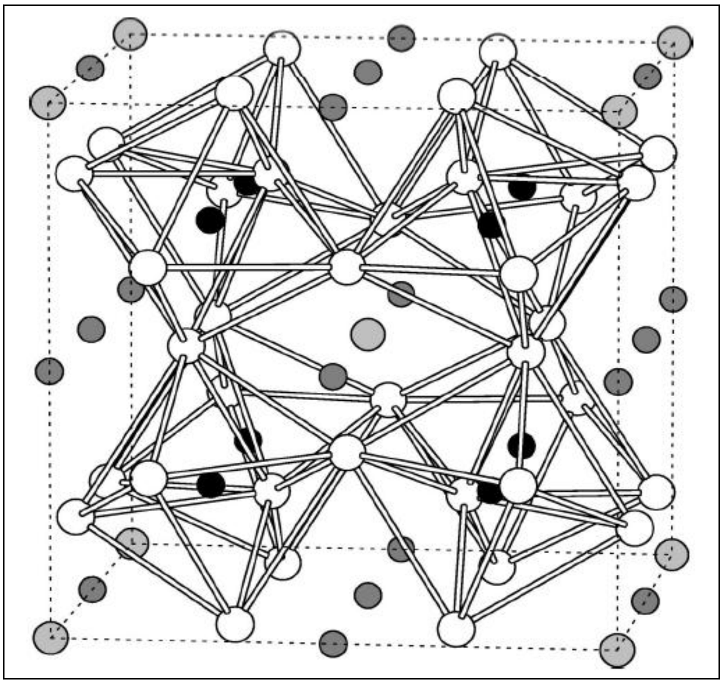

Figure 2.1: Structure of $CaCu_3Ti_4O_{12}$ CCTO showing tilted oxygen octahedra. White, light, dark, and black atoms are O, Ca, Cu, and Ti, respectively. Dashed lines indicate 40-atom primitive cell of antiferromagnetic spin structure (He *et. al.,* 2002)

Its structure can be derived from the ideal cubic perovskite structure by superimposing a body centred ordering of Calcium (Ca) and Copper (Cu) ions and a pronounced tilting of the titanium centred octahedral (tilt system $a^+a^+a^+$) can be interpreted in the terms of lattice modes (Bozin *et al.,* 2004).

2.1.2 The Origin of Dielectric Behaviour of CCTO

The CCTO ceramics is so called the giant dielectric permittivity value that is mostly temperature impendence (Barbier *et al.,* 2009). The main focus has been on perovskite based ferroelectric materials, owing to their high intrinsic dielectric constant originating from the polar polarization in addition to the electronic and ionic polarization. However, the dielectric properties of these materials are strongly temperature dependent and undergo a maximum in the vicinity of the ferroelectric to paraelectric transition temperature. The microstructure and impedance characteristic of CCTO were found strongly dependent on the sintering conditions. CCTO is a property that could make the material ideal for use in capacitors. CCTO ceramics are constituted of semi-conducting grains (pure CCTO phase) and insulating grain boundary layers. Most of the investigation into CCTO, after its dielectric properties were initially reported in the year 2007, have been mainly centered around the low temperature dielectric behaviour of the material due to the dielectric anomalies that were exhibited by it in the low temperature region (Prakash *et al.*, 2007).

This stunning dielectric behaviour of CCTO is intrinsic, while other researchers claim that it arise from the internal effects such as spatial inhomogeneity in which fine particles or clusters of them are present in an otherwise homogeneous medium, contact effect and internal barrier layer capacitors (IBLC) (Sen *et al.*, 2010). The giant dielectric constants have been variously attributed to the barrier layer capacitance arising at twin boundaries, disparity in electrical properties between grain interiors and grain boundaries and, space charge at the interfaces between the sample and the electrode contacts and, polarizability contributions from lattice distortions, (V) differences in electrical properties due to internal domains, dipolar contributions from oxygen vacancies and, the role of Cu off stoichiometry in modifying the polarization mechanisms, cation disorder induced planar defects and associated inhomogeneity or nanoscale disorder of Ca/Cu substitution giving rise to electronic contribution from the degenerate e_g states of Cu occupying the Ca site contributing to the high dielectric constant. The IBLC explanation of extrinsic mechanism is comparatively widely accepted (Patra, 2009).

2.1.3 Role of Doping

The investigation in interest of using La as doping materials will be done in this research. This research is to find the effect of La doping concentration that indicates the structures of the materials and the effect in ferroelectric. By comparing a variety of study in prepared the dielectric materials, the effect of doping on various physical