PRODUCING CALCIUM CUPRUM MANGAN OXIDE ($CaCu_3Mn_4O_{12}$) VIA WET AND DRY CHEMISTRY TECHNIQUES

NURUL HIDAYAH BINTI ISMAIL

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PRODUCING CALCIUM CUPRUM MANGAN OXIDE ($CaCu_3Mn_4O_{12}$) VIA WET AND DRY 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

NURUL HIDAYAH BINTI ISMAIL

FACULTY OF MANUFACTURING ENGINEERING
2009

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

TAJUK: **PRODUCING CALCIUM CUPRUM MANGAN OXIDE ($CaCu_3Mn_4O_{12}$) VIA WET & DRY CHEMISTRY TECHNIQUES**

SESI PENGAJIAN: 2008/2009 Semester 2

Saya **NURUL HIDAYAH BINTI ISMAIL**

mengaku membenarkan Laporan PSM ini disimpan di Perpustakaan Universiti Teknikal Malaysia Melaka (UTeM) dengan syarat-syarat kegunaan seperti berikut:

1. Laporan PSM adalah hak milik Universiti Teknikal Malaysia Melaka dan penulis.
2. Perpustakaan Universiti Teknikal Malaysia Melaka dibenarkan membuat salinan untuk tujuan pengajian sahaja dengan izin penulis.
3. Perpustakaan dibenarkan membuat salinan laporan PSM ini sebagai bahan pertukaran antara institusi pengajian tinggi.
4. **Sila tandakan (√)

☐	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia yang termaktub di dalam AKTA RAHSIA RASMI 1972)
☐	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
√	TIDAK TERHAD	

Disahkan oleh:

(NURUL HIDAYAH BINTI ISMAIL)

(DR MOHD WARIKH B ABD RASHID)

Alamat Tetap:
Lot 313, Kg Jejulok Banggu,
16150 Kota Bharu,
Kelantan.

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

Tarikh: 22 MEI 2009

Tarikh: 22 MEI 2009

** Jika Laporan PSM ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh laporan PSM ini perlu dikelaskan sebagai SULIT atau TERHAD.

DECLARATION

I hereby, declared this report entitled "Producing Calcium Cuprum Mangan Oxide ($CaCu_3Mn_4O_{12}$) via Wet and Dry Chemistry Techniques" is the results of my own research as cited in references.

Signature : ....

Author's Name : Nurul Hidayah Binti Ismail

Date : 22 MEI 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 Materials) 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

In this project, the preparation of $CaCu_3Mn_4O_{12}$ is carried out via wet-chemistry and solid state reaction methods so that at the end of this study, the differences in the characteristic of the samples produced can be clarified. In addition, in solid state reaction method, the $CaCu_3Mn_4O_{12}$ preparation is done by varying the time used for calcination process in order to investigate the effect of varying that parameter on the characteristics of the product. In order to achieve the objectives of the project, the study is divided into two tasks; preparation of the $CaCu_3Mn_4O_{12}$ samples by using sol-gel and solid state reaction method and material testing on the sample produced. In sample preparation, both methods involves the same processes such as precursor preparation; mixing, stirring, drying in sol-gel method while in solid state reaction, it involves mixing and ball milling, followed by calcination, forming and sintering process. For the second task that is for sample testing, the identification of phase formation and microstructural analysis are characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) respectively, while the characterization of electrical properties is done by using impedance analyzer. The study shows that the formation of $CaCu_3Mn_4O_{12}$ phase in x-ray diffraction pattern occurs at 600°C in sol-gel sample and at 800°C in solid state reaction sample. SEM micrograph shows the microstructure of sol-gel sample contains small particle size with high grain boundaries whereas the microstructure of sample produced via solid state reaction contains large particle size. Furthermore, experimental observation and theoretical calculation done in electrical characterization clarify that the density as well as grain boundaries are significant factors determining the electrical conductivity of $CaCu_3Mn_4O_{12}$ samples. The result shows the solid state reaction sample has higher conductivity value compared to sol-gel sample. Moreover,

the result of varying the calcination time in solid state reaction shows no significant different in their phase formation, microstructure and conductivity value.

ABSTRAK

Dalam projek ini, penyediaan $CaCu_3Mn_4O_{12}$ telah dijalankan melalui teknik kimia basah dan tindak balas keadaan pepejal supaya pada penghujung kajian, perbezaan dalam sifat-sifat sampel antara kedua-dua kaedah dapat dijelaskan. Tambahan lagi, dalam teknik tindak balas keadaan pepejal, penyediaan $CaCu_3Mn_4O$ dilakukan dengan mempelbagaikan masa yang digunakan untuk proses pengkalsinan yang bertujuan untuk menyiasat kesan kepelbagaian parameter tersebut terhadap sifat-sifat produk. Untuk mencapai objektif projek, kajian dibahagikan kepada dua bahagian; penyediaan $CaCu_3Mn_4O_{12}$ menggunakan *sol-gel* dan tindak balas keadaan pepejal dan ujian ke atas sampel yang dihasilkan. . Kedua-dua kaedah melibatkan proses yang sama iaitu penyediaan *precursor*; pencampuran, pengacauan, dan pengeringan dalam kaedah *sol-gel* manakala dalam tindak balas keadaan pepejal melibatkan pencampuran dan pengisaran bebola, diikuti dengan pengkalsinan, pembentukan dan proses pensinteran. Untuk bahagian yang kedua iaitu ujian ke atas sampel, pengenalan terhadap pembentukan fasa dan analisis ke atas mikrostruktur-mikrostruktur masing-masing dicirikan melalui pembelauan sinar-X (XRD) dan Mikroskop Elektron Pengimbasan (SEM), manakala pencirian ke atas sifat-sifat elektrik dijalankan menggunakan penganalisa impedans. Kajian menunjukkan pembentukan fasa $CaCu_3Mn_4O_{12}$ dalam pola pembelauan sinar-X berlaku pada 600°C dalam sampel *sol-gel* dan 800°C dalam sampel yang dihasilkan melalui tindak balas keadaan pepejal. Mikrograph SEM menunjukkan mikrostruktur sampel *sol-gel* mengandungi partikel-partikel yang kecil dan banyak sempadan butir manakala mikrostruktur sampel yang dihasilkan melalui tindak balas keadaan pepejal mangandungi saiz partikel yang besar. Tambahan lagi, pemerhatian eksperimen dan pengiraan secara teori yang dilakukan dalam pencirian elektrik menjelaskan bahawa ketumpatan dan bilangan sempadan butir merupakan

factor-faktor yang kuat dalam menentukan kekonduksian elektrik dalam sampel $CaCu_3Mn_4O_{12}$. Keputusan menunjukkan bahawa sampel yang dihasilkan melalui tindak balas keadaan pepejal mempunyai nilai kekonduksian yang lebih tinggi berbanding sampel *sol-gel.* Selain itu, keputusan dalam mempelbagaikan masa untuk proses pengkalsinan menunjukkan tiada perubahan yang ketara dalam pembentukan fasa, mikrostruktur dan nilai kekonduksian.

DEDICATION

For all your advice and encouragement, this thesis is gratefully dedicated to my family and my friends. Thank you very much for your continuous support and effort towards the publication of this thesis.

ACKNOWLEDGEMENT

Firstly, Syukur Alhamdulillah and all praises of Allah S.W.T which lead me to accomplish this final year project (Semester II) in a course of BMFG 4923.I would like to express my big appreciation and sincere gratitude to my supervisor, Dr. Mohd Warikh Bin Abd Rashid and to my examiner Pn. Intan Sharhida Bt Othman for their encouragement, ideas and support and for their irreplaceable unfailing patience, guidance throughout this project research. Their knowledge and experience really inspired and spurred myself. Last but least, to technician lab members and whom those involve in completing this projects who have been helping together to give idea and any flourishing suggestions, a special thanks for their sincerely and co-operations. Also big thanks for my family as well as friends without their wise counsel and dependable assistance this project research would not have been possible. Thank you very much.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

$CaCu_3Mn_4O_{12}$	-	Calcium Cuprum Mangan Oxide
TMOs	-	Transition Metal Oxides
CCMO	-	Calcium Cuprum Mangan Oxide
CuO	-	Copper (II) Oxide
$CaCO_3$	-	Calcium Carbonate
$Ca(OH)_2$	-	Calcium Hydroxide
MnO_2	-	Manganese Oxide
$KClO_3$	-	Potassium Chlorate
$Mn(NO_3)_2.4H_2O$	-	Manganese Nitrate Tetrahydrate
MR	-	Magnetoresistance
GMR	-	Giant Magnetoresistance
CMR	-	Colossal Magnetoresistance
FCC	-	Face Center Cubic
XRD	-	X-Ray Diffraction
SEM	-	Scanning Electron Microscopy
EDS	-	Energy Dispersive X-Ray Spectroscopy
RT	-	Room Temperature
σ	-	Conductivity
ICDD	-	International Center for Diffraction Data

CHAPTER 1

INTRODUCTION

1.1 Introduction to Calcium Cuprum Mangan Oxide ($CaCu_3Mn_4O_{12}$)

Materials science and engineering have been at the frontier of technological advancement since the bronze and iron ages. The present information age relies on the development of 'smart' and 'smaller' magnetic materials for memory, data storage, processing and probing. These magnetic materials can be divided into numerous categories, depending on their origin and applications. One prime example is the transition metal oxides (TMOs) having perovskite (ABO_3 type) structure, which form a vitally important class of materials from the point of view of fundamental physics as well as technological applications (Siwach *et al.*, 2008).

.

In this project, the research is carried out on one of the perovskite compounds of ABO_3 type structure which is $CaCu_3Mn_4O_{12}$ (CCMO). This compound which is also an electroceramic material was first reported by Chenavas *et al.* Among the rare ferromagnetic and half-metallic oxides, the complex perovskite $CaCu_3Mn_4O_{12}$ is interesting because it exhibits a high magnetoresistive property (Zeng *et al.*, 1999a). $CaCu_3Mn_4O_{12}$ belongs to the wide $AA'_3B_4O_{12}$ perovskite family phase; where A and B consists of different cations. In all these compounds, the crystal symmetry is cubic (space group *Im*3) with a doubling of the ideal ABO_3 perovskite cell. The superstructure is due to the ordering of the A and A' ions and the distortion of the oxygen sublattice, which leads to a three-dimensional network of strongly tilted BO_6 octahedral sharing corners (Zeng *et al.*, 1999a).

The various physical properties of several manganese perovskite materials have recently been under very active investigation because of the interesting interplay between their magnetic, electronic and structural properties. Most of these phenomena are related to magnetic, charge and orbital orderings of interpenetrating sublattices of Mn^{3+} and Mn^{4+} ions in the material. $CaCu_xMn_{7-x}O_{12}$ family is one of the very interesting classes of perovskite-type manganite materials. The interest on this group of compounds has grown since the discovery of low-field magnetoresistance in $CaCu_3Mn_4O_{12}$. The magnetoresistance of $CaCu_3Mn_4O_{12}$ at low fields around room temperature (RT) is remarkably large and stable with temperature as compared with other CMR (colossal magnetoresistance) manganite materials, which is very important in potential technical applications. $CaCu_3Mn_4O_{12}$ is also interesting from its fundamental physical properties. The crystal lattice contains only Mn^{4+} ions, so the magnetoresistance cannot be due to the double exchange mechanism which requires charge transfer along the Mn^{3+}−O−Mn^{4+} bonds (Przenioslo *et al*., 2004b).

Magnetoresistance (MR) is the change of electric resistance in the application of magnetic field. Recently, many of the researchers have found a giant magnetoresistance material such as $Pr_{0.7}Sr_{0.04}Ca_{0.26}MnO_3$ (Maignan *et al*., 1995), LaLCaMnO (L = Y, Gd) (Martinez *et al.*, 1996), nanostructure Co/Cu/Co (Sakrani *et al*., 2007) and $CaCu_3Mn_4O_{12}$ (Sanchez-Benitez *et al.*, 2006). $CaCu_3Mn_4O_{12}$ have received much attention because of their giant magnetoresistance (GMR) and charge ordering properties. GMR property of these materials finds potential applications in the field of magnetic sensors, in memory applications and in prototype disc drives employing read-head technology.

Recently, the complex perovskite $CaCu_3Mn_4O_{12}$ has attracted the attention of the CMR (Colossal Magnetoresistance) community: it is semiconducting, orders ferromagnetically at 355 K and shows good MR response at room temperature and low fields. This compound and its derivatives are suitable for practical applications due both to the magnitude and the thermal stability of their MR around room temperature (Sanchez-Benitez *et al.*, 2004).

1.2 Problem Statement

There is a wide number of publications exist in the literature on the synthesis of $CaCu_3Mn_4O_{12}$. This material can be synthesized by either via conventional solid state reaction or wet chemical method such as co-precipitation method, deposition-precipitation, impregnation, sol-gel, hydrothermal and urea methods. From the previous research, it is noted that the synthesis route of $CaCu_3Mn_4O_{12}$ have rarely been employed by using solid state reaction. This is because the powder prepared through this method is less active in sintering due to high calcination temperature used, and the homogeneity of the powder is often insufficient due to degree of mixing. However, the conventional method has the advantages of relatively low number of processing steps and low process cost (Dao *et al.*, 1992). Low process cost is due to fewer raw materials used in conventional method compared to wet-chemistry.

Producing of $CaCu_3Mn_4O_{12}$ by using wet-chemistry technique gives a lot of advantages. Through wet-chemistry technique, quality of material produced is guarantee. The wet chemical preparation method allows mixing of the components at a molecular level, resulting in materials with high compositional homogeneity and lower sintering temperature (Guohong *et al*, 2006). Besides, the powder prepared by the wet chemical method has better sintering activity (Dao *et al.*, 1992). Wet chemical preparation such as sol-gel processing also affords greater control over the formation of particular phase and higher purity of the formed phase (Shinji *et al.*, 2002). Furthermore, the wet chemical method has another advantages including preparing crystalline oxides with narrow grain size distribution, producing highly $CaCu_3Mn_4O_{12}$ fine powders without calcination at high temperature and the resulted particles form low agglomeration (Pusit *et al.*, 2004). In contrast with wet chemical preparation, the traditional mixed-oxide solid-state reaction method requires a high calcination temperature, usually leading to poor microstructure and properties due to coarsening and agglomerating (Guohong *et al*, 2006).

In this study, the producing of $CaCu_3Mn_4O_{12}$ will be accomplished by using both wet-chemistry method and conventional solid state reaction method. This is in order to study the characteristic of the samples produced through both methods.

1.3 Objectives

The objectives of this project are:

(a) To produce $CaCu_3Mn_4O_{12}$ by using wet and dry chemistry techniques.
(b) To study the phase analysis, microstructural analysis and electrical properties of $CaCu_3Mn_4O_{12}$ prepared through both methods.

1.4 Scope of the Study

In this project, there are two synthesize techniques that will be applied to produce complex manganite perovskite $CaCu_3Mn_4O_{12}$ which are wet-chemistry technique that is sol-gel method and solid state reaction method. Two tasks will be carried out in this study; sample preparation and sample testing. In sample preparation, the first method that will be employed to produce $CaCu_3Mn_4O_{12}$ is sol-gel method and the second one is solid state reaction method. For solid state reaction method, two experiments will be conducted to produce $CaCu_3Mn_4O_{12}$ where the time for calcination process for both experiments is varied into 1½ hours and 5 hours. This is in order to see the effect of varying the time for calcination towards the sample produced.

In the first method which is sol-gel method, the compound will be prepared by mixing the stoichiometric amount of the compositions of calcium carbonate, $CaCO_3$ (99%, Aldrich), copper oxide, CuO (99.9%, Aldrich), and manganese nitrate tetrahydrate, $Mn(NO_3)_2.4H_2O$ (49.7% w/w aqueous solution, Aldrich). This mixture then will be dissolved in nitric acid (35%, Aldrich), citric acid (99.8%, Aldrich), and ethylene glycol (99%, Aldrich) and hence will be evaporated and dried which then followed by calcination, forming by pressing and sintering process.

For the second method, solid state reaction, the $CaCu_3Mn_4O_{12}$ producing process involves the mixing of calcium hydroxide, $Ca(OH)_2$, copper oxide, CuO, manganese oxide, MnO_2 and the oxidizing agent that is $KClO_3$. After preparing 30g of precursor powder, the powder then is divided into two parts where one sample part will undergo calcination at 800°C for 1½ hours and another one part of powder will undergo calcination at the same temperature but for 5 hours. Then, after calcination, the powder will be ground to finite powder and formed into pellet shape by using die pressing. Sintering process of the sample pellet is carried out at 1000°C in furnace afterwards. Lastly, the samples are washed several times with deionized water under ultrasonic conditions to dissolve KCl.

For sample testing task, 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 performed by using impedance analyzer.