UNIVERSITI TEKNIKAL MALAYSIA MELAKA

PRODUCING CALCIUM COPPER MANGANESE OXIDE via WET CHEMISTRY

Thesis submitted in accordance with the partial requirements of the Universiti Teknikal Malaysia Melaka for the Degree Bachelor of Manufacturing Engineering (Engineering Materials) with Honors

By:

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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*). The members of the supervisory committee are as follow:

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ABSTRACT

Preparation of $CaCu_3Mn_4O_{12}$ (CCMO) ceramic is carried out via wet chemistry method. The wet chemistry method is employed as it has many advantages such as higher homogeneity and finer microstructure compared to conventional solid-state reaction. In this study, the wet chemistry technique that will be employed is the sol-gel method. $CaCO_3$ (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) is mixed and stirred to produce $CaCu_3Mn_4O_{12}$ which then subjected to evaporation, calcination, forming and sintering process. The compound is studied in terms of its phase transformation, electrical properties and hardness properties. Phase transformation is tested using X-Ray Diffraction (XRD) analysis shows phase evolution with different sintering parameters. The electrical properties analysis conducted using Potentiostat Machine yield conductivity value between 2.86×10^{-6} to 9.04×10^{-5}, which is much lower compared to solid-state results from previous study. Effect of sintering and calcination parameters on electrical conductivity is discussed. Hardness test is done using Vickers Microhardness Tester. Hardness value for sintered body is found to be influenced by calcination and sintering parameters.

ABSTRAK

Penghasilan $CaCu_3Mn_4O_{12}$ (CCMO) dilakukan menggunakan kaedah kimia basah. Kaedah kimia basah mempunyai pelbagai kelebihan berbanding kaedah tindakbalas pepejal seperti struktur mikro lebih baik dan kesamarataan fasa campuran. Dalam kajian ini, kaedah basah yang digunakan adalah kaedah sol-gel. $CaCO_3$ (99%, Aldrich), Copper Oxide, CuO (99.9%, Aldrich), dan Manganese Nitrate Tetrahydrate, $Mn(NO_3)_2.4H_2O$ (49.7% w/w campuran akues, Aldrich) akan dicampur bersama dan digaul yang mana kemudian akan dikeringkan dan dilakukan proses kalsinasi, pembentukan dan pensinteran. Bahan yang terhasil akan dikaji dari segi perubahan fasa, kekerasan dan sifat elektrik. Kajian terhadap perubahan fasa telah dilakukan menggunakan mesin X-Ray Diffraction (XRD) menunjukkan perubahan fasa dengan keadaan pensinteran yang berbeza. Kajian sifat elektrik dijalankan menggunakan mesin Potentiostat memperolehi nilai pengaliran elektrik di antara 2.86×10^{-6} hingga 9.04×10^{-5} yang mana nilai tersebut jauh lebih rendah daripada kaedah tindakan pepejal. Kesan keadaan pengkalsinan dan pensinteran terhadap pengaliran eletrik turut dibincangkan. Ujian kekerasan dilakukan menggunakan alat ujian Vickers Microhardness member gambaran kesan pengkalsinan dan pensinteran terhadap kekerasan bahan yang dihasilkan.

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LIST OF ABBREVIATIONS

CCMO   -   Calcium Copper Manganese Oxide

CCTO   -   Calcium Copper Titanate Oxide

GMR   -   Giant Magnetoresistance

ICDD   -   International Centre for Diffraction Data

LCMO   -   Lanthanum Copper Manganese Oxide

MR   -   Magnetoresistance

SEM   -   Scanning Electron Microscope

XRD   -   X-Ray Diffraction

CHAPTER 1
INTRODUCTION

1.1   Background

Material science and engineering is one of the most important of the engineering disciplines as it impacts nearly all the traditional field of engineering. The disciplines is concerned with the structure and properties of materials used in modern technology. This means that materials science and engineering is at the forefront of high technology for the simple reason that advancement in technology is the direct result of advances in materials. This phenomenon is no recent but has been going 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.

Perovskite-kinds of oxides $ACu_3M_4O_{12}$ have been increasingly attractive for their colossal magnetoresistance effects in $CaCu_3Mn_4O_{12}$ (CCMO) and $LaCu_3Mn_4O_{12}$ (LCMO) as well as high dielectric constant in $CaCu_3Ti_4O_{12}$ (CCTO) (Li *et al*., 2005). $CaCu_3Mn_4O_{12}$ is one of electroceramic materials that exhibit great magnetoresistance properties at a temperature close to room temperature which is 355K compared to other electroceramic materials (Zeng *et al*., 1999, Sanchez-Benitez, 2006). Although $CaCu_3Mn_4O_{12}$ was first discovered by Chevanas *et al*., on 1975, further research of this material has only been done in the late 1990's pioneered by Zeng *et al*., (1999).
$CaCu_3Mn_4O_{12}$ is from ABO_3 type and has the general formula of $AA'_3B_4O_{12}$ (family phase) having a perovskite structure and containing different sizes of A and B cation. In

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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*., 1999).

Vigorous investigation on various physical properties of several manganese perovskite has been done recently because of the interesting interplay between their magnetic, electronic and structural properties. One of the most interesting properties of $CaCu_3Mn_4O_{12}$ is the giant magnetoresistance (GMR) properties produced by the compound. GMR property of the material finds potential applications in the field of magnetic sensors, in memory applications and in prototype disc drives employing read-head technology.

1.2   Problem Statement

The synthesis of nanoscale particles has received considerable attention amongst researchers judging from numerous publications on the topic. $CaCu_3Mn_4O_{12}$ can be synthesized by either via solid state reaction or wet chemical reaction. The most common wet chemistry method for synthesizing $CaCu_3Mn_4O_{12}$ includes sol-gel method, hydrothermal process and co-precipitation method. Even though there are various processing route to synthesis $CaCu_3Mn_4O_{12,}$ solid state reaction is the less common method used judging from the number of publication on the matter. Solid state reaction provides low cost processing because it uses fewer initial materials compared to wet chemistry techniques. However, materials prepared using solid state reaction suffers from inhomogeneity and other limitations (Jin, *et al.*, 2007). It is well known that electrical properties can be considerably improved when ceramic is of homogeneous microstructure. The process also needs tedious works, requires long reaction period, high calcination temperature and the probability that secondary phase might appear in the ceramic (Liu, L. *et al.*, 2008). This agrees with Ni *et al*., (2006) who reported that a

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$CaCu_3Ti_4O_{12}$ produced via solid state reaction sintered at 1025-1125°C for 3 hours yields a ceramic with $CaCu_3Ti_4O_{12}$ as major compound but 1.92 wt% Cu_2O secondary phase was detected. In addition, the secondary phase precipitates with increasing temperature of sintering. Wet chemistry techniques have been attracting the attention of many chemist and material researchers and have been recognized as another potential route to better materials and ceramics (Klabunde, 2001). Producing $CaCu_3Mn_4O_{12}$ using wet chemistry technique offers a lot of advantages. Among the advantages of wet chemistry techniques are excellent chemical stoichiometry, compositional homogeneity and lower crystallization temperature due to mixing of liquid precursor at molecular level (Liu, L. *et al*., 2007). In comparison to solid state reaction where migration of ions to interfaced-grain boundaries involve complete disruption of structures, solution reaction of molecular precursor typically involves breaking of one atom and formation of another, sometimes simultaneously (Liu, M. *et al*., 2006). Wet chemistry synthesis of $CaCu_3Mn_4O_{12}$ takes in various processing route including hydrothermal and co-precipitation but the most common and probably the most reliable method is the sol-gel technique (Schwarz, A. *et al*., 2004). Sol-gel approach delivers good results even when a synthesis of complex structures are required (Varin, A. *et al*., 2009). Sol-gel technique enables homogeneity in the scale of nanometer, inducing fine microstructure of the sintered ceramics (Jin *et al*., 2007). Furthermore, sol-gel reaction in mixing of components at molecular scale occurs at lower temperature avoids phase transformation of the ceramic (Liu, M. *et al*., 2006). The small particle sizes obtained by this technique enhance particle contact and facilitate reaction (Zeng *et al*., 1999). In this study, $CaCu_3Mn_4O_{12}$ will be produced via sol-gel processing route and the product yielded will be studied in terms of its microstructure, phase transformation and electrical properties. It is expected that the sample produced have a fine microstructure, highly homogenous and exhibit magnetic behavior.

1.3 Objective

The objectives of this project are:

a) To produce $CaCu_3Mn_4O_{12}$ by using wet chemistry techniques (sol-gel synthesis).

b) To study the phase analysis, hardness properties and electrical properties of $CaCu_3Mn_4O_{12}$ prepared through the method.

1.4 Scope of Study

This study focuses on the production of $CaCu_3Mn_4O_{12}$ using the sol-gel method. It involves the investigation of phase transformation, hardness and electrical properties of $CaCu_3Mn_4O_{12}$ produced by the method. Phase analysis will be conducted using the X-Ray Diffraction (XRD), where hardness analysis will be conducted using Vickers Micro-hardness Test equipment. The electrical properties of the produced $CaCu_3Mn_4O_{12}$ will be tested using Potentiostat Machine.

1.5   Research Flowchart

Figure 1.1: Flowchart of Research
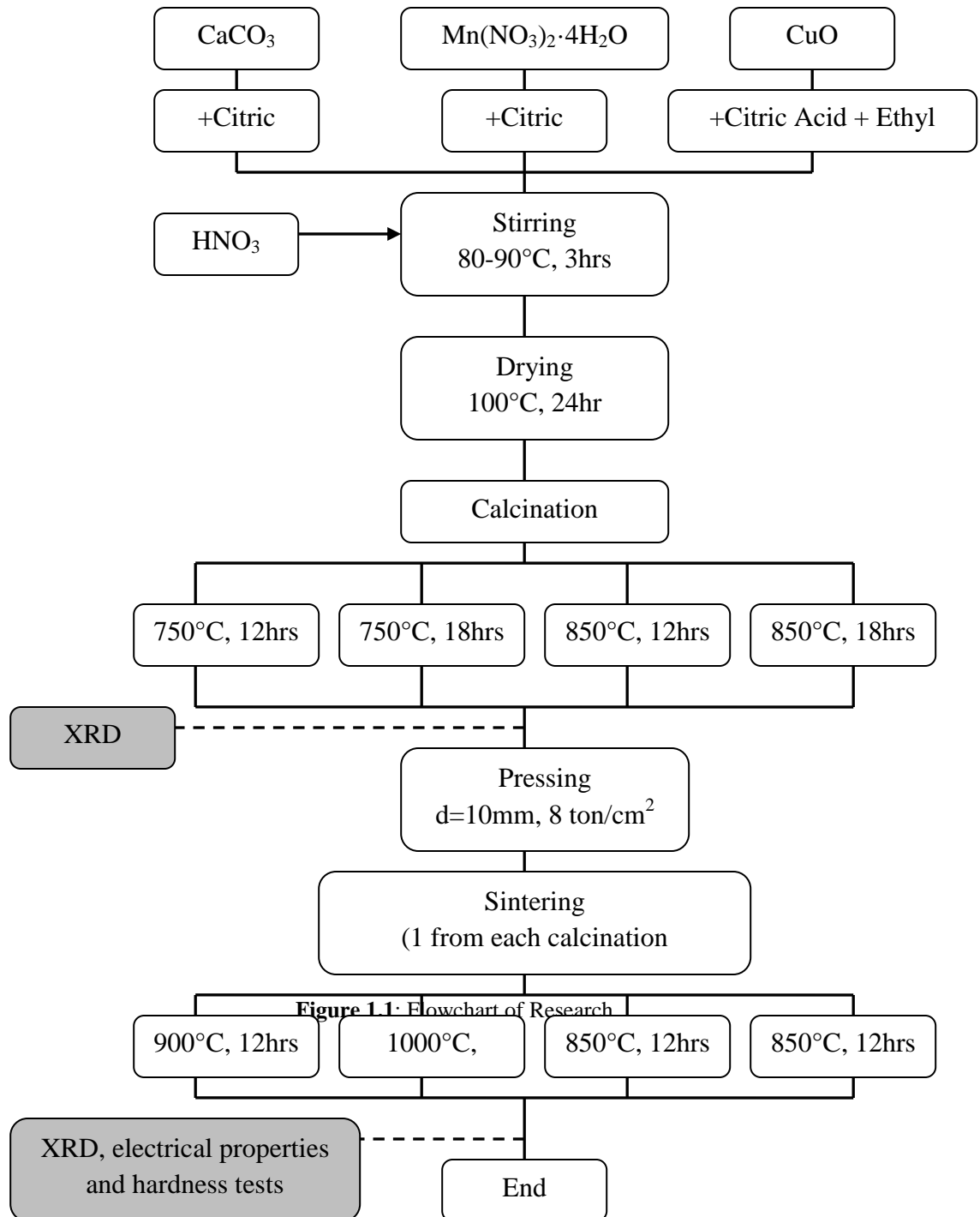
CHAPTER 2
LITERATURE REVIEW

2.1   Electroceramic Materials

Ceramics materials nowadays are used in many electronic applications including communications, energy conversion and storage, electronics and automation. These ceramic materials are classified as electroceramic materials to distinguish them from other functional ceramics. The first use of ceramics in the electrical industry took advantage of their stability when exposed to extremes of weather and to their high electrical resistivity. Whilst the obvious characteristic of ceramics in electrical use in the first half of the twentieth century was that of chemical stability and high resistivity, it was evident that the possible range of properties was extremely wide. For example, the ceramic form of the mineral magnetite, known to the early navigators as 'lodestone', was recognized as having a useful electrical conductivity in addition to its magnetic properties (Moulson and Herbert, 2003).

Electroceramic can further be classified into several other distinct groups based on their properties, namely magnetic ceramic, semiconductor, electro-optic ceramic, superconductor ceramic, piezoelectric, pyroelectric and ferroelectric. The substance group of magnetic ceramic is the complex oxide, generally called ferrite, which contains trivalent iron as the main ingredient (Somiya *et al.*, 2003). High solid solubility also enables modifying on magnetic property on the magnetic ceramics. Magnetic ceramics are used in many applications, not only magnetic but also medical uses such as magnetic recording, magnetic fluid, magnetic resonance imaging and drag carrier.

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Semiconductors are a group of materials that have electrical conductivities intermediate between those of metals and insulators. It is significant that the conductivity of these materials can be varied considerably by changes in temperature, optical excitation, and impurity content (Streetman, 2002). The valence band of semiconductors are fully filled but the band gap between the valence and conduction band is narrow, enabling electrons in the valence band to excite to the conduction band to carry electrical charges upon getting energy. Conductivity of semiconductors can be controlled according to the impurities or dopants. This variability of electrical properties makes possible the wide range of modern electronic devices such as diodes and transisors.

Electro-optic material is used as a medium to change the electric information to optic information which can be done through electrical order. The electro-optic changes the refractive index that functions as electric field source. For a ceramic to be useful as an electro-optic material it must, of course, be transparent. Ceramic dielectrics are mostly white and opaque, though thin sections are usually translucent. This is due to the scattering of incident light. Scattering occurs because of discontinuities in refractive index which will usually occur at phase boundaries (including porosity) and, if the major phase itself is optically anisotropic, at grain boundaries (Moulson and Herbert, 2003).

The history of superconductivity has its origins in the experiments of H. Kamerlingh Onnes who in 1908 succeeded in liquefying helium and reaching temperatures down to 1 K. In 1911, while pursuing the study of the electrical resistivity of metals at these very low temperatures, he discovered superconductivity in mercury (Moulson and Herbert, 2003). Since then, superconductivity was found in many other metals and in an extremely large number of metallic alloys and compounds. An abrupt change in metallic phase into the nature of conductor has been observed on mercury at temperature change of 4K. Stable cooling to achieve superconductivity for the conventional metallic superconductors is possible only by using liquid helium (4.2K)

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which makes it costly and complex. Later, Bednorz and Mueller discovered high temperature superconductivity at around 35K in La-Ba-Ca-Cu-O system (Somiya *et al.*, 2003). Since then, various researches were done in ceramic oxide superconductors and other material families were observed to exhibit superconductivity at relatively high temperature such as $YBa_2Cu_3O_y$, $Bi_2Sr_2Ca_2Cu_3O_x$ and $Tl_2Ba_2Ca_2Cu_3O_x$ (Somiya *et al.*, 2003).

All materials undergo a small change in dimensions when subjected to an electric field. If the resultant strain is proportional to the square of the field it is known as the electrostrictive effect. Some materials show the reverse effect; the development of electric polarization when they are strained through an applied stress. These are said to be piezoelectric. To a first approximation the polarization is proportional to the stress and the effect is said to be 'direct'. Piezoelectric materials also show a 'converse' effect, for example, the development of a strain x directly proportional to an applied field (Moulson and Herbert, 2003).

Pyroelectricity results from the temperature dependence of the spontaneous polarization of polar materials and is therefore shown by ferroelectric materials whether they are single-domain single crystals or poled ceramics. Because a change in polarization in a solid is accompanied by a change in surface charges, it can be detected by an induced current in an external circuit. If the pyroelectric material is perfectly electrically insulated from its surroundings, the surface charges are eventually neutralized by charge flow occurring because of the intrinsic electrical conductivity of the material. Since pyroelectric materials are polar, they are also piezoelectric, and the strain resulting from thermal expansion will result in the development of a surface charge. However, this is a small effect that seldom exceeds 10% of the primary pyroelectric effect (Moulson and Herbert, 2003).

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2.2 Perovskite Structure

Perovskite was originally named for CaTiO3 minerals discovered by Rose in 1839 after the then Russian Minister of Lands, L.A. Perovsky. The name perovskite has been later used for designation of a large ABO3 perovskite family (Lemanov *et al*., 1999). Moulson and Herbert (2003) stated that perovskite-type crystals can be viewed as consisting of a simple cubic array of corner-sharing octahedral MO_6 groups with all the interstices filled by divalent ions.

The perovskite-like structure is a ternary compound of formula ABO_3 that A and B cations differ in size. It is considered an FCC- derivative structure in which the larger A cation and oxygen together form an FCC lattice while the smaller B cation occupies the octahedral interstitial sites in the FCC array. There is only the oxygen being B cation's nearest neighbor. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes and the large cation filling the dodecahedral holes (Hsiao-Lin *et al.,* 2002). The example of unit cell of perovskite cubic structure for $BaTiO_3$ is shown below in Figure 2.1.
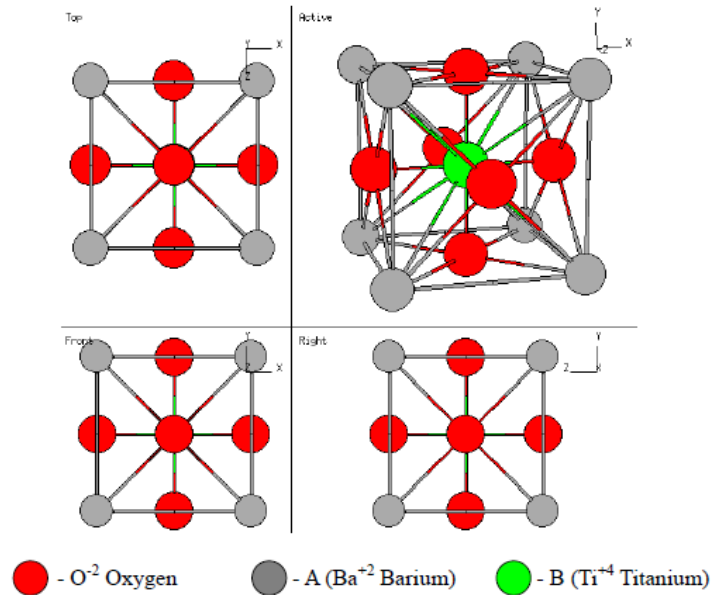

● - O^{-2} Oxygen   ● - A (Ba^{+2} Barium)   ● - B (Ti^{+4} Titanium)

Figure 2.1: Perovskite Structure (Hsiao-Lin *et al*., 2002)

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