UNIVERSITI PUTRA MALAYSIA

EFFECTS OF STRONTIUM SUBSTITUTION ON STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF POLYCRYSTALLINE AND NANOCRYSTALLINE La0.67(Ca1-xSrx)0.33MnO3

CHANG SEN CHOUNG

FS 2014 59

EFFECTS OF STRONTIUM SUBSTITUTION ON STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF POLYCRYSTALLINE AND NANOCRYSTALLINE $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$

By

CHANG SEN CHOUNG

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Master of Science

April 2014

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

EFFECTS OF STRONTIUM SUBSTITUTION ON STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF POLYCRYSTALLINE AND NANOCRYSTALLINE $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$

By

CHANG SEN CHOUNG

April 2014

Chairman: Abdul Halim Shaari, PhD
Faculty: Science

This research is aimed at studying the influences of Sr ions substitution on the structural, electrical and magnetic properties of polycrystalline and nanocrystalline $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$. The differences between polycrystalline and nanocrystalline samples were discussed.

The polycrystalline and the nanocrystalline $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ for $0 \leq x \leq 1.0$ were synthesized via the solid-state reaction and the sol gel based polymerizable complex method respectively. The X-Ray Diffraction (XRD) measurements were carried out to determine the crystal structure properties. The XRD spectrums revealed that the structural transition from orthorhombic structure to rhombohedra structure took place when the Ca ions were gradually substituted by the Sr ions in both polycrystalline and nanocrystalline samples. The lattice parameters, Mn-O bond length and Mn-O-Mn bond angle were obtained by the Rietveld refinement method. The microstructures for both polycrystalline and nanocrystalline samples were obtained from the Scanning Electron Microscope (SEM). The grain sizes were found in the ranges of 2.83 μm - 8.78 μm and 35.72 nm - 45.38 nm for polycrystalline samples and nanocrystalline samples respectively.

The temperature dependences of resistivity and magnetoresistance (MR) were measured by the four point probe method at variable magnetic field range of 0 T - 1 T for both polycrystalline and nanocrystalline samples. The metal-insulator transition temperature (T_p) for polycrystalline samples increased with the substitution of Sr ions. However, the nanocrystalline samples with high surface to volume ratio showed that its T_p varied with the grain size. The intrinsic MR around the T_p and the extrinsic MR at $T \leq T_p$ were observed in polycrystalline samples. The substitution of Sr ions shifted the intrinsic MR of polycrystalline samples towards higher temperature but lowering its magnitude whereas the intrinsic MR of nanocrystalline samples were suppressed and left behind the extrinsic MR at low temperature. The electrical transport properties for both polycrystalline and nanocrystalline samples were explained by the double exchange

interaction within the grain and the spin-polarized tunneling mechanism across the grain boundaries. The highest MR values were found to be -26.79% for polycrystalline $x = 0.0$ at 244 K and -23.37% for nanocrystalline $x = 0.0$ at 80 K. At room temperature, the highest MR for polycrystalline samples and nanocrystalline samples were found to be -8.45% at $x = 0.4$ and -4.19% at $x = 1.0$ respectively.

The field dependences of magnetization for both polycrystalline and nanocrystalline samples were carried out by the Vibrating Sample Magnetometer (VSM). The magnetization increased with the Sr ion substitution for the polycrystalline and nanocrystalline samples due to the increase of the Mn-O-Mn bond angle. The nanocrystalline samples have lower magnetization than that of the polycrystalline samples due to the loss of long-range ferromagnetic ordering in the nanocrystalline samples.

Abstrak tesis yang dikemukakan kapade Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Sarjana Sains

KESAN PENGGANTIAN STRONTIUM PADA SIFAT STRUKTUR, ELEKTRIK DAN MAGNET BAGI POLIHABLUR DAN NANOHABLUR $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$

Oleh

CHANG SEN CHOUNG

April 2014

Pengerusi: Abdul Halim Shaari, PhD
Fakulti: Sains

Tujuan penyelidikan ini adalah untuk mengaji kesan penggantian ion Sr pada sifat struktur, magnet and elektrik bagi polihablur and nanohablur $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$. Perbezaan antara polihablur dan nanohablur bagi sampel $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ telah dibincang dalam tesis ini.

Polihablur dan nanohablur bagi $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ dengan $0 \leq x \leq 1.0$ telah disintesis melalui kaedah tindak balas keadaan pepejal and kaedah "sol-gel" melalui pempolimeran kompleks masing-masing. Pengukuran belauan sinar-x (XRD) telah dilaksanakan untuk menentukan sifat struktur hablur. Spektrum XRD menunjukkan bahawa perubahan struktur daripada struktur orthrombik kepada struktur rombohedra berlaku apabila ion Ca diganti dengan ion Sr secara beransur-ansur bagi sampel polihablur dan nanohablur. Parameter kekisi, panjang ikatan Mn-O dan sudut ikatan Mn-O-Mn diperolehi daripada kaedah Rietveld. Mikrostruktur bagi sampel polihablur dan nanohablur diperolehi daripada mikroskop imbasan elektron (SEM). Saiz butiran didapati dalam lingkungan 2.83 μm - 8.78 μm dan 35.72 nm - 45.38 nm bagi sampel polihablur dan sampel nanohablur masing-masing.

Kerintangan elektrik dan magnetorintangan (MR) melawan suhu bagi sampel polihablur dan nanohablur telah diukur dengan menggunakan kaedah penduga empat titik pada medan magnet dalam lingkungan 0 T - 1 T. Suhu peralihan logam-penebat (T_p) bagi sampel polihablur didapati meningkat dengan menambahkan penggantian ion Sr. Walau bagaimanapun, sampel nanohablur yang mempunyai nisbah permukaan terhadap isipadu yang tinggi menunjukkan bahawa T_p berubah dengan saiz butiran. MR intrisik pada sekeliling T_p dan MR ekstrinsik pada $T \leq T_p$ telah diperhati dalam sampel polihablur. Penggantian ion Sr menyebabkan MR intrinsik bagi sampel polihablur beralih ke suhu tinggi tetapi magnitudnya menurun. Manakala, MR intrinsik bagi sampel nanohablur didapati ditindaskan dan hanya MR ekstrinsik yang dikekalkan pada suhu rendah. Sifat pergerakan elektrik bagi sampel polihablur dan nanohablur boleh dijelaskan dengan tindakbalas tukarganti gandaan dalam butiran dan mekanisme penerowongan spin-

terkutub melintasi sempadan butiran. Nilai MR yang tertinggi adalah -26.79% untuk polihablur x = 0.0 pada suhu 244 K dan -23.37% untuk nanohablur x = 0.0 pada suhu 80 K. Pada suhu bilik, nilai MR yang tertinggi untuk sampel polihablur dan sampel nanohablur adalah -8.45% pada x = 0.4 dan -4.19% pada x = 1.0 masing-masing.

Pemagnetan terhadap medan magnet telah dijalankan dengan menggunakan magnetometer getaran sampel (VSM). Pemagnetan bagi sampel polihablur dan nanohablur didapati meningkat dengan penambahkan penggantian ion Sr kerana sudut ikatan Mn-O-Mn meningkat. Nilai pemagnetan bagi sampel nanohablur didapati lebih rendah daripada nilai pemagnetan bagi sampel polihablur disebabkan oleh kehilangan susunan feromagnet berjulat panjang dalam sampel nanohablur.

ACKNOWLEDGEMENTS

First of all, I would like to thank and express my deepest gratitude and appreciation to my supervisor, Prof Dr. Abdul Halim Shaari for his invaluable advice, guidance, patience and support throughout this project. It is really my pleasure for having Prof Dr. Abdul Halim Shaari as my supervisor for this project.

In addition, I would like to thank and appreciate to Prof Dr. Zainal Abidin Talib and Dr. Lim Kean Pah for willing to be part of my supervisory committee members and for their guidance and assistance throughout this project.

Last but not least, I would like to give my special thanks and appreciation to all other UPM staffs and to my friends who either directly or indirectly helped me towards the success of this project.

I certify that a Thesis Examination Committee has met on 28 April 2014 to conduct the final examination of Chang Sen Choung on his thesis entitled "Effects of Strontium Substitution on Structural, Electrical and Magnetic Properties of Polycrystalline and Nanocrystalline $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Thesis Examination Committee were as follows:

Chen Soo Kien, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Jumiah binti Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Halimah binti Mohamed Kamari, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Roslan Abd. Shukor, PhD
Professor
Universiti Kebangsaan Malaysia
Malaysia
(External Examiner)

____
NORITAH OMAR, PhD
Associate Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 23 June 2014

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Abdul Halim Shaari, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Zainal Abidin Talib, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Lim Kean Pah, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

Declaration by Graduate Student

I hereby confirm that:

- this thesis is my original work;
- quotations, illustrations and citations have been duly referenced;
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions;
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia, as according to the Universiti Putra Malaysia (Research) Rules 2012;
- written permission must be obtained from supervisor and the office of Deputy Vice-Chancellor (Research and Innovation) before thesis is published (in the form of written, printed or in electronic form) including books, journals, modules, proceedings, popular writings, seminar papers, manuscripts, posters, reports, lecture notes, learning modules or any other materials as stated in the Universiti Putra Malaysia (Research) Rules 2012;
- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity is upheld as according to the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) and the Universiti Putra Malaysia (Research) Rules 2012. The thesis has undergone plagiarism detection software.

Signature: ______________________ Date: _______________

Name and Matric No: Chang Sen Choung, GS24993

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

Signature:______________________
Name of
Chairman of
Supervisory
Committee: Abdul Halim Shaari, PhD

Signature:______________________
Name of
Member of
Supervisory
Committee: Zainal Abidin Talib, PhD

Signature:______________________
Name of
Member of
Supervisory
Committee: Lim Kean Pah, PhD

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

ABS	Anti-Lock Brake System
AF	Antiferromagnetic
CA	Citric Acid
CAF	Canted Antiferromagnetic
CMR	Colossal Magnetoresistance
CNI	Spin-Canted Insulator
CO	Charge/Orbital Ordering
DTA	Differential Thermal Analysis
EDX	Energy-Dispersive X-Ray Spectroscopy
EG	Ethylene Glycol
FESEM	Field Emission Scanning Electron Microscope
FI or FMI	Ferromagnetic Insulator
FM or FMM	Ferromagnetic Metal
GMR	Giant Magnetoresistance
LFMR	Low Field Magnetoresistance
MI	Metal Ion
MR	Magnetoresistance
MRAM	Magnetoresistive Random Access Memory
PI or PMI	Paramagnetic Insulator
PM	Paramagnetic Metal
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
VPSEM	Variable Pressure Scanning Electron Microscope
VSM	Vibrating Sample Magnetometer
XRD	X-Ray Diffraction
$\langle r_A \rangle$	Average A-site ionic radius
ρ	Resistivity
G	Correction Factor
V	Voltage
V	Unit Cell Volume
T_C	Ferromagnetic-Paramagnetic Transition Temperature or Curie Temperature
T_p	Metal-Insulator Transition Temperature
T_N	Nell Temperature
I	Current
n	Integer Number
λ	wavelength of X-Ray
d_{hkl}	Interplaner Distance of (hkl) Planes
θ	Angle between Incident Ray and (hkl) Plane
t	Thickness of a Slice
T_2	Thickness Factor
$F(t,c)$	Additional Correction Factor depending on both thickness and contour
C	Contour Factor

emf	Electromotive Force
N	Number of Wire turns
s	Time
B	Magnetic Field
A	Coil Turn Area
ϑ	Angle between B Field and the Direction Normal to the Coil Surface
r_{A}	Ionic Radius of A-site Ion
r_B	Ionic Radius of B-site Ion
r_{O}	Ionic Radius of Oxygen Ion
r_{Mn}	Ionic Radius of Manganese Ion
$d_{\mathrm{A\text{-}O}}$	Distance between A-Site Ion and Oxygen Ion
$d_{\mathrm{Mn\text{-}O}}$	Distance between Manganese Ion and Oxygen Ion
t_e	Effective Transfer Integral
t_0	Normal Transfer Integral
θ_s	Angle between the Two Spin Direction
f	Goldschmidt Tolerance Factor
K	Constant Depending on the Grain Shape
β_{Size}	Full Width at Half Maxima of XRD Peak
R_H	Resistance or Resistivity in the Present of External Magnetic Field
R_0	Resistance or Resistivity in the Absence of External Magnetic Field

CHAPTER 1

INTRODUCTION

1.1 Introduction

The present high technology era strongly relies on the development of the smart and smaller magnetic material for various applications particularly in the computer industries. The discovery of the magnetoresistance (MR) effect which is defined as the ability of resistivity changed upon external magnetic field, have boosted up the development of magnetic sensor and read head sensor in data storage and electronic devices by the application of MR. One of the current technological challenges is to produce a smaller device with high sensitivity. Thus, studying the MR effect and looking for the highest MR operated at room temperature are required for next-generation devices.

During recent decades, the manganites systems have received tremendous attention in consequence of the discovered extraordinary large negative MR near the metal-insulator transition temperature (T_p) and the ferro-paramagentic transitions temperature (T_C), so-called 'Colossal' Magnetoresistance (CMR). The MR effect of the CMR materials is in the order of magnitude larger than a typical giant magnetoresistance (GMR) that is currently used in the magnetic device. Thus, the CMR manganites with enormous MR have greater sensitivity to the magnetic field, making it possible to be applied in various technologies such as magnetic sensor and the read head sensor for hard disk drive. Researchers believe that the CMR manganites are promising to be the new generation of the magnetic sensor especially the read head sensor in the hard disk drive.

A lot of researches have devoted much effort in the study of CMR properties in manganites systems, in order to have a deeper understanding of the physical origin of the CMR properties. Moreover, researchers are looking for the optimization of the CMR properties at room temperature and lower magnetic field in order to achieve their applicability to hand on devices. The ferromagnetic coupling between Mn^{3+} and Mn^{4+} plays an important role in governing the CMR properties. The mechanism is explained by the double exchange interaction where the e_g electrons from Mn^{3+} can hop to Mn^{4+} when their spins are parallel. The hopping amplitude of e_g electron via double exchange is strongly dependent on the Mn-O-Mn bond angle and Mn-O bond length in the perovskite structure (Coey et al., 1999). Radaelli et al. (1997) showed that the magnetic and electrical properties are sensitive to the average A-site ionic radius that directly influences the internal atomic structure and the electronic band width. Hence, it is possible to optimize the CMR properties by manipulating the atomic structure of perovskite manganites. Besides that, researchers have found an extrinsic MR effect at a moderately low magnetic field (<0.1T), which is contributed by the grain boundary (Hwang et al., 1996). This brings out the necessity to study the microstructure dependence of the MR properties of manganites as well.

1.2 CMR Manganites

The general formula of manganites compound is $R_{1-x}A_xMnO_3$ where R is a trivalent rare earth ion and A is a divalent alkaline earth ion. Without hole doping (x = 0), the parent manganites compound is an antiferromagnetic insulator. By the partial substitution of trivalent rare earth ions with divalent alkali earth ions, this leads to the co-existing of mix-valence Mn^{3+} and Mn^{4+} in the manganites (Jonker and Santen, 1950). Around x = 0.33, the mix-valence manganites exhibit a transition from a high-temperature paramagnetic insulator to a low-temperature ferromagnetic metal. At this transition point, an enormous change in resistivity upon external applied magnetic field is observed and attributing to the CMR effect (Jin et al., 1994; Helmolt et al., 1993).

MR is the relative change in the electrical resistance or resistivity of a material upon an external magnetic field. The MR effect is defined as the percentage of the fractional change to the zero field resistance,

$$\text{MR} = \frac{\Delta R}{R_0} \times 100\% = \left[\frac{R_H - R_0}{R_0}\right] \times 100\%, \quad (1.1)$$

where R_0 and R_H are the resistance or resistivity in the absence and the presence of external magnetic field respectively. Recent investigations have found that mix-valence manganites tend towards 100% of MR value. Thus, alternative definition of MR effect is expressed in MR ratio,

$$\text{MR ratio} = \left[\frac{R_H - R_0}{R_H}\right] \times 100\%. \quad (1.2)$$

This definition gives a better way to show how many orders of resistance magnitude can be decreased by an applied magnetic field. For example, Jin et al. (1994) observed a large negative MR as large as 99.92% in $La0_{.67}Ca_{0.33}MnO_3$ thin film at temperature 77 K and 6 T magnetic field. Alternatively, expression in term of MR ratio in this case is 127000%, which is a truly "colossal" MR factor (Dagatto et al., 2001; Raveau et al., 1998). Thus, the term "colossal" was coined because of its thousand-fold of MR ratio observed in manganites oxide.

The CMR is due to the suppression of spin fluctuations by aligning the spin parallel upon an external magnetic field which favors the double exchange interaction, consequently enhancing the mobility of charge carries. CMR effect is only observed in the appropriate doping of parent compound where the mix-valance state is present (Mn^{3+} and Mn^{4+} coexists in the manganites oxide). In this mix-valence state, the itinerant electrons can hop to the neighboring Mn^{4+} ion via the double exchange mechanism. Generally, the highest T_C was found in doped manganites at doping level x = 0.33. The most significant MR effect is observed at the vicinity of T_C.

1.3 Potential Application

The CMR manganites material has a large potential for the application based on their various physical and chemical properties. For examples: magnetoresistive read head sensor in the magnetic recording devices, magnetoresistive random access memory and speed control sensor in the anti-lock brake system.

1.3.1 Magnetoresistive Read Head Sensor in Magnetic Recording Devices

CMR manganite materials with large MR is a very good magnetic sensor that can be used as read head sensor for the magnetic recording device. In hard disk, the read head detects the change in the direction of magnetization (represents the binary data bits) emanating from the magnetic media and then changes its resistivity correspondingly. The MR effect in CMR materials are in the order of magnitude larger than the typical GMR that is currently used in magnetic device. Hence, this material has a greater sensitivity to the magnetic field and making it possible to detect smaller recorded data bit (White et al., 1994).

1.3.2 Magnetoresistive Random Access Memory (MRAM)

MRAM is a non-volatile random-access memory that can retain information for a long period of time even in the absence of electrical power. A data bit is stored in a spin valve which is composed of two ferromagnetic plates separated by a thin insulating layer. Both the ferromagnetic plates hold a magnetic field where one of the two plates is permanently magnetized in a particular orientation and the other plate changes its magnetic field according to the external field to store memory. Both data bits 1 and 0 are represented by the parallel and antiparallel moment in the spin valve and can be determined by measuring the resistance of the spin valve. Comparing with the conventional RAM chip technologies, MRAM records data in the form of magnetic moment instead of electric charge. This makes MRAM has an advantage in retaining their data over time and not necessary to refresh their contents. Hence, MRAM is expected to have much lower power consumption compared to the conventional RAM (Zhuang et al., 2002; Katti, 2000).

1.3.3 Speed Control Sensor in Anti-Lock Brake System (ABS)

The CMR materials can be used as a speed control sensor to detect the rotation and speed of the steel disc attached to the automobiles wheel and then transferring the information to a computer for monitoring the rotational speed of each wheel. If the system detects a wheel rotating significantly slower than the others, it reduces the braking pressure at the detected wheel. Conversely, if the system detects a wheel rotating faster than the others, it increases the braking pressure at the detected wheel. This condition of releasing and increasing on the braking pressure allows the wheels on the automobile keep friction contact with the road surface while braking. Hence, it is able to avoid the automobiles from uncontrolled skidding and to decrease the automobiles braking distance (Aly et al., 2011).

1.4 Problem Statement

The CMR effect in the manganites is much higher than the current employing magnetic multi-layer system, i.e. GMR. Hence, it is prospected to increase the sensitivity of the magnetic sensor and to reduce the operation power required. However, the conventional magnetic sensor requires material which is able to operate at room temperature and low magnetic field. Commercialization of the CMR is discouraged because of

- Significant CMR in manganites appears only in a high magnetic field of several Tesla range, which is considered too large for the potential use in the magnetic recording (Dagotto et al., 2001) and

- The CMR effect is rather low at room temperature.

  - Significant CMR effect is confined to a quite narrow temperature range around the T_C. The CMR effect is relatively low beyond T_C (Tokura and Tomioka, 1999).

  - CMR effect appears significant only when its T_C temperature is at low temperature. High T_C temperature will sacrifice the CMR effect (Dagotto et al., 2001).

Hence, enhancing the CMR properties of the manganite materials for utilizing in room temperature and low magnetic field will be the final goal for researchers.

1.5 Scope and Objectives of the Research

This project mainly studies the structural, electrical, magnetic and CMR properties on $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ manganites compounds with the x value ranging from 0 to 1.0. Samples with two different crystalline forms were synthesized i.e. polycrystalline bulk and nanocrytalline manganites. The polycrystalline bulk manganites were synthesized via the solid state reaction which is the most common method in synthesizing various kind of ceramic. Nanocrystalline manganites were synthesized via the sol-gel based polymerizable complex method in order to confine the crystallite size down to nano-scale. A systematic characterization was carried out upon the polycrystalline bulk and the nanocrystalline samples. Structural properties of these samples were investigated by X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX). While the MR effect in the manganite samples was measured by employing the four point probe method with applied magnetic field range of 0 T to 1 T. The magnetization of the samples was investigated by Vibrating Sample Magnetometer (VSM) at room temperature and applied magnetic field ranges from 0 kG to 10 kG. Lastly, the experiments data obtained were analyzed and the features of both polycrystalline and nanocrystalline manganites samples were studied and discussed. Hence, the objectives of this research are:

I. To characterize polycrystalline and nanocrystalline $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ samples synthesized by the solid state reaction and sol-gel based polymerizable complex method respectively.

II. To study the effects of Strontium ions substitution at Calcium site by investigating and comparing the structural, electrical and magnetic properties of the polycrystalline and nanocrystalline samples.

III. To find the optimum composition of both polycrystalline and nanocrystalline $La_{0.67}(Ca_{1-x}Sr_x)_{0.33}MnO_3$ for obtaining the highest MR effect at room temperature.

1.6 Overview of the Thesis

In the first chapter, an introduction concerning about this project is presented. Problem statements regarding to the research of CMR materials are mentioned. The scope of project and the objectives are presented. Lastly, the overview of this thesis is given.

In chapter 2, the histories of the CMR material will be presented. A review on the existing literatures related to the physical properties of CMR manganites is also given.

In chapter 3, some theories related to the CMR material will be presented. It is important to understand the theories behind the CMR phenomenon so that the experimental results can be well interpreted.

In chapter 4, the implemented methodology, the synthesis method adopted in this project will be discussed in details. Systematic characterizations are carried out. The equipments involved in this project will be introduced and the experimental settings will also be provided in chapter 4.

In chapter 5, the experimental data will be presented in the form of graphs, pictures or tables to give a clear and facilitated observation. The structural, magnetic and electrical properties of the CMR manganite samples will be discussed with respect to the analyzed graph, picture and table.

Finally, in chapter 6, the conclusion of this project will be presented. The future research will also be suggested in this chapter.

REFERENCES

Aly, A.A., Zeidan, E.S., Hamed, A. and Salem, F. (2011). An Antilock-Braking Systems (ABS) Control: A Technical Review. *Intelligent Control and Automation* 2: 186-195.

Anderson, P.W. and Hasegawa, H. (1955). Consideration of Double Exchange. *Physical Review 100*: 675-681.

Andres, A.D., Garcia-Hernandez, M. and Martinez, J.L. (1999). Conduction Channels and Magnetoresistance in Polycrystalline Manganites. *Physical Review B* 60: 7328-7334.

Berlin, J. (2011). Analysis of Boron with Energy Dispersive X-ray Spectrometry-Advances in Light Element Analysis with SDD Technology. *Imaging & Microscopy* 13: 19-21.

Burgei, W., Pechan, M.J., and Jaeger, H. (2003). A Simple Vibrating Sample Magnetometer for Use in a Materials Physics Course. *American Journal of Physics* 71: 825-828.

Chahara, K.-I., Ohno, T., Kasai, M. and Kozono, Y. (1993). Magnetoresistance in Magnetic Manganese Oxide with Intrinsic Antiferromagnetic Spin Structure. *Applied Physics Letters* 63: 1990-1992.

Cheong, S.W. and Hwang, H.Y. (2000). Ferromagnetism versus charge/orbital ordering in mixed-valent manganites. In Colossal Magnetoresitance Oxides edited by Tokura. Y. Gordon and Breach, London.

Coey, J.M.D., Viret, M. and Molnar, S.V. (1999). Mixed-Valence Manganites. *Advances in Physics* 48: 167-293.

Conceicao, L.D., Ribeiro, N.F.P., and Souza, M.V.M. (2011). Synthesis of $La_{1-x}Sr_xMnO_3$ Powders by Polymerizable Complex Method: Evaluation of Structural, Morphological and Electrical Properties. *Ceramics International* 37: 2229-2236.

Dagotto, E., Hotta, T., and Moreo, A. (2001). Colossal Magnetoresistant Material: The Key Role of Phase Separation. *Physics Reports* 344: 1-153.

De, A.K. (2003). Chemical Bonding and Structure. In *A Textbook of Inorganic Chemistry* 9th, pp106-108. New Age International (P) Ltd.

Dinesen, A.R. and Linderoth, S. (2002). Adjustable Temperature Working Range in $La_{2/3}Ca_{1/3-x}Sr_xMnO_3$ Manganites with CMR Effect. *EUROSENSORS XVI, The 16th European Conference on Solid-State Transducers*: 575-578.

Goodenough, J.B. (1955). Theory of the Role of Covalence in th Perovskite-Type Manganites [La,M(II)]MnO_3. *Physical Review* 100:564-573.

Gosnet, H.A.M. and Renard, J.P. (2003). CMR Manganites: Physics, Thin Films and Devices. *Journal of Physics D: Applied Physics 36*:127-150.

Hafner, B. (2007). Scanning Electron Microscopy Primer. Characterization Facility, University of Minnesota-Twin Cities.

Helmolt, R.V., Wecker, J., Holzapfel, B., Schultz, L. and Samwer, K. (1993). Giant Negative Magnetoresistance in Perovskitelike $La_{2/3}Ba_{1/3}MnO_x$ Ferromagnetic Films. *Physical Review Letters* 71: 2331-2333.

House, J.E. (2008). Ligand Fields and Molecular Orbitals, In *Inorganic Chemistry*, 2th pp603-604. USA, Elsevier Inc.

Hwang, H.Y., Cheong, S.W., Radaelli, P.G., Marezio, M., and Batlogg, B. (1995). Lattice Effects on the Magnetoresistance in Doped $LaMnO_3$. *Physical Review Letters* 75: 914-917.

Hwang, H.Y., Cheong, S.W., Ong, N.P. and Batlogg, B. (1996). Spin-Polarized Intergrain Tunneling in $La_{2/3}Sr_{1/3}MnO_3$. *Physical Review Letters* 77: 2041-2044.

Huang, Y.H., Yan, C.H., Wang, Z.M., Liao, C.S. and Xu, G.X. (2001). Variation of Structural, Magnetic and Transport Properties in $RE_{0.7}Sr_{0.3}MnO_3$ Granular Perovskites. *Solid State Communication* 118: 541-546.

Hueso, L.E., Rivas, J., Rivadulla. F, and Lopez-Quintela, M.A. (1999). Tuning of Colossal Magnetoresistance Via Grain Size Change in $La_{0.67}Ca_{0.33}MnO_3$ *Journal of Applied Physics* 86: 3881-3884.

Im, H., Chon, G., Lee, S.M., Koo, B., Lee, C., and Jung, M. (2007). Preparation and Characterization of $La_{0.7}AE_{0.3}MnO3$ (AE=Ca, Sr, Ba): Perovskite Structured Manganites. *Journal of Magnetism and Magnetic Material* 310: 2668-2670.

Jahn, H.A and Teller, E. (1937). Stability of Polyatomic Molecules in Degenerate Electronic State. I. Orbital Degeneracy. *Proceedings of the Royal Society A* 161: 220-235

Jin, K., Chen, C., Wang, S., Zhao, S., Wang, Y. and Song, Z. (2005). Structure and Electrical Properties in $La_{2/3}(Ca_{1-x}Sr_x)_{1/3}MnO_3$ Films. *Material Science and Engineering B* 119: 206-209.

Jin, S., Tiefel, T.H., McCormack, M., Fastnacht, R.A., Ramesh, R. and Chen, L.H. (1994). Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films. *Science* 264: 413-415.

Jirak, J., Vratislav, S. and Zajicek, J. (1979). The Magnetic Structure of $Pr_{0.9}Ca_{0.1}MnO_3$. *Physica Status Solidi (a)* 52: 39-43.

Jonker, G.H. and Van Santen, J.H. (1950). Ferromagnetic Compounds of Manganese with Perovskite Structure. *Physica* 16: 337-349.

Katti, R.R. (2000). GMRAM: Giant Magneto-Resistance Random-Access Memory. *IEEE Aerospace Conference Proceedings* 5: 371-376.

Khazeni, K., Jia, Y., Lu, L., Crespi, V.H., Cohen, M.L. and Zettl, A. (1996). Effect of Pressure on the Magnetoresistance in Single Crystal $Nd_{0.5}Sr_{0.36}Pb_{0.14}MnO_{3-\delta}$. *Physical Review Letters* 76: 295-298.

Lakshmi, Y.K., Venkataiah, G., Vithal, M., and Reddy, P.V. (2008). Magnetic and Electrical Behavior of $La_{1-x}A_xMnO_3$. *Physica B* 403: 3059-3066.

Levy, M.R. (2005). *Crystal Structure and Defect Property Predictions in Ceramic Materials*. PhD Thesis, Department of Materials, Imperial College of Science, Technology and Medicine.

Li, G., Qian, T., Feng, S.-J., Liu, F., Zhou, H.-D. and Li, X.-G. (2003). Magnetoresistance in $La_{1-x}Ca_xMnO_3$ ($0<=x<0.4$). *Solid State Communications* 128:171-176.

Lim, K.P., Ng, S.W., Halim, S.A, Chen, S.K. and Wong, J.K. (2009). Effect of Divalent Ions (A= Ca, Ba and Sr) Substitution in La-A-Mn-O Manganite on Structure, Magnetic and Electrical Transport Properties. *American Journal of Applied Sciences* 6: 1153-1157.

Loudon, J. (2003). *An Investigation of the Unconventional Phases in The $La_{1-x}Ca_xMnO_3$ System.* Phd Thesis, Department of Material Science and Metallurgy, University of Cambridge.

Madelung, O. (1996). Electron-Phonon Interaction: Transport Phenomena. In *Introduction to Solid-State Theory.* pp175-187. Springer-Verlag Berlin Heidelberg.

Mahesh, R., Mahendiran, R., Raychaudhuri, A.K. and Rao, CNR. (1995). Effect of the Internal Pressure due to the A-Site Cations on the Giant Magnetoresistance and Related Properties of Doped Rare Earth Manganates, $Ln_{1-x}A_xMnO_3$ (*Ln*=La, Nd, Gd, Y; *A*=Ca, Sr, Ba, Pb). *Journal of Solid State Chemistry* 120: 204-207.

Mahesh, R., Mahendiran, R., Raychaudhuri, A.K. and Rao, C.N.R. (1996). Effect of Particle Size on the Giant Magnetoresistance of $La_{0.7}Ca_{0.3}MnO_3$. *Applied Physics Letters* 68: 2291

Mathur, N.D., Burnell, G., Isaac, S.P., Jackson, T.J., Teo, B.S, MacManus-Driscoll, J.L, Cohen, L.F., Evetts, J.E. and Blamire, M.B. (1997). Large Low Field Magnetoresistance in $La_{0.7}Ca_{0.3}MnO_3$ Induced by Artificial Grain Boundaries. *Nature 387*: 266-268.

Mera, J., Mera, M., Cordoba, C., Paredes, O. and Moran, O. (2013). $La_{0.7}Sr_{0.3}MnO_3$ Nanoparticles Synthesized Via the (Pechini) Polymeric Precursor Method. *Journal of Superconductivity and Novel Magnetism* 26: 2553-2556.

Millis, A.J., Littlewood, P.B. and Shraiman, B.I. (1995). Double Exchange Alone Does Not Explain the Resistivity of $La_{1-x}Sr_xMnO_3$. *Physical Review Letters 74*: 5144-5147.

Millis, A.J., Mueller, R and Shraiman, B.I. (1996). Fermi Liquid to Polaron Crossover.II. Double Exchange and the Physics of Colossal Magnetoresistance. *Physical Review B* 54: 5405-5417.

Ng, S.W., Lim, K.P., Halim, S.A., Chen, S.K., and Wong, J.K. (2010). Influence of Sintering temperature on Microstructure and Electrical Properties of $La_{0.67}Ba_{0.33}MnO_3$ Ceramic. *Proceedings of the Progress of Physics Research in Malaysia: PERFIK2009,* pp. 59-62.

Niazi, A., Poddar, P., and Rastogi, A.K. (2000). A Precision, Low-Cost Vibrating,Sample Magnetometer. *Current Science* 79: 99.

Nossov, A., Pierre, J., Strobel, P., Vassiliev, V., Slobodin, B., Vladimirova, E., Machkaoutsan, V. and Ustinov, V. (1999). Extrinsic Magnetoresistance in Bulk Sintered Manganites. *Journal of Magnestism and Magnetic Material* 196-197: 461-462.

Pan, K.Y., Halim, S.A., Lim, K.P., Daud, W.M.W.Y., Chen, S.K., Navasery, M. (2013). Microstructure, Electrical and Magnetic Properties of Polycrystalline $La_{0.85}K_{0.15}MnO_3$ Manganites Prepared by Different Synthesis Routes. *Journal of Material Science: Materials in Electronics* 24: 1869–1874.

Petrykin, V. and Kakihana, M. (2005). Chemistry and Applications of Polymeric Gel Precursors, *In Sol-Gel Processing*, ed. Kozuka, H. pp. 77-104.

Pollert, E., Krupicka, S. and Kuzmicova, E. (1982). Structural Study of Pr_{1-x} Ca_xMnO_3 and $Y_{1-x}Ca_xMnO_3$ Perovskites. *Journal of Physics and Chemistry of Solids* 43: 1137-1145.

Radaelli, P.G., Iannone, G., Marezio, M., Hwang, H.Y., Cheong, S.W., Jorgensen, J.D., and Argyriou, D.N. (1997). Structural Effects on the Magnetic and Transport Properties of Perovskite $A_{1-x}A'_xMnO_3$ (x=0.25, 0.30). *Physical Review B* 56: 8265-8276.

Ramirez, A.P. (1997). Colossal Magnetoresistance. *Journal of Physics: Condensed Matter* 9: 8171-8199.

Rao, G.H., Sun, J.R., Barner, K. and Hamad, N. (1999). Crystal Structure and Magnetoresistance of Na-doped $LaMnO_3$. *Journal of Physics:Condens Matter* 11: 1523

Raveau, B., Maignan, A., Martin, C. and Hervieu, M. (1998). Colossal Magnetoresistance Manganite Perovskites: Relations Between Crystal Chemistry and Properties. *Chemistry of Materials* 10: 2641-2652.

Rostamnejadi, A., Salamati, H., Kameli, P. and Ahmadvand, H. (2009). Superparamagnetic Behavior of $La_{0.67}Sr_{0.33}MnO_3$ Nanoparticles Prepared via Sol-Gel Method. *Journal of Magnetism and Magnetic Materials* 321: 3126-3131.

Roy, B., Poddar, A., and Das, S. (2006). Electrical Transport Properties and Magnetic Cluster Glass Behavior of $Nd_{0.7}Sr_{0.3}MnO_3$ nanoparticles, *Journal of Applied Physics* 100: 1-10.

Salamon, M.B. (2001). The Physics of Manganites: Structure and Transport. *Reviews of Modern Physics 73*: 583-628.

Schuetze, A.P., Lewis, W., Brown, C. and Geerts, J. (2003). A Laboratory on The Four-Point Probe Technique. *American Journal of Physics* 72: 149-153.

Shankar, K.S., Kar, S., Subbanna, G.N., and Raychaudhuri, A.K. (2004). Enhanced Ferromagnetic Transition Temperature in Nanocrystalline Lanthanum Calcium Manganese oxide ($La_{0.67}Ca_{0.33}MnO_3$). *Solid State Communications* 129: 479-483.

Shindo, D. and Murakami, Y. (2004).Fundamentals of Characterization. In *Morphology Control of Materials and Nanoparticles.* Ed. Waseda, Y. and Muramatsu, A. pp154-180. Springer-Verlag Berlin Heidelberg.

Siwach, P.K., Goutam, U.K., Pankaj Srivastava, Singh, H.K., Tiwari, R.S. and Srivastava, O.N. (2006). Colossal Magnetoresistance Study in Nanophasic $La_{0.7}Ca_{0.3}MnO_3$ manganite. *Journal of Physics D: Applied Physics* 39: 14-20.

Siwach, P.K., Singh, H.K. and Srivastava, O.N. (2008). Low Field Magnetotransport in Manganites. *Journal of Physics: Condensed Matter* 20: 1-43.

Spaldin, N.A. (2011). Ferromagnetic Domain. In *Magnetic Material: Fundamentals and Applications* 2nd . pp79-92. Cambridge University Press, New York.

Statham, P.J. (2002). Limitations to Accuracy in Extracting Characteristic Line Intensities from X-Ray Spectra. *Journal of Research of the Natianal Institute of Standards and Technology* 107: 531-546.

Tendeloo, G.V., Lebedev, O.I., Hervieu, M., and Raveau, B. (2004). Structure and Microstructure of Colossal Magnetoresistance Materials. *Reports on Progress in Physics* 67: 1315-1365.

Tokura, Y. (2006). Critical Features of Colossal Magnetoresistive Manganites. *Reports on Progress in Physics* 69: 797-851.

Tokura, Y. and Tomioka, Y. (1999). Colossal Magnetoresistive Manganites. *Journal of Magnetism and Magnetic Material* 200: 1-23.

Topsoe, H. (1968). Geometric Factor in Four Point Resistivity Measurement, http://www.four-point-probes.com/haklor.html]

Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G. and Tokura, Y. (1995). Insulator-Metal Transition and Giant Magnetoresistance in $La_{1-x}Sr_xMnO_3$. *Physical Review B* 51: 103-109.

Van Santen, J.H. and Jonker, G.H. (1950). Electrical Conductivity of Ferromagnetic Compounds of Manganese with Perovskite Structure. *Physica* 16: 599-600.

Venkataiah, G., Krishna, D.C., Vithal, M., Rao, S.S., Bhat, S.V., Prasad, V., Subramanyam, S.V. and Reddy, P.V. (2005). Effect of Sintering Temperature on Electrical Transport Properties of $La_{0.67}Ca_{0.33}MnO_3$. *Physica B* 357: 370-379.

Volger, J. (1954). Further Experimental Investigations on Some Ferromagnetic Oxidic Compounds of Manganese with Perovskite Structure. *Physica* 20: 49-66.

White, R.L. (1994). Giant Magnetoresistance Materials and Their Potential as Read Head Sensors. *IEEE Transactions on Magnetics* 30: 346-352.

Whitten, K.W., Davis, R.E., Peck, M.L., and Stanley, G.G. (2010). Coordination Compounds. In *Chemistry,* 9^{th}*,* pp. 924-926. USA, Thomson Brooks/Cole.

Wollan, E.O and W.C. Koehler, W.C. (1955). Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds [(1-x)La,xCa]MnO3. Physical Review 100: 545-563.

Yaket, H.L. (1955). On the Structures of Some Compounds of the Perovskite Type. *Acta Crystallographica* 8: 394-398.

Yang, W.D., Chang, Y.H., and Huang, S.H. (2005). Influence of Molar Ratio of Citric Acid to Metal Ions on Preparation of $La_{0.67}Sr_{0.33}MnO_3$ Materials via Polymerizable Complex Process. *Journal of European Ceramic Society* 25: 3611-3618.

Zener, C. (1951a). Interaction Between the d-Shells in the Transition Metals. *Physical Review* 81: 440-444.

Zener, C. (1951b). Interaction Between the s-shells in the Transition Metals: II. Ferromagnetic Compounds of Manganese with Perovskite Structure. *Physical Review* 81: 403-406.

Zhou, W., Apakarian, R.P., Wang, Z.L and Joy. D. (2006). Fundamentals of Scanning Electron Microscopy. In *Scanning Microscopy for Nanotechnology: Techniques and Applications*. Ed. Zhou, W. and Wang, Z.L. Springer, New York.

Zhuang, W.W., Pan, W., Ulrich, B.D., Lee, J.J., Stecker, L., Burmaster, A., Evans, D.R., Hsu, S.T., Tajiri, M., Shimaoka, A., Inoue, K., Naka, T., Awaya, N., Sakiyama, K., Wang, Y., Liu, S.Q., Wu, N.J. and Ignatiev. A. (2002). Novel Colossal Magnetoresistive Thin Film Nonvolatile Resistance Random Access Memory (RRAM). *Electron Devices Meeting IEDM '02. International*: 193-196.