UNIVERSITI PUTRA MALAYSIA

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$_3$

CHANG SEN CHOUNG

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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

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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 ≤ $x$ ≤ 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 $T$ ≤ $T_p$ 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.
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 ekstrisik pada T \leq T_p telah diperhatikan dalam sampel polihablur. Penggantian ion Sr menyebabkan MR intrisik bagi sampel polihablur beralih ke suhu tinggi tetapi magnitudnya menurun. Manakala, MR intrisik bagi sampel nanohablur didapati ditindaskan dan hanya MR ekstrisik 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 penambahan 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.
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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)

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**BUJANG BIN KIM HUAT, PhD**  
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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

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F.3 Scanning of EDX in spot and area for nanocrystalline \( \text{La}_{0.67}\text{(Ca}_{1-x}\text{Sr}_x)_{0.33}\text{MnO}_3 \) compound at \( x = 0.4 \)

F.4 Scanning of EDX in spot and area for nanocrystalline \( \text{La}_{0.67}\text{(Ca}_{1-x}\text{Sr}_x)_{0.33}\text{MnO}_3 \) compound at \( x = 0.6 \)

F.5 Scanning of EDX in spot and area for nanocrystalline \( \text{La}_{0.67}\text{(Ca}_{1-x}\text{Sr}_x)_{0.33}\text{MnO}_3 \) compound at \( x = 0.8 \)

F.6 Scanning of EDX in spot and area for nanocrystalline \( \text{La}_{0.67}\text{(Ca}_{1-x}\text{Sr}_x)_{0.33}\text{MnO}_3 \) compound at \( x = 1.0 \)
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
<br'A'> Average A-site ionic radius
\( \rho \) 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
\( T_N \) Néel Temperature
\( I \) Current
\( n \) Integer Number
\( \lambda \) wavelength of X-Ray
\( d_{hkl} \) Interplaner Distance of (hkl) Planes
\( \theta \) 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
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>emf</td>
<td>Electromotive Force</td>
</tr>
<tr>
<td>N</td>
<td>Number of Wire turns</td>
</tr>
<tr>
<td>s</td>
<td>Time</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic Field</td>
</tr>
<tr>
<td>A</td>
<td>Coil Turn Area</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle between B Field and the Direction Normal to the Coil Surface</td>
</tr>
<tr>
<td>$r_A$</td>
<td>Ionic Radius of A-site Ion</td>
</tr>
<tr>
<td>$r_B$</td>
<td>Ionic Radius of B-site Ion</td>
</tr>
<tr>
<td>$r_O$</td>
<td>Ionic Radius of Oxygen Ion</td>
</tr>
<tr>
<td>$r_{Mn}$</td>
<td>Ionic Radius of Manganese Ion</td>
</tr>
<tr>
<td>$d_{A-O}$</td>
<td>Distance between A-Site Ion and Oxygen Ion</td>
</tr>
<tr>
<td>$d_{Mn-O}$</td>
<td>Distance between Manganese Ion and Oxygen Ion</td>
</tr>
<tr>
<td>$t_e$</td>
<td>Effective Transfer Integral</td>
</tr>
<tr>
<td>$t_0$</td>
<td>Normal Transfer Integral</td>
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<tr>
<td>$\theta_s$</td>
<td>Angle between the Two Spin Direction</td>
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<tr>
<td>$f$</td>
<td>Goldschmidt Tolerance Factor</td>
</tr>
<tr>
<td>$K$</td>
<td>Constant Depending on the Grain Shape</td>
</tr>
<tr>
<td>$\beta_{Size}$</td>
<td>Full Width at Half Maxima of XRD Peak</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Resistance or Resistivity in the Present of External Magnetic Field</td>
</tr>
<tr>
<td>$R_0$</td>
<td>Resistance or Resistivity in the Absence of External Magnetic Field</td>
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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-paramagnetic 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 La$_{0.67}$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-valence 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 nanocrystalline 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.
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