UNIVERSITI PUTRA MALAYSIA

STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES AND COLOSSAL MAGNETORESISTIVE EFFECT OF La0.67Sr0.33MnO3 PEROVSKITES WITH Dy SUBSTITUTION AT La SITE

LEE OON JEW

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By

LEE OON JEW

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LIST OF ABREVATIONS/NOTATIONS/GLOSSARY OF TERMS

$t_{2g}^3 e_g^1$	Electron configuration
<ra>	A-site ionic radius
2D	2 dimension
2Theta	Bragg diffraction angle
3D	3 dimension
a, b, c	Lattice parameter
Abbreviation	Description
ABO_3	Pervoskite
ABS	Antilock Brake System
AC	Alternating current
AFM	Atomic Force Microscope
AMR	Anisotropic magnetoresistance
CMR	Colossal magnetoresistance
D	Divalent cation or alkaline earth
$d_{A\text{-}O}$	Distance between the A site
DC	Direct current
DE	Double exchange
$d_{Mn\text{-}O}$	Shortest distance of Mn-O
Dy	Dysprosium
E_a	Activation energy
EMR	Extraordinary magnetoresistance

GMR	Giant magnetoresistance
H	Magnetic field
ICDD	International Crystal Diffraction Data
La	Lanthanum
LFMR	Low field magnetoresistance
Ln	Trivalent lanthanide cation
M	Magnetization
Mn	Mangnese
MR	Magnetoresistance
MRAM	Magnetoresistance Random Access Memory chip
$N(E_f)$	The density of states at the Fermi level
O	Oxygen
Q_1, Q_2, Q_3	Normal modes of vibration of the oxygen octahedron
R	Resistance
R_0	Resistances in the absence of a magnetic field
R_H	Resistances in the presence of a magnetic field
SPH	Small polaron hopping
SPM	Scanning Probe Microscope
Sr	Strontium
T	Tesla
t	Goldsmith tolerance factor
Tc	Curie temperature
T_f	Freezing Temperature

T_{MIT}	Metal-insulator transition temperature
TMR	Tunnelling magnetoresistance
T_N	Neel temperature
VLMR	Very large magnetoresistance
VRH	Variable range hopping
VSM	Vibrating Sample Magnetometer
XRD	X-ray diffraction
α, β, γ	Phase designations
θ	Mn-O-Mn bond angle
Θ	Paramagnetic Curie temperature
μ_0	Permeability of the free space
ρ	Resitivity
σ	Conductivity
χ	Magnetic susceptibility

To My Family and Friends.........

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

STRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES AND COLOSSAL MAGNETORESISTIVE EFFECT OF $La_{0.67}Sr_{0.33}MnO_3$ PEROVSKITES WITH Dy SUBSTITUTION AT La SITE

By

LEE OON JEW

June 2007

Chairman: **Professor Abdul Halim bin Shaari, PhD**

Faculty: **Science**

A thorough study on structural, magnetic and electrical properties and colossal magnetoresistive (CMR) effect in $La_{0.67}Sr_{0.33}MnO_3$ or generically known as LSMO manganites substituted with dysprosium (Dy) at lanthanum (La) site is the main area of research in this thesis. In the first part of this work, the samples of $(La_{1-x}Dy_x)_{0.67}Sr_{0.33}MnO_3$ (LDSMO) with x=0.00-0.90 were synthesized using standard solid state reaction method. The second part involves the characterization of the samples using X-ray Diffractometer (XRD), Vibrating Sample Magnetometer (VSM), four point probe electrical resistivity and magnetoresistance measurement system, and Atomic Force Microscope (AFM). The XRD pattern for all samples reveals a single phase pattern with rhombohedral structure. When Dy concentration increases, the magnetization value at any given temperature decreases markedly. Moreover, the magnetization (temperature dependence of magnetization and isothermally hysteresis loop) show a prominent transition corresponding to Curie temperature,T_C arising from long range ferromagnetic order to a short range nature

with paramagnetic order ($0.00 \leq x \leq 0.06$), antiferromagnetic (x=0.90) and spin glass state (x=0.80). The electrical resistivity increases with the shifting of metal-insulator transition temperature, T_{MIT} to lower temperature. Low temperature resistivity datas signify that the resistance of electrical transport mechanism in the metallic region can be ascribed as electron-electron scattering with minor attribution of magnon-electron scattering. On the other hand, the high temperature resistivity data satisfy the variable range hopping (VRH) model and small polaron hopping (SPH) model. The considerable change in the density of states at Fermi level, $N(E_f)$ and activation energy, E_a which was obtained from fitting the electrical transport data, proved that the mobility of the electron decreases proportionally with Dy concentration. The $N(E_f)$ values were found within the range of $1.53x10^{16}$ $eV^{-1}cm^{-3}$ to $1.45x10^{18}$ $eV^{-1}cm^{-3}$ whereas the E_a values were ranged from $2.96x10^{2}$ meV to $1.32x10^{3}$ meV. The T_C-T_{MIT} discrepancy is due to the fact that the former is an intrinsic characteristic, the latter depends strongly on the extrinsic factor e.g. grain size (grain boundary). The effect of grain size on the CMR mechanism is analyzed from AFM images. The grain size was found to decrease exponentially from 2.88 µm (x=0.00) to 1.34 µm (x=0.90) with the increase of Dy concentration. As the grain size decreases, the ratio of surface over volume increased. Hence, the influence of grain boundaries effect cannot be excluded and eliminated in all samples. Overall, negative CMR in ascending order had been obtained in all samples as decreasing temperature at low magnetic field. This phenomenon is known as Low Field Magnetoresistance (LFMR). Spin dependent scattering, spin polarization and tunneling between neighbouring grains and the magnetically disordered grain boundaries seems to be responsible for the LFMR effect. The highest CMR value with 62.2% is obtained in x=0.60 LDySMO sample at 90K.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

SIFAT STRUKTUR, MAGNET DAN ELEKTRIK DAN KESAN MAGNETORINTANGAN RAKSASA PEROVSKIT $La_{0.67}Sr_{0.33}MnO_3$ DENGAN PENGGANTIAN Dy PADA TAPAK La

Oleh

LEE OON JEW

Jun 2007

Pengerusi: **Profesor Abdul Halim bin Shaari, PhD**

Fakulti: **Sains**

Kajian menyeluruh tentang sifat struktur, magnet dan elektrik dan magnetorintangan raksaksa terhadap $La_{0.67}Sr_{0.33}MnO_3$ atau dikenali sebagai manganit LSMO yang digantikan dengan dysprosium (Dy) pada tapak lanthnum (La) adalah kajian utama dalam tesis ini. Dalam bahagian pertama kajian ini, sampel $(La_{1-x}Dy_x)_{0.67}Sr_{0.33}MnO_3$ (LDySMO) dengan x=0.00-0.90 telah disintesis melalui kaedah tindak balas keadaan pepejal. Manakala bahagian kedua tesis ini adalah pencirian dan pengukuran sifat sampel menggunakan alat belauan sinar-X (XRD), magnetometer getaran sampel (VSM), kaedah penduga empat titik (pengukuran kerintangan dan magnetorintangan) dan mikroskop daya atom (AFM). Corak belauan sinar-X menunjukkan fasa tunggal dengan kewujudan struktur rombohedral. Apabila kepekatan Dy meningkat, nilai kemagnetan dalam keseluruhan suhu didapati berkurang. Pengukuran kemagnetan (persandaran kemagnetan sampel terhadap suhu dan lengkung histeresis isoterma) menunjukkan peralihan suhu Curie, Tc yang menonjol dan kemunculan dari julat panjang susunan ferromagnet ke julat pendek yang berkait rapat dengan susunan paramagnet ($0.00 \leq x \leq 0.06$), antiferromagnet (x=0.90) dan keadaan spin kaca (x=0.80). Kerintangan elektrik meningkat dengan peralihan suhu logam-penebat, T_{MIT} ke suhu rendah. Data kerintangan suhu rendah menandakan mekanisme rintangan dalam bahagian logam ini boleh dikaitkan dengan penyerakkan elektron-elektron yang dilengkapi dengan sumbangan minor dari serakkan magnon-elektron. Selain itu, data kerintangan suhu tinggi pula memenuhi model Loncatan Julat Bolehubah (VRH) dan model Loncatan polaron kecil (SPH). Ketumpatan keadaan di aras Fermi, $N(E_f)$ dan tenaga pengaktifan, E_a yang diperoleh daripada data pemadanan membuktikan kelincahan elektron berkurang secara berkadar langsung dengan kepekatan Dy. Nilai $N(E_f)$ didapati berjulat antara 1.53×10^{16} $eV^{-1}cm^{-3}$ ke 1.45×10^{18} $eV^{-1}cm^{-3}$ manakala nilai E_a berubah dari 2.96×10^{2} meV ke 1.32×10^{3} meV. Perbezaan antara T_C-T_{MIT} adalah disebabkan oleh faktor intrinsik dan disusuli dengan faktor ekstrinsik seperti saiz butiran (sempadan butiran). Kesan saiz butiran terhadap mekanisme CMR dianalisis daripada imej AFM. Saiz butiran dalam kesemua sampel didapati menurun secara eksponan dari 2.88 μm (x=0.00) ke 1.34 μm (x=0.90) kerana bahan dopan tidak menyumbang kepada pertumbuhan butiran. Apabila saiz butiran berkurang, nisbah permukaan terhadap isipadu butiran adalah tinggi. Oleh demikain, pengaruh sempadan butiran tidak boleh dikecualikan. Secara keseluruhan, CMR negatif dalam urutan menaik telah dikesan dalam semua sampel ketika suhu menurun pada medan magnet yang rendah. Fenomena ini dikenali sebagai magnetorintangan medan rendah (LFMR). Serakkan spin, polarisasi spin dan penerowongan antara butiran bersebelahan melalui sempadan butiran yang tidak terjajar pada arah medan magnet adalah dipertanggungjawab terhadap kesan LFMR. Nilai CMR tertinggi sebanyak 62.2% diperolehi daripada sampel LDySMO (x=0.60) pada suhu 90K.

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I certify that an Examination Committee has met on 11th Jun 2007 to conduct the final examination of Lee Oon Jew on her Master of Science thesis entitled "Structural, Magnetic and Electrical Properties and Colossal Magnetoresistive effect of $La_{0.67}Sr_{0.33}MnO_3$ Perovskites with Dy Substitution at La site" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Master of Science degree.

Members of the Examination Committee are as follows:

Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Elias Saion, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Hishamuddin Zainuddin, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

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

HASANAH MOHD. GHAZALI, PhD
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia.

Date:

This thesis 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
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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

AINI IDERIS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 9 August 2007

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

____

LEE OON JEW

Date: 2 August 2007

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Jumiah Hassan, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Elias Saion, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Hishamuddin Zainuddin, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

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

HASANAH MOHD. GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 3 AUGUST 2007

Saya mengesahkan bahawa Jawatankuasa Peperiksaan Tesis bagi Lee Oon Jew telah mengadakan peperiksaan akhir pada 11 Jun 2007 untuk menilai tesis Master Sains beliau yang bertajuk “Sifat Struktur, Magnet dan Elektrik dan Kesan Magnetorintangan Raksasa Perovskit $La_{0.67}Sr_{0.33}MnO_3$ dengan Penggantian Dy pada tapak La” mengikut Akta Universiti Pertanian Malaysia (Ijazah Lanjutan) 1980 dan Peraturan-peraturan Universiti Pertanian Malaysia (Ijazah Lanjutan) 1981. Jawatankuasa Peperiksaan Tesis memperakukan bahawa calon ini layak dianugerahi ijazah tersebut. Ahli Jawatankuasa Peperiksaan Tesis adalah seperti berikut:

Jumiah Hassan, PhD
Profesor Madya
Fakulti Sains
Universiti Putra Malaysia
(Pengerusi)

Elias Saion, PhD
Profesor
Fakulti Sains
Universiti Putra Malaysia
(Pemeriksa Dalam)

Hishamuddin Zainuddin, PhD
Profesor Madya
Fakulti Sains
Universiti Putra Malaysia
(Pemeriksa Dalam)

Roslan Abd. Shukor, PhD
Profesor
Fakulti Sains
Universiti Kebangsaan Malaysia
(Pemeriksa Luar)

HASANAH MOHD. GHAZALI, PhD
Profesor/Timbalan Dekan
Sekolah Pengajian Siswazah
Universiti Putra Malaysia

Tarikh: 3 OGOS 2007

CHAPTER 1

INTRODUCTION

1.1 Colossal Magnetoresistance

The continually increasing demand for ultrahigh density magnetic information storage, retrieval and sensing electronic device has driven a significant effort to secure fundamental base for the future manufacturing of devices and sensors based on colossal magnetoresistance (CMR) materials. Thus, there has been intense attention, theoretical and experimental paid to these colossal magnetoresistance materials in the search for a complete understanding of the fundamental science behind the phenomena exhibited by the material.

Magnetoresistance (MR) is a change in the electrical resistance of a material when it is subjected to magnetic field and defined as:

$$\%MR = \frac{\Delta R}{R_0} = \frac{R_H - R_0}{R_0} \times 100\% \qquad (1.1)$$

where R_H and R_0 are the resistances in the presence and absence of a magnetic field respectively. In general, the MR can be classified by their origin and working principle into several types namely, anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), colossal magnetoresistance (CMR), tunnelling