UNIVERSITI PUTRA MALAYSIA

COLOSSAL MAGNETORESIST ANCE OF (La1-x Ax)0.67 Cao.33Mn03 [A=Sn, Sm and Er) PEROVSKITE

ZOHRA ALI MOHAMED GEBREL

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MASTER OF SCIENCE
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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

July 2003

DEDICATIONS

To Prof. Dr. Halim,
for his patience and guidance

To my late father, my mother for her love and support
To all my sisters and brothers for their love and concern……
To my brother Moftah for his support and understanding……

To all my family and my friends

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

COLOSSAL MAGNETORESISTANCE OF $(La_{1-x}A_x)_{0.6}Ca_{0.33}MnO_3$ [A=Sn, Sm and Er] PEROVSKITE

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July 2003

Chairman: Professor Abdul Halim bin Shaari, Ph.D.

Faculty : Science and Environmental Studies

In this work, the colossal magnetoresistance (CMR) of $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$ [LSnCMO], $(La_{1-x}Sm_x)_{2/3}Ca_{1/3}MnO_3$ [LSmCMO] and $(La_{1-x}Er_x)_{2/3}Ca_{1/3}MnO_3$ [LErCMO] ceramics samples, with x=0.0 to 0.4 were prepared by solid-state reaction technique. The structure, magnetic and electrical properties of the samples were investigated. The x-ray diffraction (XRD) spectrum for all the samples exhibit orthorhombic distorted and single-phase perovskite structures with the presence of some minor impurities. The magnetic properties were studied by measuring the susceptibility of the samples as a function of temperature at various magnetic fields. Ferromagnetic-paramagnetic phase transition temperature, T_c was determined for low doping concentration. The Curie temperature, T_c shifts to lower temperature as tin, samarium and erbium content was increased, indicating the loss of ferromagnetic order. For high tin content, the classical ferromagnetic order disappears and a cusp peak anomaly appears at 87 K, 68 K, 61 K and 55 K for x=0.1, 0.2, 0.3 and 0.4 respectively. The cusp shifts to higher temperature as the frequency increases from

125 Hz to 200 Hz and becomes sharper as magnetic field increases from 0.1 Oe to 10 Oe in agreement with spin glass behavior. However, LSmCMO system displays a classical ferromagnetic-paramagnetic transition for x = 0.0, 0.01, 0.02 and 0.04 and T_c shifts to lower temperature as samarium content increases. Also a cusp peak was observed at around 50 K for samples with x ≥0.03. However, the study of frequency dependence of susceptibility did not show any shift in T_{cusp}. Thus the samples did not exhibit the spin glass behavior and T_{cusp} is called Neél temperature, T_N. In addition, LErCMO system also demonstrated that the samples with x=0.01, 0.02 and 0.03 exhibit the spin glass behavior and the respective spin-glass transition temperatures, T_{SG} are 99.7 K, 98.7 K and 70.5 K, respectively. But, samples with x ≥ 0.1 did not show any ferromagnetic-paramagnetic transition at the range of 30 K to 300 K, possibly the Curie temperature for these samples is below 30 K. The pure sample, which exhibits T_c around 240 K and T_p around 200 K showed high level of porosity, and an average grain size of 3μm. By replacing La with Sn, Sm and Er, respectively, in the LCMO system, the colossal magnetoresistance effect appear at low temperature and the highest value of CMR effect was observed at temperature approaching Tp. The highest CMR value was observed in LErCMO system with x=0.03 at 170 K. The value is 51 %. In LSnCMO, the maximum CMR value is 49 % at 200 K for the sample with x=0.01. While in the LSmCMO system the highest CMR value is displayed at 200 K for the sample with x=0.02.

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

MAGNETORINTANGAN RAKSAKSA BAGI $(La_{1-x}A_x)_{0.67}Ca_{0.33}MnO_3$ [A=Sn, Sm and Er] PEROVSKITE

Oleh

ZOHRA ALI MOHAMED GEBREL

Julai 2003

Pengerusi : Profesor Abdul Halim Shaari, Ph.D.

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Dalam kajian ini, magnetorintangan raksasa bagi sampel seramik $(La_{1-x}Sn)_{2/3}Ca_{1/3}MnO_3$ [LSnCMO], $(La_{1-x}Sm)_{2/3}Ca_{1/3}MnO_3$ [LSmCMO], $(La_{1-x}Er_{2/3}Ca_{1/3}MnO_3$ [LErCMO], dengan x=0.0 hingga 0.4 telah disediakan menggunakan teknik tindakbalas keadaan pepejal. Struktur, sifat magnet dan sifat elektrik bagi sampel tersebut telah dikaji. Spektrum belauan sinar-x bagi semua sampel menunjukkan orthorombik tercangga dan struktur perovskite fasa tunggal dengan kehadiran bendasing. Sifat magnet telah dikaji menggunakan ketelapan sebagai fungsi suhu pada medan magnet yang berbeza. Suhu peralihan fasa feromagnet-paramagnet, Tc telah ditentukan bagi kepekatan dopan yang rendah. Suhu Curie, Tc teranjak ke suhu yang rendah apabila kandungan timah, samarium dan erbium bertambah, yang menunjukkan kehilangan tertib ferromagnet. Bagi kandungan timah yang tinggi, klasik tertib ferromagnet hilang dan kejanggalan juring puncak masing-masing muncul pada 87 K, 68 K, 61 K dan 55K bagi x=0. 1, 0.2, 0.3

dan 0.4. Anjakan juring kepada suhu tinggi berlaku apabila frekuensi meningkat dari 125 Hz ke 200 Hz dan menjadi tajam semasa medan magnet meningkat dari 0.1 Oe ke 10 Oe dalam persetujuan dengan sifat spin kaca. Walau bagaimanapun, LSmCMO sistem, menunjukkan klasik ferromagnet-paramagnet bagi x=0.0, 0.01, 0.02 dan 0.04 dan Tc beranjak ke suhu yang rendah apabila kandungan samarium meningkat. Juga puncak juring pada sekitar 50 K diperhatikan bagi sampel dengan $x \geq 0.03$ dan kajian kebergantungan terhadap frekuensi bagi susceptibiliti tidak menunjukkan sebarang perubahan dalam T_{cusp}, Oleh itu, sampel tersebut tidak menunjukkan sifat spin kaca dan T_{cusp} adalah sebagai suhu Neel, T_N. Sebagai tambahan LErCMO sistem telah menunjukkan sampel dengan x=0.01, 0.02 dan 0.03. mempamerkan sifat spin kaca dan masing-masing T_{SG} adalah 99.7 K, 98.7 K dan 70.5 K. Tetapi sampel dengan x > 0. 1 tidak memperlihatkan sebarang ferromagnet-paramagnet pada julat 30 K ke 300 K. Kemungkinan suhu Curie bagi sampel ini di bawah 30 K. Sampel tulen, yang menunjukkan Tc sekitar 240 K dan Tp sekitar 200 K mempamerkan paras porositi yang tinggi , dan purata saiz butiran 3 μm. Dengan menggantikan La dengan Sn, Sm dan Er dalam magnetorintangan perovskite bagi LCMO sistem, purata magnetorintangan raksasa timbul pada suhu rendah dan kesan magnetorintangan yang besar telah diperolehi pada suhu mencapai Tp. Nilai CMR tertinggi diperhatikan dalam LErCMO sistem dengan x=0.03 ada 170 K dan nilai tersebut adalah 51% . Dalam LSnCMO, nilai maksimum CMR adalah 49% pada 200 K bagi sampel x=0.01. Walau bagaimanapun, sistem LSmCMO menunjukkan nilai CMR tertinggi pada 200 K bagi sampel dengan x=0.02.

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Last but not least, I would like to send all my love to my whole family, specifically my great mother who encourage me till I reached this position.

I certify that an Examination Committee met on 23/7/2003 to conduct the final examination of Zohra Ali Mohamed Gebrel on her Master of Science thesis entitled "Colossal Magnetoresistance of $(La_{1-x}\ A_x\ )_{0.67}\ Ca_{0.33}MnO_3$ [A=Sn, Sm and Er] perovskite" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisor Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citation which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ZOHRA ALI MOHAMED GEBREL

Date: 20/10/2023

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LIST OF ABREVIATIONS AND KEY WORDS

T	Temperature in Kelvin
T_c	Curie temperature
T_N	Néel temperature
T_f	Freezing temperature
T_p	Phase transition temperature
T_{SG}	Spin freezing temperature
MR	Magnetoresistance
CMR	Colossal Magnetoresistance
GMR	Giant Magnetoresistance
AMR	Anisotropic Magnetoresistance
TMR	Tunnelling Magnetoresistance
EMR	Extraordinary Magnetoresistance
VLMR	Very Large Magnetoresistance
R (H)	The resistance in the magnetic field
R (0)	The resistance in zero magnetic field
DE	Double exchange
JT	Jahn-Teller
LCMO	La-Ca-Mn-O system
LSnCMO	La-Sn-Ca-Mn-O system
LSmCMO	La-Sm-Ca-Mn-O system
LErCMO	La-Er-Ca-Mn-O system
LTCMO	La-Tb-Ca-Mn-O system
LBCMO	La-Bi-Ca-Mn-O system
LDCMO	La-D-Ca-Mn-O system

LGCMO	La-Gd-Ca-Mn-O system
MI	Metal to insulator
MIT	Metal-insulator transition
AFM	Antiferromagnetic
AFI	Antiferromagnetic insulator
FMI	Ferromagnetic insulator
PMI	Paramagnetic insulator
<A>	Average ionic radius
t	Tolerance factor
d_{La-O}	La-O bond distance
d_{Mn-O}	Mn-O bond distance
XRD	X-ray diffraction
SEM	Scanning Electron Microscope
H	Applied magnetic field
M	Magnetization
K_B	Boltzman constant
E_a	Activation energy
a, b, C	Lattice Parameter
hkl	Miller indices
d_{hkl}	Distance between atom and selected 2θ
χ	Susceptibility
Θ	Paramagnetic Curie point
f	Frequency
S	Spin electron
int	Intrinsic

CHAPTER I

GENERAL INTRODUCTION

Types of Magnetoresistance

Recently it has been discovered that certain types of materials exhibit extreme changes in electrical resistivity when a large magnetic field is applied. This effect, named as magnetoresistance is utilized in many types of sensors, measuring the amount and direction of magnetic fields. During the discovery of magnetoresistance, new effects found grew in strength and were progressively named anisotropic magnetoresistance (AMR), giant magnetoresistance (GMR), and colossal magnetoresistance (CMR), the latter being the main focus of this study (Valentine et al ., 2002). The materials that exhibit CMR are manganate perovskites. In these materials the magnetoresistance arises from a difference in carrier scattering rates, depending on the relative orientation of the magnetization in the adjacent layers. The relative change in resistance, is usually defined as :

$$\frac{\Delta R}{R(0)} = \frac{[R(H) - R(0)]}{R(0)} \qquad (1.1)$$

where R(H) is the resistance at an applied field, and R(0) is the resistance at zero field.