UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF (La1-xDYx)1-yCayMnO3 (x=0.00 TO 1.00; y=1/8, 1/3, 1/2) PEROVSKITES

SHARMIWATI BINTI MOHAMMED SHARIF

MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF $(La_{1-x}Dy_x)_{1-y}Ca_yMnO_3$ (x=0.00 TO 1.00; $y={}^1/_8, {}^1/_3, {}^1/_2$) PEROVSKITES

By

SHARMIWATI BINTI MOHAMMED SHARIF

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

August 2003

DEDICATION

To my dear
Husband
for his love and support....

To my dear family
Abah, Mama, Ngah and Adik
for their love and encouragement....

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

MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF $(La_{1-x}Dy_x)_{1-y}Ca_yMnO_3$ (x=0.00 TO 1.00; y=$^1/_8$, $^1/_3$, $^1/_2$) PEROVSKITES

By

SHARMIWATI BT. MOHAMMED SHARIF

August 2003

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

Faculty: Science and Environmental Studies

A thorough study of Colossal Magnetoresistance materials of $(La_{1-x}Dy_x)_{7/8}Ca_{1/8}MnO_3$, $(La_{1-x}Dy_x)_{2/3}Ca_{1/3}MnO_3$ and $(La_{1-x}Dy_x)_{1/2}Ca_{1/2}MnO_3$ have been carried out for a full range of doping from x=0.00 to x=1.00. All samples show single-phase orthorhombic perovskite structure with some minor impurities. Paramagnetic-ferromagnetic phase transitions were observed in the χ'-temperature curves for the undoped $(La\text{-}Dy)_{7/8}Ca_{1/8}MnO_3$ and $(La\text{-}Dy)_{2/3}Ca_{1/3}MnO_3$ samples. The Curie temperature, T_C shifts to lower temperature as dysprosium increases indicating the lost of ferromagnetic order. However, dysprosium doping is observed to increase the T_C in $(La\text{-}Dy)_{7/8}Ca_{1/8}MnO_3$ system more than the effect of other systems. But for the higher doping of dysprosium, the magnetic behaviour of samples has been disturbed. For $(La\text{-}Dy)_{2/3}Ca_{1/3}MnO_3$ system, the substitution of dysprosium decreases the T_C. This is due to the buckling of MnO_6 octahedra, which increases with the increase of dysprosium concentration giving weaker double exchange interaction and describing the decreases of the electron hopping between Mn^{3+} and Mn^{4+}. $(La\text{-}Dy)_{1/2}Ca_{1/2}MnO_3$ system shows both ferromagnetism and antiferromagnetism transition for undoped sample but as the dysprosium substitutes, the

antiferromagnetism totally disappears and ferromagnetic behaviours is observed. This anomaly indicates that the change in the bond angle on Dy substitution reduces the antiferromagnetism coupling. The existence of T_P and T_C was found to be correlated. This phenomenon of coexistence was due to the double exchange interaction of Mn^{3+} and Mn^{4+} that brings the systems below T_C into metallic state. Based on the semiconductor model, $\ln(R) \alpha (-E_a/k_BT)$ it was observed that the energy gap for all samples was very small with below than 0.2 eV and thus exhibits narrow gap semiconductor properties. The measurement of temperature dependence of magnetoresistance has been studied for each sample and negative CMR values have been obtained. CMR value appears at low temperature approaching T_P. The highest CMR value is 56.9% at 150 K was observed in $(La_{1-x}Dy_x)_{7/8}Ca_{1/8}MnO_3$ system with x=0.33 and applied magnetic field at 1 Tesla.

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

KAJIAN TERHADAP MIKROSTRUKTUR AND SIFAT MAGNET BAGI $(La_{1-x}Dy_x)_{1-y}Ca_yMnO_3$ (x=0.00 HINGGA 1.00; y=$^1/_8$, $^1/_3$, $^1/_2$) PEROVSKITE

Oleh

SHARMIWATI BT. MOHAMMED SHARIF

Ogos 2003

Pengerusi: Professor Abdul Halim Bin. Shaari, Ph.D.

Fakulti: Sains dan Pengajian Alam Sekitar

Kajian menyeluruh terhadap bahan magnetorintangan raksasa $(La_{1-x}Dy_x)_{7/8}Ca_{1/8}MnO_3$, $(La_{1-x}Dy_x)_{2/3}Ca_{1/3}MnO_3$ dan $(La_{1-x}Dy_x)_{1/2}Ca_{1/2}MnO_3$ telah dilakukan dalam julat pendopan dari x=0.00 hingga x=1.00. Kesemua sampel menunjukkan kewujudan satu fasa dalam struktur perovskite ortorombik dengan sedikit bendasing. Perubahan fasa paramagnet-ferromagnet telah dicerap pada lengkung χ'-suhu untuk sampel $(La\text{-}Dy)_{7/8}Ca_{1/8}MnO_3$ dan $(La\text{-}Dy)_{2/3}Ca_{1/3}MnO_3$. Suhu Curie, T_C beralih ke suhu yang lebih rendah apabila pendopan dengan dysprosium meningkat di mana menunjukkan kehilangan fasa ferromagnet. Walau bagaimanapun, kehadiran dysprosium dalam sistem $(La\text{-}Dy)_{7/8}Ca_{1/8}MnO_3$ menunjukkan sedikit peningkatan dalam T_C berbanding dalam sistem yang lain. Tetapi untuk pendopan yang tinggi, kehadiran dysprosium dikesan mengganggu sifat magnetik bahan. Bagi sistem $(La\text{-}Dy)_{2/3}Ca_{1/3}MnO_3$, kehadiran dysprosium menyebabkan penurunan T_C. Ini kerana pembentukkan struktur oktagon MnO_6 yang semakin meningkat dengan kesan pertambahan dysprosium menyebabkan interaksi tukarganti ganda dua semakin lemah dan menggambarkan lompatan elektron di antara Mn^{3+} dan Mn^{4+} semakin berkurangan. Sistem $(La\text{-}Dy)_{1/2}Ca_{1/2}MnO_3$

menunjukkan kehadiran fasa ferromagnet dan antiferromagnet untuk sampel tanpa pendopan tetapi dengan kehadiran dysprosium, sifat antiferromagnetik hilang serta-merta dan hanya sifat ferromagnet dapat dikesan. Kesan luar biasa ini menunjukkan perubahan ke atas sudut ikatan dan dengan kehadiran dysprosium mengurangkan kesan antiferromagnetik. Kewujudan T_P dan T_C adalah saling berkait. Fenomena ini disebabkan kehadiran interaksi tukarganti ganda dua antara Mn^{3+} dan Mn^{4+} membawa sistem pada paras di bawah T_C keadaan pengalir. Berdasarkan model semikonduktor $\ln(R)\ \alpha\ (-E_a/k_BT)$ didapati jurang tenaga untuk semua sampel sangat kecil iaitu 0.2 eV ke bawah dan mempamerkan sifat jurang sempit semikonduktor separa. Suhu kebergantungan magnetorintangan telah diuji bagi setiap sampel dan nilai CMR negatif telah diperolehi. Nilai CMR didapati pada suhu rendah mendekati T_P. Nilai tertinggi CMR adalah 56.9% pada suhu 150 K dicerap dalam sistem $(La\text{-}Dy)_{7/8}Ca_{1/8}MnO_3$ untuk sampel x=0.33 dengan medan magnet 1 Tesla dikenakan.

ACKNOWLEDGEMENTS

Firstly, I would like to dedicate my special thanks to Professor Dr. Abdul Halim B. Shaari, the supervisor of my Master Project for his suggestions, interests and supports, his foresight, as well as for the facilities that he provided and the important role he played in making this project a success. I also would like to express my appreciation to my co-supervisors, Professor Dr. Wan Mahmood B. Mat Yunus and Associate Professor Dr. Hishamuddin B. Zainuddin for their valuable advice, comments and guidance.

I would like to acknowledge my indebtedness to MOSTE for the financial support through National Science Fellowship (NSF). I owe particular thanks to Mr. Razak B. Harun for technical favours, Mrs. Noriza for her kind help, staffs in the Physics Department and staffs from Electron Microscope Unit, Institute of Bioscience for their significant contributions.

I would also like to express my appreciation to the various individuals, too numerous to mention individually, who provided assistance during the course of the project especially for Dr. Lim Kean Pah, Dr. Abdullah Chik, Mr. Kabashi Kathir Kabashi, Ms. Zohra Gebrel, Mr. Ramadhan Shouib, Mr. Ali Agail, Dr. Imad Hamadneh, Mr. Azman Awang Teh, Mr. Teh Jia Yew, Ms. Nur Jannah, Ms. Masrianis, Mr. Walter Charles, Mr. Mustafa Dihom, Ms. Huda Abdullah and Ms. Ari. To my housemates, Ms. Nur Shukriyah, Ms. Nur Hidayati, Ms. Sam Azura, Ms. Roszuliza and Ms. Nurfariza, thanks to all of them. Their support and help will never forgetten.

Special thanks are due to my family; my parents Mr. Mohd. Sharif B. Kusnan and Mrs. Samiah Bt. Ismail, my sisters Ms. Sabihah Shuhada and Ms. Syazwina for their continuous support, understanding and encouragement. To my fiancé, Mr. Mohd. Annas B. Mustafa, thank you for giving me the support that I needed toward the completion the project.

My efforts would not have come to fruition if I had not had the guidance, supports and encouragement of many people from within as well as from outside the Universiti Putra Malaysia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

T	Temperature in Kelvin
T_C	Curie temperature
T_P/T_{IM}	Phase transition temperature
T_G	Spin glass temperature
T_f	Freezing temperature
T_N	Nèel temperature
Θ_P	Paramagnetic Curie temperature
C	Curie constant
R	Resistance
R_H	Resistance with presence of field
R_0	Resistance in an absence of field
ρ	Resistivity
E_a	Activation energy
k_B	Boltzman constant
MI	Metal to insulator
MIT	Metal-insulator transition
AFI	Antiferromagnetic insulator
FMM	Ferromagnetic metal
FMI	Ferromagnetic insulator
PMI	Paramagnetic insulator
MR	Magnetoresistance
CMR	Colossal magnetoresistance
AMR	Anisotropic magnetoresistance

GMR	Giant magnetoresistance
TMR	Tunneling magnetoresistance
EMR	Extraordinary magnetoresistance
VLMR	Very large magnetoresistance
BMR	Ballistic magnetoresistance
MRRAM	Magnetoresistive random access memory
x	Concentration of dopants
Ln	Lantanide group ions
A	Divalent earth ions
χ	Magnetic susceptibility
M	Magnetization
B	Applied magnetic field
H	Magnetic field
$<r_A>$	Average radius of the rare-earth ions
DE	Double exchange
JT	Jahn Teller
XRD	X-ray diffractometer
SEM	Scanning electron microscope
ι	Length of the conductor
A	Cross sectional area
θ	Glancing angle (Bragg angle)
$\mathit{\theta}$	Mn-O-Mn bond angle
a, *b*, *c*	Lattice parameter
hkl	Miller indices
d	Interplanar spacing

d_{hkl}	Distance between atom and selected 2θ
n	Order of reflection (an integer)
λ	Wave length
V	Measured root mean square (RMS voltage)
α	Calibration coefficient
υ	Volume of sample
f	Frequency of AC field

CHAPTER I

INTRODUCTION

Research Background

The discovery of colossal magnetoresistance (CMR) has received extensive studis since 1950s. As the name implies, the effect observed in these materials showed a huge change in electrical resistivity when a magnetic field was applied. The effect is typically known as magnetoresistance (MR) but the resistivity change was so large that it could not be compared with any other forms of magnetoresistance. These manganese-based perovskite materials has been the subject of a huge international research to seek suitable new materials with specific properties susceptible to be involved in numerous technological applications in magnetic recording and sensors. In 1993, the researchers at Siemens in Germany and a little later by a group at Bell Labs in New Jersey, raised expectations of a new generation of magnetic devices and sensors, and launched a frenetic scientific race to understand the cause of the effect (Fontcuberta, 1999). Even though it has not been utilized in devices yet but it development shows such great potential.

The CMR materials have the formula $Ln(_{1-x})A_xMnO3$ where Ln is usually the trivalent rare earth ions (La^{3+}, Pr^{3+}, Nd^{3+} etc.) and A is the divalent ions (Ca^{2+}, Ba^{2+}, Sr^{2+}). The reason they are called "colossal" is that their magnetoresistance ratios are many orders of magnitude larger than those of the giant magnetoresistance materials. Unfortunately, the temperatures at which the "colossal" magnetoresistance ratios