

# **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

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FSAS 2003 55

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By

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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=<sup>1</sup>/<sub>8</sub>, <sup>1</sup>/<sub>3</sub>, <sup>1</sup>/<sub>2</sub>) PEROVSKITES

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#### August 2003

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

**Faculty: Science and Environmental Studies** 

А 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  $\chi$ '-temperature curves for the undoped  $(La-Dy)_{7/8}Ca_{1/8}MnO_3$  and  $(La-Dy)_{2/3}Ca_{1/3}MnO_3$  samples. The Curie temperature, T<sub>C</sub> shifts to lower temperature as dysprosium increases indicating the lost of ferromagnetic order. However, dysprosium doping is observed to increase the T<sub>C</sub> in  $(La-Dy)_{7/8}Ca_{1/8}MnO_3$  system more than the effect of other systems. But for the higher doping of dysprosium, the magnetic behaviour of samples has been disturbed. For  $(La-Dy)_{2/3}Ca_{1/3}MnO_3$  system, the substitution of dysprosium decreases the T<sub>C</sub>. This is due to the buckling of MnO<sub>6</sub> 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-Dy)<sub>1/2</sub>Ca<sub>1/2</sub>MnO<sub>3</sub> 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,  $ln(R) \alpha$  (- $E_g/k_BT$ ) 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<sub>1-x</sub>Dy<sub>x</sub>)<sub>1-y</sub>Ca<sub>y</sub>MnO<sub>3</sub> (x=0.00 HINGGA 1.00; y=<sup>1</sup>/<sub>8</sub>, <sup>1</sup>/<sub>3</sub>, <sup>1</sup>/<sub>2</sub>) PEROVSKITE

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Kajian terhadap bahan magnetorintangan menyeluruh 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-Dy)<sub>7/8</sub>Ca<sub>1/8</sub>MnO<sub>3</sub> dan (La-Dy)<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub>. Suhu Curie, T<sub>C</sub> beralih ke suhu yang lebih rendah apabila pendopan dengan dysprosium meningkat di mana menunjukkan kehilangan fasa ferromagnet. Walau bagaimanapun, kehadiran dysprosium dalam sistem (La-Dy)<sub>7/8</sub>Ca<sub>1/8</sub>MnO<sub>3</sub> menunjukkan sedikit peningkatan dalam  $T_{\rm C}$  berbanding dalam sistem yang lain. Tetapi untuk pendopan yang tinggi, kehadiran dysprosium dikesan mengganggu sifat magnetik bahan. Bagi sistem (La-Dy)<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub>, kehadiran dysprosium menyebabkan penurunan T<sub>C</sub>. Ini kerana pembentukkan struktur oktagon MnO<sub>6</sub> yang semakin meningkat dengan kesan pertambahan dysprosium menyebabkan interaksi tukarganti ganda dua semakin lemah dan menggambarkan lompatan elektron di antara Mn<sup>3+</sup> dan Mn<sup>4+</sup> semakin berkurangan. Sistem (La-Dy)<sub>1/2</sub>Ca<sub>1/2</sub>MnO<sub>3</sub>

menunjukkan kehadiran fasa ferromagnet dan antiferromagnet untuk sampel tanpa pendopan tetapi dengan kehadiran dysprosium, sifat antiferromagnetik hilang sertamerta 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<sub>P</sub> dan T<sub>C</sub> adalah saling berkait. Fenomena ini disebabkan kehadiran interaksi tukarganti ganda dua antara Mn<sup>3+</sup> dan Mn<sup>4+</sup> membawa sistem pada paras di bawah T<sub>C</sub> keadaan pengalir. Berdasarkan model semikonduktor ln(R)  $\alpha$  (-E<sub>a</sub>/k<sub>B</sub>T) 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<sub>P</sub>. Nilai tertinggi CMR adalah 56.9% pada suhu 150 K dicerap dalam sistem (La-Dy)<sub>7/8</sub>Ca<sub>1/8</sub>MnO<sub>3</sub> 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. Nurfanza, 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.



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## LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

Т	Temperature in Kelvin
Tc	Curie temperature
$T_P/T_{IM}$	Phase transition temperature
T <sub>G</sub>	Spin glass temperature
$T_f$	Freezing temperature
T <sub>N</sub>	Nèel temperature
$\Theta_{\rm P}$	Paramagnetic Curie temperature
C	Curie constant
R	Resistance
R <sub>H</sub>	Resistance with presence of field
R <sub>0</sub>	Resistance in an absence of field
ρ	Resistivity
E <sub>a</sub>	Activation energy
k <sub>B</sub>	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	Turmeling magnetoresistance
EMR	Extraordinary magnetoresistance
VLMR	Very large magnetoresistance
BMR	Ballistic magnetoresistance
MRRAM	Magnetoresistive random access memory
x	Concentration of dopants
Ln	Lantanide group ions
Α	Divalent earth ions
χ	Magnetic susceptibility
Μ	Magnetization
В	Applied magnetic field
Н	Magnetic field
< <b>r</b> <sub>A</sub> >	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
Α	Cross sectional area
θ	Glancing angle (Bragg angle)
θ	Mn-O-Mn bond angle
a, b, c	Lattice parameter
hkl	Miller indices
d	Interplanar spacing



d <sub>hkl</sub>	Distance between atom and selected $2\theta$
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<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup> etc.) and A is the divalent ions (Ca<sup>2+</sup>, Ba<sup>2+</sup>, Sr<sup>2+</sup>). 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

