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

FSAS 2003 55
MICROSTRUCTURAL AND MAGNETIC PROPERTIES OF
(La$_{1-x}$Dy$_x$)$_{1.2}$Ca$_y$MnO$_3$ (x=0.00 TO 1.00; y=1/6, 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$_y$MnO$_3$ (x=0.00 TO 1.00; y=$1/8$, $1/3$, $1/2$) PEROVSKITES

By

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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$_x$)$_{1/8}$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)$_{1/8}$Ca$_{1/8}$MnO$_3$ and (La-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-Dy)$_{1/8}$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 $T_C$. 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-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, \( \ln(R) \propto (-E_\alpha/k_B T) \) 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 \((La_{1-x}Dy_x)_{2/3}Ca_{1/3}MnO_3\) 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$_y$MnO$_3$ (x=0.00 HINGGA 1.00; y=1/8, 1/3, 1/2) PEROVSKITE

Oleh

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Ogos 2003

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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 $\chi'$-suhu untuk sampel (La-Dy)$_{7/8}$Ca$_{1/8}$MnO$_3$ dan (La-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-Dy)$_{2/3}$Ca$_{1/3}$MnO$_3$ menunjukkan sedikit peningkatan dalam $T_C$ berbanding dalam sistem yang lain. Tetapi untuk pendopan yang tinggi, kehadiran dysprosium dihasilkan mengganggu sifat magnetik bahan. Bagi sistem (La-Dy)$_{2/3}$Ca$_{1/3}$MnO$_3$, kehadiran dysprosium menyebabkan penurunan $T_C$. Ini kerana pembentukan 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-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 $\ln(R) \propto (-E_a/k_B T)$ 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 $T_P$. Nilai tertinggi CMR adalah 56.9% pada suhu 150 K dicerap dalam sistem $(\text{La-Dy})_{78}\text{Ca}_{18}\text{MnO}_3$ untuk sampel $x=0.33$ dengan medan magnet 1 Tesla dikenakan.
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APPROVAL

I certify that an Examination Committee met on 7th August 2003 to conduct the final examination of Sharmiati Binti Mohammed Sharif on her Master of Science thesis entitled "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" 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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Date: 14 NOV 2003
DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations 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.

__________________________
SHARMIWATI BT. MOHAMMED SHARIF

Date: 26.09.2013
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### LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>T</td>
<td>Temperature in Kelvin</td>
</tr>
<tr>
<td>$T_C$</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>$T_{p/T_{IM}}$</td>
<td>Phase transition temperature</td>
</tr>
<tr>
<td>$T_G$</td>
<td>Spin glass temperature</td>
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<tr>
<td>$T_f$</td>
<td>Freezing temperature</td>
</tr>
<tr>
<td>$T_N$</td>
<td>Néel temperature</td>
</tr>
<tr>
<td>$\Theta_P$</td>
<td>Paramagnetic Curie temperature</td>
</tr>
<tr>
<td>C</td>
<td>Curie constant</td>
</tr>
<tr>
<td>R</td>
<td>Resistance</td>
</tr>
<tr>
<td>$R_H$</td>
<td>Resistance with presence of field</td>
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<tr>
<td>$R_0$</td>
<td>Resistance in an absence of field</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
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<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
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<tr>
<td>MI</td>
<td>Metal to insulator</td>
</tr>
<tr>
<td>MIT</td>
<td>Metal-insulator transition</td>
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<tr>
<td>AFI</td>
<td>Antiferromagnetic insulator</td>
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<tr>
<td>FMM</td>
<td>Ferromagnetic metal</td>
</tr>
<tr>
<td>FMI</td>
<td>Ferromagnetic insulator</td>
</tr>
<tr>
<td>PMI</td>
<td>Paramagnetic insulator</td>
</tr>
<tr>
<td>MR</td>
<td>Magnetoresistance</td>
</tr>
<tr>
<td>CMR</td>
<td>Colossal magnetoresistance</td>
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<tr>
<td>AMR</td>
<td>Anisotropic magnetoresistance</td>
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</table>
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
<ra> Average radius of the rare-earth ions
DE  Double exchange
JT  Jahn Teller
XRD X-ray diffractometer
SEM Scanning electron microscope
l Length of the conductor
A  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

xxii
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$d_{hkl}$</td>
<td>Distance between atom and selected 29</td>
</tr>
<tr>
<td>$n$</td>
<td>Order of reflection (an integer)</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wave length</td>
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<tr>
<td>$V$</td>
<td>Measured root mean square (RMS voltage)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Calibration coefficient</td>
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<tr>
<td>$v$</td>
<td>Volume of sample</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency of AC field</td>
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CHAPTER I
INTRODUCTION

Research Background

The discovery of colossal magnetoresistance (CMR) has received extensive studies 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 its development shows such great potential.

The CMR materials have the formula Ln(1-x)A_xMnO_3 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