UNIVERSITI PUTRA MALAYSIA

COLOSSAL MAGNETORESISTANCE OF Lao.67Cao.33Mn1-xAxO3 [A =V, Dy AND Zr] PEROVSKITE

KOH SONG FOO

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COLOSSAL MAGNETORESISTANCE OF $La_{0.67}Ca_{0.33}Mn_{1-x}A_xO_3$ [A=V, Dy AND Zr] PEROVSKITE

By

KOH SONG FOO

Thesis Submitted in Fulfilment of the Requirements for the degree of Master of Science in the Faculty of Science and Environmental Studies
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April 2001

DEDICATIONS

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

To my dear family,
Grandma (Tan Kua)
Mother (Tey Hong Eng @ Tey Kim Hong)
Late father (Koh Eng Chuan)
Brothers (Shuang Long and Shuang Par)
Sisters (Sok Hui, Sok Ching, Sok Theng and Sock San)
for their love and concern….

To my dear,
Girl friend (Su Cheng)
for her love, support and understanding….

Fellow friends, ex-coursemates
and University Putra Malaysia as a whole !

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 LANTHANUM MANGANITE PEROVSKITE

By

KOH SONG FOO

April 2001

Chairman : Professor Abdul Halim bin Shaari, Ph.D

Faculty : Science and Environmental Studies

The colossal magnetoresistive of $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ (LCMVO), $La_{0.67}Ca_{0.33}Mn_{1-x}Dy_xO_3$ (LCMDO) and $La_{0.67}Ca_{0.33}Mn_{1-x}Zr_xO_3$ (LCMZO), x=0.00 to x=0.30, ceramics have been studied. X-ray diffraction (XRD) patterns show single-phase perovskite structure with the presence of some minor impurities for all the samples. The systems exhibit tetragonal and orthorhombic distorted perovskite structures, which resulted from the Jahn Teller distortion. Paramagnetic - Ferromagnetic phase transitions were observed in the χ'-temperature curves for all the samples. The Curie temperature, T_C shifts to lower temperature as vanadium, dysprosium and zirconium doping increases respectively, which indicate the loss of ferromagnetic order. Zirconium doping is observed to decrease the T_C more than the effect of other dopants. For LCMVO system, samples with x=0.01, 0.02, 0.03 and 0.30 show an enhancement of volume susceptibility as the temperature increases from 110 K-140 K, 120 K-142 K, 123 K-140 K and 77 K-94 K respectively. These enhancements are due to the formation of magnetic clusters

in the samples. For LCMDO system, all the samples show the typical ferromagnetic-paramagnetic transition and no spin glass behaviour was detected. However, in LCMZO system, the samples with $x>0.05$ show ferromagnetic onset followed by a cusp when cooling from room temperature. The anomalies were due to the formation of spin glass in the sample. The transport properties show the transition of semiconducting to metallic conductivity at T_P. The existence of T_P and T_C was found correlated. This phenomenon of coexistence was due to the double exchange interaction of two electrons in Mn^{3+}-O^{2-}-Mn^{4+} and Mn^{4+}-O^{2-}-Mn^{3+} configuration that brings the system below T_C into a metallic state. The semiconductor model, $\ln(\sigma) \sim (-Ea/kT)$ was used to explain the conduction mechanism of pervoskite manganites above T_P. It was concluded that the total conductivity, σ_{tot}, consists of the intrinsic and the extrinsic components. The energy gap found for all the samples was very small and thus exhibits narrow gap semiconductor properties. The measurement of temperature dependence of magnetoresistance has been carried out for each sample. Colossal magnetoresistance value appears at low temperature and the large magnetoresistive effect was observed at temperature approaching T_P. The highest CMR value observed is in LCMZO system for sample with $x=0.14$. The value is 72.2 % at 80 K. However, in LCMVO and LCMDO systems, the observed maximum CMR values are respectively 58.0 % at 170 K for sample with $x=0.20$ and 68.8 % at 126 K for sample with $x=0.20$. For LCMVO system, the increase in CMR value at low temperature may be due to the formation of magnetic clusters.

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

MAGNETORINTANGAN RAKSAKSA BAGI SERAMIK LANTHANUM MANGANITE

Oleh

KOH SONG FOO

April 2001

Pengerusi : Profesor Abdul Halim Shaari, Ph.D

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Sifat magnetorintangan raksaksa $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ (LCMVO), $La_{0.67}Ca_{0.33}Mn_{1-x}Dy_xO_3$ (LCMDO) dan $La_{0.67}Ca_{0.33}Mn_{1-x}Zr_xO_3$ (LCMZO), x=0.00 hingga x=0.30, telah dikaji. Corak belauan sinar-x (XRD) menunjukkan kewujudan satu fasa dengan sedikit bendasing untuk semua sampel. Semua sampel menunjukkan bentuk tetragonal dan ortorombik, akibat daripada herotan Jahn Teller. Peralihan fasa paramagnet-ferromagnet ada dicerap pada lengkung χ'-suhu untuk semua sampel. Suhu Curie, T_C masing-masing beralih ke suhu lebih rendah apabila pendopan dengan vanadium, dysprosium dan zirkonium meningkat, menunjukkan kehilangan fasa ferromagnet. Pendopan dengan zirkonium menunjukkan penurunan suhu T_C lebih daripada kesan pendopan lain. Untuk LCMVO sistem, sampel dengan x=0.01, 0.02, 0.03 and 0.30 masing-masing menunjukkan perangsangan pada ketelapan isipadu apabila suhu meningkat daripada 110 K-140 K, 120 K-142 K, 123 K-140 K dan 77 K-94 K. Rangsangan ini adalah disebabkan oleh pembentukan kelompok magnet di dalam sampel

tersebut. Untuk sistem LCMDO, semua sampel menunjukkan peralihan ferromagnet-paramagnet tipikal dan tiada sifat kaca spin dikesan. Bagaimanapun, dalam sistem LCMZO, sampel dengan x>0.05 menunjukkan permulaan ferromagnet diikuti oleh pembentukan juring semasa penyejukan daripada suhu bilik. Sifat luar biasa ini adalah disebabkan oleh pembentukan kaca spin di dalam sampel. Ciri sifat angkutan menunjukkan perubahan daripada sifat kebolehaliran separa kepada sifat kebolehaliran logam pada T_P. Kewujudan T_P dan T_C didapati saling berkait. Fenomena ini disebabkan oleh interaksi tukarganti ganda dua oleh dua elektron pada konfigurasi Mn^{3+}-O^{2-}-Mn^{4+} dan Mn^{4+}-O^{2-}-Mn^{3+} yang membawa sistem pada paras di bawah T_C ke keadaan pengalir. Untuk sifat angkutan, model semikonduktor $\ln(\sigma) \sim (-Ea/kT)$ digunakan untuk menjelaskan mekanisma konduksi manganite perovskite pada suhu yang lebih daripada T_P. Secara kesimpulannya, jumlah kebolehaliran, σ_{tot} terdiri daripada komponen intrinsik dan ekstrinsik. Jurang tenaga untuk semua sampel didapati sangat kecil dan mempamerkan sifat jurang sempit kebolehaliran separa. Suhu kebergantungan magnetorintangan telah diuji bagi setiap sampel. Nilai magnetorintangan raksaksa muncul pada suhu rendah dan kesan kemagnetorintangan besar diperhatikan pada suhu dekat dengan T_P. Nilai CMR tertinggi dicerap pada sistem LCMZO, bagi sampel dengan x=0.14. Nilainya ialah 72.2 % pada 80 K. Walaupun demikian, bagi sistem LCMVO dan sistem LCMDO, nilai maksimum CMR masing-masing ialah 58.0 % pada 170 K untuk sampel x=0.20 dan 68.8 % pada 126 K untuk sampel x=0.20. Untuk sistem LCMVO, peningkatan nilai CMR pada suhu rendah barangkali disebabkan oleh pembentukan kelompok magnet.

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LIST OF ABREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

T	Temperature in Kelvin
T_C	Curie temperature
T_P	Phase transition temperature
T_{SG}	Spin freezing temperature
T_N	Néel temperature
LCMO	La-Ca-Mn-O system
LCMVO	La-Ca-Mn-V-O system
LCMDO	La-Ca-Mn-Dy-O system
LCMZO	La-Ca-Mn-Zr-O system
LCMFO	La-Ca-Mn-Fe-O system
LCMAO	La-Ca-Mn-Al-O system
LCMIO	La-Ca-Mn-In-O system
LCMCO	La-Ca-Mn-Co-O system
CMR	Colossal Magnetoresistance
MI	Metal to insulator
MIT	Metal-insulator transition
MR	Magnetoresistance
GMR	Giant Magnetoresistance
R (H)	Resistance at present of magnetic field
R (0)	Zero field resistance
AFI	Antiferromagnetic insulator
FMM	Ferromagnetic metal

FMI	Ferromagnetic insulator
PMI	Paramagnetic insulator
MRRAM	Magnetoresistive random access memory
R	Trivalent
A	Divalent
$<r_A>$	Average ionic radius
t	Tolerance factor
$d_{La\text{-}O}$	La-O bond distances
$d_{Mn\text{-}O}$	Mn-O bond distances
θ	Mn-O-Mn bond angle
θ_{ij}	Angle between spins on neighboring Mn atoms
$\mathrm{\theta}$	Bragg angle
τ_h	Electron transfer time
τ_s	Time for a localized Mn spin to relax to a new orientation
D	Demagnetization factor
E_a	Activation energy
DE	Double exchange
JT	Jahn-Teller
ρ	Resistivity
XRD	X-ray diffraction
SEM	Scanning Electron Microscope
d	Sample diameter
H	Applied magnetic field

l	Sample length
M	Magnetization
k_B	Boltzman constant
a, b, c	Lattice parameters
χ	Susceptibility
χ'	Volume susceptibility
μ_{eff}	magnetic moment
AC	Alternating Current
χ_{ac}	AC susceptibility
μ	Magnetic dipole moment
$\mathbf{B}_{ext}$	External magnetic field
C	Curie constant
V	Sample volume
Θ	Paramagnetic Curie point
LSDA	Local spin density approximation
S	Spin electron
l-spin	Localized spin
c-electron	Conduction electron
ZFC	Zero-field cooled
FC	Field-cooled
P	Density
m	Mass
f	Frequency