



**UNIVERSITI PUTRA MALAYSIA**

**COLOSSAL MAGNETORESISTANCE  
OF  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{AxO}_3$  [A = V, Dy AND Zr] PEROVSKITE**

**KOH SONG FOO**

**FSAS 2001 20**

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**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  
Universiti Putra Malaysia**

**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  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{V}_x\text{O}_3$  (LCMVO),  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Dy}_x\text{O}_3$  (LCMDO) and  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3$  (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  $\chi'$ -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,  $\ln(\sigma) \sim (-E_a/kT)$  was used to explain the conduction mechanism of perovskite manganites above  $T_p$ . It was concluded that the total conductivity,  $\sigma_{tot}$ , 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**

**Fakulti : Sains dan Pengajian Alam Sekitar**

Sifat magnetorintangan raksaksa  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{V}_x\text{O}_3$  (LCMVO),  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Dy}_x\text{O}_3$  (LCMDO) dan  $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_{1-x}\text{Zr}_x\text{O}_3$  (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  $\chi'$ -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  $110\text{ K}-140\text{ K}$ ,  $120\text{ K}-142\text{ K}$ ,  $123\text{ K}-140\text{ K}$  dan  $77\text{ K}-94\text{ K}$ . 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 jurang 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  $\ln(\sigma) \sim (-E_a/kT)$  digunakan untuk menjelaskan mekanisme konduksi manganite perovskite pada suhu yang lebih daripada  $T_P$ . Secara kesimpulannya, jumlah kebolehaliran,  $\sigma_{tot}$  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 ABBREVIATIONS/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
$\langle r_A \rangle$	Average ionic radius
$t$	Tolerance factor
$d_{\text{La-O}}$	La-O bond distances
$d_{\text{Mn-O}}$	Mn-O bond distances
$\theta$	Mn-O-Mn bond angle
$\theta_{ij}$	Angle between spins on neighboring Mn atoms
$\theta$	Bragg angle
$\tau_h$	Electron transfer time
$\tau_s$	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
$\rho$	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
$\chi$	Susceptibility
$\chi'$	Volume susceptibility
$\mu_{\text{eff}}$	magnetic moment
$AC$	Alternating Current
$\chi_{\text{ac}}$	AC susceptibility
$\mu$	Magnetic dipole moment
$B_{\text{ext}}$	External magnetic field
$C$	Curie constant
$V$	Sample volume
$\Theta$	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