



**UNIVERSITI PUTRA MALAYSIA**

**STRUCTURAL ELECTRICAL AND MAGNETIC PROPERTIES OF  
LA<sub>2/3</sub>CA<sub>1/3</sub>MNO<sub>3</sub> PEROVSKITES WITH IN, GA AND AL  
SUBSTITUTION AT EITHER LA OR CA SITE**

**ABDULLAH CHIK.**

**FSAS 2004 32**



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EITHER La OR Ca SITE**

**By**

**ABDULLAH CHIK**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,  
in Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

**March 2004**



## DEDICATIONS

Prof. Dr. Abdul Halim Shaari,  
for guidance...

To Prof. Datuk Dr. Mohd Noh Dalimin,  
for patience and understanding...

To my wife, Rojita Abdul Hamid, and my two children,  
Ahmad Luqman Afiq and Nurul Farzana Aimi  
To my mother and father, Hjh. Che Bee Mohd Arshad  
and Hj. Chik Hussain  
for their love and support...

To Universiti Malaysia Sabah for this opportunity for study leave,  
Universiti Putra Malaysia, friends and ex-coursemates !



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirements for the degree of Doctor of Philosophy

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By

**ABDULLAH CHIK**

**March 2004**

**Chairman : Professor Abdul Halim bin Shaari, Ph.D.**

**Faculty : Science and Environmental Studies**

The structure, electrical and magnetic properties of colossal magnetoresistance material  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LCMO) substituted with In, Ga and Al at both La and Ca site have been studied. Samples of  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LICMO),  $(\text{La}_{1-x}\text{Ga}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LGCMO),  $(\text{La}_{1-x}\text{Al}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LACMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{In}_x)_{1/3}\text{MnO}_3$  (LCIMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Ga}_x)_{1/3}\text{MnO}_3$  (LCGMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Al}_x)_{1/3}\text{MnO}_3$  (LCAMO) with  $x=0.0$  to  $1.0$  were prepared using solid state reaction method. X-ray diffraction (XRD) patterns shows single phase pattern at low concentration with increasing intensity of secondary phases at high concentration of dopant. All samples except sample LICMO  $x=0.6$ , exhibit orthorhombic structure. Sample LICMO  $x=0.6$  exhibits tetragonal structure. The AC susceptibility studies indicates LICMO, LGCMO, LACMO exhibit wide variety of magnetic phases. For LICMO, LACMO and LGCMO system, ferromagnetic to paramagnetic transition are observed from the undoped sample  $x=0.0$  to  $0.5$ ,  $0.4$  and  $0.3$  respectively. With further doping at La site, spin glass transition is observed followed by antiferromagnetic to paramagnetic transition with increasing dopant concentration. The Curie temperature,  $T_C$  decreases as indium, gallium and aluminum doping increases indicates weakening of



ferromagnetic interactions, but the antiferromagnetic interactions is getting stronger with increasing dopant, resulting spin glass system and antiferromagnetism with further doping concentration. With In, Ga and Al substitution at the Ca site, all samples with the exception of LCIMO  $x=1.0$ , exhibit ferromagnetic to paramagnetic transition. For LCIMO sample  $x=1.0$ , AC susceptibility study indicates antiferromagnetic to paramagnetic transition. The electrical properties show the metal to insulator transition and this property is limited to certain doping level for both La and Ca site substitution, i.e. until  $x=0.9$  for LICMO,  $x=0.8$  for LGCMO, LACMO, LCIMO and LCGMO, and  $x=0.5$  for LCAMO system. Beyond the specific doping level, the samples become insulator for La site substitution, and semiconducting behaviour for Ca site substitution. This phenomenon is due to the ionic size of dopant for La site substitution, and both ionic size of dopant and decreasing  $Mn^{4+}/Mn^{3+}$  ratio due to decreasing  $Ca^{2+}$  ions. Fitting of adiabatic small polaron hopping model to high temperature  $\ln(R/T)$ , indicates the activation energies of all samples within range of 0.03eV to 0.17eV which is consistent with reported values in the literature, confirming small polaron hopping activities beyond  $T_P$ . Magnetoresistance measurements show that magnetoresistance (MR) ratio is maximum at temperature close to  $T_P$  for all samples, and increases with increasing dopant concentration for La site substitution. However, for Ca site substitution, the magnetoresistance's maximum is not as high as La site substitution, and decreases with increasing dopant concentration for  $x > 0.3$ , because of the low  $Mn^{4+}/Mn^{3+}$  ratio that weakened the Zener double exchange interactions and thus the metallic conductivity and ferromagnetism. High MR values are 80% for LICMO sample  $x=0.4$ , 95% for LGCMO sample  $x=0.6$  and 87% for LACMO sample  $x=0.2$ , compares to 40% of LCMO sample. The Scanning Electron Microscopy (SEM) micrographs indicate



fused and denser grains for all samples. Large abnormal growth is seen only in LICMO for  $x=0.1$  and  $0.2$  samples and increasing level of porosity with increasing dopant is seen for LACMO, LCGMO and LCIMO samples. LICMO and LGCMO samples exhibit decreasing level of porosity with increasing substitution while LCAMO system has low level of porosity in all samples.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

**PENCIRIAN STRUKTUR, ELEKTRIK DAN MAGNET BAGI BAHAN  
PEROVSKIT  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  DENGAN PENGGANTIAN In, Ga dan Al PADA  
TAPAK La ATAU Ca**

Oleh

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**Mac 2004**

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Ciri-ciri struktur, elektrik and magnet bahan bermagnetorintangan kolosal  $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LCMO), digantikan dengan In, Ga dan Al pada kedua-dua tapak La dan Ca, telah dikaji. Sampel-sampel  $(\text{La}_{1-x}\text{In}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LICMO),  $(\text{La}_{1-x}\text{Ga}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LGCMO),  $(\text{La}_{1-x}\text{Al}_x)_{2/3}\text{Ca}_{1/3}\text{MnO}_3$  (LACMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{In}_x)_{1/3}\text{MnO}_3$  (LCIMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Ga}_x)_{1/3}\text{MnO}_3$  (LCGMO),  $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Al}_x)_{1/3}\text{MnO}_3$  (LCAMO) dengan  $x=0.0$  ke  $1.0$  telah disediakan dengan menggunakan kaedah tindakbalas keadaan pepejal. Corak belauan sinar X menunjukkan fasa tunggal pada kepekatan rendah dengan pertambahan keamatan fasa kedua pada kepekatan pendopan yang tinggi. Kesemua sampel-sampel kecuali sampel LICMO  $x=0.6$  mempamerkan struktur ortorombik. Sampel LICMO  $x=0.6$  mempamerkan struktur tetragonal. Kajian kerentanan AC menunjukkan LICMO, LGCMO dan LACMO memperlihatkan pelbagai jenis fasa magnet. Bagi sistem LICMO, LACMO dan LGCMO, peralihan ferromagnet kepada paramagnet masing-masing dicerap daripada sampel  $x=0.0$  ke  $0.5$ ,  $x=0.0$  ke  $0.4$  dan  $x=0.0$  ke  $0.3$ . Dengan pertambahan pendopan di tapak La, peralihan kepada kaca spin dicerap dan diikuti dengan peralihan antiferromagnet kepada paramagnet dengan penambahan kepekatan pendopan. Suhu



Curie,  $T_C$  mengurang dengan penambahan pendopan indium, gallium dan aluminum menunjukkan interaksi ferromagnet yang semakin lemah, dan interaksi antiferromagnet yang semakin kuat, lalu melahirkan sistem spin kaca dan antiferromagnet dengan penambahan kepekatan pendopan. Dengan penggantian In, Ga dan Al pada tapak Ca, kesemua sampel kecuali LCIMO  $x=1.0$ , menunjukkan peralihan ferromagnet kepada paramagnet. Interaksi ferromagnet masih berlaku dengan penambahan kepekatan pendopan Al dan Ga walaupun pada kepekatan  $x=1.0$ . Untuk sampel LCIMO  $x=1.0$ , kajian kerentanan AC menunjukkan peralihan antiferromagnet kepada paramagnet. Ciri-ciri elektrik menunjukkan peralihan logam kepada penebat dan ciri ini terhad kepada paras pengdopan tertentu bagi kedua-dua penggantian tapak La dan Ca, contohnya, sehingga  $x=0.9$  untuk LICMO,  $x=0.8$  untuk LGCMO, LACMO, LCIMO dan LCGMO, dan  $x=0.5$  untuk sistem LCAMO. Selepas paras pengdopan tersebut, sampel menjadi penebat bagi penggantian tapak La, dan bagi penggantian tapak Ca, sampel-sampel mempamerkan hanya perlakuan semikonduktor. Fenomena ini disebabkan oleh saiz ion pendopan bagi penggantian tapak La, dan kedua-dua saiz ion pendopan dan pengurangan nisbah  $Mn^{4+}/Mn^{3+}$  disebabkan oleh pengurangan ion-ion  $Ca^{2+}$ . Lekapan model lompatan polaron kecil adiabatik kepada  $\ln(R/T)$  pada suhu tinggi, menunjukkan tenaga pengujaan kesemua sampel adalah dalam lingkungan 0.03 eV ke 0.17 eV yang konsisten dengan nilai-nilai dilaporkan dalam literatur, mengesahkan aktiviti lompatan polaron kecil pada suhu melebihi  $T_P$ . Penyukatan magnetorintangan menunjukkan nisbah magnetorintangan (MR) adalah maksimum pada suhu menghampiri  $T_P$  pada semua sampel, dan bertambah dengan penambahan kepekatan pendopan pada penggantian tapak La. Walaubagaimanapun, bagi penggantian tapak Ca, megnetorintangan maksima adalah tidak setinggi penggantian pada tapak La, dan berkekurangan





dengan penambahan kepekatan pendopan  $x > 0.3$ , kerana nisbah  $Mn^{4+}/Mn^{3+}$  yang rendah melemahkan interaksi pertukaran ganda dua Zener dan seterusnya konduksi logam dan feromagnet. Nilai MR yang tinggi adalah 80% bagi sampel LICMO  $x=0.4$ , 95% bagi sampel LGCMO  $x=0.6$  dan 87% bagi sampel LACMO  $x=0.2$ , berbandingkan 40% sampel LCMO. Mikrograf Mikroskop Elektron Imbasan (SEM) menunjukkan butir-butir tercantum dan lebih tumpat untuk kesemua sampel. Pertumbuhan abnormal yang besar kelihatan hanya pada sampel LICMO  $x=0.1$  dan  $0.2$  dan penambahan paras poros dengan pertambahan pendopan dilihat pada sampel-sampel LACMO, LCGMO dan LCIMO. Sampel-sampel LICMO dan LGCMO mempamerkan penurunan paras poros dengan pertambahan penggantian manakala sistem LCMO mempunyai paras poros yang rendah bagi semua sampel.



## ACKNOWLEDGEMENTS

I would like to express my utmost gratitude and appreciation to my project supervisor, Professor Dr. Abdul Halim Shaari for his patience, supervision, guidance, and discussions. I am also very grateful to my co-supervisor, Professor Dr. Wan Mahmood Mat Yunus and Professor Dr. Mohd Maarof H.A. Mokhsin for their comments and suggestions throughout the research work.

I am also expressing my gratitude to Universiti Malaysia Sabah for granting study leave and scholarship for Ph. D study. I would like to thank Tan Sri Professor Datuk Seri Panglima Dr. Abu Hassan Othman for allowing me to complete my work at Universiti Putra Malaysia. I am also grateful to Professor Datuk Dr. Mohd Noh Dalimin for his guidance and suggestions throughout my study leave.

Sincere thanks to Dr. Lim Kean Pah, Dr. Imad Hamadneh, Mrs Iftetan, Ms. Zohra Gebrel, Mr. K.K.Kabashi, Mrs Sharmiwati and Mr Azman Awang Teh for their assistance in samples preparation method, in using resistivity machine, AC susceptometer, magnetoresistance measurements, X ray diffractometer, furnaces and fruitful discussions. I would like also to thank Mr. Razak Harun for all technical favors.

I wish to thank all staffs of Electron Microscope Unit, Faculty of Bioscience, UPM especially Mr. Raffi, Ms. Aini, and Mrs. Faridah for helping me in operating SEM and taking SEM micrographs.



At last but not least, to my loving wife, Rojita Abdul Hamid, for her understanding, caring and continuous support, and my two darling children, Ahmad Luqman Afiq and Nurul Farzana Aimi of whom I cannot live without.



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