UNIVERSITI PUTRA MALAYSIA

MICROSTRUCTURE, MAGNETIC AND ELECTRICAL PROPERTIES OF La0.67(Sr1-xBax)0.33 Mn1-yTiyO3

ZALITA BINTI ZAINUDDIN

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By

ZALITA BINTI ZAINUDDIN

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

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DEDICATION

To my dearest husband, parents, sons, family and friends.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chairman: Abdul Halim Shaari, PhD

Faculty: Science

A study on the microstructure, magnetic and electrical properties of $La_{0.67}Sr_{0.33}MnO_3$ substituted with Ba at Sr site and Ti at Mn site have been performed. Samples of $La_{0.67}(Sr_{1-x}Ba_x)_{0.33}Mn_{1-y}Ti_yO_3$ (LSBMT) with x = 0.00, 0.25, 0.50, 0.75 and 1.00; and y = 0.00, 0.05, 0.10, 0.15, 0.20, 0.40 and 0.60 were prepared using solid state reaction method. Quantitative compositional percentage data of the elements results confirmed the expected La:Sr:Ba:Mn:Ti ratios for the prepared samples. X-ray Diffractometer (XRD) spectrum showed single phase compounds, except for samples with y = 0.60 which have $La_2Ti_2O_7$ peaks. Sr substitution with Ba changed the rhombohedral *R-3c* structure to cubic *Pm3m,* however Mn substitution with Ti only increased the lattice parameters values, without changing the whole structure. Scanning Electron Microscope (SEM) images showed a few porous structured samples, with coarse and fine grains while the others showed large closely packed grains with clear shapes and grain boundaries. The magnetization studies showed that samples with y = 0.00 exhibited a transition from the ferromagnetic to the paramagnetic phase as temperature increased and the Curie temperature, T_C decreased from 371 K to 341 K when x increased from 0.00 to 1.00. T_C also decreased when y increased. Magnetization versus field patterns did not differ much with x composition. The ferromagnetic behaviour for $0.00 \leq y \leq 0.15$ change to paramagnetic when $y \geq 0.20$. Resistivity versus temperature study showed that samples with y = 0.00 had metal-like behaviour. Nearly all samples with $0.00 < y < 0.20$ showed metallic and semiconducting-like behaviour. LSBMT with $y \geq 0.20$ exhibited only semiconducting behaviour. The metal-insulator transition temperature, T_P decreased with increment of x and/or y. At $T < T_P$ the resistivity curves can be fitted with the $\rho = \rho_0 + \rho_2 T^2$ relations. For $T > T_p$ the curves can be fitted with the variable range hopping (VRH) model and small polaron hopping (SPH) model. The density of states at Fermi level, $N(E_F)$ values were between 10^{18} to 10^{22} $eV^{-1}cm^{-3}$. Polaron activation energy, E_p increased with y ranging from 47 meV to 210 meV. Magnetoresistance (MR) measurement showed an increment of the *MR %* when the magnetic field increased and temperature decreased. The maximum *MR %* was ~34 % for LSBMT with x = 0.00 and y = 0.15 at 100 K and 1.0 Tesla. Samples with $y \leq 0.10$ showed low field magnetoresistance (LFMR) effect. At 1000 Hz LSBMT with x = 0.00, 0.25 and 0.75 exhibit a ferroelectric-paraelectric transition peak at 200 K, 250 K and 225 K respectively, with the highest ε' value of 6.54×10^5 when x = 0.25, y = 0.20. The Nyquist plots of Z'' versus Z' showed depressed semicircles contributed by the grain, grain boundary and/or electrode effect. Two relaxation processes occurred in the AC conductivity curve due to the grain and grain boundary. Materials with very high dielectric constant ~ 10^5 at 1000 kHz were successfully synthesized with $x \leq 0.75$; y = 0.20 and all samples with y = 0.40. Samples with y = 0.40 have wide range of nearly frequency and temperature independent high dielectric constant. These samples are excellent for capacitors fabrication.

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

MIKROSTRUKTUR, SIFAT MAGNET DAN SIFAT ELEKTRIK
$La_{0.67}(Sr_{1-x}Ba_x)_{0.33}\ Mn_{1-y}Ti_yO_3$

Oleh

ZALITA BINTI ZAINUDDIN

Oktober 2009

Pengerusi: **Abdul Halim Shaari, PhD**

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Kajian ke atas mikrostruktur, sifat magnet dan sifat elektrik $La_{0.67}Sr_{0.33}MnO_3$ yang diganti dengan Ba di tempat Sr dan Ti di tempat Mn telah dilakukan. Sampel-sampel $La_{0.67}(Sr_{1-x}Ba_x)_{0.33}\ Mn_{1-y}Ti_yO_3$ (LSBMT) dengan x = 0.00, 0.25, 0.50, 0.75 dan 1.00; dan y = 0.00, 0.05, 0.10, 0.15, 0.20, 0.40 dam 0.60 telah disediakan mengguna kaedah tindak balas keadaan pepejal. Data peratusan komposisi kuantitatif bagi unsur mengesahkan nisbah La:Sr:Ba:Mn:Ti jangkaan bagi sampel yang disediakan. Spektrum Pembelauan Sinar-X (XRD) menunjukkan sebatian berfasa tunggal, kecuali bagi sampel dengan y = 0.60 yang mempunyai puncak-puncak $La_2Ti_2O_7$. Penggantian Sr dengan Ba mengubah struktur rhombohedral *R-3c* kepada kubik *Pm3m,* tetapi penggantian Mn dengan Ti hanya meningkatkan nilai pemalar kekisi, tanpa mengubah struktur keseluruhan. Imej Mikroskop Elektron Imbasan (SEM) menunjukkan beberapa sampel berstruktur poros, dengan butiran yang kasar dan halus manakala yang lainnya menunjukkan butiran besar yang tersusun padat dengan bentuk dan sempadan butiran yang jelas. Kajian pemagnetan menunjukkan bahawa sampel dengan y = 0.00 mempamerkan peralihan daripada fasa feromagnet kepada paramagnet apabila suhu ditingkatkan dan suhu Curie, T_C berkurang dari 371 K

kepada 341 K apabila x meningkat dari 0.00 kepada 1.00. T_C turut berkurang apabila y meningkat. Corak pemagnetan tidak banyak berubah dengan komposisi x. Sifat feromagnet bagi $0.00 \leq y \leq 0.15$ berubah kepada paramagnet bagi $y \geq 0.20$. Kajian kerintangan melawan suhu menunjukkan bahawa sampel dengan y = 0.00 mempunyai kelakuan seperti logam. Hampir kesemua sampel dengan $0.00 < y < 0.20$ menunjukkan kelakuan seperti logam dan semikonduktor. LSBMT dengan $y \geq 0.20$ hanya menunjukkan kelakuan semikonduktor. Suhu peralihan logam-penebat, T_P berkurang dengan penambahan x dan/atau y. Pada $T < T_P$ lengkung kerintangan boleh dipadankan dengan hubungan $\rho = \rho_0 + \rho_2 T^2$. Bagi $T > T_P$ lengkung boleh dipadankan dengan model Loncatan Julat Boleh ubah (VRH) dan model Loncatan Polaron Kecil (SPH). Nilai ketumpatan keadaan di aras Fermi adalah di antara 10^{18} to 10^{22} $eV^{-1}cm^{-3}$. Tenaga pengaktifanpolaron, E_p meningkat dengan y dalam julat 47 meV kepada 210 meV. Pengukuran magnetorintangan menunjukkan peningkatan MR % apabila medan magnet meningkat dan suhu berkurang. MR % maksimum adalah ~34 % bagi LSBMT dengan x = 0.00 dan y = 0.15 pada 100 K dan 1.0 Tesla. Sampel dengan $y \geq 0.10$ menunjukkan kesan magnetorintangan medan rendah (LFMR). Pada 1000 Hz sampel dengan x = 0.00, 0.25 and 0.75 menunjukkan puncak peralihan feroelektrik-paraelektrik pada 200 K, 250 K dan 225 K masing-masing, dengan nilai ε' tertinggi iaitu 6.54 x 10^5 apabila x = 0.25, y = 0.20. Plot Nyquist bagi Z'' melawan Z' menunjukkan separa bulatan terhimpit yang disumbangkan oleh butiran, sempadan butiran dan/atau elektrod. Dua proses perehatan berlaku pada lengkung kekondusian AC disebabkan oleh sempadan butiran pada frekuensi rendah dan butiran pada suhu tinggi. Bahan dengan pemalar dielektrik sangat tinggi ~ 10^5 pada 1000 kHz telah berjaya dihasilkan dengan sampel $x \leq 0.75$; y = 0.20 dan semua sampel dengan y = 0.40. Sampel dengan y = 0.40 mempunyai pemalar dielektrik tinggi yang hampir tidak bergantung pada suhu dan frekuensi dalam suatu julat yang lebar. Sampel-sampel ini sangat sesuai untuk pembuatan kapasitor.

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I certify that an examination committee has met on 12 October 2009 to conduct the final examination of Zalita binti Zainuddin on her doctor Doctor of Philosophy thesis entitled "Microstructure, Magnetic And Electrical Properties Of $La_{0.67}(Sr_{1-x}Ba_x)_{0.33}$ $Mn_{1-y}Ti_yO_3$" in accordance with 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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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Date: 14 January 2010

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.

ZALITA BINTI ZAINUDDIN

Date: 4 February 2010

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LIST OF ABBREVIATIONS

LSBMT	$La_{0.67}(Sr_{1-x}Ba_x)_{0.33}Mn_{1-y}Ti_yO_3$
x	Ba composition
y	Ti composition
LCMO	$La_{1-x}Ca_xMnO_3$
LSMO	$La_{1-x}Sr_xMnO_3$
LBMO	$La_{1-x}Ba_xMnO_3$
MR	magnetoresistance
CMR	colossal magnetoresistance
SSR	solid state reaction
FM	ferromagnetic
FMM	ferromagnetic metallic
FMI	ferromagnetic insulator
AF	antiferromagnetic
AFI	antiferromagnetic insulator
PM	paramagnetic
PMI	paramagnetic insulator
CI	canted insulating
SE	superexchange
DE	double exchange
JT	Jahn-Teller
T	temperature
T_C	Curie temperature
T_P	metal-insulator transition temperature

M	magnetization
H	magnetic field
H_C	coercive field
Q_1, Q_2, Q_3	modes of distortion
ρ	resistivity
NNH	nearest neighbour hopping
TAC	thermally activated conduction
SPH	small polaron hopping
VRH	variable range hopping
E_a	energy gap/activation energy
E_p	polaron activation energy
k_B	Boltzmann constant
f	frequency
ω	angular frequency
ω_{max}	maximum angular frequency
R_H	resistance in the presence of a magnetic field
R_0	resistance in the absence of a magnetic field
R_b	bulk/grain resistance
R_{gb}	grain boundary resistance
R_e	interface/electrode resistance
R_T	total resistance
LFMR	low field magnetoresistance
HFMR	high field magnetoresistance
Z^*	complex impedance
Z'	real impedance

Z''	imaginary impedance
ε_0	permittivity of free space = 8.854 x 10^{-12} F/m,
ε^*	complex permittivity
ε_r	relative permittivity
ε'	real part of relative permittivity
ε''	imaginary part of relative permittivity
$tan\ \delta$	loss tangent/dielectric loss/dissipation factor
Y^*	complex admittance
Y'	real part of complex admittance
Y''	imaginary part of complex admittance
M^*	complex electric modulus
M'	real part of electric modulus
M''	imaginary part of electric modulus
G	conductance
B	susceptance
τ	relaxation time
τ_0	pre-exponential factor
DC	direct current
AC	alternating current
σ_{DC}	direct current conductivity
σ_{AC}	alternating current conductivity
C_0	vacuum capacitance
C^*, $C_n(\omega)$	complex capacitance
C'	real part of capacitance

C''	imaginary part of capacitance
A	cross sectional area of the flat surface
d	thickness of pellet
χ'	real part of susceptibility
χ''	imaginary part of susceptibility
XRD	x-ray diffractometer
SEM	scanning electron microscope
EDX	energy dispersive x-ray
VSM	vibrating sample magnetometer

CHAPTER 1

INTRODUCTION

Perovskite manganite, $Ln_{1-x}A_xMnO_3$ where Ln is an element from the lanthanide group such as La, Nd, Pr, Y and A is a divalent ion such as Ca, Sr, Ba, Pb, with a Mn^{3+}/Mn^{4+} mixed valence has stimulated an increasing interest due to their unique spin-dependent magneto-transport properties. A variety of phases such as ferromagnetic metallic (FMM), antiferromagnetic insulator (AFI), ferromagnetic insulator (FMI), cluster glass and spin glass emerged due to the unique coupling among charge, spin, orbital and lattice degree of freedom of the 3d electrons in this system. From the technological point of view, the most intriguing phenomena of this manganese system is the colossal magnetoresistance (CMR) that exists near the Curie temperature, T_C where it experiences a transition from the ferromagnetic (FM) to paramagnetic (PM) state. Extensive research, experimentally and theoretically, on the properties of this material are being done by researchers worldwide (Zener, 1951; Asamitsu et al., 1996; Tokura, 2000; Ziese, 2002; Tokura, 2007) for better understanding of the principles lying behind all those phenomena and hoping that its improved feature could be useful in the technological industries.

The magnetic exchange, structure properties and electronic transport of manganites crucially depend on the Mn^{3+}/Mn^{4+} ratio and the effective ionic radius of the A-site cations. These properties are believed to be determined by a competition between the superexchange (SE) and the double exchange (DE) mechanism (Zener, 1951). Further studies of these materials have shown that other mechanism also influences