

UNIVERSITI PUTRA MALAYSIA

EFFECTS OF DIFFERENT SYNTHESIS METHODS ON PHYSICAL PROPERTIES OF La0.85K0.15MnO3

PAN KAI YAP

FS 2013 6



EFFECTS OF DIFFERENT SYNTHESIS METHODS ON PHYSICAL PROPERTIES OF La_{0.85}K_{0.15}MnO₃

PAN KAI YAP

MASTER OF SCIENCE UNIVERSITI PUTRA MALAYSIA



EFFECTS OF DIFFERENT SYNTHESIS METHODS ON PHYSICAL PROPERTIES OF La_{0.85}K_{0.15}MnO₃



Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science.

March 2013

COPYRIGHT

All material contained within the thesis, including without limitation text, logos, icons, photographs and all other artwork, is copyright material of Universiti Putra Malaysia unless otherwise stated. Use may be made of any material contained within the thesis for non-commercial purposes from the copyright holder. Commercial use of material may only be made with the express, prior, written permission of Universiti Putra Malaysia.

Copyright © Universiti Putra Malaysia



Abstract of the thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of requirements for the degree of Master of Science

EFFECTS OF DIFFERENT SYNTHESIS METHODS ON PHYSICAL PROPERTIES OF La_{0.85}K_{0.15}MnO₃

By

PAN KAI YAP

March 2013

Chair

: Abdul Halim Shaari, PhD

: Science

Faculty

The structure, microstructure, magnetic and electrical properties of La_{0.85}K_{0.15}MnO₃ polycrystalline manganites synthesized via three methods: solid state (SS), sol-gel (SG) and co-precipitation (CP) and then sintered with various sintering temperature and synthesized were investigated and reported. XRD patterns of all SS and SG sintered samples showed a pure perovskite phase of hexagonal structure while CP samples that sintered at 1000°C and 1100°C showed the appearance of secondary phases. SG samples showed pure phase at the calcination temperature of 700°C while SS and CP methods showed same structure at 800°C. SEM micrographs displayed an increase of average grain size with sintering temperature. Nevertheless, formation of melt-like structure grains was occurred at 1100°C, for all methods. The room temperature magnetization curves of all SS and SG samples showed ferromagnetic ordering behavior. The magnetization was increased with the increasing of average grain sizes. Conversely, CP samples sintered at 1000°C and 1100°C showed paramagnetic behavior due to the presence of secondary phases and exhibited less content of potassium. By comparing the magnetization through

synthesized techniques, SS sample had the highest magnetization while CP synthesized sample obtained lowest magnetization. The Curie temperature (T_c) decreased with the increase of sintering temperature. This might associated with the elongation of Mn-O bond length and narrowed of Mn-O-Mn bond angle that had the responsibility in double exchange mechanism. The electrical transport properties at zero field of SS and SG samples showed that the metal-insulator transition temperature (T_p) increased with the increase of sintering temperature. The grain growth promotion and decrease of grain boundaries caused these phenomena because grain connectivity was improved when the sintering temperature was increased. Abnormal electrical curve was observed in CP samples with sintering temperature of 1000°C and 1100°C. This might affected by the vaporization of K and the occurrence secondary phases on the structure. By comparing T_c and T_p through synthesized techniques, SS method exhibits highest T_c and T_p while CP sample shows lowest T_c and T_p. This may due to the shortest Mn-O bond length, widest Mn-O-Mn bond angle and largest average grain size that possessed by SS samples. All samples exhibited MR effect at room temperature with the raised of field from 0 to 1T. The lack of DE mechanism in CP samples sintered at 1000°C and 1100°C due to the vaporization of potassium content causing low MR effect on that both samples. Pure LKMO system exhibited ferromagnetic-insulator (FI) phase at room temperature.

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

KESAN TEKNIK-TEKNIK SINTESIS BERLAINAN KE ATAS SIFAT FIZIK La_{0.85}K_{0.15}MnO₃

Oleh

PAN KAI YAP

Mac 2013

Penyelia : Abdul Halim Shaari, PhD

: Sains

Fakulti

Struktur, mikrostruktur, sifat magnet dan elektrik bagi polihabluran La_{0.85}K_{0.15}MnO₃ yang disintesis melalui tiga teknik, iaitu tindak balas keadaaan pepejal (SS), sol-gel (SG) dan ko-pemendakan (CP) dengan suhu pensinteran yang berlainan dikaji dan dilaporkan. Corak XRD bagi semua sampel yang disintesiskan oleh teknik SS dan SG membentuk fasa tulen dengan struktur heksagon manakala fasa campuran telah diperhatikan pada sampel CP dengan suhu pensinteran 1000°C dan 1100°C. Teknik SG memperoleh fasa tulen pada suhu pengkalsinan 700°C manakala teknik SS dan CP memperoleh fasa yang sama pada suhu pengkalsinan 800°C. Mikrograf SEM memaparkan peningkatkan purata saiz butiran berkadar langung dengan peningkatan suhu pensinteran. Namun, pembentukan butiran yang tanpa sempadan dengan stuktur serupa peleburan telah berlaku bagi semua sampel yang disinter pada suhu 1100°C. Teknik SG menghasilkan polihablur LKMO yang mempunyai saiz butiran purata terkecil dan skala nano, iaitu sampel SG750 dan SG800. Ini adalah kerana teknik SG memperoleh suhu pengkalsinan dan pensinteran yang terendah jika berbanding dengan ketiga-tiga teknik tersebut. Semua sampel yang disintesiskan

oleh teknik SS dan SG memaparkan sifat ferromagnet. Nilai pemagnetan berkadar lansung dengan peningkatan saiz butiran purata. Sebaliknya, sampel CP yang disinter pada suhu 1000°C dan 1100°C mempunyai sifat paramagnet dengan kehadiran fasa campuran dan kekurangan kandungan K. Dengan membandingkan nilai pemagnetan melalui ketiga-tiga teknik tersebut, teknik SS memperoleh nilai pemagnetan yang tertinggi manakala teknik CP memperoleh nilai pemagnetan yang terendah. Penurunan suhu Curie (T_c) berkadar terus dengan peningkatan suhu pensinteran. Fenomena ini berkaitan dengan pemanjangan ikatan Mn-O dan penyempitan sudut Mn-O-Mn yang bertanggungjawab dalam mekanisme pertukaran ganda. Bagi SS dan SG sampel, sifat pengangkutan elektrik dalam medan sifar memaparkan peningkatan suhu peralihan logam-penebat (T_p) dengan peningktan suhu pensinteran. Ini adalah kerana pertumbuhan butiran digalakkan dan pengurangan sempadan butiran semasa suhu pensinteran dinaikkan. Oleh itu, sifat konduksi elektrik butiran ditingkatkan. Lengkungan elektrik yang luar biasa telah diperhatikan pada CP sampel yang disintesis dalam suhu 1000°C dan 1100°C. Hal ini mungkin disebabkan oleh pengewapan kandungan K dan kehadiran fasa campuran dalam struktur sampel tersebut. Dengan membandingkan T_c dan T_p melalui ketigatiga teknik tersebut, teknik SS memperoleh T_c dan T_p yang tertinggi manakala teknik CP memperoleh T_c dan T_p yang terendah. Ini disebabkan oleh sampel SS mempunyai ikatan Mn-O yang terpendek, sudut Mn-O-Mn dan saiz butiran purata yang terbesar. Semua sampel menunjukkan kesan MR pada suhu bilik dengan peningkatan medan dari 0 kepada 1T. Kekurangan mekanisme petukaran ganda pada sampel yang disintesiskan pada suhu 1000°C dan 1100°C (disebabkan kekurangan pengewapan kandungan K pada suhu tersebut) menyebabkan kesan MR yang rendah. Sistem LKMO yang tulen mempamerkan fasa ferromagnet-penebat pada suhu bilik.

ACKNOWLEDGEMENTS

First and foremost, I would like to express my most appreciation to my supervisor, Prof. Dr. Abdul Halim Shaari for the valuable guidance, advice, unlimited support and fully supervision in this project. Without him, this thesis would never be completed.

Next, I would like to thank to both of my co-supervisor, Assoc. Prof. Dr. Wan Mohd. Daud Wan Yusoff and Dr. Lim Kean Pah for their willingness to share thousands of greatful ideas with me.

This work was not completed in a vacuum. I worked with many brilliant persons in Superconductor and Thin Film Laboratory; together we worked hard and learned hard, and share ideas with each others. I will never forget for their support, collaboration and friendship.

I am thankful for the funding from the Ministry of Higher Education (MOHE) through Fundamental Research Grant Scheme (FRGS) and Graduate Research Fellowship (GRF), Universiti Putra Malaysia (UPM). The project is impossible to start without the financial support.

Special regard goes to my family, especially to my late father. I am proud to be your son and you always live in my heart; my mother and brother, who are always beside me all the time.

I certify that a Thesis Examination Committee has met on 18 March 2013 to conduct the final examination of Pan Kai Yap on his thesis entitled "Effects of Different Synthesis Methods on Physical Properties of $La_{0.85}K_{0.15}MnO_3$ " in accordance with the Universities and Universiti College Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

Members of the Examination Committee were as follows:

Zainal Abidin bin Talib, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairman)

Khamirul Amin bin Matori, PhD

Senior Lecturer Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Wan Mahmood bin Mat Yunus, PhD

Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Roslan Abdul Shukor, PhD

Professor School Of Applied Physics Universiti Kebangsaan Malaysia (External Examiner)

NORITAH OMAR, PhD

Associate Professor and Deputy Dean School of Graduate Studies Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti of Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Abdul Halim Shaari, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairman)

Lim Kean Pah, PhD

Senior Lecturer Faculty of Science Universiti Putra Malaysia (Member)

Wan Mohamad Daud Wan Yusoff, PhD

Associate Professor Pusat Asasi Sains Pertanian Universiti Putra Malaysia (Member)

BUJANG BIN KIM HUAT, PhD Professor and Dean School of Graduate Studies

Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is nor concurrently, submitted for any other degree at Universiti Putra Malaysia or other institutions.



TABLE OF CONTENTS

	Page
COPYRIGHT	ii
ABSTRACT	iii
ABSTRAK	V
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	Х
LIST OF TABLES	xiv
LIST OF FIGURES	XV
LIST OF ABBREVATIONS	xix

CHAPTER

1		ODUCTION	1
1	INIK		1
	1.1	Brief History of Mixed Valence Manganites	1
	1.2	Monovalent Doped Manganites	2
	1.3	Application of Mixed Valence Manganites	3
1.4	Proble	m Statement and Objectives	5
2	LITE	RATURE REVIEW	7
21	Phase	Diagram	7
2.1	211	Phase diagram of Lat. Ca Mn Ω_{2}	8
22	Effect	of Sintering Temperature	10
2.2	221	Structural properties	10
	2.2.1	Microstructural properties	11
	2.2.2	Electrical properties	12
	2.2.3 2.2.4	Magnetic properties	12
23	Effect	of Different Synthesis Techniques	14
2.5	Liteet	of Different Synthesis Teeninques	11
3	THE	DRY	17
	3.1	Perovskite Manganites	17
	3.2	LaMnO ₃ and La _{1-x} A_x MnO ₃	19
	3.3	Double Exchange	21
	3.4	Colossal Magnetoresistance (CMR) Effect	22
		3.4.1 CMR in manganites	22
		3.4.2 Intrinsic and extrinsic CMR	23
	3.5	Correlation between electrical transport and magnetic properties	25
	3.6	Magnetism	26
		3.6.1 Hysteresis loop	28
		3.6.2 Magnetic anisotropy	29
		3.6.3 Magnetic domain	30
		3.6.4 Type of magnetism	31
		3.6.4.1 Diamagnetic	32
		3.6.4.2 Paramagnetic	32
		3.6.4.3 Ferromagnetic	34

		3.6.4.4 Antiferromagnetic	36
		3.6.4.5 Ferrimagnetic	37
		3.6.4.6 Superparamagnetic	38
	3.6.5	Curie temperature	38
3.7	Sinter	ring Mechanism	39

4	MET	HODS	40
	4.1	Introduction	40
		4.1.1 Solid State Reaction	40
		4.1.2 Sol-gel and Co-precipitation	41
	4.2	Solid State Reaction Preparation	41
		4.2.1 Chemical powder weighing and mixing	41
		4.2.2 Grinding	42
		4.2.3 Calcination	42
		4.2.4 Pelletization	43
		4.2.5 Final sintering –	43
	4.3	Sol-gel	43
		4.3.1 Weighing	44
		4.3.2 Mixing process	44
		4.3.3 Calcination, Pelletization and Final sintering	45
	4.4	Co-precipitation	45
		4.4.1 Chemical Preparation	46
		4.4.1.1 Preparation for Solution A	46
		4.4.1.2 Preparation for Solution B	46
		4.4.2 Mixing process	47
		4.4.3 Filtration process	47
		4.4.4 Calcination, Pelletization and Final sintering	47
	4.5	Sample Characterization	52
		4.5.1 Powder X-ray diffraction (XRD)	52
		4.5.2 Scanning electron microscope (SEM)	53
		4.5.3 Four point probe	55
		4.5.4 Vibrating sample magnetometer (VSM)	56
		4.5.5 AC susceptibility	57
5	RESI	IT TS AND DISCUSSION	50
5	5 1	X-ray Diffraction (XRD) Patterns	59
	5.1	Microstructure Properties	64
	5.2	5.2.1 Scanning electron microscope (SFM)	64
		5.2.2 Energy-dispersive X-ray spectroscopy (EDAX)	70
	5.3	Magnetic Properties	70
			71

RESULTS AND DISCUSSION

RESU	JLTS AND DISCUSSION	59
5.1	X-ray Diffraction (XRD) Patterns	59
5.2	Microstructure Properties	64
	5.2.1 Scanning electron microscope (SEM)	64
	5.2.2 Energy-dispersive X-ray spectroscopy (EDAX)	70
5.3	Magnetic Properties	71
	5.3.1 Magnetization	71
	5.3.2 Coercivity	73
	5.3.3 Curie Temperature	76
5.4	Electrical Properties	82
5.5	Magnetoresistance	85
5.6	Correlation between T_p and T_c	88

CONCLUSION AND SUGGESTION906.1Conclusion906.2Suggestions for Future Work93

REFERENCES Appendix A Appendix B Appendix C LIST OF PUBLICATIONS BIODATA OF STUDENT

6



LIST OF TABLES

Table		Page
5.1	Structural properties of LKMO prepared by SS method at various sintering temperature.	63
5.2	Structural properties of LKMO prepared by SG method at various sintering temperature.	63
5.3	Structural properties of LKMO prepared by CP method at various sintering temperature.	64
5.4	EDAX data of LKMO via SS method/in ratio.	70
5.5	EDAX data of LKMO via SG method/in ratio.	70
5.6	EDAX data of LKMO via CP method/in ratio.	71
5.7	Magnetization data at 10 kG of LKMO samples sintered at various temperatures with synthesized techniques of SS, SG and CP.	76
5.8	Curie temperature (T_c) of LKMO sintered at various temperatures with synthesized techniques of SS, SG and CP.	82
5.9	Metal-insulator transition temperature (T_p) of LKMO sintered at various temperatures with synthesized techniques of SS, SG and CP.	85

Ĉ

LIST OF FIGURES

Figure		Page
2.1	Phase diagram of $La_{1-x}Ca_xMnO_3$ as a function of temperature.	9
2.2	(a) X-ray diffraction (XRD) patterns of La _{0.7} Sr _{0.3} MnO ₃ sintered at 600°C (T6), 700°C (T7), 800°C (T8), 900°C (T9) and 1000°C (T10). The inset shows the variation in intensity and 2 θ of the main peak intensity with sintering temperature. (b) XRD patterns of La _{0.67} Ca _{0.33} MnO ₃ sintered at 800°C (LC-8), 900°C (LC-9), 1000°C (LC-10) and 1100°C (LC-11).	11
2.3	SEM micrographs of the surface morphologies for LCMO bulks oxides sintered at: (a) 1200°C, (b) 1300°C and (c) 1400°C.	12
2.4	FESEM micrographs of (a) SS, (b) SG and (c) CP sample.	16
3.1	Ideal cubic perovskite structure with (a) B-site octahedral and (b) A-site cubotahedral as the center of unit cell.	18
3.2	Crystal field splitting of fivefold degenerate $3d$ orbitals of Mn^{3+} before and after Jahn-Teller distortion.	20
3.3	Mechanism of double exchange between the $3d_z^2$ orbitals of Mn ³⁺ and Mn ⁴⁺ ion via O ²⁻ ion.	21
3.4	Crystal structure with Mn ions spin along the <i>abc</i> axis of LaMnO ₃ .	23
3.5	Magnetoresistance ratio as a function of temperature for epitaxial and polycrystalline (3μ m average grain size) films of LCMO for magnetic field $H = 0.5, 1, 2, 3$ and 4T.	25
3.6	A typical hysteresis loop of a ferromagnetic material.	29
3.7	Spin lattice of diamagnetism.	32
3.8	Spin lattice for paramagnetism (a) without magnetic field, (b) in field.	34
3.9	Spin lattice for ferromagnetism in polycrystalline substances (a) without magnetic field, (b) in field.	35
3.10	<i>B</i> - <i>H</i> curves for (a) soft ferromagnetic, (b) hard ferromagnetic.	36
3.11	Spin lattice of antiferromagnetism.	36
3.12	Spin lattice of ferrimagnetism.	37

3.13	Magnetization hysteresis loop of (a) ferromagnetic, (b) paramagnetic and (c) superparamagnetic materials.	38
4.1	Flow chart of sample preparation by using solid state reaction method.	48
4.2	Flow chart of sample preparation by using sol-gel method.	49
4.3	Flow chart of sample preparation by using co-precipitation method.	50
4.4	Schematic diagram of Calcination Process.	51
4.5	Schematic diagram of Sintering Process.	51
4.6	Schematic diagram of Bragg's Law.	52
4.7	Schematic diagram of scanning electron microscope.	54
4.8	Schematic drawing of four point probe.	55
4.9	Schematic diagram of vibration sample magnetometer (VSM) showing: (1) mechanical vibrator, (2) sample holder, (3) sample, (4) pick up coils, (5) electromagnet and (6) magnet pole pieces.	56
4.10	Schematic diagram of magnetic sample placed inside the coaxial coils of the AC susceptometer.	57
5.1	XRD patterns of LKMO samples prepared by solid state reaction (SS) method after calcined at 800°C (SSC800) and sintered at 900°C (SS900), 1000°C (SS1000) and 1100°C (SS1100).	59
5.2	XRD patterns of LKMO samples prepared by sol gel (SG) method calcined at 500°C (SGC500), 600°C (SGC600) and 700°C (SGC700) and then sintered at 750°C (SG750), 800°C (SG800), 900°C (SG900), 1000°C (SG1000) and 1100°C (SG1100).	60
5.3	XRD patterns of LKMO samples prepared by co-precipitation (CP) method calcined at 700°C (CPC700), 750°C (CPC750) and 800°C (CPC700) and then sintered at 900°C (CP900), 1000°C (CP1000) and 1100°C (CP1100).	61
5.4	SEM micrographs together with the grain size distribution of LKMO prepared by SS method with various sintering temperature: (a) 900°C, (b) 1000°C and (c) 1100°C.	66

5.5 SEM micrographs together with the grain size distribution of 68 LKMO prepared by SG method with various sintering

temperature: (a) 750°C, (b) 800°C, (c) 900°C, (d) 1000°C and (e) 1100°C.

- 5.6 SEM micrographs together with the grain size distribution of 69 LKMO prepared by CP method with various sintering temperature: (a) 900°C, (b) 1000°C and (c) 1100°C.
- 5.7 Field dependence of magnetization curves at room temperature for LKMO calcined and sintered at various temperatures and prepared by SS method. Inset shows the coercivity of the sintered samples as the function of sintering temperature.
- 5.8 Field dependence of magnetization curves at room temperature 74 for LKMO calcined and sintered at various temperatures and prepared by SG method. Inset shows the coercivity of the sintered samples as the function of sintering temperature.
- 5.9 Field dependence of magnetization curves at room temperature 75 for LKMO calcined and sintered at various temperatures and prepared by CP method.
- 5.10 Room temperature magnetization curves for different 75 synthesized techniques in the range of ±400G magnetic field.
- (a) Temperature dependence of normalized AC susceptibility of 79 SS900, SS1000 and SS1100. (b) Gauss fit of first derivative graph of AC susceptibility as the function of temperature of SS900, SS1000 and SS1100.
- 5.12 (a) Temperature dependence of normalized AC susceptibility of 80 SG900, SG1000 and SG1100. Inset shows the temperature dependence of normalized AC susceptibility of SG750 and SG800. (b) Gauss fit of first derivative graph of AC susceptibility as the function of temperature of SG750, SG800, SG900, SG1000 and SG1100.
- (a) Temperature dependence of normalized AC susceptibility of 81
 CP900, CP1000 and CP1100. (b) Gauss fit of first derivative graph of AC susceptibility as the function of temperature of CP900, CP1000 and CP1100.
- 5.14 Temperature dependence of normalized AC susceptibility of 82 LKMO prepared by various synthesized methods and sintered at 900°C.
- 5.15 Temperature dependence of the electrical resistance for SS1000 84 and SS1100 samples between 100 and 300K. Inset shows the temperature dependence of the electrical resistance for SS900 sample between 100 and 300K.

5.16	Temperature dependence of the electrical resistance for SG750, SG800, SG900, SG1000 and SG1100 samples between 100 and 300K.	84
5.17	Temperature dependence of the electrical resistance for CP1000 and CP1100 samples between 100 and 300K. Inset shown the temperature dependence of the electrical resistance for CP900 sample between 100 and 300K.	85
5.18	Field dependence of magnetoresistance (MR) curves of SS synthesized LKMO at 300K.	87
5.19	Field dependence of magnetoresistance (MR) curves of SG synthesized LKMO at 300K.	87
5.20	Field dependence of magnetoresistance (MR) curves of CP synthesized LKMO at 300K.	88
5.21	Phase diagram of SG synthesized LKMO at various sintering temperature. The abbreviations are paramagnetic-insulator (PI), ferromagnetic insulator (FI) and ferromagnetic metal (FM).	89

LIST OF ABBREVIATIONS

х	Concentration of dopant	-
Κ	Potassium	-
T _c	Curie temperature	Κ
T _p	Metal-insulator transition temperature	K
°C	Degree Celsius	-
t	Tolerance factor	-
À	Angstrom	-
a,b,c	Lattice Parameter	-
eg	Sub-orbital of 3 <i>d</i> orbital (higher energy level)	-
t _{2g}	Sub-orbital of 3 <i>d</i> orbital (lower energy level)	-
eV	Energy in electron volt	
Т	Temperature	K
R_H, r_H	Electrical resistance in applied field	Ω
$R_{0,} r_0$	Electrical resistance in zero field	Ω
B, H	Magnetic field	Т
Т	Tesla	-
N	Number of turns	-
L	Length	m
Ι	Current	А
Wb	Weber	-
М	Extent of magnetized of materials under applied	Am ² m ⁻³
	magnetic field	
m	Magnetic moment	Am^2
V	Volume	m ³
Xm, X	Magnetic susceptibility	$m^3 kg^{-1}$
μ_0	permeability in free space	N A ⁻²
M	Magnetization	emu g ⁻¹
M_s	Magnetization saturation	emu g ⁻¹
M_r	Remanence	emu g ⁻¹
H_c	Coercivity	Т
H_{ci}	Intrinsic Coercivity	Т
~	Approximately	-

xix

<	Less than	-
>	More than	-
\leq	Less than or equal to	-
h	Hour	-
θ	Theta	-
λ	Wavelength	-
V	Potential difference	V
0	Degree	-
G	Gauss	oe
LKMO	La _{0.85} K _{0.15} MnO ₃ system	-
DE	Double exchange	-
JT	Jahn-Teller	-
MR	Magnetoresistance	-
CMR	Colossal magnetoresistance	-
LFMR	Low-field magnetoresistance	-
SS	Solid state	-
SG	Sol-gel	-
СР	Co-precipitation	-
SSC800	LKMO synthesized by solid state with calcination	
	temperature of 800°C	-
SS900	LKMO synthesized by solid state with sintering	_
	temperature of 900°C	
SS1000	LKMO synthesized by solid state with sintering	_
	temperature of 1000°C	
SS1100	LKMO synthesized by solid state with sintering	_
	temperature of 1100°C	
SGC500	LKMO synthesized by sol-gel with calcination	_
	temperature of 500°C	
SGC600	LKMO synthesized by sol-gel with calcination	_
	temperature of 600°C	
SGC700	LKMO synthesized by sol-gel with calcination	_
	temperature of 700°C	
SG750	LKMO synthesized by sol-gel with sintering	-

	temperature of 750°C	
SG800	LKMO synthesized by sol-gel with sintering	
	temperature of 800°C	-
SG900	LKMO synthesized by sol-gel with sintering	
	temperature of 900°C	-
SG1000	LKMO synthesized by sol-gel with sintering	
	temperature of 1000°C	-
SG1100	LKMO synthesized by sol-gel with sintering	
	temperature of 1000°C	-
CPC700	LKMO synthesized by co-precipitation with	
	calcination temperature of 700°C	-
CPC750	LKMO synthesized by co-precipitation with	
	calcination temperature of 750°C	-
CPC800	LKMO synthesized by co-precipitation with	
	calcination temperature of 800°C	-
CP900	LKMO synthesized by co-precipitation with sintering	
	temperature of 900°C	-
CP1000	LKMO synthesized by co-precipitation with sintering	
	temperature of 1000°C	-
CP1100	LKMO synthesized by co-precipitation with sintering	
	temperature of 1100°C	-
MRAM	Magnetoresistive random access memory	-
SOFC	Solid oxide fuel cells	-
<i>R</i> , <i>RE</i>	Rare earths ions	-
Α	Doped cations	-
IMR	Intrinsic magnetoresistance	-
EMR	Extrinsic magnetoresistance	-
XRD	X-ray diffraction	-
FWHM	Full-width half maxima	-
SEM	Scanning Electron Microscope	-
EDAX	Energy Dispersive X-ray Spectroscopy	-
VSM	Vibration Sample Magnetometer	-
DC	Direct current	-

AC	Alternate current -
ACS	AC susceptometer
FM	Ferromagnetic metal
FI	Ferromagnetic insulator
PI	Paramagnetic insulator
СО	Charge ordering -
CAF	Canted antiferromagnetic
FESEM	Field Emission Scanning Electron Microscope



CHAPTER 1

INTRODUCTION

1.1 Brief History of Mixed Valence Manganites

Mixed valence manganites are compounds with chemical composition of RE_1 . ${}_{x}A_{x}MnO_{3}$ where RE = rare earth elements such as La, Pr and Nd while A = alkali metals or alkali earth metals such as Ca, Sr, and K. The manganese ions exhibited in mixed valence states of Mn³⁺ and Mn⁴⁺ upon the doping process of A into RE. These materials were first reported by Jonker and Santen (1950) who found out that the manganites exhibit metallic properties and a transition temperature of ferromagnetic to paramagnetic (T_c) as the finite doping of LaMnO₃ by Ca, Ba and Sr. Then in 1951, Clarence Zener, an American scientist, explained this correlation of electrical and magnetic properties by a brand new concept, called "double exchange mechanism". His work was then further studies in theorectical part by Anderson and Hasegawa in 1955. Besides, Volger (1954) found out that La_{0.8}Sr_{0.2}MnO₃ has a resistivity drop in ferromagnetic state when external field is applied.

 \bigcirc

In 1955, Wollan and Koehler study the magnetic structure of $La_{1-x}Ca_xMnO_3$ (x = 0 to 1) by using neutron diffraction techniques. They found out that LaMnO₃ exhibited ferromagnetic phase at *ab*-plane and antiferromagnetic at *c*-axis which they defined antiferromagnetism; CaMnO₃ exhibited as A-type while а G-type antiferromagnetism. The intermediate doping shows variety type of antiferromagnetism and at x=0.33, the manganites are fully ferromagnetism.

Manganites received a wide attention since 1990's due to the discovery of a very large magnetoresistance in bulk $Nd_{0.5}Pb_{0.5}MnO_3$ (Kusters et al., 1989), $La_{2/3}Ba_{1/3}MnO_3$ thin films (Helmolt et al., 1993) and $La_{3/4}Ca_{1/4}MnO_3$ thin films (Chahara et al., 1993). The latter two have observed large MR at room temperature (-60% and -53%, respectively). In 1994, Jin et al. observed a negative ~1500% MR value at 200K and ~100,000% at 77K for $La_{2/3}Ca_{1/3}MnO_3$. Since that time, this large negative MR is named as colossal magnetoresistance (CMR). However, this CMR values required a high field to appear (6T) so it is not suitable for technology application. Hwang et al. (1996) studied the MR in ferromagnetic phase, and found out the different of MR behavior for single crystal and polycrystalline of $La_{2/3}Sr_{1/3}MnO_3$. He observed high negative MR values occur at low temperature even in low magnetic field (0.1 T) for polycrystalline manganites, due to the effect of spin-polarized electron tunneling between the grains. This property is latter named as extrinsic CMR.

In 21st century, researchers are interested in nano-scale materials including manganites. Manganites in nanoparticles or nanocrystallines exhibit different properties in magnetism, magnetoresistance, Curie temperature and metal-insulator transition temperature with their bulk counterparts. Sol-gel method is a very famous process to prepare nanoscale manganites by lowering the calcination and sintering temperature (Venkataiah et al., 2012).

1.2 Monovalent Doped Manganites

Monovalent cations (Li⁺, Na⁺, K⁺, Cs⁺ and Ag⁺) are also good candidates for doping with manganites (LaMnO₃), and possessed similar trend of electrical and magnetic properties with the manganites that doped with divalent cations. However, the

monovalent elements are only possessing one valence electron. Hence, every x amount of monovalent doping to the trivalent (La) site will create an amount of 2x Mn^{4+} and double up the double exchange mechanism. As a result, a small amount of monovalent doping results in a large number of charge carriers and enhanced the conductivity (Shaikh and Varshney, 2012). Furthermore, the solid solubility of monovalent cations in manganites are very narrow. Coey et al. (1999) stated that the solubility range is up to x =0.2. Besides, Teraoka et al. (2001) found that the solubility limit of potassium ion, K⁺ in La-K-Mn-O is lies between x = 0.2 and 0.25 and K₂MnO₄ appeared to be the byproduct beyond the solubility limit. Furthermore, in the investigation of Shen et al. (2009), the XRD results of the La_{0.8}Sr_{0.2}MnO₃ gives a single phase while La_{0.8}K_{0.2}MnO₃ and La_{0.8}Na_{0.2}MnO₃ shows the additional secondary phase which is defined as K₄MnO₄ and Na₄MnO₄ through analysis, respectively. This results indicating that the solubility limit of monovalent cations and the solubility limit of monovalent cations is lower than x = 0.20.

1.3 Application of Mixed Valence Manganites

The discovery of CMR effect in manganites since 1994 has made this materials become potential to apply in MR type devices such as magnetic recording, data storage technique on computer hard discs and magnetoresistive random access memory (MRAM). This large MR effect produced can increase the data storage densities of hard drive. However, manganites only show CMR effect at low temperature and high applied field, which is contradict with the practical application that need MR near room temperature and low applied field (Jin, 1997). Furthermore, the discovery of extrinsic CMR in polycrystalline manganites may fulfill the

 \bigcirc

requirement of low field and widen the temperature range of MR effect but the high MR values only produced at low temperature (Hwang et. al., 1996). Currently, many researchers are trying to find the CMR materials that can operate in low field and having high MR values at room temperature.

Manganites are potential candidates for making sensors. In 2002, polycrystalline of $La_{2/3}Sr_{1/3}MnO_3$ thick film has been investigated and the results has shown the feasible use of this material in making low-cost contactless potentiometer (Balcells et. al., 2002) manganites can also be used in making microwaves sensors and bolometric uncooled infrared sensors (Venkatesan et al., 1998).

Lanthanum strontium manganites are suitable to use as the cathode of solid oxide fuel cells (SOFC) due to its high electrical conductivity at higher temperature (Stambouli and Traversa, 2000). The advantages of SOFC include high effiency, long-term stability, environmental friendly and low emissions of NO_x, dust and noise (Joo and Choi, 2008). Manganites can also be employed in the magnetic refrigeration technology due to the exhibition of magnetocaloric effect (Dhahri et al., 2008). Spintronics is the new technology emerged nowadays which utilizes the electronic's spin of electron to carry the information. Manganites doped at x = 1/3, is half-metal ferromagnets. The high spin polarization of conduction electron is potential for spintronics devices (Felser et al., 2007).

1.4 Problem Statement and Objectives

There are several techniques to fabricate perovskite manganites, including solid state reaction, sol-gel and co-precipitation. Solid state is the most common and a traditional way to produce the homogenous ceramic by multiple grindings and extended heat treatment (Rao et al., 1993). Thus, the grain size of powders or polycrystalline samples obtained usually is large (subnano- or micro- range).

Sol-gel and co-precipitation methods have been developed to achieve better mixing of the initial product. The homogenous mixing of cations is attained on the atomic scale in the solution and enhanced the reaction during the heat treatment process (lowering the heat treatment temperature) and results a more homogenous powder (Rao et al, 1993; Hamadneh et al., 2006; Hamadneh et al, 2010). Grain size in nanometer range can achieve.

Therefore, in this project, polycrystalline $La_{0.85}K_{0.15}MnO_3$ was prepared by 3 synthesis method, i.e. solid state reaction, sol-gel and co-precipitation. The duration and rate of change of heat treatment (calcination and sintering) is fixed. The lowest calcination temperature of each synthesis techniques was investigated. The technique with the lowest calcination temperature indicates the lowest sintering temperature it can produce, and exhibits smallest grain size of polycrystalline sample.

In this work, the main objectives are list down as follow:

• To synthesize polycrystalline lanthanum potassium manganites, La_{0.85}K_{0.15}MnO₃ via three different methods: solid state reaction, sol-gel and co-precipitation.

- To investigate the effect of different synthesis methods with the difference of initial particles to the structure, microstructure, electrical and magnetic properties of polycrystalline La_{0.85}K_{0.15}MnO_{3.}
- To investigate the effect of sintering temperature to the structure, microstructure, electrical and magnetic properties of polycrystalline $La_{0.85}K_{0.15}MnO_{3.}$
- To study the relationship between the electrical and magnetic properties of polycrystalline La_{0.85}K_{0.15}MnO_{3.}



REFERENCES

- Anderson, P.W. and Hasegawa, H. (1955). Considerations on Double Exchange. *Physical Review*. 100: 675-681.
- Alonso, J.A., Martinez-Lope, M.J. and Casais, M.T. (2000). Evolution of the Jahn-Teller Distortion of MnO₆ Octahedra in RMnO₃ Perovskites (R = Pr, Nd, Dy, Tb, Ho, Er, Y): A Neutron Diffraction Study. *Inorganic Chemistry*. 39: 917-923.
- Balcells, L., Calvo, E., and Fontcuberta, J. (2002). Room-temperature Anisotropic Magnetoresistive Sensor Based on Manganese Perovskite Thick Films. *Journal of Magnetism and Magnetic Materials*. 242-245: 1166-1168.
- Brink, J.V.D., Khaliulin, G. and Khomskii, D. (1999). Charge and Orbital Order in Half-Doped Manganites. *Physical Review Letters*. 83: 5118-5121.
- Burgei, W., Pechan, M.J. and Jaeger, H. (2003). A Simple Vibrating Sample Magnetometer for Use in a Materials Physics Course. American Journal of *Physics*. 71: 825-828.
- Castro, A. and Palem, D. (2002). Study of Fluorite Phase in the System Bi₂O₃-Nb₂O₅-Ta₂O₅. *Journal of Material Chemistry*. 12: 2774-2780.
- Chahara, K., Ohno, T., Kasai, M. and Konzond, Y. (1993). Magnetoresistance in Magnetic Manganese Oxide with Intrinsic Antiferromagnetic Spin Structure. *Applied Physics Letters*. 63:1990-1992.
- Chen, Y., Yuan, H.M., Tian, G., Zhang, G.H., and Feng, S.H. (2007). Mild Hydrothermal Synthesis and Magnetic Properties of the Manganates Pr₁₋ _xCa_xMnO₃. *Journal of Solid State Chemistry*. 180: 167-172.
- Cheong, S-W. and Hwang, H. Y. (2000). Ferromagnetism Versus Charge/Orbital Ordering in Mixed-Valent Manganites. In Y. Tokura. *Colossal Magnetoresistive Oxides* (pp. 237-280). Gordon and Breach Science Publishers, Advances in Condensed Matter Science.

Chikazumi, S. (1997). Physics of Ferromagnetism. Oxford Science Publication.

- Coey, J.M.D., Viret, M. and Molnar, S.V. (1999). Mixed-valence Manganites. *Advances in Physics*. 48: 167-293.
- CryoBIND (Cryogenic Balanced Inductive Detector). (2010). AC Susceptibility Measuring System – Operating and Instruction Manual. CryoBIND Manual.
- Cullity, B.D. and Graham, C.D. (2009). Introduction to Magnetic Materials (2nd edition). WILEY.
- Dhahri, E., Bejar, M., Othmani, S., Tozri, A. and Hill, E.K. (2008). Magnetic Refrigeration: Application to the Electron Doped Manganites. *NATO Science for Peace and Security Series B: Physics and Biophysics*. 1: 31-40.

- Dutta, A., Gayathri, N. and Ranganathan, R. (2003). Effect of Particle Size on the Magnetic and Transport Properties of La_{0.875}Sr_{0.125}MnO₃. *Physical Review B*. 68: 054432(1-8).
- Egerton, R.F. (2005). *Physical Principle of Electron Microscopy: an Introduction to TEM, SEM, and AEM*. Springer.
- Felser, C., Fecher, G.H., and Balke, B. (2007). Spintronics: A Challege for Materials Science and Solid-State Chemistry. Angewandte Chemie International Edition. 46: 668-699.
- Fiorillo, F., Appino, C. and Pasquale, M. (2006). *The Science of Hysteresis*(1st edition). Academic Press.
- Galceran, M., Pujol, M.C., Aguilo, M. and Diaz, F. (2007) Sol-gel Modified Pechini Method for Obtaining Nanocrystalline KRE(WO₄)₂ (RE = Gd and Yb). *Journal of Sol-Gel Science Technologies*. 42: 79-88.
- Gaur, A. and Varma, G.D. (2006). Sintering Temperature Effect on Electrical Transport and Magnetoresistance of Nanophasic La_{0.7}Sr_{0.3}MnO₃. *Journal of Physics: Condensed Matter.* 18: 8837-8846.
- Gosnet, A.M.H. and Renard, J.P. (2003). CMR Manganites: Physics, Thin Films and Devices. *Journal of Physics D: Applied Physics*. 36: R127-R150.
- Gupta A., Gong, G.Q., Xiao G., Duncombe, R.R., Lecoeur, P., Trouiloud, P., Wang, Y.Y., Dravid, Y.P. and Sun, J.Z. (1996). Grain-boundary effects on the magnetoresistance properties of perovskite manganite films. *Physical Review B*. 54: R15629-R15632.
- Hamadneh, I., Halim, S.A. and Lee, C.K. (2006). Characterization of Bi_{1.6}Pb_{0.4}Sr₂Ca₂Cu₃O_y Ceramic Superconductor Prepared Via Coprecipitation Method at Different Sintering Time. *Journal of Materials Science*, 41: 5526-5530.
- Hamadneh, I., Khalili, F., Shaaer, M, and Rosli, A.M. (2010). Effect of Nano Sized Oxalate Precursor on the Formation of REBa₂Cu₃O_{7- δ} (RE = Gd, Sm, Ho) Ceramic Via Coprecipitation Method. *Journal of Physics: Conference Series*. 234: 012016 (1-5).
- Helmolt, R.V., Wecker, J., Holzapfel, B., Schultz, L. and Samwer, K. (1993). Giant Negative Magnetoresistance in Perovskite La_{2/3}Ba_{1/3}MnO₃ Ferromagnetic Films. *Physical Review Letters*. 71: 2331-2333.
- Hwang, H.Y., Cheong, S-W., Ong, N.P., and Batlogg, B. (1996). Spin-Polarized Intergrain Tunneling in La_{2/3}Sr_{1/3}MnO₃. *Physical Review Letters*. 77: 2041-2044.
- Jiles, D.C. (1991). *Introduction to Magnetism and Materials (2nd edition)*. Chapman & Hall.
- Jin, S. (1997). Field-induced Conductivity Changes in CMR manganites. *Journal of the Minerals, Metals and Materials Society*. 49: 61-63.

- Jin, S., Tiefel, T.H., McCormack, M., Fastnacht, R.A., Ramesh, R. and Chen, L.H. (1994). Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films. *Science*. 264: 413-415.
- Johnsson, M. and Lemmens, P. (2008). Perovskites and Thin Films-Crystallography and Chemistry. *Journal of Physics: Condensed Matter*. 20: 264001(1-6).
- Jonker, G.H. and Van Santen, J.H. (1950). Ferromagnetic Compounds of Manganese with Perovskite Structure. *Physica*. 16: 337-349.
- Joo, J.H. and Choi, G.M. (2008). Thick-film Electrolyte (thickness <20m)-Supported Solid Oxide Fuel Cells. *Journal of Power Sources*. 180: 195-198.
- Joshi, L. and Keshri, S. (2010). Enhanced CMR Properties of La_{0.67}Ca_{0.33}MnO₃ Sintered at Different Temperatures. *Phase Transitions: A Multinational Journal*. 83: 263.275.
- Kajimoto, R., Kubota, M. and Yoshizawa, H. (1996). Ferromagnetism-induced Reentrant Structural Transition and Phase Diagram of the Lightly Doped Insulator La_{1-x}Sr_xMnO₃ (x < 0.17). *Physical Review Letters*. 53: R14709-R14712.
- Kang, Suk-Joong L (2005). Sintering: Densification, Grain Growth and Microstructure. Elsevier.
- Ku, S.K. (2008). The Effect of Particle Size on Magnetoresistance of La_{0.67}Sr_{0.33}MnO₃ Prepared by Co-precipitation Method. Bachelor Thesis, Universiti Putra Malaysia.
- Kundu, S., and Nath, T.K. (2010). Size-induced Metallic State in Nanoparticles of Ferromagnetic Insulating Nd_{0.8}Sr_{0.2}MnO₃. *Journal of Physics: Condensed Matter*. 22: 506002(1-10).
- Kusters, R.M., Singleton, J., Keen, D. A., McGreevy, R. and Hayes, W. (1989). Magnetoresistance Mesurements on the Magnetic Semiconductor Nd_{0.5}Pb_{0.5}MnO₃. *Physica B: Condensed Matter*. 155: 362-365.
- Lakshmi, Y.K. and Reddy, P.V. (2009). Influence of Sintering Temperature and Oxygen Stoichiometry on Electrical Transport Properties of La_{0.67}Na_{0.33}MnO₃ manganite. *Journal of Alloys and Compounds*. 470: 67-74.
- Laurent, P., Fagnard, J.F., Vanderheyden, V., Babu, N.H., Cardwell, D.A., Ausloos, M. and Vanderbemden, P. (2008). An AC Susceptometer for the Characterization of Large, Bulk Superconducting Samples. *Measurement Science and Technology*. 19: 085705(1-10).
- Lei, L.W., Fu, Z.Y. and Zhang, J.Y. (2006). Influence of Sintering Temperature on Microstructure and Magnetotransport Properties of La_{0.8}Na_{0.2}MnO₃ Ceramics. *Materials Letters*. 60: 970-973.
- Li, C., Soh, K. C.K. and Wu, P. (2004). Formability of ABO₃ Perovskites. *Journal of Alloys and Compounds*. 372: 40-48.

- Li, Haifeng (2008). Synthesis of CMR Manganites and Ordering Phenomena in Complex Transition Metal Oxides. Julich Forschungszentrum.
- Li, X.W., Gupta, A., Xiao, G. and Gong, G.Q. (1997). Low-field Magnetoresistive Properties of Polycrystalline and Epitaxial Perrovskite Manganite Films. *Applied Physics Letters*.71: 1124-1126.
- Lim, K.P., Ng, S.W., Halim, S.A., Chen, S.K. and Wong, J.K. (2009). Effect of Divalent Ions (A = Ca, Ba and Sr) Substituition in La-A-Mn-O Manganite on Structural, Magnetic and Electrical Transport Properties. *American Journal of Applied Sciences*. 6: 1153-1157.
- Liu, R.S., Shen, C.H. and Hu, S.F. (2001). Chemical Pressure Controlled Colossal Magnetoresistance Effects in La_{0.6}(Sr_{0.4-x}Ca_x)MnO₃. *International Journal of Inorganic Materials*. 3: 1063-1072.
- Malavasi, L., Alessandri, I., Mozzati, M.C., Ghigna, P., Chiodelli, G., Azzoni, C.B. and Flor, G. (2003). Preparation, Structural and Magnetic Characterisation of RF-sputtered $La_{1-x}Na_xMnO_{3\pm\delta}$ Thin Films Manganites. *Physical Chemistry Chemical Physics*. 5(11):2274-2278.
- Mozhegorov, A.A., Gonchar, L.E. and Nikiforov, A.E. (2007). Antiferromagnetic resonance in LaMnO₃. Low Temperature Physics. 33(2): 229-233.
- Opel, M. (2012). Spintronic Oxides Grown by Laser-MBE. Journal of Physical D: Applied. Physics. 45: 033001(1-31).
- Pekala, M., Drozd, V., Fagnard J.F., Vanderbemden, P. and Ausloss, M. (2006). Magnetocaloric Effect in Nano- and Polycrystalline Manganite La_{0.7}Ca_{0.3}MnO₃. *Applied Physics A – Materials Science & Processing*. 90: 237-241.
- Rao, C.N.R., Nagarajan, R., and Vijayaraghavan, R. (1993). Synthesis of Cuprate Superconductors. *Superconductor Science and Technology*. 6: 1-22.
- Sakka, S. (2005). Handbook of Sol-Gel Science and Technology Processing, Characterization and Applications, Volume I: Sol-Gel Processing. Kluwer Academic Publishers.
- Schiffer, P., Ramirez, A.P., Bao, W. and Cheong, S.W. (1995). Low Temperature Magnetoresistance and the Magnetic Phase Diagram of La_{1-x}Ca_xMnO₃. *Physical Review Letters*. 75: 3336-3339.
- Shaikh, M.W. and Varshney, D. (2012). Structural Properties and Electrical Resistivity Behaviour of $La_{1-x}K_xMnO_3$ (x = 0.1, 0.125 and 0.15) Manganites. *Materials Chemistry and Physics*. 134: 886-898.
- Shankar, K.S., Kar, S., Subbanna, G.N. and Raychaudhuri, A.K. (2004). Enhanced Ferromagnetic Transition Temperature in Nanocrystalline Lanthanum Calcium Manganese Oxide (La_{0.67}Ca_{0.33}MnO₃). *Solid State Communications*. 129: 479-483.
- Shen, X., Xu, G. and Shao, C. (2009). The Effect of K⁺ and Na⁺ Doping on Infrared Emissivity of Lanthanum Manganites. *Solid State Communications*. 149: 852-854.

- Shimosaka, A., Ueda, Y., Shirakawa, Y. and Hidaka, J. (2003). Sintering Mechanism of Two Spheres Forming a Homogenous Solid Solubility Neck. KONA. 21: 219-233.
- Shivakumara, C. and Bellakki, M.B. (2009). Synthesis, Structural and Ferromagnetic Properties of $La_{1-x}K_xMnO_3$ (0.0 < x < 0.25) Phases by Solution Cumbustion Method. *Bulletin of Material Science*. 32: 443-449.
- Shivakumara, C., Bellakki, M.B., Prakash, A.S. and Vasanthacharya, N.Y. (2007). Rapid Synthesis of Ferromagnetic $La_{1-x}Na_xMnO_3$ ($0.00 \le x \le 0.25$) by the Solution Combustion Method. *Journal of the American Ceramic Society*. 90: 3852-3858.
- Siwach, P.K., Goutam, U.K., Srivastava, P., Singh, H.K., Tiwari, R.S. and Srivastava, O.N. (2006). Colossal Magnetoresistance Study in Nanophasic La_{0.7}Ca_{0.3}MnO₃ Manganite. *Journal of Physics D: Applied Physics*. 39: 14-20.
- Stambouli, A.B. and Traversa, E. (2002). Solid Oxide Fuel Cells (SOFCs): A Review of a Environmentally Clean and Efficient Source of Energy. *Renewable and Sustainable Energy Reviews*. 6: 433-455.
- Tejuca, L.G. and Fierro, J.L.G. (1989). Structure and Reactivity of Perovskite-Type Oxide. *Advanced in Catalysis*. 36: 237-328.
- Teraoka, Y., Kanasa, K. and Kagawa, S. (2001). Synthesis of La-K-Mn-O Perovskite-type Oxides and Their Catalytic Property for Simultaneous Removal of NO_x and Diesel Soot Particulates. Applied Catalysis B: Environmental. 34: 73.78.
- Umesh, C., Kamlesh, Y., Anurag, G. and Varma, G.D. (2010). Effect of Different Synthesis Techniques on Structural, Magnetic and Magneto-transport Properties of Pr_{0.7}Sr_{0.3}MnO₃ Manganite. *Journal of Rare Earths*. 28: 760-764.
- Urushibara, A., Moritomo, Y., Arima, T., Asamitsu, A., Kido, G. and Tokura, Y. (1995). Insulator-Metal Transition and Giant Magnetoresistance in La_{1-x}Sr_xMnO₃. *Physical Review B*. 51: 14103-14109.
- Venkataiah G., Lakshmi, Y.K. and Reddy, P.V. (2012). Influence of Sintering Temperature on Magnetotransport Behavior of Some Nanocrystalline Manganites. In Dr. Volodymyr Shatokha. *Sintering - Methods and Products* (pp. 267-292). InTech.
- Venkataiah, G. and Reddy, P.V. (2005). Electrical Behaviour of Sol-Gel Prepared Nd_{0.67}Sr_{0.33}MnO₃ Manganite System. *Journal of Magnetism and Magnetic Materials*. 285: 343-352.
- Venkataiah, G., Lakshmi, Y.K. and Reddy, P.V. (2008). Influence of Sintering Temperature on Resistivity, Magnetoresistance and Thermopower of La_{0.67}Ca_{0.33}MnO₃. *PMC Physics B*. 1: 1-12.
- Venkatesan, T., Rajeswari, M., Zhi-Wen, D., Ogale, S.B. and Ramesh, R. (1998). Manganite-based Devices: Opportunities, Bottlenecks and Challenges.

Philosophical Transactions of The Roral Society A: Mathematical Physical and Enginerring Sciences. 356: 1661-1680.

- Volger, J. (1954). Further Experimental Investigations on Some Ferromagnetic Oxidic Compounds of Manganese with Perovskite Structure. *Physica*. 20: 49-66.
- Wang, L.M., Lai, J.H. and Wu, J.L. (2007). Effects of Ru Substituition for Mn on La_{0.7}Sr_{0.3}MnO₃ Perovskites. *Journal of Applied Physics*. 102: 023915 (1-7).
- Wang, K.Y., Song, W.H., Yu, T., Zhao, B., Pu, M.H., Sun, Y.P. (1998). Colossal Magnetoresistance in Fine Particle of Layered-Perovskite La_{2-x}Ca_{1+2x}Mn₂O₇ (x = 0.3) Synthesized at Low Temperatures. *Physica Status Solidi (a)*. 171: 577-582.
- Waseda, Y. and Muramatsu, A. (2004). Morphology Control of Materials and Nanoparticles: Advanced Materials Processing and Characterization. Springer.
- Wollan, E.O. and Koehler, W.C. (1955). Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds La_{1-x}Ca_xMnO₃. *Physical Review*. 100: 545-563.
- Yang, J., Zhao, B.C., Zhang, R.L., Ma, Y.Q., Sheng, Z.G., Song, W.H. and Sun, Y. P. (2004). The Effect of Grain Size on Electrical Transport and Magnetic Properties of La_{0.9}Te_{0.1}MnO₃. Solid State Communications. 132: 83-87.
- Zener, C. (1951). Interaction between the S-shells in the Transition Metals. *Physical Review*. 81: 440-444.
- Zhang, N., Yang, W., Ding, W.P., Xing, D.Y. and Du, Y.W. (1999). Grain Size-Dependent Magnetism in Fine Particle Perovskite, La_{1-x}Sr_xMnO_z. *Solid State Communications*. 109: 537-542.
- Zhang, Y.B., Li, S., Sun, C.Q., Widjaja, S. and Hing, P. (2002). Transition Dependence of La_{2/3}Ca_{1/3}MnO₃ Oxide on Microstructure. *Journal of Materials Processing Technology*. 122: 266-271.
- Zi, Z.F., Sun, Y.P., Zhu, X.B., Yang, Z.R., Dai, J.M. and Song, W.H. (2009). Synthesis of Magnetoresistive La_{0.7}Sr_{0.3}MnO3 Nanoparticles by an Improved Chemical Coprecipitation Method. *Journal of Magnetism and Magnetic Materials*. 321: 2378-2381.

Appendix A Ratio of Samples

Atomic Mass of Starting Materials

Ś

Element	Atomic Mass (g/mol)		
La	138.906		
К	39.098		
Mn	54.938		
0	15.999		
Н	-1.008		
Ν	14.007		
С	12.001		
Standard Equation $0.425 \text{ La}_2\text{O}_3 + \text{MnO}_2 + 0.075 \text{ K}_2\text{CO}_3 \rightarrow \text{L}_2\text{O}_3$	$La_{0.85}K_{0.15}MnO_{3}$		
Materials	Atomic Mass (g/mol)		
0.425 La ₂ O ₃	138.469		
0.075 K ₂ CO ₃	10.364		
MnO ₂	86.936		
Total	235.769		

To form a 15g sample powder, 8.810g of La_2O_3 , 0.659g of K_2CO_3 and 5.531g of MnO_2 were needed.

(ii) Sol-gel

Standard Equation

 $0.425 \ La_2O_3 + MnCO_3 + 0.15 \ KNO_3 \rightarrow La_{0.85}K_{0.15}MnO_3$

Materials	Atomic Mass (g/mol)		
0.425 La ₂ O ₃	138.469		
0.15 KNO3	15.165		
MnCO ₃	114.936		
Total	268.570		

To form a 15g sample powder, 7.734g of La_2O_3 , 0.847g of KNO₃ and 6.419g of MnCO₃ were needed.

Calculation of Weight of Citric Acid and Ethylene Gylcol Used

The weight ratio of metal ions (MI), citric acid (CA) and ethylene glycol (EG) used:

MI:CA:EG = 1:4:2

Molecular weight of MI, CA and EG were 268.57 g/mol, 192.12 g/mol and 62.07 g/mol, respectively. Hence, the mass of CA used was 42.94g and EG used was 6.933 ml.

(iii) Co-precipitation

Standard Equation

 $0.85 \text{ La}(\text{CH}_3\text{COO})_3.1.5\text{H}_2\text{O} + 0.15 \text{ KNO}_3 + \text{Mn}(\text{CH}_3\text{COO})_2.4\text{H}_2\text{O} \rightarrow$

 $La_{0.85}K_{0.15}MnO_3$

Materials	Atomic Mass (g/mol)		
	291.601		
0.85 La(CH ₃ COO) ₃ .1.5H ₂ O	268.632 (without H ₂ O)		
0.15 KNO3	15.165		
	245.086		
$Mn(CH_3COO)_2.4H_2O$	173.026 (without H ₂ O)		
	603.312		
	456.823 (without H ₂ O)		

In the calculation steps of co-precipitation, we need to consider the presence of H_2O in the starting materials. Thus, to prepare 20g of $La_{0.85}K_{0.15}MnO_3$, 12.766g of $La(CH_3COO)_3.1.5H_2O$, 0.664g of KNO₃ and 10.730g of Mn(CH₃COO)₂.4H₂O were needed.

Appendix B

X-ray Diffraction Pattern (XRD) for the standard peak LKMO

Name and formula

98-005-3701

Chemical name:
Common name:
ICSD name:

Lanthanum Potassium Manganese Oxide (0.85/0.15/1/3) Lanthanum Potassium Manganese Oxide (0.85/0.15/1/3) Lanthanum Potassium Manganese Oxide (0.85/0.15/1/3)

Chemical formula: Second chemical formula: K_{0.15}La_{0.85}Mn₁O₃ (La_{0.85}K_{0.15}) MnO₃

Crystallographic parameters

Crystal system:	Hexagonal
Space group:	R -3 c
Space group number:	167
a (?):	5.5040
b (?):	5.5040
c (?):	13.3950
Alpha (°):	90.0000
Beta (°):	90.0000
Gamma (°):	120.0000
Calculated density (g/cm^3):	6.43
Volume of cell (10 ⁶ pm ³):	351.42
Z:	6.00
RIR:	5.65

Subfiles and Quality

Subfiles:

Quality:

Inorganic ICSD Pattern Calculated (C)

Comments

 \bigcirc

Structure: NdAlO3 ICSD collection code: 88441 Original ICSD space group: R3-CH X-ray diffraction (powder) Structure type : NdAlO3 Rietveld profile refinement applied The structure has been assigned a PDF number (calculated powder diffraction data): 01-089-8127 Structure type: NdAlO3 Recording date: 7/16/2001 ANX formula: ABX3 Z: 6 Calculated density: 6.43 R value: 0.014 Pearson code: hR10 Wyckoff code: e b a Publ. title: Low temperature synthesis, structure and magnetic properties of La0.85 (Na1-x Kx)0.15 Mn O3 perovskites: the role of A cation size disparity in the electronic properties of mixed-valence manganates

References

Primary reference:

Lloret, F. Beltran, D. Beltran, A. Martinez, E. Sapina, F. Coret, E. El-Fadli, Z., *Journal of Materials Chemistry*, **9**, 1793, (1999)

Peak list

No.	h	k	1	d [A]		2т]	heta[deg]	Ι[8]
1	0	1	2	3.883	349	2	2.881		19	.5
2	1	1	0	2.752	200	3	2.509		95	.9
3	1	0	4	2.740)12	3	2.654		100	.0
4	1	1	3	2.342	275	3	8.392		1	.1
5	2	0	2	2.245	537	4	0.127		25	.2
6	0	0	6	2.232	250	4	0.368		8	.7
7	0	2	4	1.941	.75	4	6.745		64	.0
8	2	1	1	1.785	53	5	1.114		0	.3
9	1	2	2	1.739	976	5:	2.560		5	.5
10	1	1	6	1.733	375	5	2.757		4	.9
11	0	3	0	1.588	387	5	8.000		26	.4
12	2	1	4	1.586	557	5	8.092		40	.7
13	0	1	8	1.579	975	5	8.367		17	.5
14	1	2	5	1.495	500	6	2.029		0	.1
15	2	2	0	1.376	500	6	8.085		17	.0
16	2	0	8	1.370	06	6	8.421		17	.0
17	1	3	1	1.315	63	7	1.677		0	.3
18	2	2	3	1.314	197	7	1.718		0	.2
19	2	1	7	1.311	.73	7	1.923		0	.1
20	1	1	9	1.309	914	7	2.087		0	.1
21	3	1	2	1.296	599	7	2.870		2	.1
22	0	3	6	1.294	150	7	3.033		2	.8
23	1	0	10	1.289	955	7	3.359		1	.2
24	1	3	4	1.229	966	7	7.575		14	.0
25	1	2	8	1.226	548	7	7.814		14	.5
26	3	1	5	1.185	553	8	1.046		0	.2
27	0	4	2	1.173	323	8	2.077		2	.1
28	2	2	6	1.171	.38	8:	2.234		4	.5
29	0	2	10	1.167	71	8.	2.549		2	.4
30	4	0	4	1.122	269	8	6.648		8	.3
31	0	0	12	1.116	525	8	7.273		2	.9
32	З	2	1	1 080	91	8	9 943		0	0

 \mathbf{G}

Structure

No.	Name	Elem.	Х	Y	Z	Biso	sof
Wyck							
1	01	0	0.46250	0.00000	0.25000	0.7000	1.0000
18e							
2	MN1	Mn	0.00000	0.00000	0.00000	0.3000	1.0000 6b
3	K1	K	0.00000	0.00000	0.25000	0.3000	0.1500 6a
4	LA1	La	0.00000	0.00000	0.25000	0.3000	0.8500 6a

Stick Pattern



Appendix C



EDAX Patterns of all Sintered LKMO