UNIVERSITI PUTRA MALAYSIA

EFFECTS OF GRAIN SIZE ON THE STRUCTURAL, ELECTRICAL, MAGNETIC AND MAGNETOTRANSPORT PROPERTIES OF POLYCRYSTALLINE $La_{0.67}Sr_{0.33}MnO_3$ SYNTHESIZED VIA DIFFERENT METHODS

CHIN HUI WEI

FS 2014 60

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master Science

EFFECTS OF GRAIN SIZE ON THE STRUCTURAL, ELECTRICAL, MAGNETIC AND MAGNETOTRANSPORT PROPERTIES OF POLYCRYSTALLINE $La_{0.67}Sr_{0.33}MnO_3$ SYNTHESIZED VIA DIFFERENT METHODS

By

CHIN HUI WEI

November 2014

Chairman: Lim Kean Pah, PhD

Faculty: Science

In recent decades, the extrinsic magnetoresistance (MR) has been widely studied due to their potential application at low field. Extrinsic MR is caused by spin polarized tunneling (SPT) and spin dependent scattering (SDS) between grains, which originates from the grain size variation and grain boundary effect. It can be enhanced by adjusting their extrinsic characteristic, for example by adding composite and size reduction. In this work, the focus is on the effect of grain size variation on $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) samples which were synthesized through solid state (SS), co-precipitation (CP) and sol-gel (SG) methods. The influence of different sintering temperature (different range of grain sizes) towards structural, magnetic, electrical and magnetotransport properties was studied, from 600˚C up until 1200 ˚C. Different sintering temperature is required to obtain pure single phase compound when different synthesis methods are used. CP and SS samples show pure $La_{0.67}Sr_{0.33}MnO_3$ (ICSD code: 156020) phase with hexagonal structure (R3c) at 1100 ˚C and 1200 ˚C, respectively. However, SG samples gave single phase compound at lower sintering temperature (600 ˚C). The increase of sintering temperature promotes significant grain growth and microstructure densification, thus grain size increases. Through SEM analysis, the smaller grain (around 42.7-194.4 nm) can be found in SG sample which was lower than 200 nm even when sintered at 1200 ºC. Magnetization decreases with grain size. Curie temperature (T_c) of SS12, CP12 and SG12 were 373 K, 375 K and 358 K, respectively. Decrease of T_c and magnetization were not only grain size (effective grain boundaries) dependent but also grain size distribution and formation. The resistivity is found to be higher for LSMO SG samples having nanograin size with higher effective grain boundaries. Thus, metal- insulator transition (T_p) shifted to lower temperature. Nanosized particles that consist of higher effective grain boundaries can enhance the magnetoresistance (MR) value but

decreases of magnetization. The highest extrinsic MR % was given by the smallest grain size (42.7 nm) in LSMO SG6 with -9.16 % in 10 kG at 80 K. It also contributes to significantly high CMR value (-19.6 %) in 10 kG at 80 K. Overall, the results show that the structure, magnetic and magnetoresistive properties are strongly dependent on their grain size distribution and formation, which is affected by synthesis methods and sintering effects. As the grain size becomes smaller, resistivity and magnetoresistence increase however magnetization decreases. T_p also shifted to lower temperature, extrinsic MR is more dominant. Vice versa, larger grain size shows lower resistivity, higher magnetization and intrinsic MR is more dominant.

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

KESAN SAIZ ZARAH TERHADAP STRUKTUR, SIFAT ELEKTRIK, KEMAGNETAN DAN MAGNETOANGKUTAN BAGI POLIHABLUR $La_{0.67}Sr_{0.33}MnO_3$ YANG DISEDIAKAN MELALUI KAEDAH YANG BERBEZA

Oleh

CHIN HUI WEI

Novamber 2014

Pengerusi: Lim Kean Pah, PhD

Fakulti: Sains

Dalam dekad-dekad kebelakangan ini, Magnetoriintangan ekstrinsik (MR Ekstrinsik) telah dikaji secara luas disebabkan potensi penggunaan di dalam medan yang rendah. MR ekstrinsik disebabkan oleh spin polarisasi terowong (SPT) and spin serakan bergantung (SDS) yang berpunca daripada perubahan saiz zarah dan sempadan zarah berkesan. Oleh demikian, magnetorintangan dapat ditingkatkan menerusi pengubahsuaian ciri-ciri fizikalnya, seperti penambahan komposit dan pengurangan saiz zarahnya. Projek ini memberi tumpuan terhadap kesan perubahan saiz zarah ke atas sampel $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) yang telah disediakan melalui kaedah tindak balas keadaan pepejal (SS), teknik pemendakan serbuk (CP) dan teknik sol- gel (SG). Kesan daripada suhu sinter (pelbagai saiz zarah) pada 600˚C hingga 1200 ˚C terhadap struktur, kemagnetan, sifat elektrik dan magnetorintangan telah dikaji. Fasa tulen boleh terbentuk pada peringkat sinter yang berbeza menerusi kaedah yang berlainan. CP and SS sampel memunjukkan fasa tulen $La_{0.67}Sr_{0.33}MnO_3$ (ICSD code: 156020) yang berstruktur heksagon pada suhu sinter yang tinggi, iaitu 1100 ˚C dan 1200 ˚C, masing- masing. Manakala SG sampel terbentuk pada suhu sinter yang agak rendah (600 ˚C). Peningkatan suhu sinter menggalakkan perkembangan zarah dan pemadatan mikrostruktur, oleh itu saiz zarah bertambah. Melalui SEM analisis, taburan zarah yang lebih kecil (sebanyak 42.7- 194.4 nm) boleh terdapat dalam SG sampel walaupun disinter sehingga mencapai 1200 ºC. Suhu Curie (T_c) bagi SS12, CP12 and SG12 ialah 373 K, 375 K dan 358 K masing-masing. Kemagnetan menurun semasa saiz zarah berkurang. Pengurangan T_c dan pemagnetan bukan sahaja bergantung pada pengurangan saiz zarah (sempadan zarah berkesan) dan juga pembentukan zarah. SG sampel yang mempunyai nano saiz zarah yang paling kecil dan sempadan zarah berkesan yang paling tinggi menunjukkan kerintangan yang paling tinggi. Oleh itu, suhu peralihan logam-penebat (T_p) mengalih ke suhu yang lebih rendah. Saiz zarah yang lebih kecil mempunyai sempadan zarah berkesan yang lebih tinngi. Ia boleh meningkatkan nilai magnetorintangan (MR) dengan pengurangan kemagnetan. MR ekstrinsik yang paling tinggi terdapat dalam saiz zarah yang paling kecil

dalam SG6 dengan nilai -9.16 % di 10 kG pada 80 K. Ia juga menyumbang nilai CMR yang tinggi (-19.6 %) di 10 kG pada 80 K. Keseluruhannya, keputusan menunjukkan bahawa struktur, kemagnetan dan magnetorintangan adalah bergantung pada taburan saiz zarah dan pembentukan zarah. Ia juga dipengaruhi oleh kesan proses penyinteran. Rintangan dan magnetorintangan meningkat manakala kemagnetan menurun semasa saiz zarah berkurang. T_p juga mengalih ke suhu yang lebih rendah, MR ekstinsik lebih dominan dalam keadaan ini. Sebaliknya, saiz zarah yang lebih besar menunjukkan rintangan yang lebih rendah, kemagnetan yang lebih tinggi dan ia mencondongi MR intrinsik.

ACKNOWLEDGEMENTS

First, I would like to express my deep appreciation to my supervisor, Dr Lim Kean Pah, for his encouragement, consideration and thoughtful suggestion that made this project complete. In addition, I would like to thank and appreciate to Prof Dr. Abdul Halim Shaari and Dr. Chen Soo Kien for willing to be part of my supervisory committee members and assistance throughout this project.

With this opportunity, I would like to extend my gratitude to all UPM staff and my lab mates and friends who either directly or indirectly helped me towards the success of this project. No word can express my gratitude to my dearest family and my partner who give me their fully support, encouragement and understanding. I am very grateful to you all for accompanying by my side.

Finally, I would like to express my deepest gratitude to anyone always care for me and give me support during the project. May you all be well and happy.

I certify that a Thesis Examination Committee has met on (date of viva voce) to conduct the final examination of Chin Hui Wei on her thesis entitled (Effects of Grain Size on the Structural, Electrical, Magnetic and Magnetotransport Properties of Polycrystalline $La_{0.67}Sr_{0.33}MnO_3$ synthesized via Different Methods) in accordance with the Universities and University Colleges 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.

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Name of Department and/or Faculty
Name of Organisation (University/Institute)
Country
(External Examiner)

(Zulkarnain Zainal, PhD)
Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

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Lim Kean Pah, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD
Professor
Name of Faculty
Universiti Putra Malaysia
(Member)

Chen Soo Kien, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

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Supervisory
Committee: Lim Kean Pah, PhD

Signature:____________________
Name of
Member of
Supervisory
Committee: Abdul Halim Shaari, PhD

Signature:____________________
Name of
Member of
Supervisory
Committee: Chen Soo Kien, PhD

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LIST OF ABBREVIATIONS AND SYMBOLS

AE	Alkaline Earth
AMR	Anisotropic Magnetoresistor
BMR	Ballistic Magnetoresistors
CA	Citric Acid
CMR	Colossal Magnetoresistance
$CoMn_2O_4$	Cobalt Manganese Oxide
CP	Co-precipitation Method
DE	Double Exchange Mechanism
EDX	Energy Dispersive X-ray Analysis
EMR	Extraordinary Magnetoresistors
FESEM	Field Emission Scanning Electron Microscope
FFM	Ferromagnetic Metallic
FM	Ferromagnetic
GMR	Giant Magnetoresistors
HFMR	High Field Magnetoresistance
ICDD	International Centre Diffraction Data
ICSD	Inorganic Crystal Structure Database
JT	Jahn Teller Distortion
LBMO	Lanthanum Barium Manganese Oxide
LCMO	Lanthanum Calcium Manganese Oxide
LFMR	Low field Magnetoresistance
LSMO	Lanthanum Strontium Manganese Oxide
MD	Multi Domain
MR	Magnetoresistance
OMR	Ordinary Magnetoresistor
PSD	Pseudo- single Domain
RE	Rare Earth
SD	Single Domain
SDS	Spin Dependence Scattering
SEM	Scanning Electron Microscope
SG	Sol-gel
SOFCs	Solid Oxide Fuel Cell
SPM	Superparamagneic
SPT	Spin Polarised Tunnelling
SS	Solid State
TGA	Thermogravimetric Analysis
TMR	Tunnel Magnetoresistors
VSM	Vibrating Sample Magnetometer
XRD	X-ray Diffraction

$\langle Ra \rangle$	Averange A-site ionic radius
T	Magnetic field

ρ	Resistivity
h	hour
α, β, γ	Angle between a,b,c
a,b,c	Lattice parameter
I	Current
V	Voltage
E	Electric field
G	Correction Factor
λ	Wave length
B	Difference in position width of broadened and standard sample
d	Lattice planes spaced
Ω	Resistance
ρ_H	Resistivity in an applied magnetic field
ρ_o	Resistivity at zero magnetic field
T_C	Curie temperature
T_S	Sintering temperature
T_P	Metal-insulator Transition
TB	Blocking Temperature
D_c	critical Range
H_c	Coercivity
t	Thickness of the sample
T	Thickness Factor
C	Contour Factor
$F(t,c)$	Additional Correction Factor
s	spacing
ΔE	specific energy value
S	Core separation
R_H	Hall coefficient
B	Magnetic flux density
m	Meter
Å	Angstrom
θ	Bragg diffraction angle
r	Hall scattering factor
°C	Degree Celsius
K	Kelvin
M	Magnetization
%MR	Percentage drop of MR at applied field
e_g	g-orbital
T_{2g}	T_{2g}-orbital

CHAPTER 1

INTRODUCTION

1.1 Introduction

Nowadays, the information age relies on the development of "smart" and "small" magnetic materials for memory, data storage, processing and probing. Magnetoresistive (MR) material which is the unique perovskite (ABO_3 type) manganite has drawn considerable attention. These perovskite (ABO_3 type) manganite also known as colossal magnetoresistance (CMR) materials, in the form of $RE_{1-x}AE_xMnO_3$, where RE and AE are trivalent rare earth (e.g. La^{3+}, Nd^{3+}, Pr^{3+}etc) and divalent alkaline-earth (e.g. Sr^{2+}, Ba^{2+}, Ca^{2+} etc) elements respectively (Chahara et al., 1993).

More sensitive and applicable CMR materials are developed as high speed information technologies, such as oxide based has been used to achieve highly sensitive heads that can process data at higher speed. Hence, CMR has been widely studied not only to understand its basic physical phenomena but also draw attention on its potential applications in electrical and electronic technology industries, for example CMR effect (Lu and Sohn, 1997), catalytic, oxygen cathode reduction (Poulsen, 2000) and field sensor (Balcells et al., 1996). Over the last few years, it has also been focused on hyperthermal studies (Thorat et al., 2013) which are a hot topic in medical field.

In general, the physical properties of samples are usually dependent on preparation routes. Preparation route influences the nature of surface region of nanograin, which plays an important role in electrical, magnetic and magnetotransport properties of system. Thus, a lot of effort has been put to discover simple cost effective routes with well-controlled, narrow grain size distribution and reproducible sample. The ability to manipulate the grain size at different scales is useful in creating or miniaturizing novel deceives.

As we know, conventional solid state reaction is hard to achieve homogeneity and nanosized product. Besides, a prolonged period (around 24 hours) tends to produce powder with bigger grain size. Thus, wet chemical routes are introduced over the past few decades. These ascribe unique advantages including lower synthesis temperature, higher purity and homogeneity. In wet chemical method, the mixing of components occurs at atomic level which contributes to lower particles sizes formation with higher homogeneity.

1.2 Problem Statement

Although CMR materials were discovered during early 1950, it did not attract much attention due to its limitation in application. This attributes to large MR obtained near

T_c and restricted to narrow temperature range. Besides, its electrical noise is relatively higher near T_c due to its larger resistivity at this temperature range (Gupta et al., 2010).

These characteristics caused CMR materials not suitable for technology application. However, the discovery of extrinsic MR (large low-field MR or LFMR) in polycrystalline manganites sample in last few decades brings new era to the actual application of this compound. It can be found that at temperature below T_c, a sharp drop of MR occurs when low magnetic field is applied.

Hwang et al. (1996) suggested that the observed extrinsic MR was due to spin polarized tunneling and spin dependent scattering between grains, which originated from the grain size variation and grain boundary effect. Core-shell effect was proposed by Zhang et al. (1997) stated that the outer layer shell becomes larger when grain size is reduced. It leads to the formation of magnetically disorder layer which enhances their MR. A lot of studies are focused on the way to enhance extrinsic MR effect through adjusting their extrinsic characteristic such as adding composite and grain size reduction. A large number of researches have been done over recent years (Chang and Ong, 2004; Dey and Nath, 2006; Wang et al., 2008), however a clear explanation of grain size distribution (from micron size to nano size) and grain boundaries effect on its physical properties of manganite compound is still insufficient.

In this project, three different methods were used to synthesize different size of particles ranging from micron to nano size. Solid state method was able to form micron size's particle, however co-precipitate and sol-gel methods tend to form submicron and nano size particle respectively. Strontium doped lanthanum manganite ($La_{0.67}Sr_{0.33}MnO_3$) was chosen in this project due to their higher electrical conductivity, catalytic activity, transition of metal-insulator (T_p) and its Curie temperature (T_c) relatively closer to room temperature (Siwach et al., 2008; Huang et al., 2000).

1.3 Objectives of the Research

The purpose of this project is to make comparative study of X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), Vibrating Sample Magnetometer (VSM), and Hall Effect measurement on the influence of grain size formation and distribution. The main objectives of the work are:

-To prepare and characterize LSMO samples with different grain size formation and distribution through different preparation methods.

-To study the grain size formation and distribution via different sintering process.

-To investigate the influence of grain size variation by measuring its changes on structure, microstructure, magnetic, electric and magnetotransport properties.

1.4 Overview of the Thesis

The first chapter of the thesis consists of a brief introduction of CMR manganites, its potential applications, problem statements and the objectives. Overview is given towards the end of this chapter.

In chapter 2, some related theories of CMR materials and nanoscience are presented. A review of existing literatures related to the grain size dependent CMR manganites properties is given as well. The experimental results can be well interpreted based on the given theories and reviews.

In chapter 3, the materials usage, every experimental procedure and steps taken in each synthesis methods are discussed. The equipment and experiment setting involved in the experiment is introduced too.

Chapter 4 presents the experiment data in the form of tables, graphs and pictures. It should give a clearer picture of the findings. In the last chapter, a conclusion concerning this project is presented. Future possible research is suggested in this chapter.

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