



UNIVERSITI PUTRA MALAYSIA

***GRAIN SIZE EFFECT ON STRUCTURAL, ELECTRICAL, MAGNETIC
AND MAGNETO-TRANSPORT PROPERTIES OF Pr-A-Mn-O (A = Sr, Ba,
Na, K) NANOMANGANITE***

NG SIAU WEI

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By

NG SIAU WEI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra
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Philosophy**

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

GRAIN SIZE EFFECT ON THE STRUCTURAL, ELECTRICAL, MAGNETIC AND MAGNETO-TRANSPORT PROPERTIES OF Pr-A-Mn-O (A= Sr, Ba, Na AND K) NANOMANGANITE

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NG SIAU WEI

October 2017

Chair: Lim Kean Pah, PhD
Faculty: Science

Colossal magnetoresistance (CMR) effect in the manganese oxide compounds are nowadays a very potential technological applications in the information storage, sensors, magnetic sensing devices and magnetic refrigeration. These CMR effects can be tuned up as the grains size is reduced to nanometers. However, the physics phenomenons of nano-sized manganites were still not yet fully understood. Although a number of works had been carried out on the effect of grain size (in nanometric regime) towards its physical properties, but less research work had been put attention in praseodymium based nano-manganese so far. Therefore, in this work, $\text{Pr}_{0.67}(\text{Sr}, \text{Ba})_{0.33}\text{MnO}_3$ and $\text{Pr}_{0.85}(\text{Na}, \text{K})_{0.15}\text{MnO}_3$ had been synthesized by sol-gel technique and sintered from 600°C to 1000°C to investigate the influence of grain size reduction from micro to nano-size. XRD results showed that all samples are polycrystalline with orthorhombic structure and no significant lattice distortion was observed as the sintering temperature increased. As the grain size increase from nano to micron-size, the resistivity of $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (PSMO) and $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ (PBMO) decreased and T_p shifted to higher value while $\text{Pr}_{0.85}\text{Na}_{0.15}\text{MnO}_3$ (PNMO) showed semiconductor behavior where T_p were estimated to be lower than 80 K. However, for $\text{Pr}_{0.85}\text{K}_{0.15}\text{MnO}_3$ (PKMO), the T_p and resistivity shifted to lower value with increasing grain size. This variation was due to the different of grain shape and grain distribution. Besides, the T_c was shifted to higher value for PSMO (278 K to 295 K), PBMO (140 K to 188 K) and PKMO (124 K to 140 K) systems as grain size increase. Substitute A-site with divalent or monovalent produce a Jahn Teller distortion of MnO_6 octahedron. By changing the ionic radius of A-site, the Mn-O-Mn angles and Mn-O lengths can be modified and hence affect the physical properties in the manganites system. From this work, we found that as the manganites system replace with monovalent, the T_c and T_p shifted to lower temperature (< 200 K) and the magnitude of MR around room temperature was relatively smaller compare with divalent system. Besides,

higher value of resistivity is observed for monovalent system as compare with divalent system. In general, every manganites system there exist an optimum grain size distribution at which the MR or LFMR reaches a maximum. This optimal grain size may vary for different system and may also depend on the synthesis technique. Out of all the four series samples under investigation, $\text{Pr}_{0.85}\text{K}_{0.15}\text{MnO}_3$ (PKS6) with average grain size of 51 nm was found to exhibit highest %MR of – 53.3% (at 80 K with magnetic field of 1 Tesla). However, the highest %MR value at room temperature (300 K) was – 2.39% for sample $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (PSS7 with average grain size of 37 nm). From a practical view-point, the high %MR values are beneficial in magnetoelectronic sensing devices.



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

KESAN SAIZ BUTIRAN TERHADAP CIRI-CIRI STRUKTUR, ELEKTRIK, MAGNET DAN MAGNETO-PENGANGKUTAN BAGI Pr-A-Mn-O (A= Sr, Ba, Na, K) NANOMANGANITE

Oleh

NG SIAU WEI

Oktober 2017

Pengerusi: Lim Kean Pah, PhD
Fakulti: Sains

Kesan magnetorintangan raksaksa (MRR) pada sebatian manganites oksida dalam aplikasi teknologi pada masa kini adalah amat berpotensi dalam bidang penyimpanan maklumat, sensor, sensor peranti magnet dan penyejukan magnet. Kesan MRR ini boleh ditala melalui pengurangan saiz butiran kepada nanometer. Walau bagaimanapun, fenomena fizikal manganites bersaiz nano masih belum difahami sepenuhnya. Walaupun beberapa kerja telah dilakukan terhadap kesan saiz butiran (dalam rejim nanometrik) terhadap sifat-sifat fizikalnya, tetapi perhatian kepada kerja penyelidikan terhadap nano-manganites berdasarkan praseodymium adalah kurang setakat ini. Dengan itu, dalam kajian ini, $\text{Pr}_{0.67}(\text{Sr}, \text{Ba})_{0.33}\text{MnO}_3$ dan $\text{Pr}_{0.85}(\text{Na}, \text{K})_{0.15}\text{MnO}_3$ telah disintesis dengan teknik sol-gel dan sinter dari 600°C ke 1000°C untuk menyiasat kesan pengurangan saiz butiran dari mikro ke nano-saiz. Keputusan XRD menunjukkan bahawa semua sampel adalah dalam bentuk polihabulur dengan struktur otorombik dan tiada perubahan ketara ke atas parameter kekisi apabila suhu persinteran meningkat. Apabila saiz butiran meningkat dari nano ke saiz mikron, kerintangan bagi $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (PSMO) dan $\text{Pr}_{0.67}\text{Ba}_{0.33}\text{MnO}_3$ (PBMO) menurun dan T_p beralih ke nilai yang lebih tinggi sementara $\text{Pr}_{0.85}\text{Na}_{0.15}\text{MnO}_3$ (PNMO) menunjukkan sifat semikonduktor di mana T_p dianggarkan lebih rendah daripada 80 K. Walau bagaimanapun, bagi $\text{Pr}_{0.85}\text{K}_{0.15}\text{MnO}_3$ (PKMO), T_p dan kerintangan beralih ke nilai yang lebih rendah dengan saiz butiran yang semakin bertambah. Perubahan ini disebabkan oleh perbezaan bentuk butiran dan pengagihan butiran. Selain itu, T_c beralih kepada nilai yang lebih tinggi bagi sistem PSMO (278 K hingga 295 K), PBMO (140 K hingga 188 K) dan PKMO (124 K hingga 140 K) dengan peningkatan saiz butiran. Gantian tapak-A dengan divalen atau monovalen menghasilkan herotan Jahn Teller bagi octahedron MnO_6 . Dengan penukaran jejari ion tapak-A, sudut Mn-O-Mn dan panjang Mn-O boleh diubah suai dan dengan itu memberi kesan terhadap sifat fizikal dalam sistem manganite. Daripada kerja ini, kami mendapati bahawa

apabila sistem manganite ganti dengan monovalen, T_c dan T_p beralih ke suhu yang lebih rendah (<200 K) dan magnitud MR lebih kecil berbanding dengan sistem divalen pada suhu bilik. Selain itu, nilai kerintangan yang lebih tinggi dapat diperhatikan bagi sistem monovalen berbanding dengan sistem divalen. Secara umumnya, setiap sistem manganite mempunyai taburan saiz butiran yang optimum untuk mencapai maksimum MR atau LFMR. Saiz butiran yang optimum ini mungkin berbeza untuk sistem yang berlainan dan mungkin juga bergantung pada teknik sintesis. Daripada semua empat siri sampel yang diasasat, $\text{Pr}_{0.85}\text{K}_{0.15}\text{MnO}_3$ (PKS6) dengan saiz purata butiran 51 nm didapati menunjukkan %MR yang paling tinggi sebanyak - 53.3% (pada 80 K dengan medan magnetik 1 Tesla). Walau bagaimanapun, nilai %MR tertinggi pada suhu bilik (300 K) adalah - 2.39% untuk sampel $\text{Pr}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (PSS7 dengan saiz bijian purata 37 nm). Dari sudut praktikal, nilai %MR yang tinggi ini adalah bermanfaat dalam peranti sensor magnetoelektronik.

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This thesis was 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:

Lim Kean Pah, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Abdul Halim Shaari, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Jumiah Hassan, PhD

Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD

Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Signature: _____
Name of Chairman of
Supervisory
Committee: Assoc. Prof. Dr. Lim Kean Pah

Signature: _____
Name of Member of
Supervisory
Committee: Prof. Dr. Abdul Halim Shaari

Signature: _____
Name of Member of
Supervisory
Committee: Assoc. Prof. Dr. Jumiah Hassan

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LIST OF ABBREVIATIONS/NOTATIONS/GLOSSARY OF TERMS

GMR	Giant magnetoresistance
MR	Magnetoresistance
CMR	Colossal magnetoresistance
LFMR	Low field magnetoresistance
HFMR	High field magnetoresistance
Pr	Praseodymium
Nd	Neodymium
Sr	Strontium
Ba	Barium
Na	Sodium
K	Potassium
Mn	Manganite
O	Oxygen
Ag	Silver
Pb	Lead
Rb	Rubidium
Li	Lithium
Y	Yttrium
Cu	Copper
T_p	Metal-insulator transition temperature
T_c	Curie temperature
PM	Paramagnetic
FM	Ferromagnetic
AFM	Antiferromagnetic
SPM	Superparamagnetic
AFM	Antiferromagnetic
DM	Diamagnetic
r_A	Averaged radii at A-site
r_B	Averaged radii at B-site
r_o	Ionic radius for oxygen
$\langle r_A \rangle$	A-site cation size
σ^2	A-site cation size mismatch
TMO	Transition-metal oxides
T_N	Neel temperature
RE	Trivalent rare earth
DE	Double exchange interaction
JT	Jahn-Teller
S	Total spin
t_{2g}	Sub-orbital of 3d orbital (lower energy level)
e_g	Sub-orbital of 3d orbital (higher energy level)
SPT	Spin dependent tunnelling
SDS	Spin dependent scattering
ρ	Electric resistivity
ρ_0	Electric resistivity at zero magnetic field
ρ_H	Electric resistivity at H magnetic field
R_o	Electrical resistance at zero magnetic field

R_H	Electric resistance at H magnetic field
$\rho_2 T^2$	Electrical resistivity due to the electron-electron scattering process
$\rho_{2.5} T^{2.5}$	Electrical resistivity due to electron-magnon scattering process in the ferromagnetic phase
$\rho_{4.5} T^{4.5}$	Electrical resistivity due to combination of electron-electron, electron-magnon and electron-phonon scattering processes
$\rho_5 T^5$	Electrical resistivity due to electron-phonon interaction
$\rho_{7.5} T^{7.5}$	Electrical resistivity originates partly from the polaron formation near the metal–semiconductor transition temperature
R^2	Square of linear correlation coefficient
VRH	Variable range hopping
SPH	Small polaron hopping
θ_D	Debye's temperature
T_o	Characteristic temperature expressed as $T_o = 16\alpha^3 / k_B N(E_F)$
k_B	Boltzman constant
β	Bohr magneton
B	Strength of the magnetic field in Tesla
g/g_{eff}	g-factor
h	Plank constant
ν	Microwave frequency
H_{pp}	Linewidth
$N(E_F)$	Density of states at the Fermi level
α	The inverse of localization length
E_p	Polaron activation energy
[CA]	Complexing agent
[METAL]	Moles of the metal cations
[EG]	Moles of ethylene glycol
C_M	Ratio of [CA]/[METAL]
C_E	Ratio of [CA]/[EG]
ABO_3	Perovskite
$d_{\text{Mn-O}}$	The Mn-O shortest distance
$d_{\text{A-O}}$	Distance between A-site ions
t_f	Tolerances factor
ω	Bandwidth
D	Crystalline size
FWHM	Line broadening at half the maximum intensity
λ	Wavelength
M	Magnetization
H	Magnetic field
χ'	AC susceptibility
XRD	X-ray diffractometer
SEM	Scanning electron microscopy
FE-SEM	Field-emission scanning electron microscopy
ESR	Electron spin resonance

ACS	AC-susceptometer
VSM	Vibrating sample magnetometer
R	Resistance
I	Current
V	Voltage
DC	Direct current
ICSD	Inorganic Crystal Structure Database
GOF	Goodness of fit



CHAPTER 1

INTRODUCTION

1.1 Overview

In the early 1990s, a new kind of MR was rediscovered in mixed-valence manganese oxides (manganites) by group of Helmolt *et al.* (1993). This manganese oxide was possible to achieve magnetoresistance values up to 60% at temperature close to ambient temperature, leading to the name of colossal magnetoresistance (CMR) to distinguish it from the giant magnetoresistance (GMR). Manganites have a general composition $A_{1-x}B_xMnO_3$ (where A is a trivalent rare-earth and B is a divalent or monovalent alkaline element) in perovskite structures. It is composed of interpenetrating simple cubic sublattices of A, B and Mn ions with O at the cube faces and edges where Mn–O–Mn bonds are formed and constitute the basis of the electrical and magnetic properties of these compounds. The occurrence of both divalent or monovalent and trivalent ions in the A site of the structure through chemical doping leads to a charge unbalance. Hence, create the appearance of Mn^{3+}/Mn^{4+} pairs. The changes of different doping levels or with different cations lead to a great variety of magnetic and transport ground states, which can be ranging from antiferromagnetic insulators to ferromagnetic metals. Zener's double-exchange (DE) model is often describing the low-temperature state and the close connection between T_C and T_p (ferromagnetic metallic state) and CMR transition (Zener, 1951). However, in the high-temperature region it has been argued that the carriers are coupled to the phonon system through a strong Jahn-Teller distortion in manganites (Millis *et al.*, 1996). Besides intrinsic CMR, low field magnetoresistance (LFMR) effect could be observed in the polycrystalline or granular manganites over a wide temperature range below T_C due to the existence of grain boundaries. It has been proposed that the spin-polarized tunneling between ferromagnetic grains through an insulating grain boundary barrier should be responsible for LFMR (Hwang *et al.*, 1996).

1.2 Motivation

Manganites offer a high degree of chemical flexibility leading to complex interplay between structural, electrical and magnetic properties. Their importance refers to their intriguing electrical and magnetic properties such as metal-insulator transition at T_p , ferromagnetic-paramagnetic transition temperature at T_c , and the magnetoresistance (MR) properties like the colossal magnetoresistance (CMR) effect and low-field magnetoresistance (LFMR) effect, which make them to be potential technological applications in the information storage field, sensors, magnetic devices, and magnetic refrigeration.

Currently, the physics of nanoscale magnetic materials has been a vivid research subject for both fundamental and technological reasons. When the size of the magnetic particles is reduced to nanometers, the magnetic particles are expected to exhibit outstanding physical properties such as superparamagnetism, small coercivity, low Curie temperature and low saturation magnetization as compared to bulk material. As the particle size decreases, the surface and interface effects become more and more important. However, a clear understanding of the physical properties for manganites at nanoscale is still lacking. Besides, nanomanganites promote formation of superparamagnetism phase which could arise in some new magnetic interaction mechanism. Hence, nano-sized reductions perturb the structural, magnetism and electrical properties of these nanomanganites.

1.3 Problem Statement

Manganites exhibit a wide range of magnetic and electric transport properties when the perovskite structure incorporates with different sized of A-site cation. The average A-site cation size of the perovskite $\langle r_A \rangle$, influences the magnetic transition temperature, T_c and the transport properties. However, the mismatch effect, represented by the variance of A-site cation radii distribution parameter σ^2 , also influences both the values of T_c and T_p . The structural disorder produces a strong local stress in MnO_6 octahedra (resulting in rotation), modifying the Mn–O–Mn angles and Mn-O lengths and thus changing lattice and electronic properties. Therefore, an effort has been made to correlate the anomalous variation of T_p and T_c observed among the samples of the present investigation with varying ionic radii of A-site cation as well as the size variance parameter, σ^2 . In this work, the size and the ration of the substitution ion on Pr-site is one of key factor influencing the different properties of manganites. Therefore, the influence of Mn-O band strength causes various changes in Mn-O bond length and the symmetry of MnO_6 .

Another important parameter that can control the magnetic and transport properties of the manganites is the structure and microstructure. In previous study, conventional solid state synthesis of manganites needs higher sintering temperature to obtain desired structure and homogenous composition. However, this method are not appropriate for many advanced applications, due to formation of large grains (in microns), agglomerates, poor homogeneity, undesirable phases, abnormal grain growth and an imprecise stoichiometric control of cations and oxygen vacancies. In contrast, the wet technique such as sol-gel process was claimed to have a potential advantage over the other methods for achieving better homogenous mixing of the components on the atomic scale and high possibility of forming nano-sized with desired structure which are of technological importance.

Beside, sintering temperature also affect the electrical properties in an efficient way for presently studied nanomanganites because different sintering temperatures provide different amounts of heat or thermal pressure to the smaller particles and grains to form larger grain that having higher impact strength and compactness.

This results in the reduction in number of boundaries between the particles and grains for higher sinter samples. The charge conduction is strongly affected by the movement of charge carriers across the defective boundaries in the lattice. Hence, boundary density plays an important key role in governing the electrical properties of presently studied nanomanganites.

1.4 Objective

Since the average A-site cation size $\langle r_A \rangle$ and synthesized condition (method and sintering temperature) significantly influence the magnetic and transport properties of the manganites system, detailed studies of $\text{Pr}_{0.67}(\text{Sr}, \text{Ba})_{0.33}\text{MnO}_3$ and $\text{Pr}_{0.85}(\text{Na}, \text{K})_{0.15}\text{MnO}_3$ systems have been carried out. Hence, the objectives of this work are:

1. To synthesize single phase of $\text{Pr}_{0.67}(\text{Sr}, \text{Ba})_{0.33}\text{MnO}_3$ and $\text{Pr}_{0.85}(\text{Na}, \text{K})_{0.15}\text{MnO}_3$ manganite via sol-gel method with different sintering temperature.
2. To investigate the influence of grain size effect on the structural, microstructural, magnetic, electrical and colossal magnetoresistance behavior on all systems.
3. To study the effect of different average A-site cation size of divalent and monovalent towards its structural, electrical, magnetic properties and colossal magnetoresistance.

1.5 Thesis Content

In Chapter 1, a brief overview of the colossal magnetoresistance, the motivation, the problem statement and the objectives of this work is included. Chapter 2 contains some literature review on previous and current work done by other researchers. The theory related to the perovskite manganites compounds is also included. In Chapter 3, the method of sample preparation and characterization process for CMR compound is discussed. For Chapter 4, the experimental results and discussion are presented. Chapter 5 includes the conclusion for the study and suggestions for the further research on CMR materials.

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