## **UNIVERSITI TEKNOLOGI MARA**

# EFFECTS OF DOPING ON MAGNETIC AND TRANSPORT PROPERTIES OF

 $La_{0.85-x}Sm_{x}Ag_{0.15}MnO_{3}, \\ La_{0.8-x}M_{x}Ag_{0.2}MnO_{3} (M=Sm^{3+}, Dy^{3+}), \\ (1-x)La_{0.8}Ag_{0.2}MnO_{3}/xBiFeO_{3}AND \\ Pr_{0.6}Ca_{0.4-x}Ba_{x}MnO_{3} MANGANITES$ 

### NORAZILA BINTI IBRAHIM

Thesis submitted in fulfillment of the requirements for the degree of **Doctor of Philosophy** 

**Faculty of Applied Sciences** 

December 2014

#### **AUTHOR'S DECLARATION**

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any other degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student	:	Norazila Binti IBrahim
Student ID No.	:	2009672166
Programme	:	Doctor of Philosophy in Science (AS990)
Faculty	:	Faculty of Applied Sciences
Thesis Title	:	Effects of Doping on Magnetic and Transport
		Properties of $La_{0.85-x}Sm_xAg_{0.15}MnO_3$ ,
		$La_{0.8-x}M_xAg_{0.2}MnO_3(M=Sm^{3+},Dy^{3+}),$
		$(1-x)La_{0.8}Ag_{0.2}MnO_3/xBiFeO_3$ and
		$Pr_{0.6}Ca_{0.4rx}Ba_xMnO_3$ Manganites.
Signature of Student	:	

Date : December 2014

#### ABSTRACT

manganites series with In this study. four starting compositions  $La_{0.85-x}Sm_xAg_{0.15}MnO_3(x=0-0.2), La_{0.8-x}M_xAg_{0.2}MnO_3$  (M=Dy<sup>3+</sup>, Sm<sup>3+</sup>, x=0-0.15).  $(1-y)La_{0.8}Ag_{0.2}MnO_{3}/yBiFeO_{3}$  (y=0wt%-3.5wt%) and Pr<sub>0.6</sub>Ca<sub>0.4-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> (x=0-0.3) were prepared by solid-state reaction method in order to elucidate their physical properties. For  $La_{0.85-x}Sm_xAg_{0.15}MnO_3$  (x=0-0.2) and  $La_{0.8-x}M_xAg_{0.2}MnO_3$  (M=Sm<sup>3+</sup>,  $Dy^{3+}$ , x=0-0.15) series, the resistivity and magnetic measurements showed all samples exhibit transition from insulating to metallic behavior accompanying a paramagnetic to ferromagnetic transition as the temperatures was decreased. For x=0, two metalinsulator, MI transition peaks were observed at  $T_{P1}$  and  $T_{P2}$  in the resistivity curves. Both peaks and Curie temperature,  $T_c$  shifted to lower temperatures with increasing  $Dy^{3+}$  and  $Sm^{3+}$ , indicating that the substitution weakened the double exchange process and enhanced the Jahn-Teller effect. The magnetoresistance peak was observed around  $T_{p1}$  for all samples. The observed double peak behavior in the  $\rho(T)$  curve is suggested to be due magnetic inhomogeneity of the samples. Our result also showed that the inhomogeneity was strongly influenced by the lattice effect. For (1-y)La<sub>0.8</sub>Ag<sub>0.2</sub>MnO<sub>3</sub>/yBiFeO<sub>3</sub> (y=0wt%-3.5wt%) composite series, the resistivity and susceptibility measurements showed both metal-insulator transition temperatures,  $T_{MI}$ and paramagnetic-ferromagnetic transition temperature,  $T_c$  decreased with increasing BFO content indicating weakening of the double exchange, DE mechanism. The MR peak was observed around  $T_{MI}$  for all samples which is ascribed to the intrinsic MR effect. Below the peak, the MR increased almost linearly with decreasing temperature for all samples and this ascribed to the phenomena of extrinsic MR. The highest MR% (at 40 K) was observed for the x=1.5% sample which showed a MR of more than twice that of the undoped (x=0%) sample. This extrinsic effect is suggested to be related to improved spin polarize tunneling of conduction electrons between grains under external field as a result of improved spin alignment. It is suggested that BFO induced some kind of magnetoelectric coupling between BFO and LAMO leading to the enhancement of the process. For  $Pr_{0.6}Ca_{0.4-x}Ba_xMnO_3$  (x=0-0.3) series the electrical and magnetic measurements showed that the x=0 sample exhibit insulating behavior and an antiferromagnetic to paramagnetic transition behavior. On the other hand, Ba-doped samples exhibit transition from insulating to metallic behavior accompanying a paramagnetic to ferromagnetic transition as the temperatures were decreased. Both  $T_c$  and  $T_{MI}$  of samples increase with increasing Ba concentration. Magnetoresistance, MR behavior indicates intrinsic MR mechanism for x=0.1 which changed to extrinsic MR for x > 0.2 as a result of Ba substitution. The weakening of charge ordering and inducement of ferromagnetic-metallic (FMM) state as well as increased in both  $T_c$  and  $T_{MI}$  indicating enhancement of double exchange mechanism which is suggested to be related to the increase of tolerance factor,  $\tau$  and increase of  $e_{g}$ -electron bandwidth as  $\langle r_{A} \rangle$  increase with Ba substitution.

#### ACKNOWLEDGEMENTS

Assalamualaikum w.b.t.

In the name of Allah, Most Gracious and Most Merciful. Alhamdulillah, all praises to Allah for giving me the strength and blessings to complete this thesis.

First and foremost, I would like to express my gratitude to my supervisor, Prof. Dr Ahmad Kamal Hayati Yahya for his invaluable support, guidance and advice. His suggestion, criticism and willingness to motivate me contributed tremendously towards the completion of this project. I would like to also thank my co-supervisor, Prof.Sunita Keshri for her contribution to the success of the project and hence the thesis. I would also like to thank Dr. Faezah Md Salleh, Prof. Madya Dr Salleh Mohd Deni, Dr Misbah Hassan and Tuan Haji Mohd Isa for sharing their knowledge and ideas.

I would also like to thank Pn. Juliana (X-Ray Diffraction), En. Hayub (Scanning Electron Microscope), and the Faculty of Applied Science's laboratory assistants at Block G who had helped me in numerous ways in accomplishing this research.

My special gratitude also to my postgraduate friends, Rozilah, Azliza, Norezan, Suhadir, Siti Azwani, Nur Baizura, Azianty, Masliyana, Shabani, Muhammad Umair, Muhamad Ikhwan and others who have given me the motivation and spiritual support throughout my research work.

The financial support provided by the Ministry of Education through scholarship and research grant are also gratefully acknowledged and appreciated here. Besides, I would also like to thank the management of the Faculty of Applied Sciences and Universiti Teknologi MARA (UiTM) for providing a good study environment and adequate research facilities to complete this project.

Finally, an honorable mention goes to my beloved family; my husband, Basri Bin Beddu, my sons, Muhammad Amirul Haziq, Muhammad Imran Haqiem, Muhammad Faris Haikal and Muhammad Nazrien Haidar and also my siblings who had given me their love, prayers, support and encouragement through my study. Without their support, it will be impossible for me to complete this study successfully. I will be forever grateful for their understanding and love, especially through the duration of the study.

Thank you.

## **TABLE OF CONTENTS**

	Page
AUTHOR'S DECLARATION	ii
ABSTRACT	iii
ACKNOWLEDGEMENTS	iv
TABLE OF CONTENTS	v
LIST OF TABLES	ix
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	XXX

CHA	PTER (	DNE: INTRODUCTION	1
1.1	Background		
1.2	Problem Statements		
1.3	Goal and Research Objectives		
1.4	4 Scope and Limitations of Study		
1.5	Signif	icance of Study	7
СНА	PTER 1	WO: LITERATURE REVIEW	9
2.1	Introd	uction	9
2.2	Electr	onics Structure of Manganites	9
	2.2.1	Structure of Manganites	10
	2.2.2	Electronic Structure and Crystal Field Splitting	10
	2.2.3	The Jahn-Teller Effect	14
2.3	2.3 Magnetic Interaction		16
	2.3.1	Double Exchange Mechanism	16
	2.3.2	Superexchange Mechanism	18
2.4	Trans	port and Magnetic Properties in Manganites	21
	2.4.1	Transport Properties	21
	2.4.2	Conduction Mechanism in the High-Temperature Insulating	21
•		Region	
		2.4.2.1 Thermal Activation or Band Gap Model	22