Electronic and structural studies of transition metal oxides

A Thesis

submitted

by

Navneet Singh

(Enrollment No: D10003)

for the award of the degree of

Doctor of Philosophy



School of Basic Sciences

Indian Institute of Technology Mandi

Mandi, Himachal Pradesh-175005

July, 2016

Declaration by the Research Guide

This is to certify that the thesis entitled "Electronic and structural studies of transition metal oxides", submitted by Mr. Navneet Singh to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

I.I.T. Mandi (H.P.)
Date:

Research Guide

Declaration by the Research Scholar

This is to certify that the thesis entitled "Electronic and structural studies of transition metal oxides", submitted by me to the Indian Institute of Technology Mandi for the award of the degree of Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of Dr. Bindu Radhamany. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

In keeping with the general practice of reporting scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

I.I.T. Mandi (H.P.)
Date:

Signature of Research Scholar

Institute of Technology Mandi

Acknowledgements

While pursuing my PhD degree, many seen and unseen hands pushed me forward; soul put me on the right path and enlightened me with their knowledge and experience. I shall remain grateful to all of them.

First of all, I would like to express my deep gratitude and profound indebtedness to my PhD advisor Dr. Bindu Radhamany for her guidance, invaluable suggestions and perceptive enthusiasm which enabled me to accomplish the task of undertaking the present study. She sets an example of a world-class researcher for her passion on research. Her wide knowledge and logical way of thinking have been of great value for me. Her understanding, encouraging and personal guidance provided me a good basis for the present thesis.

I express my sincere thanks to Dr. Sudhir Kumar Pandey, IIT Mandi for his invaluable advice and discussion during the period of research.

I am thankful to Dr. K. Maiti of TIFR, Mumbai in his laboratory I carried out some of photoemission experiments. His friendly attitude and useful discussion help me in understanding the aspects of spectroscopy. I would also like to thanks Dr. Sangeeta Thakur, Dr. Ganesh Adhikary, Dr. Deep Narayan, Nishiana and Khadiza for their help during the experiments and giving friendly atmosphere in the lab.

I am also thankful to Dr. S.R. Barman of UGC-DAE Constorium for Scientific Research, Indore where inverse photoemission experiments were carried out. His friendly attitude and useful discussion help me in understanding the aspects of spectroscopy. I would also like to thanks Dr. Sanjay Singh, Dr. Jayita Nayak, and Dr. Abhishek Rai for their help during the experiments and giving friendly atmosphere in the lab.

I am also thankful to Dr. Sayed Khalid, BNL where x-ray absorption experiments were carried out.

Faculty members from School of Basic Sciences for their invaluable advice and encouragement during course work as well as research work.

I am also very much thankful to my research group members for their invaluable support and help during my research work.

I would like to thank all my friends specially Sunil and Mohit for their continuous support and encouragement.

I express profound sense of reverence to my family for their untiring support and co-operation.

I can never forget cooperation, endless tolerance and constant encouragement from all my family members during this tough and happy moment of the journey.

Above all, all the praise is due to the Almighty God, the ultimate source of knowledge, a part of which, He reveals to man and peace is upon all his Messengers throughout the world for success and guidance of mankind. I express my gratitude and indebtedness to the Almighty for countless blessings.

Affectionately

Dedicated

To

My

Loving family

Abstract

Interest in transition metal oxides has revived since the discovery of high T_c-superconductivity and colossal magnetoresistance. The observations of intrinsic inhomogenities in these systems have revolutionized the understanding of the complex phase diagram. The present thesis is focused on two different classes of materials namely perovskite based La_{0.2}Sr_{0.8}MnO₃ and quasi one dimensional Sr₃NiRhO₆ compounds. The thesis is aimed at understanding the fundamental issues associated with both class of compounds using synchrotron based high resolution x-ray diffraction technique, inverse photoemission technique and synchrotron based x-ray absorption spectroscopy.

Our results show that La_{0.2}Sr_{0.8}MnO₃ is structurally inhomogeneous in the nanometer scale for a wide temperature region which is an intrinsic property of the system. The coexisting phases are tetragonal which is orbital ordered, insulating and cubic which is charge ordered. From the results, it appears the possibility of metallicity associated with the cubic charge ordered state. In the insulating phase, we observed unusually an increased intensity at around the Fermi level in the low temperature inverse photoemission spectra. This puzzling behaviour is attributed to the shift in the chemical potential towards the conduction band and localisation of disorder induced states closer to the conduction band.

In the case of quasi one dimensional, Sr₃NiRhO₆ compound, using Ni and Sr K-edge synchrotron x-ray absorption spectroscopy, we have observed common behaviours associated with isostructural compounds. There occurs onset of intra-chain and inter- chain magnetic interactions at temperatures much above the transition temperature and also the role played by direct *d-d* hybridization is less significant in determining the magnetic interactions.

The thesis is structured into 6 chapters. The first chapter gives details about the basic physics that is required to understand the materials under study. The chapter 2 deals with the details of the experimental techniques and computational tool that have been used for the data analysis. Chapters 3&4 discuss the results of the temperature dependent high resolution x-ray diffraction experiments and inverse photoemission experiments carried out on La_{0.2}Sr_{0.8}MnO₃. Chapter 5 discusses the results of the temperature dependent x-ray absorption experiments carried out on quasi one dimensional Sr₃NiRhO₆ compound. In Chapter 6, we summaries the results and discuss the future studies that can be done on the systems that have been studied in the thesis.

Table of Contents

Chapter 1 Introduction

1-1	Structural properties of Ruddlesden-Popper series	5
1-2	Tolerance factor	7
1-3	Electronic aspects	8
	1-3.1 Crystal Field Splitting and Jhan Teller effect	9
1-4	Exchange Interaction	11
1-5	Phase Separation	12
1-6	System under study	12
	1-6.1 La _{0.2} Sr _{0.8} MnO ₃	12
	1-6.2 Sr ₃ NiRhO ₆	15
1-7	Development of thesis	18
Refe	rences	21
	apter 2 chodology	
2-1	Sample Preparation	23
2-2	X-ray diffraction technique	26
2-3	Inverse photoemission spectroscopy	28
2-4	X-ray Absorption Spectroscopy	31
2-5	Analysis of Powder diffraction data: Rietveld method	32
	2-5.1 Criteria for fit	36

2-6	EXAFS data analysis	8
	2-6-1 Determination Structural parameters	8
2-7	Electronic structure calculation using KKR-Green's function method	0
	2-7.1 Coherent potential approximation (CPA)5	52
2-8	Density of states calculations5	;3
Refere	nces5	4
	oter 3 ence of nanoscale structural phase separation in large bandwidth $\mathrm{Sr}_{0.8}\mathrm{MnO}_3$	
3-1	Results and Discussion5	5
3-2	Conclusion6	9
Refere	nces	1
	ster 4 rese photoemission spectroscopic studies on phase separated $\mathrm{Sr}_{0.8}\mathrm{MnO}_3$	
4-1	Results and discussions	'2
4-2	Conclusion8	0
Refere	nces8	31

Chapter 5 Local structural effects in Sr ₃ NiRhO ₆ across magnetic transition		
5-1	Results and Discussions	
5-5	Conclusion	
Refe	rences	
	pter 6 mary and future work	
6-1	Evidence of nanoscale structural phase separation in large bandwidth La _{0.2} Sr _{0.8} MnO ₃ 106	
6-2	Inverse photoemission spectroscopic studies on phase separated La _{0.2} Sr _{0.8} MnO ₃ 107	
6-3	Local structural effects in Sr ₃ NiRhO ₆ across magnetic transition107	
6-3	Future studies	
Refe	rences	