Investigation of the structural connectivity with the physical properties of ilmenite and pyroxene based oxides

A Thesis

submitted

by

Rajiv Kumar Maurya

(Enrollment No. D11030)

for the award of the degree of

Doctor of Philosophy

School of Basic Sciences

Indian Institute of Technology Mandi

Mandi , Himachal Pradesh – 175005

December, 2017

Declaration by the Research Guide

This is to certify that the thesis entitled "**Investigation of the structural connectivity with the physical properties of ilmenite and pyroxene based oxides**", submitted by Rajiv Kumar Maurya to Indian Institute of Technology Mandi for the award of the degree of the Doctor of Philosophy is a bonafide record of research work carried out by him under my supervision. The contents of the 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 the scientific observation, due acknowledgements have been made wherever the work described is based on the findings of other investigators.

IIT Mandi (H.P) Research Guide

Date:

Declaration by the Research Scholar

This is to certify that the thesis entitled **"Investigation of the structural connectivity with the physical properties of ilmenite and pyroxene based oxides**", submitted by me to the Indian Institute of Technology Mandi for the award of the degree of the Doctor of Philosophy is a bonafide record of research work carried out by me under the supervision of the Dr. Bindu Radhamany. The contents of this thesis, in full of parts, have not been submitted 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 the other investigators.

IIT Mandi (H.P) Signature of Research Scholar

Date:

Acknowledgements

First of all, with the immense gratitude, I would like to thank Dr. Bindu Radhamany for their invaluable help to understand the interesting field of crystal structure of the materials, x-ray diffraction and the photoemission spectroscopy techniques. Apart from the academic life, she is very good in social life also. She also gave me the proper advice in my personal life also whenever I discussed. Because of her excellent guidance, fruitful scientific discussion and encouragement, I have become able to complete my PhD thesis work in a better way.

I express my sincere thanks to my doctoral committee members for the constant support, scientific suggestions and the encouragement during my research work. Apart from my doctoral committee members, I am also thankful to other faculty members of IIT Mandi.

I would like to thank Mr. Mohit Kumar Sharma and Mr. Surender lal Sharma for the help in the magnetic susceptibility and heat capacity measurements and for the various fruitful discussions.

I would like thank to my group members Mr. Priyamedha Sharma and Mr. Bharath M. for the various academic and non-academic discussions.

I also would like to thank all the administrative and technical staff of Advanced Material Research Centre (AMRC) for their help and support.

I am also grateful to all faculty members of School of Basic Sciences who taught me different topics to help in my research during the course work. I would like to thank all my friends of IIT Mandi who provided me friendly environment and made my life enjoyable.

I am very grateful to all my family members for their constant support and encouragement during my PhD study. I can never forget their invaluable suggestions, support and patience during this journey of my life.

Finally, I would like to thank all my teachers and friends for their invaluable contribution in my journey.

Affectionately

Dedicated

To

My

Loving

Family

Abstract

Transition metal oxides exhibit emergent phenomena like colossal magnetoresistance, high T_C superconductivity, multiferroicity etc. Such phenomena have given us ample opportunities to explore both from application and fundamental physics point of view. In this thesis, we have studied the structural link with the physical properties of doped $MnTiO_3$, $MnTiO_3$ prepared under different conditions and $LiFeSi_2O_6$ compounds. These compounds are potential ferrotoroidic materials which fall under the fourth primary ferroic order. The samples were studied using temperature dependent x-ray diffraction, dc susceptibility, heat capacity measurements, room temperature electrical resistivity, photocurrent measurements, optical absorbance spectroscopy and x-ray photoemission spectroscopy.

$MnTiO_3$, a quasi two dimensional system, stabilises in hexagonal structure with the space group $R\bar{3}$. This compound exhibits paramagnetic to antiferromagnetic transition around 64 K. This compound shows magnetoelectric property where ferroelectricity occurs with the application of magnetic field and also optical absorption in the wavelength range covering ultra-violet (UV) and visible regions. With the motivation to understand if spin lattice coupling occurs even at zero field, we have carried out temperature dependent x-ray diffraction studies on $MnTiO_3$. Our results show the signature of the onset of intra and inter layer magnetism at temperature ~ 200 K and 100 K, respectively which is much higher than reported ones. In this compound, the magnetic contribution occurs due to the Mn ion.

To understand the role of Ti ions, we have prepared $MnTi_{1-x}Ru_xO_3$ (x= 0 and 0.2) compounds. Our temperature dependent x-ray diffraction and dc susceptibility studies results show that, with Ru doping, there occurs increase in the three dimensional character.

To understand the origin of the optical absorbance in the visible region, we prepared two compounds of $MnTiO_3$. Both were prepared by the usual solid state route only with the difference that in one of the sample, the cooling was natural (MTO*uq)* while in the other it

was quenched (MTO*q*) in *liq.* nitrogen. Our combined results of room temperature structural studies, optical absorbance, core level spectra, valence band spectra and the electrical resistivity suggest even MTO*uq* sample show signature of Mn^{3+} ions in addition to Mn^{2+} ions. The fraction of Mn^{3+} ions has been found to increase on quenching. This further leads to an increase in the optical absorbance in the visible region, a persistent photo-resistance when the incident light is terminated after illuminating it and a decrease in the electrical resistivity. The features of the optical absorbance and valence band spectra were identified based on band structure calculations.

$LiFeSi_2O_6$, pyroxene family, stabilizes in monoclinic structure with C2/c space group. It undergoes structural transition from C2/c to $P2_1/c$ space group of monoclinic structure. This compound also shows magetoelectric property. This compound undergoes paramagnetic to antiferromagnetic transition around 18 K. There are reports that it shows short range magnetic ordering but the onset temperature is not clear. In this compound, it shows ferrotoroidicity in the *ab*-plane. The crystal structure of this compound suggests that it appears that its magnetism is of quasi one dimensional. But the observation of ferrotoroidicity suggests that magnetism should be three dimensional in character. Our temperature results show the clear connection between the structural parameters and the pre-ordering of magnetic interactions. The magnetism exisiting in this compound appears to be of three dimensional in character.

Table of contents