PREFACE

Ferrite materials are known for a long time and have wide applications in industry and technology due to their high resistivity and interesting magnetic properties. Hence, studies on their magnetic and electrical transport properties are of great importance. Molybdenum ferrite, Fe_2MoO_4, a cubic spinel oxide, appears to be a very interesting magnetic material and studies have shown that the magnetic interactions in this ferrite are quite complex. The present work is an attempt to study the role of molybdenum, in the magnetic interaction and also in the electrical conduction process of Fe_2MoO_4. The studies have been carried out on two series of molybdenum ferrite samples, (i) $Fe_2Mo_{1-x}Ti_xO_4$ ($0.0 \leq x \leq 1.0$) where Mo has been progressively replaced by Ti and (ii) $Fe_{2-y}Zn_yMoO_4$ ($0.0 \leq y \leq 1.0$) where Fe has been progressively replaced by Zn, and the results form the content of the thesis. The thesis comprises of six chapters.

Chapter-1 deals with a general introduction of spinel ferrites, highlighting the spinel structure and characterization of spinel ferrites by IR, thermal, electrical, magnetic and Mössbauer studies. A review of the published work on Fe_2MoO_4 and Fe_2TiO_4, and scope and objective of the present work is also given.

Chapter-2 deals with the details of sample preparation, description of the techniques used for sample characterization, and instruments used for electrical, magnetic and Mössbauer studies.

Chapter-3 deals with the results of $Fe_2Mo_{1-x}Ti_xO_4$ samples. Characterization of the samples is done by X-ray diffraction and IR spectroscopy. Thermal analyses (DTA and TG) of all the samples were carried out in air and the results of X-ray diffraction and IR studies of these samples, heated to different temperatures, is also reported. Electrical resistivity and thermoelectric power measurements were carried out in inert atmosphere in the temperature ranges 100-600K and 300-600K, respectively, for all the samples. Thermal activation energy (E_a), carrier concentration (**n**), activation energy for carrier concentration generation (E_n), and mobility (μ) values were calculated from resistivity and thermoelectric power data.

For all the samples field cooled (FC) and zero field cooled (ZFC) dc-magnetization measurements were performed in a field of ~30 Oe. Mössbauer spectra of all the samples were recorded at 295K.

Chapter-4 deals with the results of $Fe_{2-y}Zn_yMoO_4$ samples. Characterization of the samples is done by X-ray diffraction and IR spectroscopy. Electrical resistivity and thermoelectric power were carried out in inert atmosphere in the temperature range 300-600K. Thermal activation energy (E_a), carrier concentration (**n**), activation energy for carrier concentration generation (E_n), and mobility (μ) values were calculated from resistivity and thermoelectric power data. Field cooled (FC) and zero field cooled (ZFC) dc-magnetization measurements were performed for all the samples in a field of ~30 Oe. Mössbauer spectra of the samples were recorded at 295K and 340K, respectively.

Chapter-5 deals with the discussion of the results of the $Fe_2Mo_{1-x}Ti_xO_4$ samples. X-ray diffraction analysis of $Fe_2Mo_{1-x}Ti_xO_4$ samples show that single phase ferrites are formed for all values of x. IR spectra of all the samples show the presence of Mo^{4+} on the octahedral site of the spinel lattice. Thermal analyses of the samples show that, initially, all the samples undergo surface oxidation, followed by bulk oxidation to the respective oxides. The IR spectra of the ferrites show the presence of Mo^{6+} on the surface of the samples, which is confirmed by ESCA. Resistivity and thermoelectric power measurements show, that all the samples are p-type semiconductors and conduction is by hopping of charge carriers. The charge carrier concentration, mobility and the ratio of $Fe^{3+}_{oct} / Fe^{2+}_{oct}$, decreases as Mo is replaced by Ti, implying that molybdenum is also taking part in the conduction process of the ferrites. The results of FC and ZFC magnetization measurements indicate that Mo plays an important role in the magnetic interactions of these ferrites. Mössbauer studies also confirm that in the Mo containing samples, Fe is present in both divalent and trivalent states for charge balance, as Mo has a tendency to be present in both trivalent and tetravalent states, and, the concentration of the Fe^{3+} decreases as Mo is replaced by Ti. Also, the extent of reduction of Fe^{3+} on A and B sites of the spinel lattice is not the same. Such a change in Fe^{3+}_B and Fe^{3+}_A is also indicated in the results of the resistivity measurements.

Chapter-6 deals with the discussion of the results of the $Fe_{2-y}Zn_yMoO_4$ samples. X-ray diffraction analyses of the samples show that single phase spinel ferrites are formed for all values of y, except for y=1.0, and the lattice parameter decreases with increasing y. The $FeZnMoO_4$ (y =1.0) sample shows some characteristic lines of $Fe_2Mo_3O_8/Zn_2Mo_3O_8$ in the X-ray pattern. The small increase in the room temperature resistivity values with increasing y indicates that the substitution of Fe by Zn does not alter the charge carrier concentration. The charge carrier concentration, mobility, and the ratio of $Fe^{3+}_{oct} / Fe^{2+}_{oct}$, calculated from resistivity and thermoelectric power data, confirms that in all the samples Fe is present both in divalent and trivalent states and that Mo is taking part in the conduction process. The FC and ZFC magnetization data indicate that during substitution of Fe^{2+}_A by diamagnetic Zn^{2+}_A, there is a net increase in the magnetization value. Reduction in the A-site magnetic ions also leads to a decrease in T_C, and disappearance of compensation temperature. For y>0.4 samples, the concentration of Fe^{2+}_A becomes too small to sustain the Néel ferrimagnetism and in these ferrites, ferromagnetic as well as antiferromagnetic interactions introduce a complex magnetic order in the B-site moment. The Mössbauer spectra show that, in all the samples, iron is present in trivalent as well as divalent states.

The results suggest that in all the molybdenum containing samples Mo and Fe are present as Mo^{3+}, Mo^{4+} and Fe^{2+}, Fe^{3+}. Presence of all these ions, both in the octahedral and tetrahedral sites of the spinel lattice gives rise to complex magnetic interactions and high electrical conductivity of Fe_2MoO_4. The replacement of Mo and Fe by diamagnetic ions like Ti^{4+} and Zn^{2+} causes the changes in the magnetic interactions, leading to interesting results.