PREFACE

Ferrites have wide applications in industry and technology due to their high resistivity and interesting magnetic properties and thus study of ferrites is of great importance. Due to their small size nanocrystalline ferrites exhibit novel material properties, which largely differ from the bulk crystalline ferrites and they have potential applications in technology and industry. Nanocrystalline spinel ferrites have some unusual magnetic properties like high coercivity, reduced magnetization and saturation magnetization, high Curie temperature and superparamagnetism. Below a critical particle size, nanocrystalline ferrites show superparamagnetic behaviour as collective behaviour of magnetic nanoparticles are blocked at a particular temperature known as blocking temperature. Both $CoFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$ are important magnetic materials and the ultrafine ferrites are recently being investigated.

The first part of the present work is an attempt to study the changes in the properties of nanocrystalline $CoFe_2O_4$, when Co^{2+} is replaced by nonmagnetic Zn^{2-} ions. The second part of the present work is to investigate $Li_{0.5}Fe_{2.5}O_4$ in the nanocrystalline phase when the synthesis is carried out by a citrate precursor gel formation method. The thesis comprises of six chapters.

Chapter -1 deals with a general introduction of the spinel oxides, their crystal structure, cation distribution, electrical transport properties and their characterization by FTIR, thermal, magnetic and Mössbauer studies. A review of the published work on nanocrystalline materials, particularly $CoFe_2O_4$, $ZnFe_2O_4$ and $Li_{0.5}Fe_{2.5}O_4$ and scope of the present work are also given.

Chapter-2 deals with 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 nanocrystalline $Co_{1-x}Zn_xFe_2O_4$ ($x = 0.2,0.4,0.6,0.8$) samples prepared by co-precipitation method followed by sintering at 393K, 573K,673K,773K,873K,973K and 1173K. Characterization of the samples is done by X-ray diffraction, FTIR, TEM and SEM. X-ray diffraction patterns of all the nanocrystalline $Co_{1-x}Zn_xFe_2O_4$ samples show that the samples are single phase, cubic and the crystallite size of the samples increases with increasing sintering temperature. FTIR of all the

nanocrystalline $Co_{1-x}Zn_xFe_2O_4$ samples show that water is present in samples sintered upto 873K. Average particle size of the $Co_{0.2}Zn_{0.8}Fe_2O_4$ samples is measured from TEM micrographs. Cation distribution of the nanocrystalline samples is determined from XRD. Thermal analyses (DTA and TG) of all the samples in air show one endothermic and one exothermic peak in DTA curves and TG curves show that both the peaks are accompanied with weight loss. Magnetization of all the nanocrystalline $Co_{1-x}Zn_xFe_2O_4$ samples in 1Tesla field shows that with increase in sintering temperature i.e. crystallite size, magnetization increases for $Co_{0.8}Zn_{0.2}Fe_2O_4$ and $Co_{0.6}Zn_{0.4}Fe_2O_4$ samples but for $Co_{0.4}Zn_{0.6}Fe_2O_4$ and $Co_{0.2}Zn_{0.8}Fe_2O_4$ samples magnetization increases with increasing sintering temperature upto 773K and samples sintered above this temperature show some anomalous behaviour. Zero field cooled (ZFC) and Field cooled (FC) magnetization measurements have been done on the samples between 7K and 300K. Magnetization data shows that the ZFC magnetization (M_{ZFC}) gradually increases with increasing temperature and then a broad maxima appears followed by a decrease. On heating the samples, the FC curve does not follow the ZFC curve below the temperature of maxima in the ZFC plots. ZFC plots of the samples sintered at higher temperatures differ from the ZFC plots of the samples sintered at lower temperatures and show large broadening below the irreversibility temperature (T_{irr}) of ZFC and FC plots. Room temperature Mössbauer spectra of the nanocrystalline $Co_{0.2}Zn_{0.8}Fe_2O_4$ samples sintered upto 873K, show the presence of a doublet. In the 973Kand 1173K sintered samples a sextet pattern along with a doublet appears in the spectra. Low temperature Mössbauer spectra of samples sintered below 773K show sextet patterns and in samples sintered above 773K along with a sextet a doublet is present. Similar results were shown by the other samples. Low temperature hysteresis measurements show the presence of loops at lower temperatures.

Chapter 4- deals with the results of the nanocrystalline $Li_{0.5}Fe_{2.5}O_4$ samples prepared by the citrate precursor gel formation method followed by sintering at 573K and 773K. Characterization of these samples was done by XRD, FTIR and TEM. The XRD patterns show that both the sintered samples are single phase cubic spinel oxides and extra lines expected for 1:3 ordering are absent. Average particle size of the nanocrystalline lithium ferrite samples is measured from TEM micrographs. Cation distribution of the

nanocrystalline samples was determined from XRD. FTIR of the samples show that both the nanocrystalline lithium ferrite samples are disordered spinel ferrite. Thermal analyses (DTA and TG) of the samples in air show two exothermic DTA peaks accompanied with weight loss. Room temperature Mössbauer spectra of both the nanocrystalline lithium ferrite samples show sextet patterns.

Chapter-5 deals with the discussion of the results of the $Co_{1-x}Zn_xFe_2O_4$ samples. X-ray diffraction analyses of $Co_{1-x}Zn_xFe_2O_4$ samples show that single phase ferrites are formed for all values of x. XRD patterns of all the samples show that with increase in sintering temperature line broadening of the XRD peaks decreases and crystallite size of the samples increases. TEM pictures show that particle size of the samples sintered upto 873K range between 3 nm to 13 nm but samples sintered above 873K show a sudden increase in particle size. FTIR shows that the spinel ferrites retain water in the grain boundaries and is not removed completely by sintering upto 873K. Thermal analysis of the samples show that the endothermic peak in DTA below 423K is due to loss of adsorbed water and the first exothermic peak accompanied with large weight loss in TG is due to decomposition of metal hydroxide and formation of the spinel ferrite. The second exothermic hump in DTA accompanied with small weight loss in TG indicates removal of grain boundary water and crystallization of the sample. The sudden change in particle size above 873K is due to removal of grain boundary water. SEM micrographs of all the samples show very uniform distribution of the particles on the surface of the sample and with increase in the sintering temperature crystallinity of the samples improve with no change of morphology. Magnetization at 1 Tesla of $Co_{0.8}Zn_{0.2}Fe_2O_4$ and $Co_{0.6}Zn_{0.4}Fe_2O_4$ samples increase with increasing particle size but for $Co_{0.4}Zn_{0.6}Fe_2O_4$ and $Co_{0.2}Zn_{0.8}Fe_2O_4$ samples sintered above 873K, magnetization shows some anomalous changes which is attributed to the changed cation distribution in these samples. The results of FC and ZFC magnetization measurements of $Co_{0.2}Zn_{0.8}Fe_2O_4$ samples indicate that samples sintered upto 873K are superparamagnetic with a blocking temperature and samples sintered above this temperature are also superparamagnetic but has an additional cluster glass phase. The samples with smaller amounts of Zn in the ferrite, however, do not show the cluster glass phase. Low temperature hysterisis measurements of all the samples show the presence of hysterisis loop below the blocking temperature.

Magnetization measurements of all the samples show that magnetization saturation cannot be obtained even upto a field of 9 Tesla. These results indicate that all the ferrite samples are superparamagnetic. Room temperature and low temperature Mössbauer studies also confirm that all the Cobalt Zinc ferrite samples sintered upto 873K are superparamagnetic and higher temperature sintered samples have superparamagnetic and cluster glass phase, due to change in the cation distribution.

Chapter-6 deals with the discussion of the results of nanocrystalline $Li_{0.5}Fe_{2.5}O_4$ samples. X-ray diffraction analysis of the samples show the formation of single phase cubic spinel ferrites. Absence of extra peaks in XRD patterns, expected for 1:3 ordering, indicate the samples are in the disordered phase. No extra lines in FTIR also confirm the formation of disordered nanocrystalline lithium ferrite. Cation distribution of lithium ferrite samples shows that the amount of Li^+ on octahedral site is less than the amount required for 1:3 ordering in the spinel ferrite. During the preparation of lithium ferrite samples by citrate precursor method a viscous gel followed by fluffy mass formation occurs which allows random distribution of Li^{+1} between the octahedral and tetrahedral sites during sintering, and hence the absence of ordering. In the thermal analysis of the gel sample the first exothermic peak in DTA accompanied with large weight loss in TG is due to decomposition of metal citrate precursor with simultaneous evolution of CO and CO_2 gas and formation of the fluffy mass. The second exothermic peak accompanied with small weight loss in TG is due to formation and crystallization of the ferrite phase. Room temperature Mössbauer spectra of nanocrystalline lithium ferrite samples also confirm the disordered phase of lithium ferrite.