Synopsis

From a fundamental point of view, the peculiar magnetic properties of the nanoscale ferrite particles have been of particular interest for a long time. A variety of methods have been reported for the synthesis of nanocrystalline ferrites like co-precipitation, co-sputtering, citrate precursor etc. But neither of the methods is so useful for the production of nano-ferrites in mass scale. Still there is an urgent demand for a convenient method for preparing nanocrystalline ferrites.

It was reported earlier that the doping of La^{3+} ions could suppress the long-range ferroelectric order in PZT system. The results were explained in terms of generation of vacancies in some cation sites that appeared to destroy the long-range order and form nanostructured ferroelectrics. A similar approach is taken in the present case to prepare nanocrystalline spinel ferrites. The objective of this thesis was to develop a suitable low cost method for synthesizing nanocrystalline ferrites and to develop novel magnetic properties in the system. Doping of pure spinel ferrites by suitable aliovalent ions was explored in order to synthesize nanocrystalline ferrites. These doping brings vacancies in some cation sites and these destroy the long-range order to form nanostructured ferrite materials. The thesis contains eight chapters. A short review on this subject followed by the experimental methods and results are presented in the chapters.

CHAPTER-l presents the review on spinel ferrite nanoparticles. Modified structures of different types of nanostructured spinel ferrite also have been discussed. Various synthesis procedures have been briefly mentioned. The physical properties of these nanostructured ferrites are also reported. Depending on present state of knowledge on this subject, the objective of this thesis is selected.

CHAPTER-2 describes the method for the preparation of the nanostructured spinel ferrites specimens by the method of doping with suitable elements. Different measurement techniques to characterize the structural, magnetic, dielectric and electrical properties of the specimens are discussed. Weighed amount of the precursor powders (AR grade) were mixed in a mortar and calcined at a temperature around 1073K. The calcined powders were compacted and sintered at high temperature. Target composition can be represented by $D_xM_{1-x}Fe_2O_3$. D is the doping materials such as Nb_2O_5, TiO_2 and M is divalent metal oxides (simple and compound) namely ZnO, NiO, (MnZn)O, (NiMn)O etc. with x is a variable. The crystalline phases precipitated were identified taking X-ray diffractogram of the specimens. The grain size in the specimens was primarily calculated from X-ray pattern by using Scherrer's formula. The microstructures of the samples were investigated with Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). The variation of saturation magnetization and coercive field with the grain size was estimated. The magnetic measurements were carried out varying the temperature to extract the parameters like Curie temperature, Blocking temperature etc. The D.C. electrical behavior of the materials, as a function of temperature, was carried out to know about the power loss factor in the materials. The variation of dielectric permittivity as a function of frequency and temperature was noticed.

CHAPTER-3 explains the effect of niobium ions doping on structure and physical properties of nickel ferrites. Nano-sized particles of $NiFe_2O_4$ are synthesized by the method of doping with Nb^{5+} ions. Particle diameters of $NiFe_2O_4$ are found to decrease with increasing dopant content. Typically, the diameter of $NiFe_2O_4$ decreases from 67 nm to 30 nm as the Nb_2O_5 doping is increased from 10 to 20%. Since the ionic radius of Nb^{5+}(0.07nm) is quite close to that of Ni^{2+}, Nb^{5+} substitutes the Ni^{2+} sites with the creation of vacancy. The presence of Nb^{5+} ions and the resultant vacancies in the specimens are believed to break the coupling of ferrimegnetically active oxygen polyhedra. An increase of coercive field and a decrease of magnetization are observed as the size of $NiFe_2O_4$ is reduced. This behavior is explained introducing core-shell model of magnetic nanoparticles. Mossbauer spectra show the existence of superparamagnetic doublet. The splitting may arise due to the presence of smaller sized ferrite particles in the specimens. The DC resistivity of the doped specimen with $x = 0.1$ decreases by at least five orders of magnitude compared to the pure sample. This is ascribed to the presence of an interfacial amorphous phase formed by the nanoparticles of ferrites.

CHAPTER-4 describes the preparation of nanocrystalline $MnFe_20_4$ by doping withTi^{4+} ions using the same synthesis route. The particle sizes range from few micrometers to 30 nm as estimated from TEM. The substitution of Ti^{4+} ions creates vacancy at Mn^{2+} sites and the coupling of ferrimagnetically active oxygen polyhedra is broken. Thus nanoscale regions of the ferrites are created. The reduction of magnetization for decreasing particle size and nonattainment of the saturation magnetization supports the presence of core ($MnFe_2O_4$ grains) - shell (Ti^{4+} doped $MnFe_2O_4$ phase) model of magnetic nanoparticles where the spin glass like shell is generated due to breaking of bonds creating randomness in the exchange interaction.

The DC resistivities of the doped specimens indicate the presence of an interfacial amorphous phase formed by the nanoparticles. Zero field cooled and field cooled curves from 30 nm sized particles show a peak at T_B (~125 K), typical of superparamagnetic blocking temperature. The semiconducting behavior in those samples probably arises due to small polaron hopping between Fe^{2+} and Fe^{3+} sites.

CHAPTER-5 shows the effect of Ti^{4+} ions doping on microstructure and DC resistivity of nickel ferrites. Nanostructured nickel ferrites were prepared by doping with Ti^{4+} ions. Lowest grain size of 55 nm was achieved in the specimens with 20 mole % TiO_2 doping and sintered at 1050^0C. Average size of the crystallites increases slightly with increasing sintering temperature. Magnetization in the specimens decreases with decreasing grain sizes. Lower volume fractions of ferrite phase, due to dissociation of the magnetic phase into smaller particles by the disruption of super exchange interaction by the titanium substitution, results a decrease in magnetizations. Coercivity shows an increasing trend. This is explained as arising due to multidomain/monodomain magnetic behavior of magnetic nanoparticles. Doped specimens are found to have lower resistivity. This is ascribed to the presence of an interfacial amorphous phase between the sites. Specimens containing 20 mole % of TiO_2 and sintered at 1300^0C contain $NiTiO_3$ as a secondary phase and show unusual dc conductivity. The DC conductivity of the specimens is analyzed by using Mott's small polaron hoping model.

CHAPTER-6 presents the dielectric anomaly in nanocrystalline nickel zinc ferrite prepared by doping with Ti^{4+} ions for different sintering temperature. Nanocrystalline $Ni_{0.5}$ $Zn_{0.5}$ Fe_2O_4 of dimension 40-50 nm have been produced by a ceramic processing route with a doping of TiO_2. The latter substitutes the Ni^{2+} and Zn^{2+} ions in the ferrite structure. The composite shows the usual ferromagnetic behavior with the coercivity decreasing as the ferrite phase size is reduced. The high electrical conductivity exhibited by these materials is ascribed to a small polaron hopping mechanism between Fe^{2+} and Fe^{3+} sites. A peak in dielectric permittivity of the doped specimens is indicative of a ferroelectric transition. Such materials exhibiting both ferromagnetic and ferroelectric transitions will have wide applications.

CHAPTER-7 describes the dielectric behavior of cobalt ferrites doping with Ti^{4+} ions of different concentrations. Nanocrystalline cobalt ferrites ($CoFe_2O_4$) of particle sizes in the range of 55-35 nm are prepared using doping technique where TiO_2 is used as dopant. $CoFe_2O_4$ particles are found to evolve with increasing Ti^{4+} concentration in the specimens.

The composites show very unusual dielectric behavior. Dielectric constants versus temperature plot measured at 10 kHz show a peak at 430 K. But the undoped specimen does not show such dielectric behavior. This is believed to arise due to the presence of a phase in between the ferrites phases. The former has lattice symmetry lower than cubic which probably causes the presence of dipole moment in the unit cell.

CHAPTER-8 presents the conclusion of the thesis. A series of spinel ferrites like $NiFe_2O_4$, $MnFe_2O_4$, and $(NiZn)Fe_2O_4$ are developed by doping with Nb^{5+}/Ti^{3+} ions using conventional ceramic processing route. Nanostructured ferrite particles are found to evolve with increasing the concentration of dopant ions. Since the ionic radius of the dopant is quite close to that of Ni^{2+}or Mn^{2+} or Zn^{2+} ions, it substitutes the ions with the creation of vacancy. The presence of dopant ions and the resultant vacancies are believed to break the coupling of ferrimagnetically active oxygen polyhedra. Saturation magnetization and coercive field show a strong dependence on the size of the ferrite grains. The Mössbauer spectrum of nanostructured $NiFe_2O_4$ with 30 nm particle size shows superparamagnetic doublet that confirms the presence of smaller sized particles in the specimens. Zero field cooled and field cooled curves from 30 nm sized $MnFe_2O_4$ particles showed a peak at T_B (~125 K), typical of superparamagnetic blocking temperature. These results are explained in terms of core/shell structure of the materials. The DC resistivity of the doped specimens decreases by at least five orders of magnitude compared to pure sample. This is ascribed to the presence of an interfacial amorphous phase between the sites. Nanostructured Nickel ferrites specimens containing 20 mole % of TiO_2 sintered at 1300^0C contain $NiTiO_3$ as a secondary phase and show unusual dc conductivity. Few composites show very uncommon dielectric behavior. Dielectric constants versus temperature plot shows that there is a transition of the phase at a particular temperature. Such materials exhibiting both ferromagnetic and ferroelectric transitions will have wide applications.