Preface

In recent years various fields of science has witnessed the growth and development in the field of nanotechnology. The magnetic nanoparticles show interesting properties when compared to bulk particles. The progress of technology and quality of life of mankind has always been closely knit with the progress in material science and material processing technology. Most of the material processing techniques are based on the breaking up large chunk of a material into desired shapes and sizes, inducing strain, lattice defects and other deformations in the processed material. Recent developments in nanotechnology and the demonstration of various quantum sizes effects in nanoscaleparticles, implies that most of the novel devices of the future will be based on properties of nanomaterials. Each nanoparticle contains only about $3\text{-}10^7$ atoms/molecules. Lattice defects and other imperfections induced by the traditional material processing techniques will no longer be diluted by sheer number of atoms, when used for synthesizing nanoparticles. Furthermore, it is difficult to achieve size selective synthesis of such small particles, by using the traditional approach. In magnetic nanoparticles some of the new phenomena like, superparamagnetism and spin counting can be realized, whereas the same does not exist in bulk magnetic particles. Some physical properties like saturation magnetization of the magnetic nanoparticles is found to have less value when compared to bulk magnetic particles. The coercivity also varies with particle size.

Ferrites are an important class of magnetic materials. The term ferrites denotes a group of iron oxides, which have general formula $MO.Fe_2O_3$, where M is a divalent metal ions such as Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, and Cd^{2+}.

The typical ferrite is magnetite Fe_2O_4 (Or Fe_2O_3) that has been a well-known magnetic oxide since advance times. Nano size ferrite particles have interesting properties as compared to bulk particles in material processing and technological applications. These particles have improved magnetic, dielectric, catalytic properties, as they possess high resistivity and negligible eddy current losses. The preparation technique also plays important role in surface properties and Curie temperature (T_c) can also be varied by substitution of non-magnetic cations. Nano- magnetic particles exhibit some interesting properties such as high frequency devices, magnetic fluids, high density recording, colour imaging etc. In this thesis we reported the synthesis, structural and magnetic properties of Ni-Zn and Cu-Zn Ferrite Nanoparticles.

Till now there has been an extensive investigation on the nanoferrites in the literature. Nanoferrites such as Ni, Mn, Cu, Co, Mg, Zn ferrites have been prepared by different synthesis techniques and their structural and magnetic properties were extensively investigated and the corresponding results are very well presented. But, to our knowledge very few ferrite nanoparticle have been synthesized by sol-gel method. Also the doping of non-magnetic into magnetic materials and its underlying properties has not been reported clearly. Therefore to clearly understand the role of non-magnetic element such as zinc into the magnetic element nickel ferrite and its effect on the structural and magnetic properties have motivated to take up the present work. Also the annealing conditions showed the remarkable effect on the structural and magnetic of nonmagnetic zinc ferrite Nanoparticles.

This investigations involve the synthesis, structural and magnetic characterization of $Ni_{1-x}Zn_xFe_2O_4$ and $Cu_{1-x}Zn_xFe_2O_4$ samples with x = 0.0, 0.2, 0.4, 0.6 and 0.8. A detailed crystal structure and ferrite phase formation analysis is carried out using X-ray diffraction (XRD) data. Further the phase formation has been confirmed using the Infrared analysis.

The effect of Zn doping on to the structural and magnetic properties on Ni and Cu ferrite are carefully studied. Furthermore, the results of magnetic studies clearly indicated the change in the magnetic ordering with the increase in the non-magnetic zinc substitution in magnetic nickel ferrite nanoparticles.

In general ceramic method is used for the preparation of spinel ferrites, which involve high temperature sintering. Ceramic method has some drawbacks like low surface area, loss of metal oxides, addition of impurities during grinding process etc. In order to overcome such draw backs, numbers of wet chemical methods are developed to prepare spinel ferrites at relatively low temperatures. Number of techniques such as microwave refluxing, hydrothermal, glass crystallization, salt melt, sol-gel, etc. is employed in obtaining mono phase spinel ferrites.

The sol-gel auto-ignition method is used to speed up the synthesis of complex materials. It is a simpler process, a significant in saving time and energy consumption over the traditional methods, characterizes this method and small crystalline size of the resultants, later of which may have an important influence on the particles of the materials prepared. This method is employed to obtain improved powder characteristics, more homogeneity and has a narrow particle size, there by influencing structural, electrical, and magnetic properties of spinel ferrites.

(a) X-ray Diffraction (XRD):

To study crystalline nature and to find the desired phase of the samples, all the samples are characterized using XRD (X-ray Diffraction method). In our work, INEL X-ray diffractometer with Co-kα radiation has been used (2θ range 30^0 to 80^0). These studies revealed that prepared samples are mono phase from the phase identification and crystal parameter determination.

X-ray diffraction can also be used for the determination of crystallite size from the analysis of peak broadening. As the particle size is decreased, effectively the number of diffraction centers is reduced and the peak is broadened. The crystalline size of the samples is measured from the line broadening using Scherer formula.

$$D=0.9\lambda / \beta \cos\theta$$

Where D is the average crystalline size, λ is the X-ray wavelength used, β the angular line width of half maximum intensity and θ the Bragg angle in degrees. By employing the above equation and by using the profile of high intensity peak (311) the particle size has been found and the particle size ranges from 50 nm to 6 nm for all the samples.

(b) Scanning and Transmission Electron microscopy (SEM /TEM):

While XRD gives the crystal structure and the average crystalline size, transmission electron microscopy (TEM) shows the particle morphology and its size distribution. The TEM instrument used is Philips CM-12 Transmission Electron Microscope. It has been found that all the samples shows nanocrystalline nature ranging from 40 nanometers to 6 nanometers. Thus the nano particle nature will have strong influence in magnetic and electrical properties. The particle size found by XRD employing Scherrer equation has a good agreement with the TEM micrographs.

(c) Fourier Transform Infrared spectrometer (FTIR):

IR spectroscopic analysis is carried to find the chemical and structural changes taking place in combustion reaction. The IR spectrum shows the characteristic bands corresponding to O–H group, Carboxyl group and NO_3^- ion respectively. The IR spectra of the calcined powders show the absorption bands near 600cm^{-1}, which is a characteristic feature of spinel ferrite.

(d) Thermo gravimetric and differential thermal analysis (TG-DTA):

The decomposition process has been studied by TG – DTA for precursor powders in the temperature range of 25 to 800^{0}C in static air at 10^0 C/min. The Tg-Dta experimental observations showed that the citric acid and metal nitrates exhibited self – propagating combustion behavior. Using TG-DTA data the formation of the spinel phase takes place at 500^{0}C

(a) Vibrating Sample magnetometer (VSM):

In order to look for the response of an applied magnetic field, using vibrating sample magnetometer experiment was performed using (Lakeshore vibrating sample magnetometer VSM 7410.) at an applied field of 10kOe, with both positive and negative fields. The parameters like saturation magnetization (Ms), remanance or remanent magnetization (Mr), Coercivity (Hc) has been found by this system. The above parameters vary depending on the sample preparation technique and mostly on the particle size.

Detailed results and discussions are made in chapters 4, 5 and 6. The results are interpreted on the basis of earlier theories and reports. The relative applicability of the theories, references are brought into focus at various stages of the work.

The references are indicated serially at appropriate places and also at the end of each chapter. At the end of the dissertation the overall conclusions are presented systematically.