CHAPTER 6

SUMMARY AND CONCLUSIONS

This chapter consists of the summary of work done and the conclusive remarks made on the observations. The main objective of this work is to synthesis of some ferrite nanomaterials by sol-gel combustion method and their characterization.

Recently nanotechnology has become one of the most important and exciting forefront fields in science and technology. Development of the ample range of applications of nanoferrites in the emerging fields of science and technology such as magnetic recording media, sensors, activators etc., has induced the author’s interest and led to the present research work in the field of nanomagnetic materials.

In the recent research activities in search of nanomaterials, temperature and compositions have played a vital role. Considering the importance of nanocrystalline ferrites, the present research work aims at the synthesis and characterization of three different ferrites, namely, \( \text{Ni}_1-x\text{Mn}_x\text{Fe}_2\text{O}_4 \) (\( x = 0.25, 0.5 \text{ and } 0.75 \)), \( \text{Co}_1-x\text{Mn}_x\text{Fe}_2\text{O}_4 \) (\( x = 0.25, 0.5 \text{ and } 0.75 \)) and \( \text{Ni}_1-x\text{Co}_x\text{Fe}_2\text{O}_4 \) (\( x = 0.6, 0.8 \text{ and } 0.9 \)) prepared at various calcination temperatures (300°C, 500°C, 700°C and 900°C). The studies carried out in the present work are:

- Structural, morphological, thermal and magnetic properties of the \( \text{Ni}_1-x\text{Mn}_x\text{Fe}_2\text{O}_4 \) nanoparticles have been synthesized by
sol-gel combustion method and the results have been analysed as a function of temperature and concentration of manganese (Mn) (discussed in Chapter 3).

- Structural, morphological, thermal and magnetic properties of the Co\textsubscript{1-x}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} nanoparticles have been synthesized by sol-gel combustion method and have been analyzed the results as a function of temperature and concentration of manganese (Mn) (discussed in Chapter 4).

- Structural, morphological, thermal and magnetic properties of the Ni\textsubscript{1-x}Co\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} nanoparticles have been synthesized by sol-gel combustion method and analyze the results as a function of temperature and Cobalt content (Co) (discussed in Chapter 5).

The Ni\textsubscript{1-x}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} nanoparticles have been prepared using sol-gel combustion technique for different contents of Mn, viz., x=0.25, x=0.5 and x=0.75. An ample range of nanosize particles have been obtained and polyvinyl alcohol has been used as a capping agent. The size of the particles and morphology of the ferrites have been studied through XRD, TEM and AFM studies. The observed peaks in FTIR spectra confirm the presence of functional groups, while ionic distribution and the phase identification have been carried out using the Mössbauer spectra.

The percentage of weight loss and gain has been obtained at different temperatures from the thermal properties of Ni\textsubscript{1-x}Mn\textsubscript{x}Fe\textsubscript{2}O\textsubscript{4} nanoparticles. From TGA-DTA studies, it is found that ferritization temperature decreases with increasing Mn concentration ($T_{Fe}$ for Mn ($x = 0.25$) = 973.29°C, $T_{Fe}$ for Mn ($x = 0.5$) = 927.81°C and $T_{Fe}$ for Mn ($x = 0.75$) = 898.45°C). The magnetic coercivity increases with calcination temperature initially due to thermally activated surface and interfacial defects.
and then decreases for further increase in calcination temperature which can be attributed to the growth of magnetic domains with the increase of grain size. Further, Mössbauer studies reveal that the observed results indicate that the quadrupole splittings of the system is very small. Therefore, there is no distribution of A and B sites. The first order quadrupole splitting are averaged to zero, which is one of the characteristics of the spinel ferrites. The values of quadrupole splitting for all samples have been found to be negligibly small indicating the presence of cubic point symmetry at both sites. The present study reveals that sol-gel combustion technique was found to be one of the simplest effective chemical routes for preparing wide range of nanoparticles for diverse applications.

Synthesis of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanocrystals have been carried out and the crystallite sizes are found to be in the range 20-95 nm. The sizes of the nanoparticles are measured both by XRD and TEM and were in very good agreement with each other and that the size distribution of the prepared samples has been found to be uniform. Further, the morphology of $\text{Co}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ nanoparticles was studied using Atomic Force Microscope (AFM). The size of the nanoparticles has appeared to increase linearly with calcination temperature and time which is due to the coalescence that increases with increasing temperature of calcination. It is evident that the particle size and its distribution may be controlled both by controlling the rate of reaction and the calcination temperature. The results reveal the decreasing of particle size with the increase of weight percentage of Mn.

The magnetic properties of the nanoferrites have also been strongly influenced by calcination temperature. The magnetic coercivity increases with calcination temperature initially due to thermally activated surface and interfacial defects and then decreases for further increase in calcination temperature which can be attributed to the growth of magnetic domains with
grain size. The saturation magnetization shows a decreasing trend in general but for high calcination temperature (500°C and 900°C), for Mn concentration x =0.5 the saturation magnetization has decreased and this may attributed to the presence of divalent cations (Mn$^{2+}$) in the B-sublattice; for further increase in Mn concentration, x = 0.75, the saturation magnetization has increased at high calcinations temperature (500°C and 900°C). The observed values of quadrupole splitting (QS) of this system are almost zero. Therefore, there is no distortion of A and B sites for each of the Mn–substituted samples. The Isomer Shift (IS) values of A and B are almost constant. These facts show that despite the substitutions of Mn cations, there are no changes in covalency between metal ions and oxygen anions. Since the values of IS are included in 3+ valence state of Fe cation, it is concluded that Fe$^{3+}$ cation exists only in Co$_{1-x}$Mn$_x$Fe$_2$O$_4$ system.

The Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ (x =0.6, 0.8 and 0.9) nanoparticles have been synthesized with various sizes (ranging from 15 nm to 65 nm) depending on the calcination treatments and composition (Cobalt content) using sol-gel combustion method. The size of nanoparticles is controlled by calcinations temperature, and hence the magnetic property of ferrite has also been controlled. Morphology and particle sizes of the Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ have been analysed by using AFM and TEM studies. The presence of functional groups has been identified by Fourier Transform Infrared spectra (FTIR). From TGA-DTA studies, the weight gains in the Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ nanoparticles have been observed and it might be due to accumulation of oxygen resulting from the oxidation reaction with capping organic molecules at temperatures above 200°C.

Magnetic properties of the Ni$_{1-x}$Co$_x$Fe$_2$O$_4$ particles have been analysed and it is found that the saturation magnetization (Ms) has increased with particle size and coercivity (Hc) increased initially with the increase of
size and then decreases. On the other hand, the Ms and Hc values have also been found to decrease with increase of cobalt content in Ni$_{1-x}$Co$_x$Fe$_2$O$_4$. It might be due to migration of Co$^{2+}$ ions from A to B- lattice. From the Mossbauer studies, the isomer shift ($\delta$) values of A-sites is less than that of B-sites. The values of quadrupole splitting ($\Delta E$) indicate the degree of deviation from cubic symmetric structure (i.e anisotrophy developed). The absolute values of $\Delta E$ has increased with decreasing particle sizes, and the asymmetrical electric fields surrounding the Mössbauer nucleus has strengthened along with the decreasing of particle sizes. It is due to incomplete crystallization at small particles (from 15 nm to 65nm). Nevertheless, the value of B is larger than that of A. This is attributed to the increase in magnetic domain volume with increase in the crystallite sizes. The fraction of Fe ions at the tetrahedral A and octahedral B sites have been determined using the area of Mössbauer spectra. For stoichiometric ferrite it is easy to estimate the cation distribution from the area of absorption peaks, but it is a formidable task for mixed ferrites used in the present work, since they contain mixtures of more than one cation other than iron.

6.1 SUGGESTIONS FOR FUTURE WORK

Improvement of the synthesis and chemical substitutions of other materials such as transition metal, rare earth materials in ferrite based nanomaterials will help to enhance the magnetic properties of these materials along with particle size and hence to make advancement in the applications of nanoferites. In order to have a proper understanding of the control of particle size of the nanomaterials, in terms of the pH of the solutions used and the temperature conditions during preparation of sample, more such studies have to be carried out and the procedure needs to be standardized.