CHAPTER 6

CONCLUSIONS AND FUTURE PERSPECTIVES

This chapter deals with important conclusions drawn from the observed results carried out under the thesis. On the basis of presented work, some suggestions are also reported for further research on the related research work.

6.1 Conclusions

Main objectives of the research work were considered to carry out various investigations under the thesis and experimentally prepared and synthesized results have been successfully analysed for structural and magnetic properties of pure $CoFe_2O_4$: SiO_2 nanocomposites along with rare earth Gd^{3+} and Nd^{3+} ions doped $CoFe_2O_4$: SiO_2 nanocomposites prepared by wet chemical route, coprecipitation and sol-gel method (from chapter 3 to chapter 6).

The third chapter deals with the preparation of silica embedded cobalt ferrites by coprecipitation method. The post heat treatment at different temperatures was also carried out to analyse the effect of heat treatment on the $CoFe_2O_4$: SiO_2 nanocomposites. The as prepared sample of $CoFe_2O_4$: SiO_2 was further heat treated at 250^{o}C, 500^{o}C, 750^{o}C and 1000^{o}C.

XRD results exposed that crystallization of silica dispersed cobalt ferrite is achieved at comparatively high temperature of 750 ^{o}C . Desirable samples of silica embedded cobalt-ferrite nanocomposites were confirmed on the basis of their characterization results. With the help of XRD data, the lattice constant has been found to increase from 8.032 Å to 8.069 Å by increasing the calcinations temperature from 250°C to 750°C respectively. Presence of silica was confirmed by a broad hump appeared at 2θ positioned around 21-25^o in all the XRD pictures. Particle sizes for the synthesized samples were examined by Debye- Scherrer equation and also by Williamson- Hall method that includes the effects of stress/strain. The particle size is reported by W-H method 20.26 nm, 28.75 nm and 38.76 nm at temperatures 250 ^{o}C,500 ^{o}C and 750 ^{o}C respectively, supported by TEM results. TEM investigation conclude aggregation of particles leading to an increase in particle size. Nearly about 75% of crystallites are having the size range 30-42 nm at 750 ^{o}C from TEM investigations, indicates a

wide grain size distribution of crystallites. Also spherical behaviour of nanoparticles was seen from TEM analysis of samples at 750^{o}C and 1000^{o}C. Results of our research concluded that there is an increase in particle size, crystallinity, surface morphology and microstructure of nanocomposites with increasing calcinations temperature.

FTIR spectra has provided significant knowledge about the structural transformation, composition of phase and bonding among the ions in the samples. At high temperature, elimination of water molecule and Si-OH volatiles from the sample leads to densification of $CoFe_2O_4$:SiO_2 system. The spectra of as prepared sample of $CoFe_2O_4$: SiO_2 nanocomposite confirms the presence of water (H-O-H) and surface silanol group (Si-OH) bands at 3398.5 cm^{-1} and 3404cm^{-1}. The IR spectrum changes significantly at 750 ^{o}C comparatively to samples thermally treated at much lower temperatures. The poor development of ferrite structure in as-prepared sample is in agreement with XRD results. At high temperature, elimination of water molecule and Si-OH volatiles from the sample leads to densification of $CoFe_2O_4$:SiO_2 justifying the formation of nanocomposites which is confirmed by XRD.

SEM study analyzed about the morphology of nanocomposites for their microstructure. The SEM image shows agglomeration of nanoparticles at 250 ^{o}C, Whereas better sphericity of nanocomposites was noticed at high temperature of 750^{o}C.

Effect of heat treatment on precursor's decomposition and development to a stable structure was concluded from TGA analysis. A weight loss of 24% was observed throughout the process. At high temperature negligible weight loss indicates about formation of stable structure. From DTG curve, appearance of strong peak at temperature 217°C indicates the decomposition of water molecules in the form of moisture and also of residual nitrates.

Further, the value of saturation magnetization (M_s) is reported 53.6±0.1 emu/g and 63.7±0.1 emu/g corresponding to the calcinations temperature 250°C and 1000°C respectively. On the basis of VSM results at room temperature, it can be concluded that magnetic properties such as retentivity, saturation magnetization and coercivity revealed a strong dependence on the crystallite size and heating temperature.

Furthermore, non-uniform behaviour of residual magnetization may be related to surface canting or spin's non-colinearity in our synthesized nanocomposites.

In chapter 4, the sol-gel route was employed to synthesize $CoFe_{2-x}$ Gd_xO_4:SiO_2 nanocomposites ($0<x<0.1$) successfully. $CoFe_{2-x}$ Gd_xO_4:SiO_2 nanocomposites were prepared for Gd^{3+} content x= 0.00, 0.025, 0.050,.0.075 and 0.1 respectively. Change in parameters of prepared samples was also observed with different temperatures to analyze thermal heating effects. An increment in lattice parameter was observed from 8.375 Å to 8.489 Å with raising Gd^{3+} ion content from 0.00 to 0.1 and reported positive slop for the plot of lattice parameter and Gd^{3+} ion concentration. While particle size has been noticed to reduce from 48.18nm (x= 0.00) to 30.36nm (x=0.1) and indicated negative slop for the variation of particle size with Gd^{3+} ion concentration. However, particle size is found to increase with increasing temperature by keeping Gd^{3+} ion concentration at a constant value.

Presence of band reflection at 457.94 cm^{-1} is assigned to Si–O–Si or O–Si–O vibrations from FTIR spectra. The absorption bands for Gd^{3+} doped in $CoFe_{2-x}Gd_xO_4$:SiO_2 nanocomposites have been found to present in an array of 559 cm^{-1} to 580 cm^{-1}. The strong absorption at 678.59cm^{-1} is associated with Co-O stretching reflections of $CoFe_2O_4$ .The appearance of bands at 860.09 cm^{-1} and 586.57 cm^{-1} contribute to Si–O–Fe.

In the present study, it is revealed from TEM results that with raising doping concentration, a narrow size distribution is seen and also crystallite size decreases because of higher ionic radius of Gd^{3+} ions as compared to Fe^{3+} ions. Size of nanocrystallites decreased from 42 nm to 30 nm with increasing $Gd3^{+}$ ion concentration from x=0.00 to x= 0.1 at 1000 ^oC and 32 nm to 28 nm for a variation in concentration from x= 0.075 to 0.1 at 750 ^{o} C. Gadolinium tends to restrict grain growth and accumulates on boundaries of crystal. Silica also plays an important role in the development of sphericity of particles as it has shielded the embedded particles from external agents. Also cobalt ferrites being magnetic in nature, attracts each other and consequently produced smaller size of crystallites. Histogram of $CoFe_{2-x}$ Gd_xO_4:SiO_2 nanocomposites reveal the size range in which maximum particles reside.

Nanocomposites with concentration of Gd^{3+} ions , x= 0.050 and 0.1 were examined for thermal effects.TGA characterization results has indicated stability in structures

approximately above 750^{o}C for Gd^{3+} ions concentration, x=0.1 and above 800 ^{o}C for x= 0.050 in $CoFe_{2-x}$ Gd_xO_4:SiO_2 nanocomposites. Maximum weight loss as a consequence of moisture evaporation was noticed in temperature range of 201-350 ^{o}C for both the samples. TGA analysis concludes that no weight loss was observed when the sample was further heated beyond 750^{o}C. This confirmed about full decomposition of precursors and formation of the stable structures of the $CoFe_{1.95}Gd_{0.050}O_4$:SiO_2 and $CoFe_{1.9}$ $Gd_{0.1}O_4$:SiO_2 nanocomposites. Maximum weight loss as a consequence of moisture evaporation was noticed in temperature range of 201-350 ^{o}C for both the samples. In DTG curve, strong peaks at the temperature 214°C and 217° corresponds to decomposition of the water molecules in the form of moisture and also of residual nitrates..

Magnetic analysis was carried out via VSM technique. Saturation magnetization ,Ms follows a decreasing trend with increasing doping concentration of Gd^{3+} ions. Ms value decreases from 54.65±0.1emu/gat x=0.00 to 37.24±0.1emu/g at x=0.1.These variations in value of the saturation magnetization for different doping concentrations of Gd^{3+} ion was explained on the basis of core- shell model, that describe about the finite size effects of nanoparticles that merge from the spin tilting effect in ferromagnetism. The value of remnant magnetization, Mr at x= 0.00 is calculated to be 15.8025 emu/g and increased value of 19.75emu/g observed at x= 0.025which further decreased to 12.495emu/g for x= 0.1. This non linear behaviour of Mr may be interpreted due to spin canting. While the variations in Hc values depend on many factors like crystallite size, anisotropy, microstructure and micro-strain.

In the fifth chapter, nanocomposites of $CoFe_{2-x}Nd_xO_4$:SiO_2 were prepared by sol-gel route for different concentrations of Nd^{3+} ions at different annealing temperatures. Prepared samples for each concentration were further heat treated at 250 ^{o}C, 500 ^{o}C, 750 ^{o}C and 1000 ^{o}C. Structural evaluation of nanocomposites was carried out by XRD, FTIR and TEM characterization techniques. XRD patterns indicate improvement in crystallinity of $CoFe_{2-x}Nd_xO_4$:SiO nanocomposites samples with the increase in concentration of Nd^{3+} ions. Findings of this research revealed that with increasing Nd^{3+} concentration, particle size was found to increase that may be concluded because of replacement of smaller size(0.67Å) Fe^{3+} by larger size Nd^{3+} ions(0.995Å). The particle size determined by W-H method are reported 28nm,37nm,42nm and 48nm by taking Nd^{3+} concentration 0.00, 0.050,0.075 and

0.1 respectively.TEM results are also reported in good agreement for particle size 26nm,35nm,39nm and 47nm at Nd^{3+} ions concentration 0.00,0.050,0.075 and 0.1 respectively. Effect of strain on particle size has also been investigated to have values 0.00242 and 0.00257 with Nd^{3+} concentration 0.00 and 0.025 respectively. By increasing doping concentration of Nd^{3+} ion from 0.025 to 0.1 in our samples, lattice parameter has increased from 8.367 Å to 8.381 Å indicated a change in properties.

From FTIR spectra, broad hump in as prepared samples of $CoFe_{2-x}Nd_xO_4$:SiO_2 nanocomposites corresponds to deformation of water molecules. Presence of silica network is evident from the spectra of all the synthesized samples. Bonding between metal ions is also observed. On the analysis of TGA- DTG curve, a maximum weight loss in all the samples has been recorded in the temperature range of 201^{o}C-350^{o}C due to maximum evaporation of water and decomposition of precursors. The maximum weight loss is also supported by the sharp peaks centred at 232^{o}C (x=0.00), 228 ^{o}C (x= 0.075) and 228 ^{o}C (x= 0.1) temperature positions in DTG curves for Nd^{3+} ions concentration effect. Afterwards a small weight loss has indicated the formation of stable structures in our samples. Moreover, DTG and TGA curves also support one another. The peak positions present in DTG curve indicate the weight loss in that region.

Formation of spherical shape of nanoparticles has been noticed from TEM results. In TEM results, particle size is increased with increasing doping concentration thus supported by XRD results. This may be believed due to the replacement of small size iron ions with bigger size Nd^{3+} ions. As the doping concentration is raised, more of Nd^{3+} ions occupy position of Fe^{3+} ions and has contributed to increase size of nano crystallites. Findings of TEM results show aggregation of nanocomposites for all the samples at different concentrations that may be concluded due to attraction of particles towards each other by their magnetic behaviour.

6.2 Future Perspectives

On the basis of contributed research some important suggestions have also been presented for further research work in the related field. Findings of the thesis work have indicated for usefulness of the data for further research on these materials that may also be with improved quality under better experimental conditions. Effect of other lanthanides like Eu, Er , Y and actinides as dopants could also be examined.

Further, Raman ,Mossbauer and Photoluminescence like investigations may provide the insight of more important new features about these materials. Furthermore, EDS and UV characterizations could be investigated for a more broad view of our investigations to make use of our experimental data by tailoring made properties of these ferrites in various fields of science, engineering and technology.