Chapter V

Summary and Conclusion
5.1 Summary

The work presented in this thesis involves a detail study of two ferrite systems Co-Zn and Co-Ni ferrite. These magnetic materials have been prepared via two different synthetic techniques, i.e. precursor combustion method and combustion method. Both methods yield the product in nano form and hence are well suited for the preparation of nanomaterials. The ferrites have been studied in their nano form as well as in the bulk state. Various characterization techniques were employed to do a comparative study of the ‘as prepared’ nanoferrite with its bulk counterparts. The influence of the synthesis method on the physico-chemical properties of the material was also demonstrated. A concise report of all the findings of this study is given below.

The ‘as prepared’ nano and the sintered bulk samples of Co$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0-1.0) in steps of 0.1 were characterized by spectroscopic and solid state techniques inorder to get a better understanding of the properties and its behavior. Interesting facts have been observed as the material dimensions are reduced to nanoscale. Also much knowledge can be derived from the results obtained when a nonmagnetic ion like Zn is added to the magnetic cobalt ferrite. Although both methods yield nanoparticles of the oxide, the combustion method produced 8-12 nm size particles of the ferrite while the particle size of the samples prepared by precursor combustion method was found to be 10-20 nm and more agglomerated in appearance this is the reason for the lower BET surface area values of the samples prepared by this method. From FTIR spectra it was found that as Co$^{2+}$ gets replaced by Zn$^{2+}$, the $v_1$ which is attributed to the intrinsic stretching vibrations of the metal at the tetrahedral site,
shifts to lower wavenumber. Also, the nanoferites showed lower \( v_1 \) and \( v_2 \) values which shifted to higher wavenumber upon sintering.

The XRD data confirms the formation of monophasic oxide without any impurity peaks. The peak broadening is noticeable in case of the ‘as prepared’ samples indicating nanosize nature of the samples. As Zn concentration increases the lattice parameter increases in accordance with the Vegard’s law. The lattice constant of nanoferites was found to be less than that of its bulk counterpart. The X-ray density and other parameters like bond lengths and ionic radii were found to increase with increase in Zn concentration. However the values were slightly lesser for the nanoferites. The particle size of the ‘as prepared’ ferrites calculated from the XRD data matches with that obtained from TEM images.

The magnetic hysteresis measurements carried out on the samples revealed less saturation magnetization values for the nano samples as compared to the bulk. Also, the saturation magnetization was found to increase with the increase in Zn concentration upto \( x=0.3 \) which then decreased with further Zn addition. The coercivity values were also found to be higher in case of the nanoferites and more specifically in the cobalt rich samples. The nature of the magnetic particles was more clearly seen from the a.c. susceptibility studies. The nano samples showed superparamagnetic behavior whereas the bulk samples showed single domain behaviour. The superparamagnetic behavior of the samples was also unmistakably seen in the Mossbauer spectra. The Curie temperature was also determined from the a.c. susceptibility measurements. The \( T_c \) of the nanoferites was found to be less than the corresponding bulk one in case of the samples prepared by precursor combustion method. However the nano samples prepared by combustion method showed higher \( T_c \) than its bulk counterpart. Here, the influence of the synthesis method was quite evident.
The d.c. electrical resistivity was found to increase with increase in Zn^{2+} ions from 0.0-1.0. The 'as prepared' nano samples showed higher resistivity as compared to the bulk. The samples showed mainly n-type semiconductivity which changes to p-type at higher temperatures for some samples which was determined from the Seebeck coefficient measurements.

The influence of synthesis conditions was also prominently felt from the dielectric constant measurements. The dielectric constant was found to be quite high, in the order of $10^5$ for the nano samples as compared to the bulk prepared by the precursor method. The samples by combustion method showed comparatively lesser values wherein, for the nanosamples they were in the order of $10^3$ while for the bulk samples they were much lesser. The dielectric loss tangent was found to decrease with increasing frequency however, a maxima in the plot was seen for all the samples. The frequency at which it appeared was composition dependent.

The initial permeability, $\mu_i$, for the 'sintered' samples was measured at varying frequency as well as at varying temperature. It was observed that $\mu_i$ initially increases slightly at lower frequencies and then decreases and almost remains constant at higher frequencies. The $\mu_i$–T plot was obtained for different compositions and was observed that $\mu_i$ increases gradually at first and then rapidly as it approaches $T_c$. At the Curie point the $\mu_i$ drops sharply, and then remains constant with further increase in temperature. The temperature variation is observed prominently for the mid-compositions only, however for the end compositions the $T_c$ is not discernable. The Curie temperature obtained from this measurements match closely with those obtained by ac susceptibility measurements. The permeability increased upto $x=0.7$ in the series and then decreased.
The Mössbauer studies also showed some differences in the magnetic character of the nanosize 'as prepared' ferrites due to the synthesis method employed. The Mössbauer spectra of the nanoferrites showed the presence of a central doublet and two magnetically split sextets for all values of $x$ (except $x = 1$). The relative area of the central paramagnetic doublet increased whereas the relative area of magnetic sextets decreased with increase in the zinc doping. However it was observed that, the doublet character was more pronounced in case of the 'as prepared' samples by combustion method as compared to the same samples by precursor combustion method. This was due to the superparamagnetic state in dominant part of the particles. Hence the nanosize samples by combustion method are more superparamagnetic than those prepared by precursor combustion method. However there was no much difference in the bulk samples of both. Isomer shift values of all samples indicate that Fe is in the Fe$^{3+}$ ionic state and the Quadrupole splitting ($\Delta$) values for tetrahedral and octahedral sites of the 'as prepared' and sintered ferrites are nearly 0.00 mm/s indicating the overall presence of cubic symmetry at both sites.

The influence of the synthesis method on the properties was felt more while checking the gas sensing potential of the materials so synthesized. The thick films of the 'as prepared' Co-Zn ferrite were tested for different gases like CO$_2$, NH$_3$, LPG, H$_2$, ethanol, H$_2$S and Cl$_2$. The samples showed sensitivity to different test gases at varying operating temperature, but no two samples with same composition showed the same behavior. If the sensitivity to a particular gas was common, then its operating temperature varied. This was observed for the samples with composition $x=0.5$, the sample prepared by both the methods showed sensitivity to H$_2$S, but their operating temperature was quite different. The sample prepared by precursor method showed maximum response at 250°C whereas the one prepared by combustion
method gave maximum response at room temperature. Their response and recovery time was also seen to differ. Similarly, the composition with x=0.8, the sample prepared by precursor method showed sensitivity to NH$_3$ whereas the one prepared by combustion method was sensitive to CO$_2$. Difference was also observed in the performance of the x=0.2 sample, the one prepared by precursor method did not show sensitivity towards any test gases, but the sample prepared by combustion method showed response towards ethanol. The films also showed quick response and fast recovery. Thus, the method of synthesis is a deciding factor for certain applications like gas sensing.

Albeit similar but nonetheless important conclusions can be drawn from the results obtained for the Co$_{1-x}$Ni$_x$Fe$_2$O$_4$ (x=0-1.0) system which were also prepared by precursor combustion method and combustion method. Both methods gave nanoparticles of the ferrite, but the particle size was much smaller in case of combustion synthesis and also gave better compositional homogeneity and purity of the final product. Finer particle size and less agglomeration of the ferrite powder was the reason behind the higher surface area. The lattice parameter, $a$, decreased with increase in nickel concentration, however, the $a$ values for nanoferrites were less than the bulk. From FTIR spectroscopy, it was observed that the $v_1$ increases linearly with increase in nickel concentration. It is found that on sintering, $v_1$ and $v_2$ shifts to higher wavenumber.

Magnetic measurements showed that, the saturation magnetization decreases with increase in nickel concentration. The values obtained for the samples by precursor combustion method were higher as compared to those obtained by combustion method. Other parameters like $M_r$ and $H_c$ were also relatively higher for the samples by precursor combustion method. The nanoferrites showed lesser values as compared to the bulk. The Curie temperature, $T_c$, of
the studied Co-Ni ferrites was found to increase with increase in nickel concentration. The $T_c$ was lower for the nanoferrites as compared to the bulk for samples obtained by both methods. However, the $T_c$ values were found to be slightly higher for the samples prepared by the precursor combustion method.

The d.c. electrical resistivity studies indicate that the resistivity increases with increases in nickel concentration. The nano samples showed lower resistivity as compared to the bulk counterparts. This was observed for both types of samples, though a slight anomalous behavior was observed at higher temperatures in case of the 'as prepared' samples by precursor combustion method. This anomaly was more discernable in case of the 'as prepared' samples by combustion method.

Dielectric measurements on the samples showed that the dielectric constant decreases with increase in nickel concentration. The values decrease with increasing frequency as expected and also increases with increase in temperature, however the increase is prominent only at lower frequencies. The dielectric values obtained for the nanosize samples by precursor combustion method were three times lesser than those prepared by combustion method. The dielectric loss decreases with increasing frequency however it increases at a certain frequency and then decreases. This maxima in the dielectric loss is compositional dependent hence tends to vary.

The initial permeability, $\mu_i$, studies of the sintered samples carried out at room temperature showed that $\mu_i$ initially increases at lower frequency and then decreases as frequency is increased and almost remains constant at higher frequencies. The initial permeability measured with varying temperature shows an increase in values as temperature
is increased, it increases sharply as it approaches Curie temperature and then drops at the Curie point.

The room temperature Mössbauer spectra for all samples show a double sextet pattern. However, the nano ‘as prepared’ samples prepared by combustion method, show a prominent doublet at the center of spectra along with a weak sextet pattern. The doublet is indicative of the superparamagnetic behavior of the small sized particles. Isomer shift values of all samples indicate that Fe is in the Fe$^{3+}$ ionic state and the Quadrupole splitting ($\Delta$) values for tetrahedral and octahedral sites of the ‘as prepared’ and sintered ferrites are nearly 0.00 mm/s indicating the overall presence of cubic symmetry at both sites.

EXAFS studies carried out on the ‘as prepared’ and sintered Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite samples prepared by precursor method and combustion method revealed distortion in the nanoferrites especially the one prepared by precursor method. The bond distances, coordination number and the disorder factor calculated using the theoretical model matches with the expected value except for the nanoferrites. Similar observations were made for the Co-Ni samples viz. Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ ferrite samples prepared by precursor method and combustion method. By comparing the $\sigma^2$ values (Debye–Waller factor) we found that the nanomaterial samples were more disordered than the bulk samples. Also the bulk samples synthesized by the precursor method showed more disorder than the ones prepared by combustion method.

Gas sensing studies carried out on the thick films of some of the selected samples. The samples showed sensitivity towards various test gases but mostly towards H$_2$S and NH$_3$. Some of the samples showed good gas sensing activity even at lower gas concentrations and at room temperature. The gas response towards a particular gas and the operating temperature
was found to differ depending on the method of synthesis, though the sensitivity towards a particular gas was common. Fast response and quick recovery were also some of the features of the sensors.

5.2 Conclusion

A marked effect of size reduction was observed on the structural, magnetic and electric properties of the cobalt-zinc and cobalt-nickel ferrite. A comparison between the ‘as prepared’ nanoferrites and bulk ‘sintered’ ferrites provides rich insights into the fundamentals of nanomagnetism particularly superparamagnetism observed in the nanoferrites. Structurally, apart from the obvious difference in the particle sizes of bulk and nanoferrites, much knowledge could be gained from the XRD lattice parameters and the Mössbauer spectroscopy data. Bond lengths tend to contract at the free surfaces, so the average lattice parameter of nanoparticles is reduced. The room temperature Mössbauer spectra of ‘as prepared’ and sintered ferrite show a transition from the magnetically ordered ferromagnetic state to a paramagnetic state with increasing concentration of zinc in case of Co-Zn ferrites. The spectra of the nanosize ferrites acquire a doublet character indicative of the superparamagnetic state in the dominant part of the particles. In contrast, the sextet is retained in the bulk ferrites though the respective hyperfine fields are largely reduced and broadly distributed for A and B sites. However in case of Co-Ni ferrites superparamagnetic behavior was seen only incase of the ‘as prepared’ ferrite prepared by combustion method. From Mössbauer data it was concluded that the Fe is in the Fe$^{3+}$ state. Size effects were also quite noticeable for d.c. resistivity of the samples and the dielectric measurements, wherein the nanoferrites showed higher resistivity than its bulk counterparts for Co-Zn samples. Incase of Co-Ni samples, the nanoferrites showed lower resistivity as compared to the bulk. The dielectric constant was
found to be quite high for the nanosamples as compared to the bulk, the synthesis method also seemed to play a role. The AC susceptibility studies revealed that the nanoferrites exhibited higher $T_c$ than the bulk Co-Zn ferrites contrary to popular belief that $T_c$ decreases with particle size. Whereas, in the case of Co-Ni ferrites, the nano samples showed Curie temperature suppression. Thus, the results vary depending on the mode of preparation and subsequent heat treatment, a fact acknowledged by most investigators. Thus, addressing the key issues raised by these size dependent studies promises further advancement in understanding the properties of these materials in the nanometer regime.

The study also demonstrated the influence of the synthesis method on the physico-chemical properties of the Co-Zn and Co-Ni ferrite. This is noticed in almost all the properties studied and was also quite evident in the gas sensing performance of the thick films. The films fabricated by using the ‘as prepared’ ferrites showed sensitivity towards various test gases but particularly towards $\text{H}_2\text{S}$ and $\text{NH}_3$. The gas response and the operating temperature varied depending on the synthesis method and the subsequent heat treatment. Undoubtedly, the method of synthesis plays a vital role in governing the properties of a material.

The study of magnetic nanoparticles is a fertile area of research with many unresolved scientific problems as well as many existing and potential technological applications. To those interested, there is room for much more work in this area.