CHAPTER 4

Synthesis and Characterization of Ni-Co ferrite nanoparticles
4.1 INTRODUCTION

Nickel ferrite is a soft magnetic material with low saturation magnetization and low coercivity while cobalt ferrite is well known hard magnetic material with relatively high saturation magnetization and coercivity. Due to their unique properties these ferrite materials have variety of applications in biomedical, electronics as well recording technology [1-9]. The magnetic character of the ferrite nanoparticles depends upon the size, purity, shape and magnetic stability of these nanoparticles. The nanoparticles should be of single domain, of pure phase, suitable coercivity, moderate magnetization. From the application point of view in the field of data recording these nanoparticles must have the superparamagnetic blocking temperature well above the room temperature and for applications in biomedical for target drug delivery the nanoparticles used should be magnetically in superparamagnetic unblocked state with relatively low coercivity and blocking temperature [10]. So it is very important to tailor the magnetic properties of the ferrite nanoparticles according to the requirement which can be done either by varying the size of the nanoparticles or by adjusting the concentration of hard (e.g. cobalt) and soft (e.g. nickel) magnetic phases in these materials. Obviously due the interesting and useful properties of spinel ferrites it is more important to look into their preparation and reporting a number of investigations. The present chapter describes the synthesis of nickel doped cobalt ferrite nanoparticles with various compositions by chemical co-precipitation method and characterization by various analytical techniques to investigate the structural, morphological and magnetic properties.

4.2 EXPERIMENTAL

4.2.1 Synthesis of Ni-Co Ferrite Nanoparticles

Nanocrystalline $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ particles with compositions ($x = 0.5, 0.75, 0.9$) have been synthesized by chemical co-precipitation method. AR grade Sigma Aldrich $\text{NiCl}_2\cdot6\text{H}_2\text{O}$, $\text{CoCl}_2$ and $\text{FeCl}_3$ salts were taken for the synthesis. 1M aqueous solution of the salts were
mixed in their stoichiometric ratio and homogenized at 60° C with constant stirring. In next step, addition of base (ammonia solution) was carried out by maintaining pH 9.5 of solution mixture. The precipitated particles were then washed several times with double distilled water to remove the unwanted salt residues and other impurities. The precipitated particles were dried at 80° C to obtain the powder. The ferrite formation takes place by conversion of metal salts into hydroxides and then the transformation of hydroxides into ferrites. The overall chemical reactions can be summarized as:

\[
xNi^{2+} + (1-x)Co^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow xNi(OH)_{2}.(1-x)Co(OH)_{2}.2Fe(OH)_{3} (4.1)
\]

\[
xNi(OH)_{2}.(1-x)Co(OH)_{2}.2Fe(OH)_{3} \xrightarrow{80^\circ C} Ni_{x}Co_{1-x}Fe_{2}O_{4} + 4 H_{2}O (4.2)
\]

### 4.3 CHARACTERIZATION

The developed materials were analyzed for structural characterization which includes the study of crystallinity, desired phase, determination of structural parameters viz. lattice parameter, volume of unit cell, X-ray density, porosity and particle shape, size determination. The crystal structure and type of phases were identified by means of X-ray powder diffraction at room temperature using Rigaku make powder X-ray diffractometer with Cu K\(_\alpha\) (\(\lambda = 1.54059\) Å) radiations generated at 40kV and 30mA power setting. The data was collected with a scanning speed of 2° per minute and step size of 0.02° over the angular range 2θ (20° < θ < 70°). The Fourier transform infrared spectroscopy measurements on the synthesized samples were carried out on NICOLET 5700 FTIR spectrometer. IR transmission spectra were recorded in the range 4000 cm\(^{-1}\) to 400 cm\(^{-1}\). The samples were taken in KBr pellet form and each spectrum was an average of 32 number of scans. All recorded spectra have been corrected for background features arising from air. The shape and size distribution of the samples were studied by transmission electron microscope model (Jeol CX 200). The magnetic properties viz. saturation magnetization, coercivity and retentivity of samples have been determined from the magnetic moment versus magnetization curve recorded for various samples with the help of a vibrating sample magnetometer (VSM). The EPR measurements were
carried out at room temperature by a Varian E-line Century X-band EPR spectrometer (Model-E-112). The measurements were done at 9.36 GHz at 100 kHz modulation frequency in the 4000 ± 4000 G region at 1.25×10 receiver gain and 1×1 modulation amplitude. The ac susceptibility measurements were carried out on these samples by an ac suseceptometer in the 77-300 K temperature range to determine the blocking temperature of the synthesized samples.

4.4 RESULT AND DISCUSSION

4.4.1 X-ray Diffraction Analysis

The XRD patterns of the synthesized samples are shown in Fig. 4.1. All the patterns exhibit the major peaks related to spinel crystallite structure without any impurity and indicate the ultrafine nature of the particles. The peak intensity and ‘d’ values of the entire observed diffraction peaks perfectly match with single crystalline phase of cubic spinel form of nickel-cobalt ferrite (JCPDS card number 03-864) [11]. The XRD pattern of as synthesized particles shows very broad diffraction peaks indicating ultrafine nature of the samples. The average crystallite size was calculated using Williamson-Hall equation (as shown in Fig. 4.2) [12]. The average crystallite size of the nanoparticles lies in the range 8 to 11 nm. The lattice parameter was calculated correspond to the main (311) peak of the cubic spinel structure. Equation $a = \frac{d\sqrt{h^2 + k^2 + l^2}}$, where ‘d’ is the interplanar distance, ‘h’, ‘k’ and ‘l’ are the miller indices [13]. The lattice parameter decreases from 8.395 Å to 8.331Å with the increase in nickel content. The higher value of lattice parameter in Ni₅₀Co₅₀Fe₂O₄ sample can be attributed to the larger ionic radii of cobalt ions as compared to nickel ions. The decrease in lattice parameter with the increase in Ni²⁺ ion concentration is due to replacement of large ionic radii Co²⁺ cation (0.78Å) by smaller ionic radii Ni²⁺ ion (0.63Å) [14]. The variation of lattice parameter and crystallite size with nickel ion concentration is shown in Fig 4.3. The X-ray density is calculated by the relation [15, 16].

$$\rho_x = \frac{8M}{Na^3}$$ (4.3)
Where N is Avogadro number, M is the molecular weight of the sample, ‘a’ is the lattice parameter and the measured density ($\rho_m$) is calculated by the relation $\rho_m = \frac{m}{\pi r^2 h}$, where m is the mass, r is radius, h is the height of cylindrical pallets of the sample. Porosity (P) is determined using the relation [17].

$$P = 1 - \frac{\rho_m}{\rho_x} \quad (4.4)$$

All the parameters calculated from the XRD pattern are listed in table 4.1. The X-ray density increases with nickel ion concentration which is due to the increase in molecular weight and decrease in lattice parameter for $x = 0.5$ to $x = 0.9$. The measured density shows the decreasing trend with increasing Ni$^{2+}$ ion content. Porosity increases with Ni$^{2+}$ ion concentration which is due to smaller molecular mass of nickel (58.293 g) as compared to cobalt (58.933 g) atoms. The variation of X-ray density with nickel content is shown in Fig. 4.4.

**Figure 4.1**: XRD pattern of as-synthesized Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ samples, (a) $x = 0.5$, (b) $x = 0.75$, (c) $x = 0.9$. 
Fig. 4.2: Williamson-Hall plot of Ni$_{0.5}$Co$_{0.5}$Fe$_2$O$_4$ Sample

Fig. 4.3: Variation of Lattice Parameter and Crystallite Size with Ni$^{2+}$ ion Concentration.

Table 4.1: XRD analysis of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ ($x=0.5, 0.75, 0.9$) samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>X-ray density $\rho_x$ (gm/cc)</th>
<th>Physical Density $\rho_m$ (g/cc)</th>
<th>Porosity P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{0.5}$Co$</em>{0.5}$Fe$_2$O$_4$</td>
<td>8.10</td>
<td>8.3959</td>
<td>5.292</td>
<td>1.56</td>
<td>0.7036</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Co$</em>{0.25}$Fe$_2$O$_4$</td>
<td>9.87</td>
<td>8.3554</td>
<td>5.338</td>
<td>1.52</td>
<td>0.7153</td>
</tr>
<tr>
<td>Ni$<em>{0.9}$Co$</em>{0.1}$Fe$_2$O$_4$</td>
<td>10.13</td>
<td>8.3310</td>
<td>5.354</td>
<td>1.48</td>
<td>0.7374</td>
</tr>
</tbody>
</table>
Fig. 4.4: Variation of X-Ray density with Ni$^{2+}$ ion Concentration.

4.4.2 Fourier transforms infrared spectroscopy (FTIR) studies

Fig. 4.5: FTIR spectra of as synthesized Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ samples, (a) x = 0.5, (b) x = 0.75, (c) x = 0.9.

IR transmittance spectra of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ (x = 0.5, 0.75 and 0.9) samples were recorded in 3500 - 400 cm$^{-1}$ region at ambient temperature. Fig. 4.5 shows the FTIR spectra of all
the compositions. In the wavenumber range of 1000-400 cm\(^{-1}\), main broad metal-oxygen bands are seen in the infrared spectra of all spinels. The higher one (\(v_1\)) generally observed in the range 600–550 cm\(^{-1}\), is caused by the stretching vibrations of the tetrahedral metal–oxygen bond [18]. The lowest band (\(v_2\)) usually observed in the range 450–385 cm\(^{-1}\), is caused by the metal–oxygen vibrations in the octahedral sites. The spectra show prominent bands near 3400cm\(^{-1}\) and 1600cm\(^{-1}\), which are attributed to the stretching modes and H–O–H bending vibrations of the free or absorbed water. The intensity and position of these modes of vibration vary with nickel and cobalt concentration due to change in crystalline filed effect and strain in the lattice. C-H symmetric stretching and antisymmetric stretching of -CH\(_2\)- group are observed as a double band at 2800- 2930 cm\(^{-1}\) in all the three samples.

### 4.4.3 Transmission electron microscopic (TEM) images

The shape, size distribution and morphology of the particles were examined by using transmission electron microscope (TEM). The TEM images of all the samples are shown in Fig. 4.6 (a, b, c). It is observed from the TEM images that the particles are slightly agglomerated. The particles are tending to agglomerate due to their magnetic nature. TEM images shows that, almost all the particles are spherical in shape and the particle size varies in the range 5-20 nm.

![TEM images](image)

**Fig 4.6 (a)** : TEM images of Ni\(_{0.5}\)Co\(_{0.5}\)Fe\(_2\)O\(_4\) sample
Fig 4.6(b): TEM images of Ni$_{0.75}$Co$_{0.25}$Fe$_2$O$_4$ sample

Figure 4.6(c): TEM image of Ni$_{0.9}$Co$_{0.1}$Fe$_2$O$_4$ sample

4.4.4 Electron paramagnetic resonance (EPR) Studies
EPR spectroscopy of ferrite nanoparticles is important for investigating the magnetic properties and spin dynamics of magnetic materials at high frequency (Microwave X-band region). EPR spectra were recorded by inserting a sample into TE$_{102}$ rectangular cavity for microwave irradiation at constant frequency $\nu$ and sweeping the external magnetic field ($H$) until the resonance condition is fulfilled. The line and the shape of the resonant signal give information about the magnetic and electronic state of the paramagnetic centers present in the material. The EPR spectra of as synthesized nickel doped cobalt ferrite nanopowdered samples are shown in Fig. 4.7. All spectra were analyzed by considering Lorentzian distribution of the obtained broad resonance signal to calculate $\Delta H_{pp}$, $g$-value and $N_s$, EPR parameters and their values are listed in Table 4.2. The spectra of these samples show a single broad signal with $g$-value $\sim$ 2.1, indicating the presence of Fe$^{3+}$, Co$^{2+}$, Ni$^{2+}$ ions with dominance of Fe$^{3+}$ ions signal.

![EPR spectra of Ni$_x$Co$_{1-x}$Fe$_2$O$_4$ samples, (a) $x=0.5$, (b) $x=0.75$ and (c) $x=0.9$](image)

The variation in EPR parameters such as peak-to-peak linewidth ($\Delta H_{pp}$), $g$-value, spin concentration of paramagnetic centres present in these ferrites is discussed in terms of the interparticle magnetic dipole–dipole interactions and super-exchange interactions [19-28]. The interparticle superexchange interaction between magnetic ions (through oxygen)
can reduce the value of peak-to-peak linewidth. The magnitude of this interaction is determined by the relative position of metallic and oxygen ions. When the distance between the metallic and oxygen ions is short, the metal cations have half-filled orbital, and the angle between these two bonds is about to 180°, the superexchange interaction is maximum [19]. The g-value increases on increasing Ni^{2+} ions concentration (x = 0.5 to 0.9) in these ferrite samples due to strengthening of superexchange interaction via magnetic ordering within each sublattice of ferrite [20–22] through rearrangement of cation between A site and B site [23, 24]. The surface anisotropy and formation of spin glass state are the additional parameters which are also playing an active role in shifting the magnetic resonance field value (H_R) to lower magnetic field [25]. H_R decreases with increase in the Ni^{2+} content in these ferrite analogues with the increase in intensity. The decrease in line width i.e. narrowing of resonance derivative signal with respect to increase in Ni^{2+} content has been attributed to the occupation of Ni^{2+} ions at the octahedral B site. The presence of Ni^{2+} ions in the octahedral B site causes a decrease in the magnetic moment of B sublattice. This causes an overall decrease in total magnetic moment. This decrease in the magnetic moment of samples may be the reason for decrease in the line width of samples.

Table 4.2: Various parameters as calculated from the EPR spectra of Ni_xCo_{1-x}Fe_2O_4 (x= 0.5, 0.75 and 0.9) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔH_{PP} (Gauss)</th>
<th>g-value</th>
<th>N_S (Spin/gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{0.5}Co_{0.5}Fe_2O_4</td>
<td>1309.4</td>
<td>2.0015</td>
<td>1.866x10^{20}</td>
</tr>
<tr>
<td>Ni_{0.75}Co_{0.25}Fe_2O_4</td>
<td>1289.7</td>
<td>2.1008</td>
<td>2.573x10^{20}</td>
</tr>
<tr>
<td>Ni_{0.9}Co_{0.1}Fe_2O_4</td>
<td>1240.8</td>
<td>2.1164</td>
<td>2.828x10^{20}</td>
</tr>
</tbody>
</table>

4.4.5 Magnetization Studies

Magnetization measurements were carried out on these samples at room temperature using vibrating sample magnetometer. Fig 4.8 displays the hysteresis loops for all the samples exhibiting the coercivity ($H_c$), saturation magnetization ($M_s$) and remanence magnetization ($M_r$) for each sample. As seen from $M$–$H$ loops of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ( $x= 0.5, 0.75$ and $0.9$) samples, coercivity of the samples decreased with increasing $x$ values. This is due to lower magneto-crystalline anisotropy of $\text{Ni}^{2+}$ with respect to that of $\text{Co}^{2+}$ [29]. Table 4.3 shows the decrease of $M_s$ values of the samples as the nickel content ($x$) increases.

![Magnetization curves](image)

Fig 4.8 Magnetization curves of $\text{Ni}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ samples, (a) $x= 0.5$, (b) $x= 0.75$, (c) $x= 0.9$.

A similar trend of decrease in saturation magnetization with $\text{Ni}^{2+}$ ion substitution in Co ferrite has been already reported [30, 31]. This decrease in $M_s$ with increasing nickel content is attributed to the smaller magnetic moment of $\text{Ni}^{2+}$ (2 μB) at octahedral sites as compared to larger magnetic moment of $\text{Co}^{2+}$ (3 μB) and $\text{Fe}^{3+}$ (5 μB) ions are uniformly equally distributed between tetrahedral and octahedral sites and this gives a net magnetic moment of 2 μB per formula unit for Ni-ferrite and 3 μB per formula unit for Co-ferrite.
So, by increasing Ni content, Ms values of the samples are decreased. This phenomenon could be attributed to two reasons: (1) the synthesized particles are large enough to support the domain walls, and the coercivity (Hc) of nanoparticles could be reduced by magnetization reversal through the domain wall [31]; (2) with the increasing of the x value, the magnetic anisotropy decreases, leading to the easier reversal of moments and a lower Hc value. Then the decrease of Ms owes to a small magnetic moment of nickel than that of cobalt [32–35]. This is more likely due to inert or dead layer at the surface (shell) of nanoparticles that prevents the core ferromagnetic spins to align along the field direction. As a result the saturation magnetization in case of nanoparticles decreases. Another reason for the decreased magnetization in nanoparticles is the canted spins or spin glass like layer [36, 37] at the surface of the nanoparticles that arises due to the larger fraction of surface to volume atoms in small particles. These canted spins basically reduce the saturation magnetization in these nanoparticles. Due to this effect (canted spins) at the surface (shell) of nanoparticles, no true saturation in these particles is achieved even at very high applied field [38] causing the reduction of magnetization in the smaller particles.

**Table 4.3:** Various magnetic parameters as calculated from the Magnetization curve of NiₙCo₁₋ₙFe₂O₄ (n = 0.5, 0.75 and 0.9) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Saturation Magnetization Ms (emu/gm)</th>
<th>Remanence Magnetization Mr (emu/gm)</th>
<th>Coercivity Hc (Gauss)</th>
<th>Blocking Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₀.₅Co₀.₅Fe₂O₄</td>
<td>30.40</td>
<td>7.85</td>
<td>134.54</td>
<td>230</td>
</tr>
<tr>
<td>Ni₀.₇₅Co₀.₂₅Fe₂O₄</td>
<td>20.45</td>
<td>5.27</td>
<td>116.07</td>
<td>286</td>
</tr>
<tr>
<td>Ni₀.₉Co₀.₁Fe₂O₄</td>
<td>17.88</td>
<td>2.97</td>
<td>108.46</td>
<td>315</td>
</tr>
</tbody>
</table>
4.4.6 AC Susceptibility Studies

The ac susceptibility of ferromagnetic/ferromagnetic materials reveals valuable information about the dynamic magnetization process. Measurements of temperature dependence ac susceptibility give information on possible phase transition. The temperature dependence of ac susceptibility of these samples in the 230-315 K temperature range is plotted in figures 4.9, 4.10 and 4.11 for Ni\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}, Ni\textsubscript{0.75}Co\textsubscript{0.25}Fe\textsubscript{2}O\textsubscript{4} and Ni\textsubscript{0.9}Co\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} respectively. From Fig. 4.9 it is seen that Ni\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} sample shows a sharp transition starting at T= 230 K. As the Ni content increases the onset of transition shifts towards higher temperature and found to be at 286 K for Ni\textsubscript{0.75}Co\textsubscript{0.25}Fe\textsubscript{2}O\textsubscript{4} samples. For Ni\textsubscript{0.9}Co\textsubscript{0.1}Fe\textsubscript{2}O\textsubscript{4} sample transition is observed at 315 K. The blocking temperature ($T_B$) was determined by taking the derivative of the $\chi$ -T data and the values of $T_B$ are listed in Table 4.4. From the measured data it is seen that the blocking temperature increases with increase of nickel content.

![Graph showing temperature dependence of d\chi/dT of Ni\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} sample.]

**Fig 4.9:** Temperature dependence of $d\chi/dT$ of Ni\textsubscript{0.5}Co\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} sample.
Fig 4.10: Temperature dependence of d\(\chi/dT\) of Ni\(_{0.75}\)Co\(_{0.25}\)Fe\(_2\)O\(_4\) sample.

Fig 4.11: Temperature dependence of d\(\chi/dT\) of Ni\(_{0.9}\)Co\(_{0.1}\)Fe\(_2\)O\(_4\) sample.

4.4 CONCLUSIONS

Ni\(_x\)Co\(_{1-x}\)Fe\(_2\)O\(_4\) (x = 0.5, 0.75, 0.9) were synthesized by chemical co-precipitation method. X-ray powder diffraction confirms the formation of single-phase crystalline structure without any trace of impurity. Lattice constant decreased due to the difference in ionic radii of Fe\(^{3+}\) and Co\(^{3+}\) ions. The average crystallite size varies in the range 8-10 nm. The
particle size calculated from TEM images lies in the range of 5-20 nm. Infrared transmission spectra confirm the bonding present in the spinel ferrite structure. The g-value increases on increasing Ni\textsuperscript{2+} ions concentration (x = 0.5 to 0.9) in these ferrite samples due to strengthening of superexchange interactions. The coercivity and saturation magnetization were found to decrease linearly with increasing Ni\textsuperscript{2+} concentration in cobalt ferrite that has been attributed to the lower magneto-crystalline anisotropy of Ni\textsuperscript{2+} ions as compared to cobalt. The larger coercivity in case of nanoparticles has been attributed to the increased effective anisotropy constant (K\textsubscript{eff}) due to the enhanced role of the surface and its associated anisotropies in these nanoparticles. The blocking temperature has been found to increases with increasing Ni\textsuperscript{2+} content due to the lower magnetocrystalline anisotropy of nickel ions as compared to cobalt ions that increases the chance of a jump across the anisotropy energy barrier.
REFERENCES

[22]. Y. A. Koksharov, D. A. Pankratov, S. P. Gubin, I. D. Kosobudsky, M. Beltran,


