CHAPTER 3

STRUCTURAL, MAGNETIC AND ELECTRICAL
CHARACTERIZATION OF NICKEL SUBSTITUTED
COBALT ZINC NANOFERRITES

3.1 INTRODUCTION

CoFe$_2$O$_4$ is an inverse spinel structure with high coercivity, moderate magnetization and great physical and chemical stability hence suitable for magnetic recording audio videotapes and high density digital recording disc. The recording disc materials should be single domain of pure phase having low grain size. As the grain size becomes smaller the magnetization direction of the ferrite powder cannot be fixed as in large crystals, but fluctuate spontaneously. It is very important to grow ferrite particles with homogenous magnetic particles. Co-Zn ferrite is one of the soft ferrite used in electronic devices such as transformer cores, electric motors and generators.

Synthesis of nanoparticles with single phase, narrow diameter distribution and good control over particle size has been a challenge for many researchers. Co-precipitation and templated synthesis using reverse micelles are two methods widely used in the synthesis of magnetic nanoparticles. Many studies on Co-Zn ferrites in the bulk crystalline form were prepared by the usual ceramic technique. Effect of laser irradiation on the cation
distribution mechanism of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ ferrite was explained by Tawfik et al (2002). Gul et al (2007) have prepared nanoparticles of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ with stoichiometric proportion varying from 0.0 to 0.6 by the chemical co-precipitation method. Gozak et al (2009) synthesized nano cobalt zinc ferrite by (PEG)-assisted hydrothermal route and their magnetization measurements shows that the materials with high zinc substitution are superparamagnetic at room temperature, whereas with less Zn substitution are ferromagnetic below room temperature while the former is ferromagnetic at temperatures lower than the blocking temperature.

Dey and Ghose (2003) prepared $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ by co-precipitation method and found magnetization decreases with increasing particle size. Arulmurugan et al (2005a) suggested that substitution of $\text{Co}^{2+}$ with $\text{Zn}^{2+}$ lead to improved magnetic properties in nanocrystalline ferrites. They also observed a decreasing behavior of saturation magnetization and the particle size of the Co-Zn substituted ferrite nanoparticles with increasing Zn concentration. Islam et al (1998) reported that saturation magnetization decreases with zinc concentration in cobalt zinc ferrites prepared by ceramic technique. Vaidyanathan et al (2007) also reported decrease in magnetic properties such as $M_s$, $H_s$, $H_c$, and $M_r$ with increase in zinc substitution. Single phase and monodispersed nanocrystalline Zn substituted cobalt ferrites with grain size of 3 nm were prepared by Duong et al (2007) using forced hydrolysis method and they found that the ferrites were superparamagnetic at room temperature and ferrimagnetic at lower temperatures. Waje et al (2010) reported that $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles, prepared by mechanical alloying and sintering show a constant value of permittivity within a measured frequency range but vary with sintering temperature. However, in general the permeability values vary with both frequency and sintering temperature.
Josyulu et al (1980) have studied the dielectric behavior as a function of temperature and frequency for Co-Zn, and Mg-Zn ferrites, the dielectric behavior is attributed to the Maxwell-Wagner polarization. The electrical conductivity of these ferrites is explained by the hopping mechanism. Sharma et al (2005) has reported the synthesis of chromium substituted nanoparticles in the range 2 to 7 nm of cobalt zinc ferrites by co-precipitation method and confirmed the presence of superparamagnetic relaxation by Mossbauer studies. An exponential decrease in the superparamagnetic blocking temperature, with increasing chromium concentration, is observed for all the samples. Tomar et al (2005) reported that Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ shows no remanent and coercive magnetization and behaves as superparamagnetic at 300 K. Omprakash et al (2007) prepared Ni$_{0.25}$Co$_{0.25}$Zn$_{0.5}$Fe$_2$O$_4$ with different particle sizes by chemical co-precipitation technique. The decrease in saturation magnetization values with an increase in annealing temperature is explained by the variation in proportions of superparamagnetic phase and also the redistribution of cations in these ferrite nanoparticles. The variation in coercivity with annealing temperatures is explained in terms of the size effect.

Hence the present work is devoted to know the effect of nickel substitution in Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ ferrite.

3.2 PREPARATION PROCEDURE FOR Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ NANOFERRITES

Nanoparticles of Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ with x- varying from x = 0.0 to 0.3 were prepared by co-precipitation method. FeCl$_3$, ZnSO$_4$.7H$_2$O, CoCl$_2$.6H$_2$O and NiCl$_2$.6H$_2$O are taken in the respective stoichiometry (100 ml of solution containing (0.5-x) M CoCl$_2$, (x) M NiCl$_2$, 0.5 M ZnSO$_4$ and
100 ml of 2 M FeCl₃) were mixed thoroughly using magnetic stirrer at 80°C. It was then transferred immediately into a boiling solution of NaOH (0.55 M dissolved in 1330 ml of distilled water) under constant stirring and a pH of 12 is maintained throughout the reaction. Conversion of metal salts into hydroxides and subsequent transformation of metal hydroxide into nanoferrites takes place upon 100°C and maintained for 60 minutes until the reaction is complete. The nanoferrites thus formed were isolated by centrifugation and washed several times with deionized water followed by acetone and then dried at room temperature. The dried powder is ground thoroughly in a clean agate mortar, and then the material is pelletized at 5 ton pressure for about 3 min. The pellet and the powder were sintered at 500°C in a furnace for about 2hrs. The powder samples were used for the analysis of XRD, FTIR, TEM, SEM and magnetic studies, whereas the pelletized sample is used for the analysis of dielectric studies.

3.3 STRUCTURAL ANALYSIS OF Co₉(0.5-x)NiₓZn₀.₅Fe₂O₄ COMPOUNDS

3.3.1 XRD analysis of Co₉(0.5-x)NiₓZn₀.₅Fe₂O₄ compounds

3.3.1.1 Lattice parameter

The powder X-ray diffraction patterns of the as prepared and sintered at 500°C compound for the composition Co₉(0.5-x)NiₓZn₀.₅Fe₂O₄ (where x = 0 to 0.3) are shown in Figure 3.1a and 3.1b. All the as prepared and sintered samples show the formation of single phase spinel ferrite. The broad peaks in XRD patterns indicate that the ferrite particles are in nanoscale. All the peaks in the diffraction pattern have been indexed and the lattice parameter was refined through PowderX indexing software (Dong 1999).
The crystalline size of each composition were calculated from line width of (311) peak using Scherrer formula (Cullity 1959). The average particle size was found to be in the range of 15 nm measured from TEM images for the compound Co$_{0.3}$Ni$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$, this result matches with result calculated from the XRD using Scherrer equation. The lattice constant and particle size for the as prepared sample and sintered samples were calculated from the powder X-ray diffraction data are given in Table 3.1. It was observed that for the lattice parameter for as prepared and sintered samples of Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ was found to be 8.354(3) Å and 8.377(2) Å respectively.

![Figure 3.1a XRD pattern of the as prepared Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ samples](image)

Figure 3.1a  XRD pattern of the as prepared Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ samples
Figure 3.1b XRD pattern of the Co\(_{(0.5-x)}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) compounds sintered at 500°C for 2 hour

Arulmurgan et al (2005b) reported similar value of 8.356 Å for Co\(_{0.51}\)Zn\(_{0.5}\)Fe\(_{1.9}\)O\(_4\) compound and this value is found to be less for bulk compounds (8.37 Å) by Pandya et al (1991). This decrease in lattice constant in the nanosize when compared with bulk may be explained as follows. In nanosize there is variation in cation distribution when compared with bulk material. Usually Zn\(^{2+}\) occupies A-site and Co\(^{2+}\) occupies B-site in bulk material. But in nanosize a small portion of Zn\(^{2+}\) and Co\(^{2+}\) occupies B and A site respectively which forces the Fe\(^{3+}\) to the tetrahedral A-site against the chemical preferences. Since Fe\(^{3+}\) ions have smaller ionic radius (0.64 Å),
occupying the tetrahedral site in place of larger divalent ions leads to a variation in lattice parameter in nanoferrite.

Hence the lattice parameters are found to be less than bulk materials similar redistribution of cation in nanosize was discussed by Chandan Upadhyay et al (2004). The lattice constant for sintered sample at 500°C for Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ is 8.377(3) Å. This is similar to the values reported by Pandya et.al (1991) and Ana Maria et al (2006) for the compound sintered at 400°C. The increase in lattice parameter for the sintered sample is a temperature effect which may leads to the increase in particle size.

From Table 3.1 the lattice parameters are found to decrease with increase in nickel concentration up to $x = 0.3$. The decrease in lattice parameter can be explained on the basis of cation stoichometry. The ionic radius of Ni$^{2+}$ ions (0.69 Å) is smaller than the ionic radius of Co$^{2+}$ cations (0.72 Å). Hence the replacement of cobalt by nickel in Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$ causes a decrease in lattice constant by obeying Vegard’s law (Denton and Ashcroft 1991). Similar behavior is also observed for sintered sample up to the concentration $x = 0.2$. However the lattice parameter found to increases for the concentration $x = 0.3$ for the sintered sample at 500°C. The increase in lattice parameter for the value of $x = 0.3$ in the sintered sample is due to the formation of Fe$^{2+}$ in the octahedral sites. Since ionic radius of Fe$^{2+}$ (0.74 Å) ion is larger than Fe$^{3+}$ ion (0.64 Å), the lattice constant may increases slightly for the sintered sample, which may be due to thermal effect.
Table 3.1  Structural and magnetic parameters of Co\(_{(0.5-x)}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) compounds

<table>
<thead>
<tr>
<th>Composition</th>
<th>Average particle size ‘t’ nm</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Saturation Magnetization at 15 kOe (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As prepared sample</td>
<td>Sintered sample at 500°C</td>
<td>As prepared sample</td>
</tr>
<tr>
<td>x = 0</td>
<td>12</td>
<td>16</td>
<td>8.354(2)</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>11</td>
<td>15.5</td>
<td>8.333(2)</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>14</td>
<td>15</td>
<td>8.329(3)</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>15</td>
<td>15.5</td>
<td>8.310(1)</td>
</tr>
</tbody>
</table>

3.3.1.2  Cation distribution

In order to determine the cation distribution and its variation with composition, X–ray intensity calculations were carried out using formula suggested by Buerger (1960).

\[
I_{(hkl)} = |F_{hkl}|^2 \cdot m \cdot L_p
\]  

(3.1)

Where, \(I_{(hkl)}\) is the relative integral intensity, \(F_{hkl}\) the structure factor, \(m\) the multiplication factor and \(L_p\) is the Lorentz polarization factor. The distribution of divalent and trivalent cations among octahedral and tetrahedral sites in the Co\(_{(0.5-x)}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) compound was determined from the ratio of X-ray diffraction lines \(I_{(220)}/I_{(400)}\), \(I_{(220)}/I_{(440)}\) and \(I_{(400)}/I_{(440)}\). These ratios are considered to be sensitive to the cation distribution (Ohnishi and Teranishi 1961). The absorption and temperature factors are not taken into
account in the calculations because these factors do not affect the relative intensity calculations for spinels at room temperature.

The structure factor formula for the individual planes (hkl) was taken from those reported by Furuhashi et al (1973). The multiplicity and Lorentz polarization factors are taken from the literature (Otero Arean et al 1990). The cation distribution for which the experimental ratios agree well with observed intensity ratios is taken as a correct one. It is known that there is a correlation between the ionic radius and lattice parameter. The distribution of divalent and trivalent cations among octahedral and tetrahedral sites in the Co\(_{0.5-x}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) compound was determined from the relation suggested by Mazen et al (1992). The lattice parameter can be calculated theoretically from the relation.

\[
a_{th} = \frac{8}{3\sqrt{3}} \left[ (r_A + R_0) + \sqrt{3}(r_B + R_0) \right]
\]  

(3.2)

Where \(R_0\) is the radius of oxygen ion (1.32Å), \(r_A\) and \(r_B\) are the ionic radii of tetrahedral (A-Site) and octahedral (B-Site) respectively. The ionic radius for each site was calculated according to

\[
r_A = \left[ C_{A\text{Co}} r(\text{Co}^{2+}) + C_{A\text{Ni}} r(\text{Ni}^{2+}) + C_{A\text{Zn}} r(\text{Zn}^{2+}) + C_{A\text{Fe}} r(\text{Fe}^{3+}) \right] \quad (3.3)
\]

\[
r_B = \left[ C_{B\text{Co}} r(\text{Co}^{2+}) + C_{B\text{Ni}} r(\text{Ni}^{2+}) + C_{B\text{Zn}} r(\text{Zn}^{2+}) + C_{B\text{Fe}} r(\text{Fe}^{3+}) \right] +
\frac{C_{B\text{Fe}} r(\text{Fe}^{2+})}{2}
\]

where, \(r\text{Co}^{2+}\), \(r\text{Ni}^{2+}\), \(r\text{Zn}^{2+}\) and \(r\text{Fe}^{3+}\) are the cationic radius of Co, Ni, Zn and Fe respectively. The ionic radii for calculating the lattice parameter \(a_{cal}\) was taken from the work of Shannon (1976). The agreement between calculated value lattice parameter and observed lattice parameter
value from X-ray data intensity supports the cation distribution. It is seen that there is a reasonable agreement between experimental and theoretically calculated value of lattice parameter suggesting that the estimated cation distribution is in close agreement with the real distribution.

The distribution of cation for as prepared samples was determined from the lattice parameter from X-ray diffraction data shown in the Table 3.2. It was found that there is a deviation in cation preferences in nanosized particles when compared with bulk particles. Usually $\text{Zn}^{2+}$ and $\text{Fe}^{3+}$ occupies A-site and $\text{Co}^{2+}$, $\text{Ni}^{2+}$ and $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ occupies B-site, but in the nanoscale some of the nickel, cobalt and zinc occupies both A-site and B-site leading to a metastable state and statistically disordered cation distribution.

Table 3.2  Cation distribution analysis of $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ as prepared samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>A- Site</th>
<th>B- Site</th>
<th>I(220)/I(440)</th>
<th>I(220)/I(440)</th>
<th>I(400)/I(440)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs</td>
<td>cal</td>
<td>obs</td>
<td>cal</td>
<td>obs</td>
</tr>
<tr>
<td>x = 0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}<em>{0.25}\text{Zn}</em>{0.26}\text{Fe}^{3+}_{0.49}$</td>
<td>$\text{Co}<em>{0.25}\text{Zn}</em>{0.24}\text{Fe}^{3+}_{1.51}$</td>
<td>0.65</td>
<td>0.64</td>
<td>1.45</td>
<td>1.44</td>
</tr>
<tr>
<td>x = 0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}<em>{0.2}^{2+}\text{Zn}</em>{0.3}^{2+}\text{Fe}^{3+}_{0.5}$</td>
<td>$\text{Ni}<em>{2}^{2+}\text{Co}</em>{0.2}^{2+}\text{Zn}<em>{2}^{+}\text{Fe}^{3+}</em>{1.5}$</td>
<td>0.64</td>
<td>0.62</td>
<td>1.44</td>
<td>1.43</td>
</tr>
<tr>
<td>x = 0.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}<em>{0.17}\text{Zn}</em>{0.31}^{2+}\text{Fe}^{3+}_{0.52}$</td>
<td>$\text{Ni}<em>{2}^{2+}\text{Co}</em>{0.2}^{2+}\text{Zn}<em>{2}^{+}\text{Fe}^{3+}</em>{1.48}$</td>
<td>0.60</td>
<td>0.60</td>
<td>1.41</td>
<td>1.40</td>
</tr>
<tr>
<td>x = 0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}<em>{0.15}\text{Zn}</em>{0.32}^{2+}\text{Fe}^{3+}_{0.53}$</td>
<td>$\text{Ni}<em>{2}^{2+}\text{Co}</em>{0.3}^{2+}\text{Zn}<em>{2}^{+}\text{Fe}^{3+}</em>{1.47}$</td>
<td>0.57</td>
<td>0.58</td>
<td>1.31</td>
<td>1.32</td>
</tr>
</tbody>
</table>
The cation distribution parameter for the sintered sample is shown in Table 3.3. It is observed that there is a change in occupation of cations in tetrahedral (A-site) and octahedral (B-site). During the process of heating Zn\(^{2+}\) ions migrate from octahedral (B site) to tetrahedral (A site) and Fe\(^{3+}\) ion migrates from tetrahedral (A site) to octahedral (B site). This suggest that sintering can facilitate cation redistribution and hence the metastable cation distribution in the as synthesized particles starts transforming to a thermally induced stable distribution as is evident from the increase in the lattice constant.

The increase in lattice parameter upon sintering can be explained with the help of ideal spinel structure. In an ideal spinel structure of bulk ferrite material, a metal cation with a radius $\leq 0.03\text{nm}$ occupies the tetrahedral site, while cations with radius $\leq 0.055\text{ nm}$ can occupy the octahedral sites. In order to accommodate cations like Co\(^{2+}\) and Zn\(^{2+}\) having larger ionic radius (more than 0.03nm) in the tetrahedral site, the lattice has to expand. It is observed from the Table 3.3 that there is a migration of Zn\(^{2+}\) and Co\(^{2+}\) ions from octahedral (B) sites to tetrahedral (A) sites and Fe\(^{3+}\) ions migrate from tetrahedral (A) to octahedral (B) site. Since the ionic radius of Zn\(^{2+}\)(0.60nm) and Co\(^{2+}\)(0.58nm) ions in tetrahedral sites are larger than the Fe\(^{3+}\) (0.485nm) ions, there is an expansion of lattice parameter as observed in all of our sintered samples.
Table 3.3  Cation distribution analysis of Co\(_{0.5-x}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) sintered samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>A- Site</th>
<th>B- Site</th>
<th>$I(220)/I(440)$</th>
<th>$I(220)/I(400)$</th>
<th>$I(400)/I(440)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.0</td>
<td>Co(<em>{0.1})Zn(</em>{0.4})Fe(<em>{0.50})(</em>{3+})</td>
<td>Co(<em>{0.4})Zn(</em>{0.1})Fe(<em>{1.4})Fe(</em>{0.1})(_{2+})</td>
<td>0.66</td>
<td>0.65</td>
<td>1.21</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>Ni(<em>{2+})(</em>{0.02})Co(<em>{2+})(</em>{0.1})Zn(<em>{2+})(</em>{0.4})Fe(_{0.48})</td>
<td>Ni(<em>{2+})(</em>{0.08})Co(<em>{2+})(</em>{0.3})Zn(<em>{2+})(</em>{0.1})Fe(<em>{1.42})Fe(</em>{0.1})(_{3+})</td>
<td>0.67</td>
<td>0.66</td>
<td>1.34</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>Ni(<em>{2+})(</em>{0.07})Co(<em>{2+})(</em>{0.1})Zn(<em>{2+})(</em>{0.39})Fe(_{0.44})</td>
<td>Ni(<em>{2+})(</em>{0.13})Co(<em>{2+})(</em>{0.2})Zn(<em>{2+})(</em>{0.11})Fe(<em>{1.56})Fe(</em>{0.1})(_{3+})</td>
<td>0.70</td>
<td>0.68</td>
<td>1.38</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>Ni(<em>{2+})(</em>{0.02})Co(<em>{2+})(</em>{0.2})Zn(<em>{2+})(</em>{0.38})Fe(_{0.58})</td>
<td>Ni(<em>{2+})(</em>{0.02})Co(<em>{2+})(</em>{0.2})Zn(<em>{2+})(</em>{0.38})Fe(_{0.58})</td>
<td>0.63</td>
<td>0.62</td>
<td>1.42</td>
</tr>
</tbody>
</table>

3.3.2 Fourier Transform Infrared Spectra studies on Co\(_{0.5-x}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)

Infrared spectra of the as prepared compositions Co\(_{0.5-x}\)Ni\(_x\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) with x = 0 to 0.3 are shown in Figure 3.2. The existence of absorption bands at 550–600 and 420–450 cm\(^{-1}\), are the metal–oxygen bonds and attributed to the formation of the ferrite phase in IR spectra. On inspection of Figure 3.2, it is found that the spectra consist of two significant absorption bands, first at about 590 cm\(^{-1}\) and second at about 450 cm\(^{-1}\). Absorption bands observed within this limit reveal the formation of single phase spinel structure having two sublattices, tetrahedral (A) site and octahedral (B) site (Waldron 1955). The absorption band, $\nu1$, observed at about 590 cm\(^{-1}\) is attributed to the tetrahedral site, whereas that of $\nu''$ observed at about 450 cm\(^{-1}\) is assigned to octahedral group complexes.
3.3.3 Electron microscopic studies

3.3.3.1 Transmission Electron Microscopic analysis for Co$_{0.3}$Ni$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$

Figure 3.3 TEM images for the sample Co$_{0.3}$Ni$_{0.2}$Zn$_{0.5}$Fe$_2$O$_4$
The particle size and morphology of the concentration \( x = 0.2 \) for the sintered sample is shown in Figure 3.3. The average particle size is around 15 nm. TEM analysis revealed that the particles are nearly spherical. The particle size determined from TEM was found to be in close agreement with that obtained from XRD studies.

### 3.3.3.2 Surface morphology and compositional analysis of \( \text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \)

The structural features and elemental composition of the as prepared powder samples coated with gold to have contact were observed by using Hitachi S-3400 scanning electron microscope with energy dispersive X-ray analysis setup. The SEM images and EDX spectrum of the samples are shown in Figure 3.4(a-h). The SEM images clearly show the materials are small size in nanoregion. Chemical analyses through EDX were also carried out on powder samples \( \text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) with \( x = 0 \) to 0.3 compounds.

The EDX analysis Figure 3.4 (e-h) shows the wt% of cobalt and nickel in the powder sample is 14.73, 12.34, 9.93, 7.92 and 1.99, 4.01, 6.42, respectively, which shows the decreasing trend in cobalt and increasing behavior of nickel. The wt% of iron and zinc remain almost constant. The EDX spectrum of the samples shows that all the samples are of nearly expected elemental composition and reveal the presence of the substitution elements Ni, Co, Zn, Fe and Oxygen for the compound \( \text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) (\( x = 0 \) to 0.3).
Figure 3.4 SEM images and EDX spectra for $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$
3.4 MAGNETIC STUDIES

3.4.1 Variation in Magnetic Moment at FC and ZFC conditions

The magnetization behavior of Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0 to 0.3) nanoparticles were observed when cooled in the presence of external magnetic field (field cooled case FC) and also in zero field (zero field cooling case ZFC). The temperature dependence of (ZFC) and (FC) magnetization for the samples Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ (x = 0 to 0.3) is shown in Figure 3.5. FC data measurements were recorded in the presence of 300 Oe applied field for the compound Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ i.e x = 0 whereas for all other concentration x = 0.1, 0.2 & 0.3 a constant field of 100 Oe was maintained. The ZFC magnetization increases with temperature to a maximum corresponding to the mean blocking temperature ($T_B$) and then decreases, while the FC magnetization continuously decreases with temperature and coincides with the ZFC magnetization at a certain temperature. In general, this temperature represents the maximum blocking temperature ($T_{\text{max}}$), i.e., the blocking temperature of particles with the highest energy barrier. The difference between $T_B$ and $T_{\text{max}}$ corresponds to the width of the blocking temperature and also the particle size distribution. It was observed that the net magnetic moment gradually increases and shows a broad maximum at 150 K and 167 K for the nickel content of x = 0 and 0.1, which is a characteristic feature of superparamagnetism. The increase in blocking temperature is due to the applied field; as the field increases the blocking temperature increases. Similar effects are also observed by Zhang (1998). Below this temperature the thermal activation energy is not sufficient enough to overcome the magneto crystalline anisotropy energy of the nanoparticles.
Figure 3.5  Magnetic moment for the compound $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$
from room temperature down to 2K in ZFC and FC

Hence magnetic moment is blocked by the quantum wells, showing decreasing trend in magnetic moment, which is reported in the literatures as blocking temperature by Pettit and Forester (1971). Tomar et al (2005) reported $\text{Co}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ has blocking temperature $T_B$ at 150 K which coincides with our result. Any temperature above $T_B$, the particles have sufficient thermal energy to overcome the energy barrier and thus the magnetic spins are free to fluctuate between orientations. Above the blocking temperature the particles obey Curie-Weiss law (Adam Rondinone et al 1999). The data shows irreversibility between ZFC and FC at 230 K and 260 K for the nickel concentration $x = 0$ and 0.1, the samples behaves superparamagnetic above 150 K and 167 K respectively and ferrimagnetic below these temperatures for the composition $x = 0$ and 0.1. Whereas for the concentration $x = 0.2$ and 0.3 ZFC and FC does not separate up to 300K, hence superparamagnetism is not seen up to 300K. In order to ascertain this
result hysteresis loop analysis for the concentration $x = 0.2$ and 0.3 shows coercivity at 300 K which is shown in Figure 3.6. As the concentration increases, the blocking temperature is found to increase; the increase in blocking temperature may not only due to increase in applied field but also may be due to variation in cation distribution or particle size.

### 3.4.2 Variation in Magnetization with Applied Magnetic Field

The variation of magnetization with respect to the applied field at 300 K for the composition $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (where $x = 0$ to 0.3) is shown in Figure 3.7. As a normal behavior the magnetization increases with increase in applied field and attains maximum value for field higher than 50 KOe. As the Ni ion concentration increases, the saturation magnetization decreases from 49.6 to 33.3 emu/g for the concentration $x = 0.1$, and then saturation magnetization starts increasing with increase in cobalt concentration from 33.3 emu/g to 74.2 emu/g for the concentration $x = 0.2$ and 0.3.

![Hysteresis loop for the compound $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300K](image)

**Figure 3.6** Hysteresis loop for the compound $\text{Co}_{(0.5-x)}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 300K
Arulmurugan et al (2005a) reported 39.6 emu/g at 10 KOe for the compound Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. This value is found to match our present investigation value 43 emu/g for the compound Co$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$. It was observed that with an increase in the concentration of x (i.e., Ni$^{2+}$ ion (with 2$\mu_B$)) at Co-site (with 3$\mu_B$) there was a decrease in the saturation magnetization values for the concentration x = 0.1. This decrease in the saturation magnetization is due to the migration of Fe$^{3+}$ ion from A-site to B-site, due to this the magnetic moment of the B-site decreases and hence the net magnetization decreases.

However for the sample x = 0.2 and x = 0.3, the migration of Fe$^{3+}$ ions increases from A-site to B-site. Due to this, the interaction between A-site cations increases and this reduces the spin canting in the B-site (since the net magnetic moment is equal to $M_B - M_A$). This is also due to the increase in particle size. Similar behavior were reported in Mg$_{0.95}$Mn$_{0.05}$Fe$_2$O$_4$ by Sharma (2007); Ichiyanagi (2005).
Saturation magnetization ($M_S$) is not achieved even at 50 kOe for all the composition and this may be explained by core shell morphology of nanoparticles in which the surface to volume ratio is large. The core consists of ferrimagnetically aligned spins and the surface with disordered spins, the increase in magnetic field has effect only on the surface causing slow down in magnetization. However, these magnetization values are found to be less than that of bulk materials for all compositions. Coey and Khalafella (1972) explained the smaller values of $M_S$ due to the existence of random canting of particles, surface spins caused by competing antiferromagnetic exchange interactions due to a symmetry in the environment of these spins. Pankhurst and Pollard (1991) claimed that the lower magnetization values are due to non–saturation effects because of random distribution of the small particles with enhanced values of magneto-crystalline anisotropy.

Hysteresis loop of $\text{Zn}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ and $\text{Ni}_{0.1}\text{Zn}_{0.5}\text{Co}_{0.4}\text{Fe}_2\text{O}_4$ in Figure 3.6 reveals that neither coercivity nor remnant magnetization, suggesting superparamagnetic behavior at room temperature (Tomar et al 2005). Hysteresis loop at various temperatures down to 10 K is shown in Figure 3.8 for the $\text{Co}_{0.4}\text{Ni}_{0.1}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ compound. It is observed that the coercivity decreases as the temperature increases and becomes almost zero near to 150 K and becomes zero at the 200 K. This clearly indicates that below $T_B$ i.e. up to 167 K hysteresis loop exist and above $T_B$ it disappears. Seema Verma et al (2004) also observed similar behavior in Mn ferrite prepared by microwave hydrothermal process, where coercivity becomes zero above the blocking temperature ($T_B$). The magnetization also found to decrease with increase in temperature. With the increase in concentration the coercivity increase may be due to the irreversible domain moment.
3.5 DIELECTRIC STUDIES

3.5.1 Variation of dielectric constant with applied field at room temperature

From Figure 3.9, it is observed that the dielectric constant decreases with increase in frequency, showing dispersion in low frequency range. All samples show dispersion due to Maxwell-Wagner polarization and are also in agreement with the Koop’s phenomenological theory (Koops 1951; Maxwell
The decrease in dielectric constant at higher frequency can be explained on the basis that the material is assumed as composed of well conducting grains and is separated by non conducting grain boundaries, when electrons reach such non conducting grain boundaries through hopping the resistance of the grain boundary is high, hence the electron pile up at the grain boundaries and produce polarization. At higher frequency beyond a particular limit, the electron does not follow the applied alternating field. This decreases the probability of electrons reaching the grain boundary and as result polarization decrease. The decrease in dielectric constant with increase in nickel concentration may be due to the migration of Fe\(^{3+}\) ions from octahedral site to tetrahedral site.

![Figure 3.9 Variation of dielectric constant with frequency for the compound Co\(_{(0.5-x)}\)Ni\(_{x}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) at 300 K](image)

The dielectric constant is found to be less than bulk sample for a frequency of 100 KHz at room temperature. The dielectric constant for bulk Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) as reported by Ahmed et al (1997) is 105, whereas in the present investigation the dielectric constant for Co\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) with particle
size 15 nm is calculated as 28. This low dielectric loss is attributed to homogeneity, better symmetry and small grain size when compared with bulk sample (Mathur et al 2008). This decreases the hopping and hence decreases the polarization up to \( x = 0.2 \). The increase in dielectric constant for the concentration \( x = 0.3 \) may be due to the formation of \( \text{Fe}^{2+} \) ions in octahedral site. The increase in \( \text{Fe}^{2+} \) ions in octahedral site increases the hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) and hence increases the polarization. This results in the local displacement of electrons in the direction of applied field thereby increasing the dielectric constant.

### 3.5.2 Variation of dielectric constant with temperature at 1MHz

The variation of dielectric constant at 1 MHz with temperature for mixed \( \text{Co}_{0.5-x}\text{Ni}_x\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \) (where \( x = 0.0 \) to 0.3) as shown in Figure 3.10. The dielectric constant increases gradually with increase in temperature up to a certain temperature designated as dielectric transition temperature \( (T_d) \). However beyond this temperature, the values of the dielectric constant were found to decrease continuously, a similar temperature variation of the dielectric constant has been reported by Ravinder and Vijaya kumar (2001); Olofa (1994). This change in the dielectric behavior beyond transition temperature may be due a magnetic transition from ferrimagnetic to paramagnetic.

The increase in the dielectric constant with temperature can be explained on the basis that as the temperature increases the hopping between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) ions on the octahedral sites is thermally activated this electron hopping causes local displacement in the direction of the external applied field and as a result the dielectric polarization increases. Therefore the dielectric constant increases. However beyond the transition temperature, the
ions and electrons are less oriented towards the field direction and hence the dielectric constant deceases.

![Figure 3.10 Variation of dielectric constant with temperature for the compound Co_{(0.5-x)}Ni_{x}Zn_{0.5}Fe_{2}O_{4} at 1MHz](image)

**3.5.3 Variation of dielectric loss tangent with applied field at room temperature**

Figure 3.11 shows the variation of dielectric loss tangent $\tan(\delta)$ with frequency at room temperature in all the cases there is decrease in dielectric loss initially followed by resonance peak with increase in frequency. The appearance of a resonance peak can be explained as follows: If an ion has more than one equilibrium position, say two positions tetrahedral (A-site) and octahedral B-site, of equal potential energies, separated by a potential barrier, the probabilities of jumping of ions from A-site to B-site and from B-site to A-site are the same. Depending upon this probability, the ion
exchanges position between the two states matches with the natural frequency of jump between the two positions. When an external alternating electric field of the same frequency is applied, maximum electrical energy is transferred to the oscillating ions and power loss shoots up, thereby resulting in resonance according to Debye relaxation theory (Trivedi et al 2005). The loss peak occurs when the applied field is in phase with the dielectric and the condition $\omega \tau = 1$ is satisfied, where $\omega = 2\pi f$, $f$ being the frequency of the applied field and $\tau$ the relaxation time is related to jumping probability per unit time $p$, by an equation $\tau = p/2$ or $f_{\text{max}} \propto p$.

![Figure 3.11 Variation of dielectric loss with log frequency for the compound Co$_{(0.5-x)}$Ni$_x$Zn$_{0.5}$Fe$_2$O$_4$ at T = 300 K](image)

From Figure 3.11 it is seen that the increase in $f_{\text{max}}$ with increasing nickel content indicates the hopping or jumping probability per unit time increases. The shifting of relaxation peak towards higher frequency side is due to increase in nickel concentration since nickel prefers B-site which
strengthens the dipole-dipole interaction leading to hindrance to the rotation of the dipoles (Amarendra et al 2002).

3.5.4 Variation of a.c. conductivity with applied field at room temperature

Figure 3.12 Variation of a.c. conductivity with log frequency for the compound Co\(_{(0.5-x)}\)Ni\(_{x}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) at T = 300 K

Figure 3.12 shows the variation of ac conductivity log(\(\sigma_{ac}\)) with frequency at 300 K. The entire sample shows increase in conductivity with increase in frequency, which is the normal behavior of ferrites.

A consolidated summary of the above studies is given in chapter 6.