CHAPTER-III

RESULTS ON STRUCTURAL, ELECTRICAL AND MAGNETIC PROPERTIES OF Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ and Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$
NANOCRYSTALLINE FERRITES

3.1 Introduction

Based on the detailed discussion in the chapter-1 on general introduction of ferrites such as importance of magnetic core, essential requirements of materials were clearly understood. Due to increasing trend of smart technology, wide ranges of electronic device applications are also improved. Over the years spiel ferrites plays an efficient role in various electromagnetic applications. In these way nano crystalline magnetic materials exhibits tremendous magnetic properties as compared then the bulk systems [1-2]. Poly crystalline Ni-Zn ferrites are extensively investigated due to their high electrical resistivity, high saturation magnetization, high initial permeability, low magnetic and eddy current losses etc. These unique properties make them suitable for various electromagnetic applications like inductors, magnetic storage tapes, Multi Layer Chip Inductor (MLCI) applications [3-5].

In this chapter the nanocrystalline Ni-Zn ferrite powders with the composition Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) were prepared by the auto combustion method. The detailed method of preparation is discussed in earlier chapter-II. The obtained powders were sintered at 900$^\circ$C for 4 h in air atmosphere. The as-prepared and the were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Scanning electron microscopy (SEM), Energy dispersive spectra, magnetization studies, electrical and dielectrical studies. X-ray diffraction studies confirm that the single phase cubic structure was formed. An increase in the crystallite size and a slight decrease in the lattice constant with sintering temperature were observed, whereas microstrain was observed to be negative for all the samples. Two significant absorption bands in the wave number range of the 400 cm$^{-1}$ to 600 cm$^{-1}$ have been observed in the FT-IR spectra for all samples which is the distinctive feature of the spinel ferrites. The force constants were found to vary with sintering temperature, suggesting a cation redistribution and modification in the unit cell of the spinel. The grain size is increased with decreasing of Ni concentration. The M-H
loops indicate smaller coercivity, which is the typical nature of the soft ferrites. The observed variation in the saturation magnetization and coercivity with sintering temperature has been attributed to the role of surface, inhomogeneous cation distribution, and increase in the crystallite size. The electrical resistivity is increased with increasing of sintering temperature. The dielectrical properties of all sintered samples were done in the frequency range of 1 kHz to 10 MHz.

3.2 Structural properties

3.2.1 X-ray diffraction studies

The XRD patterns of the as prepared powder samples of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) shown in Figure 3.1 and Figure 3.2. From Figures 3.1&3.2 it is very clear that the formation of the spinel ferrite phase, suggesting the solubility of the cations into their respective lattice sites. The interplanar spacing has been obtained using the Bragg’s law. The lattice parameter corresponding to each peak of the diffraction pattern was plotted against the Nelson–Riley error function [6]

$$F(\theta) = \frac{1}{2} \left( \frac{\cos^2 \theta}{\sin \theta} \right) + \left( \frac{\cos^2 \theta}{\theta} \right)$$

The accurate lattice parameter, corresponding to zero error, was obtained by the least square fit. The obtained values of lattice parameters were reported in Table 1.

![X-ray diffractogram of Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$](image.png)
The variations in the lattice parameter can be explained on the basis of differences between ionic radii of replace and replaced ions. In present case the lattice parameter is increased with decreasing of Ni content which is due to Ni$^{2+}$ (0.69 Å) ionic radius smaller than that of Zn$^{2+}$ (0.74Å). The crystallite size of the all powder samples were determined by using the following Scherrer formula [6].

$$D_{311} = \frac{0.9\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength, $\theta$ is the Diffraction angle, $\beta$ is the FWHM (full width at half maximum) of diffraction profile in radians on 2$\theta$ scale, and $k$ is a constant called as shape factor approximately equal to unity [7]. The estimated crystallite sizes are listed in Table 3.1.

Density plays very important key role in polycrystalline ferrites. Density and porosity are strongly influence the electrical and magnetic properties of ferrites. The X-ray density ($d_x$), bulk densities ($d_b$) and percentage of porosity are calculated using standard formula [8].

$$d_{bulk} = \frac{m}{v}$$
\[ d_{\text{x-ray}} = \frac{8M}{Na_0} \]

Where ‘M’ is the molecular weight, ‘N’ is the Avogadro's number, and ‘a₀’ is the experimental lattice constant of spinel ferrite. The densities of all the samples sintered at 900°C were presented in Table 3.1. From the Table 3.1 it is evident that both bulk and X-ray densities increases with increasing Zn content. The changes in the density is due to the atomic weight of Zn (65.409 amu) is greater than that of Ni (58.693 amu). Therefore, replacement of Ni ion by Zn ion improves the density. The porosity of the present investigation is decreased with increasing of Zn concentration. The obtained values of porosity were reported in Table 3.1.

**Table 3.1: Lattice parameter, crystallite size, bulk density, X-ray density and porosity of Ni_{1-x}Zn_xFe_2O_4 (x=0.35 and 0.50).**

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice parameter (Å)</th>
<th>Crystallite size D (nm)</th>
<th>Bulk density (g/cc)</th>
<th>X-ray density (g/cc)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>8.381</td>
<td>23.8</td>
<td>3.09</td>
<td>5.35</td>
<td>42.24</td>
</tr>
<tr>
<td>0.50</td>
<td>8.3963</td>
<td>20</td>
<td>3.37</td>
<td>5.33</td>
<td>36.83</td>
</tr>
</tbody>
</table>

The cation distribution in spinel ferrites has been the subject of immense interest among various researchers as the imperative properties of ferrites suitable for technological applications remarkably depend on the nature of the cation and the type of the interstitial site it dwells in. The site occupancy of a cation in the spinel lattice in general depends on several factors such as cation radius, crystal field effects, polarization effects, electrostatic energies, and temperature [9]. Moreover, finite particle size effects, methods of preparation, and sintering conditions play a vital role in deciding the site occupancy, wherein an inhomogeneous distribution is observed in several ferrispinels [10-12] with the cations occupying sites departing from their usual site preferences and thereby exhibiting several different structural, magnetic, and electrical properties at the nanoscale. Hence, in this study, examining the differences in the saturation magnetization, lattice strain, and lattice constant it is
required to propose a suitable cation distribution, which could suffice the observed results. The cation distribution in spinels can be well verified in a direct, easier, and straightforward manner using the method suggested by Buerger [13] using the XRD line intensities, because the intensities of the X-ray diffracted peaks depend directly on the position of the atoms in the spinel unit cell, whereas the position of the XRD lines depends on the size of the unit cell [14]. Hence, this method is widely utilized in determining the cation distributions in several systems. According to Buerger et al., the relative integrated intensity of X-ray reflections because of the lattice plane \((h k l)\) is according to the relation,

\[ I_{hkl} = |F_{hkl}|^2 \cdot P \cdot L_p \]

Where \(I_{hkl}\) is the relative integral intensity, \(F_{hkl}\) is the structure factor, \(P\) is multiplicity factor (no of lines in a family that have the same spacing) and \(L_p\) is the Lorentz polarization factor.

The obtained intensities are valid strictly at 0 K, whereas the diffraction pattern is recorded at room temperature, and hence a temperature correction might be necessary. However, the spinel ferrites, which are relatively high melting point oxides, the thermal vibration of atoms at room temperature would not significantly differ from that at 0 K. Hence, the intensity calculations were performed neglecting the temperature factor [15-16]. Best information regarding the distribution can be obtained on comparing experimental and calculated intensity ratios for reflections which are

(i) Nearly independent of the oxygen parameter,

(ii) Vary inversely with cation distribution,

(iii) Do not differ significantly [15].

In this study, the planes \((220), (422), (400), (440)\) are considered for cation distribution, as these planes are sensitive to distribution of cations among the tetrahedral and octahedral sites of the spinel lattice. The reflections from the planes \((220)\) and \((422)\) are sensitive to cations in the tetrahedral sites, whereas the reflections from the planes \((400)\) and \((440)\) are sensitive to cations on both the sites [14].
Therefore, the theoretical and experimental intensity ratios corresponding to I400/I422 and I220/I400 have been considered to arrive at an appropriate cation distribution. The structure factors (F_{hkl}) was calculated using the relations available in the literature [16-17] and are represented in the following equations.

\[ F_{220} = 8F_A \]
\[ F_{311} = 2\left(4F_A + 4\sqrt{2}F_B\right) \]
\[ F_{400} = \left(8F_A - 16F_B - 32F_O\right) \]
\[ F_{440} = \left(8F_A + 16F_B + 32F_O\right) \]

Where F_A is atomic scattering factor of tetrahedral (A) site, F_B is atomic scattering factor of octahedral (B) site and F_O is atomic scattering factor of oxygen. For cubic system the multiplicity factor P, the cation distribution of present system were reported in Table 3.2.

**Table 3.2: Cation distribution of Ni_{1-x}Zn_xFe_2O_4 (x=0.35 and 0.50)**

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>A-Site</th>
<th>B-Site</th>
<th>I_{400}/I_{422}</th>
<th>I_{400}/I_{422}</th>
<th>I_{220}/I_{400}</th>
<th>I_{220}/I_{400}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>Zn_{0.35}Fe_{0.65}</td>
<td>Ni_{0.65}Fe_{1.35}</td>
<td>0.867</td>
<td>1.068</td>
<td>1.109</td>
<td>0.827</td>
</tr>
<tr>
<td>0.50</td>
<td>Zn_{0.5}Fe_{0.4}Ni_{0.1}</td>
<td>Ni_{0.4}Fe_{1.6}</td>
<td>0.91</td>
<td>1.01</td>
<td>1.07</td>
<td>1.03</td>
</tr>
</tbody>
</table>

It is known that there is a correlation between the ionic radii of both A-and B-sublattices and the lattice parameter. Then, the lattice parameter can be calculated theoretically using the following equation [6].

\[ a_t = \frac{8}{3\sqrt{3}}(r_A + r_o) + \sqrt{3}(r_B + r_o) \]

Where r_o is the radius of the oxygen ion (1.38 Å) and r_A and r_B are the ionic radii of tetrahedral (A-site) and octahedral (B-site), respectively. The calculated values of theoretical lattice parameter were reported in Table 3.3. The obtained theoretical
lattice parameter ($a_{th}$) and experimental lattice parameter of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x=0.35$ and 0.50) ferrite are almost same. This indicates that the estimated cation distribution is valid.

The bond lengths ($d_{AL}$, $d_{BL}$) and shared ($d_{AE}$, $d_{BE}$), unshared bond edges ($d_{BEU}$) and Oxygen positional parameter of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x=0.35$ and 0.50) has been calculated by using the following relations.

$$d_{AE} = a_o \sqrt{2}(2u - 0.5)$$

$$d_{AL} = a_o \sqrt{3}(u - 0.25)$$

$$d_{BE} = a_o \sqrt{2}(1 - 2u)$$

$$d_{BEU} = a_o \sqrt{4u^2 - 3u + \frac{11}{16}}$$

$$d_{BL} = a_o \sqrt{3u^2 - \frac{11}{4}u + \frac{43}{64}}$$

$$u^{43_{m}} = 0.3876 \left(\frac{r_B}{r_A}\right)^{-0.07054}$$

Where $R$ is the ratio of the bond lengths at octahedral and tetrahedral sites respectively, given by,

$$R = \frac{(B-O)}{(A-O)} = \frac{r_B + R_O}{r_A + R_O}$$

Where $r_B$ is the average cation radii of B-site and $r_A$ is the average cation radii of A-site of proposed cation distribution and $r_O$ is the radius of Oxygen.

To shift the origin from tetrahedral site to octahedral site the following expression can be used.

$$u^{43_{m}} = u^{3_{m}} + \frac{1}{8}$$
The obtained values of shared tetrahedral edge (d$_{AE}$), octahedral edge (d$_{BE}$) and unshared octahedral edge (d$_{BEU}$), tetrahedral bond length (d$_{AL}$), octahedral bond length (d$_{BL}$), oxygen positional parameters of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) ferrite were reported in Table 3.3.

By using the experimental lattice constant ‘a$_{exp}$’ and oxygen positional parameter (u) various structural parameters such as cation-anion (M$_e$-O) (p, q, r and s), cation-cation (M$_e$-M$_c$) (b, c, d, e and f) distances and interionic bond angels ($\theta_1$, $\theta_2$, $\theta_3$, $\theta_4$ and $\theta_5$) were calculated using following standard relations [14].

**Interionic distances**

\[
b = \left(\frac{a}{4}\right)\sqrt{2}
\]
\[
c = \left(\frac{a}{8}\right)\sqrt{11}
\]
\[
d = \left(\frac{a}{4}\right)\sqrt{3}
\]
\[
e = \left(\frac{3a}{8}\right)\sqrt{3}
\]
\[
f = \left(\frac{a}{4}\right)\sqrt{6}
\]

**Interionic bond angles**

\[
\theta_1 = \cos^{-1}\left(\frac{p^2 + q^2 - c^2}{2pq}\right)
\]
\[
\theta_2 = \cos^{-1}\left(\frac{p^2 + r^2 - e^2}{2pr}\right)
\]
\[
\theta_3 = \cos^{-1}\left(\frac{2p^2 - b^2}{2p^2}\right)
\]
\[
\theta_4 = \cos^{-1}\left(\frac{p^2 + s^2 - f^2}{2ps}\right)
\]
\[
\theta_5 = \cos^{-1}\left(\frac{r^2 + q^2 - d^2}{2rq}\right)
\]
The changes in the bond lengths and bond angles between the cation-cation (Me-Me) (b, c, d, e and f) and cation-anion (Me-O) (p, q, r and s) alters the overall strength of the magnetic interactions such as A-A interaction, B-B interaction and A-B interaction. The bond angles and bond lengths between cation-anion and cation-cation are influence the magnetic interaction between sublattices. It is well known that the bond length inversely related to the strength of the magnetic interaction and also the bond angle is directly related to the magnetic interaction. The electromagnetic properties of ferrites are completely depending on the distance between magnetic ions over tetrahedral (A) and octahedral (B) sites. The obtained values of interionic distances and interionic bond angles were reported in Table 3.4 and Table 3.5 respectively.
Table 3.3: Compositional variation of $r_A$, $r_B$, $a_{Ba}$, $a_{La}$, $d_{Ba}$, $d_{La}$, $d_{BaE}$, $d_{LaE}$, $d_{BaFe}$, $d_{LaFe}$, $u_{A}$, $u_{B}$, $u_{BaE}$, $u_{LaE}$, $u_{BaFe}$, $u_{LaFe}$, $L_A$ and $L_B$ of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.35</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_A$</td>
<td>0.529</td>
<td>0.551</td>
</tr>
<tr>
<td>$r_B$</td>
<td>0.66</td>
<td>0.654</td>
</tr>
<tr>
<td>$a_{Ba}$</td>
<td>8.374</td>
<td>8.394</td>
</tr>
<tr>
<td>$a_{La}$</td>
<td>1.906</td>
<td>1.933</td>
</tr>
<tr>
<td>$d_{Ba}$</td>
<td>2.042</td>
<td>2.034</td>
</tr>
<tr>
<td>$d_{La}$</td>
<td>3.107</td>
<td>3.157</td>
</tr>
<tr>
<td>$d_{BaE}$</td>
<td>2.801</td>
<td>2.779</td>
</tr>
<tr>
<td>$d_{LaE}$</td>
<td>2.9651</td>
<td>2.971</td>
</tr>
<tr>
<td>$d_{BaFe}$</td>
<td>0.2566</td>
<td>0.2579</td>
</tr>
<tr>
<td>$d_{LaFe}$</td>
<td>0.3816</td>
<td>0.3829</td>
</tr>
<tr>
<td>$u_{A}$</td>
<td>3.6291</td>
<td>3.6356</td>
</tr>
<tr>
<td>$u_{B}$</td>
<td>2.9597</td>
<td>2.9597</td>
</tr>
<tr>
<td>$u_{BaE}$</td>
<td>0.3816</td>
<td>0.3829</td>
</tr>
<tr>
<td>$u_{LaE}$</td>
<td>0.2566</td>
<td>0.2579</td>
</tr>
<tr>
<td>$u_{BaFe}$</td>
<td>2.9651</td>
<td>2.971</td>
</tr>
<tr>
<td>$u_{LaFe}$</td>
<td>0.2566</td>
<td>0.2579</td>
</tr>
<tr>
<td>$L_A$</td>
<td>5.1323</td>
<td>5.1323</td>
</tr>
<tr>
<td>$L_B$</td>
<td>5.1323</td>
<td>5.1323</td>
</tr>
</tbody>
</table>

Table 3.4: Compositional variation of interionic distances of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.35</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
<td>2.04</td>
<td>2.0331</td>
</tr>
<tr>
<td>$q$</td>
<td>1.9102</td>
<td>1.9322</td>
</tr>
<tr>
<td>$r$</td>
<td>3.6578</td>
<td>3.6998</td>
</tr>
<tr>
<td>$s$</td>
<td>3.661</td>
<td>3.6738</td>
</tr>
<tr>
<td>$b$</td>
<td>2.9631</td>
<td>2.9685</td>
</tr>
<tr>
<td>$c$</td>
<td>3.4746</td>
<td>3.4809</td>
</tr>
<tr>
<td>$d$</td>
<td>3.6291</td>
<td>3.6357</td>
</tr>
<tr>
<td>$e$</td>
<td>5.4436</td>
<td>5.4436</td>
</tr>
<tr>
<td>$f$</td>
<td>5.1323</td>
<td>5.1323</td>
</tr>
</tbody>
</table>

Table 3.5: Compositional variations of interionic bond angles of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.35</th>
<th>0.50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_1$</td>
<td>144.1441</td>
<td>142.7733</td>
</tr>
<tr>
<td>$\theta_2$</td>
<td>93.165</td>
<td>93.8005</td>
</tr>
<tr>
<td>$\theta_3$</td>
<td>126.007</td>
<td>126.1468</td>
</tr>
<tr>
<td>$\theta_4$</td>
<td>73.986</td>
<td>72.916</td>
</tr>
<tr>
<td>$\theta_5$</td>
<td>54.986</td>
<td>54.986</td>
</tr>
</tbody>
</table>
3.2.2 FTIR studies

To verify the correctness of the proposed cation distribution using XRD and magnetization measurements, room temperature FT-IR spectral studies in the wavenumber range 300-1,000 cm\(^{-1}\) were performed on the sintered powders of Ni\(_{0.65}\)Zn\(_{0.35}\)Fe\(_2\)O\(_4\) and Ni\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\) were shown in Figure 3.3 and Figure 3.4 respectively. The spectra of all the as prepared powders show the existence of two principal absorption bands, in which one peak is concentrated at the wavenumber 400 cm\(^{-1}\), whereas the other peak is concentrated at ~600 cm\(^{-1}\). According to Waldron et al. [18], IR spectrum in inverse or normal spinels consists of two fundamental absorption bands in the wavenumber range 400-600 cm\(^{-1}\), corresponding to intrinsic vibrations of the Me–O bond in two different environments. The low frequency band \(\gamma_2\) concentrated at ~400 cm\(^{-1}\) is attributed to the stretching Me–O bonds at the octahedral sites, whereas the high frequency band \(\gamma_1\) positioned at ~600 cm\(^{-1}\) corresponds to the intrinsic stretching of the Me–O bonds at the octahedral sites. Such an IR wavenumber absorption difference can be expected, because of the difference in the bond length (Me–O) at both the sites. Smaller Me–O distance in the tetrahedral complex (~1.92 Å) than that in the octahedral complex (~2.03 Å) indicates a higher covalency between metal cations and surrounding oxygen at A-sites, and hence larger IR absorption frequency [19].

![FTIR spectra of Ni\(_{0.65}\)Zn\(_{0.35}\)Fe\(_2\)O\(_4\)](image)

**Figure 3.3:** FTIR spectra of Ni\(_{0.65}\)Zn\(_{0.35}\)Fe\(_2\)O\(_4\)
No splitting or the presence of additional shoulders in the IR absorption bands corresponding to $v_1$ and $v_2$ were observed for all the sintered powders, indicating a near absence of the Fe$^{2+}$ ions at both the octahedral and tetrahedral sites of the spinel lattice. This is due to the fact that local deformations can occur in the Fe$^{2+}$ ions because of the Jahn-Teller effect, which can lead to a noncubic component of the crystal field potential, and hence splitting of the band was not observed in this study [20].

The force constants of Ni-Zn ferrites systems were suggested by Waldron [13] for both tetrahedral and octahedral sites $K_t$ and $K_o$ respectively are calculated by using the following expressions.

$$K_t = 7.62 \times M_1 \times v_1^2 \times 10^{-3} \text{ dynes/cm}$$

$$K_o = 10.62 \times \frac{M_2}{2} \times v_2^2 \times 10^{-3} \text{ dynes/cm}$$

Where, $M_1$ and $M_2$ are molecular weights of cations on A and B sites respectively. The force constants in Table 3.6 usually represent the strength of the bonding and vary with the cation site radius. The higher force constant at the octahedral sites is ascribed to the fact that under favorable conditions the oxygen ions can form bonds even at larger internuclear separations.
Table 3.6: Force constants of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50)

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$K_1 \times 10^5$ dyne/cm</th>
<th>$K_0 \times 10^5$ dyne/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>577</td>
<td>467</td>
<td>1.501</td>
<td>1.314</td>
</tr>
<tr>
<td>0.50</td>
<td>569.98</td>
<td>403.13</td>
<td>1.507</td>
<td>0.973</td>
</tr>
</tbody>
</table>

3.2.3 Scanning Electron Microscopy (SEM) studies

Study of Micro structure is very important to understand the electrical properties of polycrystalline ferrites. The scanning electron microscopic (SEM) images of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) ferrite sintered at different sintering temperatures was shown in Figure 3.5 (a-b). From SEM images it was observed that sintered samples contain grooves, pores, layers, cracks and sheet like patterns having some small aggregations within the available resolution. The observed sheet like structures gradually decreases to increasing of sintering temperature which leads to increase in grain size with increasing of sintering temperature. The grain size of all samples measured by linear intercept method [21]. The obtained values are found to be in the range of below 200 nm. The obtained grain size values are very smaller than those reported in conventionally synthesized ferrites [22]. The observed smaller grain size values of sintered pellets can be explained on the basis of open and closed pores in the microstructure. Open pores are more effective at pinning than closed pores to restrict the growth of grain [23].
Figure 3.5: SEM images of (3.5.a) Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ and (3.5.b) Ni$_{0.5}$Zn$_{0.5}$Fe$_2$O$_4$
3.3 Electrical properties

3.3.1 Dc electrical properties

Electrical resistivity is an important property of ferrite for MLCI application. The substitution of Zn ion improves the electrical resistivity. The study on electrical resistivity in mixed ferrites was extensively made by Verwey et. al. [24], Van Uitert [25]. The conduction mechanism in ferrites is attributed to hopping of electrons between the ions of the same element present in more than one valence state randomly over crystallographic ally equivalent lattice sites. Since the distance between B-B state in spinel structure is smaller than the distance between A-A sites which is smaller than the distance between A and B sites, the probability of hopping taking place is the greatest at octahedral sites. The hopping probability depends on (i) separation between the ions and (ii) the activation energy. Figure 3.6 depicts the Dc electrical resistivity as a function of temperature. It is clear that the resistivity is increased with increasing of Zn concentration. The activation energies are calculated and are found to be in the range 0.65 and 0.53 for x=0.35 and x=0.50 samples respectively.

![Figure 3.6: 1000/T vs log_e(ρ) of Ni_{1-x}Zn_xFe_2O_4 samples (x=0.35 and 0.50)]
3.3.2 Dielectric properties

The spinel ferrites usually exhibit a high dielectric constant at lower frequencies and the dielectric properties of these ferrites are very sensitive to method of preparation, grain size, heat treatment temperature and the cation distribution. The dielectric constant of the Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite samples (x=0.35 and 0.50) sintered at 900 °C has been calculated by using the following relation,

$$\varepsilon' = \frac{C d}{\varepsilon_0 A}$$

Where $\varepsilon'$ is the dielectric constant, C is the capacitance, “A” and “d” are the area and thickness of the sample and $\varepsilon_0$ is the permittivity of free space.

The dielectric loss tangent of the material is calculated by following relation.

$$\tan \delta = \frac{\varepsilon'}{\varepsilon''}$$

Where $\varepsilon'$ is the dielectric constant and $\tan \delta$ is dielectric loss tangent of the material.

The ac conductivity of the all samples were calculated from the known values of dielectric constant, dielectric loss tangent, permittivity of free space and applied frequency using the relation

$$\sigma_{ac} = \omega \varepsilon_0 \varepsilon'. \tan \delta$$

The variation of the room temperature dielectric constant, dielectric loss tangent and a.c resistivity of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite (x=0.35 and 0.50) samples with frequency were shown in Figure 3.7, Figure 3.8 and Figure 3.9 respectively. The decrease in dielectric constant with the increase of frequency of the samples shows a normal dielectric behavior and in accordance with the Maxwell-Wagner theory of interfacial polarization [26]. The dielectric dispersion is clearly observed in low frequency region and at high frequencies; the dielectric dispersion is almost independent of the frequency of the applied field. The dielectric constant of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) samples were observed to increase with the increase in the concentration of Zn ions.
Figure 3.7: frequency variation of dielectric constant of \( \text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \) 
\((x=0.35 \text{ and } 0.50)\) ferrite

Figure 3.8: frequency variation of dielectric loss tangent of \( \text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4 \) 
\((x=0.35 \text{ and } 0.50)\) ferrite
The dielectric loss tangent as a function of frequency is depicting in Figure 3.8. It is clear that the loss tangent has been found to be very low and decreases with increasing frequency for all the samples. Dielectric loss tangent arises when the polarization lag behind the applied alternating field which is caused by the impurities and imperfections in the crystal.

The mechanism involved in ac resistivity and dielectric constant is similar lines, since both are electrical transport properties. The interdependency of these properties is confirmed by many researchers [27]. The room temperature frequency variation of ac resistivity of Zn substituted Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x=0.35 and 0.50) ferrite was shown in Figure 3.9. From the Figure 3.9 it is very clear that the ac resistivity is decreased with increasing of frequency.
3.4 Magnetic properties

The M-H loops of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x=0.35$ and $0.50$) recorded at room temperature Figure 3.10 shows a nonsaturated specific magnetization of as obtained powders even under a high magnetic field of 1.5T. The samples showed a near magnetic saturation, and a complete saturation of the M-H loop was observed.

![M-H loops of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$](image)

Figure 3.10: Saturation magnetization of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x=0.35$ and $0.50$) ferrite

The observed values of saturation magnetization are 59.68 and 61 emu/gm for $x=0.35$ and $x=0.50$ respectively. The lower saturation magnetization was observed Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ $x=0.35$ (59.68emu/gm) and 0.50 (61 emu/gm) ferrite nanoparticles compared to the bulk (70 emu/gm) is attributed to the finite particle size effects arising at the nanoscale. Saturation magnetization curves of all the samples exhibit soft ferromagnetic behaviour with low coercivity.

The experimental magnetic moment ($n_B$) is determined from the saturation magnetization data using the following formula

$$n_B (\mu_B) = \frac{M.Wt \times M_s}{5585}$$
Where M.Wt is the molecular weight of the sample and $M_S$ is the saturation magnetization in emu/g. From the values of saturation magnetization it is clear that the magnetization increases with increasing Zn concentration. This observed variation in the saturation magnetization can be understood from the Neel’s two sub-lattice model [28]. In spinel ferrites the magnetization is known to be strongly influenced by the exchange interaction between the magnetic ions in the tetrahedral (A) and octahedral (B) crystallographic sites i.e. inter sub-lattice interaction between (A-B) and inter sub-lattice exchange interaction between (A-A) and (B-B). Among these three exchange interaction, intra sub-lattice interaction (A-B) is predominant over inter sub-lattice interactions. Therefore the resultant magnetic moment is the difference between magnetic moment of A and B sites i.e. $M_B - M_A$. In general, as discussed above Zn$^{2+}$ ions are preferentially occupying A-sites while Ni$^{2+}$ and Fe$^{3+}$ ions have a strong preference to occupy the B-sites [29]. It is known that the magnetic moment of Ni$^{2+}$ in spinel ferrite is 3µB [30]; however, the magnetic moment of Zn$^{2+}$ (0µB) and Fe$^{3+}$ (5µB). In the present work as Zn ions occupy A-site results in the migration of some of the Fe$^{3+}$ ions in to octahedral sites. This arrangement decreases the magnetic moment of A–site and increases net magnetic moment. The uncompensated electron spin in spinel ferrites results in net magnetic moment. In present work substitution of Zn enhancing the magnetization.
3.5 References


