Estimating the Cation Distributions in Ni$_{0.65-x}$Zn$_{0.35}$Co$_x$Fe$_2$O$_4$ Ferrites Using X-Ray, FT-IR, and Magnetization Measurements

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The fundamental requirements for the shift of critical frequency to microwave frequencies are smaller grains with single domain, high resistivity, high saturation magnetization, moderate permeability, moderate magnetic anisotropy, and low spin relaxation time. With these guidelines an attempt to produce high performance ferrite for high frequency applications the present work aimed to synthesize cobalt substituted Ni-Zn ferrites using sol-gel method. Investigation of effects of cobalt on crystallite size, saturation magnetization, initial permeability, magnetic anisotropy, and spin relaxation time reveal the suitability of these materials for high frequency applications. Further in this paper cation distribution was proposed from the basis of variations in these properties. The results of this paper are thus useful to tailor the properties apt for high frequency applications.

1. Introduction

Ferrites are the most widely used cores in high frequency power electronics, broadband transformers, pulse transformers, antennas, and sensors because of their excellent magnetic and electrical properties. The extensive study on mixed ferrite systems revealed that Ni-Zn ferrite was the only core material suitable for high frequency applications up to 100 MHz due to its high value of saturation magnetization, moderate permeability, and high resistivity. The increasing demand for materials with improved efficiency and reduced size and cost necessitates high operational frequencies beyond 100 MHz. However, at higher frequencies, magnetic cores with improved resistivity, high saturation magnetization, and high permeability are inevitable to minimize eddy current losses and magnetic losses [1–4]. The high frequency limit for ferrites is governed by Snoek’s law according to which there exists an effective limit for the product of critical frequency and permeability [5]. The limiting frequency is controlled by spin rotation of domains and as such the use of ferrite core in the GHz range is considered to be a complicated task. The recent developments in nanotechnology signify that the electrical resistivity can be increased manyfold with the generation of a vast number of grains and grain boundaries if the material is produced in nanoform [6, 7]. The improvement in saturation magnetization can be achieved by modifying the crystallite size of the material comparable to characteristic length, a responsible parameter for exchange coupling to take place among the nanograins [8, 9]. The efficient performance of the core at higher frequencies is expected to be synchronized with the rotation of domains under a small AC field and the process of rotation is known to be critically affected by magnetic anisotropy [10]. The magneto crystalline anisotropy determines the direction and stability of the magnetization within the material. Critical size below which a spherical particle exists as a single-magnetic domain depends on magnetic anisotropy. Also, the coercivity and the permeability are controlled by the magnetic anisotropy constant. Thus in order to shift the critical frequency of operation to GHz range, it is necessary to achieve the best
combination between saturation magnetization, resistivity, particle size, and initial permeability which requires a wide range of variations in magnetic anisotropy.

Cobalt ions with their slight higher magnetic moment as compared to that of nickel have a tendency to occupy both tetrahedral (A) and octahedral (B) interstitial sites of nickel zinc ferrite keeping the majority of cobalt ions at B-site [II]. The presence of cobalt at B-site, in general, produces a large positive magnetic anisotropy due to trigonal distortion of the lattice [12, 13]. The incorporation of cobalt in nickel zinc ferrite of negative uniaxial anisotropy ensures the combination of low or vanishing magneto crystalline anisotropy and adjustable induced anisotropy. The wide range of variation (small negative value to high positive value) in magnetic anisotropy due to cobalt substitution in nickel zinc ferrites permits understanding clearly the changes taking place in saturation magnetization, coercivity, and initial permeability with reference to shift of critical frequency.

2. Experimental

The method of preparation of samples was described elsewhere [14]. The XRD measurements were carried out using Bruker D8 Advance X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha) and 0.178 (Co K-alpha). The X-rays were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector). The TEM (Hitachi H-7500) at required magnifications is used on silicon strip technology (Bruker LynxEye detector). The X-rays were produced using a sealed tube and the wavelength of X-ray was 0.154 nm (Cu K-alpha) and 0.178 (Co K-alpha). The X-rays were detected using a fast counting detector based on silicon strip technology (Bruker LynxEye detector). The TEM (Hitachi H-7500) at required magnifications is used on silicon strip technology (Bruker LynxEye detector). The accuracy of the measurement was found to be about ±2°C.

3. Results and Discussions

3.1. X-Ray Diffraction Analysis. X-ray diffraction patterns of Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ and Ni$_{0.65-x}$Zn$_{0.35}$Co$_x$Fe$_2$O$_4$ samples are shown in Figures 1(a) and 1(b). The intense sharp peaks indicate well crystalline single phase spinel structure. No peaks corresponding to any additional crystalline component are detected in the patterns. The peaks observed in the pattern matched well with characteristic reflection of Ni-Zn JCPDS Card number 08-0234. Accurate estimation of lattice constant has been done from the extrapolation of calculated lattice constant against the Nelson-Riley function [16]:

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

for which the function is zero. The crystallite size ($D$) for all the samples was calculated from X-ray peak broadening of the (3 1 1) peak using Scherrer’s formula from the full width at half maximum (FWHM) given by

$$D = \frac{0.9 \lambda}{\beta \cos \theta},$$

where $\lambda$ is the wavelength of Cu $K_a$ (1.5406 Å), $\theta$ is the angle of the Bragg diffraction, and $\beta$ is the full width at half maximum corrected by the given instrumental line broadening. Figures 2(a) and 2(b) show the variation of lattice constant and crystallite size with cobalt concentration.

An increase in lattice constant from 8.3708 Å to 8.384 Å as shown in Figure 2(a) is noticed with increasing cobalt substitution. Because the ionic radius of Co$^{2+}$ ion (0.745 Å) is greater than that of Ni$^{2+}$ ion (0.69 Å) [17, 18] the replacement

![Figure 1: (a) X-ray diffraction patterns of Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$. (b) X-ray diffraction patterns of Ni$_{0.65-x}$Zn$_{0.35}$Co$_x$Fe$_2$O$_4$ (x = 0.04 to 0.28).](image-url)
of Ni$^{2+}$ by Co$^{3+}$ ions is expected to increase the lattice constant of ferrite samples. The crystallite size was observed to increase from 99 nm to 111 nm (Figure 2(b)) with increasing cobalt content. The steep increase in crystallite size has been noticed for initial concentrations and a small increase at higher concentrations. The observed increase in crystallite size is may be due to increase in the dimension of the unit cell with replacement of Ni$^{2+}$ by Co$^{3+}$ ions.

3.2. Transmission Electron Microscopy. Transmission electron micrographs of basic and cobalt substituted nickel-zinc ferrites annealed at 1000°C are shown in Figures 3(a) to 3(h). The average particle size has been estimated from volume averages of number of TEM pictures for a particular sample. Figure 2(b) shows the variation in particle size with cobalt concentration. The increase in particle size can be attributed to the agglomeration of particles besides an increase in lattice parameter. The observed increase in magnetic moment with increase in cobalt concentration also supports the agglomeration of particles. The particle size has been observed to be higher than the crystallite size for any cobalt substituted ferrite composition and the difference may be attributed to agglomeration of particles due to increase in saturation magnetization as evident from TEM pictures.
Table 1: Saturation magnetization ($M_s$), magnetic moment per formula unit in the Bohr magneton ($n_B$), coercivity ($H_c$), residual magnetization ratio ($M_r/M_s$), and anisotropy constant ($K$) for Ni$_{0.65-x}$Zn$_{0.35}$Co$_x$Fe$_2$O$_4$ system.

<table>
<thead>
<tr>
<th>x</th>
<th>Particle size (nm)</th>
<th>$M_s$ (emu/gm)</th>
<th>$H_c$ (Oe)</th>
<th>$K$ (erg/cm$^3$)</th>
<th>$M_r$</th>
<th>$n_B$</th>
<th>$M_r/M_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>114.4</td>
<td>71.0</td>
<td>30.8</td>
<td>1122</td>
<td>5.1</td>
<td>3.01</td>
<td>0.071</td>
</tr>
<tr>
<td>0.04</td>
<td>113.4</td>
<td>72.0</td>
<td>30.0</td>
<td>1102</td>
<td>4.8</td>
<td>3.05</td>
<td>0.065</td>
</tr>
<tr>
<td>0.08</td>
<td>149.2</td>
<td>73.3</td>
<td>34.5</td>
<td>1233</td>
<td>5.6</td>
<td>3.10</td>
<td>0.078</td>
</tr>
<tr>
<td>0.12</td>
<td>208.4</td>
<td>74.1</td>
<td>42.9</td>
<td>1595</td>
<td>6.1</td>
<td>3.14</td>
<td>0.082</td>
</tr>
<tr>
<td>0.16</td>
<td>214.4</td>
<td>75.9</td>
<td>44.1</td>
<td>1652</td>
<td>6.8</td>
<td>3.21</td>
<td>0.090</td>
</tr>
<tr>
<td>0.20</td>
<td>224.1</td>
<td>76.0</td>
<td>49.0</td>
<td>1872</td>
<td>9.4</td>
<td>3.22</td>
<td>0.123</td>
</tr>
<tr>
<td>0.24</td>
<td>228.5</td>
<td>77.0</td>
<td>63.7</td>
<td>2427</td>
<td>10.2</td>
<td>3.26</td>
<td>0.133</td>
</tr>
<tr>
<td>0.28</td>
<td>286.2</td>
<td>78.0</td>
<td>79.3</td>
<td>3131</td>
<td>10.4</td>
<td>3.30</td>
<td>0.132</td>
</tr>
</tbody>
</table>

Figure 4: FT-IR absorption spectra of Ni$_{0.65-x}$Co$_x$Zn$_{0.35}$Fe$_2$O$_4$ ferrites.

3.3. Fourier Transform Infrared Analysis. The Fourier transform infrared spectra of all the samples in the range 400 cm$^{-1}$–4000 cm$^{-1}$ are shown in Figure 4. It is well known that normal and inverse cubic spinels have two fundamental absorption bands: the first band is due to tetrahedral and the second is due to octahedral complexes. Further, the first band observed at higher frequency of $\sim$590 cm$^{-1}$ ($\nu_1$) is attributed to the stretching vibration of tetrahedral group Fe$^{3+}$O$^{2-}$ and the second band observed at lower frequency of $\sim$405 cm$^{-1}$ ($\nu_2$) is attributed to the stretching vibration of octahedral group Fe$^{3+}$O$^{2-}$.

The existence of two wide bands $\nu_1$ and $\nu_2$ reveals that these samples are single phase spinel ferrites. In the spectra it has been observed that both $\nu_1$ and $\nu_2$ shift slightly towards lower frequencies but not in a systematic trend with Co addition. The difference in frequencies between $\nu_1$ and $\nu_2$ may be attributed to the changes in bond lengths (Fe$^{3+}$O$^{2-}$) within the tetrahedral and octahedral sites [22]. The IR bands and their intensities for all samples under investigation are plotted with cobalt content x and are shown in Figure 5(a).

The force constant ($F_k$) decreases (Figure 5(b)) with increasing cobalt content. As larger radius Co$^{2+}$ ions replace the smaller Ni$^{2+}$ ions, the bond lengths at both A- and B-sites increase consequently the decrease in force constant at both sites.

The observed variations in wave numbers ($\nu_1$, $\nu_2$) and force constant at both sites indicate the tendency of cobalt ions to occupy both A- and B-sites.

3.4. Magnetic Properties. Room temperature hysteresis loops of Ni-Co-Zn ferrites recorded up to 20 kOe (Figure 6) indicate narrow hysteric soft ferromagnetic behaviour with increasing coercivity. The magnetic properties associated with the hysteresis loops such as particle size, saturation magnetization $M_s$, remnant magnetization $M_r$, coercivity $H_c$, and the loop squareness ratio ($M_r/M_s$) values of ferrite samples are listed in Table 1.

The dependence of saturation magnetization and coercivity as a function of Co$^{2+}$ concentrations is shown in Figure 7. An increase in saturation magnetization and coercivity is noticed with increasing cobalt concentration. The observed variations can be understood on the basis of super exchange interactions among the tetrahedral (A) and octahedral (B) site ions in the spinel lattice [24]. Saturation magnetization depends on the type and the number of ions located at the tetrahedral (A) and octahedral (B) sites in the spinel structure because this distribution affects the magnetizations, $M_A$ and $M_B$ of the A and B sublattices, respectively. The net magnetization is given as $M_B - M_A$. The Zn$^{2+}$ and Ni$^{2+}$ ions have strong preferences for the A- and B-sites, respectively; while the Fe$^{3+}$ ions are distributed over both sites [25]. Co$^{2+}$
ions also tend to occupy both sites [18]. When the cobalt ions are introduced in the spinel lattice replacing nickel ions, some of the cobalt ions entering into A-sites tend to push some of the iron ions into B-sites. These iron ions migrating from A-sites to B-sites and the cobalt ions (3μ₉) entering directly into B-sites in place of nickel ions (2μ₉) collectively increase the magnetic moment of the B sublattice.

As cobalt ions produce large anisotropy in Ni-Zn ferrite [26, 27], magneto crystalline anisotropy has been estimated from the following formula:

$$H_c = \frac{2K}{M_s}$$  \hspace{1cm} (4)

where $M_s$ is saturation magnetization and $H_c$ is coercive field. The magnetic anisotropy increases with increasing cobalt concentration as shown in Figure 8. The magnetic anisotropy is directly proportional to the coercive force and a large variation in coercive force has been noticed with increasing cobalt concentration. The large increase in magnetic anisotropy for higher cobalt concentrations suggests that higher amount of cobalt tends to occupy B-site.

A gradual decrease in Curie temperature has been noticed with increasing cobalt concentration as shown in Figure 8. The observed changes in Curie temperature have been explained on the basis of super-exchange interactions among A- and B-sites in the spinel lattice.

The exchange interaction between ions lying on A- and B-sites depends on the magnetic moments of the ions occupying the sublattices and the distance between the ions. The distance between the A- and B-sites increases with the occupancy of cobalt ions at both the sites consequently weakening the A-B super-exchange interactions [28, 29]. Therefore the thermal energy required to offset the alignment of the magnetic moment decreases, leading to decrease in Curie temperature. Another factor which determines the Curie temperature is the stabilizing energy of the ions occupying a particular site. Cobalt ions have lesser values of stabilization energies at B- and A-sites compared to those of nickel ions. The decrease in stabilization energy results in the decrease of Curie temperature.

3.5. Cat Ion Distribution. It is well known that Zn²⁺ ions have strong preference for A-site and Ni²⁺ and Co²⁺ ions have preference for the B-site while Fe³⁺ ions occupy both A- and B-sites. On the basis of this site preference and from the variations in wave numbers ($v_1, v_2$), force constant, saturation

![Figure 5](image1.png)

**Figure 5:** (a) Variation in wave number at $A$- and $B$-sites with cobalt concentration. (b) Variation in force constant at $A$- and $B$-sites with cobalt concentration.

![Figure 6](image2.png)

**Figure 6:** Hysteresis loops of cobalt substituted Ni-Zn ferrites.
Table 2: Estimated cation distribution of the ferrite Ni$_{0.65-x}$Zn$_{0.35}$Co$_x$Fe$_2$O$_4$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>A-site</th>
<th>$B$-site</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>Ni ($y$)</td>
</tr>
<tr>
<td>0.0</td>
<td>0.35</td>
<td>0.015</td>
</tr>
<tr>
<td>0.04</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>0.08</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>0.12</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>0.16</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>0.20</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>0.24</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>0.28</td>
<td>0.35</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 7: Saturation magnetization and coercivity of cobalt substituted Ni-Zn ferrites.

magnetization, and magnetic anisotropy an approximate cation distribution for the series has been proposed (Table 2).

The mean radii of the tetrahedral and octahedral sites ($r_A$ and $r_B$) are calculated using the following expressions and plotted as a function $x$, depicted in Figure 6:

\[
\begin{align*}
    r_A &= 0.35r_{\text{Zn}} + yr_{\text{Ni}} + zr_{\text{Co}} + (0.65 - y - z) r_{\text{Fe}}, \\
    r_B &= \frac{1}{2} \left( (0.65 - y - x) r_{\text{Ni}} + (x - z) r_{\text{Co}} + (1.35 + y + z) r_{\text{Fe}} \right).
\end{align*}
\]

To ensure the exactness of the proposed distribution, lattice constant for the Ni-Co-Zn ferrite has been estimated theoretically using $r_A$ and $r_B$ from the following relation:

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

where $R_O$ is the radius of oxygen ion.

A close agreement between the theoretical lattice constant and experimental lattice constant from X-ray diffraction measurements (Figure 2(a)) shows the correctness of the proposed distribution.

The entry of cobalt into both the sites has been further verified calculating bond lengths ($d_{AO}$, $d_{BO}$) and site edges ($d_{AE}$, $d_{BE}$, and $d_{BEU}$) of the spinel lattice considering theoretical lattice constant and oxygen parameter. The oxygen parameter $u$ can be determined using the relation

\[
r_A = a\sqrt{3} (u - 0.25) - R_O. \tag{7}
\]

For face centered cubic structure the value of oxygen parameter is 0.375. The values of “$u$” obtained are higher than this value. Substitution of larger radius ion will cause distortion in the cubic lattice and therefore the oxygen parameter may differ from its usual value 0.375. The increase in $u$ reveals the increasing effect of that trigonal distortion at $B$-sites [17].

The tetrahedral and octahedral bond lengths ($d_{AO}$, $d_{BO}$) were obtained using the relations [18]

\[
\begin{align*}
    d_{AO} &= a\sqrt{3} (u - 0.25), \\
    d_{BO} &= a\left( 3u^2 - \frac{11}{4} u + \frac{43}{64} \right)^{1/2}. \tag{8}
\end{align*}
\]

The tetrahedral edge $d_{AE}$, octahedral edge $d_{BE}$, and unshared edge $d_{BEU}$ have been calculated using the relations

\[
\begin{align*}
    d_{AE} &= a\sqrt{2} (2u - 0.25), \quad d_{BE} = a\sqrt{2} (1 - 2u), \\
    d_{BEU} &= a\left( 4u^2 - 3u + \frac{11}{16} \right)^{1/2}. \tag{9}
\end{align*}
\]
The hopping lengths $L_A$ and $L_B$ between the magnetic ions at the A-site and B-sites were estimated using the relations (see [22, 23])

$$L_A = \frac{a\sqrt{3}}{4}, \quad L_B = \frac{a\sqrt{2}}{4}.$$ (10)

The obtained values of $u$ and other above mentioned parameters are represented in Figures 9 and 10. These plots indicate that tetrahedral bond length $d_{AO}$, tetrahedral edge $d_{AE}$, and unshared octahedral edge $d_{BEO}$ meagerly increase with increase in $x$. Octahedral bond length $d_{BO}$ and octahedral edge $d_{BE}$ increase profusely with increasing Co$^{2+}$ substitution (Figure 11). From this fact it can be concluded that relatively larger quantity of cobalt enters into B-sites compared to that of A-sites. Similar observation is also reflected in variation in hopping lengths (Figure 12) with increasing cobalt content.
The number of Bohr magnetons per formula unit is calculated by considering saturation magnetization and molecular weight of each composition using the following relation [30]:
\[
n_B = \frac{M_s \times \text{Mol.wt}}{5585}. \tag{11}\n\]

The trends in the variation in number of Bohr magnetons per formula unit obtained from the proposed cation distribution and that from the saturation magnetization measurements are found to be in agreement (Figure 13). The difference in value of the number of Bohr magnetons is due to the fact that the number of Bohr magnetons obtained from the saturation magnetization measurements is at room temperature and that obtained from cation distribution calculations corresponds to low temperature.

4. Conclusion

In the present paper the effect of cobalt substitution on structural and magnetic properties in Ni\(_{0.65-x}\)Zn\(_{0.35}\)Co\(_x\)Fe\(_2\)O\(_4\) ferrites has been investigated. XRD patterns revealed the formation of single phase cubic spinel structure. X-ray analysis, FT-IR, theoretical lattice constant calculations and saturation magnetization measurements suggest that Co\(^{2+}\) ions occupy both tetrahedral (A) and octahedral (B) sites from which Cation distribution for Ni\(_{0.65-x}\)Zn\(_{0.35}\)Co\(_x\)Fe\(_2\)O\(_4\) is proposed. The site occupancy of cations helps in understanding the variation in magnetic anisotropy and hence permits understanding clearly the changes taking place in saturation magnetization, coercivity, and initial permeability with reference to shift of critical frequency.

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