Chapter - 3

Synthesis and Characterization of Ni²⁺ Substituted Cobalt Ferrite Nanoparticles

This chapter presents detailed study of structural, electrical and magnetic properties of a series of polycrystalline $\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ni}_{0.5+1.0x}\text{O}_{4}$ ($0.0 \leq x \leq 0.4$) ferrite nanoparticles, prepared through sol-gel auto combustion process. The effect of Ni substitution in $\text{Co}_{0.5}\text{Fe}_{2-x}\text{Ni}_{0.5+1.0x}\text{O}_{4}$ has been studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), vibrating sample magnetometer (VSM), Fourier transform infrared spectroscopy (FTIR), frequency dependent dielectric and impedance spectroscopy and Mössbauer spectroscopy techniques.
3.1 Introduction

The design, characterization, synthesis and application of materials, devices and systems with control and having a fundamental organization in nanometric dimensions is ever expected challenges for researchers. In this range, some of the properties of materials such as optical, magnetic and electrical alter in surprising ways. This results in exciting different characteristics that can produce a vast array of novel products. Nanocrystalline materials show properties vastly superior to those exhibited by single crystalline, conventional polycrystalline and amorphous materials. The study of ferrites on nanometer scale have generated more interest as well as curiosity in the scientific community to understand the basic physics of the ferrites, involving drastic changes in electrical and magnetic properties due to the change in size and their potential applications in modern technology. Ferrite nanoparticles are gaining attraction due to many important applications such as: tone generating circuitry of push button telephones, load coils in transmission lines to reduce signal loss over long distances, ferrofluids, magnetic drug delivery, hyperthermia for cancer treatment, high density information storage system, magneto caloric refrigeration, medical diagnostics, magnetic resonance imaging enhancement and gas sensors [1,2].

The properties of ferrite nanoparticles are strongly influenced by the composition and microstructure, which are sensitive to the preparation methodology used in their synthesis [3,4]. Spinel ferrites are one of the best semiconductors which have great importance in telecommunication, microwave and electronic engineering. The synthesis of spinel ferrite nanoparticles has been intensively studied in the recent years and the principal role of the preparation conditions on the morphological and structural features of the ferrites is discussed. Many reports proved that the property of spinel ferrites can be improved by doping metal elements in $\text{MFe}_2\text{O}_4$. There are several different synthesis methods used to generate ferrites as reported in the literature including sol-gel [5], co-precipitation [6], hydrothermal [7], mechanochemical [8], refluxing [9], precursor [10] and auto-combustion [11], citrate gel auto combustion [12] methods. The role of substituent in modifying the properties of basic ferrites has been widely studied. Development of high quality, low cost and low loss at high frequency ferrite material for power applications is an ever challenging aspect for researchers.
The cobalt ferrite (CoFe2O4) material is considered to be mostly an inverse spinel structure represented as (Co2Fe1-x)[Co1-xFe1-x]O4, where x depends on thermal treatment and preparation conditions [13]. Nickel ferrite (NiFe2O4) is an important member of the spinel family and it is found to be the most versatile technological materials suited for high-frequency applications due to its high resistivity. In the bulk state, this material possesses an inverse spinel structure, in which tetrahedral (A) sites are occupied by Fe3+ ions and octahedral (B) sites by Fe3+ and Ni2+ ions. It exhibits ferrimagnetism that originates from the antiparallel orientation of spins on (A) and (B) sites [14, 15]. Recently, the preparation methods and applications of one-dimensional (1D) Ni-Co alloy materials have been paid to more attention due to their unique properties of low dimensionality [16-17]. As important magnetic materials, Ni-Co alloys have potential application in ferrofluids technology, microwave absorber and electromagnetic shielding material. In the present work we have substituted Ni ions for Fe ions; this could affect the structural, electrical and magnetic properties of Co-ferrite. Ni2+ ions will control the magnetic properties with its lower magnetic moment and may alter the saturation magnetization and remanent ratio. At the same time Ni2+ ions will modify the resistivity and dielectric properties of the compound. These modifications in the properties of Co-Ni ferrite could be important from the point of view for their above mentioned applications. This work is to demonstrate a general, efficient and environmental friendly synthetic strategy for obtaining Co0.5Fe2.5Ni0.5+1.5xO4 (0.0 ≤ x ≤ 0.4) microspheres via a simple sol-gel auto combustion method. The structural, electrical and magnetic studies of the spinel Co-Ni ferrite microspheres were investigated. The inspiration behind this research in pure and Ni2+ doped cobalt ferrite nanoparticles was: (i) to proliferate the nanoparticles of the ferrite materials, as it is well recognized from the literature that the size discomfiture introduce the phenomenal changes in the physical and transport properties of materials. (ii) it is well known that doping of various elements in ferrite enhances their structural, electrical and magnetic properties. Among the various spinel ferrites, we have chosen cobalt ferrite matrix because cobalt ferrite has large magnetocrystalline anisotropy and high coercivity, which has applications in high density recording media, high performance electromagnetic and spintronic devices. Such properties of cobalt ferrite suggest that this material is a good aspirant for the various technological applications. Therefore,
by keeping this view, we have proposed this material and the detailed investigations are presented in this chapter.

3.2 Results and Discussion

3.2.1 Structural Properties

3.2.1.1 X-ray Diffraction

The structure and phase purity of as prepared products were confirmed by analyzing the observed powder X-ray diffraction (XRD) patterns. Fig. 3.1 depicts the observed powder XRD patterns of the Co$_{0.5}$Fe$_{2-x}$Ni$_{0.5+x}$O$_4$ (0.0 ≤ x ≤ 0.4) compositions. All the observed reflections of the Ni substituted cobalt ferrite samples could be assigned to cubic spinel lattice indicating their single phase nature. The planes (2 2 0), (3 1 1), (2 2 2), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) in the diffraction patterns confirm the formation of pure cubic spinel ferrite structure. The broadened diffraction peaks can be attributed to the nanocrystallite size of as prepared product. Unit cell parameters i.e. lattice constant (a) were determined by indexing the observed reflections of the XRD patterns. The variation of lattice constant 'a' with the Ni$^{2+}$ doping is determined from the XRD data and is shown in Fig. 3.1. It is observed that the unit cell parameter of the Ni substituted Co ferrite phase gradually increases with increasing Ni content in the composition, obeying Vegard's law. The slow linear increasing trend in the unit cell parameter is attributed to the replacement of Fe$^{3+}$ (0.67 Å) ion by Ni$^{2+}$, a slightly larger ion (0.69 Å). The average crystallite size of the nano phase particles was determined by using the Debye-Scherrer formula [18];

$$t = \frac{0.98\lambda}{\beta\cos\theta}$$  \hspace{1cm} (3-1)

where 0.98 is the Scherrer's constant, \(\lambda\) is the wavelength of the CuK\(\alpha\) radiation (\(\lambda=1.5406\) Å) and \(\beta\) is the full width at half maximum (FWHM) in radians calculated using Gaussian fitting and \(\theta\) denotes the Bragg angle. The average crystallite size as shown in Fig. 3.2 decreases from 43 to 22 nm with increase in Ni$^{2+}$ substitution. This effect is due to the precipitation of Ni$^{2+}$ ions on the grain boundary during sintering leading to the reduction of grain size which favoured the formation of new nuclei preventing further growth of particles. Hence, preparation condition plays an effective role to control the particle size. The variation of lattice parameter will
lead to the lattice strains which produce internal stress [19]. Such stress binder the growth of grains, and the grains size of the samples doped with Ni$^{2+}$ become smaller than that of Co-Ni ($x = 0.0$) ferrite.

![Fig.3.1: Powder XRD patterns of as-synthesized Co$_{0.3}$Fe$_{2.4}$Ni$_{0.5}$t-1.0O$_{4}$.](image)

The X-ray density or theoretical density was estimated by using the relation:

$$d_{x} = \frac{\sum A}{N \times V}$$

(3-2)

where $A$ is sum of the atomic weights of all the atoms in the unit cell, $V$ is volume of the unit cell and $N$ is the Avogadro’s number. Since each primitive unit cell of the spinel structure contains eight molecules, the theoretical density, $d_{x}$ was determined according to the following relation:

$$d_{x} = \frac{8M}{Na^{3}}$$

(3-3)

where $M$ is molecular weight of the sample, $N$ the Avogadro’s number, $a$ lattice parameter, $8$ represents the number of molecules per unit cell and $a^{3}$ is the volume of the cubic unit cell.

It is observed from Table 3.1 that the X-ray density decreases with Ni substitution, which may be due to the fact that the atomic weight of Ni$^{2+}$ is 58.71, which is lesser than that of Fe$^{3+}$ ion (58.93). The apparent density (experimental) is found by assuming the circular shape of the pellets by using the following relation:

$$d = \frac{m}{V} = \frac{Na^{3}m}{\pi r^{2}h}$$

(3-4)
where \( m, V, r \) and \( h \) represent the mass, volume, radius and thickness of the samples, respectively. From Table 3.1 it can be seen that the apparent densities of the samples decrease with increase in Ni\(^{2+}\) substitution. This may be related to decrease in particle size with Ni\(^{2+}\) substitution. Further, the higher value of X-ray density than that of the apparent density is due to the existence of pores that depend on the sintering condition [20].

![Graph](image)

**Fig.3.2:** Variation of crystallite size and lattice constant with Ni concentration.

**Table 3.1:** Lattice volume (\( V \)), X-ray density (\( d_x \)), Apparent density (\( d \)), Specific surface area (\( S \)), Porosity (\( P \)) of Co\(_{0.5}\)Fe\(_{2-x}\)Ni\(_{0.5+x}\)O\(_{4}\) ferrite nanoparticles.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>( x = 0.0 )</th>
<th>( x = 0.1 )</th>
<th>( x = 0.2 )</th>
<th>( x = 0.3 )</th>
<th>( x = 0.4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V (\text{Å}^3) )</td>
<td>605</td>
<td>606</td>
<td>607</td>
<td>608</td>
<td>609</td>
</tr>
<tr>
<td>( d_x (\text{g/cm}^3) )</td>
<td>5.14</td>
<td>5.14</td>
<td>5.13</td>
<td>5.12</td>
<td>5.11</td>
</tr>
<tr>
<td>( d (\text{g/cm}^3) )</td>
<td>4.20</td>
<td>4.13</td>
<td>4.08</td>
<td>3.96</td>
<td>3.86</td>
</tr>
<tr>
<td>( P (%) )</td>
<td>18.21</td>
<td>19.57</td>
<td>20.59</td>
<td>22.50</td>
<td>24.57</td>
</tr>
<tr>
<td>( S (\text{m}^2/\text{g}) )</td>
<td>33</td>
<td>39</td>
<td>44</td>
<td>30</td>
<td>77</td>
</tr>
</tbody>
</table>

It is also evident from the Table 3.1 that the unit cell volume increases with the substitution of Ni\(^{2+}\) ions, this may be due to the formation of Fe\(^{2+}\) (0.83Å) ions to maintain the charge neutrality in the system. The percentage porosity was calculated using the relation:

\[
P = 1 - \frac{d}{d_x}
\]  

(3-5)
It is evident from Table 3.1 that porosity increases with Ni$^{2-}$ substitution. This behavior of porosity is understandable since the density and particle size decreases with increase in Ni$^{2+}$ substitution. Specific surface area (S) was calculated from the diameter of the particle in nm and the measured density in g/cm$^3$ by using the following relation:

$$S = \frac{6000}{t \times d}$$  \hspace{1cm} (3-6)

where $t$ is the diameter of the crystallites in nm and $d$ is the apparent density. The variation of specific area is given in Table 3.1. The increase in S is due to decrease in particle size with increase in substitution of Ni$^{2-}$ ions.

### 3.2.1.2 Field Emission Scanning Electron Microscopy (FE-SEM)

Scanning electron microscopy has a large depth of field, which allows a huge amount of the sample to be in focus at one time and produces an image that is a good representation of the three-dimensional sample. The mixture of higher magnification, larger depth of field, greater resolution, compositional and crystallographic information makes this one of the most heavily used instruments in research areas and industry. Field emission scanning electron microscopy (FE-SEM) images were obtained using a TESCAN, MIRA II LMH microscope. The morphology and shape of our ferrite powder was observed by using this technique of as obtained nanoparticles, and is presented in Fig. 3.3. The composition was determined by using energy dispersive X-ray spectroscopy (EDAX, Inca Oxford, attached to the FE-SEM). For the FE-SEM and EDAX measurements, the nanoparticles of Co$_{0.5}$Fe$_{2-x}$Ni$_{0.5+x}$O$_4$ (0.0 $\leq x \leq 0.4$) ferrite were dispersed homogeneously in ethanol using ultrasonic treatment. A minute drop of nanoparticles solution was cast on to a glass slide followed by subsequently drying in air before transfer it into the microscope. The FE-SEM micrographs were taken at different magnifications at different parts of the samples. The uniform nature of the ferrite particle is showing fine grain growth in the samples along with some agglomeration. It is clear from the FE-SEM micrographs that the microstructure changes with Ni$^{2+}$ substitution. By having a closer look at these microstructures, it is found that structure gets improved and grains in all samples are spherical in shape. Also, it is observed that Ni substitution increases the porosity and
the individual grains are parted from each other and the effective area of grain contact decreases.

Fig. 3.3: FE-SEM micrographs of $\text{Co}_{0.5}\text{Fe}_{2.0}\text{Ni}_{0.5+1.0x}\text{O}_4$ ferrite nanoparticles.
3.2.1.3 Energy Dispersive X-ray Analysis (EDAX)

The composition of the nanocrystalline metal oxides has been determined using the energy dispersive analysis of X-ray (EDAX). The X-ray spectrum for \( x = 0.0, 0.1, 0.2 \) and 0.3, compositions are highlights in Fig. 3.4. The quantitative analysis of EDAX spectrum revealed the relative atomic ratio of Co: Ni: Fe are close to the expected values for \( \text{Co}_{0.5}\text{Fe}_{2.5}\text{Ni}_{0.5+1.0x}\text{O}_4 \).

![Typical EDAX spectra for different compositions](image)

**Fig. 3.4:** The typical EDAX spectra of the composition \( \text{Co}_{0.5}\text{Fe}_{2.5}\text{Ni}_{0.5+1.0x}\text{O}_4 \) for \( x = 0.0, 0.1, 0.2 \) and 0.3 specimens.

3.2.1.4 Fourier Transform Infrared Spectroscopy (FT-IR)

FTIR spectroscopy is a powerful method for identifying unknown materials, the quality or consistency of a sample and the amount of components in a mixture. Different types of chemical bonds in a molecule are determined by producing an infrared absorption spectrum that is like a molecular fingerprints by which we find out the position of ions in the crystal through the crystal's vibrational modes due to the changes in the \( \text{Fe}^{3+}-\text{O}^2- \) bond during heat treatment or when some foreign atom is introduced in the parent compound. The absorption bands in spinel ferrites mostly occur as of lattice vibrations of oxygen ions with cations. The frequencies of the
vibrations depend on cation-oxygen bonding, lattice parameters and cation mass. The two most prominent absorption bands at $v_1$ and $v_2$, found in almost all spinel ferrites, are approximately around at 600 and 400 cm$^{-1}$, respectively, such that their existence reveals the creation of spinel ferrite phase. Absorption at $v_1$ is caused by stretching vibrations of tetrahedral metal ion and oxygen bonding, while $v_2$ can be assigned to the divalent metal ion-oxygen complexes in the octahedral sites. The FT-IR spectra as shown in Fig. 3.5 were recorded at room temperature in the frequency range 400-4400 cm$^{-1}$ for all samples. Present study for our samples of infrared absorption spectrum focuses to get information about the positions of the ions in the crystal through the crystal’s vibrational modes. Inset of Fig. 3.5 shows the expanded view of the lower region of wave number to give the clear idea of low frequency bands ($v_1$ and $v_2$). It is observed that, there are two main frequency bands, namely, high frequency band ($v_1$) is observed at 584-610 cm$^{-1}$ whereas the lower frequency band ($v_2$) is observed at 412-418 cm$^{-1}$. These two observed bands $v_1$ and $v_2$ correspond to the intrinsic vibrations of tetrahedral and octahedral Fe$^{3+}$-$O^{2-}$ complexes, respectively, and are the characteristics of all the ferrite material [21]. It explains that the normal mode of vibration of tetrahedral cluster is higher than that of octahedral cluster. It should be attributed to the shorter bond length of tetrahedral cluster and longer bond length of octahedral cluster [22]. The FTIR spectrum shows absorption bands in the region 1100 to 1300 cm$^{-1}$ corresponding to NO$_3^-$ ions, absorption bands corresponding to carboxyl group (COO$^-$) is observed at 1400-1700 cm$^{-1}$ and one more at 3400 cm$^{-1}$ corresponding to hydrogen bonded O-H groups. Owing to the high temperature generated during combustion process all the carboxyl, hydroxyl and nitrate groups appear with less intensity.

A comparison of the observed vibrational frequencies of all the studied compositions indicates that the $v_1$ remains almost unmodified with increasing Ni$^{2+}$ content. However, $v_2$ is seen to decrease smoothly with increase in Ni$^{2+}$ substitution. The difference in frequencies between $v_1$ and $v_2$ may be attributed to the changes in bond lengths Fe$^{3+}$-$O^{2-}$ within octahedral and tetrahedral sites.

The Ni$^{2+}$ preferably enters the octahedral site affecting the force constant and bond lengths, without any change in tetrahedral site. It is also observed from Fig. 3.5 that the intensity of the bands decreases while broadening increases on increasing doping ion concentration. Such broadening can be attributed to the statistical
distribution of Fe at A (tetrahedral) and B (octahedral) sites. Reports are there that the system in more disorder state gives broader and less intense band in IR spectra [23].

Fig. 3.5: FT-IR spectra of Co$_{0.5}$Fe$_{2-x}$Ni$_{0.5+1.0x}$O$_4$ ferrite nanoparticles. Inset of Fig. shows the expanded view of the lower region of wave number.

3.2.1.5 Resistivity

The variations in log $\rho$ with 1000/T for all the compositions of the ferrite system Co$_{0.5}$Fe$_{2-x}$Ni$_{0.5+1.0x}$O$_4$ are presented in Fig. 3.6. Resistivity decreases continuously with increasing temperature, revealing the semiconducting nature of the prepared samples. In the present series all the samples are in good agreement with Arrhenius relation [24]. According to this relation resistivity and temperature may be expressed as,

$$\rho = \rho_0 \exp\left(\frac{-\Delta E}{kT}\right)$$  \hspace{1cm} (3-7)

where, $\rho$ is the d.c. electrical resistivity at temperature $T$, $\rho_0$ is the pre-exponential factor with the dimensions of $\Omega$-cm, $k$ is the Boltzmann constant ($8.6173439 \times 10^{-5}$ eV/K), $\Delta E$ is the activation energy, and $T$ is the absolute temperature. The resistivity of the sample was calculated using the relation,
\[ \rho_{dc} = R \pi r^2 / t \]  

where,

\( R \) = ohmic resistance of the pellet  
\( r \) = radius of the pellet  
\( t \) = thickness of the pellet

The conduction mechanism of ferrites can be explained on the basis of the Verwey de Boer [25] mechanism that involves exchange of electrons between the ions of the same elements present in more than one valence state and distributed randomly over crystallographic lattice sites. A very small amount of Fe\( ^{2+} \) and Ni\( ^{3+} \) ions are formed during the sintering process, and electron exchange is believed to be between the iron ions and nickel ions [26] which can be written as:

\[ \text{Ni}^{2+} + \text{Fe}^{2+} \leftrightarrow \text{Ni}^{3+} + \text{Fe}^{2+} \]  

The decrease in resistivity with increase in temperature is due to the increase in drift mobility of the charge carriers. Also conduction in ferrites is attributed to hopping of electrons from Fe\( ^{3+} \) to Fe\( ^{2+} \) at elevated temperatures [27].

![Fig. 3.6: Variation of resistivity with temperature of Co\(_{0.5}Fe_{2-x}Ni_{0.5-1.0}O_4 \) (for \( x = 0.0, 0.1, 0.3, 0.4 \)) ferrite nanoparticles.](image)

It is observed from Fig. 3.6 that, resistivity initially increases for \( x = 0.1 \) and then it shows decreasing trend with increase in Ni\( ^{3+} \) substitution. It is evident from the compositions of all the samples in the system contain a fixed quantity of Co\( ^{2+} \). The electron exchange between Co\( ^{2+} \) and Fe\( ^{3+} \) can be illustrated as follows:

\[ \text{Co}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Co}^{3+} + \text{Fe}^{2+} \]  

(3-10)
It is known that Co sup+ ions invariably reside on octahedral sites [28], they are expected to lock up with the Fe sup+ ions that developed in the course of preparation, which is inevitable to maintain the charge balance. This locking process reduces hopping between iron ions such as Fe sup+ + \leftrightarrow Fe sup+ in octahedral sites and contributes to increase the resistivity initially for x = 0.1. Since Ni sup+ ions are known to have preference for B-sites [29], the substitution of Ni sup+ replaces Fe sup+ ions at octahedral site and this replacement of Fe sup+ ions (0.67 Å) by Ni sup+ ions (0.69 Å) obviously pushes the oxygen ions around it, thus, reducing the distance between two metal ions in B-sub lattice, which increases the hopping probability. This process contributes to decrease in resistivity for higher Ni sup+ substitution.

The breaks in resistivity plots denote two regions of resistivity and the temperature corresponding to the break was found to be at Curie temperature (Tc) of the sample. The activation energies are calculated from the slopes of resistivity plots. The lower temperature region below Tc corresponds to the ordered ferrimagnetic region (E_r) with low activation energy while the higher temperature region above Tc corresponds to a paramagnetic disordered region (E_p) with comparatively high activation energy. The resultant activation (\Delta E) is the difference between the activation energy of para and ferrimagnetic region. The activation energies thus calculated are listed in Table 3.2. In the Table E_r is the activation energy corresponding to ferrimagnetic region and E_p that corresponding to paramagnetic region. It is noted from the Table that the activation energies in paramagnetic region is higher than those in ferrimagnetic region.

Table 3.2: Curie temperature (Tc) and activation energy (\Delta E) from DC resistivity plots of Co_{0.5}Fe_{2-x}Ni_{0.5+x}O_4.

<table>
<thead>
<tr>
<th>Comp. ((x))</th>
<th>Tc (K)</th>
<th>E_r (eV)</th>
<th>E_p (eV)</th>
<th>\Delta E (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>355</td>
<td>0.34</td>
<td>0.24</td>
<td>0.1</td>
</tr>
<tr>
<td>0.1</td>
<td>351</td>
<td>0.32</td>
<td>0.21</td>
<td>0.11</td>
</tr>
<tr>
<td>0.3</td>
<td>345</td>
<td>0.31</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>0.4</td>
<td>342</td>
<td>0.28</td>
<td>0.14</td>
<td>0.14</td>
</tr>
</tbody>
</table>

This could be attributed to the disordered states of the paramagnetic region and the ordered states of the ferrimagnetic region. It is seen from Table 3.2 that values of activation energy (\Delta E) increase with Ni sup+ substitution. This increase in activation
energy can be related with the increase in lattice constant ‘a’ with Ni$^{2+}$ substitution. The increase in the value of ‘a’ manifests itself as increase in inter-ionic distances in the ferrite and consequently, in an increase in the barrier height encountered by the hopping electrons [30].

Curie temperature (Tc) obtained using the resistivity plots are given in Table 3.2. It can be seen from Table 3.2 that the Curie temperature decreases with the increase in Ni$^{2+}$ substitution. Since the Curie temperature is determined by an overall strength of the AB exchange interaction, the weakening of the Fe$^{3+}$(A)-O$^{2-}$-Fe$^{3+}$(B) interaction results in a decrease of the Curie temperature, when the concentration of the Ni$^{2+}$ ions increases successively in the samples. dc conductivity was also calculated using the resistivity plots and its variation is shown in Fig. 3.7.

![Figure 3.7: Variation of dc conductivity with temperature of Co$_{0.5}$Fe$_{2-x}$Ni$_{0.5+1.0x}$O$_4$ (for x = 0.0, 0.1, 0.3, 0.4) ferrite nanoparticles.](image)

3.2.1.6 Impedance Spectroscopy

The charge transport behaviour of the ferrites and its relation to the microstructure has been studied by impedance spectra. The impedance spectra can be obtained by using the equivalent circuit consisting of series connecting parallel resistance (R) and capacitance (C) [31, 32]. The impedance spectrum is usually represented as imaginary component of impedance (Z") against real component of impedance (Z'). It is referred to as Nyquist plot or Cole-Cole plot. The Cole-Cole plot
is particularly useful for materials, which possess one or better separated relaxation processes with comparable magnitudes and obeying the Cole-Cole functional forms.

![Nyquist plots](image)

**Fig. 3.8:** Nyquist plots for all samples of $\text{Co}_{0.5}\text{Fe}_{2-\text{x}}\text{Ni}_{0.5+\text{x}}\text{O}_4$ ferrite nanoparticles.

These measurements give us information about the resistive (real part) and reactive (imaginary part) components in a material. The Cole-Cole plot can give two semicircles, the first semicircle at low frequency represents the resistance of grain boundary. The second one obtained for high frequency domain corresponds to the resistance of grain or bulk properties.

**Table 3.3:** Impedance parameters of as obtained by using Cole-Cole plot for $\text{Co}_{0.5}\text{Fe}_{2-\text{x}}\text{Ni}_{0.5+\text{x}}\text{O}_4$ ferrite nanoparticles at room temperature for grain boundary.

<table>
<thead>
<tr>
<th>Comp. ($\chi$)</th>
<th>$R_{gb}$</th>
<th>$C_{gb}$</th>
<th>$\tau_{gb}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>4239</td>
<td>1.83E-7</td>
<td>7.43E-3</td>
</tr>
<tr>
<td>0.1</td>
<td>3781</td>
<td>3.21E-7</td>
<td>2.42E-3</td>
</tr>
<tr>
<td>0.2</td>
<td>6247</td>
<td>3.14E-7</td>
<td>2.12E-4</td>
</tr>
<tr>
<td>0.3</td>
<td>10322</td>
<td>1.79E-8</td>
<td>3.42E-2</td>
</tr>
<tr>
<td>0.4</td>
<td>11053</td>
<td>1.3E-9</td>
<td>2.13E-4</td>
</tr>
</tbody>
</table>

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The complex impedance of a system at an applied frequency can be written as sum of the real and imaginary parts:

\[ Z'(\omega) = Z'(\omega) + iZ''(\omega) \quad (3-11) \]

where \( Z' \) and \( Z'' \) of the impedance can be written as:

\[
Z' = \frac{R_g}{(1 + \omega_g C_g R_g)^2} + \frac{R_{gb}}{(1 + \omega_{gb} C_{gb} R_{gb})^2} \quad (3-12)
\]

\[
Z'' = \frac{R_g^2}{1 + (\omega_g C_g R_g)^2} + \frac{R_{gb}^2}{1 + (\omega_{gb} C_{gb} R_{gb})^2} \quad (3-13)
\]

where \( R_g \) and \( C_g \) stand for the resistance and capacitance of the grain and \( R_{gb} \) and \( C_{gb} \) symbolize the corresponding terms for grain boundary, as \( \omega_g \) and \( \omega_{gb} \) are the frequencies at the peaks of the semicircles for grain and grain boundary correspondingly. The resistances are intended from the circular arc intercepts on the Z' axis, whereas the capacitances are derived from the maximum height of the circular arcs. The maximum height in each semicircle is \( Z' = -Z'' \), therefore, by using this condition and using (3-12) and (3-13) relations, the relaxation times for grain and grain boundary are given as:

\[
\tau_g = \frac{1}{\omega_g} = C_g R_g \quad (3-14)
\]

\[
\tau_{gb} = \frac{1}{\omega_{gb}} = C_{gb} R_{gb} \quad (3-15)
\]

Typical impedance spectra for the present samples are shown in Fig. 3.8. A well-resolved semicircle is observed for each sample between the frequency range 42 Hz to 5 MHz. It is also observed from Fig. 3.8 that only single semicircle was obtained for all the samples under investigation, which suggests a predominance of the contribution from the grain boundary and that contribution from the grain is not resolved for these samples. By other means, the grain boundary contribution cannot be separated from the grain or bulk contribution by the impedance spectroscopy measurements. Also, it could be due to the presence of some additional time constants, which appeared outside the measured frequency range [34]. The various electrical parameters calculated using the relations discussed elsewhere [31-33], are shown in Table 3.3.
3.2.1.7 Dielectric Measurements

The value of real dielectric constant \( (\varepsilon') \) has been calculated by using the following relation:

\[
\varepsilon' = \frac{C_p \times t}{\varepsilon_0 A}
\]

(3-16)

where \( \varepsilon_0 = 8.85 \times 10^{-14} \text{ F/cm} \), known as permittivity of the free space, \( t \) is the thickness of pellet, \( A \) is the cross sectional area of the flat surface of the pellet and \( C_p \) is the capacitance of the pellet in (F). The frequency dependence of dielectric constant \( (\varepsilon') \) at room temperature in the frequency range 42Hz-5MHz is shown in Fig. 3.9. Plots of the dielectric constant \( (\varepsilon') \) show a continuous decrease with increase in frequency with pronounced dispersion at lower frequency and almost remains independent of applied external field at high-frequency division.

![Fig. 3.9: Variation of dielectric constant (\( \varepsilon' \)) with log (f) of Co\(_{0.5}\)Fe\(_{2-x}\)Ni\(_{0.5-x}\)O\(_4\) ferrite nanoparticles at room temperature.](image)

It is well known that the variation of dielectric constant with frequency in ferrites is mainly due to the variation of Fe\(^{2+}\) and Fe\(^{3+}\) ion concentration. In the low frequency region, the polarization is predominately due to the electronic exchange between Fe\(^{2+} \leftrightarrow \)Fe\(^{3+}\) ions present on the octahedral site in the ferrite lattice. Beyond a certain frequency of the externally applied electric field, the electronic exchange between ferrous and ferric ions, i.e., Fe\(^{2+} \Leftrightarrow \)Fe\(^3\), cannot follow the alternating field.
According to Maxwell and Wagner two-layer model [35-37], the dielectric material is assumed to have well conducting grains, which are separated by highly resistive grain boundaries, where the applied voltage drop leads to the building up of space charge polarization. The first layer which is a conducting layer having of large ferrite grains and second one being the grain boundaries that are poor conductors. The electrical conduction in ferrite is explained by the Verwey mechanism of electron hopping [25, 38], where conduction takes place by hopping of electrons between ions of the same element present in more than one valence state distributed randomly over crystallographically equivalent lattice sites.

![Plot of dielectric loss tangent (tanδ) versus Log f of Co0.5Fe2-xNio.5+1.0xO4 ferrite nanoparticles.](image)

**Fig. 3.10:** Plot of dielectric loss tangent (tanδ) versus Log f of Co0.5Fe2-xNio.5+1.0xO4 ferrite nanoparticles.

In the present study, the substitution with Ni2+ ions produces a change in the polarization so developed, as can be understood by considering the cationic formula; 

\[(\text{Fe})^3[\text{Co}_0.5\text{Fe}_2-x\text{Ni}_{0.5+1.0x}]^3\].

As Ni2+ content is increased there is a decrease in Fe3+ ions and increase in Ni2+ ions at the B site. However, the exchange process of \(\text{Ni}^{2+} \leftrightarrow \text{Ni}^{3+}\) is weak compared to \(\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}\) hence \(\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}\) is assumed to be the dominant mechanism.

The decrease in Fe3+ ions at the B site, therefore, decreases the hopping motion of electrons. This in turn decreases the piling up of electrons at the grain boundary, hence impeding the buildup of space charge polarization. Therefore, the value of
dielectric constant decreases with increase in Ni$^{2+}$ substitution. The loss tangent has been calculated from the following relation:

$$\tan\delta = \frac{1}{2\pi f \varepsilon_0 \varepsilon' \rho}$$

(3-17)

![Graph showing variation of dielectric loss (e'') with log (f) of Co$_{0.5}$Fe$_{2.5}$Ni$_{0.5+1.0x}$O$_4$ ferrite nanoparticles.](image)

Dielectric loss is an important part of the total core loss in ferrites [39]. The complex dielectric constant has been calculated by the following relation:

$$\varepsilon'' = \varepsilon' \tan\delta$$

(3-18)

where \(\tan\delta\) is the dielectric loss tangent which is proportional to the "loss" of energy from the applied field into the sample (in fact this energy is dissipated into heat) and, therefore, denoted as dielectric loss. Fig. 3.10 and 3.11 shows the variation of dielectric loss tangent factor (\(\tan\delta\)) and dielectric loss (\(\varepsilon''\)), respectively, with log frequency at room temperature. The loss tangent exhibits the normal behaviour with frequency and decreases as the frequency of applied field increases.

3.2.1.8 Magnetic Properties

To determine the magnetic properties of the samples the M-H loops of as synthesized samples were performed to obtain the saturation magnetization (Ms), remanent magnetization (Mr) and coercivity (Hc). It is observed from Fig. 3.12 and Fig. 3.13 that the saturation magnetization (Ms) decreases with increase in Ni$^{2+}$
substitution. It is known that in ferrites, the magnetic moment comes mainly from the parallel uncompensated electron spin of individual ion. The intensity of magnetization is, therefore, explained by considering the metal ion distribution and anti-parallel spin alignment of the two sub-lattice sites as given by Neel's Model \([41]\). According to Neel's model, of the three types of interactions A-A, A-B and B-B. The inter sub-lattice A-B super-exchange interaction is the strongest. The net magnetization is, thus, given by \(M_s = M_A - M_B\) where \(M_A\) and \(M_B\) are the magnetization of the sub-lattices A and B, respectively. In the present system, magnetic \(Fe^{3+}\) ions of \(5\mu_B\) are replaced by less magnetic \(Ni^{2+}\) ions of \(2\mu_B\) magnetic moment. The observed decrease in magnetization is attributed to decrease in A-B interaction. On the other hand, the magnetic properties may also be affected by the grain size and bulk density, and enhanced by the increase of particle size \([3]\). The particle size is obviously found to decrease by \(Ni^{2+}\) substitution as evidenced from Fig. 4. This may also be the reason for the drop of saturation magnetization \(M_s\) of the ferrites. Pores act as pinning centers for the electron spins, thereby lowering the saturation magnetization. These results indicate that an optimum microstructure must be taken into account to obtain ferrites with high performance. Remanence is a structure-sensitive parameter.

![Fig. 3.12: Magnetic hysteresis loops for \(Co_{0.5}Fe_{2.0}Ni_{0.3+1.0}\) system.](image)

For the present system, we got experimentally that the values of remanent magnetization \(M_r\) decreases from 17 to 10 emu/g with increase in \(Ni^{2+}\) substitution (Fig. 3.13). The remanent ratio \(R = M_r/M_s\) is a characteristic parameter of a
material. Higher and lower remanent ratios denote different material responses and, accordingly, determine where the material will be applied. It is desirable to have higher remanent ratios for magnetic recording and memory devices. It was observed that the values of $R$ increase from 0.26 to 0.56 with increasing Ni$^{2+}$ substitution (Fig. 3.13).

![Graph](image)

**Fig. 3.13:** Variation of magnetization ($M_s$), remanence magnetization ($M_r$) and remanent ratio ($R$) with Ni content $x$.

### 3.2.1.9 Mössbauer Spectroscopy

The Mössbauer spectra of the series $\text{Co}_0.5\text{Fe}_{2-x}\text{Ni}_{0.5+1.0}\text{O}_4$, for the values of $x = 0.0$ and 0.3 were taken at 300 K. The Mössbauer spectrum could be interpreted as the superposition of two sextets, one from the tetrahedral sites and the other from the octahedral sites. The spectra of the typical samples are shown in Fig. 3.14, exhibit well-resolved six finger patterns. The + bullets represent the experimental points and the full curve is the least squares fit of the experimental spectrum. The lines inside each spectrum indicate the position of the A-site and B-site resonance lines. As indicated from the Fig. 3.14, the width of the splitting changes with Ni$^{2+}$ substitution, which evidences a change in the magnetic hyperfine field. The line width of the tetrahedral sites becomes broader than that of the octahedral site with the increase of the Ni$^{2+}$ contents at the octahedral site. Such broadening is, in fact, expected due to a distribution of the hyperfine fields at the A-site caused principally by a random...
distribution of Ni$^{2+}$, Fe$^{3+}$ and Co$^{2+}$ ions at the B-site, since the Fe$^{3+}$ A-sites would feel different configurations of Ni$^{2+}$, Fe$^{3+}$ and Co$^{2+}$ ions occupying the 12 nearest neighbours B-sites. The results of data fitting are represented in Table 4. The hyperfine field (BHF) was 54.22 and 55.34 Tesla for A- and B-sites, respectively. When Ni$^{2+}$ is added to the system, the BHF decreases to 52.44 Tesla for A-site and 53.03 Tesla for B-site. Further, it is also observed from Table 4 that the BHF for B-site is larger to that of A-site. In most of the ferrites, B site hyperfine magnetic field is generally larger than that of A site, which is attributed to the dipolar field resulting due to deviation from cubic symmetry and covalent nature of tetrahedral bond. The decrease in the BHF when magnetic Fe$^{3+}$ ion is replaced by Ni$^{2+}$ ion, which is less magnetic. Therefore, the substitution of Ni$^{2+}$ ion for Fe$^{3+}$ ion will produce a decrease in the super transferred hyperfine interactions contribution at both sites.

Magnetization measurements for these samples (Figs. 3.12 and 3.13) show that the magnetization of the sample decreases with increasing Ni$^{2+}$ substitution. The isomer shift (IS) results from the electrostatic interaction between the charge distribution of the nucleus and those electrons that have a finite probability of being found in the region of the nucleus. Only s-electron wave functions have a finite value inside the nucleus and these electrons are, therefore, responsible for this interaction. It can be clearly seen from Table 4 that IS(A) < IS(B). It is known that IS for octahedral site is more than that of the tetrahedral sites since in cubic spinel ferrites the bond separation Fe$^{3+}$-O$^{2-}$ is larger for octahedral sites as compared to that for tetrahedral sites, due to which the overlapping of orbitals of Fe$^{3+}$ ions is smaller at B sites and thus a larger IS and hence more s-electron density at B site emerges [42-44]. The IS is a physical parameter for probing the valency state of the Mössbauer atom. For example, Fe$^{2+}$ and Fe$^{3+}$ have electron configurations of (3d)$^6$ and (3d)$^5$, respectively. The ferrous ions have lesser s-electron density at the nucleus due to the greater screening of the d-electron. This produces a positive IS that is greater in ferrous ions than in ferric [45]. Any asymmetry at the A- and/or B-site environment of Fe$^{3+}$ ions gives rise to nonzero quadrupole splits (QS). QS in compounds containing Fe$^{3+}$ at A site is attributed to the asymmetric charge distribution associated with the random distribution of divalent and trivalent ions on the neighboring 12 B sites which surround the A site. In the present case, the distribution of Ni$^{2+}$ and Fe$^{3+}$ ions on the B sites creates an asymmetry at the A site and gives rise to a QS.
The observed QS at the B site is attributed to the trigonal field created by the distortion due to the oxygen parameter \((u)\) present in such compounds [46]. The quadrupole splitting (QS) for both sites increase linearly with the substitution of Fe\(^{3+}\) by Ni\(^{2+}\) in the spinel structures because of increased distortion in the symmetry of the electric field gradient.

**Table 4:** Line width \((\Gamma)\), isomer shift (IS), quadruple splitting (QS), hyperfine field (BHF) and % area \((I_{rel})\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>(\Gamma) (mm/s)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>BHF (Tesla)</th>
<th>(I_{rel}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>A</td>
<td>0.470±0.017</td>
<td>0.193±0.007</td>
<td>-0.06±0.01</td>
<td>54.22±0.04</td>
<td>75.0</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.373±0.034</td>
<td>0.543±0.014</td>
<td>0.135±0.021</td>
<td>55.34±0.09</td>
<td>25</td>
</tr>
<tr>
<td>0.3</td>
<td>A</td>
<td>0.533±0.051</td>
<td>0.168±0.021</td>
<td>0.111±0.035</td>
<td>52.44±0.09</td>
<td>61.7</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.663±0.106</td>
<td>0.535±0.052</td>
<td>0.243±0.077</td>
<td>53.03±0.19</td>
<td>38.3</td>
</tr>
</tbody>
</table>
3.3 Conclusion

To summarize, the effect of Ni\textsuperscript{2+} in cobalt ferrite nanoparticles has been investigated on a series of Co\textsubscript{0.5}Fe\textsubscript{2-x}Ni\textsubscript{x}O\textsubscript{4}, (x=0.0, 0.1, 0.2, 0.3, & 0.4), synthesized by so-gel auto combustion method. Structural analysis with XRD confirms that all the samples have single phase cubic spinel structure without the signature of any impurity peak. The contents of the metal in the resulting spinel ferrites are close to the theoretical values. Surface morphology of all the samples reveals that the microstructure is going to improve and grains in all samples are spherical in shape. IR spectra show two prominent vibrational bands at $v_1$ (584-610 cm\textsuperscript{-1}) and $v_2$ (412-422 cm\textsuperscript{-1}), and these bands are assigned to the tetrahedral and octahedral sites, respectively. The resistivity measurement with temperature indicates a semiconducting behaviour. The dielectric constant showed decreasing trend with increasing frequency. The hopping of localized electrons between Fe\textsuperscript{2+}$\leftrightarrow$Fe\textsuperscript{3+} and Ni\textsuperscript{2+}$\leftrightarrow$Ni\textsuperscript{3+} ions on octahedral sites is responsible for electric conduction and dielectric polarization. The Cole-Cole plots show a single semi-circle for all the samples which exhibited that polycrystalline ferrites are composed of well conducting grains and poorly conducting grain boundaries. Decrease in saturation magnetization and in hyperfine field suggests that the weakening in A-B interactions takes place due to Ni\textsuperscript{2+} substitution. The Mössbauer measurements showed well-resolved magnetic spectra for the tetrahedral and octahedral sites. Mössbauer spectra show that there is an insignificant change in the values of Isomer shift. The hyperfine magnetic field at both the sub lattices decreases with the introduction of increasing Ni\textsuperscript{2+} ions by breaking the coupling bonds between Fe\textsuperscript{3+}A-O-Fe\textsuperscript{3+}a interactions. The as obtained nano ferrites are found to have high quality and good stoichiometric composition which sanctifies the preference of this method.
References


