Chapter – 4

Results and Discussion on \( \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4 \) \( (0.0 \leq x \leq 1.0) \) Ferrite Nanoparticles

This chapter highlights detailed study of structural, electrical and magnetic properties of a series of polycrystalline \( \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4 \) \( (0.0 \leq x \leq 1.0) \) ferrite nanoparticles, prepared using the citrate-gel method. The effect of Cr substitution on \( \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{O}_4 \) has been studied by using x-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy analysis (EDAX), vibrating sample magnetometer (VSM), Fourier transformation infrared spectroscopy (FTIR), frequency dependent dielectric and impedance spectroscopy and Mössbauer spectroscopy measurements.
4.1 Introduction

The last two decades have witnessed a tremendous increase in the interest of the academics and the industry in materials that are aptly described by this new terminology nano-structured materials. Naturally this made the study of ferrites at nanoscale quite interesting subject both from the fundamental and application point of view. Nano-structured materials show the properties that are vastly superior to those exhibited by single crystalline, conventional polycrystalline and amorphous materials. Properties of nano-structured materials are of great theoretical and technological importance. The crystallographic, electrical and magnetic properties of these ferrites substantially depend on their method of preparation, chemical composition, sintering temperature, substitution, and grain size [1-3], which controls the microstructure forming high resistive boundaries between the constituent grains. Properties of ferrites have also been strongly affected when the particle size approaches a critical diameter, below the critical diameter each ferrite particle considered as a single domain [4]. Ferrites with AB2O4 formula crystallize either in a normal spinel structure or in an inverse spinel structure. In a normal spinel structure, the A2+ cations occupy the tetrahedral site, whereas the B3+ cations occupy the octahedral site. In an inverse spinel structure, half of the octahedral coordination sites are occupied by A2+ cations and the remaining half as well as all the tetrahedral coordination sites are occupied by the B3+ cations. In this cubic symmetry the metal ions are distributed over the two lattice sites; namely tetrahedral A-sites and octahedral B-sites. The tetrahedral site is surrounded by four oxygen ions while octahedral site is surrounded by six oxygen ions. Commonly, metal ions used for enhancing the properties of spinel ferrites are Ni, Mg, Mn, Zn, Ti, Co, Cu, Mg, etc. Ni–Mg ferrites are among the most widely used soft magnetic materials because of their use in high frequency applications as they possess high electrical resistivity and low eddy current losses [5]. Khalid et al. have reported the finite size effect and influence of temperature on electrical properties of nanocrystalline Ni–Cd ferrites [6]. Kharabe et al. have studied the dielectric and magnetic properties of Cd substituted Li–Ni ferrites [7]. Soibam et al. have reported the high value of magnetization for Ni–Li–Zn ferrites [8]. The electrical properties of Li–Ni–Eu and Li–Mg–Ti ferrites have been reported by Al-Hilli et al. [9] and by Bellad and Chougule [10], respectively. Both the NiFe2O4 and MgFe2O4 are well-known inverse spinel structures with Mg2+ and Ni2+ ions located on the B sites and
Fe$^{3+}$ ions distributed equally over A and B sites [11,12]. Recently, several methods have been employed to synthesize highly crystalline and uniformly sized magnetic nanoparticles of ferrite [13-15]. The citrate-gel method has gained scientific and technological importance during the last three decades. Citrate-gel method offers many advantages compared to that of conventional double sintering method, such as low temperature processing for the synthesis of nano-range particles. Several researchers have studied the effects of Cr$^{3+}$ substitution in the spinel structure of ferrites [16,18]. In this chapter, we have investigated the Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ (0 $\leq$ x $\leq$ 1.0) system synthesized using citrate-gel method to examine the influence of the substitution of Cr$^{3+}$ ion on the structural, electrical and magnetic properties of the Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ ferrite system.

4.2 Results and Discussion

4.2.1 Structural Properties

Identification of the single-phase FCC spinel structure was made by X-ray diffraction technique. The crystallinity, structure and crystallite size of Cr doped Ni-Mg ferrite nanoparticles were obtained by X-ray powder diffraction (XRD) on a Rikagu Miniflex (II) using CuK$_\alpha$ radiation ($\lambda$=0.15406 nm) in 2$\theta$ range from 20$^\circ$-70$^\circ$. Fig. 4.1 displays the structural characterization for all the samples. All the samples have single phase cubic spinel structure and no detrimental intermediate phase is observed. The linear variation of lattice constant with Cr$^{3+}$ ion substitution is observed. The linear variation in lattice constant is due to the ionic radii of the doped and the replaced ion. The substitution of Cr$^{3+}$ ions in Ni-Mg ferrite decreases the lattice constant of the ferrite system. This reduction in unit cell size is attributed to the ionic radius of 6-fold-coordinated Cr$^{3+}$ being smaller (0.64 Å) than that of 6-fold-coordinated high-spin Fe$^{3+}$ (0.67 Å). The values of lattice constant as a function of chromium concentration are given in Table 4.1, for various Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ ferrites. It can be seen that the lattice constant decreases proportionally to the doping contents. The decrease in lattice constant value can be explained on the basis of Vegard's law [19].
The average crystallite size of the nano phase synthesized particles was
determined by using the following Debye-Scherrer formula [20] and found in the
range 30-35 nm as shown in Table 4.1,

\[
I_{hkl} = \frac{0.98 \lambda}{\beta_{hkl} \cos \theta_{hkl}} \quad \ldots(4.1)
\]

where \(\lambda\) is X-ray wavelength of the CuK\(\alpha\) radiation (\(\lambda=1.5406\) Å), \(\theta_{hkl}\) is the
Bragg diffraction angle and \(\beta_{hkl}\) is the full width at half maximum (FWHM) in radians
of the main peak in the X-ray diffraction pattern calculated by using Gaussian fitting.

\[\text{Fig. 4.1: X-ray patterns of Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4 \quad (a) x = 0.0, \ (b) x = 0.2, \ (c) x = 0.4, \]
\[\quad (d) x = 0.6, \ (e) x = 0.8, \ and \ (f) x = 1.0\]

The X-ray density (\(d_x\)) of the prepared samples was calculated by using the
following relation [21].

\[d_x = \frac{8M}{Na^3} \quad \ldots..(4.2)\]
where $M$ is molecular weight of the sample, $N$ the Avogadro's number, $a$ lattice constant and 8 (in ferrites) represents the number of molecules in a unit cell of spinel ferrite.

The apparent density ($d_{\text{exp}}$) was calculated by assuming the circular shape of the pellets by using the following relation:

$$d_{\text{exp}} = \frac{m}{V} = \frac{Na^3m}{\pi r^2h}$$

......(4.3)

where $m$, $V$, $r$ and $h$ represent the mass, volume, radius and the thickness of the samples, respectively. The X-ray density depends on the lattice constant and the molecular weight of the sample, while the apparent density of the samples is being calculated from the geometry and mass of the samples. Both densities as a function of Cr contents are given in Table 4.1. X-ray density decreases with Cr substitution, which may be due to the fact that the density and atomic weight of Cr are 7.19 gm/cm$^3$ and 51.99, respectively, which are greater than that of Fe ions (6.98 gm/cm$^3$, 55.84). The apparent densities of the samples show the same general behaviour like that of theoretical density. The higher value of X-ray density than that of the apparent density is due to the existence of pores that depends on sintering condition. The variation of the porosity of samples with composition is given in Table 4.1.

**Table 4.1:** Lattice constant (a), X-ray density ($d_x$), apparent density ($d_{\text{exp}}$), porosity (P), and crystallite size (t) of $\text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$a$ (Å)</th>
<th>$d_x$ (g/cm$^3$)</th>
<th>$d_{\text{exp}}$ (g/cm$^3$)</th>
<th>P (%)</th>
<th>t (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.450</td>
<td>4.781</td>
<td>3.643</td>
<td>23.80</td>
<td>35.5</td>
</tr>
<tr>
<td>0.2</td>
<td>8.436</td>
<td>4.787</td>
<td>3.426</td>
<td>28.43</td>
<td>35.6</td>
</tr>
<tr>
<td>0.4</td>
<td>8.431</td>
<td>4.779</td>
<td>3.207</td>
<td>32.89</td>
<td>33.9</td>
</tr>
<tr>
<td>0.6</td>
<td>8.428</td>
<td>4.767</td>
<td>3.132</td>
<td>34.29</td>
<td>34.4</td>
</tr>
<tr>
<td>0.8</td>
<td>8.425</td>
<td>4.755</td>
<td>3.110</td>
<td>34.59</td>
<td>33.1</td>
</tr>
<tr>
<td>1.0</td>
<td>8.423</td>
<td>4.741</td>
<td>3.100</td>
<td>34.61</td>
<td>30.6</td>
</tr>
</tbody>
</table>

The porosity of the samples increases with composition; this is due to the lower density of Cr$^{3+}$ ions. It may be depicted that the size of the particles decreases;
the porosity increases in the range of 23.8-34.6%. EDAX measurements were performed to determine the chemical composition of the sample to support our observations on the structure of the Ni-Mg ferrite. EDAX measurements were carried out on the same point with electrons to give the chemical composition of essentially the core of the particle. Results of EDAX analysis of the investigated samples are given in Fig. 4.2. It is observed from Figs. that, the Fe$^{3+}$ has very high concentration as would be expected for undoped ($x = 0.0$) Cr$^{3+}$ ions. As the Cr$^{3+}$ content goes on increasing, the percentage of Fe$^{3+}$ ions decreases. The atomic and weight percentages of various cations in the Ni$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$ are shown in Table 4.2. The elemental analysis as obtained from EDAX is in close agreement with the starting composition used for the synthesis. The EDAX quantification can be influenced by the surface crystalline defects of nanoparticles. This can also be taken into account to explain the difference between the values of the atomic ratio as determined by EDAX and the expected value. Typical SEM micrographs of the Cr$^{3+}$ substituted Ni-Mg ferrites are shown in Fig. 4.3. The grains were of cubic-shaped platelets. The average grain size obviously tends to decrease with Cr$^{3+}$ content. It is thus reasonable to note that the Cr$^{3+}$ substitution results in inhibiting grain growth in the prepared ferrite samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Chemical composition (EDAX)</th>
<th>Wt %</th>
<th>At %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$</td>
<td>Ni</td>
<td>Mg</td>
<td>Fe</td>
</tr>
<tr>
<td>0.0</td>
<td>13.75</td>
<td>06.63</td>
<td>49.72</td>
</tr>
<tr>
<td>0.2</td>
<td>13.46</td>
<td>06.66</td>
<td>44.73</td>
</tr>
<tr>
<td>0.4</td>
<td>12.32</td>
<td>06.80</td>
<td>37.98</td>
</tr>
</tbody>
</table>

Fig. 4.3 shows the SEM images of powder samples while Fig. 4.4 shows the photographs of sintered pellets of the typical compositions of Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$. It is observed from Figs. 4.4 that the SEM images of the sintered pellets sample show dense structure as compared to that of powder sample (Fig. 4.3). Fig. 4.5 shows the AFM micrographs where we have observed that the grains of different shape and sizes. The shape, size and morphology of the particles were examined by direct
observation via transmission electron microscopy. The typical TEM micrographs for
the $x = 0.4$, 0.6 and 1.0, samples are shown in Fig. 4.6. The observations reveal that
the particles are approximately spherical in shape and agglomerated. Fig. 4.6 also
shows the selected area electron diffraction (SAED) pattern for $x = 0.4$, 0.6 and 1.0,
samples. The polycrystalline nature of as prepared samples can be clearly seen in the
SAED pattern (Fig.4.6). Fig. 4.7(a-c) shows the typical histograms of size distribution
for Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ nanoparticles, indicating the quality of spherical
Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ nanoparticles are very high in terms of size distribution.

4.2.2 Cation Distribution

The cation distribution in spinel ferrite can be obtained from an analysis of the
X-ray diffraction pattern. In the present work, the Bertaut method [22] is used to
determine the cation distribution. This method selects a few pairs of reflections
according to the expression:

$$\frac{I_{\text{Obs.}}^{\text{Calc.}}}{I_{\text{Calc.}}^{\text{Calc.}}} = \frac{I_{\text{Calc.}}^{\text{Calc.}}}{I_{\text{Calc.}}^{\text{Calc.}}}$$

(4.4)

where $I_{\text{Obs.}}^{\text{Calc.}}$ and $I_{\text{Calc.}}^{\text{Calc.}}$ are the observed and calculated intensities for reflection
(hkl), respectively. The best information on cation distribution is achieved when
comparing experimental and calculated intensity ratios for reflections whose
intensities (i) are nearly independent of the oxygen parameter, (ii) vary with the cation
distribution in opposite ways and (iii) do not differ significantly. In the present work,
(220), (400), (440) were used to calculate intensity ratio. These planes are assumed to
be sensitive to the cation distribution. The temperature and absorption factors are not
taken into account in our calculations as they do not affect the intensity calculation. If
an agreement factor ($R$) is defined as in Eq. (4.5), the best-simulated structure which
matches the actual structure of the sample will lead to a minimum value of $R$ and the
corresponding cation distribution is obtained for each hkl and h'k'l' reflection pair
considered.

$$R = \left( \frac{I_{\text{Obs.}}^{\text{Calc.}}}{I_{\text{Calc.}}^{\text{Calc.}}} \right)$$

(4.5)
Energy - keV

(x = 0.0)

Counts

Energy - keV

(x = 0.2)

Counts

Energy - keV

(x = 0.4)
Fig. 4.2: EDAX analysis of $x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0.
Fig. 4.3: SEM images of the powder samples (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$ and (f) $x = 1.0$. 

96
Fig. 4.4: SEM images of the sintered pellets of the typical samples $\text{Ni}_{0.5} \text{Mg}_{0.5} \text{Fe}_2$. $\text{Cr}_x \text{O}_4$ (a) $x = 0.2$, (b) $x = 0.4$, (c) $x = 0.6$ and (d) $x = 0.8$. 
\[ 8'0 = x(p) \quad \text{and} \quad 9'0 = x(c) \]

- Z \; 0 = x(a), 9'0 = x(a) \text{ for } a \in \mathbb{R}^2.
Fig 4.6: TEM and their respective SAED images of the typical Ni$_{0.5}$Mg$_{0.3}$Fe$_{2-x}$Cr$_x$O$_4$ samples (a) $x = 0.4$, (b) $x = 0.6$ and (c) $x = 1.0$. 
Fig. 4.7: Size distribution of nanoparticles from TEM images (a) $x = 0.4$, (b) $x = 0.6$ and (c) $x = 1.0$.

The intensities of these are nearly independent of the oxygen parameters. The calculations were made for various combinations of cations. For the calculation of the relative integrated intensity of a given diffraction line from powder specimens as observed in a diffractometer with a flat-plate sample holder, the following formula is valid.

$$I_{hkl} = |F_{hkl}|^2 P L_P$$

......(4.6)

where, $F$ is structure factor, $P$ is multiplicity factor, $L_P$ the Lorentz polarization factor and

$$L_P = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

......(4.7)
The atomic scattering factor for various ions was taken from the literature [23]. The cation distribution for each concentration and the site preferences of cations distributed among the tetrahedral A- sites and octahedral B- sites are presented in Table 4.3.

**Table 4.3: Cation distribution, ionic radii of tetrahedral ($r_A$) and octahedral ($r_B$), theoretical lattice constant ($a_0$) site.**

<table>
<thead>
<tr>
<th>Comp. $x$</th>
<th>Cation distribution</th>
<th>$r_A$ (Å)</th>
<th>$r_B$ (Å)</th>
<th>$a_0$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>(Mg$<em>{0.1}$Fe$</em>{0.9}$)$<em>A$ [Ni$</em>{0.8}$Mg$<em>{0.4}$Fe$</em>{1.1}$]$_B$ O$_4$</td>
<td>0.675</td>
<td>0.685</td>
<td>8.419</td>
</tr>
<tr>
<td>0.2</td>
<td>(Mg$<em>{0.1}$Fe$</em>{0.9}$)$<em>A$ [Ni$</em>{0.8}$Mg$<em>{0.4}$Cr$</em>{0.2}$Fe$_{0.9}$]$_B$ O$_4$</td>
<td>0.675</td>
<td>0.682</td>
<td>8.411</td>
</tr>
<tr>
<td>0.4</td>
<td>(Mg$<em>{0.1}$Ni$</em>{0.0}$Fe$<em>{0.87}$)$<em>A$ [Ni$</em>{0.47}$Mg$</em>{0.4}$Cr$<em>{0.4}$Fe$</em>{0.73}$]$_B$ O$_4$</td>
<td>0.676</td>
<td>0.679</td>
<td>8.403</td>
</tr>
<tr>
<td>0.6</td>
<td>(Mg$<em>{0.1}$Ni$</em>{0.0}$Fe$<em>{0.87}$)$<em>A$ [Ni$</em>{0.43}$Mg$</em>{0.4}$Cr$<em>{0.5}$Fe$</em>{0.73}$]$_B$ O$_4$</td>
<td>0.676</td>
<td>0.675</td>
<td>8.395</td>
</tr>
<tr>
<td>0.8</td>
<td>(Mg$<em>{0.1}$Ni$</em>{0.1}$Cr$<em>{0.2}$Fe$</em>{0.8}$)$<em>A$ [Ni$</em>{0.47}$Mg$<em>{0.4}$Cr$</em>{0.7}$Fe$_{0.73}$]$_B$ O$_4$</td>
<td>0.676</td>
<td>0.673</td>
<td>8.387</td>
</tr>
<tr>
<td>1.0</td>
<td>(Mg$<em>{0.1}$Ni$</em>{0.1}$Cr$<em>{0.8}$Fe$</em>{0.6}$)$<em>A$ [Ni$</em>{0.38}$Mg$<em>{0.36}$Cr$</em>{0.95}$Fe$_{0.31}$]$_B$ O$_4$</td>
<td>0.678</td>
<td>0.669</td>
<td>8.380</td>
</tr>
</tbody>
</table>

In this Table, the fraction of Fe$^{3+}$ ions in either site is shown. The results demonstrate that Ni$^{2+}$ and Mg$^{2+}$ ions occupy B sites. The Mg$^{2+}$ ions have the probability to occupy the tetrahedral site (A) or octahedral site (B), with high preference for the B sites. Cr$^{3+}$ preferentially replaces Fe$^{3+}$ from octahedral sites because of favourable crystal-field effects (Cr$^{3+}$/6$\Delta_0$, Cr$^{3+}$/0$\Delta_0$) [24]. It is observed from Table 4.3 that the Cr$^{3+}$ ions predominately occupy the octahedral sites, which is consistent with the preference for large octahedral-site energy. With increasing Cr$^{3+}$ content, the fraction Cr$^{3+}$ ions in octahedral sites increases, whereas the fraction of Fe$^{3+}$ ions in octahedral sites decreases linearly.

The values of $r_A$ and $r_B$ are given in Table 4.3. It is shown that $r_A$ remains almost constant and $r_B$ decreases with increasing Cr$^{3+}$ content. The decrease in $r_B$ is due to the increasingly high occupation of the B site by the smaller ionic radii of Cr$^{3+}$ (0.64 Å), replacing Fe$^{3+}$ (0.67 Å). The values of theoretical lattice parameter ‘$a_0$’ are
shown in Table 4.3. The variation of theoretical values is similar to that observed for the experimentally determined lattice parameter.

4.2.3 FT-IR Spectroscopy

The FT-IR spectra of Cr$^{3+}$ substituted Ni-Mg ferrite were recorded at room temperature in the frequency range of 400-2000 cm$^{-1}$ and the obtained results are shown in Fig. 4.8. The higher frequency band ($v_1$) (584-675 cm$^{-1}$) and lower frequency band ($v_2$) (434-465 cm$^{-1}$) are assigned to the tetrahedral and octahedral sites, respectively [25-29].

![FT-IR spectra of Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ for x = 0.0, 0.2, 0.4, 0.6 and 1.0 ferrite nanoparticles.](image)

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 [30]. It has been observed in the present system that the band positions $v_1$ and $v_2$ change slightly. This may be due to the distribution of Cr$^{3+}$ ions (ionic radius 0.64 Å) which are replacing Fe$^{3+}$ ions (ionic radius 0.67 Å) at octahedral [B] site, thus, making some changes in the size of tetra and octa-hedron. It can be seen that the frequency $v_2$ is shifted to higher frequencies with increasing Cr$^{3+}$ content. The shift in the band position, by increasing Cr$^{3+}$ content, may be due to the variation in the cation-oxygen bond length of the octahedral lattice of the spinel. The replacement of Fe$^{3+}$ ions by smaller Cr$^{3+}$ ions will result into a somewhat decrease in the metal-oxygen bond length and
consequently increase the wave number of \( v_2 \) band. The splitting of the \( v_2 \) band into bands of medium intensity may be logically attributed to the increasing quantity of \( \text{Cr}^{3+}-\text{O}^{2-} \) complexes as the \( \text{Fe}^{3+} \) content decrease at B-site. Similar splitting of spectra have been reported in literature for \( \text{Cr}^{3+} \) substituted ferrite system \[31\].

4.2.4 Magnetic Properties

Fig. 4.9 shows the variation of magnetization as a function of applied magnetic field for various \( \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4 \) samples at 300 K.

![M-H curve](image)

**Fig. 4.9:** \( M-H \) curves of \( \text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4 \) (for \( x = 0.0, 0.2, 0.4, 0.6, 0.8 \)) ferrite nanoparticles samples at room temperature.

M-H curve helps in understanding the magnetic response of synthesized material and provides the information regarding the magnetic parameters such as saturation magnetization (\( M_s \)), coercivity (\( H_c \)) and remanence magnetization (\( M_r \)) as shown in Fig. 4.10.
Fig. 4.10: Variation of saturation magnetization (Ms), remanence magnetization (Mr) and coercivity (Hc) with Cr content x.

For Cr$^{3+}$ substituted Ni-Mg ferrite, the Fe$^{3+}$ ions are replaced by Cr$^{3+}$ ions, leading to a decrease in the B-site sub-lattice magnetization. The decrease in magnetization is explained by the A-B interaction. In the present case, Cr$^{3+}$ ions of low magnetic-moment values (3\(\mu_B\)) replace Fe$^{3+}$ ions of high magnetic moment (5\(\mu_B\)). The observed magnetic moment (n$_{Bohr}$) per formula unit in Bohr magneton (\(\mu_B\)) was calculated by using the relation [32, 33]:

\[
n_{Bohr} = \frac{\text{Mol. wt} \times M_s}{5585}\]

where n$_{Bohr}$ is the observed magnetic moment of the samples expressed in Bohr magneton, Ms is the saturation magnetization. Fig. 4.11 shows that observed magnetic moment decreases with increase in Cr$^{3+}$ ions, the observed decrease in magneton number is attributed to decrease in A-B interaction.

The applicability of Neel's model has been tested for all the samples of the presently investigated ferrite system. According to Neel's two sub-lattice model of ferrimagnetism, calculated magnetic moment (n$_{Cal}$) per formula unit in \(\mu_B\) is expressed as [33]:

\[
n_{Cal} = M_B(x) - M_A(x)\]

where M$_B$ and M$_A$ are the B and A sub-lattice magnetic moments in \(\mu_B\). The \(n_B^N\) (\(\mu_B\)) values for Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ were calculated using cation distribution
Table 4.3 and ionic magnetic moment of Fe$^{3+}$, Ni$^{2+}$, Mg$^{2+}$ and Cr$^{3+}$ i.e. 5\(\mu_B\), 2\(\mu_B\), 0\(\mu_B\) and 3\(\mu_B\), respectively.

![Graph](image)

**Fig. 4.11:** Variation of observed and calculated magneton number with Cr content x.

The calculated values of magneton number are shown in Fig. 4.11. It is seen that both observed and calculated values of magneton number show decreasing trend. As shown by Hastings and Corliss [34] good agreement between observed and calculated saturation moments can be obtained for a series of mixed ferrites if some of the Cr$^{3+}$ moments (situated at the B-sites) are aligned parallel rather than antiparallel to the A-sites moments. It is observed from Fig. 4.10 that remanence magnetization (Mr) and coercivity (Hc) decreases with increasing Cr$^{3+}$ content x. The deviation from the calculated magnetic moment (using Néel model) may be due to the canted magnetic system.

### 4.2.5 Mössbauer Spectroscopy

Mössbauer spectra of Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ ferrites were recorded at room temperature (300 K). The spectra of all the samples are shown in Fig. 4.12; spectra could be resolved into two well defined sextets each. One of the sextets is attributed to Fe$^{3+}$ ions at tetrahedral (A) site due to its smaller isomer shift and smaller hyperfine field of the Zeeman pattern and the second sextet has been attributed to Fe$^{3+}$ ions at octahedral [B] site due to its larger isomer shift and larger hyperfine field of the Zeeman pattern [35]. The presence of six finger pattern in the spectra of all the samples shows that the samples are magnetically ordered. The values of the Line
width (Γ), isomer shift (IS), quadruple splitting (QS) and hyperfine field (BHF) corresponding to tetrahedral (A) and octahedral (B) sites for all the samples are given in Table 4.4. The line width of the tetrahedral sites becomes broader than that of the octahedral site with the increase of the Cr contents at the octahedral site. Such broadening is, in fact, expected due to a distribution of the hyperfine fields caused principally by a random distribution of Ni²⁺, Fe³⁺ and Cr³⁺ ions at the A and B-site (as evidenced by Table 4.4), since the Fe³⁺ A-sites would feel different configurations of Ni²⁺, Fe³⁺ and Cr³⁺ ions occupying the 12 nearest neighbours B-sites [36]. The observed values of isomer shift show within experimental error, an insignificant change with increasing substitution of Cr³⁺ ions. It implies that the s-electron charge density of Fe³⁺ ions is not influenced by increased Cr³⁺ substitution in Ni-Mg ferrites. It is observed from Table 4.4 that isomer shift value for octahedral sites is greater than that for tetrahedral sites. In cubic spinel ferrites, the bond separation Fe³⁺-O²⁻ is larger for octahedral sites when compared to that for tetrahedral sites.

![Fig. 4.12: Mössbauer spectra of all the samples of Ni₀.₅Mg₀.₅Fe₂₄Cr₅O₄](image)

Due to this, overlapping of orbital of Fe³⁺ ions is small at B-sites and thus a larger isomer shift at B-sites was expected [37,38]. The range of values of isomer shift indicates that iron exists in Fe³⁺ valence state with high spin configuration in the prepared samples [39]. The values of quadrupole splitting (Table 4.4) for hyperfine spectra of all the samples are found to be negligibly small and attributed to the fact
that overall cubic symmetry is maintained between Fe\(^{3+}\) ions and their surroundings with the substituted Cr\(^{3+}\) ions in the present Ni-Mg ferrites. The variations in hyperfine magnetic field at tetrahedral (A) and octahedral (B) sites as a function of Cr\(^{3+}\) substitutions in Ni-Mg ferrites are given in Table 4.4. 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 bonds [33,36].

Table 4.4: Line width (Γ), isomer shift (IS), quadruple splitting (QS) and hyperfine field (BHF)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Site</th>
<th>Γ (mm/s)</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>BHF (Tesla)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>A</td>
<td>0.625±0.025</td>
<td>0.112±0.008</td>
<td>-0.111±0.013</td>
<td>49.11±0.04</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.491±0.028</td>
<td>0.444±0.008</td>
<td>0.194±0.067</td>
<td>49.85±0.05</td>
</tr>
<tr>
<td>0.2</td>
<td>A</td>
<td>0.601±0.039</td>
<td>0.106±0.012</td>
<td>-0.170±0.042</td>
<td>48.08±0.06</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.590±0.056</td>
<td>0.412±0.023</td>
<td>0.188±0.038</td>
<td>48.68±0.08</td>
</tr>
<tr>
<td>0.4</td>
<td>A</td>
<td>0.607±0.103</td>
<td>0.056±0.082</td>
<td>-0.254±0.133</td>
<td>46.57±0.12</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.715±0.059</td>
<td>0.312±0.041</td>
<td>0.179±0.106</td>
<td>46.93±0.07</td>
</tr>
<tr>
<td>0.6</td>
<td>A</td>
<td>0.794±0.106</td>
<td>0.041±0.139</td>
<td>-0.297±0.265</td>
<td>42.00±0.12</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.919±0.091</td>
<td>0.338±0.117</td>
<td>0.162±0.245</td>
<td>42.34±0.09</td>
</tr>
<tr>
<td>0.8</td>
<td>A</td>
<td>0.725±0.034</td>
<td>0.093±0.047</td>
<td>-0.299±0.093</td>
<td>39.62±0.05</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.783±0.042</td>
<td>0.363±0.062</td>
<td>0.285±0.122</td>
<td>39.67±0.03</td>
</tr>
<tr>
<td>1.0</td>
<td>A</td>
<td>1.121±0.025</td>
<td>0.133±0.010</td>
<td>-0.169±0.019</td>
<td>44.67±0.03</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>0.677±0.038</td>
<td>0.547±0.017</td>
<td>0.721±0.038</td>
<td>44.86±0.05</td>
</tr>
</tbody>
</table>

The observed variations in hyperfine magnetic field at A and B sites with increasing Cr\(^{3+}\) substitutions in Ni-Mg ferrites can be qualitatively explained using Neel’s super-exchange interactions [33]. According to Neel’s model, inter sublattice exchange interactions, i.e., AB exchange interactions are stronger than intra sublattice exchange interactions, i.e., AA or BB exchange interactions. As both A and B sites
are occupied by Fe$^{3+}$ ions, so the interaction of Fe$^{3+}$ is possible with Ni$^{2+}$, Mg$^{2+}$ and Cr$^{3+}$ ions. The net magnetic field is mainly due to strong Fe$^{3+}$-$O$-Fe$^{3+}$ interactions. In the present series, Fe$^{3+}$ ions with larger magnetic moment (i.e. 5µB) are replaced by Cr$^{3+}$ ions with smaller magnetic moment 3µB. This results in decrease of magnetic linkages in Fe$_A^{3+}$-$O$-Fe$_B^{3+}$, Fe$_A^{3+}$-$O$-Mg$_D^{2+}$ and Fe$_A^{3+}$-$O$-Ni$_B^{2+}$ and consequently Fe$^{3+}$ ion experience a decrease in the magnetic field at A and B sites. Therefore, hyperfine magnetic field is expected to decrease with increase of Cr$^{3+}$ concentration. In general, the decrease in hyperfine fields is due to decrease in the super-transfer field that arises from the magnetic ions (Fe and Cr) surrounding a given Fe$^{3+}$ ion [40] and in Fermi contact field that is proportional to the magnetic moment of Fe ions [41]. This argument is suitable for Cr$^{3+}$ substitution up to x = 0.8, it is observed from Table 4.4 that hyperfine field shows increased values for x = 1.0 as compared to x = 0.8. With the increase of Cr content (x > 0.8), competition for the octahedral sites takes place between Fe$^{3+}$, Ni$^{2+}$ and Cr$^{3+}$. We assert that Cr$^{3+}$ displaces some of Ni$^{2+}$ from the octahedral sites to tetrahedral site. Usually the saturation magnetization is proportional to the hyperfine field which agrees well with hysteresis measurements [42]. Relation between hyperfine field, H, and the average of sublattice magnetization M can be represented [43] by H = AM, where A is the hyperfine coupling constant and M is the magnetization. Therefore, the magnetization is lowered due to the decrease in hyperfine field.

### 4.2.6 Dielectric Measurements

The dielectric properties of ferrites strongly depend on the several factors, including the method of preparation, chemical composition, and grain size. Fig. 4.13 and 4.14 depicts the variation of real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of the dielectric constant as a function of an ac field at room temperature in the frequency range of 42Hz - 5MHz. It is clearly evident from these Figs. that the dielectric constant initially decreases rapidly in the low frequency region but at very high frequencies; its value becomes so small that it becomes independent of applied frequency. The low-
frequency dispersion in ferrites is observed due to a space-charge effect [44-45]. The imaginary part of dielectric constant ($\varepsilon''$) decreases with increasing frequency at a faster rate than that of real part of dielectric constant ($\varepsilon'$). The observed behaviour can be explained on the basis of interfacial polarization suggested by Koops [46]. During the sintering process the presence of majority $\text{Fe}^{3+}$ ions and minority $\text{Fe}^{2+}$ ions makes ferrite material dipolar, as $\text{Fe}^{2+}$ ions are usually formed due to the partial reduction of $\text{Fe}^{3+}$ ions during the synthesis process. The electron exchange interaction between the ferrous ($\text{Fe}^{2+}$) and ferric ($\text{Fe}^{3+}$) ions results in the local displacement of the electrons in the direction of the applied field, which determines the polarization in ferrites.

![Figure 4.13](image)

**Fig. 4.13:** Variation of real part of dielectric constant ($\varepsilon'$) as a function of log $f$.

The decrease in dielectric constant with increasing frequency is explained to be due to the decrease of polarization of the dipoles when electric field propagates with high frequency. In other words, beyond a certain frequency region or electric field the electron exchange does not follow the applied alternating field. The high value of the dielectric constant at lower frequency region is due to the existence of $\text{Fe}^{2+}$ ions, oxygen vacancies, grain boundary defects, etc [47,48]. While the decrease in dielectric constant with frequency is natural, i.e., any species contributing to the polarizability is found to show lagging behind the applied field at higher frequencies [49]. A plot of dielectric loss tangent ($\tan \delta$) versus frequency at room temperature is
shown in Fig. 4.15. The value of tan δ measures the loss of electrical energy from the applied electric field into the samples at different frequencies. It is observed that the tan δ shows a decreasing trend with increase in frequency. All the samples show normal behaviour except x=0.0. In the case of pure Ni-Mg ferrite (x=0.0) normal behaviour is obtained up to 2 MHz after that the peaking behavior is observed. This type of peaking behavior (Debye-type relaxation) observed when the jumping frequency of the Fe^{2+} and Fe^{3+} ions exactly equal to the frequency of applied field [50]. The dielectric loss is more at high frequency because of increase in interruption to the passage of electric field through the sample due to the interaction of it with the oscillating majority charge carriers of the dipoles.

Further, it is observed from Figs. 4.13 - 4.15 that the dielectric constant, dielectric loss and dielectric loss tangent decreased with Cr^{3+} substitution. This behaviour can be explained by using the assumption of the mechanism of dielectric polarization is similar to that of conduction in ferrites. According to this, the electronic exchange interaction between Fe^{3+} ↔ Fe^{3+} results in a local displacement of the electrons in the direction of an electric field which determines the polarization of ferrites.
The presence of Fe$^{2+}$ ions in excess amount favours the polarization effects [51]. Thus, the more dispersion observed in the sample with low Cr$^{3+}$ ion substitution and can be attributed to the presence of more Fe$^{2+}$ ions in excess amount. As the Cr$^{3+}$ ions substitution increased which replaces Fe$^{3+}$ ions, as the Fe$^{3+}$ ions are reduced in the samples there is less possibility of electronic exchange interaction between Fe$^{2+}$ ↔ Fe$^{3+}$, results in decrease in dielectric parameters.

4.2.7 Frequency Dependence of ac-conductivity

Conductivity is the physical property of a material which characterizes the conducting power inside the material. The electrical conductivity in ferrite is mainly due to the hopping of electrons between the ions of the same element present in more than one valence state and distributed randomly over crystallo-graphically equivalent sites.

The total frequency dependence of ac conductivity is expressed as:

$$\sigma_{\omega \tau} = \sigma_{0} (T) + \sigma (\omega, T) \quad \ldots (4.10)$$

where the first term is dc conductivity which is due to the band conduction and is frequency independent.
Fig. 4.16: Variation of $\sigma_{ac}$ conductivity with log $f$.

The second term is pure ac conductivity due to the hopping process at the octahedral site and it is frequency dependent function. The first term is predominant at low frequencies and at high temperature, while the second term is predominant at high frequencies and at low temperature. The frequency dependence of the second term $\sigma_{ac}$ can be written as:

$$\sigma_{ac} = A\omega^n$$

(4.11)

where $A$ is a constant having the units of conductivity, and the exponent `$n$' is a temperature dependent constant, $\sigma$ is the real part of the conductivity, $\omega$ is angular frequency ($\omega = 2\pi f$).
To understand the effect of the conduction and types of polaron contributing for conduction, the variation of ac conductivity of nano phase chromium substituted nickel magnesium ferrites were studied at different frequencies (42Hz-5Hz) and is illustrated in Fig. 4.16.

Fig. 4.17 shows the variation of lnσ versus lnω in the frequency range of 42Hz to 5MHz, measured at room temperature. The ac conductivity shows an increasing trend with the increase in frequency for all the compositions. Its value first increases linearly according to the power law Eq. (4.11). It is seen that the conductivity of as prepared ferrite shows a gradual rise at low frequencies whereas at higher frequencies the conductivity rises steeply. This behavior can be explained on the basis of that, at low frequencies the conductivity is found low due to the grain boundary effect which acts as hindrance for mobility of the charge carriers. At high frequency regions the conductivity is mainly due to the ionic part which masks the effect due to the grain boundaries. The linear increase in ac conductivity with the frequency confirms the polaron type of conduction [52]. The materials having low conductivity may be good candidates for the microwave applications that require negligible eddy currents [53].

### 4.2.8 Impedance Spectroscopy

The concept of impedance was first introduced by Oliver Heaviside. Impedance spectroscopy is a specific branch of the tree of electrical measurements [54]. It has been among the most useful investigating techniques, since the impedance of the grains can be separated from the other sources of impedance, namely grain boundaries and electrode effects [55]. Impedance analysis provides an opportunity for understating the electrical transport in detail by assuming their resistive and reactive components, separately.

The experimental data can be analysis in terms of four possible complex formalisms such as the complex impedance ($Z^*$), the electric complex modulus ($M^*$), the complex admittance ($Y^*$), and the complex permittivity ($ε^*$). Fig. 4.18 shows the complex impedance or Cole-Cole plot as a function of frequency at room temperature. There is no complete semicircle obtained except $x = 0.0$. All the samples show one semicircle that is due to the conduction of the grain boundary, suggesting that a predominant conduction is through the grain boundary volume. The size of semi circles change with the grain size. In general, different types of dipoles contained in
the material are characterized by their own relaxation time. Therefore, the Cole-Cole plot generally is not exactly semi circular and varies with various degrees of distortions. The centers of these semicircles being dispersed under the real axis by an angle. Furthermore, contribution from the grain is not well resolved in all the samples. It is therefore, concluded that the conductivity for all the samples is mainly due to the grain boundary contribution.

![Cole-Cole plot](image)

**Fig. 4.18:** Cole-Cole plot of $\text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ ferrite nanoparticles at room temperature.

### 4.3 Conclusion

$\text{Ni}_{0.5}\text{Mg}_{0.5}\text{Fe}_{2-x}\text{Cr}_x\text{O}_4$ (0.0 ≤ $x$ ≤ 1.0), ferrite successfully synthesized using a citrate-gel combustion route. The contents of the metal ions ($x$) in the resulting spinel ferrites are close to the theoretical values as shown by EDAX measurements. Structural analyses with XRD reveal that the system confirms the formation of single phase cubic spinel structure of Ni-Mg ferrite. It is also observed that the lattice constant decreases with increase in Cr$^{3+}$ substitution. Infrared spectra show two prominent bands corresponding to spinel ferrite phase. Magnetic analyses confirm that the samples show the ferrimagnetic behaviour. The Mössbauer measurements showed well resolved magnetic spectra for the tetrahedral and octahedral sites. The
hyperfine magnetic field at both the sub lattices decreases with the introduction of increasing Cr\(^{3+}\) ions by breaking the coupling bonds between Fe\(^{3+}\) —O—Fe\(^{3+}\) interactions. The dielectric constant and loss factors decrease with increasing frequency for all the samples. The dielectric parameters also decreased with increase in Cr\(^{3+}\) substitution. The ac conductivity data show that the conduction process is the hopping type. Impedance analysis shows that the conduction mechanism is due to the grain boundary.
References


