Chapter 5

Gadolinium Substitution Induced Changes in the Dielectric and Magnetic Behaviour of Nickel Ferrite Nanoparticles

Structural, magnetic and electrical properties of gadolinium substituted nan.nickel ferrites are presented. XRD technique is used for the structural analysis. Magnetic characterization using VSM revealed that the samples lost its soft magnetic nature due to doping. DC resistivity of the samples is measured as a function of temperature and is found to increase with doping. All the compositions exhibited semiconducting nature. Dielectric measurements are done using impedance analyzer. Dielectric dispersion, absorption and ac conductivity are studied as a function of temperature, frequency and composition.
5.1 Introduction

It is reported that the properties of nanoferrites can be tuned by suitable addition of small amount of divalent or trivalent metal ions. In the past decades, research community was interested on the properties of mixed ferrites and the material science literature is rich in reports regarding this [1,2]. Up to some extent, they succeeded in tuning and optimizing the properties using mixed ferrites. Now-a-days interest is on trivalent rare earth metal ion doped ferrites and the resulting changes in properties. In the previous chapter we have seen that Tb$^{3+}$ ion doping has resulted in structural changes and improvement in electrical as well as magnetic properties of nanocrystalline nickel ferrite.

Reports on the properties of rare earth doped nano ferrites are rather rare in the literature. E. Melagiriyappa et al. [3] have studied the dielectric properties and AC conductivity of samarium substituted Mg-Zn ferrite. Increase in DC resistivity and decrease in dielectric loss has been reported in zinc ferrite by Nd$^{3+}$ substitution [4]. Electric and dielectric properties of Gd$^{3+}$ doped magnesium ferrite has been reported [5]. M. Ishaque et al. [6] have investigated the effect of Yttrium doping on the structural and electrical properties of nickel ferrite prepared by ceramic technique. They observed improvement in the structural and transport properties of NiFe$_2$O$_4$ by the substitution. K. Kamala Bharathi et al. [7] have reported the improvement in dielectric constant and magnetic capacitance of nickel ferrite by the minor doping of Gd and Nd ions. Recently they again reported the synthesis of dysprosium doped nickel ferrite thin films and their structural and optical properties [8]. They reported increase in density, grain size, lattice constant, lattice strain and changes in electronic structure leading to the enhancement in energy gap by Dy$^{3+}$ substitution. Improved magnetic permeability and decreased magnetic loss has been reported for gadolinium doped NiFe$_2$O$_4$ prepared by auto combustion method [9].

In this context, a systematic study on the complete properties of Gd$^{3+}$ doped NiFe$_2$O$_4$ nanoparticles has significance. Thus, in this chapter, the synthesis
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of NiGd\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} system by sol-gel technique and the influence of rare earth metal ion Gd\textsuperscript{3+} doping on the properties of NiFe\textsubscript{2}O\textsubscript{4} nanoparticles is described in detail.

5.2. Experimental

Sol-gel technique has been used for the synthesis of gadolinium doped nickel ferrite samples with general formula NiGd\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} (x=0, 0.1, 0.2 and 0.3). AR grade Ferric nitrate, Nickel nitrate and Gadolinium nitrate (99.9% pure MERK) were used. Details of the method have been presented in section 2.1.1. The obtained powder was ground well and sintered for two hours in a muffle furnace at 400\textdegree C. For DC resistivity and dielectric measurements, cylindrical pellets of the samples (10mm diameter and 2-3mm thickness) were made using a hydraulic press by applying uniform pressure of 5 ton. Silver paste was used as electrode material.

5.3 Results and Discussion

5.3.1 Structural properties

The X-ray diffraction patterns of NiGd\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} (x= 0, 0.1, 0.2 and 0.3) ferrite system are depicted in figure 5.1. All the patterns show diffraction peaks corresponding to polycrystalline cubic spinel structure without any impurity peak, which confirms the single phase nature of the samples. The lattice constants of all the compositions are calculated from the \(d\)-spacing values. The X-ray density, apparent density and porosity of the samples are calculated using equations 4.1, 4.2 and 4.3 respectively. Average grain sizes of the samples corrected for micro strain, estimated from the Hall-Williamson plots [10], average lattice constant (\(a\)), X-ray density (\(\rho_x\)), apparent density (\(\rho_d\)) and porosity of the studied samples are tabulated in table 5.1.
Figure 5.1 XRD Patterns of NiGdₓFe₂₋ₓO₄ ferrite system.

Table 5.1 Structural parameters of NiGdₓFe₂₋ₓO₄ ferrite system.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice parameter (Å)</th>
<th>Crystallite size (nm)</th>
<th>X-ray density (g/cm³)</th>
<th>Apparent density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.332</td>
<td>18.1±1.2</td>
<td>5.382</td>
<td>3.039</td>
<td>43.53</td>
</tr>
<tr>
<td>0.1</td>
<td>8.342</td>
<td>17.2±1.3</td>
<td>5.595</td>
<td>2.790</td>
<td>50.13</td>
</tr>
<tr>
<td>0.2</td>
<td>8.331</td>
<td>15.2±0.8</td>
<td>5.850</td>
<td>2.836</td>
<td>51.52</td>
</tr>
<tr>
<td>0.3</td>
<td>8.303</td>
<td>13.6±1.1</td>
<td>6.145</td>
<td>3.822</td>
<td>54.07</td>
</tr>
</tbody>
</table>

It can be seen from the table that the grain size is decreasing with the increase in gadolinium concentration. Similar results are reported elsewhere [11-13]. It is an established fact that the grain growth depends on grain boundary mobility. A possible reason for the decrease in grain size is the segregation of Gd³⁺ on or near the grain boundaries, which hampers its movement [6].
The lattice constant ($a$) is observed to increase initially up to $x=0.1$, and for higher gadolinium concentrations, it decreases. An increase in the lattice constant with increasing gadolinium content is expected because of the large ionic radius of Gd$^{3+}$ (0.0938nm) compared to that of Fe$^{3+}$ (0.067nm) [6-9, 11]. Gd$^{3+}$ ions are expected to replace Fe$^{3+}$ ions and occupy the octahedral (B) sites, which results in an internal stress to make the lattice distorted and an expansion of the unit cell. J. Jing et al. [14] have reported a decrease in lattice parameter of the LiNi$_{0.5}$Gd$_x$Fe$_{2-x}$O$_4$ system when Gd content ($x$) exceeds 0.04, and which is explained in terms of the compression of the spinel lattice induced by the secondary phase (GdFeO$_3$). In our case, this possibility is omitted because of the single-phase nature of the samples. The transfer of Ni$^{2+}$ ions from octahedral sites to the tetrahedral sites due to the increased concentration of Gd$^{3+}$ ions may be one of the reasons for the decrease in lattice constant for $x > 0.1$ [15]. Moreover, the lattice constant does not solely depend on the ionic radii [16]. There may be contributions from many other factors such as the long range attractive Coulomb force, bond length et., the calculation of which requires precise knowledge of the shape and surface structure of the particles as well as the existence of any surface energy [1,17,18].

Figure 5.2 presents the Hall-Williamson plots of the present ferrite system. As we know, negative slope in the plot is an indication of compressive strain and positive slope represents tensile strain in the nanoparticles. It can be seen from the figure that, the compressive strain in the undoped NiFe$_2$O$_4$ sample is changed to tensile strain due to gadolinium doping. As the doping concentration is increased, the tensile strain in the particles decreased and finally for the sample with $x=0.3$, again the strain became compressive. As expected the X-ray density is increased with increase in Gd content, while the apparent density exhibited an irregular variation. The porosity of the samples is found to increase with increase in Gd$^{3+}$ concentration.
5.3.2 FTIR analysis

The FTIR spectra of ferrite system NiGd$_x$Fe$_{2-x}$O$_4$ ($x = 0, 0.1, 0.2$ and $0.3$) are shown in figure 5.3. FTIR analysis helps to confirm the formation of spinel structure in ferrite samples. As we know, the IR spectra of ferrites are expected to exhibit two major absorption bands in the wave number range $1000-300\text{ cm}^{-1}$. The higher frequency band ($V_1$) is usually observed in the range $600-550\text{ cm}^{-1}$, and is caused by the stretching vibrations of the tetrahedral (A) metal- oxygen bond. The lower one ($V_2$) is in the range $450-385\text{ cm}^{-1}$, and is due to the metal- oxygen vibrations in the octahedral (B) sites [19]. These band positions mainly depend on the bond lengths and the nature of the cations involved. The band positions
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obtained for the studied samples are given in table 5.2 and are found to be in the range reported for nickel ferrite [20, 21].

Figure 5.3 Infrared spectra of NiGd$_x$Fe$_{2-x}$O$_4$ ferrites.

Table 5.2 Magnetic parameters and vibrational frequency band positions of NiGd$_x$Fe$_{2-x}$O$_4$ system.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>$M_S$ (emu/g)</th>
<th>$M_R$ (emu/g)</th>
<th>$H_C$ (Oe)</th>
<th>$V_1$ (cm$^{-1}$)</th>
<th>$V_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>31.44</td>
<td>3.25</td>
<td>86.87</td>
<td>587.15</td>
<td>410.9</td>
</tr>
<tr>
<td>0.1</td>
<td>20.22</td>
<td>13.56</td>
<td>444.84</td>
<td>588.8</td>
<td>407.3</td>
</tr>
<tr>
<td>0.2</td>
<td>17.90</td>
<td>6.46</td>
<td>470.90</td>
<td>592.5</td>
<td>409.0</td>
</tr>
<tr>
<td>0.3</td>
<td>15.98</td>
<td>13.06</td>
<td>462.30</td>
<td>596.1</td>
<td>410.0</td>
</tr>
</tbody>
</table>

It can be seen from the table that for gadolinium doping up to $x = 0.1$, frequency band position $V_1$ is almost constant, while $V_2$ is decreased. It is well known that increased site radius reduces the fundamental frequency and therefore the centre frequency should shift towards lower frequency side [22]. Increase in site radius is expected at the octahedral sites due to the replacement of smaller Fe$^{3+}$ by larger
Gd\(^{3+}\) ions. As the doping concentration is further increased, it is observed that, \(V_1\) is increased and \(V_2\) remains the same. It is already observed that the lattice constant is decreased when the doping concentration, \(x\) is greater than 0.1. This result in decreased site radius and therefore the vibration frequency band positions are increased.

5.3.3 Magnetic Characterization

The room temperature magnetic hysteresis curves of NiGd\(_x\)Fe\(_{2-x}\)O\(_4\) (\(x = 0, 0.1, 0.2\) and 0.3) samples are depicted in figure 5.4. Measured magnetic parameters such as saturation magnetization \((M_S)\), coercivity \((H_C)\) and remanence \((M_R)\) are given in table 5.2. It is evident from the table that, the magnetic properties of nanocrystalline NiFe\(_2\)O\(_4\) is considerably affected by gadolinium doping. As we have observed in case of terbium doped nickel ferrite in chapter 4, the \(M_S\) values are found to decrease with gadolinium concentration. Gd\(^{3+}\) ions are expected to occupy the octahedral (B) sites in place of Fe\(^{3+}\), owing to their large ionic radius. We know that the rare earth metal ions are nonmagnetic and make no contribution to the magnetization of doped ferrite at room temperature [14]. The reduction in B sub-lattice magnetization and the resulting decrease in A-B interaction due to the presence of Gd\(^{3+}\) ions on B-sites cause \(M_S\) to decrease [13, 23, 24]. Increase in porosity and decrease in particle size due to Gd\(^{3+}\) doping may be another reason for the reduction in \(M_S\) with gadolinium content. It is known that porosity is inversely proportional, while the particle size is directly proportional to the magnetization for nano ferrites [25].

A large increase in coercivity is observed for the sample with \(x = 0.1\); the rate of increase then slow down and finally \(H_C\) became almost constant. It is evident from figure 5.4 that, NiFe\(_2\)O\(_4\) lost its soft magnetic nature by gadolinium doping. Coercivity of ferrite nanoparticles are reported to be dependent on factors such as micro strain, particle morphology and size distribution, anisotropy, porosity and magnetic domain size [14]. The increase in coercivity can be
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attributed to the increased porosity and decreased particle size of NiGd$_x$Fe$_{2-x}$O$_4$ system due to doping. Strain developed in the nanoparticles due to Gd$^{3+}$ doping may be another reason. High value of coercivity together with moderately high magnetization and remanence is desirable for ferrites which are used in magnetic recording and memory devices. From table 5.2, it is obvious that minor gadolinium doping ($x = 0.1$) can make NiFe$_2$O$_4$ nanoparticles suitable for such applications.

Figure 5.4 Room temperature hysteresis curves of NiGd$_x$Fe$_{2-x}$O$_4$ ferrite nanoparticles
(a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$ and (d) $x = 0.3$. 

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5.3.4 Electrical Properties

5.3.4.1 DC resistivity

Figure 5.5 presents the plots between $\ln \rho$ and reciprocal of absolute temperature of gadolinium doped NiFe$_2$O$_4$. The variation of dc resistivity is similar to that of terbium doped nickel ferrite. Like terbium doping, gadolinium doped nickel ferrite samples exhibited increase in resistivity with increasing temperature in the range 300-330K. Above 330K all the samples exhibited the usual semiconducting nature of ferrite. As expected resistivity of the samples are observed to increase with the gadolinium concentration. The rise in the room temperature resistivity is not prominent (24.2M$\Omega$cm to 60.5M$\Omega$cm), although at 330K there is a large increase in resistivity (up to 125M$\Omega$cm) by 15% gadolinium substitution. Activation energy values are observed to increase from 0.487eV to 0.593eV (for $x=0.3$) by gadolinium substitution. The variation of resistivity with temperature and composition can be understood in terms of the drift mobility of charge carriers and the hopping conduction mechanism in ferrites; a detailed description of which is given in section 4.3.4.1. Increased porosity and decreased particle size of the samples due to gadolinium doping may be another reason for the enhanced resistivity. High resistivity is desirable in high frequency applications of ferrite as it reduces the eddy current loss.

![Figure 5.5](image)

**Figure 5.5** The relation between dc resistivity and absolute temperature for Ni-Gd system.
5.3.4.2 Dielectric Constant

Figure 5.6 shows the variation of dielectric constant as a function of frequency at room temperature for all the samples in the frequency range 100Hz to 20MHz. All the compositions exhibited normal dielectric behaviour. The values of dielectric constant are high at low frequencies and then decreases rapidly as the frequency increases and ultimately attain constant values, which is a general trend shown by all ferrites [2,3,26,27]. As we know in ferrites, the mechanism of electric conduction and dielectric polarization are similar [28, 29]. Thus, hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions and hopping of holes between Ni$^{3+}$ and Ni$^{2+}$ ions on the octahedral sites, which facilitate electrical conduction, give local displacement of electrons in the direction of applied electric field and results in dielectric polarization. The observed dielectric dispersion of NiGd$_x$Fe$_{2-x}$O$_4$ ferrite system can be well explained using Koop’s phenomenological theory, which considers the dielectric structure of ferrite as a heterogeneous medium of Maxwell-Wagner type. A detailed description of the theory is given in section 4.3.4.2.

![Figure 5.6 Variation of dielectric constant with frequency.](image-url)
The temperature dependence of dielectric constant of the sample with \( x = 0.1 \), at selected frequencies is shown in figure 5.7. All other compositions show similar behaviour. Dielectric constant initially decreased in the temperature range 300-340K, and then increased with temperature with a transition peak around 430K.

![Figure 5.7 Variation of dielectric constant with temperature at selected frequencies for NiGd_0.1Fe_1.9O_4 sample.](image)

The initial decrease in dielectric constant, which is absent in pure nickel ferrite sample, is an effect of the elastic and inelastic scattering due to the rare earth ions. The increase in temperature enhances the drift mobility of charge carriers and thus the hopping rate increases which results in increased dielectric constant. It is well known that, in ferrites, the dielectric constant is inversely proportional to the square root of resistivity [30]. This is evident in the present work, as the temperature variation of dielectric constant is exactly opposite to that of DC resistivity. The observed transition around 430K, as we have seen in previous chapter, may be due to the low ionization potential of nickel.

It is evident from figure 5.8 that gadolinium doping has resulted in a reduction in the dielectric constant of NiFe_2O_4. The replacement of Fe^{3+} in the octahedral sites by Gd^{3+} ions of stable valency, decreases the rate of hopping and hence the dielectric constant decreases with composition [31, 32]. It is observed
that the decrease is prominent for minor doping and the rate of decrease slows down as the doping concentration rises.

Figure 5.8 Variation of dielectric constant with composition at different frequencies.

5.3.4.4 Dielectric loss ($\varepsilon''$)

Figure 5.9 shows the variation of dielectric loss ($\varepsilon''$) at room temperature, as a function of frequency for the studied gadolinium doped nickel ferrite samples. All the compositions exhibit normal dielectric behaviour. The dielectric loss decreases rapidly at the low frequency region. The rate of decrease slows down as the frequency increases and finally $\varepsilon''$ becomes almost frequency independent. Such behaviour can be explained on the basis of Koop’s phenomenological theory. In the low frequency region, poorly conducting grain boundaries are active and so hopping of electrons require more energy. At high frequencies, highly conducting grains become active and hence energy needed for hopping decreases [33, 34]. From figure 5.10 it is clear that the dielectric loss decreases with increasing gadolinium concentration and this can be attributed to the increase in resistivity. Similar results are reported for yttrium doped nickel ferrite [6] and gadolinium doped magnesium ferrite [5].
Figure 5.9 $\varepsilon''$ versus ln $f$ graphs of NiGd$_x$Fe$_{2-x}$O$_4$ ferrite system.

Figure 5.10 $\varepsilon''$ versus composition graphs for NiGd$_x$Fe$_{2-x}$O$_4$ ferrite system.

5.3.4.5 AC Conductivity

AC conductivities of all the compositions are calculated from the dielectric data using equation 2.18. Figure 5.11 presents the frequency
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dependence of AC conductivity at room temperature for all the samples. It is observed that, AC conductivity is increased with increase in frequency. The frequency dependence of AC conductivity can be explained with the help of Maxwell-Wagner two-layer model of polycrystalline ferrites [35, 36]. In the low frequency region, as we know, grain boundaries are more active and due to their high resistance, conductivity is less. Similar results are reported [37, 38]. In the high frequency region, conductive grains become active and so the conductivity also becomes high. Almost linear nature of the AC conductivity plots confirms the conduction due to small polaron hopping in the studied gadolinium doped nickel ferrite samples [39].

![Figure 5.11](image)

Figure 5.11 Plots showing frequency dependence of AC conductivity of NiGd_xFe_{2-x}O_4 ferrite system.

Variation of AC conductivity with absolute temperature for the sample with x = 0.1, at different frequencies is depicted in figure 5.12. All other samples show similar behaviour. As expected, the variation of AC conductivity is similar to that of the dielectric constant, since, for ferrites dielectric constant is directly proportional to the square root of conductivity [6, 30]. It is clear from
the figure that, conductivity is more frequency dependent in the lower temperature region and the frequency dependence decreases at high temperatures, which is in accordance with equation 2.19. Moreover, dispersion is observed in the low temperature region and the conductivity became less temperature dependent at high temperatures. In the lower temperature region, the drift mobility of charge carriers is low. Thus, the mobility and hence the conductivity increases rapidly by the increase in temperature as it increases the hopping frequency.

Figure 5.12 Temperature dependence of AC conductivity at selected frequencies.

Figure 5.13 Variation of AC conductivity with gadolinium content for NiGd_xFe_{2-x}O_4 system.
In the high temperature region, huge thermal energy causes large lattice vibrations and the scattering of charge carriers due to their collisions with the vibrating lattice is expected to damp the mobility and hence the conductivity becomes less temperature dependent. From figure 5.13 it is obvious that, the conductivity is decreased with increasing gadolinium doping concentration. This is expected since, as we know, the replacement of Fe$^{3+}$ ions on the octahedral sites by Gd$^{3+}$ inhibits the hopping conduction. The rate of decrease is observed to increase with gadolinium concentration.

5.4. Conclusion

Using sol-gel technique, gadolinium ions are successfully incorporated in to NiFe$_2$O$_4$, keeping its spinel structure and without the formation of any impurity phase. Gadolinium addition has made structural deformation and remarkable improvement in electrical and magnetic properties of nickel ferrite. Grain size of Ni-Gd ferrite samples is found to decrease with gadolinium concentration. Lattice parameter is observed to increase with gadolinium content initially, owing to the large ionic radius of Gd$^{3+}$, and for higher doping concentration it decreased. The X-ray density and porosity of the samples are increased with increase in gadolinium concentration.

Gadolinium doping greatly influenced the magnetic properties of nickel ferrite nanoparticles. Saturation magnetization is found to decrease with increase in gadolinium concentration. Doping has resulted in a large increase in coercivity and as a result nickel ferrite lost its soft magnetic nature. High value of coercivity together with moderate magnetization and remanence make these Ni-Gd ferrites suitable for magnetic recording and memory devices.

The temperature variation of DC resistivity of all the samples exhibited usual semiconducting nature of ferrites and the resistivity is observed to increase with gadolinium concentration. All the compositions exhibited normal dielectric behaviour of ferrites. The observed increase in AC conductivity and
dielectric constant with temperature is explained in terms of increase in drift mobility of charge carriers. The linear nature of AC conductivity versus frequency plots confirmed small polaron type hopping conduction in the present Ni-Gd ferrite system. Gadolinium doping decreased the dielectric loss of nickel ferrite nanoparticles.
References:

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