Chapter 3

Influence of Preparation Methods on Structural, Magnetic and Electrical Properties of Nanocrystalline Nickel Ferrite

The properties of ferrite nanoparticles are influenced by the composition and microstructure that are sensitive to the preparation methodology used. Hence, a comparative study of the properties of nano ferrite synthesised by different techniques has significance. Nickel ferrite nanoparticles of very small size were prepared by sol-gel combustion and co-precipitation techniques. The study of intrinsic properties of materials may lead to important new ideas and the origin of new theories. Hence, structural, magnetic and electrical properties of nanoparticles synthesized by these two methods were analyzed and compared in this chapter.
3.1 Introduction

During the last few years, ferrite nanoparticles have drawn widespread attention because of their technological importance in high density magnetic storage, electronic and microwave devices, telecommunication equipments, magnetic fluids, magnetically guided drug delivery and gas sensors [1-6]. Among various ferrites, which form a major constituent of the magnetic ceramic materials, nano sized nickel ferrite possess attractive properties for the application as soft magnets, core materials in power transformers and low loss materials at high frequencies [7]. High permeability in the radio frequency region, high electrical resistivity, high Curie temperature and low eddy current lose are the important properties of nickel ferrites, which make them suitable for wide range of applications [8]. Being a technologically important material, Ni-ferrites as well as Ni-based mixed ferrites are extensively investigated by various researchers [1, 9-11].

Nickel ferrite has inverse spinel structure. The crystal structure is face centred cubic with the unit cell containing 32 O²⁻, 8 Ni²⁺ and 16 Fe³⁺ ions. The oxygen ions form 64 tetrahedral and 32 octahedral sites, where 24 cations are distributed. The eight Ni²⁺ and the eight Fe³⁺ cations occupy half of the octahedral sites and the other eight Fe³⁺ ions occupy eight tetrahedral sites [12, 13]. Ferrimagnetic property of the material arises from magnetic moments of anti-parallel spins between Fe³⁺ ions at tetrahedral sites and Ni²⁺ & Fe³⁺ ions at octahedral sites [14].

The magnetic and electrical properties of ferrites are sensitive to their composition and processing techniques. In order to see the role of different synthesis techniques on the growth, structural morphology and the intrinsic properties of Ni-ferrite, in the present work, ultra fine nickel ferrite nanoparticles were prepared by sol-gel and co-precipitation methods and their structural, magnetic and electrical properties were thoroughly investigated.
3.2 Experimental

Nickel ferrite samples were prepared using sol-gel as well as co-precipitation techniques. Details of the synthesis techniques are already presented in section 2.1. In order to study the effect of sintering temperature on properties, different portions of the same sample are sintered at 400°C, 600°C and 800°C for 2 hour using a muffle furnace. For dielectric and resistivity measurements, cylindrical disc shaped pellets (10mm diameter and 2-3mm thickness) were made by applying a uniform pressure of 5 ton using a hydraulic press.

3.3 Results and Discussion

3.3.1 Structural Properties

Figure 3.1 shows the XRD patterns of NiFe₂O₄ (a) co-precipitation derived samples and (b) sol-gel derived samples. The patterns were compared with standard data (JCPDS PDF card No.074-2081) and the formation of cubic NiFe₂O₄ nanoparticles in all the samples was confirmed. Sol-gel derived samples sintered at 600°C and 800°C as well as co-precipitated sample sintered at 800°C show some extra peaks, indicating minor presence of Hematite (Fe₂O₃) phase in the samples. Crystallite size of the samples were calculated for the (311) peak using Scherrer formula [15]. Grain size of the samples, corrected for microstrain was calculated from Hall-Williamson plots [16, 17]. The actual (x-ray) density of the synthesized NiFe₂O₄ nanoparticles was calculated using the formula [18],

\[ \rho_x = \frac{8M}{N\alpha^3} \]  

Where, \( M \) is the molecular weight (kg) of the sample, \( N \) is the Avogadro’s number (per mol) and \( \alpha \) is the lattice constant (Å). The apparent density of the samples is determined using the formula

\[ \rho_a = \frac{m}{\pi r^2 h} \]  

Where, \( m \) is the mass, \( r \) is the radius and \( h \) is the thickness of the pellet.
Percentage porosity $P$ of the ferrite samples were then determined employing the relation [18],

$$P = (1 - \frac{\rho_o}{\rho_x}) \times 100$$

The crystallite size of the samples obtained using Scherrer formula, particle size estimated from Hall-Williamson plots, X-ray density, apparent density and the porosity are tabulated in table 3.1.

It is obvious from the table that co-precipitation yields Ni-ferrite nanoparticles with very small size; while sol-gel technique yields nanoparticles with moderate size. Similar results have been reported earlier in case of magnesium ferrite [19]. Thus it is clear that sol-gel derived particles attain better crystallinity even at lower sintering temperature.

![Figure 3.1 X-ray diffraction pattern of Ni-ferrite nanoparticles prepared by (a) co-precipitation and (b) sol-gel technique, sintered at (i) 400°C (ii) 600°C and (iii) 800°C.](image)

In sol-gel as well as co-precipitation, the crystallite size is observed to be increasing with temperature. It has been reported earlier that annealing process generally decreases lattice defects and strains; however, it can also cause coalescence of smaller grains that results in an increase in the average grain size of nanoparticles [20]. X-ray density is observed to be less than that reported for
nickel ferrite produced by ceramic technique; but it is greater than the apparent density of Ni-ferrite which is in accordance with literature [18].

<table>
<thead>
<tr>
<th>Technique</th>
<th>Sintered temperature (°C)</th>
<th>Crystallite size (Scherrer formula) (µm)</th>
<th>Lattice parameter (Hall-Williamson plot) (Å)</th>
<th>X-ray density (g/cc)</th>
<th>Apparent density (g/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol-gel</td>
<td>400</td>
<td>16.3</td>
<td>18.1±1.2</td>
<td>8.732</td>
<td>5.382</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>18.7</td>
<td>21.4±0.9</td>
<td>8.313</td>
<td>5.384</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>39.6</td>
<td>49.24±1.7</td>
<td>8.337</td>
<td>5.372</td>
</tr>
<tr>
<td>Co precipitation</td>
<td>400</td>
<td>7.66</td>
<td>9.57±1.1</td>
<td>8.338</td>
<td>5.371</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>18.1</td>
<td>19.7±0.7</td>
<td>8.334</td>
<td>5.378</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>23.8</td>
<td>30.84±1.4</td>
<td>8.341</td>
<td>5.365</td>
</tr>
</tbody>
</table>
Calculated values of lattice parameter of Ni-ferrite samples are listed in table 1, which are in close agreement with standard data (8.34Å) [12]. It is clear from the table that the lattice constant is almost constant, showing negligible variation with sintering temperature in both methods. Figure 3.2 depicts Hall-Williamson plots for all the samples. Negative slopes in these plots indicate the presence of compressive strain and positive slope is an indication of tensile strain in the nanoparticles [17]. In the present case, at lower sintering temperature slopes are negative indicating the presence of compressive strain. However, plots of the samples sintered at higher temperature show positive slopes, indicating tensile strain developed in the particles.

Figure 3.2 Hall-Williamson plots of Ni-ferrite synthesized by (i)sol-gel technique and (ii) co-precipitation sintered at (a)400°C, (b)600°C and (c)800°C.

The stoichiometry of the powder samples in both the methods was checked by EDX analysis. EDX patterns of the samples are shown in Figure 3.3 and composition of the elements present is given in Table 3.2. Both samples show expected stoichiometry; while co-precipitation derived sample indicates a little deficiency of iron and the excess presence of nickel. No trace of any impurity was found which indicates the purity of the samples.
Figure 3.3 EDX spectra of (a) co-precipitation and (b) sol-gel derived samples.

Table 3.2 EDX analysis results of NiFe$_2$O$_4$ samples prepared by co-precipitation and sol-gel techniques.

<table>
<thead>
<tr>
<th>Element present</th>
<th>Co-precipitation</th>
<th>Sol-gel technique</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expected (atomic %)</td>
<td>EDX (atomic %)</td>
</tr>
<tr>
<td>Ni</td>
<td>14.29</td>
<td>15.033</td>
</tr>
<tr>
<td>Fe</td>
<td>28.57</td>
<td>26.494</td>
</tr>
<tr>
<td>O</td>
<td>57.14</td>
<td>58.493</td>
</tr>
</tbody>
</table>
Morphology and particle size of the synthesized samples were investigated using High Resolution Transmission Electron Microscope (HRTEM). Figure 3.4 presents HRTEM images of Ni-ferrite nanoparticles synthesized by (a) co-precipitation and (b) sol-gel techniques, sintered at 400°C. From Fig.3 (a) it is observed that sol-gel derived particles are slightly agglomerated with almost spherical shape and a particle size of 20-30nm, which confirm the XRD analysis. Co-precipitation derived particles are of irregular shape with a wide particle size distribution of 10-25nm. Thus, it is evident that sol-gel synthesis gives Ni-ferrite particles of moderate size and a narrow particle size distribution. Grains in the co-precipitation derived sample can be clearly viewed in the two dimensional and three dimensional AFM images shown in figure 3.5. Grain sizes obtained from the AFM analysis is in the nanometre regime. Figure 3.7 presents SEM image of sol-gel derived nickel ferrite sample pellet. It is clear from the figure that the grain sizes are in the nanometre range and are agglomerated.
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Figure 3.5 Grain sizes of co-precipitation derived nickel ferrite nanoparticles sintered at 400°C from AFM height mode.

Figure 3.6 Surface morphology of co-precipitation derived Ni-ferrite nanoparticles from AFM 3D mode.
3.3.2 FTIR Analysis

Fourier Transform Infra Red (FTIR) spectra analysis helps to confirm the formation of spinel structure in ferrite samples. The FTIR spectra of the investigated NiFe$_2$O$_4$ samples are shown in figure 3.8. In the wave number range of 1000-300 cm$^{-1}$, two main broad metal-oxygen bands are seen in the infrared spectra of all spinels, especially ferrites. The higher one ($V_1$) generally observed in the range 600-550 cm$^{-1}$, is caused by the stretching vibrations of the tetrahedral metal-oxygen bond. The lowest band ($V_2$) usually observed in the range 450-385 cm$^{-1}$, is caused by the metal-oxygen vibrations in the octahedral sites [21]. The vibrational frequencies of IR bands $V_1$ and $V_2$ of samples prepared by both co-precipitation and sol-gel are given in table 3.3, which are in perfect agreement with reported values [22, 23]. The spectra show prominent bands near 3400 cm$^{-1}$ and 1600 cm$^{-1}$, which are attributed to the stretching modes and H-O-H bending vibrations of the free or absorbed water. The band near 1400 cm$^{-1}$ is due to the anti-symmetric NO-stretching vibrations arising from the nitrate group which is present as residue in the samples [22]. This band is very weak in the spectra of
sol-gel derived sample, indicating the purity of Ni-ferrite nanoparticles synthesized by this method.

![FTIR spectra of Ni-ferrite samples](image)

**Figure 3.8** FTIR spectra of Ni-ferrite samples prepared by co-precipitation and sol-gel techniques.

### 3.3.3 Magnetic Properties

Magnetic characterization of the samples was performed by Vibrating Sample Magnetometer (VSM) at room temperature with maximum applied field of 15kOe. Figure 3.9 shows the typical magnetic hysteresis loops of Ni-ferrite samples prepared by (a) co-precipitation and (b) sol-gel technique, heat treated at (i) 400°C and (ii) 600°C.

It is obvious from the Figure that saturation magnetization ($M_s$) is not attained even in the maximum field of 15kOe, which indicates the presence of some paramagnetic oxides. FTIR analysis indicated the presence of NO as impurity in the sample and is paramagnetic in nature. The $M_s$ values of all the samples were calculated by extrapolating the inverse of the field versus magnetization ($M$) graph to $1/H = 0$ [24]. The saturation magnetization ($M_s$), coercivity ($H_c$) and remanence ($M_r$) of all the samples are given in table 3.3.
Figure 3.9 Room temperature hysteresis loops of Ni-ferrite samples synthesized by (a) co-precipitation and (b) sol-gel techniques; heat treated at (i) 400°C and (ii) 600°C.

It is observed that co-precipitation derived Ni-ferrite particles sintered at 400°C are not exhibiting hysteresis with almost immeasurable remanence and coercivity. This is a unique property of superparamagnetism [25, 26, 27] and the particles are of single domain nature. However, as it is evident from figure 3.9(a), when heated at 600°C, particle grows and became multi domain in nature and hence exhibits hysteresis with a considerable rise in magnetization. This is expected since at higher temperature, there is increase in particle size as it is clear from X-ray diffraction analysis.

Co-precipitation derived sample heated at 600°C has very small $M_r$ and $H_C$ values but almost equal $M_S$ value compared with the corresponding sol-gel derived sample. Sol-gel derived samples are ferrimagnetic with moderately high saturation magnetization. Comparatively less increase in $M_S$ values for sol-gel derived samples may be due to the presence of Fe$_2$O$_3$ or due to its comparatively small increase in particle size. The low value of saturation magnetization compared with that of bulk Ni-ferrite in both methods (56emu/g) [10, 28] can be understood on the basis of core-shell model, which explains that the finite size effects of the nanoparticles lead to a canting of spins on their surface and thereby reduces its magnetization [22, 29].
Table 3.3
Magnetic and electrical characterization results and IR frequency band positions of nickel ferrite samples

<table>
<thead>
<tr>
<th>Technique</th>
<th>Sintered temperature (°C)</th>
<th>$M_s$ (emu/g)</th>
<th>$H_C$ (Oe)</th>
<th>$M_r$ (emu/g)</th>
<th>Activation Energy (eV)</th>
<th>Resistivity ($\Omega \cdot cm$)</th>
<th>IR frequency bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sol-gel</td>
<td>400</td>
<td>30.838</td>
<td>86.665</td>
<td>3.25</td>
<td>0.487</td>
<td>24.2</td>
<td>584</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>31.626</td>
<td>113.995</td>
<td>3.88</td>
<td>0.503</td>
<td>31.8</td>
<td>---</td>
</tr>
<tr>
<td>Co-precipitation</td>
<td>400</td>
<td>14.222</td>
<td>---</td>
<td>---</td>
<td>0.462</td>
<td>19.08</td>
<td>597.5</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>30.899</td>
<td>38.785</td>
<td>1.59</td>
<td>0.483</td>
<td>25.7</td>
<td>---</td>
</tr>
</tbody>
</table>
3.3.4. Electrical Properties

3.3.4.1. DC Resistivity

The temperature variation of DC resistivity of sol-gel as well as co-precipitation derived nickel ferrite samples are depicted in figure 3.10. Resistivity of the samples is found to decrease with increase in temperature. This semi conducting nature, generally observed for ferrites, is due to the increase in thermally activated drift mobility of charge carriers [30, 31]. The rate of decrease is slow in the low temperature range, where the contribution from impurities and lattice defects dominates. As we have seen in section 1.4, conduction in ferrite can be explained by the hopping model of electrons [32]. The electric conduction in NiFe$_2$O$_4$ is due to the electron hopping between Fe$^{2+}$ and Fe$^{3+}$ and the hole hopping between Ni$^{3+}$ and Ni$^{2+}$ [30, 33]. It is also observed that sintering at high temperature has increased the rate of decrease of resistivity after the transition temperature.

Resistivity of ferrites is known to depend upon the purity of the starting compounds and the preparation details such as sintering temperature and atmosphere, which also influence the micro structure and the composition of the prepared samples. The grain size, grain boundaries, porosity and stoichiometry are important factors in this regard [34].

Figure 3.10 Temperature dependence of DC resistivity of nickel ferrite prepared by (a) co-precipitation and (b) sol-gel technique.
As we observed in the present system, grain size of ferrite samples is generally found to increase with increase in firing temperature. It has been reported [35, 36] that the resistivity of polycrystalline materials in general decreases with increase in particle size; smaller grains imply larger number of insulating grain boundaries which acts as barriers to the flow of electrons. Besides, smaller grains have smaller grain-grain surface contact area and therefore a reduced electron flow. Thus resistivity of ferrites is expected to decrease with increase in sintering temperature. However, in contradiction to this, the resistivity of the present system of nickel ferrite samples is observed to increase with increase in sintering temperature. Mathew George et al [36] have reported similar results and they explained this in terms of the localized stage in the forbidden energy gap which arises due to lattice imperfections. Presence of these states effectively lowers the energy barriers for the flow of electrons. Increased sintering temperature results in more uniform crystal structures with reduced imperfections thereby increasing the sample resistivity. A similar trend in resistivity was reported by Van Uitert [37]. He also explained it in terms of increased homogeneity and structural perfection with increase in sintering temperature.

The room temperature resistivity values and activation energy calculated from Arrhenius plots using equation 1.20 are presented in table 3.3. The sol-gel derived nickel ferrite samples are observed to be more resistive and this may be due to the increased particle size and reduced structural imperfections. The transition observed around 430K may be due to the small ionization potential of Ni (176kCal) [38]. Accordingly one can expect that, Ni$^{2+}$ ions play a significant role in the polarization and conduction process in the low temperature region.

### 3.3.4.2. Dielectric Constant

Ferrites are dipolar due to the presence of majority Fe$^{3+}$ and minority Fe$^{2+}$ ions. The rotational displacements of the dipoles result in orientational polarization. The rotation of Fe$^{3+}$-Fe$^{2+}$ dipoles may be visualized as the exchange
of electrons between the ions so that the dipoles align themselves with the applied field. The existence of inertia to the charge movement would cause relaxation of the polarization [39].

![Figure 3.11 Variation of dielectric constant with frequency for NiFe₂O₄, synthesized by (a) co-precipitation and (b) sol-gel techniques.](image)

The variation of real part of dielectric permittivity ($\varepsilon_r$) with frequency (100Hz to 20MHZ) at room temperature for the synthesized ferrite samples are shown in figure 3.11. From the figure it is clear that the dielectric constant initially decreases rapidly with increase in frequency and then decreases slowly at higher frequencies. The decrease in dielectric constant with frequency is a normal dielectric behaviour of soft ferrites. Similar results were reported by several authors [40, 41]. The frequency variation of dielectric constant reveals the dispersion due to Maxwell-Wagner type [42, 43] interfacial polarization, which is in agreement with Koop’s phenomenological theory [44]. According to this model, the dielectric structure of the ferrite is supposed to be composed of two layers; well conducting grains which are separated by poorly conducting grain boundaries. The grain boundaries are more effective at low frequencies, but grains are effective at high frequencies [44].
It is well known that, in ferrites the mechanism of electric conduction and dielectric polarization are similar [45]. In NiFe$_2$O$_4$ hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ ions and hopping of holes between Ni$^{3+}$ and Ni$^{2+}$ ions on octahedral (B) sites, that facilitate the electrical conduction, give local displacements of electrons in the direction of the applied electric field and that results in the polarization [33]. During the hopping process, electrons must pass through the grains and grain boundaries of the dielectric medium. Due to the high resistance of the grain boundaries, electrons accumulate on the grain boundaries and produce space charge polarization which results in high value of dielectric constant at low frequencies [39, 46, 47]. As the frequency of the alternating electric field increases, grains come into action and dielectric constant reduces rapidly due to the decrease in dielectric polarization. At high frequencies, even though the conductivity is high, hopping of electrons cannot follow the alternating field and so the dielectric constant becomes very small and almost frequency independent [48, 49].

In the present work, it is observed that the dielectric constant is decreased with the increase in sintering temperature for both sol-gel and co-precipitation derived samples. This is expected, since the resistivity of the samples is increased with increase in sintering temperature. It is already reported that, for ferrites the dielectric permittivity is inversely proportional to the square root of resistivity [50]. The value of dielectric constant is comparatively less for NiFe$_2$O$_4$ synthesized by sol-gel technique and this is due to the high resistivity of these samples.

In order to study the effect of temperature on dielectric properties, dielectric constant is measured as a function of temperature at selected frequencies and is presented in figure 3.12. As expected the temperature variation of dielectric constant is found to be exactly opposite to that of DC resistivity. The increase in $\varepsilon_r$ can be related to the increase in drift mobility of electrons.
Hopping of electrons is thermally activated by the increase in temperature and so the hopping frequency increases. This results in an increase in space charge polarization, leading to an increase in the dielectric constant with temperature [47, 51]. The dielectric constant of any material is due to dipolar, electronic, ionic and interfacial polarizations. At low frequencies, dipolar and interfacial contributions are dominant and both these polarizations are temperature dependent. This explains the rapid increase in dielectric constant with temperature at low frequencies. Electronic and ionic polarizations dominate at higher frequencies and their temperature dependence is insignificant [52]. The plots exhibit dispersion peaks with transition around 430K for both samples and which is attributed to the low ionization potential of nickel [38]. Similar behaviour is reported for doped Ni-Zn and Cr-Zn ferrite [38, 41, 51]. Beyond the transition temperature, the thermal energy added to the system overcomes the field effect and decreases the internal viscosity of the system, giving more degrees of freedom to the dipoles, and increasing the entropy of the system, which results in a decrease in $\varepsilon_r$ [53]. There after the dielectric constant is observed to increase slowly towards the second transition peak where ferromagnetic to paramagnetic transition is reported to happen in spinel ferrites [51, 54]. However, in the present case this transition temperature (Curie temperature) is beyond the measured temperature range.

![Figure 3.12](image-url)  

**Figure 3.12** Temperature dependence of dielectric constant at selected frequencies for nickel ferrite prepared by (a) co-precipitation and (b) sol-gel technique.
Energy absorption within a dielectric medium is characterized by the imaginary part of dielectric permittivity ($\varepsilon''$). The variation of $\varepsilon''$ with frequency at room temperature for the synthesized Ni-ferrite samples is depicted in figure 3.13. All the samples exhibit normal dielectric behaviour. Dielectric loss decreases rapidly at the low frequency region. As the frequency increases, the rate of decrease slow down and the loss factor becomes almost frequency independent. The high value of $\varepsilon''$ at lower frequencies corresponds to high resistivity due to grain boundaries. Hence more energy is required for the hopping of electrons, resulting in high energy loss. However, in the high frequency region, which corresponds to the high conductivity of grains, energy required for the hopping of electrons is less and thereby $\varepsilon''$ becomes small [55, 56]. None of the samples exhibit loss peak. The loss maxima occurs when the hopping frequency of electrons become equal to the frequency of the applied alternating electric field [48].

![Figure 3.13 Frequency dependence of dielectric loss ($\varepsilon''$) for (a) co-precipitation and (b) sol-gel derived NiFe$_2$O$_4$ samples.](image)

It is obvious from the figure that $\varepsilon''$ is decreased with increase in sintering temperature in both the methods and this can be explained in terms of the
variation of resistivity of the samples with sintering temperature. Dielectric loss is a major part of the total core loss in ferrites [57]. Hence for minimising core loss, ferrite material with low dielectric loss is desirable. In the present work, it is observed that the sol-gel derived NiFe$_2$O$_4$ samples exhibit comparatively less dielectric loss in the measured frequency range and this can be attributed to the high resistivity of these samples. Thus, it is concluded that sol-gel method is much better for the production of ferrites for high frequency applications.

### 3.3.4.4 AC Conductivity

The AC conductivity of the samples was calculated from the dielectric data using equation 2.18. The variation of AC conductivity as a function of frequency at room temperature for the synthesized Ni-ferrite samples is represented in figure 3.14. It is clear from the figure that the AC conductivity remains almost constant in the low frequency region for all the samples, however exhibits dispersion for high frequencies which is well in accordance with equation 2.19. The plots are observed to be almost linear, confirming the small polaron type conduction in the samples. The formation of small polaron may be due to the defect levels or oxygen vacancies created during sintering. In most of the disordered solids AC conductivity is directly proportional to the frequency, confirming the linear nature [49, 58]. In the present study, it has been observed that, the AC conductivity gradually increases as the frequency of the applied AC field increases. Since the increase in frequency enhances electron hopping frequency, conductivity increases. The frequency dependence of AC conductivity can be explained with the help of Maxwell- Wagner [45, 46] two-layer model of polycrystalline ferrites. When the applied frequency is low, poorly conducting grain boundaries are more effective and so the conductivity is less. As the frequency rises, conductive grains become active and hence hopping conduction increases [46, 49]. As expected, Ni-ferrite samples synthesized by co-precipitation are exhibiting higher conductivity than the corresponding sol-gel
derived ones. It is also evident from figure 3.14 that, the conductivity is decreased with the increase in sintering temperature in both the preparation methods and this is in accordance with the resistivity changes.

![Figure 3.14](image)

**Figure 3.14** Variation of AC conductivity with frequency for NiFe$_2$O$_4$ prepared by (a) co-precipitation and (b) sol-gel technique.

According to the correlated barrier hopping model [59], AC conductivity is

\[
\sigma(\omega) = \frac{\pi^3}{24} N^2 \varepsilon_r R_\omega^6 \omega
\]

Where, \( N \) is the concentration of defect sites contributing to the hopping mechanism, \( \varepsilon_r \) is the dielectric permittivity and \( R_\omega \) is the hopping distance. Increase in sintering temperature can increase the structural improvement. Increased sintering temperature results in more uniform crystal structures with reduced imperfections and thereby decrease the value of \( N \), which ultimately reduces the value of AC conductivity. Hence samples fired at high temperature possess low value of conductivity. A similar trend in conductivity was reported by Van Uitert [37], who also explains it in terms of increased homogeneity and structural perfection with increase in sintering temperature.
Figure 3.15 Variation of AC conductivity with temperature at selected frequencies for NiFe$_2$O$_4$ Prepared by (a) co-precipitation and (b) sol-gel techniques.

Figure 3.15 presents curves that correlate $\ln \sigma_{ac}$ with absolute temperature at selected frequencies for (a) co-precipitation and (b) sol-gel derived samples. In both figures, the AC conductivity profiles are similar to those of dielectric constant, since, as we know for ferrites, the dielectric permittivity is directly proportional to the square root of conductivity [48]. At lower temperatures, conductivity gradually increases with temperature and then a rapid increase is observed with transition peaks around 430K, which can be attributed to the increase in drift mobility of charge carriers. 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. It is also obvious from the figure that in both the methods, the conductivity becomes frequency independent at high temperature region [41, 47, 51].
3.4 Conclusion

Nanocrystalline nickel ferrite was successfully synthesized by sol-gel and co-precipitation techniques. Both methods produced single phase cubic NiFe$_2$O$_4$ nanoparticles with expected stoichiometry. However, sol-gel derived samples sintered at high temperatures ($\geq 600^\circ$C) exhibited an additional hematite (Fe$_2$O$_3$) phase. Co-precipitation technique produced nanoparticles of very small size with a wide size distribution and super paramagnetic nature. Ni-ferrite samples prepared by sol-gel technique are of comparatively larger size with narrow size distribution and are ferrimagnetic. Magnetic properties including saturation magnetization, coercivity and remanence are observed to be increasing with increase in sintering temperature in both the methods and this can be attributed to the increase in particle size. When heated at higher temperatures, co-precipitation derived sample lost its super paramagnetic nature and became ferrimagnetic.

The temperature variation of DC resistivity of the samples reflects usual semiconducting nature of ferrites, which is explained using the hopping conduction model. The increase in resistivity with sintering temperature in both the methods is explained in terms of localized states in forbidden energy gap which arises due to lattice imperfections. Sol-gel synthesized NiFe$_2$O$_4$ samples are found to be more resistive than the corresponding samples prepared by co-precipitation technique. Eddy current loss in ferrite materials mainly depends on the eddy current circuit dimensions and electrical resistivity. Hence eddy current loss will be less for nickel ferrite prepared by sol-gel technique. All the samples demonstrate normal dielectric behaviour. The observed dielectric dispersion is explained in terms of Maxwell-Wagner two-layer model, in accordance with Koop’s phenomenological theory and the electron hopping mechanism. Almost linear increase in AC conductivity with temperature suggests that the conduction in the present system of ferrite is due to small polaron hopping. Nickel ferrite nanoparticles synthesized by sol-gel technique exhibited comparatively less dielectric loss in the measured frequency range of applied AC field. Thus it can be
concluded that sol-gel technique is suitable for the production of ferrites with high frequency applications, while co-precipitation is appropriate for the synthesis of super paramagnetic particles.
References

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