CHAPTER-4

SYNTHESIS, STRUCTURAL AND MAGNETIC PROPERTIES OF
Ni_{0.65}Zn_{0.35}Al_{x}Fe_{2-x}O_{4}(x=0.25,0.45,0.65,0.85) NANOFERRITES

4.1 INTRODUCTION

The changes in the structural properties like particle size, lattice constant, density, porosity and presence of different phases, imperfections etc. in the nanomaterials significantly alter the extrinsic properties of these materials. It is therefore essential to make detailed structural analysis of the nanoferrites for any suitable technological applications. The microstructural properties of Al^{3+} substituted Ni-Zn ferrites have been studied by using X-Ray Diffraction analysis and Transmission Electron Micrographs apart from measurements of their densities and porosities.

Nanostructured materials (or materials with particle size in the range of 1 to 100 nm) have a number of desirable electromagnetic and mechanical properties and can play a significant role in improving key antenna parameters like radiation efficiency, directivity and mechanical robustness. Electromagnetic absorption properties can be controlled by changing the particle distribution in nano-materials. Eddy-current and magnetic losses are minimized in nano-materials. A major innovation in using nanomaterials for antennas is the high mechanical robustness that can be achieved. Nano-materials are best known for their superior mechanical properties associated with the increased surface area. Magnetic nanoparticles are other class of materials which find applications in frontiers of materials science including medical diagnosis. In addition to their high surface to volume ratio and quantum size effect, magnetic nanoparticle dramatically change some of the magnetic properties and exhibit superparamagnetic phenomenon, because each particle can be considered as a single magnetic domain.

The performance characteristic of device made ferrite materials is the dependent on their magnetic and electrical properties. Ferrites are a very important class of magnetic materials. The useful magnetic properties of the spinel structure are
governed by the choice of the cations and their distribution between the tetrahedral (A-site) and octahedral (B-site). In spinel structure, the antiferromagnetic superexchange A-O-B interaction is much stronger than ferromagnetic A-A and B-B interactions. In general, the spins of the magnetic ions in the same sublattice are parallel and the spins of the cations on the dissimilar sublattice are antiparallel. The octahedral site are double of those of tetrahedral sites, a net non-compensated magnetic moment is expected, if all the cations are magnetic in nature. So a detailed investigation of these properties in the ferrites is essential from the point of view of their applications [1-8].

This chapter deals with the detail description about the methodology of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites, structural and magnetic properties of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites.

4.2 RESULTS AND DISCUSSION

4.2.1 Composition

Ni-Al-Zn nanoferrites have been prepared where in Fe$^{3+}$ ions were replaced by Al$^{3+}$ ions in the Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nano ferrites. These nanoferrites are prepared by modified sol-gel method by using high purity nitrates and aloe vera plant extracted solution.

4.2.2 Preparation of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nano ferrite samples by modified sol-gel method using high purity metal nitrates and aloe vera plant extracted solution

The compound with chemical composition Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) have been prepared by the modified sol-gel method. In this study Zn(NO$_3$)$_2$.6H$_2$O, Ni(NO$_3$)$_2$.6H$_2$O, Al(NO$_3$)$_2$.6H$_2$O and Fe(NO$_3$)$_2$.9H$_2$O purchased from Himedia (A. R. Grade) were used as the starting materials. In a typical procedure, 60 ml of aloe vera plant extract, instead of toxic organic polymers, was mixed with 40 ml distilled water under vigorous stir until homogenous solution was obtained. According to this formula Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85), each metal nitrate was added slowly to the aloe vera extract solution under vigorous stirring for 2 hours to obtain a well–dissolved solution. Then the mixed solution was evaporated by heating on the hot plate at 100°C under vigorous stirring for several
hours until a dried precursor was obtained. The dried precursor was crushed into powder using mortar and pestle. Then the dried precursor was calcinated in a muffle furnace at 800°C for 2 hours. The processing of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45, 0.65,0.85) nano ferrites as shown in Figure 4.1

![Diagram of processing steps](image)

**Figure 4.1** Processing of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45, 0.65,0.85) nano ferrites

### 4.3 STRUCTURAL PROPERTIES

#### 4.3.1 XRD spectra of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45, 0.65,0.85) nano ferrites

The fine particles of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45, 0.65,0.85) were characterized by XRD for structural determination and estimation of crystallite size. All experimental peaks were matched with theoretically generated one and indexed. The XRD patterns of all the samples are shown in Figure 4.2. The XRD patterns were
analyzed and confirmed single phase cubic spinel structure in all the samples. The broad XRD line indicates that the ferrite particles are in nano size. The crystallite size for each composition are calculated from XRD line width of the (311) peak using Scherrer’s formula [9-16]. The average crystallite sizes are decreased from 29.5 nm to 20.4 nm when the partial substitution of Al increased from $x = 0.25$ to $x = 0.85$.

Figure 4.2 XRD spectra of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$($x=0.25,0.45,0.65,0.85$) nano ferrites

4.3.1.1 Effect of the doping on particle size of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$($x=0.25$, 0.45, 0.65,0.85) nano ferrites

Particle size of the Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$($x=0.25,0.45,0.65,0.85$) nano ferrites calcined at $800^\circ$C for 2 hours calculated by using Scherrer’s formula. The particle
size was found to be decrease from 29.5 nm to 20.4 nm for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ series as the value if $x$ increased from 0.25 to 0.85 as shown in Fig. 4.3. Such a sharp decrease in the value of the particle size for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ series is expected because replacement of Fe$^{3+}$(0.65 Å$^0$) ions of larger radius, by Al$^{3+}$(0.54 Å$^0$) ions of the smaller radius [17-18].

![Figure 4.3 Variation of particle size [D(nm)] with aluminum concentration (x) in Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.8.5) nanoferrites](image)

**Table 4.1** Crystallite size for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.8.5) nanoferrites

<table>
<thead>
<tr>
<th>Al Concentration(x)</th>
<th>Crystallite Size (D) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>29.5</td>
</tr>
<tr>
<td>0.45</td>
<td>24.3</td>
</tr>
<tr>
<td>0.65</td>
<td>20.9</td>
</tr>
<tr>
<td>0.85</td>
<td>20.4</td>
</tr>
</tbody>
</table>
4.3.1.2 Effect of the doping on the lattice parameter of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ (x=0.25,0.45,0.65,0.85) nanoferrites

The observed variations of calculated values of lattice constant of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites calcinated at 800°C for 2 hours are given in Table 4.2. Table shows that a continuous decrease in the value of lattice constant take place from value 8.304 Å$^0$ to 8.269 Å$^0$ as the concentration Al$^{3+}$ ions was increased from 0.25 to 0.85. Such as decrease in lattice parameter in Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nano ferrites calcinated at 800°C for 2 hours can be understood on the basis of the ionic radius of the substituted cation. This is due to the fact that the replacement of larger Fe$^{3+}$(0.65Å$^0$) cation by smaller Al$^{3+}$(0.54 Å$^0$) cation, causing a shrinkage in the unit cell dimensions of the spinel lattice. Therefore as the concentration of Al$^{3+}$ ions increases the lattice constant decreases. It shows that a decrease in the dimension of unit cell is mainly governed by the size or radii of cation present in the unit cell of the ferrites. The graph between aluminum concentration and lattice constant is shown in Figure 4.4

![Figure 4.4 Variation of the lattice constant a (Å$^0$) with aluminum concentration (x) of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites](image-url)
Table 4.2 Lattice constant \( a (\text{Å}) \) and unit cell volume \( a^3 (\text{Å}^3) \) for \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 (x=0.25,0.45,0.65,0.85) \) nanoferrites

<table>
<thead>
<tr>
<th>Aluminum Concentration(x)</th>
<th>Lattice Constant ( a (\text{Å}) )</th>
<th>Unit Cell Volume ( a^3 (\text{Å}^3) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>8.304</td>
<td>584.019</td>
</tr>
<tr>
<td>0.45</td>
<td>8.272</td>
<td>580.810</td>
</tr>
<tr>
<td>0.65</td>
<td>8.271</td>
<td>578.425</td>
</tr>
<tr>
<td>0.85</td>
<td>8.269</td>
<td>574.063</td>
</tr>
</tbody>
</table>

4.4 TRANSMISSION ELECTRON MICROSCOPE (TEM)

4.4.1. Transmission Electron Microscope (TEM) for \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 (x=0.25,0.45,0.65,0.85) \) nanoferrites

The Transmission Electron Micrograph of the samples of the series of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 (x=0.25,0.45,0.65,0.85) \) nanoferrites calcinated at 800\(^\circ\)C for 2 hours were obtained. The TEM images of the nanoferrites are shown in Figures 4.5. A study of these micrographs also indicates that the samples have almost uniform sized crystalline with almost spherical shape [19-21]. The average particle size obtained is in range of 20.4 nm to 29.5 nm which is good agreement as obtained from XRD data.
Figure 4.5 TEM images for $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_{x}\text{Fe}_{2-x}\text{O}_4$($x=0.25,0.45,0.65,0.85$) nanoferrites

4.5 FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY ANALYSIS

4.5.1 Fourier Transform Infrared spectroscopy (FTIR) for $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_{x}\text{Fe}_{2-x}\text{O}_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites

The FTIR spectra of the pallets formed from the mixture of the synthesized compound and KBr are recorded. The FTIR Spectra of $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_{x}\text{Fe}_{2-x}\text{O}_4$ ($x=0.25,0.45,0.65,0.85$) were reproduced in the Figure 4.6. The spectrum was recorded in the range 400 cm$^{-1}$ up to 4000 cm$^{-1}$. Two main broad metal–oxygen bands are seen in the infrared spectra of all spinels, especially ferrites. The highest one, ($\nu_1$), generally observed in the range 600–620 cm$^{-1}$, is caused by the stretching vibrations of the tetrahedral metal–oxygen bond. The lowest band ($\nu_2$) usually observed in the range 430–442 cm$^{-1}$, is caused by the metal–oxygen vibrations in the octahedral site. This difference in the spectral positions is expected because of the difference in the
Fe$^{3+}$-O$^{2-}$ distance for the octahedral and tetrahedral compounds [22-23]. This is confirmed from FTIR that the structure remains cubic spinel after aluminum substitution in nickel-zinc nanoferrite [24-25]. The weak absorption broad band at 3400 cm$^{-1}$ represents a stretching mode of H$_2$O molecules. The weak band around 1340 cm$^{-1}$-1600 cm$^{-1}$ corresponds to the H-O-H bending and corresponds to the molecular water absorbed or incorporated into the crystalline lattice. The peak around 2900 cm$^{-1}$ may be due to C-H stretching bond.
Figure 4.6 FTIR spectra of $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 (x=0.25,0.45,0.65,0.85)$ nanoferrites
4.6 MAGNETIC STUDIES

4.6.1 Variation of magnetization with applied field at room temperature for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

The variation of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ nanoferrites with the (x=0.25, 0.45, 0.65, 0.85) (Figure 4.7) can be understood on the basis of Neel’s theory. According to Neel there are three kinds of exchange interactions between unpaired electrons of two ions. These are: (1) both ions at tetrahedral (A) sites (A-A interactions) (2) both ions at octahedral (B) sites (B-B interactions), and (3) one at (A) site and other at (B) site (A-B interaction). As we know A-B interaction (super exchange interaction) is strongest among A-A and B-B interactions. The A-B interaction aligns all the magnetic spins at tetrahedral (A) site in one direction and those at octahedral (B) site in the opposite direction.

The net magnetic moment of the lattice is therefore the difference between the magnetic moments at (B) and (A) sublattice, i.e. $M = M_B - M_A$. Where $M_A$ is the magnetic moments at tetrahedral (A) site and $M_B$ is the magnetic moments at octahedral (B) site respectively.

To explain the observed variation in saturation magnetization, the following possibilities may be considered:

(a) If Al$^{3+}$ ions occupy octahedral (B) site and replace Fe$^{3+}$ ions.
(b) If Al$^{3+}$ ions replace tetrahedral (A) site Fe$^{3+}$ ions.
(c) If Al$^{3+}$ ions occupy tetrahedral (A) sites and push Zn$^{2+}$ ions from (A) to (B) sites.
(d) If Al$^{3+}$ ions occupy both tetrahedral (A) and octahedral (B) sites.

If aluminum ions occupy octahedral (B) sites and replace Fe$^{3+}$ ions, the magnetization of (B) sublattice decreases keeping the magnetization of tetrahedral (A) sublattice constant. Thus, the resultant magnetization according to $M = M_B - M_A$ is expected to decrease which is contrary to the observed rise in the saturation magnetization for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ nanoferrites. Therefore, possibility (a) is not applicable here. For lower concentration, if Al$^{3+}$ ions occupy tetrahedral (A) sites and replace Fe$^{3+}$ ions, (A) sublattice magnetization decreases and the resultant magnetization, therefore increases. For higher concentration, x>0.45 if aluminum ions
continues to occupy (A) sites, the magnitude of (A) sublattice would decrease rapidly which in turn weaken A-B exchange interactions considerably and material may turn into the paramagnetic. Thus the saturation magnetization decreases for higher concentration of aluminum ion. However at higher concentration, of aluminum ions some of them migrates to the B site also, which reduces the overall saturation magnetization of the particles. Same results are reported earlier by many researcher for aluminum doped ferrites [26-29]. The observance of hysteresis loops for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$($x=0.25,0.45,0.65,0.85$) nanoferrites at room temperature is consistent with the occurrence of ferromagnetic or a ferromagnetic ordering in these samples (Figure 4.7).

![Figure 4.7 Variation of magnetization with applied field at room temperature for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$($x=0.25,0.45,0.65,0.85$) nanoferrites](image)

Also it has already been observed with other nanoferrite particles and is due to an increase in the disorder of magnetic moments orientation in the various sites when the ratio surface volume increases [30-32]. The reduced magnetization measured for nanoferrite samples is attributed to the effect of spin canting and small particle size.
The saturation magnetization of ferromagnetic and ferromagnetic materials usually decreases with the decreasing particle size due to the existence of spin canting in small particles. There are two mechanisms which explain the origin of spin canting: one is the surface or interface effect and other is the finite size effect. Saturation magnetization (Ms), coercivity (Hc) and remanent magnetization (Mr) decreases with increase in aluminum concentration as shown in Figures 4.8 to 4.10 respectively. At room temperature coercivity (Hc) decreases with decreasing particle size due to superparamagnetic relaxation effect.

Figure 4.8 Variation of saturation magnetization (Ms) of $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.25, 0.45, 0.65, 0.85$) nanoferrites with aluminum concentration.

$O_4(x=0.25, 0.45, 0.65, 0.85)$ nanoferrites with aluminum concentration

Figure 4.9 Variation of coercivity (Hc) of $\text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4$ ($x=0.25, 0.45, 0.65, 0.85$) nanoferrites with aluminum concentration ($x$)
Figure 4.10 Variation of remanent magnetization (Mr) of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$  
\((x=0.25, 0.45, 0.65, 0.85)\) nanoferrites with aluminum concentration \(x\)

Table 4.3 Calculated values of Saturation Magnetization (Ms), Coercivity (Hc), Remanent Magnetization (Mr) and Squareness ratio for Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$  \((x=0.25, 0.45, 0.65, 0.85)\) nanoferrites

<table>
<thead>
<tr>
<th>Ni concentration ((x))</th>
<th>Magnetic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Saturation Magnetization (Ms)(emu/gm)</td>
</tr>
<tr>
<td>0.25</td>
<td>0.121</td>
</tr>
<tr>
<td>0.45</td>
<td>32.87</td>
</tr>
<tr>
<td>0.65</td>
<td>26.19</td>
</tr>
<tr>
<td>0.85</td>
<td>17.33</td>
</tr>
</tbody>
</table>

From Table 4.3 it is seen that the squareness ratio \((Mr/Ms)\) is very small at room temperature. It is due to the increasing fraction of superparamagnetic particles.
4.7 CONCLUSIONS

In the summary We have successfully synthesized single phase polycrystalline cubic spinel nanoparticles of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) ferrite, with an average particle size of 20.4 nm–29.5 nm through modified sol-gel method with aloevera extract solution followed by calcination at 800°C for 2 hours. The effect of \( \text{Al}^{3+} \) ion on structural and magnetic properties of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) was studied by using X-Ray Diffraction, Transmission Electron Microscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Vibrating Sample Magnetometer (VSM) measurements.

(a). X-Ray Diffraction studies confirmed the formation of nanoferrite samples of the spinal phase.

(b). TEM analysis shows surface morphology of ferrite nanoparticles.

(c). TEM analysis shows that particles are nearly spherical and confirm the size obtained from XRD analysis.

(d). FTIR confirmed that the structure remains cubic spinel after aluminum substitution. 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 (\( \nu_1 \)) generally observed in the range 600–620 cm\(^{-1}\), is caused by the stretching vibrations of the tetrahedral metal–oxygen bond. The lowest band (\( \nu_2 \)) usually observed in the range 430–442 cm\(^{-1}\), is caused by the metal–oxygen vibrations in the octahedral sites. This difference in the spectral positions is expected because of the difference in the Fe\(^{3+}\)-O\(^{2-}\) distance for the octahedral and tetrahedral compounds.

(e). Vibrating Sample Magnetometer is used to investigate the magnetic properties of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites. Saturation magnetization first increases and then decreases with increase in \( \text{Al}^{3+} \) concentration at room temperature. Nanoferrite samples of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites having particle size 20.4-29.5 nm exhibit ferromagnetic coupling at room temperature. The coercivity of \( \text{Ni}_{0.65}\text{Zn}_{0.35}\text{Al}_x\text{Fe}_{2-x}\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites is found to
decreases with particle size. Which means superparamagnetic character increases with Al$^{3+}$ concentration. The squareness ratio Mr/Ms has been found to be too small. Which supported the presence of strong interactions in these nanoferrite samples. From the data it can be concluded that magnetic properties of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ (x=0.25,0.45,0.65,0.85) nanoferrites are strongly affect by the size of the particles.

To our knowledge, this is the first report which highlights synthesis and the structural properties of Ni$_{0.65}$Zn$_{0.35}$Al$_x$Fe$_{2-x}$O$_4$ (x=0.25,0.45,0.65,0.85) nanoferrites synthesized by modified sol- gel technique with aloe vera extracted solution.
REFERENCES

7. A. Sharma, Pallavi, S. Kumar, Research journal of pharmaceutical biological and chemical science, 3 (2012) 1340.