CHAPTER-5

SYNTHESIS, STRUCTURAL AND MAGNETIC PROPERTIES OF 
$\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 (x=0.25, 0.45, 0.65, 0.85)$ NANOFERRITES

5.1 INTRODUCTION

Ferrites are stable and easily manufactured and possess environmental stability. The usefulness of ferrite is influenced by the physical and chemical properties of the materials and depends on many factors including the preparation conditions, such as sintering temperature, sintering time, rate of heating and cooling and grinding time [1-7]. The magnetic and electric properties of ferrite materials strongly depend on their chemical compositions and additives/substitutions. A small amount of foreign ions in the ferrite can dramatically change the properties of ferrites.

Cu-Zn Ferrites can be used as deflection yoke core in television picture tubes, memory core devices in computers and antenna cores, inductors, memory and switching devices, microwave latching devices, transformers, etc. At microwave frequencies, ferrites are extensively used in a number of microwave devices such as isolators, circulators, gyrators and phase shifters. Soft ferrites are the most widely used magnetic materials for low-cost, high-performance, and high-frequency applications [8-13].

Magnetic and electrical properties of ferrites are having fundamental and technological and potential applications. Potential applications are high density information storage in computers, ferrofluid technology, magneto-caloric refrigeration, magnetic resonance imaging (MRI) enhancement, magnetic guided drug delivery, microwave devices and magnetic recording media and magnetic sensors. Cu-Zn ferrite (superparamagnetic) nanoparticles also have been used in biomedicine and bio-technology as contrast agents in magnetic resonance imaging (MRI) and as drug carriers for magnetically guided drug delivery. Nanocrystalline magnetic materials display a variety of unusual and interesting magnetic properties that are not present in the bulk systems. Below some critical size, magnetic particles become single domain and show superparamagnetic (SPM) behavior [14-15]. The magnetic
properties of such particles as well explained by Neel model [16], where the magnetic anisotropy energy is a key factor in deciding the magnetic behavior of nanoparticles. In fact, superparamagnetism is a unique feature of magnetic nanoparticle system and they exhibit interesting phase transition from superparamagnetism (SPM) to ferri/ferro magnetic state or vice versa with the variation of temperature. The magnetic behavior of the nanoparticles has a marked dependence with the decrease in the particle size and the surface effects start to dominate [17]. In nanoparticles with large surface to volume ratio, the spin disorder may eventually modify the magnetic properties. This spin disorder is mainly due to the lower coordination of the surface atoms, broken exchange bonds that produces a spin-glass like state of spatially disordered spins in the surface cations. Owing to strong modification in surface effects, electronic state and magnetic interactions in the nanometer range, the nanocrystalline ferrites possesses some of the most distinct features like the enhanced/reduced saturation magnetization, low/high coercivity, superparamagnetism (SPM) relaxations compared to the bulk ferrites [18-20]. Due to such a wide range of features, the magnetic nanoparticles have been usually applied in magnetic recording media, ferrofluids and catalysis.

The magnetic properties of Cu-substituted ferrites have attracted considerable attention because of the importance of these materials for high-frequency applications. Therefore, Cu-substitution Cu-Zn ferrite is expected to modify the magnetic properties. In this chapter, we study the methodology of sample preparation, structural properties and hysteresis parameters of Cu-Zn nanoferrites.

5.2 RESULTS AND DISCUSSION

5.2.1 Composition

The Cu-Zn nanoferrites have been prepared by replacing the divalent metal ion (M^{2+}) in the M.Fe_{2}O_{4} ferrite by fractional amount of Cu^{2+} and Zn^{2+} ions to form the desired Cu_{x} Zn_{1-x}Fe_{2}O_{4}(x=0.25,0.45,0.65,0.85) nanoferrites. We have prepared all samples of Cu-Zn nanoferrites, with aloevera extract solution. The method used to prepare Cu-Zn nanoferrites is modified sol-gel method by using high purity nitrates and aloevera plant extracted solution.
5.2.2 Preparation of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25,0.45,0.65,0.85) nano-ferrites samples by modified sol-gel method using high purity metal nitrates and aloe vera plant extracted solution

The compound with chemical composition Cu$_x$Zn$_{1-x}$Fe$_2$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, Cu(NO$_3$)$_2$.3H$_2$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 Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25,0.45,0.65,0.85), each metal nitrate was added slowly to the aloe vera 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 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. Figure 5.1 shows the processing of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25,0.45,0.65,0.85) nanoferrites.

![Figure 5.1 Processing of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25,0.45,0.65,0.85) nanoferrites](image)
5.3 STRUCTURAL PROPERTIES

5.3.1 X-Ray Diffraction spectra of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites

The XRD patterns of all the samples are shown in Figure 5.2. The XRD patterns are 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 [21]. The average crystallite size decreases from 33.0 nm to 25.0 nm, when the partial substitution of Cu increases from x = 0.25 to x = 0.85 as shown in Table 5.1.

![XRD spectra of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites](image)

Figure 5.2 XRD spectra of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$(x=0.25,0.45,0.65,0.85) nanoferrites
5.3.1.1 Effect of the doping on particle size of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

Particle size of the Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites calcinated at 800°C for 2 hours are calculated by using Scherrer’s formula [21]. The particle size was found to decrease from 33.0 nm to 25.0 nm for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ series as the value of x increased from 0.25 to 0.85 as shown in Fig. 5.3. Such a sharp decrease in the value of the particle size for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) series is due to the replacement of Zn$^{2+}$ ions of larger radius, 0.84 Å, by Cu$^{2+}$ ions of the smaller radius 0.72 Å.

![Figure 5.3](image)

**Figure 5.3** Variation of particle size [D(nm)] with copper concentration (x) in Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

**Table 5.1** Crystallite size for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

<table>
<thead>
<tr>
<th>Copper Concentration (x)</th>
<th>Crystallite Size (D) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>33.0</td>
</tr>
<tr>
<td>0.45</td>
<td>30.9</td>
</tr>
<tr>
<td>0.65</td>
<td>25.3</td>
</tr>
<tr>
<td>0.85</td>
<td>25.0</td>
</tr>
</tbody>
</table>
5.3.1.2 Effect of the doping on the lattice parameter of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

The variations of the lattice constant a (Å) with Cu concentration (x) of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites calcinated at 800°C for 2 hours are given in Table 5.2. Table shows that a continuous decrease in the value of lattice constant take place from value 8.335 Å to 8.280 Å as the concentration Cu$^{2+}$ ions was increased from 0.25 to 0.85. Such as decrease in lattice parameter of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites can be understood on the basis of the ionic radius of the substituted cation. This is due to the fact that the radius of Cu$^{2+}$ ions (0.72 Å) is smaller than that of Zn$^{2+}$ ions (0.82 Å) causing a shrinkage in the unit cell dimensions of the spinel lattice. Therefore as the concentration of copper ions increases, the lattice constant decreases. It shows that decrease in the dimension of unit cell is mainly governed by the size or radii of cation present in the unit cell of the ferrite [22]. The graph between copper concentration and lattice constant is shown in Figure 5.4.

![Figure 5.4 Variation of the lattice constant a (Å) with Cu concentration (x) of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites](image)
Table 5.2. Lattice constant \( a(A^0) \) and unit cell volume \( a^3(A^0) \) for \( \text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites

<table>
<thead>
<tr>
<th>Nickel Concentration(x)</th>
<th>Lattice Constant a (( A^0 ))</th>
<th>Unit Cell Volume a(^3) (( A^0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>8.335</td>
<td>579.050</td>
</tr>
<tr>
<td>0.45</td>
<td>8.331</td>
<td>578.217</td>
</tr>
<tr>
<td>0.65</td>
<td>8.310</td>
<td>573.856</td>
</tr>
<tr>
<td>0.85</td>
<td>8.280</td>
<td>567.663</td>
</tr>
</tbody>
</table>

5.4 Transmission Electron Microscope (TEM)

5.4.1 Transmission Electron Microscope (TEM) for \( \text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites

The particle size and morphology of prepared \( \text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4 \) (\( x=0.25,0.45,0.65,0.85 \)) nanoferrites calcinated at 800\(^\circ\)C for 2 hours were estimated from high resolution Transmission Electron Microscopy. The TEM images of the nanoferrites are shown in Figure (5.5). It is clear from TEM pictures that the particles are almost spherical and almost uniform. The average particle size obtained is in range of 33.0 nm to 25.0 nm which is good agreement as obtained from XRD data.
Figure 5.5 TEM for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

5.5 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS

5.5.1 Fourier Transform Infrared Spectroscopy (FTIR) of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites

FTIR spectral analysis helps to confirm the formation of spinel structure in ferrite samples. The FTIR spectra of the investigated samples Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) calcinated at 800°C for two hours are shown in Figure 5.6. In the wave number range of 400–600 cm$^{-1}$, two main broad metal–oxygen bands are seen in the infrared spectra of all spinels, and ferrites in particular. The higher one ($\nu_1$) generally observed in the range 581–587 cm$^{-1}$, corresponds to intrinsic is stretching vibrations of the metal at the tetrahedral site, $M_{\text{tetra}}$↔O and the lowest band ($\nu_2$) usually observed in the range 428–420 cm$^{-1}$, corresponds to $M_{\text{octa}}$↔O [23]. This is confirmed from Fourier Transform Infrared spectroscopy (FTIR) that the structure remains cubic spinel after copper substitution in zinc nanoferrite [24]. The difference between $\nu_1$ and $\nu_2$ is due to the change in the bond length (Fe$^{3+}$-O$^{2-}$) at octahedral site. The spectra show prominent bands near 3432 - 3435 cm$^{-1}$, which are attributed to the stretching modes of the water molecules. The band around 1634 cm$^{-1}$ bending and
correspond to the bending mode of water molecules [25]. The peak around 2924 cm\(^{-1}\) may be due to C-H stretching bond.

Figure 5.6  FTIR spectra of  \(\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4(x=0.25,0.45,0.65,0.85)\) nanoferrites
5.6 MAGNETIC STUDIES

5.6.1 Variation of magnetization with applied field at room temperature for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites

Variation of saturation magnetization with applied magnetic field is a time dependent property, which measures the magnetic moment of a sample in a hysteretic fashion. From the hysteresis curve one can get information such as saturation magnetization ($M_s$), coercivity ($H_c$), remanance magnetization ($M_r$) and squareness ratio ($M_r/M_s$) for a given sample. The magnetic properties of the Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites powder sample can be determined at room temperature using Vibrating Sample Magnetometer (VSM) with applied field up to 6000 Oe. Figure 5.7 shows the variation of magnetization with applied field for all four Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites. The hysteresis curve (Figure 5.7) recorded at room temperature shows very low coercivity and remanence prove that the particles are superparamagnetic at room temperature. Nanoferrites do not attain saturation in applied field.

Figure 5.7 Variation of magnetization with applied field at room temperature for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites
Table 5.3 Calculated values of Saturation Magnetization (Ms), Coercivity (Hc), Remanent Magnetization (Mr) and Squareness ratio for Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$(x=0.25, 0.45, 0.65,0.85) nanoferrites

<table>
<thead>
<tr>
<th>Cu concentration (x)</th>
<th>Magnetic Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Saturation Magnetization (Ms)(emu/g)</td>
<td>Remanent Magnetization (Mr)(emu/gm)</td>
</tr>
<tr>
<td>0.25</td>
<td>20.25</td>
<td>2.04</td>
</tr>
<tr>
<td>0.45</td>
<td>48.94</td>
<td>6.71</td>
</tr>
<tr>
<td>0.65</td>
<td>69.62</td>
<td>9.7</td>
</tr>
<tr>
<td>0.85</td>
<td>60.41</td>
<td>7.6</td>
</tr>
</tbody>
</table>

It is observed from Figure 5.7 that magnetization increases initially (up to x=0.65) and then decreases as Cu$^{2+}$ content increases. This increase is explained by the change in magnetic ion distribution in the spinellic network of Zn ferrite where the Fe$^{3+}$ ions are equally distributed in tetrahedral (A) and octahedral (B) positions, while the Cu$^{2+}$ ions take tetrahedral (A) site. This result in decreasing magnetic moment of A- site. The increase in magnetization up to x=0.65 can be explained on the basis of Neel’s theory, where Ms = M$_B$-M$_A$. If copper ion continue 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 to paramagnetic. Thus, the net magnetization increases. But with further increase in Cu$^{2+}$ content above x=0.65 the magnetization decreases from 69.62-60.41 emu/g. At higher concentration, of copper ions some of them migrates to the B site also, which reduces the overall saturation of magnetization of the particles. This can also be explained on the basis of Yafet Kittle (spin-canting model), according to which the exchange interaction between A and B sites get lowered, which results in strengthening of B-B interaction and which leads to decrease in magnetization [26-35].

From Table 5.3 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.
Figure 5.8 Variation of saturation magnetization (Ms) of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ 
(x=0.25, 0.45, 0.65, 0.85) nanoferrites with copper concentration (x)

Figure 5.9 Variation of remanent magnetization (Mr) of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$
(x=0.25, 0.45, 0.65, 0.85) nanoferrites with copper concentration (x)

The variation of saturation magnetization (Ms) and remanent magnetization (Mr) with the copper concentration are shown above in Figures 5.8 to 5.9 respectively, which shows saturation magnetization (Ms) and remanent magnetization (Mr) decreases with increase in copper ion concentration.

5.7 CONCLUSIONS

In the summary we have successfully synthesized single phase polycrystalline cubic spinel of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ (x=0.25, 0.45, 0.65, 0.85) nanoferrites, with an average particle size of 25.0 nm–33.0 nm through modified sol-gel method with aloevera
extract solution followed by calcination at 800°C for 2 hours. The effect of Cu$^{2+}$ ion on structural and magnetic properties of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$($x=0.25,0.45,0.65,0.85$) nanoferrites was studied by using X-Ray Diffraction, Transmission Electron Microscopy, Fourier Transform Infrared Spectroscopy and Vibrating Sample Magnetometer (VSM) measurements.

(a). X-Ray Diffraction studies confirmed the formation of nanoferrite samples of the spinel 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 copper substitution. In the wave number range of 300–1000 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 550–600 cm$^{-1}$, is caused by the stretching vibrations of the tetrahedral metal–oxygen bond. The lowest band ($\nu_2$) usually observed in the range 385 – 450 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). Magnetic properties of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$($x=0.25,0.45,0.65,0.85$) was studied by using Vibrating Sample Magnetometer. Magnetic ordering of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25,0.45,0.65,0.85$) nanoferrites decreases with increases in copper concentration. Saturation magnetization first increases and then decreases with increase in copper concentration at room temperature. Samples of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$($x=0.25,0.45,0.65,0.85$) nanoferrites having particle size 25.0 nm to 33.0 nm attain improved saturation magnetization and exhibit ferromagnetic coupling at room temperature. This behavior makes these nanoferrites important for technological applications.

(f). 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 Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$($x=0.25, 0.45,0.65,0.85$) nanoferrites are strongly affect by the size of the particles.
Among the studied nanoferrite Cu$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ has the highest magnetization.

To our knowledge, this is the first report which highlights synthesis and the structural properties of Cu$_x$Zn$_{1-x}$Fe$_2$O$_4$ ($x=0.25, 0.45, 0.65, 0.85$) nanoferrites synthesized by modified sol-gel technique with aloevera extract solution.
REFERENCES


