Studies on Cu-Zn ferrite nanoparticles

The studies of nanoparticles of copper and copper containing ferrites have been of continued interest because of their interesting electrical and magnetic properties and crystal structure changes that take place due to heat treatment [1]. Chemical techniques are suitable for the synthesis of ultrafine materials with homogeneous composition and adequate morphology for their use in multiple technological purposes [2]. Coprecipitation method has been extensively used for the preparation of nanosized particles of spinel ferrite materials [3,4]. In this chapter the crystal structure and magnetic properties of Cu-Zn ferrite nanoparticles synthesized by coprecipitation method are presented. These studies have been very useful in finding out the role of Cu$^{2+}$ and Cu$^{1+}$ ions in controlling the magnetic and dielectric properties of these ferrites.

4.1 Crystal structure

Figure 4.1 shows the typical XRD patterns of the Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ (0.0 ≤ x ≤ 1.0) powder samples coprecipitated at 80 °C followed by heat treatment in air at 850 °C for 6 hrs. For all the samples, the spinel phase is obtained and the main peak is (311), which is in agreement with our studies on corresponding bulk samples [Chapter 3]. As can be seen from the XRD pattern no other phase is present. The average particle size of the as-coprecipitated Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ (x > 0) samples estimated using Scherrer formula vary in the range 8–12 (±1) nm. The as-coprecipitated sample of CuFe$_2$O$_4$ (x = 0) is found to be amorphous.

The lattice parameters of the samples were calculated using the combination of Bragg’s law of diffraction and the relation $a = d_{hkl} \sqrt{h^2 + k^2 + l^2}$ for cubic symmetry where h, k, and l are the miller indices, $a$ represents lattice parameter and $d_{hkl}$ is interplanar spacing. With increase in Zn content the lattice parameter increases similar to what is observed in the case of bulk samples. The estimated values of ‘a’ for the samples with x = 0.4 and 0.8 are
8.36 and 8.38 Å respectively. This can be attributed to the difference in radii of Zn$^{2+}$ (0.82 Å) and Cu$^{2+}$ (0.72 Å) which means that the larger the ion greater the lattice parameter [5]. The relative concentration of Cu and Zn in the ferrite structure not only influences the particle size and lattice parameter but also causes deviation in the distribution of cations at the lattice sites of the nanoparticles. The cation distribution is influenced by the strong chemical affinity of certain cations to occupy either A- or B-sites and the metastable cation distribution in nanosized particles. It is also influenced by change in the stoichiometry when large number of small ions replaces ions having larger radii.

![Figure 4.1: X-ray powder diffraction patterns of Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ synthesized by coprecipitation method and calcined at 850 °C for 6 hrs.](image)

**Figure 4.1:** X-ray powder diffraction patterns of Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ synthesized by coprecipitation method and calcined at 850 °C for 6 hrs.

### 4.2 Microstructure analysis

The surface morphology of the calcined copper-zinc ferrite nanoparticles have been studied by scanning electron microscopy (SEM). Figure 4.2 represents the SEM images for the compositions with $x =$ (a) 0.0 (b) 0.4, (c) 0.6 and (d) 1.0. The difference in
microstructure is clearly seen in terms of grain size and morphology. The figure suggests the presence of aggregates of small grains at the surface of the higher Zn containing samples. The samples have a homogeneous microstructure of equiaxed grains. It can be seen that the morphology varies significantly with composition. Energy-dispersive x-ray spectroscopy (EDAX) was used to determine the final composition of the samples. The synthesis procedure was optimized until it produced samples with uniform microstructure and chemical homogeneity.

![SEM photographs of calcined Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples at 850 C for 6 hrs with x value of (a) 0.0 (b) 0.4, (c) 0.6 and (d) 1.0](image)

**Figure 4.2:** SEM photographs of calcined Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples at 850 C for 6 hrs with x value of (a) 0.0 (b) 0.4, (c) 0.6 and (d) 1.0

The EDAX measurements (Figure 4.3) performed randomly at several spots across the samples show no microphase separation or compositional inhomogeneities at a submicrometer level. It reveals that the Cu:Zn:Fe ratio in the matrix is close to the nominal compositions with an overall a slight excess of Fe observed. No trace of any impurities is found in the samples confirming the phase purity of the samples. The EDAX results suggest that the precursors have undergone the chemical reaction fully to form the expected ferrite materials.
Figure 4.3: EDAX results confirm the formation of calcined Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite crystallites in the heat treated samples at 850 °C for 6 hrs with x value of (a) 0.0 (b) 0.4, (c) 0.6 and (d) 1.0.

4.3 Magnetic properties

Figure 4.4 indicates the composition dependence of the magnetization (M) vs. applied field (H) for Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ (0.0 $\leq x \leq 1.0$) samples synthesized by coprecipitation method followed by calcination at 850 °C for 6 hrs. With the increase in Zn content, the saturation magnetization (M$_s$) initially increases reaching the maximum value of about 67 emu/g at x = 0.4 followed by a decreasing trend with further increase in zinc content. This trend is similar to that of the bulk Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples (3rd chapter) and for M-Zn ferrite system (see for eg. [5,6]).

The improvement in M$_s$ with the addition of Zn ions into the CuFe$_2$O$_4$ compound is attributed to the preferential occupation of nonmagnetic Zn$^{2+}$ ions of A-sites and consequent displacement of equivalent number of magnetic Fe$^{3+}$ ions to B-sites. The
increment of B-site population with the magnetic Fe$^{3+}$ on account of displacement from A-sites develops the difference of magnetic moments which leads to the enhancement of Fe$^{3+}$(A)-O-Fe$^{3+}$(B) superexchange interaction and magnetization [7]. However, with further increase in zinc content ($x > 0.4$) after reaching a maximum, $M_S$ starts to decrease irrespective of increase in the number of Fe$^{3+}$ ions on B-sites. The increment of Fe$^{3+}$ ions on B-sites leads to decrease in the superexchange interaction between A and B sites. At this stage the Fe$^{3+}$ spins start canting on B-sites. The canting increases with increase in the zinc content leading to full antiparallel alignment at $x = 1$ (ZnFe$_2$O$_4$) [7-9].

**Figure 4.4:** Magnetization vs. magnetic field curves at 300 K for the Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ samples prepared by coprecipitation method and calcined at 850 °C for 6 hrs.
With the increase in Zn concentration, the coercivity $H_C$ decreases monotonously. The decline in coercivity can be due to decreasing crystal anisotropy with increase in Zn concentration [10]. Similar results have been reported in the literature for substitution of magnetic ions by non magnetic Zn in mixed ferrites [11].

The slightly higher $M_S$ values for the nanoparticle compared to the bulk materials (Figure 4.5) can be attributed to the change in the cation distribution of the coprecipitated samples. For the bulk material Cu$^{2+}$ ions are apt to locate in the octahedral sites while Zn$^{2+}$ in the tetrahedral sites. However, in the coprecipitated samples some fraction of Cu$^{2+}$ ions occupy the tetrahedral sites while fraction of Zn ions occupy the octahedral sites resulting in an increase in the magnetic moment [10].

**Figure 4.5:** M-H plots of Cu$_{0.6}$Zn$_{0.4}$Fe$_2$O$_4$ and Cu$_{0.4}$Zn$_{0.6}$Fe$_2$O$_4$ (a) bulk sample prepared by solid state reaction at 1000 °C for 12hrs (b) nanoparticles synthesized by coprecipitation method with calcination at 850 °C for 6hrs.

### 4.4 FMR studies

Figures (4.6-4.8) show the temperature dependent ESR data for the as-coprecipitated Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticle ($x = 0.4, 0.6, 0.7, 0.8$ and 1.0) samples with cubic shapes. It can be seen that ESR measurements show only one FMR signal at $g \sim 2$, in the high temperature range. The FMR signal splits into two resonances. The single FMR lines of Lorentzian shape at high temperature can be assigned to a paramagnetic (PM) phase. With decrease in temperature the resonance absorption appearing at lower field can be assigned to a ferromagnetic phase. The resonance at high field can be assigned to the presence of one or two magnetic phases (PM, spin glass or antiferromagnetic) [12].
In the present systems, the splitting of the FMR spectra at lower temperature can be assigned to the formation of ferromagnetic (FM) clusters in paramagnetic (PM) and antiferromagnetic (AFM) backgrounds. The preparation of these materials as nanosized particles leads to change in their magnetic properties. Some of Zn$^{2+}$ and Fe$^{3+}$ ions redistribute partially among A- and B-sites which cause local superexchange interactions via oxygen ions between Fe$^{3+}$ ions on both sites leading to local ferromagnetic phases \[13\]. With decreasing temperature more FM centers form and consequently increase the FM phase. This indicates that the FM-PM transition is not complete. The PM phase may still survive in a certain temperature range below $T_C$. The formation of AFM phase could not be ruled out. We believe that the AFM phase plays a major role in the splitting of FMR signal. This is evident from the decrease signal intensity with decrease in temperature. The disappearance of the high-field signals in the sample containing high Cu content (Figure 4.8) where the Para-to-ferromagnetic phase transition occurs in a very narrow temperature range confirms the absence or the highly reduced AFM phase in these samples compared to the sample having high zinc content.

**Figure 4.6:** FMR spectra of as-coprecipitated ZnFe$_2$O$_4$ nanoparticles at pH value of 12.
For zinc ferrite, the temperature dependence of FMR spectra (Figure 4.6) shows substantial changes near the transition temperature due to the existence of multi-magnetic phases (para-, ferro- and antiferromagnetic phases) over a wide temperature range. The splitting of the ESR signal could be due to the size distribution of the local effective magnetic fields ($H_{\text{eff}}$) which lead to the appearance of two or more preferred directions of the orientation of local magnetic moments (ensembles of particles with specific shape or size distributions). This leads to superparamagnetic behavior as can be understood from M-H and M-T plots shown in figures 4.22 and 4.23. When these ferromagnetic phases are formed, the resonance field $H_R$ due to the spins in the ferromagnetic phase shifts towards the lower field with decreasing temperature due to the ferromagnetic exchange interaction. Whereas for the spins in the PM or AFM backgrounds $H_R$ shifts towards the higher field with decreasing temperature due to the demagnetizing field from the ferromagnetic phases.

The presence of two well resolved absorption lines in a wide temperature below Curie point $T_C$ was observed in La-manganite single crystal [14,15] and in polycrystalline samples [16]. The low field resonance is assigned to the FM state which appears below $T_C$. The decrease in the resonance field $H_R$ with decreasing temperature is associated with anisotropic interactions, namely, with increasing magnetocrystalline anisotropy and shape anisotropy. The other line assigned to the paramagnetic state changes its position insignificantly and its resonance field $H_R$ does not depend on the sample shape and the orientation of the external magnetic field. The slight increase in $H_R$ with decrease in temperature may be associated with a change in the g factor caused by local lattice distortions initiated by strong electron-phonon coupling.
The analysis of the resonance absorption of ESR signal for the samples of doped perovskite manganites (either single crystalline or polycrystalline) in which para- and ferromagnetic phases coexist over a wide temperature region was carried out by Dzhezherya and Tovstolytkin [12]. It was found that by taking into account the mutual
influence of coexisting phases gives rise to the appearance of substantial changes in the curves of line shape and $H_R$ values of resonance fields, as well as to the geometry of a phase distribution dependent on an external magnetic field. Near the temperature boundaries of the phase coexistence region, the resonance field for the paramagnetic phase becomes dependent on the shape of the sample, the saturation magnetization and the fraction of ferromagnetic phase.

Figure 4.8: FMR spectra of (a) $Cu_{0.4}Zn_{0.6}Fe_2O_4$ and (b) $Cu_{0.6}Zn_{0.4}Fe_2O_4$ nanoparticles.
The ESR measurements carried out on spinel compounds Fe$_{1+x}$Cr$_{2-x}$S$_4$ by Z. Yang et al. [17] show that only one ESR signal, with a $g \sim 2$, appears at temperatures above $T_C$ (the PM state). Below $T_C$ ESR spectra splits into two resonances. The ESR spectra analysis indicates that the PM-FM transition is not complete and the PM phase may still survive in a certain temperature range below $T_C$.

This phenomenon was also observed in magnetic ferrofluids. One of the first experimental results regarding the effect of the particle size distribution on the ferromagnetic resonance line was reported by Sharma and Waldner [18]. They showed that at room temperature the ferromagnetic resonance line of some magnetic fluids has a two line pattern, consisting of a narrow line superposed to a broad line. They assumed that the broad line is due to the large particles within the magnetic fluid and the narrow line is due to the small particles, which are in superparamagnetic state. Similar experimental results were reported in Ref. [19,20].

The influence of the temperature on the ferromagnetic resonance behavior of magnetic fluids was investigated by different authors [20–23]. The experimental results have shown that by increasing the temperature, the ferromagnetic resonance line becomes narrower and the resonance field shifts towards larger values. The explanation to the mentioned experimental results was supplied by the effective-field model of Raikher et al. (RSS model) [24,25]. The particles are assumed to be ultrafine (several nanometers in size), hence single-domain and considerably influenced by superparamagnetism. Under these circumstances the shape of the FMR absorption line is determined as interplay of two main mechanisms: thermofluctuational motion of particle magnetic (homogenous broadening) and orientational spreadout of the particle anisotropy axes (inhomogeneous broadening). These sources of the line shape have different temperature and field dependences.

The thermal and the particle size distribution effects on the ferromagnetic resonance of diluted magnetic fluids were theoretically investigated by Marin [26], neglecting possible effects due to the viscosity of the carrier liquid. The model originates from the theory of the ferromagnetic resonance of single-domain particle systems, which was modified in order to take into account the orientation mobility of the particles within the fluid and the finite size of magnetic particles. Under these circumstances the shape of the resonance line, the resonance field and the line width of magnetic fluids are found to be strongly affected by the temperature and by the particle size distribution.
Figure 4.9 shows the temperature dependence of FMR spectra of the as-coprecipitated CuFe$_2$O$_4$ nanoparticles in the temperature range 300 to 470K. The FMR data shows a single resonance line fitted by a Lorentzian function corresponding to a $g$-value of 2.044 at room temperature. Beside the main resonance line there is a very weak signal corresponding to $g \sim 4.3$ for residual Fe$^{3+}$ ions in close contact with spinel Cu-ferrites. The FMR data support the superparamagnetic nature in this sample.

![FMR spectra of as-coprecipitated CuFe$_2$O$_4$ nanoparticles recorded at various temperatures.](image)

**Figure 4.9:** FMR spectra of as-coprecipitated CuFe$_2$O$_4$ nanoparticles recorded at various temperatures.

Figure 4.10 displays the temperature dependence of resonance field ($H_r$) and peak-to-peak linewidth ($\Delta H_{pp}$) of the as coprecipitated CuFe$_2$O$_4$ nanoparticles. It is found that $\Delta H_{pp}$ decreases with increase in temperature up to 370K followed by increasing trend with further increase in temperature. The peak to peak width ($\Delta H_{pp}$) of the FMR signal depends on the magnetic interactions and relaxation times which in turn are influenced by the microstructure of the ferrite material [27]. It could be the slight weakening of magnetic moment that is responsible for the observed reduction in the linewidth when temperature increases to 370 K. The increase of $\Delta H_{pp}$ above 370 K could be due to thermal broadening. The resonance field $H_r$ plotted in Figure 4.10 shows weak temperature dependence throughout the temperature range. This is in agreement with the magnetization data which shows that the sample is weak superparamagnet at room temperature.
4.5 Dielectric properties

The variation of the dielectric constant ($\varepsilon'$) and dielectric loss tangent ($\tan\delta$) of the Cu-Zn ferrite nanoparticle samples has been done as a function of frequency and composition as presented in figure 4.11 and figure 4.12. All the samples show normal behavior where both $\varepsilon'$ and $\tan\delta$ decrease with increasing frequency. The values of $\varepsilon'$ and $\tan\delta$ decrease with increase in frequency rapidly in the lower frequency range and marginally in the MHz frequency range. This behavior can be explained on the basis of Koops' model [28] which is based on the Maxwell-Wagner type interfacial space charge polarization for inhomogeneous multi-layer dielectric structure [29,30]. According to this model, the dielectric structure (ferrite) is composed of well conducting grains, which are separated by poorly conducting thin layer grain boundaries, such as an equivalent of a resistor and a capacitor.

There are two types of charge carrier exchange in this system i.e. $\text{Fe}^{2+} = \text{Fe}^{3+}$ and $\text{Cu}^{1+} = \text{Cu}^{2+}$. When an electric field is applied, it could induce a local displacement of charge carriers through hopping to accumulate at the separating boundaries. The building up of charge carriers at the interfaces corresponds to charge polarization and dielectric constant. At high frequencies, the jumping frequency of electric charge carriers cannot
follow the alteration of applied AC electric field beyond a critical frequency and the probability of charge carriers reaching the grain boundaries decreases resulting in decrease of polarization and dielectric constant [30-32].

**Figure 4.11**: Frequency dependence of dielectric constant of Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ nanoparticles.

The Loss factor decreases with the increase in frequency as shown in Figure 4.12. The values of tan $\delta$ depend on a number of factors such as stoichiometry, Cu$^+$ and Fe$^{2+}$ contents and structural homogeneity, which in turn depend on the composition and sintering temperature of the samples [29]. The initial decrease of tan $\delta$ with an increase in frequency can also be explained on the basis of Koops’ phenomenological model [28].
Figure 4.12 shows that the $\varepsilon'$ and $\tan\delta$ decrease with increase in Zn content up to $x = 0.6$ followed by increasing trend with further addition of Zn. The variation of dielectric parameters with zinc content can be explained on the basis of two types of charge carrier model [33]. The decrease in $\varepsilon'$ and $\tan\delta$ with increase in Zn content can be assigned to the decrease in Cu charge carriers. The increase in the $\varepsilon'$ values with increasing Zn content ($x > 0.6$) suggests the presence of increasing concentration of Fe$^{2+}$ ions [34]. The Fe$^{2+}$ ions being more easily polarizable than the Fe$^{3+}$ ions, an increase in Fe$^{2+}$ concentration would result in an increase in dielectric constant.

The real part of complex permittivity ($\varepsilon'$) of the nanocrystalline copper and zinc ferrites prepared by solid state reaction (bulk) and coprecipitation methods (nanoparticles) is shown in Figure 4.13 (a) and (b). The frequency dependence of dielectric constants ($\varepsilon'$) for the coprecipitated samples show little dispersion unlike for the corresponding bulk ferrites. The figure also shows the low values of dielectric constant observed in the coprecipitated CuFe$_2$O$_4$ sample compared to those obtained for ferrite bulk ceramics. Different behavior is obtained for the ZnFe$_2$O$_4$ where the coprecipitated sample shows higher values compared to the bulk one. The higher values could be attributed to the nanometer size effect of the particles. The dielectric enhancement is attributed to dipoles associated with the interfaces of the nanometer-sized particles. These dipoles result from different types of point defects at the particle interfaces [35]. The effect of particle size on the dielectric
constant of nanocrystalline ZnFe$_2$O$_4$ has been studied by Ghatak et al. [36] where $\varepsilon'$ is high for the smallest particles.

**Figure 4.13**: Frequency dependence of $\varepsilon'$ of (a) bulk samples sintered at 1000 °C/12h and (b) coprecipitated samples calcined at 850 °C/6h of CuFe$_2$O$_4$ and ZnFe$_2$O$_4$.

4.6 **Effect of heat treatment**

4.6.1 **Copper ferrite nanoparticles**

4.6.1.1 **Crystal structure**

The XRD patterns of CuFe$_2$O$_4$ nanoparticles synthesized by coprecipitation method are shown in figure 4.14. It can be seen that the as-synthesized powder does not show any XRD peaks which is an indication of amorphous nature of the sample. The as-coprecipitated powder is not expected to be pure CuFe$_2$O$_4$ as it may contain some adsorbed water and amorphous copper and iron hydroxides. Similar behavior has been reported by Tao et al. [37] and Sun et al. [38].
Figure 4.14: the calcination effect on the XRD patterns of CuFe$_2$O$_4$ nanoparticles prepared by coprecipitation method.

The crystalline phase of the powder improves when the calcination temperature is increased. Diffraction patterns of the calcined powder show that the crystallization process starts when the calcination is done for 6 hrs at temperatures between 700 and 850 °C. This result is in good agreement with that obtained using metal citrate precursor [2]. The sample calcined at 850 °C is highly crystalline and the position and the relative intensity of peaks match well with that of standard tetragonal CuFe$_2$O$_4$ pattern (JCPDS No. 34-0425) where the patterns display the fundamental peaks of tetragonal structure with I4$_1$/amd space group regarded as a distorted cubic spinel structure. The d$^9$ electronic configuration state in Cu$^{2+}$ ions favors the Jahn-Teller effect due to the elongation of the ligand axis along the d orbital [2,39]. The lattice parameters $a = 8.232$ Å and $c = 8.618$ Å (for standard $a = 5.844$, $c = 8.630$) were calculated from the position of the principal peaks using a standard least squares routine. The results are also in good agreement with values obtained by other workers [39-41]. We were not able to estimate the average particle size
from the Debye–Sherrer formula due to the amorphous state of the as prepared sample and the large crystallite size of the calcined sample as observed in SEM images ($\langle D \rangle \sim 1 \, \mu m$).

### 4.6.1.2 Microstructural analysis

Figure 4.15 shows the SEM micrographs of as-coprecipitated and calcined samples at 850 °C for 6 hrs. The SEM micrographs show that the as-coprecipitated samples have dominant spherical polydispersed particles with some monodispersed grains linked together with average particle sizes of the order of 60 nm.

![SEM micrographs of CuFe$_2$O$_4$ nanoparticles.](image)

**Figure 4.15**: SEM micrographs of CuFe$_2$O$_4$ nanoparticles. (down) as coprecipitated (above) calcined at 850 °C for 6 hrs.
The calcined sample shows changes in the microstructure from a non-uniform agglomeration to highly crystalline structure. The average grain size is about 1 µm and density \( \sim 5 \text{ g/cm}^3 \) which is close to that of bulk sample obtained by sintering at 1000 °C for 12 hrs [Chapter 3] and higher than that obtained for samples synthesized by ball milling and sintered at higher temperature [42]. The grain coarsening is mainly attributed to sintering that forms dense structure. Similar effect was observed by Sun et al. [38].

The EDAX data of the as-coprecipitated sample shows that the Fe/Cu ratio deviates from the stoichiometry at different position in the sample. However, the chemical composition of the sample \( \text{CuFe}_2\text{O}_4 \) heat treated at 850 °C is found to confirm the chemical homogeneity. The chemical signatures obtained are identical within experimental accuracy (5-8%) and only Cu, Fe, and O elements are observed with the expected molar ratio for \( \text{CuFe}_2\text{O}_4 \).

4.6.1.3 Magnetic properties

The magnetic properties of ferrite materials are mainly dependant on the preparation method, particle size, sintering temperature, measuring temperature, microstructure and external field. Nanocrystalline ferrites are characterized by a lack of long range atomic order, similar to that of the liquid state. The lack of crystallinity causes nanocrystalline materials to have a very low magnetic anisotropy [43] and lower coercivity.

Figure 4.16 shows the effect of annealing temperature on the M-H plots of \( \text{CuFe}_2\text{O}_4 \) nanoparticles. The magnetization of the as-coprecipitated sample is much smaller than the corresponding bulk sample and it shows superparamagnetic behavior at room temperature with zero coercivity and remanance. The substantial reduction of the magnetization could be related to the large surface area that arises in the imperfect structure of nanosized particles [44]. This leads to possible local canting of magnetic ions and formation of magnetic dead layer on the surface of particles [45,46]. The spherical nanoparticle can be thought of having core-shell structure with shell of finite and constant thickness made of weak-magnetic layer i.e. magnetically dead layer. It has been found that the shell layer can have thickness approximately equal to one lattice constant, which means that the magnetic nature of the first crystalline layer on the nanoparticles is weakened by surface adsorption of nonmagnetic ions but the magnetic properties of the core remains intact and resembles
to bulk magnetization [47]. The superparamagnetic behavior of the sample suggests that the thermal energy can overcome the anisotropy energy barrier of a single particle, and the net magnetization of the particle assemblies in the absence of external magnetic field is zero [48].

Table 4.1: Magnetic parameters of copper ferrite prepared by coprecipitation method.

<table>
<thead>
<tr>
<th></th>
<th>$M_S$ (emu/cc)</th>
<th>$H_C$ (Oe)</th>
<th>$M_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As coprecipitated</td>
<td>1.92</td>
<td>0.35</td>
<td>0</td>
</tr>
<tr>
<td>Calcined at 700 °C</td>
<td>30</td>
<td>350</td>
<td>8</td>
</tr>
<tr>
<td>Calcined at 850 °C</td>
<td>33</td>
<td>450</td>
<td>13</td>
</tr>
<tr>
<td>Bulk</td>
<td>35</td>
<td>435</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The samples calcined at 700 and 850 °C exhibit hysteresis behavior at RT typical of ferrimagnetism, with coercivity, $H_C$, of 350 and 450 Oe, remanence, $M_R$, of 8 and 13 emu/g, and saturation magnetization, $M_S$, of 30 and 33 emu/g respectively. The $M_S$ values obtained by extrapolating the high field region of the $M(H)$ curve to infinite field ($M$ vs. $1/H$ to $1/H = 0$). The values of $H_C$, $M_S$ and $M_R/M_S$ (squareness) ratio for sample calcined at 700 °C are less than the corresponding values for the bulk sample whereas the values obtained for the sample calcined at 850 °C are close to the bulk sample values. For the calcined copper ferrite, the improvement in magnetic properties such as saturation magnetization, remanent magnetization and coercivity are attributed to the increase in grain size, decrease in the defects and impurities and change in cation distribution[49]. This suggests that the calcination at 850 °C for 6 hrs is optimum for this compound to be synthesized by coprecipitation method. The larger value of $H_C$ for the sample calcined at 850 °C compared to that of the bulk sample could be due to several sources including magnetic anisotropy, shape, stress, and surface effects.
The magnetization vs magnetic field plots for as-prepared and calcined CuFe$_2$O$_4$ nanocrystalline samples 80 and 300K are shown in Figure 4.17. The as-coprecipitated sample does not show hysteresis even at 80 K and does not saturate in applied field up to 10 kOe suggesting that the as-prepared sample is superparamagnetic at RT and 80 K. The relatively low magnetization (M) values found at high fields may be linked to the magnetic disorder due to the poor crystalline state of the CuFe$_2$O$_4$ [50].

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**Figure 4.16:** M-H plots of CuFe$_2$O$_4$ nanoparticles measured at room temperature-The annealing effect.

**Figure 4.17:** M-H plots of CuFe$_2$O$_4$ nanoparticles annealed at 850 °C.
The EDAX data of the as-coprecipitated sample does not show the stoichiometric ratio of 1:2 between Cu and Fe for various pieces of the sample. This could be due to the presence of residual CuO and Fe₂O₃ phases in close contact with spinel Cu-ferrite as confirmed by ESR spectra (Figure 4.9) which show weak signal corresponding to isolated Fe³⁺ ions. The magnetization loop measured at 300 K displays a smaller Hₐ, a reduction of ~20% of the value at 80 K. The reduction in Hₐ and Mₛ indicates the existence of residual disorder in the sample.

### 4.6.2 Zinc ferrite nanoparticles

#### 4.6.2.1 Crystal structure (XRD analysis)

To study the effect of particle size on the properties, the as-coprecipitated ZnFe₂O₄ samples were calcined at 500, 700 and 850 °C for 6hrs. XRD patterns of the as-prepared, heat treated and the bulk samples are shown in figure 4.18. The XRD patterns for all the samples display the characteristic peaks of ZnFe₂O₄ which match well with cubic spinel Franklinite [JCDPS file No. 22-1012]. The fundamental peaks of ZnFe₂O₄ as shown in the figure are indexed as (111), (220), (311), (222), (400), (422), (511) and (440). The cell parameters of the samples calculated from the position of the principal peaks using a standard least squares routine are listed in table 4.2. The lattice parameter value of as-synthesized ZnFe₂O₄ particles is 8.47 Å which is larger than the JCPDS table value of 8.441 Å. The cell parameter of the calcined samples decreases with increase in calcination temperature reaching a value of 8.447 Å which is comparable to the value of 8.44 Å obtained for sample synthesized by ceramic method [chapter 3]. These results agree very well with earlier reports [51,52].
Broad XRD peaks corresponding to single-phase spinel zinc ferrite are observed. The broadening in XRD peaks may come from other sources in addition to the main contributions from the reduced particle size and strain in the crystal. The broadening decreases as heat treatment temperature increases. This indicates the improvement of crystallinity in the powders as well as the particle size growth with increase in heat treatment temperature. The mean particle size \( \langle D \rangle \) of the crystallites was estimated from the full width at half maximum of the most intense reflection peak using Scherrer’s formula \( \langle D \rangle = \frac{0.9 \lambda}{\beta_{1/2} \cos \theta} \) [53] where \( \langle D \rangle \) is the average particle size, \( \lambda \) is the wavelength, \( \theta \) is the diffraction angle of the most intense peak (311) and \( \beta_{1/2} \) is given by \( \beta_{1/2} = \sqrt{\left(\beta_{1/2}^0\right)^2 - b_0^2} \) [53] where \( \beta_{1/2}^0 \) is the full width at half maximum (FWHM) of the (311) peak and \( b_0 \) is same for larger crystallites. The value of \( \beta_{1/2}^0 \) was obtained from the fitting of the (311) peak to the Lorentzian function. The uncertainty in particle
size determination was estimated from the errors in the fitting procedures, which is in the range ± 1 nm. These studies reveal that with the increase in the calcination temperature the crystallite size gradually increases for all the powder samples. The estimated average particle size for various powder samples calcined at different temperatures are listed in Table 4.2.

**Table 4.2**: Effect of heat treatment on the particle size and lattice parameter of ZnFe₂O₄ nanoparticles prepared by coprecipitation method.

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Particle size (nm)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared (80)</td>
<td>8</td>
<td>8.471</td>
</tr>
<tr>
<td>500</td>
<td>15</td>
<td>8.461</td>
</tr>
<tr>
<td>700</td>
<td>20</td>
<td>8.455</td>
</tr>
<tr>
<td>850</td>
<td>30</td>
<td>8.447</td>
</tr>
<tr>
<td>Ceramic Standard (1000)</td>
<td>5 µm</td>
<td>8.440</td>
</tr>
</tbody>
</table>

### 4.6.2.2 Microstructural analysis

Figure 4.19 shows EDAX spectra of various samples. The chemical signatures for Zn, Fe an O are within the expected stoichiometry of ZnFe₂O₄ with an experimental error of (3-6%). This confirms the formation of ferrite crystallites in the as-synthesized sample. XRD and EDAX studies demonstrate that the as-coprecipitated samples were nanoparticles of crystalline ZnFe₂O₄ ferrite.
Figure 4.19: EDAX results confirm the formation of ferrite crystallites in the as-synthesized sample. The chemical signatures obtained are identical.

The Figure 4.20 shows the SEM micrographs of as-coprecipitated and the samples calcined at 500 °C, 700 °C and 850 °C for 6 hrs.

Figure 4.20: SEM micrographs of ZnFe$_2$O$_4$ nanoparticles (pH = 10) as a function of heat treatment (a) as-coprecipitated, and calcined at (b) 500, (c) 700 and (d) 850 °C.

The SEM micrographs show that the samples have nanocrystalline structures with average particle sizes ~ 50 nm. The samples calcined at 500- 850 °C show changes in the
microstructure from a uniform agglomeration to grain coarsening without densification. The grain coarsening is mainly attributed to sintering process.

### 4.6.2.3 Magnetic properties

Figure 4.21 shows room temperature magnetization (M) measurements of coprecipitated and calcined samples of ZnFe$_2$O$_4$ prepared at pH values of 10 and 12. It can be seen that the magnetization of as-prepared samples does not saturate up to a magnetic field of 10 kOe. The M values at 10kOe are 2 and 8 emu/g for the samples synthesized at pH values of 10 and 12 respectively. At RT the sample is paramagnetic having slightly higher M values compared to the bulk sample. This could be due to the existence of ferromagnetic mixed phases in paramagnetic background [54]. The heat treatment significantly decreases the magnetization value. The figure shows large decrease in M value for sample calcined at 850 °C. The higher value of M for sample prepared at pH 12 could be attributed to the redistribution of Zn$^{2+}$ and Fe$^{3+}$ cations in the ZnFe$_2$O$_4$ lattice sites. The value of magnetization is related to the inversion parameter $\delta$. Higher magnetization corresponds to higher inversion parameter $\delta$. The cation redistribution has changed from normal to the mixed spinel type structure. Hence, some percentage of Fe$^{3+}$ cations are pinned in tetrahedral sites due to small size effect, which cause the formation of A-B exchange interaction between Fe$^{3+}$ ions on both the sites to give rise to ferrimagnetic ordering of small clusters depending on the inversion parameters. These results are in good agreement with the data on ZnFe$_2$O$_4$ nanoparticles reported earlier [54-57].

![Figure 4.21](image.png)

**Figure 4.21**: Room temperature M-H plots of ZnFe$_2$O$_4$ nanoparticles (pH = 10 and 12) as a function of heat treatment.
Figure 4.22 shows the M-H plots of as-coprecipitated and calcined ZnFe$_2$O$_4$ nanoparticles (pH = 10 and 12) recorded at 80 and 300K. The M-H curves at 80 K show high values of M with $H_C$ and $M_R$ close to zero suggesting that the samples are superparamagnets [58]. Similar behavior was observed by Upadhyay et al. [59].

![M-H plots](image)

**Figure 4.22:** M-H plots of as-coprecipitated and calcined ZnFe$_2$O$_4$ nanoparticles (pH = 10 and 12) recorded at 80 and 300K.

Figure 4.23 shows the magnetization (M) as a function of temperature (80-300K) for the as-prepared sample at pH value of 12 at constant magnetic fields($H_{dc}$) of 20, 100 and 5 kOe in the FC-ZFC modes. In this temperature range the superparamagnetic blocking temperature is not observed and it could be below 80 K. The nanoparticles trapped inside magnetic pores show superparamagnetic behavior.
Figure 4.23: M-T curves for ZnFe$_2$O$_4$ nanoparticles prepared at pH value of 12

Figure 4.24 shows the effect of pH-value on the magnetic properties of ZnFe$_2$O$_4$ nanoparticles. The magnetization value (M) of the as-coprecipitated ZnFe$_2$O$_4$ nanoparticles increased significantly by increasing the pH-value. This result can be explained by the fact that the cationic distribution in the nanocrystalline ZnFe$_2$O$_4$ is disordered: Zn$^{2+}$ ions occupy B sites and Fe$^{3+}$ ions occupy both A and B sites in the AB$_2$O$_4$ spinel structure. The occupation of Fe$^{3+}$ ions on both sites leads to super-exchange spin interaction between A and B sites which give rise to a weak ferrimagnetic behavior. The disorder of cations increases with pH-value and thereby increases the magnetic moment. However, disordered Zn and Fe ions move back to their thermodynamically stable sites during subsequent heat treatment leading to dissappearance of ferrimagnetism and ZnFe$_2$O$_4$ becoming normal spinel like the corresponding bulk sample.
Figure 4.24: Room temperature M-H plots of as-coprecipitated ZnFe$_2$O$_4$ nanoparticles prepared at pH = 10, 12 and 13.

### 4.6.2.4 ESR study

Figure 4.25 shows the ESR spectra of zinc ferrite nanoparticles as a function of particle size. All the spectra show a single broad signal indicating the complete formation of the compound and absence of isolated Fe$^{3+}$ ions. The peak to peak resonance linewidth ($\Delta H_{pp}$) increases with increase in particle size. There is no significant change in g–value as a function of particle size. A good correlation is noticed between $\Delta H_{pp}$ and particle size in this compound.
Figure 4.25: EPR spectra of zinc ferrite nanoparticles coprecipitated at a pH-value of 10 as a function of thermal heat treatments.

The temperature dependence of $\Delta H_{pp}$ and resonance field $H_r$ for sample with 8 nm particle size is shown in figure 4.26. The $\Delta H_{pp}$ decreases with increasing temperature up to 250K followed by increasing trend with further increase in temperature. The reduction in $\Delta H_{pp}$ with decreasing temperature is due to the variation of both the magnetization and anisotropy [60]. The large values of $\Delta H_{pp}$ and g-factor at low temperature are attributed to stronger dipole-dipole interactions. With increasing temperature, this interaction decreases resulting in decreasing of $\Delta H_{pp}$ and increase in $H_r$. The increase of $\Delta H_{pp}$ with temperature above room temperature could be due to thermal broadening. The resonance field $H_r$ decreases slightly with decreasing temperature down to 230 K followed by a rapid decrease at lower temperatures (Figure 4.25). The non-linear temperature dependency of $H_r$ in nanometer size ZnFe$_2$O$_4$ suggests that the surface anisotropy becomes dominant on the magneto-dynamics of nanoparticles when the
diameter of the nanoparticle is smaller than the critical size (the effect of large surface area to volume ratio) [23].

**Figure 4.26**: Temperature dependence of EPR parameters of Zn-ferrite nanoparticles—Effect of annealing.
References


