Chapter 4: Optimization of Zn concentration in
\( \text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4 \) ferrite (x=0.0≤0.6)

4.1 Introduction
Nanocrystalline magnetic particles with particular properties can be synthesized by various chemical techniques [1-4]. Such types of characteristics are robustly based on size, dimension, crystal structure as well as allotment of the cation amongst the tetrahedron A as well as octahedron B position of the ferrite formation. The use of nanoparticles for desired applications has engrossed attention in present years, as nanoparticles offer high surface area-to-volume ratios [5-6]. Magnetic particles are deriving attention due to miscellaneous technological applications namely ferrofluids, high density information storage nanodevices, residential cooling, magnetic refrigeration, bio-medical applications like biosensors, magnetic separations, resonance imaging, targeted and control drug delivery and hyperthermia. Thus, ferrites are especially prominent due to their magnetic nature that may be used to suit the requirement by chemical changes [7-11]. The progress of the new techniques for advances of the magnetic and the structural properties of soft magnetic spinel ferrites has been the objective of various studies in preceding decades. Presently Ni-Cu-Zn spinel ferrites with nanometric dimensions were extensively studied in order to develop multilayer chip inductors (MLCs) [12-14]. Many procedure, such as sol-gel self propagating technique and ceramic method were utilized to prepare Nickle-Copper-Zinc spinel ferrite. Out of this, sol-gel auto-combustion route has distinctive benefits viz good proportion, lower temperature processing, low production cost as well as better results.

In this contribution, we report the sol-gel self propagating analysis of Nickle-Copper-Zinc ferrite. The Nickle-Copper spinel ferrite material allows the introduction of Zn\(^{2+}\) cation in the spinel matrix, which causes the change in structure and surface morphology considerably. Optimization of Zn\(^{2+}\) concentration with respect to Ni\(^{2+}\) will be investigated. Correlation between compositions of Ni-Cu-Zn spinel ferrites and sintering temperature on structural, infrared and morphological behavior has been carried out.

4.2 Experimental Techniques
A spinel ferrite compositions of \( \text{Ni}_{0.8-x}\text{Zn}_x\text{Cu}_{0.2}\text{Fe}_2\text{O}_4 \) where x lies in the interval of 0.00 to 0.60, nanoparticles are formulated by the sol-gel route from purified analytical rated liquids of above
mentioned chemicals. The fuel used was citric acid. The counted quantities of these salts are mixed in purified water and the solvent sintered for 30 mins. This solvent then mixed to fuel in a manner that in the final sample, containing one mole of a substance with ratio of nitrates and citric acid (fuel) turn out to be 1:3. A little quantity of ammonia is substituted drop by drop to keep the alkalinity of the solvent to 7 with continuous shaking the solution. The as-prepared ferrite materials are heated at 400 and 700º C for two hours after confirmation by TG/DTA analysis. The schematic of chemical reaction involved in the present investigated ferrite system is represented in Fig. 4.1.

\[
\text{Ni(NO}_2\text{)}_{(II)}^{(0.8-x)} + \text{Zn(NO}_2\text{)}_{(II)}^{(x)} + \text{Cu(NO}_2\text{)}_{(II)}^{(0.2-x)} + \text{Fe(NO}_3\text{)}_{(III)} + \text{HOOC} \rightarrow \text{NiO}_{(II)}^{(0.8-x)} + \text{ZnO}_{(II)}^{(x)} + \text{CuO}_{(II)}^{(0.2-x)} + \text{Fe}_2\text{O}_3_{(III)} + \text{COOH} + \text{COOH} + \text{OH}
\]

Neutralising reaction mass using liquid Ammonia

Fig. 4.1: Chemical reaction of \(\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4\)

The general nitrate-citrate combustion reaction may be written as:

\[(0.8-x)\text{Ni(NO}_3\text{)}_2.6\text{H}_2\text{O} + 0.2\text{Cu(NO}_3\text{)}_2.3\text{H}_2\text{O} + x\text{Zn(NO}_3\text{)}_2.6\text{H}_2\text{O} + 2\text{Fe(NO}_3\text{)}_3.9\text{H}_2\text{O} + 3\text{C}_6\text{H}_8\text{O}_7 \rightarrow (\text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4) + 4\text{N}_2 \uparrow + 18\text{CO}_2 \uparrow + 36\text{H}_2\text{O} \uparrow \]

The thermal behavior analysis of as-prepared sample was carried out on PERKIN ELMER, USA (Model Diamond TG/DTA) in air atmosphere in the temperature varying between ambient to 1000º C. The X-ray diffractometer is utilized for identification and composition synthesis of the heat tempered test samples are carried out by XRD. The structural investigation are done with SEM (JSM-7600F) with varying potential difference from 0.1 to 30 KV and transmission electron microscopy technique on PHILIPS (Model CM200) operated at 20-200 KV with resolution of 2.4 Å. The FTIR Spectroscopy was done with Nicolet Instruments Corporation, United States of America (type MAGINA 550) in the interval 390-4000 cm\(^{-1}\).
4.3 Structural Aspects

To study the thermal growth process of \( \text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4 \) nanophases, a quality that differentiates between similar thermal and thermal-gravimetric analysis (TG/DTA) of the as-prepared powder sample were carried out from 30 to 1000\( ^\circ \)C. The typical TG-DTA curve for the test sample \( x = 0.4 \) is graphically plotted in Fig. 4.2.

![TGA and DTA curves](image)

Fig. 4.2: TG/DTA Plot of test sample at \( x = 0.4 \)

TGA analysis shows, a complete mass failure of \( \sim 35\% \) as the test sample annealed within ambient to 1000\( ^\circ \)C. A mass failure of \( \sim 10\% \) took place during 30 to 300\( ^\circ \)C that can be attributed to removal of surface vapor and solutions that stayed in the material after drying. The major weight loss at 300 to 400\( ^\circ \)C assigned to the loss of water and the disintegration of organic compounds and nitrates. As projected, the disintegration reaction is robustly exothermic. The DTA curve shows, an exothermic occurrence at 370\( ^\circ \)C related to the rotting of organic material organized using chemical combination of 2 or more than 2 elements in the structure due to crystallization of spinel ferrite material is relatively sharp and intense. The weight loss about 3\% at 400 to 600\( ^\circ \)C is because of the dehydroxylation of the ferrite samples, which takes place at high temperatures, followed by the collapse of the pores and the compaction of the nanoparticles.

Figure 4.3 represent the distinctive patterns of X-ray diffraction for the heat treated test sampling at 400 and 700\( ^\circ \)C which support the arrangement of single phase cubic spinel ferrite.
Fig. 4.3: X-ray diffraction patterns for Ni<sub>0.8-x</sub>Cu<sub>0.2</sub>Zn<sub>x</sub>Fe<sub>2</sub>O<sub>4</sub> (0.00 ≤ X ≤ 0.60).

The crystallinity from the test samples enhances but crystal structure does not change during heat treatment. The lesser peak intensity and enlargement in XRD patterns shows the nanocrystalline behavior of the materials. The XRD analysis depicts a pointed structured indicating the enhancement in crystalline behavior of the sintered test samples. The XRD peak having line width of (311) is considered for finding out the average crystalline size by applying Scherrer equation,

\[ D = \frac{0.9\lambda}{\beta\cos\theta} \]

D - crystallite diameter, 
\( \lambda \) - radiation wavelength, 
\( \theta \) - incidence angle [15] and these values are presented in chart 4.1.

<table>
<thead>
<tr>
<th>Zn&lt;sup&gt;2+&lt;/sup&gt; content</th>
<th>Lattice constant(Å)</th>
<th>Crystallite size(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400°C</td>
<td>700°C</td>
</tr>
<tr>
<td>0.0</td>
<td>8.334</td>
<td>8.351</td>
</tr>
</tbody>
</table>
It is evident from Table 4.1 that average homogeneous crystalline spinel phase enhances as the doping of Zn$^{2+}$ ions and sintering temperature increases. The change of lattice constant with composition(x) computed by using interphase spacing (d) and Miller indices (hkl) are shown in Table 4.1.

Microstructural and chemical alteration taking place in the system during heat treatment and Zn$^{2+}$ substitutions are noticeable in the Figs. 4.4 – 4.8.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Average Homogeneous Crystalline Spinel Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>8.360</td>
</tr>
<tr>
<td>0.4</td>
<td>8.386</td>
</tr>
<tr>
<td>0.6</td>
<td>8.407</td>
</tr>
</tbody>
</table>

Fig. 4.4: Scanning electron microscopy images for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (annealed at 400°C).
Fig. 4.5: Scanning electron Microscopy images for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (annealed at 700$^\circ$C.)

Fig. 4.6: Transmission electron microscopy images for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (as burnt).
Fig. 4.7: Transmission electron microscopy images for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (at 400°C).

Fig. 4.8: Transmission electron microscopy images for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (at 700°C).
The scanning electron microscope images of the samples obtained after heat treatment at 400 and 700°C presented in Figs. 4.4 to 4.5 shows nanocrystalline nature and crystallinity increases as annealing temperature increases. This may be credited to the reality that the development of the crystal takes place in various orientations. The crystallographic pictures point out that the particles are piled on top of each other due to their common magnetic interactions.

The TEM images together with SAED pattern (x=0.2) for representative compound results of \( \text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4 \) (x=0.2 to 0.6) nanoparticles are predicted in Figs. 4.6 – 4.8. It is noticed that after annealing and metal substitution the nanoparticles are combined. The equivalent lattice outer boundary is found as consistently elongated throughout the major units, pores and grain edges in the test samples heated to 700°C towards every composition as shown in inset of Figure. Hence, it concludes that by distributing symmetrical lattice planes the nanoparticles are arranged into a similar oriented structure [16].

The FTIR range of the powder test samples during interval 4000-400 cm\(^{-1}\) were presented within Fig. 4.9(a) – 4.9(c).

\[ \text{Fig. 4.9(a): FT-IR spectra } \text{Ni}_{0.8-x}\text{Cu}_{0.2}\text{Zn}_x\text{Fe}_2\text{O}_4 \]
The FTIR spectroscopy is a powerful technique to derive not only the structural studies and rearrangement of cations among octahedral and tetrahedral sites of ferrite nanoparticles but also the lattice vibrational modes [17]. The FTIR spectra of all sample shows two major absorption bands at wave numbers 600 cm\(^{-1}\) and 400 cm\(^{-1}\) corresponds to situated within lattice oscillations of ferrite structure for tetrahedral A position and octahedral B position[18]. A impurity peak is noticed around 1380 cm\(^{-1}\) in all the test samples. The observed peak is credited to carboxyl group.
of C-O bonding. This is because of unreacted citric acid composite, which is used as energy. The band near 1600 cm\(^{-1}\) belongs to the twisting mode of H\(_2\)O molecules and another observed at 3100-3450 cm\(^{-1}\) belonging to O-H chemical groups. During combustion process the elevated degree of hotness is produced, all carboxyl and hydroxyl groups appear with less intensity and disappears when the heat treatment enhances confirming single phase characteristics of test samples as evident as of XRD results. The enhancement in the band breadth and area of 564 cm\(^{-1}\) is credited to the increase in crystallinity after the heat treatment, the reverse observations are observed of FTIR data shows that the peak intensity at octahedral site decreases as annealing temperature and Zn\(^{2+}\) contents increases showing that cations are migrates to octahedral B-position to tetrahedral A-position. This observation is also supporting the cation distribution obtained from XRD results and exothermic peak observed at 370\(^\circ\)C in DTA analysis.

4.4 Dielectric Properties

![Dielectric Properties Graph](image)

**Fig. 4.10:** Room temperature variation of \(\varepsilon\) with frequency for ferrite test sampling calcined at 700\(^\circ\)C.

Fig 4.10 depicts change of \(\varepsilon\) along frequency for test samplings heated to 700\(^\circ\)C. In the beginning \(\varepsilon\) reduces with rise in the number of occurrences within a given time period and finaly at higher ‘n’ approaching a steady amount for every constitutions. This result is in corelation with the conception that variety adding in conjunction with polarizability are falling back the enforced field for high ‘n’. The change of dielectric constant with ‘n’ exposes distribution because of Maxwell-Wagner [19-21] kind interfacial condition having polarity, which agrees with koop’s phenomenological hypothesis. As per suggetsed framework, the insulating substance with a varied form might be supposed to be microstructure comprising of well- behaving
granuals divided into very resistant single thickness coating grain edges. The space charge polarization monitors free charges available on the grain edges and the conductivity of the test samples. As per Koop proposition influence of grain edges is major at lesser ‘n’. The quantity of insulator rises as the grain boundary becomes thinner. The applied external field does not change the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ ions and this leads to the decrease of $\varepsilon$ with rise in ‘n’[22].

![Graph](image_url)

**Fig. 4.11: Room temperature variation of loss tangent with frequency for Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ (x= 0.0 to 0.6)**

Figure 4.11 shows change of tan $\delta$ along with frequency for the Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$ for the as-prepared test sampling. Fig. 4.11 depicts that tan $\delta$ reduces with rise in frequency with shoulder type. The inspection of shoulder points the occurrence of resonance among the hopping frequencies of the point charge carrier and ‘n’. In the decided frequency interval the other test samples do not shows shoulder nature. The reason behind this may be the resonant ‘n’ for remaining test sampling falls away from the frequency interval. The amount of tan $\delta$ decresases
for the test sampling with proportion of x=0.00 and x = 0.60 equated to other composition. The distributed behavior found can be justified in same way as of $\xi$ change with ‘n’.

4.5 Magnetization

![Hysteresis Plot](image)

**Fig.4.12** Room temperature hysteresis plot for (Ni$_{0.8-x}$Cu$_{0.2}$Zn$_x$Fe$_2$O$_4$) with x=0.0 using VSM.

Magnetization is significant and elementary parameters of oxide magnetic materials that decide upon their applications. Ceramic magnets are fabricated artificially to the required degree of magnetization by changing the concentration of constituents. The study on hysteresis provides valuable information about saturation magnetization, permeability, coercivity and remenance.

The materials with low H$_c$ are called ‘soft’ magnetic substances and utilized in greater frequency applications. For making permanent magnets, ‘hard’ magnetic materials with large H$_c$ are used. The coercive force of ferrites is found to vary from $10^1$ to $10^3$ Oe [23]. The magnetic properties are very much responsive to their chemical composition, microstructure and crystal structure. These properties may be controlled by heat treatment, rate of cooling and sintering atmosphere. The porosity and grain size are found to be the influencing factors in controlling the magnetic nature of ferrites [24-25]. The basic magnetic nature of ferrites can be characterized by hysteresis technique, A.C. susceptibility and permeability.

The magnetic induction in ferrites results to distribution and alignment of magnetized ions on the octahedral and tetrahedral position. If magnetic ions were sufficiently nearer to each other, spontaneous magnetization (M$_s$) occurs still in the lack of external field. The electron can
undergo an exchange interaction between neighbouring magnetic atoms or ions. This may be direct or may take place via an interaction. It may be either +ve or –ve and it is based on parallel and antiparallel alignment of the spins of neighbouring atoms respectively. When the exchange interaction is +ve it is ferromagnetic and the alignment is parallel and when it is –ve, then it is either anti-ferromagnetic or ferromagnetic moments within the crystals. Gorter arrived at a scheme of spin ordering on the basis of Anderson’s concept of super exchange coupling to arrive at a reasonably good value of saturation magnetization.

Fig. 4.12 shows the magnetic hysteresis curve for prepared ferrite sample. The saturation magnetization was highest at the composition X=0 for as prepared samples. The magnetization reduces with rise in temperature which is because of the improved densification. The decreasing magnetization was also due to the decreasing net magnetic moment of the crystal.

4.6 Conclusions
Nanocrystalline synthesis of Zn$^{2+}$ substituted Ni-Cu spinel ferrite was effectively accomplished by Sol-gel self propagating route. Thermal performance of the as-formed test samples is confirmed by TG-DTA study. The pattern of X-ray diffraction brings out development of unique state cubic spinel microstructure for every composition and temperatures. Crystallization size of the product observed as in nanometric dimensions. Analysis of insulating behavior with frequencies at normal temperature serves in accepting the electrical nature of test sample. The magnetization reduces with rise in temperature which is because of the improved densification. The novel morphological results with variation in the composition and sintering conditions are promising candidate for MLC technological application. The chemical examination and infrared spectral investigation of prepared material affirms the arrangement of the spinel ferrite phase and effect of preparation aids.

References


[25] Patankar KK, Mathe VL, Patil AN, Patil SA, Lotke SD, Kolekar YD, Joshi PB, (2001), Electrical conduction and magnetoelectric effect in CuFe$_{1.8}$Cr$_{0.2}$O$_4$-Ba$_{0.8}$Pb$_{0.2}$TiO$_3$ composites, *J Electroceram*, **2**:115-122.