Chapter-3
Synthesis and characterization of Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ mixed spinel ferrite system

3.1 INTRODUCTION

The magnetic ordering and ferromagnetic resonance properties of NiZn[1,2] and FeZn[3,4] spinel ferrites have been studied by a number of workers. These have been satisfactorily explained [5] on the basis of Yafet-Kittel type of spin ordering on the B-sublattice. It is well known [6,7,8] that crystal distortion arising from John-Teller effect occurs whenever an ion like Cu$^{2+}$ is present at the octahedral site.

Smit and Wijn [9] have systematically and elaborately studied the electric and magnetic properties of the ferrites NiFe$_2$O$_4$ and CuFe$_2$O$_4$. They have reported that the saturation magnetization value of NiFe$_2$O$_4$ is 300 Gauss at 0$^\circ$K and its curie temperature is 585$^\circ$C. For the ferrite CuFe$_2$O$_4$ the values are 160 Gauss and 455$^\circ$C respectively. Similarly Arrot and Goldman [10] and Hartmann-Boutron and Imbert [11] have studied ZnFe$_2$O$_4$ magnetically and have found out ZnFe$_2$O$_4$ is antiferromagnetic below 10$^\circ$K. Many attempts have been made to lower the curie temperature of NiFe$_2$O$_4$ and CuFe$_2$O$_4$ and for increasing the transition point of ZnFe$_2$O$_4$ thereby suitably tailoring the saturation magnetization, resistivity, chemical
stability and mechanical hardness. Such attempts have been made possible by mixing the end member ferrites namely NiFe$_2$O$_4$ and CuFe$_2$O$_4$[12]. NiFe$_2$O$_4$ and ZnFe$_2$O$_4$[13-29]and ZnFe$_2$O$_4$ and CuFe$_2$O$_4$[30-36].

Continuing on the same lines, several reports of earlier researchers [37-39] on mixed ferrites of Ni-Zn-Cu have motivated to prepare ferrites of ternary mixtures to provide optimum electric and magnetic data. It is of interest to dope Zn$^{2+}$ and Ni$^{2+}$ ions in some of the sites of Fe$^{2+}$ ions in Ni-Cu mixed ferrite system. It is known that the magnetic behavior of Ni-Cu ferrite is largely governed by Fe-O-Fe interaction and Ni-O-Fe interaction (the coupling of spins of the 3d electrons). Introducing Zn$^{2+}$ and Ni$^{2+}$ ions in the spinel lattice is expected to bring in a substantial change in magnetization, Curie temperature and electric properties. In the last chapter we have studied Ni-Zn-Cu ferrite by varying the concentration of Zn. Interestingly a definite contribution of Jahn-Teller effect and crystal field distortions are found to exist in the octahedral sites of the ferrites. The present chapter is an attempt to prepare and investigate mixed ferrite with a chemical formula Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2.2x}$O$_4$. In the present case value of x is increased i.e. concentration of Zn$^{2+}$ is increased which should in turn increase Ni$^{2+}$ and thereby reduce Fe$^{3+}$ ions. It is expected that Ni$^{2+}$ ions and Fe$^{2+}$ ions are the neighbours of Cu$^{2+}$ ions in octahedral site. The new situation helps finding the variation of crystal field and Jahn-Teller effects as well as spin canting.
3.2 PREPARATION OF THE SAMPLE

In the present chapter a system of ferrite of chemical formula \( \text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4 \) is prepared and subjected to magnetic and electric study. The values of \( x \) are 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5. The systematic procedure of preparation falls into four categories. They are

1. Powder preparation
2. Compact formation
3. Heat treatment processes and
4. Machining to final shape.

3.2.1 POWDER PREPARATION

The composite oxides of \( \text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4 \) system are A.R grade NiO, ZnO, CuO and Fe\(_2\)O\(_3\). They are taken in stochiometric proportions as given below:

\[
\begin{align*}
  &x = 0.0 \Rightarrow 0.5[\text{NiO}] + 0.0[\text{ZnO}] + 0.5[\text{CuO}] + 1.0[\text{Fe}_2\text{O}_3] \to \text{Ni}_{0.5}\text{Zn}_{0.0}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4 \\
  &x = 0.1 \Rightarrow 0.6[\text{NiO}] + 0.1[\text{ZnO}] + 0.5[\text{CuO}] + 0.9[\text{Fe}_2\text{O}_3] + 0.05[\text{O}_2] \to \text{Ni}_{0.6}\text{Zn}_{0.1}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4 \\
  &x = 0.2 \Rightarrow 0.7[\text{NiO}] + 0.2[\text{ZnO}] + 0.5[\text{CuO}] + 0.8[\text{Fe}_2\text{O}_3] + 0.1[\text{O}_2] \to \text{Ni}_{0.7}\text{Zn}_{0.2}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4 \\
  &x = 0.3 \Rightarrow 0.8[\text{NiO}] + 0.3[\text{ZnO}] + 0.5[\text{CuO}] + 0.7[\text{Fe}_2\text{O}_3] + 0.15[\text{O}_2] \to \text{Ni}_{0.8}\text{Zn}_{0.3}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4 \\
  &x = 0.4 \Rightarrow 0.9[\text{NiO}] + 0.4[\text{ZnO}] + 0.5[\text{CuO}] + 0.6[\text{Fe}_2\text{O}_3] + 0.2[\text{O}_2] \to \text{Ni}_{0.9}\text{Zn}_{0.4}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4 \\
  &x = 0.5 \Rightarrow 1.0[\text{NiO}] + 0.5[\text{ZnO}] + 0.5[\text{CuO}] + 0.5[\text{Fe}_2\text{O}_3] + 0.25[\text{O}_2] \to \text{Ni}_{1.0}\text{Zn}_{0.5}\text{Cu}_{0.5}\text{Fe}_{1.0}\text{O}_4
\end{align*}
\]

The powders of reactants are mixed and ground well using an agate mortar. The acetone is only used for cleaning the mortar after each concentration is ground.
Well ground powder is fired at 900 °C for 20 hours and furnace cooled approximately at the rate of 100 °C per hour. This process is termed as pre-sintering.

3.2.2 COMPACT FORMATION

The pre-sintered powders are again ground well and are pelletized using hydraulic press at a constant pressure of 70 Kg/cm².

This powder pressing is an important and commonly used ceramic forming technique that warrants a brief treatment. In essence, the process is the compaction of a powdered mass into a desired shape. The degree of compaction is maximized and fraction of void space is minimized by coarse and fine particle mixed in appropriate proportion.

3.2.3 HEATING SCHEDULES

In the present study, the synthesis of polycrystalline mixed ferrite is undertaken through two heat treatment methods.

A. Sintering (Double sintering) and

B. Quenching (First sintering then quenching)

Accordingly the study of these ferrites, prepared by differing heat treatments, is presented in two sections. They are:

Section A: Characterization of the Sintered system and

Section B: Characterization of the Quenched system.
SECTION A

CHARACTERIZATION OF THE SINTERED Ni_{0.5+x}Zn_{x}Cu_{0.5}Fe_{2-x}O_{4} SYSTEM.

Sintering is the heating process by which atomic mobility of the compact is sufficient to permit the decrease of the free energy associated with the grain boundaries. Sintering is by far the most critical and an extensive step. If carefully executed, it yields the required crystal structure, Oxidation State, microstructure, and physical condition of the ferrite core.

High sintering temperature assures the more densification or less porosity. The samples in the form of pellets (three specimens for each concentration) are fired at 1050 °C for 15 hour and then furnace cooled at the rate of 100°C per hour. This procedure is called second sintering.

3.3A EXPERIMENTAL

3.3.1A X-RAY DIFFRACTION STUDY

An X-ray powder diffraction pattern is a set of lines or peaks, each of different intensity and position [d-spacing or Bragg angle θ], on a length of chart paper. For a given substance, the peak positions are essentially fixed and are characteristic of that substance. The intensities may vary from sample to sample, depending on the method of sample preparation and the instrumental conditions. For identification purpose, principal note is taken of line position together with a semi-quantitative consideration of intensities.
A fingerprint proof is provided for XRD in comparison with Powder diffraction files of JCPDS (Joint Committee on Powder Diffraction Standards) for similar ferrites. Experimental determination of lattice constants, molecular densities, particle size and oxygen parameter is taken up following the procedure highlighted in chapter-I.

PROPOSAL FOR THE SITES OF CATIONS

A prior knowledge of the site preference of the constituent ions of a ferrite is an important requirement for working out the spinel structure. Secondly an accurate data of ionic size of the constituent ions is advantageous. In the present system of ferrite Cu²⁺,Ni²⁺,Zn²⁺ and Fe²⁺ are the constituent cations. Using knowledge of site preference of the ions and the ionic size data of the respective ions viz., TABLE-3.1 and substituting the ions in A and B sites of spinel structure. A systematic calculation of radii of individual sites \( r_a \) and \( r_b \) is proceeded. Theoretical values of lattice constants are estimated permuting the \( r_a \) and \( r_b \) values in the modified formula for lattice constant calculation of Bhongale et.al.[40]

\[
a = \left\{ (r_a/\sqrt{3} + 2.0951r_o) + \left[ (r_a/\sqrt{3} + 2.0951r_o)^2 - 1.866 \left( 1.333r_a^2 + 0.0675r_o^2 - 0.6r_ar_o \right) \right]^{1/2} \right\} / 0.933 \quad \text{.....(3.1)}
\]

An appropriate set of values of lattice constants is estimated according to the criteria of Vegard's law[41]

1. Change of lattice constant with concentration
### TABLE - 3.1

Ionic radii and magnetic moments of the cations used in the present study*

<table>
<thead>
<tr>
<th>Cations</th>
<th>Ionic radius ($\text{A}^0$)</th>
<th>Magnetic moment ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>0.64</td>
<td>5.92</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.74</td>
<td>4.90</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.69</td>
<td>2.84</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>0.74</td>
<td>0.0</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.72</td>
<td>1.73</td>
</tr>
</tbody>
</table>

*CRC Hand book data.
XRD spectra of the sintered $\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2.2x}\text{O}_4$ system

Figure-3.1A
### TABLE - 3.2A

Experimental and theoretical lattice constants, particle size, porosity, molecular and macroscopic densities and 

\( u \)-parameter of sintered \( \text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4 \) ferrite system

<table>
<thead>
<tr>
<th>Concentration ( x )</th>
<th>Lattice constant ( \alpha ) A(^0)</th>
<th>Particle size A(^0)</th>
<th>Molecular density ( \rho_m ) Kg/m(^3)</th>
<th>Macroscopic density ( \rho_A ) Kg/m(^3)</th>
<th>Porosity ( P ) %</th>
<th>( 'u' ) Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.539</td>
<td>8.5222</td>
<td>350</td>
<td>5052</td>
<td>4572</td>
<td>9.5</td>
</tr>
<tr>
<td>0.1</td>
<td>8.527</td>
<td>8.5499</td>
<td>428</td>
<td>5082</td>
<td>3792</td>
<td>25.38</td>
</tr>
<tr>
<td>0.2</td>
<td>8.508</td>
<td>8.5660</td>
<td>431</td>
<td>5124</td>
<td>4505</td>
<td>12.08</td>
</tr>
<tr>
<td>0.3</td>
<td>8.574</td>
<td>8.5876</td>
<td>427</td>
<td>5018</td>
<td>4538</td>
<td>9.56</td>
</tr>
<tr>
<td>0.4</td>
<td>8.507</td>
<td>8.6095</td>
<td>334</td>
<td>5146</td>
<td>4801</td>
<td>6.70</td>
</tr>
<tr>
<td>0.5</td>
<td>8.588</td>
<td>8.6300</td>
<td>213</td>
<td>5012</td>
<td>4615</td>
<td>7.92</td>
</tr>
</tbody>
</table>
### TABLE - 3.3A

Proposed Cations distribution for sintered $\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4$ System

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>Tetrahedral site (A)</th>
<th>Octahedral site [B]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>$\text{Zn}<em>{0.0}\text{Fe}</em>{1.0}$</td>
<td>$\text{Ni}<em>{0.5}\text{Cu}</em>{0.5}\text{Fe}_{1.0}$</td>
</tr>
<tr>
<td>0.1</td>
<td>$\text{Zn}<em>{0.05}\text{Cu}</em>{0.025}\text{Fe}_{0.925}$</td>
<td>$\text{Ni}<em>{0.6}\text{Zn}</em>{0.05}\text{Cu}<em>{0.475}\text{Fe}</em>{0.875}$</td>
</tr>
<tr>
<td>0.2</td>
<td>$\text{Zn}<em>{0.1}\text{Cu}</em>{0.05}\text{Fe}_{0.85}$</td>
<td>$\text{Ni}<em>{0.7}\text{Zn}</em>{0.1}\text{Cu}<em>{0.45}\text{Fe}</em>{0.75}$</td>
</tr>
<tr>
<td>0.3</td>
<td>$\text{Zn}<em>{0.15}\text{Cu}</em>{0.075}\text{Fe}_{0.775}$</td>
<td>$\text{Ni}<em>{0.8}\text{Zn}</em>{0.15}\text{Cu}<em>{0.425}\text{Fe}</em>{0.625}$</td>
</tr>
<tr>
<td>0.4</td>
<td>$\text{Zn}<em>{0.2}\text{Cu}</em>{0.1}\text{Fe}_{0.7}$</td>
<td>$\text{Ni}<em>{0.9}\text{Zn}</em>{0.2}\text{Cu}<em>{0.4}\text{Fe}</em>{0.5}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$\text{Zn}<em>{0.25}\text{Cu}</em>{0.125}\text{Fe}_{0.625}$</td>
<td>$\text{Ni}<em>{1.0}\text{Zn}</em>{0.25}\text{Cu}<em>{0.375}\text{Fe}</em>{0.375}$</td>
</tr>
</tbody>
</table>
2. A close agreement of lattice constant for each concentration with its experimental value. This procedure helps to propose a good fit set of cations and their respective sites of spinel structure.

The theoretical and experimental lattice constants are tabulated in TABLE-3.2A. The porosity, particle size, molecular density and u-parameter are also listed in the same table. In order to appreciate the variation of lattice constant with concentration a graph is drawn between them, which is given in Figure-3.2A. The proposed cation distribution is given in TABLE-3.3A.

3.3.2 LOW FIELD MEASUREMENTS

Curie temperature is measured for the samples using the Low Field Susceptibility Bridge as explained in Chapter-I. As per the procedure given in Chapter-I samples of thickness 5 mm and diameter 15 mm are introduced in the balancing coil of the bridge to measure a signal proportional to the actual moment of the sample. The values of the moment corresponding to each temperature are noted for different concentrations. A graph is plotted between susceptibility ratio i.e. $\chi_T / \chi_{RT}$ versus temperature in °K for different concentrations and it is shown in the Figure-3.3A. The temperature corresponding to the minimum value of $\chi_T / \chi_{RT}$ gives the curie temperature of the sample. The values of Curie temperature for different concentrations are given in the TABLE 3.4A. A graph is drawn between concentration and Curie temperature and it is given in the Figure-3.4A.
3.3.3A HIGH FIELD MEASUREMENTS

Hysteresis loops are traced using the A.C High Field Hysteresis Loop Tracer in the field ranging up to 3600 Oe. A sample of approximately 3 mm thickness and 15 mm diameter is placed in the upper part of the pick-up coil and pushed back into the pole gap. When the current is increased, the hysteresis loop of the sample will be seen on the oscilloscope screen. Vertical and horizontal sensitivities of the scope could be adjusted to get a suitable size of the hysteresis loop. The representative loops for the present study is given in Figure-3.5A. The parameters calculated from the hysteresis loop are given in TABLES-3.5A and 3.6A.

3.3.4A A.C CONDUCTIVITY MEASUREMENTS

A.C conductivity values are measured at different frequencies i.e. from 40 Hz to 100 kHz with a desired interval of frequency steps at different temperatures for all the concentrations of Ni$_{0.5-x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system. The variation of conductivity ($\sigma_{ac}$) with frequency log ($\omega$), for all the concentrations, for one particular temperature, is shown in the Figure-3.7A.

The dielectric loss factor tan$\delta$ and the dielectric constant of the materials are measured at different temperatures and at different frequencies. The values of the quantities measured by electrical studies are reported for 10 kHz frequencies and at 150 °C, for all the concentrations, which are given in the TABLE-3.7A. In order to appreciate the behavior of dielectric constant and tan$\delta$ with frequency, curves are drawn and are shown in the Figures-3.8A and 3.9A respectively.
The values of activation energy \((E_a)\) are estimated, from the slopes of the set of plots of \(\log (\sigma_{ac})\) versus \(1000/T\) (Figure-3.10A) drawn for a particular frequency of 10kHz, for all the concentrations. The values of activation energy are tabulated as in TABLE-3.7A. A graph is drawn between concentration and activation energy \((E_a)\), at 10kHz, which is shown in the Figure-3.11A. The site preference factor ‘n’ and the grain boundary conductivity ‘B’ are calculated from the \(\log (\sigma_{ac} - \sigma_{dc})\) versus \(\log (\omega)\) plot for all the concentrations. The variation of ‘B’ and ‘n’ with concentration is shown in the Figures-3.12A and 3.13A respectively.

3.3.5A FTIR STUDY

The FTIR spectra are taken for all the samples of \(\text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4\) system using SHIMADZU-8700 FTIR Spectrometer. The spectra are shown in the Figure-3.14A. The vibration frequencies are given in TABLE-3.9A.

3.4A RESULTS AND DISCUSSION

The observed XRD patterns of the samples of the present study are shown in the Figure-3.1A. It is seen from Figure-3.1A that X-ray intensity patterns are separated and distinguished. This observation enable to state that the samples prepared is in single phase and polycrystalline nature. The measured values of diffraction angles lie between 34° - 35° for the characteristic peak of 311 plane. The presence of 311 reflection plane in these ferrites is the first evidence of the phase centered cubic structure (FCC). The values of experimental lattice constant given in TABLE-3.2A are found to range between 8.507Å to 8.588Å for the spinel ferrites.
The variation of experimental lattice constants is well depicted from Figure-3.2A. Figure-3.2A clearly indicates that there is an increase of lattice constants with increase of concentration (x). According to the plan of preparation of the spinel ferrite system Fe$^{3+}$ ions are replaced by a proportionate substitution of Zn$^{2+}$ and Ni$^{2+}$ ions when concentration x is increased. It is wise to relate the increase of Zn$^{2+}$ and Ni$^{2+}$ ions at the expense of Fe$^{3+}$ ions with the increase of lattice constant as concentration increases. Actually the ionic radii of Zn$^{2+}$ and Ni$^{2+}$ ions are (0.74Å and 0.69Å) larger than that of the Fe$^{3+}$ ions (0.64 Å), which legitimately conforms the increase of lattice constant as concentration, increase.

The measured values of particle size of the spinel ferrite lie in-between 213Å and 431Å. They are in good agreement with the values reported earlier for similar ferrites prepared by double sintering methods [15]. The values of % of porosity vary from 6.7 to 25.38. The range of values of % of porosity of the present samples reflects a good schedule of heat treatment of ceramics. Further the values of porosity are found to be well within the range of values reported by the earlier workers [14,18].

The values of molecular density determined using experimental lattice constant data are also given in the TABLE-3.2A. Molecular density of the spinel ferrites is found to vary between 5012 Kg/m³ and 5146Kg/m³ which show good agreement with the molecular density of similar ferrites. It may be concluded that the polycrystalline ferrite of the present study has a good compaction. The values of
Variation of lattice constant with concentration for the sintered samples of Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system.

![Graph of lattice constant vs. concentration](image1)

Variation of Susceptibility ratio with temperature for the Sintered samples of Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system.

![Graph of susceptibility ratio vs. temperature](image2)
Oxygen parameter change from 0.396 to 0.399 which is clearly found to be close to the ideal value of Oxygen parameter 0.375. It means that the spinel ferrites of the present study have a good amount of loose packing. This explanation is in agreement with the ones suggested by porosity, molecular density and particle size measurements.

TABLE-3.3A provides a picture of distribution of cations in the A and B sites. It is noticed from the TABLE-3.3A that Zn$^{2+}$ ions show equal preference for A and B sites and the Cu$^{2+}$ ions tends to encroach B site. In order to explain the site preference of transition metal ions two theories have been proposed which differ in the concept of chemical bonding in oxides. Dunitz and Orgel [42] have used crystal field theory, which is based on purely ionic type of bonding, where as Blasse[43] has used a simplified molecular orbital approach, taking into account, the covalent bonding between oxygen and transition metal atoms. Normally large divalent ions like Zn$^{2+}$ tend to occupy the tetrahedral sites as this is favored by polarization effects. Daniels' [44] and Matsui et.al.[45] have explained that Ni$^{2+}$ and Cu$^{2+}$ ions have a tendency to occupy octahedral sites. The proposed cations distribution of spinel ferrites of the present study is in vogue with the criteria reported earlier. However an equal % of Zn$^{2+}$ ions is found to occur in the octahedral sites for compensating the condition of valency. Theoretical value of lattice constant is also plotted with respect to concentration and shown in the same Figure-3.2A for comparison. Both the curves of theoretical and experimental lattice constants show a
straight line behavior and an increasing trend with concentration. Such an observation on theoretical and experimental lattice constants certifies that the proposed cation distribution is an equivalent of actual distribution of the ions in this spinel ferrites system. It is also noticed in Figure-3.2A that there is an appreciable gap between the two straight-line curves of theoretical and experimental lattice constants. Further the curves for experimental lattice constant lies below the theoretical lattice constant curve. A judicious incorporation of the rules of packing of ions reveals that

1. The presence of crystal field distortions is unavoidable, as there are Cu$^{2+}$ ions in B site.

2. The Jahn-Teller distortion due to Cu$^{2+}$ ion makes the neighboring ions in B site to shift to the exited state.

Therefore the occurrence of crystal field distortions and Jahn-Teller effect are estimated as the cause mechanism of the gap between the theoretical and experimental lattice constants. It is also understood that the increasing trend of lattice constants with concentration is solely attributed to that part of Zn$^{2+}$ and Ni$^{2+}$ ions replacing Fe$^{3+}$ ions in the B site. Replacement of Fe$^{2+}$ ions by the doped Zn$^{2+}$ and Cu$^{2+}$ ions in the A sites contributes for the expansion of the lattice.

Figure-3.3A shows the thermal variation of $\chi_T / \chi_{RT}$ with temperature for the Ni$_{0.5}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system. It is seen from Figure-3.3A that there is a sudden fall of susceptibility ratio at the transition point followed by a plateau region when the
temperature increases from the room temperature values. It is explained as a standard phase transition of second order in which the ferrites undergo a change of phase from paramagnetic to ferrimagnetic phases. It is believed that the height of the plateau region of the curve is the measure of the magnetic energy in ferrites [46]. The steep decrease of $\chi_T / \chi_{RT}$ near the Curie temperature confirms the absence of impurity phases and formation of single phase ferrite, the fact supported by X-ray diffraction (XRD) analysis of these samples.

Generally a polycrystalline magnetic material may consist of four types of domain states namely 1. Multidomain (MD) 2. Single domain (SD) 3. Superparamagnetic particles (SP) and 4. Cation deficient phases (CD). Rathakrishnamoorthy et al. [47] and Bean [48] systematically characterized magnetic materials and postulated different nature of curves as the indirect evidences for the presence of varying domain states. According to the postulate of Bean [48], it is stated that the nature of the curves is indicative of the presence of multidomain states.

Other important result of thermal variation of A.C susceptibility is the measurement of Curie temperature which is the phase transition point. Measured values of Curie temperatures in TABLE-3.4A show a proportionate decrease with the increase of concentration. The parameter Curie temperature is the sincere function total magnetic moment contribution of the spinel. The decrease of Curie temperature with concentration is explained to be due to the increase in the
TABLE-3.4A

Curie temperature of the samples of sintered $\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4$ system

<table>
<thead>
<tr>
<th>Concentration ($x$)</th>
<th>Curie Temperature ($T_c$) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>741</td>
</tr>
<tr>
<td>0.1</td>
<td>717</td>
</tr>
<tr>
<td>0.2</td>
<td>701</td>
</tr>
<tr>
<td>0.3</td>
<td>646</td>
</tr>
<tr>
<td>0.4</td>
<td>615</td>
</tr>
<tr>
<td>0.5</td>
<td>569</td>
</tr>
</tbody>
</table>
concentration of Zn$^{2+}$ and Ni$^{2+}$ ions whose relative magnetic moment at A and B sites amounts to a reduction in $T_C$.

From the TABLE-3.4A it is seen that the $T_C$ values range from 741$^0$K to 569$^0$K. The values of Curie temperature of the end member ferrites is 585$^0$C and 455$^0$C for NiFe$_2$O$_4$ and CuFe$_2$O$_4$ ferrites respectively[9]. For the ZnFe$_2$O$_4$ ferrite the transition temperature is 10 $^0$K [49] also for the Ni-Zn ferrite the transition temperature is 770 $^0$K [13]. The transition temperature of Cu-Ni ferrite is 797 $^0$K [12] and for Cu-Zn ferrite $T_C$ is 473 $^0$K [30]. It is clear that the range of values of Curie temperature is well within the values reported earlier. It is established that the substitution of Zn$^{2+}$ and Ni$^{2+}$ ions sufficiently reduces the transition temperature of Ni-Zn-Cu spinel ferrites. From the knowledge of ions present in the A and B sites of the ferrite it is positively interpreted that the crystal field faces a concise reduction due to Cu$^{2+}$ ions as the neighbor of the ions in B sites. Thus the reduction of $T_C$ with concentration explains that the interaction of crystal field and Jahn-Teller splitting.

In the present study the parameters of primary importance are saturation magnetization, coercive field, remanance magnetization and magnetic moment. The shape of magnetic hysteresis loop renders explanation for the nature of a magnetic domain and type of the magnetic materials. Bean[48] has shown from theoretical considerations that the hysteresis loops of dilute magnetic materials of various size of particles would be different. It has been worked out that the shapes of the loops will be divided into four categories. Each kind of loop is found to be indicative of
Variation of Magnetic moment with concentration for the sintered samples of Ni$_{0.5+x}$Zn$_x$Cu$_{0.8}$Fe$_{2.2-x}$O$_4$ system.

![Graph showing the variation of Curie temperature with concentration](image)

**Figure-3.4A**

![Graph showing the variation of Magnetic moment with concentration](image)

**Figure-3.6A**
one type domain or mixed types of domains. The types of the domains so
categorized are single-domain (SD), multidomain (MD), superparamagnetic domain
(SP) and cation deficient states (CD). The reason for the occurrence of different
domain states is well established in the literature[50].

According to the fairly well established criteria for domains, the loops obtained
for the Ni_{0.5-x}Zn_{x}Cu_{0.5}Fe_{2-x}O_{4} system (Figure-3.5A) of the present study are
indicative of multidomains. The values of coercive field vary between 22.94 Oe and
25.03 Oe. It is seen from the TABLE-3.5A that the coercive field is found to be
fairly low and there is no much change with respect to concentration. Low value of
coevasive field is effected due to soft nature of the ferrite. It is found to be insensitive
to concentration variation. The values of remanance ratio range from 0.348 to 0.433.
Therefore it is understood that the ferrites prepared in the present study are
multidomain cases. The values of saturation magnetization (M_s)(TABLE-3.6A)
values vary from 47 Gauss to 166 Gauss and the specific magnetization (σ) values
are form 13 to 36 emu/g . These values are in good agreement with the values
reported by Smit and Wijn [9], Wisvanathan and V.R.K. Murthy [51] and Derek
Craik et.al [52] for the similar types of ferrites.

According to Neel's two sublattice model [53] of ferrimagnetism, theoretical
magnetic moments can be calculated by the relation

\[ n_{B} (\text{Neel}) = M_B - M_A \]  \hspace{1cm} (3.2)
\( M_B \) and \( M_A \) are the B and A sublattice magnetic moments respectively. In the present studies \( n_B \) values are calculated using ionic magnetic moments of \( \text{Fe}^{3+}, \text{Ni}^{2+}, \text{Zn}^{2+}, \text{and Cu}^{2+} \). The observed magnetic moments are compared with the theoretical (Neel's model) magnetic moment and are summarized in TABLE-3.6A. In the earlier studies [54], agreement between the observed and theoretical magnetic moment values have been found confirming the collinear spin ordering and disagreement also found indicating the non-collinear order. The present discrepancy between observed and theoretical \( n_B \) values can be understood in terms of significant non-collinear behavior.

The discrepancy between observed and theoretical \( n_B \) values suggests the dominant role of canted spin (non-collinear) on B sites existing and Yafet-Kittel angles having strong influence on the \( M_S \) variation with \( x \). The values of canting angle \( (\theta_{\text{YK}}) \) have been obtained from the observed \( n_B \) variation with \( x \) by the relation [55]

\[
\text{n}_B(x)_{\text{obs}} = M_B(x)\cos\theta_{\text{YK}} - M_A(x) \tag{3.3}
\]

These values are also given in TABLE-3.6A. Thus the observed \( M_S \) variation has been explained on the basis of Yafet-Kittel angles existing on the B site spin besides two sub lattice models. \( \text{Zn}^{2+} \) ions going into B sites decrease the magnetic moment of the B sub lattice and also modify the exchange interactions of A and B sites. Hence, the net magnetization, \( M_S \) decreases. However studies using Mossbauer spectrometer would give clear information about the magnetic structure of the
Hysteresis loops of the sintered $\text{Ni}_{0.5+1}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4$ system
### TABLE - 3.5A

Saturation induction, remanance induction, $B_r \backslash B_s$ ratio and coercive field of sintered $\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-x}\text{O}_4$ system

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>Saturation induction $B_s$ (Gauss)</th>
<th>Remanance induction $B_r$ (Gauss)</th>
<th>$B_r \backslash B_s$ Ratio</th>
<th>Coercive field $H_c$ Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2077</td>
<td>831</td>
<td>0.399</td>
<td>24.33</td>
</tr>
<tr>
<td>0.1</td>
<td>590</td>
<td>206</td>
<td>0.348</td>
<td>23.98</td>
</tr>
<tr>
<td>0.2</td>
<td>872</td>
<td>312</td>
<td>0.357</td>
<td>22.94</td>
</tr>
<tr>
<td>0.3</td>
<td>1308</td>
<td>518</td>
<td>0.396</td>
<td>23.98</td>
</tr>
<tr>
<td>0.4</td>
<td>1376</td>
<td>570</td>
<td>0.414</td>
<td>22.94</td>
</tr>
<tr>
<td>0.5</td>
<td>775</td>
<td>336</td>
<td>0.433</td>
<td>25.03</td>
</tr>
</tbody>
</table>
TABLE - 3.6A

Saturation magnetization, magnetic moment, Y-K angle, exchange energy, molecular field coefficient and exchange field of sintered Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2.2x}$O$_4$ system

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>Sat. magnetisation $M_s$ (Gauss)</th>
<th>$\sigma$ (emu/gm)</th>
<th>Magnetic moment $\eta_B$</th>
<th>Y-K Angle (Degrees)</th>
<th>Exchange energy $E$ ($\times 10^{-16}$ ergs)</th>
<th>Mol. Field coeff. $\lambda_W$</th>
<th>Exchange field $B_e$ ($\times 10^3$ Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>166</td>
<td>36</td>
<td>1.525</td>
<td>24° 51'</td>
<td>219.54</td>
<td>2546</td>
<td>421.4</td>
</tr>
<tr>
<td>0.1</td>
<td>47</td>
<td>13</td>
<td>0.530</td>
<td>38°16'</td>
<td>1757.6</td>
<td>20356</td>
<td>956.73</td>
</tr>
<tr>
<td>0.2</td>
<td>70</td>
<td>16</td>
<td>0.659</td>
<td>36° 42'</td>
<td>1112</td>
<td>12880</td>
<td>895.16</td>
</tr>
<tr>
<td>0.3</td>
<td>104</td>
<td>23</td>
<td>0.980</td>
<td>31° 50'</td>
<td>463.64</td>
<td>5372</td>
<td>558.68</td>
</tr>
<tr>
<td>0.4</td>
<td>110</td>
<td>23</td>
<td>0.982</td>
<td>31° 24'</td>
<td>440.04</td>
<td>5096</td>
<td>558.0</td>
</tr>
<tr>
<td>0.5</td>
<td>62</td>
<td>14</td>
<td>0.577</td>
<td>38° 05'</td>
<td>1177.2</td>
<td>13636</td>
<td>838.61</td>
</tr>
</tbody>
</table>
ferrites to understand in terms of Neel's two sub lattice model and canting spin on B sites.

Magnetic moment contribution and magnetic energy bear direct relation to $n_B$ and Curie temperature. From Figures-3.4A and 3.6A it is confirmed that $T_C$ and magnetic moment decrease with concentration.

In order to check the validity of molecular field theory for the present system of ferrites, the values of exchange energy, molecular field coefficient and exchange field are obtained and reported in TABLE-3.6A. The value of exchange energy lies between $219.84 \times 10^{-16}$ and $1757.6 \times 10^{-16}$ ergs. The molecular field coefficient ranges between 2546.28 and 20356, and the exchange field varies from $421.4 \times 10^3$ to $956.73 \times 10^3$ Gauss. The order of values of these parameters shows that the spinel ferrite prepared is ferrimagnetic in nature.

The TABLE-3.7A shows that the values of conductivity measured in the present study lie between $9.621 \times 10^{-5}$ and $1.59 \times 10^{-3}$ at $150^\circ C$ and 10 kHz frequency. The dielectric constant and $\tan\delta$ values, at $150^\circ C$ and 10 kHz, ranges from 34.099 to 196.128 and 0.681 to 14.592 respectively. The order of the values is indicative of well organized grain formation for the sintering condition adopted in the present work. The activation energy $E_{ac}$ measured at 10kHz frequency spreads from 0.223 to 0.519 eV. The site preference factor ‘n’ lies between 0.4018 and 0.5598. Similarly the grain boundary conductivity ‘B’ ranges from $5.855 \times 10^{-8}$ to $1.316 \times 10^{-6}$ s cm$^{-1}$. 

103
# TABLE-3.7A

Conductivity, dielectric constant, tan\(\delta\), activation energy, site preference factor and grain boundary conductivity of sintered \(\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4\) system

<table>
<thead>
<tr>
<th>Concentration (x)</th>
<th>Conductivity at (150^\circ\text{C}) (\sigma_{\text{ac}}) at 10 kHz (\text{s cm}^{-1})</th>
<th>At (150^\circ\text{C}) and 10 kHz frequency</th>
<th>Activation energy (E_{\text{ac}}) (\text{eV}) at 10kHz</th>
<th>Site preference Factor (n)</th>
<th>Grain boundary Conductivity (B) (\text{m cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.352×10^{-4}</td>
<td>195.646</td>
<td>2.1902</td>
<td>0.348</td>
<td>0.486</td>
</tr>
<tr>
<td>0.1</td>
<td>9.621×10^{-5}</td>
<td>96.7112</td>
<td>1.789</td>
<td>0.345</td>
<td>0.514</td>
</tr>
<tr>
<td>0.2</td>
<td>1.505×10^{-5}</td>
<td>45.2941</td>
<td>0.5975</td>
<td>0.397</td>
<td>0.428</td>
</tr>
<tr>
<td>0.3</td>
<td>1.038×10^{-5}</td>
<td>34.0998</td>
<td>0.5474</td>
<td>0.519</td>
<td>0.401</td>
</tr>
<tr>
<td>0.4</td>
<td>1.59×10^{-3}</td>
<td>196.128</td>
<td>14.5929</td>
<td>0.223</td>
<td>0.431</td>
</tr>
<tr>
<td>0.5</td>
<td>3.062×10^{-5}</td>
<td>80.767</td>
<td>0.6818</td>
<td>0.486</td>
<td>0.559</td>
</tr>
</tbody>
</table>
The frequency dependence of conductivity, dielectric constant and $\tan\delta$ are presented in the Figures-3.7A, 3.8A and 3.9A respectively for the present spinel system. Figure-3.7A shows a slow change of the values of conductivity at low frequencies and a steady rising up at higher frequencies. Conversely Figure-3.8A shows a clear fall of values of permittivity with frequency. Figure-3.9A shows that the $\tan\delta$ values rise up at lower frequencies. The trend of conductivity explains that the mixed ferrites have more electrons available for transport at higher frequencies. The variation of dielectric constant with frequency in these materials is explained to be due to the effective value of polarization caused by inter-ionic, molecular and grain boundary effects at low frequencies. The low values of dielectric constant at high frequencies are attributed to a less contribution of polarization due to exclusively inter ionic type.

Curves of $\tan\delta$ in Figure-3.9A provide a picture of the absorption of energy carried by electromagnetic field when it propagates through the ferrite. The values of $\tan\delta$ with frequency reflect the subsiding nature subsequently leading to a gradual limping up of effect of conduction at high frequencies.

It may be explained so because of the release of charge carriers from the clutches of polarization at high frequency. The behavior of polarization with frequency can be explained using a principle laid down by Koop [56] i.e. the dielectric constants is reciprocal of root mean square of conductivity. Verwey and de Boer [57] have established that in oxides, containing one ion of variable valence, the
Variation of conductivity ($\sigma_{ac}$) with frequency for the Sintered samples of Ni$_{0.6}$Zn$_x$Cu$_{0.4}$Fe$_{2-x}$O$_4$ system.

at 150°C

Figure-3.7A

Variation of dielectric constant with frequency for the Sintered samples of Ni$_{0.6}$Zn$_x$Cu$_{0.4}$Fe$_{2-x}$O$_4$ system.

at 150°C

Figure-3.8A
conduction takes place by hopping via activation of states involving cations changing valence as

$$\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^{-} \quad \ldots \ldots (3.4)$$

and vice versa. The presence of nickel ion on the octahedral sites favors the conduction mechanism as proposed by Van Uitert [58], viz.

$$\text{Ni}^{2+} + \text{Fe}^{2+} \Leftrightarrow \text{Ni}^{3+} + \text{Fe}^{2+} + 2e^{-} \quad \ldots \ldots (3.5)$$

which explains the predominant conduction mechanism of Ni-Zn-Cu system of present investigation. The conduction mechanism for the samples of present study is due to hole transfer from Ni$^{3+}$ to Ni$^{2+}$ ions [59,60]. According to Mossbauer study carried out by Daniels and Rosencwaig [61], the cation distribution of Ni-Zn ferrites is given as

$$\text{Zn}^{2+}_x \text{Fe}_{1-x}^{3+} [\text{Ni}^{2+}_{1-x} \text{Fe}^{3+}_{1+x} \text{O}_2 \text{O}_4] \quad \ldots \ldots (3.6)$$

As zinc is a non-magnetic element and ZnFe$_2$O$_4$ is a normal ferrite, Zn$^{2+}$ ions occupy tetrahedral A-site, while in NiFe$_2$O$_4$, a predominantly inverse ferrite, Ni$^{2+}$ ions occupy octahedral B-site. In samples sintered at higher temperature, Ni$^{3+}$ may also be present along with Ni$^{2+}$ and hopping of holes from Ni$^{3+}$ to Ni$^{2+}$ is also probable according to the mechanism given above. So, in samples sintered at higher temperature, the conduction mechanism is enhanced and the conductivity of such samples is changed by an order of $10^{-2}$.

The curves of log($\sigma$) versus 1000/ T at 10 kHz for different concentration of Zn in the mixed ferrites are shown in the Figure-3.10A. It is seen from the Figure-
Variation of $\tan \delta$ with frequency for the Sintered samples of Ni$_{0.4+x}$Zn$_x$Cu$_{0.4}$Fe$_{2.2x}$O$_4$ system.

at 150°C

Figure-3.8A

Variation of conductivity($\sigma_{ac}$) with temperature for the Sintered samples of Ni$_{0.4+x}$Zn$_x$Cu$_{0.4}$Fe$_{2.2x}$O$_4$ system.

at 10 kHz

Figure-3.10A
3.10A that conductivity is a direct exponential function of temperature, which is the inherent property of a semi-conductor. It is explained on the basis of hopping of electrons between localized 3d bands of ions in these mixed ferrites. The slope of the lines in the Figure-3.10A should be a measure of activation energy ($E_{ac}$). A hopping activation energy of the order of 0.1 eV is associated with the drift mobility of electrons [62]. However, if the observed values of activation energies are $\approx 0.2$ eV suggest [63,64] that the conduction mechanism observed is due to hopping of electron of the type $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$. For ferrites possessing Cu and Ni in octahedral sites the value of activation energy has been reported to be $= 0.3797$ eV[64]. Thus there is a good agreement of activation energy of the spinel system of the present study.

The measured values of activation energy versus concentration(Figure-3.11A) would be able to throw more light on the changes in the position of the energy bands due to incorporation of Zn$^{2+}$. This range of values is suggestive of hopping and the present system behaves like a semiconductor with intermittent energy levels in the localized d bands of neighboring Fe ions of B site. Based on these results we conclude that the Fe-3d electrons are important in the conduction process.

Conductivity measurement is indicative of the presence of Ni$^{3+}$ and Fe$^{2+}$ ions in B site. The rising up of activation energy ($E_{ac}$) with concentration is attributed to the widening of the band gap of 3d band of ions mainly in B site. The increase of concentration alters the composition of Ni and Zn. Particularly Ni$^{2+}$ ion growth in B
site compete with the Cu ions and pushes them to A site. Generally Cu$^{2+}$ ion in B site is the cause of Jahn-Teller effect which makes the neighboring ions to go to the exited state.

Normally electrical conduction is explained by mobile charge carriers i.e. electrons or holes in semiconductors. The mobility of excess charge carriers accounts for conductivity. From the curves of concentration dependence of conductivity and activation energy, it is inferred that Cu and Zn ions does not remain as a passive ion but behave in a trivial manner in trimming the energy band separation.

The variations of 'B' and 'n' with respect to concentration (Figures-3.12A and 3.13A) show difference in the particle formation as the materials are prepared by ceramic techniques. Phenomenologically conductivity is explained to be dependent on the composition of ions making ferrites and the grain size of the samples. The explicit expression relating these physical quantities is

$$\sigma(\omega) = B\omega^n$$

...(3.7)

where, 'B' is the parameter decided by the organization of grains, $\omega$ is the frequency and 'n' is the parameter depending on the composition of the samples. It is inferred form the Figures-3.12A that the size of the grain increases with the concentration of Zn. But in Figure-3.13A the site preference factor 'n' indicates gradual raise with respect to Zn concentration. Of the two parameters 'B' is found to change less
Variation of activation energy (\(E_a\)) with concentration for the sintered samples of \(\text{Ni}_{0.8+x}\text{Zn}_{x}\text{Cu}_{0.4}\text{Fe}_{2.2x}\text{O}_4\) system.

![Graph showing variation of activation energy with concentration](image1)

Variation of Grain boundary conductivity (\(B\)) with concentration for the Sintered samples of \(\text{Ni}_{0.8+x}\text{Zn}_{x}\text{Cu}_{0.4}\text{Fe}_{2.2x}\text{O}_4\) system.

![Graph showing variation of grain boundary conductivity with concentration](image2)
Variation of Site preference factor (n) with concentration for the sintered samples of Ni$_{0.85}$Zn$_{0.15}$Cu$_{0.4}$Fe$_{0.6}$O$_4$ system.
sensitively with the variation of Zn. However deviation of ‘B’ and ‘n’ is attributed to the ceramic method of preparation of the system of spinel ferrites.

The ferrites prepared in the present study crystallize in the natural spinel form with the space group $Fd_3m$($O_h$). On the basis of group theoretical calculations, spinel ferrites exhibit four IR active fundamentals ($T_{nu}$) in the vibrational spectra of normal as well as inverse spinel ferrites. It has been reported that the first three IR bands are due to the tetrahedral ($T_d$) and octahedral ($O_h$) coordination compounds, while the fourth one is due to some type of lattice vibrations involving tetrahedral cation [65].

The infrared spectra of $\text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4$ mixed ferrite samples are shown in the Figure-3.14A for different concentrations. The absorption bands obtained in the present investigation are found to be in the range reported for similar type of ferrites[66,30]. The position of the bands together with their shoulders is given in the TABLE-3.9A.

From Figure-3.14A, it can be seen that the IR spectra of the present system exhibit five principal bands. The principal bands $v_1$ and $v_2$ shift gradually towards low frequency side, mainly the high-frequency band($v_1$) and second absorption band($v_2$) are found to be in the range 680-670 and 580-565 cm$^{-1}$ respectively. A comparison of FTIR charts at different concentrations provides information about decrease in transmittance and increase in broadness.

These features are explained on the basis of cation distribution in A and B sites of mixed Ni-Zn-Cu ferrites. Waldron [67] has attributed the occurrence of $v_1$ and $v_2$
<table>
<thead>
<tr>
<th>Ferrite</th>
<th>( v_1 )</th>
<th>( v_2 )</th>
<th>( v_3 )</th>
<th>( v_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>660</td>
<td>587</td>
<td>396</td>
<td>340</td>
</tr>
<tr>
<td>Cu</td>
<td>620</td>
<td>565</td>
<td>400</td>
<td>330</td>
</tr>
<tr>
<td>Zn</td>
<td>660</td>
<td>550</td>
<td>415</td>
<td>338</td>
</tr>
<tr>
<td>Fe</td>
<td>640</td>
<td>590</td>
<td>410</td>
<td>350</td>
</tr>
</tbody>
</table>

*Courtesy Ref.[67]*

**TABLE - 3.8A**

FTIR spectral frequencies of some end member ferrites

*Courtesy Ref.[67]*
FTIR Spectra of the sintered Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system.

Figure - 3.14 A
TABLE - 3.9A

Center frequency of the bands of FTIR spectra of the sintered Ni\(_{0.5+x}\)Zn\(_x\)Cu\(_{0.5}\)Fe\(_{2.2}\)O\(_4\) system

<table>
<thead>
<tr>
<th>Concentration (x)</th>
<th>(v_1)</th>
<th>(v_2)</th>
<th>(v_3)</th>
<th>(v_4)</th>
<th>(v_5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>682.6</td>
<td>578.26</td>
<td>-</td>
<td>-</td>
<td>382.60</td>
</tr>
<tr>
<td>0.1</td>
<td>-</td>
<td>578.26</td>
<td>469.56</td>
<td>395.65</td>
<td>378.26</td>
</tr>
<tr>
<td>0.2</td>
<td>673.91</td>
<td>578.26</td>
<td>469.56</td>
<td>395.65</td>
<td>386.95</td>
</tr>
<tr>
<td>0.3</td>
<td>682.60</td>
<td>573.91</td>
<td>486.95</td>
<td>400.00</td>
<td>373.91</td>
</tr>
<tr>
<td>0.4</td>
<td>682.60</td>
<td>573.91</td>
<td>486.95</td>
<td>404.34</td>
<td>386.95</td>
</tr>
<tr>
<td>0.5</td>
<td>673.91</td>
<td>565.21</td>
<td>491.30</td>
<td>395.65</td>
<td>382.60</td>
</tr>
</tbody>
</table>
bands to the intrinsic vibrations of the tetrahedral (T_d) and octahedral (O_h) coordination compounds. Both these high frequency bands have been attributed to the intrinsic lattice vibrations of E-symmetry. The third absorption band v_3 is attributed to the Cu^{2+} - O^{2-} complexes at octahedral sites. The frequency of the (v_4 and v_5) bands depend on the mass of tetrahedral metal ion complexes[68] and hence it is attributed to the vibrations of ions at the tetrahedral site. The low frequency bands are attributed to vibrations of T_{2g} -symmetry.

The cation distribution of mixed Ni-Zn-Cu ferrites is:

\[
(Zn^{2+}_{x-y} Fe^{3+}_{1-x+y-z} Cu^{2+}_z)_{A}[Ni^{2+}_{0.5-x} Zn^{2+}_y Cu_{0.5-y} Fe^{3+}_{1-x+y-z}]_{B} O^{2-}_4. \quad (3.8)
\]

Where \( x = 0.1, 0.2, 0.3, 0.4 \) and 0.5, \( y = 50\% \) of \( x \) and \( z = 50\% \) of \( y \).

As the content of Zn increases Zn^{2+} ions consistently replace Fe^{3+} ions from A to B site. At the same time Ni^{2+} ions on the octahedral site increases. This disturbs the order on the octahedral site with increase in zinc. The disordered systems give rise to broad bands in their spectrum[69]. TABLE-3.9A shows high frequency band in the range 680-670 cm \(^{-1}\) which is found to decrease to a small extent with the increase of concentration. Consequently the changes in the high frequency band \( v_1 \) is correlatable to \( Zn^{2+} - O^{2-} \) bond stretching. The agreement of the value of frequency of \( v_1 \) band with the literature value is illustrated in TABLE-3.8A. On the other hand second absorption band \( v_2 \) (580-565 cm \(^{-1}\)) which may be attributed for \( Zn^{2+} - O^{2-} \) at octahedral sites as it clearly indicates an appreciable decrease of

109
frequency with increase of Zn concentration. The sites A and B are explained to possess other ions also in this mixed ferrites along with Zn. But the shifting of the band frequency is explained to be due to Zn ion concentration affecting the distribution of other ions. Based on these observations it is accounted for by that the expansion of B sites is larger than the expansion of A site. It is in agreement with the suggestion made out of X-ray diffraction studies of the present samples. Third absorption band \( v_3 \) explains John-Teller effect due to the presence of \( \text{Cu}^{2+} \) ion in octahedral sites. The presence of \( \text{Cu}^{2+} \) ions and the John-Teller splitting makes the companions ions of B site to exist in their exited states. It means that \( \text{Ni}^{2+} \) and \( \text{Fe}^{2+} \) ions in B sites may be shifted to \( \text{Ni}^{3+} \) and \( \text{Fe}^{3+} \) states. The explanation of this kind is in accordance with the inference of conductivity measurements. Consequently these results are in support of hopping of charge carriers from 3d bands of Ni and Fe ions.

The variation of activation energy with concentration (x) has established that the band gap of localized 3d band widens. Widening of the band gap of 3d bands with x is correlatable to the relative strength of Jahn-Teller splitting and crystal field in the octahedral site of spinel ferrite.

It is seen from the TABLE-3.9A the frequencies of the bands \( v_4 \) and \( v_5 \) are found to be shifted from their corresponding values of end member ferrites namely \( \text{NiFe}_2\text{O}_4, \text{CuFe}_2\text{O}_4, \text{ZnFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \)[TABLE-3.8A]. The larger difference in the frequency of \( v_5 \) band found between end members and the present spinel ferrite may be attributed to the presence of many ion complexes and their masses in B site.
SECTION: B

CHARACTERISATION OF THE QUENCHED Ni_{0.5+x}Zn_{x}Cu_{0.5}Fe_{2.2}O_{4} SYSTEM

The interesting physical and chemical properties of spinel ferrites arise from the ability of these compounds to distribute the cations among the available tetrahedral and octahedral sites. This distribution of cations depends on the method of preparation of samples. The ferrites synthesized by different techniques have been found to exhibit different chemical, structural and magnetic properties [70]. Particularly the structural and magnetic properties of ferrites depend upon the cooling rate employed during the synthesis of samples.

We study the change in the properties of the spinel ferrite Ni_{0.5+x}Zn_{x}Cu_{0.5}Fe_{2.2}O_{4} by changing the rate of cooling. This section deals with the characterization of the quenched samples of Ni_{0.5+x}Zn_{x}Cu_{0.5}Fe_{2.2}O_{4} spinel system. For the quenching process the same procedure is adopted as the one followed for sintering method (section-A) up to pre-sintering process. The pressed samples are fired at 1050 °C for 15 hours and they are immersed in the ice bath immediately after taken out of the furnace. The ice quenching operation is carried after the pressing operation.

3.3B EXPERIMENTAL

3.3.1B X-RAY DIFFRACTION STUDY

The XRD spectra for all the samples, of the quenched spinel system of the present study, are noted. Experimental determination of lattice constant, molecular
density, particle size and oxygen parameter is taken up following the procedure highlighted in SECTION-A of this chapter.

**PROPOSAL FOR THE SITES OF CATIONS**

The theoretical lattice constants for the quenched samples of the present study are calculated as per the procedure mentioned in SECTION-A. The theoretical and experimental lattice constants are tabulated in TABLE-3.2B. The porosity, particle size, molecular density and u- parameter are also listed in the same table. In order to appreciate the variation of lattice constant with concentration a graph is drawn between them, as shown in Figure-3.2B. The proposed cation distribution is given in TABLE-3.3B.

**3.3.2B LOW FIELD MEASUREMENTS**

Curie temperature is measured for the quenched samples using the Low Field Susceptibility Bridge as explained in Chapter-1. A graph is plotted between susceptibility ratio i.e. $\chi_T / \chi_{RT}$ versus temperature in K for different concentrations and it is shown in the Figure-3.3B. The temperature corresponding to the minimum value of $\chi_T / \chi_{RT}$ gives the curie temperature of the sample. The values of Curie temperature for different concentrations are given in the TABLE 3.4B. A graph is drawn between concentration and Curie temperature and it is given in the Figure-3.4B.
XRD spectra of the quenched Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2.25}$O$_4$ system

Figure-3.1B
TABLE - 3.2B

Experimental and theoretical lattice constants, particle size, porosity, molecular and macroscopic densities and 'u'-parameter of quenched Ni_{0.5+x}Zn_xCu_{0.5}Fe_{2-2x}O_4 ferrite system

<table>
<thead>
<tr>
<th>Concentration x</th>
<th>Lattice constant a A^0</th>
<th>Particle size A^0</th>
<th>Molecular density ( \rho_m ) Kg/m^3</th>
<th>Macroscopic density ( \rho_A ) Kg/m^3</th>
<th>Porosity P %</th>
<th>'u' Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Theoretical</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>8.4366</td>
<td>8.5222</td>
<td>371</td>
<td>5238</td>
<td>4492</td>
<td>14.24</td>
</tr>
<tr>
<td>0.1</td>
<td>8.4531</td>
<td>8.5499</td>
<td>351</td>
<td>5217</td>
<td>3658</td>
<td>29.88</td>
</tr>
<tr>
<td>0.2</td>
<td>8.4214</td>
<td>8.566</td>
<td>361</td>
<td>5286</td>
<td>4786</td>
<td>9.45</td>
</tr>
<tr>
<td>0.3</td>
<td>8.4053</td>
<td>8.5876</td>
<td>311</td>
<td>5326</td>
<td>4965</td>
<td>6.77</td>
</tr>
<tr>
<td>0.4</td>
<td>8.4732</td>
<td>8.609</td>
<td>421</td>
<td>5209</td>
<td>4872</td>
<td>6.46</td>
</tr>
<tr>
<td>0.5</td>
<td>8.4702</td>
<td>8.630</td>
<td>429</td>
<td>5224</td>
<td>4957</td>
<td>5.11</td>
</tr>
</tbody>
</table>
TABLE - 3.3B

Proposed Cations distribution for
quenched Ni_{0.5+x}Zn_{x}Cu_{0.5}Fe_{2-2x}O_{4} System

<table>
<thead>
<tr>
<th>Concentration x</th>
<th>Tetrahedral site (A)</th>
<th>Octahedral site [B]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>Zn_{0.0} Fe_{1.0}</td>
<td>Ni_{0.5} Cu_{0.5} Fe_{1.0}</td>
</tr>
<tr>
<td>0.1</td>
<td>Zn_{0.05} Cu_{0.025} Fe_{0.925}</td>
<td>Ni_{0.6} Zn_{0.05} Cu_{0.475} Fe_{0.875}</td>
</tr>
<tr>
<td>0.2</td>
<td>Zn_{0.1} Cu_{0.05} Fe_{0.85}</td>
<td>Ni_{0.7} Zn_{0.1} Cu_{0.45} Fe_{0.75}</td>
</tr>
<tr>
<td>0.3</td>
<td>Zn_{0.15} Cu_{0.075} Fe_{0.775}</td>
<td>Ni_{0.8} Zn_{0.15} Cu_{0.425} Fe_{0.625}</td>
</tr>
<tr>
<td>0.4</td>
<td>Zn_{0.2} Cu_{0.1} Fe_{0.7}</td>
<td>Ni_{0.9} Zn_{0.2} Cu_{0.4} Fe_{0.5}</td>
</tr>
<tr>
<td>0.5</td>
<td>Zn_{0.25} Cu_{0.125} Fe_{0.625}</td>
<td>Ni_{1.0} Zn_{0.25} Cu_{0.375} Fe_{0.375}</td>
</tr>
</tbody>
</table>
3.3.3B HIGH FIELD MEASUREMENTS

Hysteresis loops are traced using the A.C High Field Hysteresis Loop Tracer in the field ranging up to 3600 Oe. The representative loops for the present study is given in Figure-3.5B. The parameters calculated from the hysteresis loop are given in TABLES-3.5B and 3.6B.

3.3.4B A.C CONDUCTIVITY MEASUREMENTS

A.C conductivity values are measured at different frequencies i.e. from 40 Hz to 100 kHz with a desired interval of frequency steps at different temperatures for all the concentrations of \( \text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2.2x/2}\text{O}_4 \) quenched system. The variation of conductivity \( (\sigma_{ac}) \) with frequency \( \log(\omega) \), for all the concentrations, at one particular temperature, is shown in the Figure-3.7B.

The dielectric loss factor \( \tan\delta \) and the dielectric constant of the materials are measured at different temperatures and at different frequencies. The values of these quantities measure by electrical studies are reported for 10 kHz frequency and at \( 150^\circ\text{C} \), for all the concentrations, which are given in the TABLE-3.7B. In order to appreciate the behavior of dielectric constant and \( \tan\delta \) with frequency, curves are drawn and are shown in the Figures-3.8B and 3.9B respectively.

The values of activation energy \( (E_{ac}) \) are estimated, from the slopes of the set of plots of \( \log(\sigma_{ac}) \) versus \( 1000/T \) (Figure-3.10B) drawn for a particular frequency of 10kHz, for all the concentrations. The values of activation energy are tabulated as in TABLE-3.7B. A graph is drawn between concentration and activation energy.
at 10kHz, which is shown in the Figure-3.11B. The site preference factor ‘n’ and the grain boundary conductivity ‘B’ are calculated from the log \((\sigma_{ac} - \sigma_{dc})\) versus \(\log (\omega)\) plot for all the concentrations. Variation of ‘B’ and ‘n’ with concentration is shown in the Figures-3.12B and 3.13B respectively.

3.3.5 FTIR STUDY

The FTIR spectra are taken for all the samples of Ni\(_{0.5}\)Zn\(_{x}\)Cu\(_{0.5}\)Fe\(_{2-2x}\)O\(_4\) quenched system using SHIMADZU-8700 FTIR Spectrometer. The spectra are shown in the Figure-3.14B. The vibration frequencies are given in TABLE-3.8B.

3.4 RESULTS AND DISCUSSION

The observed XRD patterns of the samples of the present study are shown in the Figure-3.1B. It is seen from Figure-3.1B that there are separated and distinguished peaks with varying intensities. This observation simply ensures that the samples prepared are in single phase and polycrystalline nature. The measured values of diffraction angle lie between 34° and 35° for the characteristic peak of 311 planes. The presence of 311 reflection plane for these ferrites provides the first evidence of the phase centered cubic structure (FCC). The values of experimental lattice constants given in TABLE-3.2B are found to range between 8.405A\(^0\) to 8.473A\(^0\) for the spinel ferrites. The variation of experimental lattice constants is well depicted from Figure-3.2B. Figure-3.2B clearly indicates that there is an increase of lattice constants with increase of concentration (x). According to the plan of preparation of the spinel ferrite system Fe\(^{2+}\) ions are replaced by a proportionate
Variation of lattice constant with concentration for the quenched samples of Ni$_{0.6+x}$Zn$_x$Cu$_{0.6}$Fe$_{2.2x}$O$_4$ system.

![Graph showing variation of lattice constant](image)

Variation of Susceptibility ratio with temperature for the quenched samples of Ni$_{0.6+x}$Zn$_x$Cu$_{0.6}$Fe$_{2.2x}$O$_4$ system.

![Graph showing variation of susceptibility ratio](image)

Figure-3.2B

Figure-3.3B
substitution of Zn$^{2+}$ and Ni$^{2+}$ ions when concentration $x$ is increased. It is wise to relate the increase of Zn$^{2+}$ and Ni$^{2+}$ ions at the expense of Fe$^{3+}$ ions with the increase of lattice constant as concentration increases. Actually the ionic radii of Zn$^{2+}$ and Ni$^{2+}$ ions are (0.74Å and 0.69Å) larger than that of the Fe$^{3+}$ ions (0.64 Å), which legitimately conforms the increase of lattice constant as concentration, increase.

The measured values of particle size of the spinel ferrite lie in-between 311Å and 429Å. They are in good agreement with the values reported earlier for similar ferrites prepared by double sintering methods [15]. The values of % of porosity vary from 5.11 to 29.88. The range of values of % of porosity of the present samples reflects a good schedule of heat treatment of ceramics. Further the values of porosity are found to be well with in the range of values reported by the earlier workers [14,18].

The values of molecular density determined using experimental lattice constant data are also given in the TABLE-3.2B. Molecular density of the spinel ferrites is found to vary between 5209 Kg/m$^3$ and 5326Kg/m$^3$ which show good agreement with the molecular density of similar ferrites. It may be concluded that the polycrystalline ferrite of the present study has a good compaction. The value of Oxygen parameter ranges from 0.397 to 0.399, which is clearly found to be close to the ideal value of Oxygen parameter 0.375. It means that the spinel ferrites of the present study have a good amount of loose packing. This explanation is in
agreement with the ones suggested by porosity, molecular density and particle size measurements.

TABLE-3.3B provides a picture of distribution of cations in the A and B sites. It is noticed from the TABLE-3.3B that Zn$^{2+}$ ions show equal preference for B site and Cu$^{2+}$ ions tend to encroach B site. The proposed cations distribution of spinel ferrites of the present study is in vogue with the criteria reported earlier[32]. Theoretical and experimental values of lattice constants is plotted with respect to concentration and shown in the Figure-3.2B for comparison. Both the curves of theoretical and experimental lattice constants show straight line behavior and increasing trend with concentration. Such an observation on theoretical and experimental lattice constants certifies that the proposed cation distribution is an equivalent of actual distribution of the ions in this spinel ferrites system. It is also noticed in Figure-3.2B that there is an appreciable gap between the two straight line curves of theoretical and experimental lattice constants.

The occurrence of crystal field distortions and Jahn-Teller effect are estimated as the cause mechanism of the gap between the theoretical and experimental lattice constants. It is also understood that the increasing trend of lattice constants with concentration is solely attributed to that part of Zn$^{2+}$ and Ni$^{2+}$ ions replacing Fe$^{3+}$ ions in the B site. Replacement of Fe$^{3+}$ ions by the doped Zn$^{2+}$ ions in the A sites contributes for the expansion of the lattice.
**TABLE-3.4B**

Curie Temperature of the samples of quenched Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system

<table>
<thead>
<tr>
<th>Concentration (x)</th>
<th>Curie Temperature $T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>767</td>
</tr>
<tr>
<td>0.1</td>
<td>742</td>
</tr>
<tr>
<td>0.2</td>
<td>708</td>
</tr>
<tr>
<td>0.3</td>
<td>667</td>
</tr>
<tr>
<td>0.4</td>
<td>615</td>
</tr>
<tr>
<td>0.5</td>
<td>613</td>
</tr>
</tbody>
</table>
Figure-2.3B shows the thermal variation of $\chi_T / \chi_{RT}$ with temperature for the Ni$_{0.5}$Zn$_{0.5}$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system. It is seen from Figure-3.3B that there is a sudden fall of susceptibility ratio at the transition point followed by a plateau region when the temperature increases from the room temperature values. It is explained as a standard phase transition of second order in which the ferrites undergo a change of phase from para magnetic to ferrimagnetic phases. It is believed that the height of the plateau region of the curve is the measure of the magnetic energy in ferrites [46]. It is observed from the set of curves for $\chi_T / \chi_{RT}$ versus temperature ordered magnetic phase is well settled in the members of the spinel ferrites. According to the postulate of Bean [48], it is stated that the nature of the curves is indicative of the presence of multi domine states.

Other important result of thermal variation of A.C susceptibility is the measurement of Curie temperature, which is the phase transition point. Measured values of Curie temperatures in TABLE-3.4B show a proportionate decrease with the increase of concentration. The parameter Curie temperature is the sincere function of total magnetic moment contribution of the spinel. The decrease of Curie temperature with concentration is explained to be due to the increase in the concentration of Zn$^{2+}$ ion, which is non-magnetic [15]. From the TABLE-3.4B it is seen that the $T_C$ values range from 613°K to 767°K. It is clear that the range of values of Curie temperature is well within the values reported earlier for similar ferrites [9,12,13,30,49]. It is established that the substitution of Zn$^{2+}$ and Ni$^{2+}$ ions
sufficiently reduces the transition temperature of Ni-Zn-Cu spinel ferrites. From the knowledge of ions present in the A and B sites of the ferrite it is positively interpreted that the crystal field faces a concise reduction due to the occurrence of Cu$^{2+}$ ions as the neighbor of the ions in B sites. Thus the reduction of $T_C$ with concentration explains that the interaction of crystal field and Jahn-Teller splitting.

In the present study the parameters of primary importance are saturation magnetization, coercive field, remanence magnetization and magnetic moment. The shape of magnetic hysteresis loop renders explanation for the nature of a magnetic domain and type of the magnetic materials. According to the fairly well established considerations, the loops obtained for the Ni$_{0.5-x}$Zn$_x$Cu$_{0.5}$Fe$_{2-x}$O$_4$ quenched system (Figure-3.5B) of the present study are indicative of multi domains. The value of coercive field varies between 21.90 Oe and 23.60 Oe. It is seen from the TABLE-3.5B that the coercive field is found to be fairly low and there is no much change with respect to concentration. Low value of coercive field is effected due to soft nature of the ferrite. It is found to be insensitive to concentration variation. The values of remanence ratio range from 0.322 to 0.386. Therefore it is understood that the ferrites prepared in the present study are multi domain cases. The saturation magnetization ($M_s$) values ranges from 53 Gauss to 174 Gauss and the specific magnetization ($\sigma$) values are form 12 to 35 emu / gm. These values are in good agreement with the values reported by Smit and Wijn [9], Viswanathan and V.R.K. Murthy [51] and Derek Craik et.al [52] for the similar types of ferrites.
Hysteresis loops of the quenched Ni_{0.51}Zn_{0.45}Cu_{0.04}Fe_{2.31}O_{4} system

Figure-3.5B
TABLE - 3.5B

Saturation induction, remanance induction, $B_r / B_s$ ratio and coercive field of quenched $\text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2.21}\text{O}_4$ system

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>Saturation induction $B_s$ (Gauss)</th>
<th>Remanance induction $B_r$ (Gauss)</th>
<th>$B_r / B_s$ Ratio</th>
<th>Coercive field $H_c$ Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>666</td>
<td>227</td>
<td>0.340</td>
<td>23.60</td>
</tr>
<tr>
<td>0.1</td>
<td>879</td>
<td>274</td>
<td>0.322</td>
<td>21.90</td>
</tr>
<tr>
<td>0.2</td>
<td>813</td>
<td>276</td>
<td>0.339</td>
<td>23.27</td>
</tr>
<tr>
<td>0.3</td>
<td>1264</td>
<td>421</td>
<td>0.333</td>
<td>23.27</td>
</tr>
<tr>
<td>0.4</td>
<td>964</td>
<td>338</td>
<td>0.350</td>
<td>22.21</td>
</tr>
<tr>
<td>0.5</td>
<td>2178</td>
<td>842</td>
<td>0.386</td>
<td>23.27</td>
</tr>
</tbody>
</table>
### TABLE - 3.6B

Saturation magnetization, magnetic moment, Y-K angle, exchange energy, molecular field coefficient and exchange field of quenched Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-2x}$O$_4$ system

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>Sat.magnetisation $M_s$ Gauss</th>
<th>$\sigma$ emu/gm</th>
<th>Magnetic moment $\eta_\text{B}$ $\mu_\text{B}$</th>
<th>Y-K angle Degrees</th>
<th>Exchange energy $J \times 10^{-16}$ ergs</th>
<th>Mol. Field coeff. $\lambda_w$</th>
<th>Exchange field $B_e \times 10^3$ Gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>53</td>
<td>12</td>
<td>0.508</td>
<td>2.285</td>
<td>38° 25’</td>
<td>2046.4</td>
<td>23704</td>
</tr>
<tr>
<td>0.1</td>
<td>70</td>
<td>19</td>
<td>0.807</td>
<td>2.186</td>
<td>34° 49’</td>
<td>786</td>
<td>9104</td>
</tr>
<tr>
<td>0.2</td>
<td>65</td>
<td>14</td>
<td>0.574</td>
<td>2.088</td>
<td>37° 49’</td>
<td>1480</td>
<td>17144</td>
</tr>
<tr>
<td>0.3</td>
<td>101</td>
<td>20</td>
<td>0.852</td>
<td>1.989</td>
<td>33° 52’</td>
<td>633.2</td>
<td>7336</td>
</tr>
<tr>
<td>0.4</td>
<td>77</td>
<td>16</td>
<td>0.662</td>
<td>1.891</td>
<td>36° 41’</td>
<td>968</td>
<td>11212</td>
</tr>
<tr>
<td>0.5</td>
<td>174</td>
<td>35</td>
<td>1.497</td>
<td>1.792</td>
<td>18° 31’</td>
<td>188.6</td>
<td>2184</td>
</tr>
</tbody>
</table>
The theoretical magnetic moment \((n_B)\) values are calculated as per the formula given in SECTION-A of this chapter. In the present studies, discrepancies between observed and theoretical \(n_B\) values are increased with the dopant concentration \((x)\). With the increase of \(x\), the increased discrepancy of \(n_B\) values suggest the dominant role of canted spin (non-collinear) on B sites existing, and Yafet-Kittel angles having strong influence on the \(M_S\) variation with \(x\).

The values of canting angle are also given in TABLE-3.6B. Thus the observed \(M_S\) variation has been explained on the basis of Yafet-Kittel angles existing on the B site spin besides two sublattice models. \(\text{Zn}^{2+}\) ions going into B sites decrease the magnetic moment of the B sublattice and also modify the exchange interactions of A and B sites. Hence, the net magnetization, \(M_S\) decreases. Thus these studies indicate the modification of A-B and B-B exchange interactions. However, the studies using Mossbauer spectrometer would give clear information about the magnetic structure of the ferrites to understand in terms of Neel’s two-sublattice model and canting spin on B sites.

Magnetic moment contribution and magnetic energy bear direct relation to \(n_B\) and Curie temperature. From Figures-3.4B and 3.6B it is noticed that \(T_c\) decreases with concentration where as magnetic moment increases. Increase of moment and the gap between theoretical and experimental values of moments are explained on the basis of canting between the spin of B site ions. The values of Y-K angel
Variation of Curie temperature with concentration for the quenched samples of Ni$_{0.5+x}$Zn$_{0.5}$Cu$_{0.5}$Fe$_{2-2x}$O$_6$ system.

![Curie temperature graph](image)

Variation of Magnetic moment with concentration for the quenched samples of Ni$_{0.5+x}$Zn$_{0.5}$Cu$_{0.5}$Fe$_{2-2x}$O$_6$ system.

![Magnetic moment graph](image)
determined are large which is attributed to the some other additional interactions. A reciprocal function of $T_c$ with moment for concentration variation envisages the magnetic energy reduction at the site of spinel ferrite. The magnetic energy change is caused by spin orbit interaction.

In order to check the validity of molecular field theory for the present system of ferrites, the values of exchange energy, molecular field coefficient and exchange field are obtained and reported in TABLE-3.6B. The value of exchange energy lies between $188.6 \times 10^{-16}$ and $2046.4 \times 10^{-16}$ ergs. The molecular field coefficient ranges between 2184 and 23704, and the exchange field varies from $378.92 \times 10^1$ to $1256.3 \times 10^3$ Gauss. The order of values of these parameters shows that the spinel ferrite prepared is ferrimagnetic in nature.

The TABLE-3.7B shows that the conductivity values of the present system lie between $4.855 \times 10^{-5}$ and $2.48 \times 10^{-3}$ at 150°C and at 10 kHz frequencies. The dielectric constant and $\tan \delta$ values, at 150°C and at 10 kHz, range from 54.30 to 159.26 and 0.724 to 29.42 respectively. This order is indicative of well-organized grain formation for the samples in the present work. The activation energy $E_a$, measured at 10 kHz frequency spreads from 0.173 to 0.482 eV. The site preference factor 'n' lie between 0.316 and 0.755. Similarly the grain boundary conductivity 'B' range form $7.013 \times 10^{-9}$ to $2.845 \times 10^{-6}$ s cm$^{-1}$. 
TABLE - 3.7B

Conductivity, dielectric constant, tan\(\delta\), activation energy, site preference factor and grain boundary conductivity of quenched \(\text{Ni}_{0.5+x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-x}\text{O}_4\) system

<table>
<thead>
<tr>
<th>Concentration (x)</th>
<th>Conductivity at 150(^{\circ})C (\sigma_{ac}) at 10 kHz (\text{s cm}^{-1})</th>
<th>Dielectric constant (\varepsilon')</th>
<th>(\tan\delta)</th>
<th>Activation energy (E_{ac}) eV at 10kHz</th>
<th>Site preference Factor (n)</th>
<th>Grain boundary Conductivity (B) (\text{s cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.683(\times)10(^{-4})</td>
<td>159.26</td>
<td>1.90</td>
<td>0.349</td>
<td>*0.544</td>
<td>1.798(\times)10(^{-7})</td>
</tr>
<tr>
<td>0.1</td>
<td>2.48(\times)10(^{-3})</td>
<td>112.92</td>
<td>29.42</td>
<td>0.173</td>
<td>0.346</td>
<td>2.845(\times)10(^{-6})</td>
</tr>
<tr>
<td>0.2</td>
<td>2.1873(\times)10(^{-5})</td>
<td>54.30</td>
<td>0.724</td>
<td>0.216</td>
<td>0.723</td>
<td>7.013(\times)10(^{-9})</td>
</tr>
<tr>
<td>0.3</td>
<td>2.891(\times)10(^{-5})</td>
<td>61.96</td>
<td>0.839</td>
<td>0.436</td>
<td>0.380</td>
<td>1.597(\times)10(^{-6})</td>
</tr>
<tr>
<td>0.4</td>
<td>3.8048(\times)10(^{-5})</td>
<td>79.76</td>
<td>0.857</td>
<td>0.194</td>
<td>0.755</td>
<td>4.029(\times)10(^{-9})</td>
</tr>
<tr>
<td>0.5</td>
<td>4.855(\times)10(^{-5})</td>
<td>65.51</td>
<td>1.332</td>
<td>0.482</td>
<td>0.316</td>
<td>1.584(\times)10(^{-6})</td>
</tr>
</tbody>
</table>
Variation of conductivity ($\sigma_{\infty}$) with frequency for the quenched samples of Ni$_{0.4+x}$Zn$_x$Cu$_{0.6}$Fe$_{2.2}$O$_4$ system.

Variation of dielectric constant with frequency for the quenched samples of Ni$_{0.4+x}$Zn$_x$Cu$_{0.6}$Fe$_{2.2}$O$_4$ system.

Figure-3.7B

Figure-3.8B
The frequency dependence of conductivity, dielectric constant and tanδ are presented in the Figures-3.7B, 3.8B and 3.9B respectively for the present spinel system. Figure-3.7B shows a slow change of the values of conductivity at low frequencies and a steady rising up at higher frequencies. Conversely Figure-3.8B shows a clear fall of values of permittivity with frequency. Figure-3.9B shows that the tanδ values rise up at lower frequencies. The trend of conductivity explains that the mixed ferrites have more electrons available for transport at higher frequencies. The variation of dielectric constant with frequency in these materials is explained to be due to the effective value of polarization caused by inter-ionic, molecular and grain boundary effects at low frequencies. The low values of dielectric constant at high frequencies are attributed to a less contribution of polarization due to exclusively inter ionic type.

Curves of tanδ in Figure-3.9B provide a picture of the absorption of energy carried by electromagnetic field when it propagates through the ferrite. The variation of tanδ with frequency reflects the subsiding nature subsequently leading to a gradual limping up effect of conduction at high frequencies. It may be explained so because of the release of charge carriers from the clutches of polarization at high frequency. The behavior of polarization with frequency can be explained using a principle lay down by Koop [56]. The presence of nickel ion on the octahedral sites favors the conduction mechanism as proposed by Van Uitert [58], which explains the predominant conduction mechanism of Ni-Zn-Cu system of present
Variation of $\tan \delta$ with frequency for the quenched samples of Ni$_{0.8+x}$Zn$_{0.2}$Cu$_x$Fe$_{2.2}$O$_4$ system.

![Graph showing variation of $\tan \delta$ with frequency](image)

Variation of conductivity ($\sigma$) with temperature for the quenched samples of Ni$_{0.8+x}$Zn$_{0.2}$Cu$_x$Fe$_{2.2}$O$_4$ system.

![Graph showing variation of conductivity with temperature](image)
The conduction mechanism for the samples of present study is due to hole transfer from Ni$^{3+}$ to Ni$^{2+}$ ions [59,60]. According to Mossbauer study carried out by Daniels and Rosencwaig [61], in samples sintered at higher temperature, Ni$^{3+}$ may also be present along with Ni$^{2+}$ and hopping of holes from Ni$^{3+}$ to Ni$^{2+}$ is also probable. So, in samples sintered at higher temperature, the conduction mechanism is enhanced and the conductivity of such samples is changed by an order of 10$^2$.

The curves of log($\sigma$) versus 1000/ T at 10 kHz for different concentration of Zn in the mixed ferrites are shown in the Figure-3.10B. It is seen from the Figure-3.10B that conductivity is a direct exponential function of temperature, which is the inherent property of a semi-conductor. It is explained on the basis of hopping of electrons between localized 3d bands of ions in these mixed ferrites. The slope of the lines in the Figure-3.10B should be a measure of activation energy($E_a$). A hopping activation energy of the order of 0.1 eV is associated with the drift mobility of electrons [62]. However, if the observed values of activation energies are $\approx$ 0.2 eV suggest [63,64] that the conduction mechanism observed is due to hopping of electron of the type Fe$^{2+} \Leftrightarrow$ Fe$^{3+}$. For ferrites possessing Cu and Ni in octahedral sites the value of activation energy has been reported to be $= 0.3797$ eV[64]. Thus there is a good agreement of activation energy of the spinel system of the present study.
The measured values of activation energy versus concentration (Figure-3.11B) would be able to throw more light on the changes in the position of the energy bands due to incorporation of Zn$^{2+}$ and Ni$^{2+}$. This range of values is suggestive of hopping and the present system behaves like a semiconductor with intermittent energy levels in the localized d bands of neighboring Fe ions of B site. Based on these results we conclude that the Fe-3d electrons are important in the conduction process.

The variations of 'B' and 'n' with respect to concentration (Figures-3.12B and 3.13B) show difference in the particle formation as the materials are prepared by ceramic techniques. Phenomenologically conductivity is explained to be dependent on the composition of ions making ferrites and the grain size of the samples. The explicit expression relating these physical quantities is

$$\sigma(\omega) = B \omega^n$$

where, 'B' is the parameter decided by the organization of grains, \(\omega\) is the frequency and 'n' is the parameter depending on the composition of the samples. It is inferred from the Figures-3.12B that the size of the grain increases with the concentration of Zn. But in Figure-3.13B the site preference factor 'n' indicates gradual decrease with respect to Zn concentration. Of the two parameters 'B' is found to change less sensitively with the variation of Zn. However deviation of 'B' and 'n' is attributed to the ceramic method of preparation of the system of spinel ferrites.
Variation of grain boundary conductivity (B) with concentration for the quenched samples of Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{1.2x}$O$_{4}$ system.

Variation of activation energy (ac) with concentration for the quenched samples of Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{1.2x}$O$_{4}$ system.
Variation of Site preference factor ($n$) with concentration for the quenched samples of Ni$_{0.6+1.5}$Zn$_{0.4}$Cu$_{0.6}$Fe$_{0.2}$O$_{4}$ system.
The ferrites prepared in the present study crystallize in the natural spinel form with the space group $Fd_{3m}$(Oh). On the basis of group theoretical calculations, spinel ferrites exhibit four IR active fundamentals ($T_d$) in the vibrational spectra of normal as well as inverse spinel ferrites. It has been reported that the first three IR bands are due to the tetrahedral ($T_d$) and octahedral ($O_h$) coordination compounds, while the fourth one is due to some type of lattice vibrations involving tetrahedral cation [57].

The infrared spectra of $\text{Ni}_{0.5-x}\text{Zn}_x\text{Cu}_{0.5}\text{Fe}_{2-2x}\text{O}_4$ mixed ferrite samples are shown in the Figure-3.14B. The absorption bands obtained in the present investigation are found to be in the range reported for similar type of ferrites[66,30]. The positions of the bands together with their shoulders are given in the TABLE-3.8B.

From Figure-3.14B, it can be seen that the IR spectra of the present system exhibit five principal bands. The principal band $v_1$ and $v_2$ shifts gradually towards low frequency site mainly the high-frequency band($v_1$) and second absorption band($v_2$) are found to be in the range 675-670 and 580-560 cm$^{-1}$ respectively. A comparison of FTIR charts at different frequencies provides information about decrease in transmittance and increase in broadness.

These features are explained on the basis of cation distribution in A and B sites of mixed Ni-Zn-Cu ferrites. Waldron [67] has attributed the occurrence of $v_1$ and $v_2$ bands to the intrinsic vibrations of the tetrahedral ($T_d$) and octahedral ($O_h$) coordination compounds. Both these high frequency bands have been attributed to
the intrinsic lattice vibrations of E-symmetry. The third absorption band \( v_4 \) is attributed to the \( \text{Cu}^{2+} - \text{O}^{2-} \) complexes at octahedral sites. The frequency of the \( (v_4 \text{and } v_5) \) bands depend on the mass of tetrahedral metal ion complexes[68] and hence it is attributed to the vibrations of ions at the tetrahedral site. The low frequency bands are attributed to vibrations of \( T_{2g} \)-symmetry.

The cation distribution of quenched Ni-Zn-Cu ferrites is:

\[
(Zn^{2+}\text{x,y Fe}^{3+}\text{1-x+y-z Cu}^{2+}\text{z})_A [\text{Ni}^{2+}\text{0.5-x Zn}^{2+}\text{x Cu}^{0.5-x} \text{Fe}^{4+}\text{1-x-z}]_B \text{O}^{2-} \ldots(3.10)
\]

Where \( x = 0.1, 0.2, 0.3, 0.4 \) and 0.5, \( y = 50 \% \) of \( x \) and \( z = 50 \% \) of \( y \)

As the content of Zn increases \( \text{Zn}^{2+} \) ions consistently replace \( \text{Fe}^{3+} \) ions from A to B site. At the same time \( \text{Ni}^{2+} \) ion on the octahedral site increases. This disturbs the order on the octahedral site with increase in zinc. The disordered systems give rise to broad bands in their spectrum[69]. TABLE-3.8B shows high frequency bands in the range 670-665 cm\(^{-1}\) which is found to decrease to a small extent with the increase of concentration. Consequently the changes in the high frequency band \( v_1 \) are correlatable to \( \text{Zn}^{2+} - \text{O}^{2-} \) bond stretching. The agreement of the value of frequency of \( v_1 \) band with the literature value is illustrated in TABLE-3.8A. On the other hand second absorption band \( v_2 \) (580-560 cm\(^{-1}\)) which may be attributed for \( \text{Zn}^{2+} - \text{O}^{2-} \) at octahedral sites as it clearly indicates an appreciable decrease of frequency with increase of Zn concentration. The sites A and B are explained to posses other ions also in this mixed ferrites along with Zn. But the shifting of the
FTIR Spectra of the quenched Ni$_{0.5+x}$ Zn Cu Fe$_{2-2x}$ O$_4$ system

Figure - 3.14 B
### TABLE - 3.8B

**Center frequency of the bands of FTIR spectra of quenched Ni$_{0.5+x}$Zn$_x$Cu$_{0.5}$Fe$_{2-x}$O$_4$ system**

<table>
<thead>
<tr>
<th>Concentration $x$</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$v_4$</th>
<th>$v_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>669.56</td>
<td>578.26</td>
<td>-</td>
<td>386.95</td>
<td>369.56</td>
</tr>
<tr>
<td>0.1</td>
<td>-</td>
<td>560.86</td>
<td>439.12</td>
<td>391.30</td>
<td>369.56</td>
</tr>
<tr>
<td>0.2</td>
<td>673.91</td>
<td>578.26</td>
<td>486.95</td>
<td>391.30</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>673.91</td>
<td>573.91</td>
<td>456.52</td>
<td>400.00</td>
<td>382.60</td>
</tr>
<tr>
<td>0.4</td>
<td>665.21</td>
<td>565.21</td>
<td>469.56</td>
<td>408.69</td>
<td>386.95</td>
</tr>
<tr>
<td>0.5</td>
<td>669.56</td>
<td>565.21</td>
<td>465.21</td>
<td>391.30</td>
<td>382.60</td>
</tr>
</tbody>
</table>
band frequency is explained to be due to Zn ion concentration affecting the
distribution of other ions. Based on these observations it is accounted for by that the
expansion of B sites is larger than the expansion of A site. It is in agreement with
the suggestion made out of X-ray diffraction studies of the present samples. Third
absorption band \( v_3 \) explains John-Teller effect due to the presence of \( \text{Cu}^{2+} \) ion in
octahedral sites. The presence of \( \text{Cu}^{2+} \) ions and the John-Teller splitting makes the
companions ions of B site to exist in their exited states. It means that \( \text{Ni}^{2+} \) and \( \text{Fe}^{2+} \)
ions in B sites may be shifted to \( \text{Ni}^{3+} \) and \( \text{Fe}^{3+} \) states. The explanation of this kind is
in accordance with the inference of conductivity measurements. Consequently these
results are in support of hopping of charge carriers from 3d bands of Ni and Fe ions.
It is seen from the TABLE-3.8B the frequencies of the bands \( v_4 \) and \( v_5 \) are found to
be shifted from their corresponding values of end member ferrites namely \( \text{NiFe}_2\text{O}_4 \),
\( \text{CuFe}_2\text{O}_4 \), \( \text{ZnFe}_2\text{O}_4 \) and \( \text{Fe}_3\text{O}_4 \)[TABLE-3.8A]. The larger difference in the frequency
of \( v_5 \) band found between the end members and the present spinel ferrite may be
attributed to the presence of many ion complexes and their masses in B site.

It is interesting to note that the John-Teller distortion due to \( \text{Cu}^{2+} \) ions and the
consequent change in the ionic states of \( \text{Ni}^{2+} \) and \( \text{Fe}^{2+} \) ions are the responsible
mechanism for the decrease of Curie temperature (Figure-3.4B) although the
moment values increased with concentration (Figure-3.6B).
REFERENCES


34) D. Ravinder, K. Vijaya kumar and B.S. Boyanov, Materials Letters 38, 22 (1999)
43) G. Blasse, Philips Research Report Supplement, 3, 13 (1964)

129
57) E.J.W. Verwey and J.H. De Boer, Rec. Trav Chim Phys, 55, 531 (1936)