Chapter 5

Quenched CuAl$_x$Fe$_{2-x}$O$_4$ system
5.1 Structural analysis, cation distribution and structural parameters determination.

(A) X-ray powder diffraction patterns analysis

The room temperature (300K) x-ray diffraction (XRD) patterns of the samples were obtained by x-ray powder diffractometry. Indexing and refinement of XRD patterns were carried out using powder-X software [1]. An attempt to fit the XRD spectra in a single phase fcc spinel structure (space group $O_h^7 Fd\bar{3}m$) or single phase tetragonal spinel with space group I4$_1$/amd, fail to large extent. Figure 5.1 shows x-ray powder diffraction patterns for un-substituted CuFe$_2$O$_4$ ($x = 0.0$) fitted assuming (a) fcc spinel structure, with lattice constant value, $a = 8.390$ Å (b) tetragonal structure, with lattice parameters values $a = b = 5.945$ Å, $c = 8.225$ Å and $c/a = 1.38$ by keeping 2$\theta$ error, 0.05.
Quenched CuAlFe$_2$O$_4$ system

5.3

Figure 5.1 X-ray powder diffraction patterns for copper ferrite (*indicates un-indexed diffraction peak).

Figure 5.2 X-ray powder diffraction pattern at room temperature for CuFe$_2$O$_4$. 
For the sake of comparison, x-ray diffraction pattern of tetragonal structured (space group I4₁/ amd) and c/a ~ 1.449 [2] CuFe₂O₄, is shown in Figure 5.2. In spite of the fact that a quench cooling process usually leads to the cubic structure of CuFe₂O₄ [3], from structural analysis results based on the powder diffraction data we confirmed that the rapidly quenched samples of the system CuAlₓFe₂₋ₓO₄ (x = 0.0, 0.2, 0.4 and 0.6) posses a tetragonally distorted spinel structure with non-standard face-centered space group F4₁/ddm. Figure 5.3 displays Rietveld fitted (using general scattering analysis software (GSAS) [4]) XRD patterns for the selected compositions with x = 0.2, 0.6. One of the most important Rietveld error indices is that of χ² [5].
The $\chi^2$ values (1.3 - 1.6) obtained in the present analysis suggest good refinement of the data. The samples showed a dominant cubic phase with a minor tetragonal component. The lattice parameters obtained from the above mentioned refinements are given in Table 5.1, from which it is seen that the lattice parameters ($a = b$ and $c$) decrease with increasing $\text{Al}^{3+}$ - concentration ($x$) in the system. The linear decrease in lattice constants is due to the replacement of larger $\text{Fe}^{3+}$ - ions with ionic radius of 0.645 Å by smaller $\text{Al}^{3+}$ - ions with ionic radius of 0.535 Å in the system.

The axial ratio ($c/a$) for $\text{CuAl}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0.0$) is found to be 1.037 and it increases to 1.050 for $x = 0.6$ composition, suggests enhancement of tetragonal distortion with increasing Al- content ($x$). The JCPDS card gives $c/a = 1.06$ for $\text{CuFe}_2\text{O}_4$ while Naik et al. [6] have reported values ranging between 1.01 and 1.06. According to other authors [7], crystal cell parameters may vary from $a = b=$
8.20 to 8.30 Å and c = 8.544 to 8.692 Å, but axial ratio (c/a) remains almost constant (1.03 – 1.05). The axial ratio ((c/a) = 1.037) found for CuFe$_2$O$_4$ (Table 5.1) lies in the expected range. The c/a ratio can be changed via decreasing the copper concentration, or alternatively, by heat treatment temperature and cooling rate [8]. The structure of pure CuFe$_2$O$_4$(x = 0.0) and Al$^{3+}$ substituted CuFe$_2$O$_4$ (x = 0.2 - 0.6) is considered as that of a tetragonally deformed spinel stretched along the ⟨011⟩ direction. According to theorem of Jahn-Teller (JT), molecules with orbitally degenerate electronic ground state are unstable in the symmetric configuration. The molecule will always find at least one vibrational coordinate along which it can distort to split the degeneracy and lower its energy. The transition metal ions having one, two, four, six, seven and nine 3d-electrons will have orbitally degenerate ground state, but only for the Cr$^{2+}$, Mn$^{3+}$,Fe$^{4+}$ (3d$^4$) and Cu$^{2+}$ (3d$^9$) configurations the degeneracy occurs in the strongly anti bonding orbits and the distortion are large unless the long-range elastic coupling between the sites clearly favours another [9]. The commonly observed distortions are of the prolate tetragonal type i.e. octahedraon is elongated so that four ligands lie close to the cation while two are further removed as shown in Figure 5.4.
Figure 5.4 Tetragonal distortion of MO₆ octahedron and the 3d orbital energy splitting by the octahedron (oₜ) and the tetrahedral site symmetries for Cu²⁺ (d⁹) ion under D₄h symmetry

Goodenough and Loeb [10] interpreted the migration of Cu-ions to the A-sites in terms of their square-bond formation although Cu-ions are more stable in the B-sites of the spinel lattice. The ground state of Cu²⁺ ion in the octahedral crystal field is an orbital doublet 2E₉ (t⁶₂e³), and so subject to a Jahn-Teller effect which removes the degeneracy of the ground state. Thus, Cu²⁺- ions at the octahedral (B-) sites tend to suffer from a tetragonal distortion [11]. According to Kim et al. [11], for an octahedral Cu²⁺ compound (C₄X₆) with a d⁶e₃ configuration, a strong Jahn-Teller distortion (Oₜ – D₄h) is expected due to its 2E₉ ground state. With dγ electron expressed in terms of d₉² and dₓ²–y² there are only two possibilities, (d₉²)²(dₓ²–y²)¹ and (d₉²)¹(dₓ²–y²)². In case of (d₉²)¹(dₓ²–y²)² configuration, a distortion to a compressed tetragonal structure (c/a < 1) is expected. On the other hand, in case of (d₉²)²(dₓ²–y²)¹, configuration, four ligand ions in the xy-plane
are attracted by the central ions on the z-axis, resulting in a distortion of the octahedraon to an elongated tetragonal structure \((c/a > 1)\). However, the elongated distroion rather than the compressed one used to be observed [12].

A precise knowledge of the distribution of cations among the available crystallographic sites of the spinel lattice is essential to understand the various physical properties of ferrites. There is good contrast in the atomic scattering factor of \(\text{Al}^{3+}\) to that of \(\text{Fe}^{3+}\) and \(\text{Cu}^{2+}\), but the scattering factor of \(\text{Cu}^{2+}\) is close to that of \(\text{Fe}^{3+}\) [13]. Thus, it is not possible to obtain the distribution of \(\text{Fe}^{3+}\) and \(\text{Cu}^{2+}\) between the A- and B-sites using XRD technique. The x-ray scattering factor of \(\text{Al}^{3+}\) is significantly low compared to those of the other cations. So, the distribution of \(\text{Al}^{3+}\) between the two types of sites can be obtained with good accuracy from x-ray analysis. We have used values of axial ratio \((c/a)\) to determine the occupancy of \(\text{Cu}^{2+}\) ions at the B-sites.

In 1951, the lattice parameters and the cation ordering parameter, \(\lambda\), for \(\text{CuFe}_2\text{O}_4\) as a function of temperature was studied by Bertaut et al. [14]. The parameter \(\lambda\) is the fraction of octahedral interstices occupied by JT ions \((\text{Cu}^{2+})\). The correlation between the axial ratio \((c/a)\) and the concentration of \(\text{Cu}^{2+}\) ions at the B-sites is well established.

Quantitative correlation between Bertaut’s observed axial ratio \((c/a)\) and \(\lambda\) produces the relation: \((\lambda - 0.26) = 3[(c-a)/a]\) for \(\lambda \geq 0.26\). The factor \((\lambda - 0.26)\) is a measure of the stress induced by square-bond formation, while the strain is given by: \((c-a)/a\) (Table 5.1). This equation expresses a linear stress-strain relationship (Hooke’s law). We have used here \(c/a\) ratio to determine the concentration of
Cu\(^{2+}\) ions ( = \(2\lambda\)) on the B-sites using the simple relation: \(\lambda = 3(c/a) - 2.74\).

Once the concentration of Cu\(^{2+}\) ions on the B-sites and corresponding concentration of Cu\(^{2+}\) ions on the A-sites, have been fixed, the distribution of Al\(^{3+}\) and Fe\(^{3+}\) ions have been determine from x-ray diffraction line intensity calculations using the formula suggested by Buerger [15]. The details are given in the Chapter 4.

**Illustrative calculations for the fraction of Cu\(^{2+}\) ions on the B-sites, Stress-Strain determination**

\[\begin{align*}
x & = 0.4, \; c/a = 1.055 \; (\text{Cu}_{0.15}\text{Fe}_{0.67}\text{Al}_{0.18})[\text{Cu}_{0.85}\text{Fe}_{0.93}\text{Al}_{0.22}] \\
\text{From the relation: } \lambda & = 0.26 = 3[(c-a)/a] \\
\lambda & = 3[(c/a)-1]+0.26 \\
& = 3(c/a) - 3 +0.26 \\
\lambda & = 3(c/a) - 2.74 = 3(1.055) - 2.74 = 0.425 \\
\text{Concentration of JT Cu}^{2+} \text{- ions on the B-sites} & = 2\lambda = 2(0.425) = 0.850 \\
\text{Stress: } \lambda & = 0.26 = 0.425 - 0.26 = 0.165 \\
\text{Included by square band formation} \\
\text{Strain: } (c/a) - 1 & = 1.055 - 1 = 0.055
\end{align*}\]

The final cation distributions, thus, determined for different compositions are given by:

\[\begin{align*}
x & = 0.0 \; (\text{Cu}_{0.26}\text{Fe}_{0.74})^A[\text{Cu}_{0.74}\text{Fe}_{1.26}]^B\text{O}_4 \\
x & = 0.2 \; (\text{Cu}_{0.20}\text{Fe}_{0.71}\text{Al}_{0.09})^A[\text{Cu}_{0.80}\text{Fe}_{1.09}\text{Al}_{0.11}]^B\text{O}_4 \\
x & = 0.4 \; (\text{Cu}_{0.15}\text{Fe}_{0.67}\text{Al}_{0.18})^A[\text{Cu}_{0.85}\text{Fe}_{0.93}\text{Al}_{0.22}]^B\text{O}_4 \\
x & = 0.6 \; (\text{Cu}_{0.10}\text{Fe}_{0.62}\text{Al}_{0.28})^A[\text{Cu}_{0.90}\text{Fe}_{0.78}\text{Al}_{0.32}]^B\text{O}_4
\end{align*}\]

Thus, the observed increase in tetragonal distortion \((c/a)\) (Table 5.1) is mainly due to the increasing concentration of in JT Cu\(^{2+}\) -ions on the B-sites.
Earlier, it has been reported that the critical number of the B-site Cu\(^{2+}\) ions per spinel formula unit for a cooperative Jahn-Teller distortion to tetragonal symmetry (\(c/a > 1\)) in copper ferrospinel is \(\sim 0.8\) [8]. The B-sites Cu\(^{2+}\) ions per formula unit in the range 0.74 – 0.90 is consistent with the critical number \(\sim 0.8\).

**Table 5.1 Lattice parameters. axial ratio, stress and strain for CuAl\(_x\)Fe\(_{2-x}\)O\(_4\) system.**

<table>
<thead>
<tr>
<th>Al(^{3+})-content (x)</th>
<th>Lattice constants ±0.002Å</th>
<th>c/a</th>
<th>(\lambda)</th>
<th>Stress</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.288 8.595</td>
<td>1.037</td>
<td>0.370</td>
<td>0.110</td>
<td>0.037</td>
</tr>
<tr>
<td>0.2</td>
<td>8.202 8.588</td>
<td>1.047</td>
<td>0.400</td>
<td>0.140</td>
<td>0.047</td>
</tr>
<tr>
<td>0.4</td>
<td>8.135 8.582</td>
<td>1.055</td>
<td>0.425</td>
<td>0.165</td>
<td>0.055</td>
</tr>
<tr>
<td>0.6</td>
<td>8.067 8.575</td>
<td>1.063</td>
<td>0.450</td>
<td>0.190</td>
<td>0.063</td>
</tr>
</tbody>
</table>

**Structural Parameters**

The compositions of the system under investigation CuAl\(_x\)Fe\(_{2-x}\)O\(_4\) posses small deviation from the cubic symmetry, the formula for the various structural parameters determination for fcc structured materials are thus, applicable to this system also with small uncertainty. However, our aim is to study the variation of different structural parameters with Al\(^{3+}\)-substitution and relative change in the magnitude. The structural parameters are calculated using the formulae presented in Chapter 4, are summarized in Tables 5.2 – 5.5.
Table 5.2. Lattice constants, molecular weight (M), x-ray density (\(\rho_x\)), bulk density (\(\rho\)), pore fraction (f) and porosity (P) for quenched Cu-Fe-Al-O system.

<table>
<thead>
<tr>
<th>Al-content (x)</th>
<th>(a^*) (Å) ±0.002Å</th>
<th>M (kg x 10^{-3})</th>
<th>(\rho_x) (kg/m^3 x 10^3)</th>
<th>(\rho) (kg/m^3)</th>
<th>f</th>
<th>P (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>8.389</td>
<td>239.23</td>
<td>5.385</td>
<td>4.820</td>
<td>0.105</td>
<td>10.49</td>
</tr>
<tr>
<td>0.2</td>
<td>8.329</td>
<td>233.46</td>
<td>5.369</td>
<td>4.691</td>
<td>0.126</td>
<td>12.62</td>
</tr>
<tr>
<td>0.4</td>
<td>8.281</td>
<td>227.69</td>
<td>5.328</td>
<td>4.442</td>
<td>0.166</td>
<td>16.63</td>
</tr>
<tr>
<td>0.6</td>
<td>8.233</td>
<td>221.92</td>
<td>5.285</td>
<td>4.638</td>
<td>0.122</td>
<td>12.24</td>
</tr>
</tbody>
</table>

\(a^*=(a^2c)^{1/3}\)

Table 5.3 Ionic radius (r), lattice constant (a) and oxygen positional parameter (u) for Cu-Fe-Al-O system.

<table>
<thead>
<tr>
<th>Al^{3+}-content (x)</th>
<th>(r_A) (Å)</th>
<th>(r_B) (Å)</th>
<th>(a_{th}) (Å)</th>
<th>(u_{\frac{3}{4}m}) (1/4,1/4,1/4)</th>
<th>(u_{\frac{3}{8}m}) (3/8, 3/8, 3/8)</th>
<th>Eq.(9)</th>
<th>Eq.(10)</th>
<th>Eq.(11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.6671</td>
<td>0.6765</td>
<td>8.3833</td>
<td>0.2621</td>
<td>0.3871</td>
<td>0.3868</td>
<td>0.3872</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.6521</td>
<td>0.6730</td>
<td>8.3509</td>
<td>0.2615</td>
<td>0.3865</td>
<td>0.3867</td>
<td>0.3867</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>0.6380</td>
<td>0.6690</td>
<td>8.3186</td>
<td>0.2611</td>
<td>0.3861</td>
<td>0.3865</td>
<td>0.3863</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>0.6227</td>
<td>0.6657</td>
<td>8.2861</td>
<td>0.2605</td>
<td>0.3855</td>
<td>0.3862</td>
<td>0.3858</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4 Edge length and bond length for Cu-Fe-Al-O system

<table>
<thead>
<tr>
<th>Al^{3+}-content (x)</th>
<th>(d_{AE}) (Å)</th>
<th>(d_{BE}) (Å)</th>
<th>(d_{BE_u}) (Å)</th>
<th>(d_{AL}) (Å)</th>
<th>(d_{BL}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>3.2525</td>
<td>2.6795</td>
<td>2.9729</td>
<td>1.9917</td>
<td>2.0011</td>
</tr>
<tr>
<td>0.2</td>
<td>3.2168</td>
<td>2.6727</td>
<td>2.9510</td>
<td>1.9698</td>
<td>1.9907</td>
</tr>
<tr>
<td>0.4</td>
<td>3.1872</td>
<td>2.6683</td>
<td>2.9335</td>
<td>1.9517</td>
<td>1.9828</td>
</tr>
<tr>
<td>0.6</td>
<td>3.1560</td>
<td>2.6656</td>
<td>2.9160</td>
<td>1.9326</td>
<td>1.9754</td>
</tr>
</tbody>
</table>
Table 5.5 Interionic distances (b, c, d, e, f and p, q, r, s) and bond angles (θ) for Cu-Fe-Al-O system

<table>
<thead>
<tr>
<th>Al&lt;sup&gt;3+&lt;/sup&gt;-content (x)</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>2.9659</td>
<td>2.9447</td>
<td>2.9277</td>
<td>2.9108</td>
</tr>
<tr>
<td>c</td>
<td>3.4779</td>
<td>3.4530</td>
<td>3.4331</td>
<td>3.4132</td>
</tr>
<tr>
<td>d</td>
<td>3.6324</td>
<td>3.6065</td>
<td>3.5857</td>
<td>3.5649</td>
</tr>
<tr>
<td>e</td>
<td>5.4487</td>
<td>5.4097</td>
<td>5.3785</td>
<td>5.3473</td>
</tr>
<tr>
<td>f</td>
<td>5.1370</td>
<td>5.1003</td>
<td>5.0709</td>
<td>5.0415</td>
</tr>
<tr>
<td>p</td>
<td>1.9960</td>
<td>1.9861</td>
<td>1.9785</td>
<td>1.9716</td>
</tr>
<tr>
<td>q</td>
<td>1.9917</td>
<td>1.9698</td>
<td>1.9517</td>
<td>1.9326</td>
</tr>
<tr>
<td>r</td>
<td>3.8139</td>
<td>3.7720</td>
<td>3.7374</td>
<td>3.7007</td>
</tr>
<tr>
<td>s</td>
<td>3.6909</td>
<td>3.6620</td>
<td>3.6386</td>
<td>3.6149</td>
</tr>
<tr>
<td>θ₁</td>
<td>121.42</td>
<td>121.59</td>
<td>121.74</td>
<td>121.91</td>
</tr>
<tr>
<td>θ₂</td>
<td>137.13</td>
<td>137.76</td>
<td>138.32</td>
<td>138.99</td>
</tr>
<tr>
<td>θ₃</td>
<td>95.97</td>
<td>95.69</td>
<td>95.44</td>
<td>95.15</td>
</tr>
<tr>
<td>θ₄</td>
<td>126.59</td>
<td>126.53</td>
<td>126.48</td>
<td>126.41</td>
</tr>
<tr>
<td>θ₅</td>
<td>69.51</td>
<td>69.92</td>
<td>70.29</td>
<td>70.72</td>
</tr>
</tbody>
</table>

(Distances in Å and angles in degrees)

The variation of various structural parameters with Al<sup>3+</sup>- substitution (x) is similar to that for slow cooled system, and thus can be explain based on the similar arguments. The observed small difference in the magnitude of parameters is mainly due to change in cation distribution as result of different thermal history of the compositions.

5.2 Microstructural Characterization

SEM analysis

Scanning electron microscopy (SEM) was employed to study the grain morphology of the samples. SEM microphotographs of fractured surface of pellets for all the compositions are shown in Figure 5.5. It is seen that grain
morphology (grain size, uniformity, homogeneity) is greatly influenced by Al\(^{3+}\) substitution for Fe\(^{3+}\) in the system.

![SEM photographs](image)

**Figure 5.5** The SEM photographs of the fractured surface for the polycrystalline Cu-Al ferrite, CuAl\(_x\)Fe\(_{2-x}\)O\(_4\); x = 0.0, 0.2, 0.4 and 0.6.

We have observed well define grain structure for x = 0.0 and 0.2 compositions. With small addition of Al\(^{3+}\) - ions (x = 0.2), average grain size increases, inter granular voids are found to decrease. The spinel ferrite compositions with x = 0.4 and 0.6 show diffused grain structure. Thus, no attempt has been made to determine the grain size, but, certainly average grain size is observed to decrease with increase in Al\(^{3+}\)- content(x) for x > 0.2. The grain size for x = 0.0 composition is found to vary between 20-25 µm while it is found to vary between 25 - 30 µm for x = 0.2 composition. The observed increase in grain
size with Al\(^{3+}\) - substitution (x = 0.2) is attributed to larger solid solubility of Al\(^{3+}\) ion in the ferrite structure that enhances the grain growth.

The decrease in grain size for x > 0.2 compositions can be explained on the similar line of argument as for slow cooled system [16]. The observed difference in grain morphology for slow cooled and quenched systems of copper-ferri-aluminates may be due to different heat treatment employed.

We have observed exaggerated grain growth for x = 0.0 and 0.2 compositions. When the grain growth rate is very high, pores may be left behind by rapidly moving grain boundaries, resulting in pores that are trapped inside the grains. The intragranular porosity is practically impossible to eliminate, leading to poor magnetic and mechanical properties. Samples with giant grain and included pores owing to exaggerated grain growth still have good magnetic and mechanical properties then those with normally grown grains provided the distances between pores were the same [17]. We feel that in the present system same mechanism is responsible for excellent magnetic properties of x = 0.0 and 0.2 compositions (Table 5.6).

5.3 Magnetic properties of quenched CuAl\(_x\)Fe\(_{2-x}\)O\(_4\) system

(A) M-H loop characteristics and dc magnetization studies

In a unit cell of spinel lattice, eight of the 64 available tetrahedrally oxygen-coordinated A-sites and 16 out of the 32 octahedrally coordinated B-sites are occupied by metal ions or by 1 tetrahedral and 2 octahedral for each formula unit. The type, valence and distribution of these metal ions ultimately control the
physical properties in general and magnetic, electronic properties in particular, of the system.

In the ideal inverse spinel configuration the eight divalent metal ions occupy the B-sites, while the 16 trivalent Fe ions are equally distributed among the A- and B-sites. The magnetic moments of the ions in both A- and B-sublattices are ferromagnetically ordered, while the magnetizations of the these two sublattices are antiparallel with respect to each other.

If CuFe$_2$O$_4$ possesses an ideal inverse spinel structure: (Fe$^{3+}_{1.0}$)$_A$[Cu$^{2+}_{1.0}$Fe$^{3+}_{1.0}$]$^B$O$_{2-4}^-$, its net magnetization can be attributed to the Cu$^{2+}$ ion, amounting to 8µ$_B$ per unit cell or 1µ$_B$ per formula unit. Here, it is assumed that Cu$^{2+}$ ion contribute 1 Bohr magneton.

The replacement of one A-site Fe$^{3+}$ ion by one B-site Cu$^{2+}$ ion: (Cu$^{2+}_{0.125}$Fe$^{3+}_{0.875}$)$_A$[Cu$^{2+}_{0.875}$Fe$^{3+}_{1.25}$]$^B$O$_{2-4}^-$, results in a net-magnetic moment of 16µ$_B$ per unit cell (≅ 2µ$_B$ / formula unit), assuming each Fe$^{3+}$ ion to contribute 5µ$_B$. Thus, the migration of a single Cu$^{2+}$ ion from the B- to the A-site doubles the magnetic moment. It has been shown that the magnetic moment of CuFe$_2$O$_4$ cannot be increased much beyond 2µ$_B$ per formula unit, since the activation energy for the process increases with the presence of on Cu$^{2+}$ at the tetrahedral site, making the transfer of further copper ions increasing unlikely [18].

Recently, enhanced magnetization (3µ$_B$ at 5K) has been reported for nano particles and thin films of copper ferrite [18]. The role of anisotropy ion, Fe$^{2+}$, in enhancing and tailoring the magnetization CuFe$_2$O$_4$ nanoparticles synthesized from a citrate precursor has been discussed by Thapa et al [18]. The observed
large magnetic moment (80 Am²/kg) for nanosized Cu₀.₂₅Co₀.₂₅Zn₀.₂₅Fe₂O₄ has been explained in terms of the enhancement in the B-B interaction because of the distortion in the B-sites due to the presence of the Jahn-Teller cation, Cu²⁺, at this site [19]. It is interesting to note that a high magnetization has also been recently observed in sputter deposited Cu-ferrite grown in a reducing atmosphere [20], sputtering in an oxygen environment followed by subsequent annealing leads to reduced magnetization. On the other hand, 42% increase over the bulk equilibrium value of magnetization has been reported for cation-disordered-enhanced magnetization in pulsed-laser-deposited CuFe₂O₄ films by Harris et al [21]. They have found that Cu²⁺ ion population on the A-sites is systematically increased compared to the bulk value of 0.15 to ~0.45. As a result, the room temperature saturation magnetization is increased as much as 42%. They speculate that lattice strain from both a mismatch in lattice parameter and thermal expansion coefficient between the film and substrate may be responsible for enhancing cation-disorder effect.

![Magnetic field dependence of magnetization at 10K; main panel, inset at 300K, for quenched Cu-Fe-Al-O samples.](image)
In Figure 5.6, we show the M-H loops recorded at 10K, while hysteresis loops recorded at 300K are shown in the inset for $x = 0.0, 0.2, 0.4$ and 0.6 compositions. In Table 5.6, the values of saturation magnetization, $\sigma_s$ (emu/g), and the magneton number, $n_B$, (saturation magnetization per formula unit in Bohr magneton, $\mu_B$) at 10K and 300K are given. Figure 5.6 displays that there is high field slope to magnetization curve for all the compositions which suggest strong evidence for a canted spin structure, and canting angle varies with applied magnetic field. The observed features may be thought of arising from non-collinear spin arrangement. The high field slope has been established arising due to the high magnetic anisotropy also [22]. Since, all the compositions under study may have very low concentration of magnetic anisotropy ion ($Fe^{2+}$), this fact does not applicable to the system. The negligible coercivity for different compositions also suggests that these are low anisotropic compounds [23]. From the observed magnetic moment it is clear that the samples show ferrimagnetism behaviour, which decreases with increasing $Al^{3+}$-content ($x$) in the system.

The applicability of Neel's two sub-lattice model of ferrimagnetism has been tested for all the samples of the series $CuAl_xFe_{2-x}O_4$. Accordingly, Neel's magnetic moment, $n_B^N$, per formula unit in $\mu_B$ is expressed as:

$$n_B^N = M_B(x) - M_A(x)$$

where, $M_B$ and $M_A$ are the B- and A-sublattice magnetic moments in $\mu_B$. The $n_B^N$ ($\mu_B$) values for $CuAl_xFe_{2-x}O_4$ were calculated using cation distribution and ionic magnetic moment of $Fe^{3+}$, $Cu^{2+}$ and $Al^{3+}$ with their respective values 5 $\mu_B$, 1 $\mu_B$ and 0 $\mu_B$. The experimental values of magnetic moment ($n_B$) at 10 K are found
lower than the magnetic moment calculated from the Neel’s model \( n^N_B \). This suggests significant canting of the B-site moments or structure to be non-collinear.

The magneton number, \( n_B \), is related to canting angle, \( \theta_c \) by:

\[
n_B(x) = M_B(x) \cdot \theta_c - M_A(x)
\]

The experimental values of canting angle, \( \theta_c \), obtained from the above equation, using measured \( n_B \) values (Table 5.6) are listed in Table 5.6.

For a chemically disordered system such as CuAl\(_x\)Fe\(_{2-x}\)O\(_4\) it is quite possible that the canting is not uniform but instead is locally dependent upon the statistical distribution of non-magnetic neighbouring ions. Therefore, the increase in Al\(^{3+}\)-substitution leads to the localized non-collinearity of the ferrimagnetic phase. In this region effective moments are created with ferrimagnetic structure by local canting around the magnetic imperfections introduced by aluminium substitution. Therefore, the disagreement between the observed and calculated \( n_B \) values can be explained in terms of a random canting of spins (RCS) model proposed by Rosencewaig [24] should be used. According to this model, the B-sites magnetic ions can be considered to be canted with an average canting \( \theta_C \) due to non-magnetic Al\(^{3+}\)-substitution which, in the average nearest neighbour approximation is estimated to be:

\[
\cos \theta_{RCS} = \left( \frac{M_A}{M_B} \right) \frac{J_{AB}}{J_{BB}}
\]

Here, \( J_{AB} \) and \( J_{BB} \) are exchange integrals. The magnetic coupling, \( J_{AB}/J_{BB} \), remains nearly constant for \( x = 0.0 - 0.2 \) and thereafter it is getting weakened for
x > 0.2 indicates change in the magnetic structure. Furthermore, \( J_{AB}/J_{BB} \) is found to be greater than unity for all the compositions and decreases with increase in \( \text{Al}^{3+}\)-content (x). These suggest \( J_{AB} > J_{BB} \) and strength of \( J_{AB} \) interaction and relative strength of \( J_{AB}/J_{BB} \) interaction decrease with magnetic dilution by non-magnetic \( \text{Al}^{3+}\)-substitution in the system.

**Table 5.6 Magnetic parameters for quenched \( \text{CuAl}_x\text{Fe}_{2-x}\text{O}_4 \).**

<table>
<thead>
<tr>
<th>( x )</th>
<th>( M_B ) (( \mu_B ))</th>
<th>( M_A ) (( \mu_B ))</th>
<th>( n_B^n ) (emu/g) (10K)</th>
<th>( \sigma_s ) (emu/g) (10K)</th>
<th>( \phi = \cos^{-1} \frac{n_B + M_A}{M_B} )</th>
<th>( J_{AB}/J_{BB} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>7.04</td>
<td>3.96</td>
<td>3.08</td>
<td>71.34</td>
<td>3.06</td>
<td>4.32°</td>
</tr>
<tr>
<td>0.2</td>
<td>6.25</td>
<td>3.75</td>
<td>2.50</td>
<td>57.04</td>
<td>2.38</td>
<td>11.25°</td>
</tr>
<tr>
<td>0.4</td>
<td>5.50</td>
<td>3.50</td>
<td>2.00</td>
<td>39.34</td>
<td>1.60</td>
<td>21.99°</td>
</tr>
<tr>
<td>0.6</td>
<td>4.80</td>
<td>3.22</td>
<td>1.58</td>
<td>29.13</td>
<td>1.16</td>
<td>24.15°</td>
</tr>
</tbody>
</table>

**DC magnetization study**

Magnetic measurements (field-cooled (FC) and zero-field-cooled (ZFC) magnetization) were performed using the physical property measurement system (PPMS, quantum design). The ZFC magnetization was recorded by first cooling the sample from 325 to 4K in zero magnetic fields, then applying the magnetic field and warming the sample up to 325K in the presence of the magnetic field (10mTesla) and recording the magnetic moment (emu/g) during the warming cycle. Field cooled patterns were obtained by first cooling the sample from 325K down to 4K in the external magnetic field and then warming it up to 325K and recording the magnetic moment.

Data on temperature dependence of magnetization (M-T) recorded in zero-field-cooled (ZFC) and field cooled (FC) modes in and external magnetic
field of 10mTesla for ‘virgin’ (CuFe₂O₄) and Al³⁺-substituted (x = 0.2, 0.4 and 0.6) samples are shown in Figure 5.7.

![Graph showing temperature dependence of FC and ZFC modes with marked temperatures and Al³⁺ substitution](image)

Figure 5.7 Temperature dependence of M_{FC} and M_{ZFC} of Cu-Fe-Al-O system. Inset shows the expanded version of the ZFC mode near the magnetic transition.
Table 5.7 Magnetic transition temperature (T) for quenched CuAl$_x$Fe$_{2-x}$O$_4$ system.

<table>
<thead>
<tr>
<th>Al$^{3+}$-content (x)</th>
<th>$T_{irr.}$ (Kelvin)</th>
<th>$T_S$ (Kelvin)</th>
<th>$T_{comp.}$ (Kelvin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>46</td>
<td>46</td>
<td>-</td>
</tr>
<tr>
<td>0.2</td>
<td>55</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>0.4</td>
<td>210</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>0.6</td>
<td>220</td>
<td>65</td>
<td>22</td>
</tr>
</tbody>
</table>

The following features can be seen from these figures.

(1) All the compositions have shown divergence between FC and ZFC magnetization (i.e. thermo-magnetic irreversibility (TMI)).

This is the characteristic feature of all magnetic systems exhibiting magnetic hysteresis behaviour. The FC – ZFC curves bifurcate at about 46K, 55K, 210K and 220K for $x = 0.0$, 0.2 0.4 and 0.6 compositions respectively. This temperature is referred to as the temperature of irreversibility above with $[(M_{FC}/M_{ZFC}) - 1]$ is less than 1%. This suggests that the system is chemically and magnetically homogeneous.

(2) The observed small difference between the FC and ZFC magnetization, flat response of FC magnetization as a function of temperature confirm that all the ferrite compositions studied are low anisotropic materials [25].

(3) We have observed a very broad hump in magnetization curve for $x = 0.4$ and 0.6 compositions in vicinity to temperature of irreversibility ($T_{irr.}$).

This suggests that coercivity for these compositions is much less than the applied magnetic field strength and materials under study are low anisotropy compounds.
(4) For x = 0.6 composition ZFC magnetization decreases slowly with decrease in temperature, shows hump centred around 60K, then decreases rapidly, passes through a zero value of magnetization (M = 0) at the compensation temperature (T = 22K) (Inset figure). Below this temperature, the magnetization is negative, down to the lowest temperature (4K).

This is due to copper ion moment, with a net effect antiparallel to that of the Fe$^{3+}$ ions with different temperature dependence giving rise to a compensation effect.

(5) We have observed that for all the four compositions, the ZFC curve bifurcate from the FC curve below the temperature, $T_{irr.}$, suddenly falls below $T_S$ and finally saturates at $T_F$.

Such anomalies at $T_S$ and $T_F$ on the ZFC curves are due to coexistence and interplay between the ferrimagnetic long rang ordering and short range ordering in the system [26].

(B) Low field ac susceptibility measurements

Plots of relative low field (0.5 Oe) ac susceptibility, $\chi_T/\chi_{RT}$, ($RT =$ room temperature) against temperature (T) for x = 0.0, 0.2, 0.4 and 0.6 compositions are shown in Figure 5.8 which exhibit normal ferrimagnetic behavior.
The Neel temperatures ($T_N$) determined from ac susceptibility measurements are listed in Table 5.8. It is evident from Table 5.8 that there is a fast decrease in Neel temperature for small addition of aluminum which is due to the decreasing $\text{Fe}^{3+}$-$\text{O}^2$-$\text{Fe}^{3+}$ super-exchange linkages resulting from replacement of $\text{Fe}^{3+}$ by $\text{Al}^{3+}$ in the spinel lattice. In other words the decrease in $T_N$ with increasing $\text{Al}^{3+}$ - content ($x$) suggests reduction in ferrimagnetic ordering and weakening of magnetic coupling.

The Neel temperatures estimated theoretically for the samples with $x = 0.2, 0.4$ and $0.6$ using the cation distributions and statistical models based on the modified molecular field theory [27] as described in Chapter 4 (Section 4.4), are in good agreement with the measured values and are given in Table 5.8. The observed difference between experimental and theoretically calculated Neel temperature values is due to the random variation of number of super-exchange
interactions per magnetic ion because of the random distribution of Al$^{3+}$- ions at the A- and B-sites.

**Illustrative calculations for \( n(x) \) and \( T_N(x) \) determination**

\[
x = 0.4 \quad (\text{Cu}_{0.15} \text{Fe}_{0.67} \text{Al}_{0.18})^A[\text{Cu}_{0.85} \text{Fe}_{0.93} \text{Al}_{0.22}]^B \text{O}_4
\]

\[
T_N(x) = \frac{n(x)}{n(x=0)} \cdot T_N(x=0)
\]

\[
n(x=0.4) = \frac{24}{1+5(2-0.4)} \left[ \frac{(0.85+0.93)^2}{2} \frac{(0.15+0.67)}{1} \right]
\]

\[
= 2.67 \times [0.89 \times 0.82]
\]

\[
n(x=0.4) = 1.95
\]

\[
n(x=0.0) = 2.18
\]

\[
T_N(x=0.4) = (1.95 / 2.18) \times 650 \text{ K} = 581 \text{ K}
\]

**Table 5.8 Neel temperature (\( T_N \)) for the quenched CuAl\(_x\)Fe\(_{2-x}\)O\(_4\) system.**

<table>
<thead>
<tr>
<th>( \text{Al}^{3+} ) content (x)</th>
<th>n(x)</th>
<th>Neel temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( T_N(K) \pm 2K )</td>
</tr>
<tr>
<td>0.0</td>
<td>2.18</td>
<td>650</td>
</tr>
<tr>
<td>0.2</td>
<td>2.06</td>
<td>620</td>
</tr>
<tr>
<td>0.4</td>
<td>1.95</td>
<td>580</td>
</tr>
<tr>
<td>0.6</td>
<td>1.83</td>
<td>515</td>
</tr>
</tbody>
</table>

All the samples are showing a decrease in normalized susceptibility nearly to zero at Neel temperature indicating that impurity phases are not present in the samples and there is single phase formation. The fact is also evidenced by XRD analysis (section 5.1).

The transition from ferrimagnetic to paramagnetic state is sharp (Figure 5.8), that suggests good quality of structural and microstructural properties as well as presence of magnetic long range order in the samples as evident by large magnetic moment (Table 5.6).
Quenched CuAl\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4} system

A high temperature asymmetric peak corresponds to ferrimagnetic to paramagnetic transition temperature is result of the two competing agencies, an ordering of spins within the domains and domain wall pinning mechanism [28].

The Neel temperatures for the quenched system are much lower than the slow cooled system of same compositions. Replacement of magnetic Fe\textsuperscript{3+} (5\(\mu\)B) with non-magnetic Al\textsuperscript{3+} (0\(\mu\)B) and weak magnetic Cu\textsuperscript{2+} (1\(\mu\)B) on the B-sites, as evident by cation distributions, decreases [Fe\textsuperscript{3+} - O\textsuperscript{2-} - Fe\textsuperscript{3+}] linkages and therefore transition temperature \(T_N\) is decreased. This agrees with previous studies for super-exchange interactions for various oxides [29], which indicated that: Neel temperature or Curie temperature depends primarily upon the number of [Fe\textsuperscript{3+} - O\textsuperscript{2-} - Fe\textsuperscript{3+}] linkages. The Neel temperature, \(T_N = 650\) K (Table 5.8) for un-substituted ferrite (CuFe\textsubscript{2}O\textsubscript{4}) is in excellent agreement to the Neel temperature reported for tetragonal structured (CuFe\textsubscript{2}O\textsubscript{4}) [29].

5.4 Variation of dc resistivity (\(\rho_{dc}\)) as a function of Al\textsuperscript{3+} - content (x) and temperature (T).

The dc resistivity values have been corrected for the pore fraction (f) using the relations [f]:
\[
\rho_{dc} = \rho_p [1+f(1+f^{2/3})^{-1}].
\]
Here, \(\rho_p\) is measured values of dc resistivity. It is important to note that this equation seems to hold good for \(f < 0.4\). In the present studies \(f\) is much less than 0.4, (Table 5.2) one can expect successful application of the above equation.

The compositional dependence of dc resistivity at 403K, is shown in Figure 5.9. It is found that \(\rho_{dc}\) (403K) increases with increase in Al\textsuperscript{3+} - content (x) in the system: CuAl\textsubscript{x}Fe\textsubscript{2-x}O\textsubscript{4}. 

5.25
Figure 5.9 Compositional dependence of electrical dc resistivity ($\rho_{dc}$) at 403K for quenched CuAl$_x$Fe$_{2-x}$O$_4$ system.

It is known that non-magnetic cations such as Al$^{3+}$ do not participate in the conduction process. Thus, the substitution of Al$^{3+}$ for magnetic Fe$^{3+}$ (5$\mu_B$) limits the degree of Fe$^{2+}$ - Fe$^{3+}$ (or electron exchange) conduction that takes place at the octahedral sites of the spinel lattice.

If the hole exchange between Cu$^{1+}$ - Cu$^{2+}$ at the tetrahedral sites of the spinel lattice is responsible for the electrical conduction, then, substitution of Al$^{3+}$ for Fe$^{3+}$, replace magnetic Cu$^{2+}$ ions (1$\mu_B$) from the A-sites to the B-sites as evident from cation distributions. Thus, observed increase in $\rho_{dc}$ value is rather expected. The high values of resistivity of the order of $\sim 10^3$ - $10^4$ $\Omega$-cm near room temperature (300K), suggesting that the ferrite compositions under investigation are good insulators of electricity at 300K.

Phase transition studies on CuFe$_2$O$_4$ have been reported extensively in literature [30]. At low temperatures, it exhibits a body centered
tetragonal (I41/amd) crystal structure with unit cell lattice parameters \( a = 8.25 \, \text{Å} \) and \( c = 8.65 \, \text{Å} \). Above a phase transition temperature about 663-673K, the crystal structure is face centered cubic (Fd\( \bar{3} \)m) with \( a = 8.40 \, \text{Å} \). The variation in phase transition temperature was either studied as a function of quenching temperature [31] or annealing conditions [32] and was correlated with the variation in cation distributions or oxygen vacancies.

But for \( \text{CuFe}_2\text{O}_4 \), prepared by ceramic techniques, a lower transition temperature is found. For example, associated anomalies in the temperature dependence of the magnetization [33], the permeability [34], and the specific heat [35] have all been reported near 633K.

Physical properties show variation at phase transformation temperature [30]. Murthy et al [31] have carried out two probe resistivity measurements on \( \text{CuFe}_2\text{O}_4 \) and observed a well defined deviation from the linear decrease in resistivity between 615K and 693K followed by a decrease in resistivity at the phase transition temperature of 693K. For the present samples, we determined the dc resistance at different temperatures. The variations in dc electrical resistivity, \( \rho_{dc} \), with respect to temperature for the pure (\( \text{CuFe}_2\text{O}_4 \) \( x = 0.0 \)) and \( \text{Al}^{3+} \)-substituted \( \text{CuFe}_2\text{O}_4 \) (\( x = 0.2, 0.4 \) and 0.6) are compared in Figure 5.10.
The important features observed from this figure are summarized as: 

1. All the compositions show typical semiconducting behaviour, i.e. resistivity decreases with increasing in temperature. 
2. The Arrhenius plots for the electrical resistivity for the different ferrite compositions show non-linear variation with temperature. This may be due to the variation in axial ratio (c/a) with temperature [36]. We feel that non-linear variation dc resistivity as a function of temperature is characteristic feature of tetragonal structured copper ferrite based system. 
3. We have observed change in the slope in vicinity to temperature that strongly supports the influence of magnetic upon the conduction process [37].
Conclusions

We have investigated the effect of Al$^{3+}$- substitution on structural, microstructural, magnetic and electrical properties of quenched CuFe$_2$O$_4$ system with general chemical formula: CuAl$_x$Fe$_{2-x}$O$_4$ ($x = 0.0, 0.2, 0.4$ and $0.6$). It has found that

1. The ferrite compositions posses tetragonally distorted spinel structure, due to rapid thermal quenching induced large B-site occupancy of Jahn-teller ion (Cu$^{2+}$) in system.

2. The axial ratio ($c/a$) can be used to determine the concentration of Cu$^{2+}$ ion on the octahedral site of the spinel lattice, stress, strain produced due to square bond formation.

3. The magnetic measurements suggest that the ferrite compositions are low anisotropy compounds, the negative magnetization for $x = 0.6$ composition is due to the copper ion moment with a net effect antiparallel to that of the Fe$^{3+}$- ions with different temperature dependence giving rise to a compensation effect.

4. The anomalies at $T_S$ and $T_F$ on the ZFC curves are due to coexistence and interplay between the ferrimagnetic long range ordering and short range ordering in the system.

5. The non-linear thermal dependence of dc resistivity is due to the variation in axial ratio ($c/a$) with temperature.

6. Finally it is concluded that the thermal history and heat treatments play an important role in controlling the materials properties.
References


[17] Alex Goldman, Modern ferrite technology, 2002, 2nd Ed, Pittsburgh, PA, USA.


