Chapter 3

Structural, Magnetic and Electrical Properties of CoIn$_x$Fe$_{2-x}$O$_4$ ($x$=0, 0.15) Nanoparticles

In this chapter, synthesis and characterization of CoIn$_x$Fe$_{2-x}$O$_4$ ($x$=0, 0.15) nanoparticles is reported. These nanoparticles were prepared by sol-gel citrate route and various experimental techniques were used to investigate the structural, magnetic properties at room temperature, resistivity as a function of temperature and ac conductivity, dielectric as a function of frequency and temperature.
3.1 Introduction:

There are numerous reports on the pristine and chemically doped CFO system, ranging from single crystals [1-3] to thin films [4-9] and nanoparticles [10-18]. The physical properties of these materials are influenced by many factors such as processing temperature and history of heat treatment, compositions, cation distributions, microstructures such as grain size, porosity, presence of defects etc [19-22]. A clean separation of these sets of parameter is not possible because the processing temperature or history of heat treatment affect both the chemical and microstructural aspects of ferrites. Substitution of non-magnetic or magnetic metals for Fe in CFO has been proposed in order to tailor the magnetic, electrical and magnetomechanical properties of such materials. This is considered to be due to the differences in cation site occupancy preferences of the elements within the spinel crystal structure; Mn$^{3+}$ and Cr$^{3+}$ prefer the octahedral (B) sites, whereas Ga$^{3+}$ and Zn$^{2+}$ prefers the tetrahedral (A) sites [19]. The enhancement in electrical properties CFO with the substitution of Zn was reported by Reddy et. al. [23] and Bayoumi et. al. [24]. Kriebel et. al. [25] and Paulsen et. al. [26] reported that magnetic and magnetomechanical properties can be tailored by varying the concentration of Mn. Song et. al. [27] reported on the variation of the Curie temperature $T_C$ and hysteresis properties with the variation of gallium content in CFO. Sometimes, limitations on the desirable properties may be more easily overcome by control of microstructure than by choice of chemistry. Gyergyek et. al. [28] studied the influence of synthesis method on structural and magnetic properties of CFO nanoparticle having uniform particle size around 8 nm, synthesized through three different methods: simple co-precipitation from aqueous solutions and a co-precipitation in an environment of microemulsions which are low temperature methods (50$^\circ$C) and a thermal decomposition of organo-metallic complexes at elevated temperature of 290$^\circ$C. Wang et. al. [29] investigated the effects of heat treatment on two samples one slowly cooled and other quenched after annealing at 1000$^\circ$C and exhibited very different magnetic behaviors. The quenched sample had a much higher saturation magnetization with a relatively low coercivity. Finite size effects on the electrical properties of sol–gel synthesized CFO powders have been studied by George et. al. [10] and found higher permittivity and conductivity for smaller grains.
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In this chapter, pure and 15% Indium doped CFO were prepared by sol-gel citrate route. Structural, magnetic and electrical properties were investigated.

3.2 Experimental details:

The stoichiometric amount of nitrates of Fe, Co, In and citric acid were dissolved into deionized water to form mixed solution and heated at 80°C under constant stirring on the magnetic stirrer to allow evaporation until it is converted into gel, containing all cations homogeneously mixed together at atomic level. These gels were heated at 100°C for 24 h in an oven to form loose fluffy powder. The powder was grinded for half an hour and sintered at 600°C for 6 hrs and again grinded for half an hour. To confirm the formation of phase, XRD and Raman spectroscopy were carried out. SEM equipped with EDS was employed to examine the microstructural features and chemical composition of the samples. Magnetic hysteresis loops were measured at room temperature using a VSM with maximum field of 22 kOe. The DC electrical resistivities were measured by two probe method in the temperature range 250K–400K. Dielectric properties were studied as a function of frequency and temperature in the range 75KHz–1MHz and 80K–400 K, respectively. For these measurements, the samples were pelletized and silver was coated on both the faces making parallel plate capacitor geometry with ferrite material as the dielectric medium.

3.3 Results and discussions:

3.3.1 Structural properties:

The structural studies of undoped and 15% In doped CFO were performed by XRD and the results are shown in figure 3.1. The XRD patterns reveal that all the peaks correspond to the characteristic peaks of cubic spinel lattice of CoFe$_2$O$_4$ (JCPDS File No. 22 – 1086) indicating that the samples have a single – phase spinel structure and no unreacted constituents or impurity phases were present in the samples. The average grain size of both the samples was determined from XRD peak broadening using Scherrer’s formula [31]

$$d = \frac{\alpha \lambda}{\beta \cos \theta}$$

(3.1)
where $d$ is the average crystallite size, $\beta$ is the full width at half maximum (FWHM) of the diffraction line of most intense peak measured in radians, $\lambda$ is the X-ray wavelength of the Cu $K_{\alpha} = 1.54 \ \text{Å}$, and $\theta$ is the Bragg's angle. The value of X-ray density was determined according to the relation [32]

$$D_x = \frac{8M}{N\alpha^2} \quad (3.2)$$

where $N$ is the Avogadro’s number and $M$ is the molecular weight of the sample. The apparent density ($D_m$) was determined from mass and the bulk volume of the sample.

Figure 3.1: XRD pattern of CoIn$_x$Fe$_{2-x}$O$_4$ ($x=0, 0.15$) with the inset showing broadening and shifting of (311) peak.

The percentage of porosity ($P$) of the samples was calculated from $D_x$ and $D_m$ values using the expression

$$P = \left(1 - \frac{D_m}{D_x}\right) \times 100 \quad (3.3)$$
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Assuming all the particles to be spherical, the specific surface area was calculated from the relation [10]

\[
S = \frac{6000}{d\rho}
\]  

(3.4)

where \(d\) is the diameter of the crystallite in nm and \(\rho\) is the density of the particle. The calculated X-ray density, apparent density, porosity and surface specific area are given in table 3.1. The average grain size decreases whereas the lattice parameter expands which may be due to larger ionic radii In\(^{3+}\) (0.78 Å) replaces the smaller Fe\(^{3+}\) (0.69 Å) ions.

Table 3.1: Structural parameters of the In doped CFO nanoparticles.

<table>
<thead>
<tr>
<th>Sample CoIn(<em>x)Fe(</em>{2-x})O(_4)</th>
<th>Grain Size (nm)</th>
<th>Lattice parameter (Å)</th>
<th>Theoretical Density (D_t) (gm/cm(^3))</th>
<th>Apparent Density (D_m) (gm/cm(^3))</th>
<th>Porosity (%)</th>
<th>Specific Surface Area (m(^2)gm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td>44.43</td>
<td>8.37</td>
<td>5.32</td>
<td>3.02</td>
<td>43</td>
<td>44.65</td>
</tr>
<tr>
<td>x=0.15</td>
<td>22.37</td>
<td>8.39</td>
<td>5.47</td>
<td>2.84</td>
<td>47</td>
<td>99.44</td>
</tr>
</tbody>
</table>

Table 3.2: Composition of the In doped CFO nanoparticles measured from EDS.

<table>
<thead>
<tr>
<th>Sample CoIn(<em>x)Fe(</em>{2-x})O(_4)</th>
<th>Composition measured from EDS</th>
<th>Co (at %)</th>
<th>Fe (at %)</th>
<th>In (at %)</th>
<th>Fe/Co</th>
<th>In/Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.0</td>
<td></td>
<td>15.10</td>
<td>30.27</td>
<td>-</td>
<td>2</td>
<td>-</td>
</tr>
<tr>
<td>x=0.15</td>
<td></td>
<td>14.44</td>
<td>23.71</td>
<td>4.6</td>
<td>1.81</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The SEM images and EDS spectra of the samples are shown in figure 3.2. The SEM images clearly show that the samples are in the nano-regime and the EDS spectra confirmed the presence of all constituent elements with nearly expected elemental composition as given in table 3.2.
Figure 3.2: SEM micrograph and EDS spectra of Coln$_x$Fe$_{2-x}$O$_4$ (a & b) x=0 and (c & d) x=0.15.

For confirmation of phase purity of pure and doped nanoparticles, Raman spectra were also recorded at room temperature as presented in figure 3.3. Ferrites crystallizes in cubic spinel structures belonging to the space group $Fd3m$ ($O^7_b$ No. 227). Group theory predicts following phonon modes for the spinel structure

$$A_{1g}(R) + E_g(R) + T_{1g} + 3T_{2g}(R) + 2A_{2u} + 2E_u + 4T_{1u} (IR) + 2T_{2u}$$  \hspace{1cm} (3.5)

Out of these phonon modes five are Raman active ($A_{1g} + E_g + 3T_{2g}$) and four infrared active modes ($4T_{1u}$). All the five Raman active modes were observed at ambient conditions. The modes above 600 cm$^{-1}$ correspond to the modes of tetrahedral group
(A – sites) that reflects the local lattice effect in the tetrahedral sublattice and those below 600 cm\(^{-1}\) represent the modes of octahedral group (B – sites) and reflects the local lattice effect of the octahedral sublattice. This is consistent with the previously reported studies [33, 34] therefore it is confirmed that the samples are single phase cubic spinel structure. The modes exhibit a red shift with broadening of FWHMs in the doped sample which may be due to the strain developed in the lattice and the decrease of grain size [34, 35]. The doping of larger ionic radius In\(^{3+}\) ions (0.78Å) forces the lattice to expand which develop a strain in the lattice. The development of strain in the lattice is also seen in the XRD spectrum shown in figure 3.1 as a shift of the diffraction peaks and expansion of lattice constant given in Table 3.1. Chandramohan et. al. [34] reported that red shift with broadening of peak are due to the decrease of grain size. In nano – crystals, unlike the crystalline materials, due to lack of long range order, not only the phonons with q=0 but also those with q > 0 take part in the scattering process leading to broadening and shift of peak position in the Raman Spectra.

![Figure 3.3: Raman Spectra of ColnFe\(_{2-x}\)O\(_4\) (x=0, 0.15).](image-url)
3.3.2 Magnetic Properties:

Magnetization measurements were performed at the room temperature and the results are shown in figure 3.4. The value of coercivity ($H_C$), remnant magnetization ($M_r$), saturation magnetization ($M_s$) are listed in Table 3.3. In ferrites, magnetic properties are strongly influenced by the site preference of cations in the spinel lattice [20]. There are three kinds of exchange interactions between the magnetic ions lying on two different sublattices of ferrite i.e. AA interaction, BB interaction and AB interactions. AB interaction predominates over AA or BB interactions [36]. The net magnetic moment is the difference in moments of B and A sublattices i.e. $M = M_B - M_A$. Magnetic properties of ferrite depend not only on the chemical composition which determines the intrinsic properties, but also on various extrinsic factors such as grain sizes, porosity and density [36]. In the literature [21, 37] it is reported that In$^{3+}$ ions prefer to occupy A sites at lower concentrations (upto x = 0.3). If In$^{3+}$ ions occupy A – sites and replace Fe$^{3+}$ ions, the A sublattice magnetization will decrease and the net magnetization will therefore increase. In the present case the magnetization decreases and coercivity increases in the In$^{3+}$ doped sample which are contrary to the previous observation of Indium doping as reported by Shirsath et. al. [21] and Lakshman et. al. [37]. Therefore, the observed result may be attributed to the decrease of grain size and increase of porosity. The coercivity of fine particles has striking properties on their size. As the grain size decreases, the coercivity increases, goes through a maximum then decreases and become zero for a very small size known as superparamagnetism. The change in coercivity is due to the change of the multidomain nature to single domain. In the multidomain region the size dependence of coercivity is expressed as [38]

$$H_c = a + \frac{b}{D}$$

(3.6)

where $a$ and $b$ are constants and $D$ is the diameter of the particle. A porous sample also implies lesser number of magnetic moments in the specified volume which results in the decrease of magnetization. The saturation magnetization is related to $H_c$ through Brown’s relation [20]

$$H_c = \frac{2K_1}{\mu_0 M_s}$$

(3.7)
According to this relation $H_c$ is inversely proportional to $M_s$ which is consistent with our experimental results. The increase in coercivity in the doped sample shows that hard ferrite nature retains with In substitution.

**Table 3.3: Electric and Magnetic Properties of the synthesize nanoparticles.**

<table>
<thead>
<tr>
<th>Sample CoIn$<em>x$Fe$</em>{2-x}$O$_4$</th>
<th>Electric Properties</th>
<th>Magnetic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Resistance (Ω)</td>
<td>Activation energy (eV)</td>
</tr>
<tr>
<td>$x=0.0$</td>
<td>$8 \times 10^6$</td>
<td>0.19</td>
</tr>
<tr>
<td>$x=0.15$</td>
<td>$3 \times 10^7$</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Figure 3.4: Hysteresis loops of CoIn$_x$Fe$_{2-x}$O$_4$ ($x=0.0$, 0.15) at room temperature.

### 3.3.3 Electrical Properties:

Temperature variation of DC electrical resistivity ($\rho$) has been studied and figure 3.5 shows the results measured in the temperature range of 250K – 400K. It is observed that the resistivity decreases with increasing temperature which reflects the semiconductor behavior. The decrease in resistivity with temperature is due to the
increase in the drift mobility of the charge carriers which are thermally activated upon increasing the temperature. In ferrites, the electrons are localized with little probability of overlapping of wavefunctions of ions located at adjacent sites. However, in the presence of lattice vibrations, the ions come close enough and the transfer of electrons from one ion to another occurs with high probability [39]. Hence the mobility is enhanced with temperature. The activation energies are obtained by fitting the DC resistivity data with the Arrhenius relation

$$\rho = \rho_0 \exp \left( \frac{E_a}{kT} \right)$$

(3.8)

where $E_a$ is the activation energy and $k$ is the Boltzmann constant. The activation energy of the samples is given in table 3.3. It is also observed that DC resistivity increases in the $\text{In}^{3+}$ ions doped sample which may be due to the decrease of grain sizes. Smaller grains imply a larger number of insulating grain boundaries which hindered the motion of charge carriers. Smaller grains also reduce the grain to grain surface contact area and therefore reduce the motion of charge carriers hence the resistivity increases.

![Graph](image)

Figure 3.5: The variation of log $\rho$ with temperature of $\text{CoIn}_x\text{Fe}_{2-x}\text{O}_4$ ($x = 0, 0.15$).
The electric conductivity of a dielectric material is a summation of two terms [40]

\[
\sigma = \sigma_0(T) + \sigma(\omega, T) \tag{3.9}
\]

The first term \(\sigma_0(T)\) is frequency independent or dc conductivity which is related to the drifting of charge carriers and follows an Arrhenius relation. The second term \(\sigma(\omega, T)\) is frequency dependent function and is related to the dielectric relaxation caused by the localized electric charge carriers which obeys the empirical power law [41]

\[
\sigma(\omega) = A\omega^n \tag{3.10}
\]

where the constants A and n are both temperature and composition dependent parameters; n is dimensionless whereas A has units of conductivity and \(\omega\) is angular frequency. Figure 3.6 shows the variation of ac conductivity with frequency at room temperature. Initially, ac conductivity increases with the increase of frequency but at higher frequency conductivity tend to decrease with further increase of frequency.
Figure 3.7: The variation of $\sigma_{dc}$ with temperature at selected frequencies of CoIn$_x$Fe$_{2-x}$O$_4$ (a) $x=0$ and (b) $x=0.15$.

The conduction mechanism in ferrites is explained on the basis of hopping of electron between Fe$^{2+}$ and Fe$^{3+}$ ions at octahedral sites. As the frequency of applied field increases the hopping frequency of electron enhances which cause an increase in the mobility of charge carriers. Thus we observe a gradual increase in conductivity with frequency. But at higher frequencies, the hopping of electron cannot follow the applied field frequency and it lags behind it which results to the decrease of
conductivity. The increase in conductivity does not mean the increase in charge concentration but increase in mobility of charge carriers. The relaxation frequency in ac conductivity is observed to decrease with the doping of In$^{3+}$ ions. Since the doped sample has smaller grain size and higher grain boundaries present in them, the conductive grain volume which become more active at higher frequencies is lesser than the undoped sample. Thus conductivity begins to decrease at lower frequency.

Variations of ac conductivity with temperature at selected frequencies for the pure and doped sample are shown in figure 3.7 (a) and (b) respectively. The ac conductivity increases with the increase of temperature for all frequencies. However such an increase is more rapid at higher frequencies. This increase in the conductivity with the increase in temperature is due to the increase in drift mobility of the charge carrier thereby enhancing the charge hopping.

![Graph showing conductivity variation](image)

Figure 3.8: The variation of $\varepsilon'$ with frequency of Coln$_x$Fe$_{2-x}$O$_4$ (x = 0, 0.15) at room temperature.

The dielectric properties were investigated as a function of frequency and temperature. The dielectric constant is represented by
\varepsilon = \varepsilon' - j\varepsilon'' \quad (3.11)

where \(\varepsilon'\) is the real part which represents the stored energy and \(\varepsilon''\) is the imaginary part which represents the dissipated energy. The dielectric properties of ferrite materials are influenced by many factors like method of preparation, structural homogeneity, cation distribution, grain size, density, porosity, history of sintering etc [20, 21]. Figure 3.8 illustrates the frequency dependence of real part of dielectric constant at room temperature. The dielectric constant decreases with increase in frequency which is common behavior in ferrites. The observed dispersion is qualitatively due to interfacial polarization in accordance with the Maxwell – Wagner model [42]. In this model, the dielectric materials are assumed to be composed of conducting grains separated by poorly conducting grain boundaries. The mechanism of polarization in polycrystalline ferrite is reported to be the hopping of electrons between ions of the same element in different oxidation states at B – site [43, 44]. When a field is applied the electron flow in the direction of the field within the grain through hopping and pile up at the grain boundaries to produce polarization. If the frequency of the field increases, the electrons cannot keep up with the field and the alteration of their direction lags behind that of the field. As a result, the probability of electrons reaching the grain boundaries decreases. This decreases the polarization and hence the dielectric constant. Iwauchi [45] pointed out that there is a strong correlation exists between the conduction mechanism and the dielectric behavior of the ferrites, i.e., the mechanism of polarization in ferrites is a similar process to that of conduction. Jonker [44] studied the electrical conduction of a series of ferrites \(Co_{1-x}Fe_{2+x}O_4\) and observed that the conduction in ferrites is the result of electron hopping between \(Fe^{3+} - Fe^{2+}\) ions and hole hopping between \(Co^{2+} - Co^{3+}\) ions. As the field frequency increases the electronic exchange between \(Fe^{3+} - Fe^{2+}\) and \(Co^{2+} - Co^{3+}\) cannot follow the rapid field variation and it lags more and more behind the field therefore the polarization decreases. The dielectric constant in the present study is of the order of \(10^2\) which is an order of magnitude higher as compared to that reported by Sivakumar et. al. [11] and George et. al. [10] at the same temperature and frequency. Introduction of small amount of \(In^{3+}\) ions (\(x = 0.15\)) results in the increases of dielectric constant which can be attributed to the decrease in grain size. Decrease in grain size results in larger number of both grains and grain boundaries. These grain
boundaries act as a scattering center. Also, smaller grains provide large surface polarization resulting from large surface area of individual grains. As discuss above that In$^{3+}$ ion replace Fe$^{3+}$ ion in the A – sites, it is reasonable to assume that the number of Fe$^{3+}$ - Fe$^{2+}$ and Co$^{2+}$ - Co$^{3+}$ ions retains in the B – sites. Therefore, microstructures play a dominant role in determining the dielectric property.

The dielectric loss $(\tan \delta)$ in ferrites is a measure of lag in the polarization with respect to the alternating field. Variations of dielectric loss as a function of frequency are shown in figure 3.9. The behavior of dielectric loss is normally reflected in the resistivity measurement; with the high-resistivity materials exhibit low dielectric losses and vice – versa.

![Figure 3.9: The variation of $\tan \delta$ with frequency of CoIn$_x$Fe$_{2-x}$O$_4$ ($x = 0.15$) at room temperature.](image)

The temperature dependence of the dielectric constant at selected frequencies is shown in figure 3.10. At low temperature both the dielectric constant and dielectric loss are independent of temperature whereas at higher temperature there is an increase with temperature for all frequencies. This is due to the fact that at higher temperatures extra thermal energy supplied by the temperature boost the mobility of charge carrier
hence their rate of hopping is enhanced while the thermal energy supplied at lower temperature are not enough for the increase of mobility of charge carriers. The dielectric polarization therefore increases at higher temperature causing an increase in dielectric constant and dielectric loss with temperature.

It is observed that the temperature dependence of the dielectric constant is different at various frequencies, the increase being more rapid at lower frequencies than at higher frequencies. Dielectric constant is a result of the contribution of four

![Graph](image)

Figure 3.10: The variation of $\varepsilon'$ with temperature at selected frequencies of CoIn$_{2}$Fe$_{1-x}$O$_{4}$ (a) $x=0$ and (b) $x=0.15$. 
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Figure 3.11: The variation of $\tan \delta$ with temperature at selected frequencies of $\text{CoIn}_{x}\text{Fe}_{2-x}\text{O}_{4}$ (a) $x=0$ and (b) $x=0.15$.

types of polarizations namely interfacial, dipolar, ionic and electronic [46]. The rapid increase in dielectric constant at lower frequencies is due to interfacial and dipolar polarization. These types of polarizations show strong dependence on frequency and temperature. At high frequencies contribution to dielectric constant is due to electronic and ionic polarization only, which are independent of temperature. Hence, the effect of temperature on high frequency dielectric constants is of little significant resulting in low dispersion of dielectric constant. This explains the observed
temperature dependence of dielectric constant at various frequencies. The temperature dependence of dielectric loss at selected frequencies is illustrated in figure 11. It is observed that the behavior is similar to that of the dielectric constant which can also be explain in similar way as in the case of dielectric constant.

3.4 Conclusion:

Nanoparticles of CFO and 15% In CFO were prepared by citrate – gel method. The substitution of In ions at Fe sites results in significant changes in the physical properties of cobalt ferrite. It is observed that the average grain size decreases whereas lattice constant, porosity and specific surface area increase in the In doped sample. Magnetization measurements show that saturation magnetization decreases whereas there is an increase in the coercivity which is attributed to the decrease of grain size and increase of porosity. The results of dc conductivity, dielectric spectroscopy study have shown that there is improvement in the electrical properties. The high resistivity and low dielectric loss led the material suitable for power application at higher frequencies. The present investigation clearly point out that the physical properties of cobalt ferrite depends on the extrinsic factors like grain size, microstructure etc.
References:


