CHAPTER 6

RESULTS AND DISCUSSION ON COBALT FERRITE NANO-PARTICLES: EFFECT OF ANNEALING TEMPERATURE

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Abstract

Cobalt ferrite nanoparticles with average particle size of the order of 32 to 48 nm were prepared by sol-gel auto-combustion technique using high purity metal nitrates and L-Ascorbic acid as a fuel. X-ray diffraction, scanning electron microscopy and infra-red spectroscopy techniques were employed to characterize the prepared cobalt ferrite nanoparticles. The crystallite size, lattice constant, X-ray density, porosity etc structural parameters were evaluated and their behavior as a function of annealing temperature is reported in this work. The magnetic properties were studied at room temperature using M-H hysteresis plots and effect of annealing temperature is presented. The effect of annealing temperature on electrical and dielectric properties is discussed in this work.
6.1: INTRODUCTION:
Nanocrystalline materials are of great importance in the recent years from the research and technological application point of view due to their interesting physical and chemical properties which are different than that of bulk counter parts [1, 2]. Nanocrystalline materials exhibit unique crystallo-graphical structure e.g., high surface area and high volume fraction of atoms at interfacial regions. The resulting properties namely super-paramagnetism, super-plasticity, catalatic activity etc are distinctly different from those of their micrometer sized counterparts [3]. The physical and chemical properties are greatly influenced by the synthesis root and various synthesis parameters.

Metal oxide nanoparticles in particular spinel ferrites are of current focus because of their interesting, unique optical, electronic, mechanical, structural and magnetic properties and have large number of promising technological applications in high density recording media, ferrofluids, drug delivery, magnetic refrigerators, high frequency devices [4,5] etc.

In the family of spinel ferrite, cobalt ferrite (CoFe$_2$O$_4$) with inverse spinel structure has been widely studied [6, 7] as they display attractive magnetic properties as well as electrical and other properties making them useful in wide range of applications.
Cobalt ferrite possess high Curie temperature, high magnetocrystalline unisotropy, high permeability, high coercivity, high saturation magnetization, good magnetic mechanical properties, excellent chemical stability etc and therefore is subject of interest of researchers. The compositional and micro-structural properties are sensitive to the preparation method used for their synthesis. The magnetic nanoparticles of cobalt ferrite cab be obtained by variety of methods including sol-gel [8], hydrothermal [9], co-precipitation [10], microemulsion [11] etc. The magnetic nanoparticles with a higher surface area to volume ratio provide higher sensitivity, better targeting and improvement of the colloidal stability of the nanostructures [12].

Sol-gel auto-combustion synthesis method is an easy and convenient method for obtaining nanoparticles of spinel ferrite. Sol-gel technique offer enhanced controlled over homogeneity, elemental composition and powder morphology. Like synthesis methods, synthesis parameters and synthesis conditions also strongly influences the physical and chemical properties of spinel ferrite nanoparticles. In order to obtain materials with desired properties, it is necessary to obtain high density powder with small and uniform grain size and controlled stoichiometry. This can be achieved by using sol-gel synthesis and annealing the obtained as prepared powder at suitable temperature.
In the literature, there are reports on the effect of fuel additives [13],
chelating agent [14], and aging time [15] on structural,
microstructural and magnetic properties of cobalt ferrite
nanoparticles. The influence of heat treatment on cobalt ferrite
ceramic powder was reported by Juliana B. Silva et.al [16]. The effect
of variation of annealing temperature on the structure, morphology,
magnetic, electric and dielectric properties of cobalt ferrite
nanoparticles is not systematically reported in the literature to our
knowledge.

In the present investigation, cobalt ferrite nanoparticles were
prepared by sol-gel auto-combustion method relatively at low
temperature using L-Ascorbic acid as a fuel and maintaining metal
nitrates to fuel ratio as 1:3. The prepared powder of cobalt ferrite was
annealed at different temperatures viz 600°C , 800°C and 1000°C to
understand the effect of varying annealing temperature on the
structural, electrical, magnetic etc. properties of cobalt ferrite
nanoparticles investigated by X-ray diffraction, scanning electron
microscope, infra-red spectroscopy techniques. The magnetic
properties were investigated through M-H hysteresis loop technique
method. The electrical properties were studied by two probe method
as a function of temperature. The dielectric properties were measured
using LCR-Q meter as a function of frequency and measured at room
temperature. The results of presented in this chapter.
6.2 EXPERIMENTAL DETAILS:

Preparation of cobalt ferrite nano-particles

The nano-powders of cobalt ferrite were synthesized by well known sol-gel method using metal nitrates of respective ions and L-Ascorbic acid, as a fuel. Amounts of Co (NO$_3$)$_2$, Fe (NO$_3$)$_3$ with molar ratio Co$^{2+}$/Fe$^{3+} = \frac{1}{2}$ were dissolved completely in de-ionized water. The aqueous solution containing Co$^{2+}$ and Fe$^{3+}$ ions was poured into L-ascorbic acid with the total cations/L-Ascorbic acid molar ratio 1:3 and the initial pH of the solution was measured. To increase the pH up to 7, ammonia hydroxide in aqueous form was added to the mixed solution drop by drop. The mixture was stirred using magnetic stirrer and evaporated at 80$^\circ$C to form a gel. The temperature of the gel was further increased to 110$^\circ$C for 1-2 hours. The gel burns rapidly and turned into brown loose powder. The obtained powder was annealed at 600$^\circ$C, 800$^\circ$C and 1000$^\circ$C and was used for further characterization. Cobalt ferrite nano-particles synthesized by sol-gel auto-combustion method at 600$^\circ$C, 800$^\circ$C and 1000$^\circ$C were named as CF6, CF8 and CF10 respectively.

Characterizations

The X-ray diffraction technique was employed to confirm the phase purity and nano crystalline nature of the prepared cobalt ferrite nano-particles. The X-ray diffraction pattern was recorded into 2θ range of 20$^0$-80$^0$ at room temperature using Cu-Kα radiation. The surface
morphological studies were carried out using scanning electron microscopy technique. Infra-red spectra of all the samples were taken at room temperature in the wave number 1000- 350cm⁻¹. The magnetic measurements were recorded at room temperature using pulse field hysteresis loop technique. The DC electrical resistivity measurements were carried out in the temperature range 300-600K using two probe techniques. A silver paste was applied on the surfaces of pellet to ensure the good ohmic contact. The dielectric constant measurements were carried out at room temperature as a function of frequency (100Hz – 1MHz) using LCR-Q meter (Model 4192, HP make).

6.3: RESULTS AND DISCUSSION:

X-RAY Diffraction

Figure 6.1(a, b, c) represents the X-ray diffraction (XRD) pattern of cobalt ferrite samples annealed at temperatures namely CF6, CF8 and CF10 respectively. All the XRD patterns exhibit similar kind of nature except the peak intensity and broadening. The reflections present in the XRD pattern belongs to cubic spinel structure. The analysis of XRD pattern was made through computer program and it indicates that all the samples possess single phase cubic spinel structure with no extra peaks. A careful examination of the XRD pattern shows that the intensity of Bragg’s reflection increases with increase in annealing temperature. Besides that the broadening of the most intense peak
(311) of the XRD pattern slightly decreases with increasing annealing temperature. The increase in broadening, intensity and sharpness is attributed to increasing annealing temperature.

Using XRD data the lattice constant (a) was determined for all the samples (CF6, CF8 and CF10) using the standard relation for cubic symmetry given by

\[ a = d\sqrt{N} \] ........................6.1

where, notations have their usual meaning. The values of lattice constant are presented in Table 6.1. It can be observed from Table that, the lattice constant increases as annealing temperature increases. Similar behavior of lattice constant was reported in the literature [17].

The X-ray density \( d_x \) was determined for all the samples under investigation using the following relation,

\[ d_x = \frac{ZM}{NV} \] ........................6.2

where, \( Z = 8 \) for cubic spinel ferrite, \( M \) is molecular weight, \( N \) Avogadro’s Number and \( V \) is volume of the unit cell.

The values of X-ray density are presented in Table 6.1. It is found from table that X-ray density decreases with increase in annealing temperature. The decrease in X-ray density is attributed to increasing unit cell volume due to increase in lattice constant.

The bulk density \( (d_B) \) was determined through Archimedes Principle and their values are reported in the Table 6.1. It is evident from table that bulk density decreases with increasing temperature. Due to increase in temperature lattice constant increases and hence unit cell
volume also increases. The increase in volume overtakes increase in mass and hence bulk density decreases.

The porosity (P) of the samples was determined through the values of X-ray density and bulk density. Table 6.1 shows the values of percentage porosity for all the samples under investigation. The porosity decreases with increase in annealing temperature. The highest porosity of 34% is observed for the sample CF6 may be due to more agglomeration. The lowest density of 29% is observed for the samples CF10 may be due to higher annealing temperature causing the reduction in number of pores.

The crystallite size (t) of all the samples was calculated using Scherer’s formula [18], for which the most intense peak (311) was considered. The values of crystallite size are presented in Table 6.1. It is evident from Table 6.1 that the crystallite size increases as annealing temperature increases.

Thus, the increase in annealing temperature results in increase in crystallite size their by affecting the structural properties of the cobalt ferrite.

**Scanning Electron Microscope**

The microstructure and surface morphology of the present samples was studied using scanning electron microscopy (SEM) technique. Figure 6.2 shows the SEM images of the samples CF6, CF8 and CF10. The analysis of SEM image shows that the microstructures of the
nanoparticles were almost regular in shape and dispersed uniformly. The agglomeration of particles at 600 °C that is for sample CF6 is more as compared to CF8 and CF10. Using the SEM image the grain size (G) was calculated using linear intercept method. Table 6.2 provides the values of grain size as a function of annealing temperature. It is observed from Table 6.2 that, the grain size of all the samples is in nanometer range and increases with increasing annealing temperature. Our results on scanning electron microscopy technique are in good agreement with the literature reports [19]. Thus, the nanocrystalline nature of the samples was confirmed through grain size values.

**Infra-red Spectroscopy**

The IR spectra of all the samples were recorded in the wave number of 350 – 1000 cm\(^{-1}\) at room temperature and is shown in Figure 6.3 (a,b,c) The spectra show one broad absorption band near 600cm\(^{-1}\), exhibiting the characteristics feature of spinel ferrite. Actually the spectra should show two bands one near 400 cm\(^{-1}\) and other at 600 cm\(^{-1}\). In the present case the spectra range starts from 500 cm\(^{-1}\) onwards, hence one absorption band near 400 cm\(^{-1}\) is invisible. The IR spectra of the present samples are of similar nature to that reported in the literature [20]. The value of high frequency absorption bands \(v_1\) is presented in Table 6.2. It is observed from spectra that the absorption
band shift towards lower wave number due to increase in annealing temperature.

**Magnetic properties**

The magnetic properties tested by pulse field hysteresis loop technique at room temperature for different produced cobalt ferrite annealed samples show strong influence of annealing temperature. The magnetization (M) versus applied magnetic field (H) that is M-H plots for all the samples are shown in Figure 6.4. The plot indicates the normal hysteresis loop and is used to evaluate the values of saturation magnetization (Ms), remanence magnetization (Mr) and coercivity (Hc). Table 6.3 illustrates the values of all these magnetic parameters for different annealing temperature. It can be noticed from Table 6.3 that the saturation magnetization increases whereas coercivity and remanence magnetization decreases with increasing annealing temperature. The increase in annealing temperature increases the crystallite size of the samples, which results in increasing the saturation magnetization and decreasing remanance magnetization and coercivity.

The magneton number \( n_B \) (the saturation magnetization per formula unit in \( \mu_B \)) was calculated for all the samples using the following relation.

\[
\frac{n_B^A}{n_B} = \frac{M_s \times \text{Molecular weight}}{5585}
\]
The observed values of magneton number are listed in Table 6.3 as a function of annealing temperature. It can be observed from table that the magneton number increases with increasing annealing temperature. Similar results of magnetic properties are reported in the literature [21, 22].

**D.C. Electrical Resistivity**

The d.c. electrical resistivity of all the samples was obtained using two probe techniques in the temperature range 300K to 850K. The plot of logarithm of resistivity versus reciprocal of temperature for all the samples is shown in Figure 6.5. It is evident from figure that as temperature increases resistivity decreases exhibiting the semiconducting behavior of the samples. The resistivity plot shows anomalous behavior. The resistivity at room temperature decreases with increase in annealing temperature decreases as noticed from the Table 6.4. The activation energy was calculated using resistivity plots and the Arrhenius relation [23]. The values of activation energy are presented in Table 6.4. It is observed from the values of activation energy that as annealing temperature increases activation energy decreases.

**Dielectric Constant (ε’)**

The dielectric constant (ε’) and dielectric loss tangent (tan δ) for the present samples were studied as a function of frequency. Figure 6.6 shows the frequency dependence of the dielectric constant at room
temperature for the studied samples. The Figure depicts that all the
samples exhibit dielectric dispersion. At low frequency the dielectric
constant shows maximum value and at high frequency the dielectric
constant shows minimum value. The decrease in dielectric constant is
exponential in nature. The dielectric behavior of the present samples
can be explained on the basis of Koop’s model [24] and Maxwell’s-
Wagner polarization theory [25, 26].
The values of dielectric constant measured at different frequency for
varying annealing temperature are presented in Table 6.5. It can be
observed from this table and Figure 6.6 that the dielectric constant
increases as annealing temperature increases. The increase in
dielectric constant is attributed to increase in grain boundaries due to
increase in annealing temperature. The behavior of dielectric constant
of the present samples is in confirmation with the reported data [27].

**Dielectric Loss Tangent (tan δ)**

Figure 6.7 displays the variation of dielectric loss tangent as a function
of applied frequency. It can be seen from this figure that the dielectric
loss tangent also decreases with increase in frequency in same fashion
to that of dielectric constant. The maximum dielectric loss tangent is
observed at lower frequency and minimum dielectric loss tangent is
observed at higher frequency. The values of dielectric loss tangent tan
δ measured at different frequency increases with increase in annealing
temperature. Due to increase in annealing temperature the crystallite
size of the cobalt ferrite sample decreases which results in increasing the dielectric constant of the studied samples. The behavior of the dielectric loss tangent as a function of frequency of the present sample is similar to that reported in the literature [28].

6.4: CONCLUSIONS:

Cobalt ferrite nanoparticles were successfully synthesized using sol-gel auto-combustion method taking L-ascorbic acid as a fuel. The characterization of all the samples annealed at different temperature was carried out using X-ray diffraction, scanning electron microscope and infra-red spectroscopy techniques, which confirms the nanocrystalline nature of the studied samples. The lattice constant, crystallite size, grain size increases with increase in annealing temperature. The saturation magnetization increases while the coercivity decreases with increase in annealing temperature. The magneton number also increases with increasing temperature. The resistivity plot displays semiconducting nature for all the samples under investigation. The activation energy decreases with increase in annealing temperature. The dielectric constant and dielectric loss tangent both decreases exponentially with increase in applied frequency. The values of dielectric constant and dielectric loss tangent both shows increasing trend with respect to annealing temperature.
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Fig 6.1 (a): XRD Patterns of cobalt ferrite nano-particles prepared by sol-gel auto-combustion method using L-Ascorbic Acid as a fuel sintered at 600°C and 800°C
Fig 6.1 (b): XRD Patterns of cobalt ferrite nano-particles prepared by sol-gel auto-combustion method using L-Ascorbic Acid as a fuel sintered at 1000°C.
Fig 6.2: Scanning electron micrograph (SEM) of cobalt ferrite nano-particles prepared by sol-gel auto-combustion method.
Fig 6.3 (a): Infrared spectra of cobalt ferrite nano-particles prepared by sol-gel auto-combustion method using L-ascorbic acid as a fuel annealed at 600°C and 800°C
Fig 6.3 (b): Infrared spectra of cobalt ferrite nano-particles prepared by sol-gel auto-combustion method using L-ascorbic acid as a fuel annealed at 1000°C.
Figure 6.4: M-H plots of cobalt ferritenano-particles prepared by sol-gel auto-combustion technique.
**Figure 6.5:** Variation of DC electrical resistivity with temperature of cobalt ferrite nanoparticles prepared by using sol-gel auto-combustion technique.
Figure 6.6: Variation of dielectric constant ($\varepsilon'$) with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique.
Figure 6.7: Variation of dielectric loss tangent (tan δ) with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique
Figure 6.8: Variation of dielectric loss ($\varepsilon''$) with frequency of cobalt ferrite nanoparticles prepared by sol-gel auto-combustion technique.
Table 6.1:

Lattice constant (a), X-ray density (d_x), Bulk density (d_b), Porosity (P), and Crystallite size (t) for cobalt ferrite nanoparticles as function of annealing temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>'a' (Å)</th>
<th>'d_x' (gm/cm³)</th>
<th>'d_b' (gm/cm³)</th>
<th>'P' (%)</th>
<th>'t' (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF6</td>
<td>8.357</td>
<td>5.365</td>
<td>3.561</td>
<td>34</td>
<td>33</td>
</tr>
<tr>
<td>CF8</td>
<td>8.382</td>
<td>5.293</td>
<td>3.654</td>
<td>31</td>
<td>42</td>
</tr>
<tr>
<td>CF10</td>
<td>8.388</td>
<td>5.281</td>
<td>3.773</td>
<td>29</td>
<td>48</td>
</tr>
</tbody>
</table>
Table 6.2:
Crystallite size (t) and Grain Size (G) for cobalt ferrite prepared by sol-gel auto-combustion technique as function of annealing temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>‘G’ (nm)</th>
<th>( v_1 (\text{cm}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF6</td>
<td>76.2</td>
<td>566.43</td>
</tr>
<tr>
<td>CF8</td>
<td>80.2</td>
<td>547.79</td>
</tr>
<tr>
<td>CF10</td>
<td>82.3</td>
<td>536.81</td>
</tr>
</tbody>
</table>
Table 6.3:

Saturation magnetization (Ms), Remenance Magnetization (Mr), Coercivity (Hc) and Magneton number (nB) for cobalt ferrite prepared by sol-gel auto-combustion technique as function of annealing temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ms (emu/gm)</th>
<th>Mr (emu/gm)</th>
<th>Mr/Ms</th>
<th>Hc (Oe)</th>
<th>nB</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF6</td>
<td>80.21</td>
<td>69.27</td>
<td>0.864</td>
<td>2444</td>
<td>3.37</td>
</tr>
<tr>
<td>CF8</td>
<td>81.62</td>
<td>68.37</td>
<td>0.838</td>
<td>1069</td>
<td>3.42</td>
</tr>
<tr>
<td>CF10</td>
<td>86.22</td>
<td>66.22</td>
<td>0.768</td>
<td>998</td>
<td>3.62</td>
</tr>
</tbody>
</table>
Table 6.4:
Room temperature resistivity ($\rho_0$) and Activation energies ($\Delta E$), for cobalt ferrite prepared by sol-gel auto-combustion technique as function of annealing temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_0 \times 10^9$ (ohm m)</th>
<th>$\Delta E$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF6</td>
<td>1.70</td>
<td>0.806</td>
</tr>
<tr>
<td>CF8</td>
<td>0.65</td>
<td>0.769</td>
</tr>
<tr>
<td>CF10</td>
<td>0.50</td>
<td>0.662</td>
</tr>
</tbody>
</table>
Table 6.5:
Room temperature dielectric constant ($\varepsilon'$), dielectric loss ($\varepsilon''$) and dielectric loss tangent ($\tan \delta$) for cobalt ferrite prepared by sol-gel auto-combustion technique as function of annealing temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>f = 100 Hz</th>
<th>f = 1 MHZ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($\varepsilon'$)</td>
<td>($\varepsilon''$)</td>
</tr>
<tr>
<td>CF6</td>
<td>704</td>
<td>2816</td>
</tr>
<tr>
<td>CF8</td>
<td>864</td>
<td>7162.56</td>
</tr>
<tr>
<td>CF10</td>
<td>934</td>
<td>9377.28</td>
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