Structural and Magnetic properties of Cobalt Ferrite (CoFe$_2$O$_4$) Nanoparticles by Sol-Gel Technique using Yeast

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Abstract. The aim of the present work is to synthesize cobalt ferrite nanoparticles by sol-gel technique using yeast. The source culture is prepared using yeast, carbon and nitrogen. Three samples are prepared by mixing the source culture with ferric nitrate (0.2 M) and cobalt nitrate (0.15, 0.2, 0.25M) and stirred for suitable duration to get the gel. The final product is heated at 600°C to get the cobalt ferrite nanopowder. Structural analysis reveals the cubic phase of cobalt ferrite nanoparticles with the peaks corresponding to the plane (220), (311), (400), (511) and (440) matches with the PDF data. The peaks are sharp showing the crystalline nature of the prepared samples. From the microstructural parameters calculated for the prominent peak (311) shows the average crystallite size is 44 nm. The lattice constant is found to be around 8.350 Å which is close to the bulk value of cobalt ferrite nanoparticle (8.373Å). The calculated X-ray density is more than their bulk counterpart and is attributed to the formation of pores throughout the synthesis method. FTIR analysis shows the existence of functional groups within the prepared sample. EDAX analysis shows the rise in the atomic weight percentage of cobalt with increase in weight proportion of cobalt nitrate. SEM analysis shows the surface morphology of the prepared sample and the ferromagnetic behavior of the cobalt ferrite nanoparticle is observed by VSM studies.

1. Introduction
Nanoscience is developing exponentially in the field of science due to its broader spectrum of applications and unique functional properties. The wide varieties of potential applications of magnetic nanoparticles include smart drug delivery, data storage, magnetic resonance imaging, sensing, medical devices and high - density information storage [1 - 4]. The spinal ferrites with the formula M (Fe$_2$O$_4$), crystallizes either in normal form or inverse spinal form [5] with M being the divalent cation (Co$^{2+}$). The gas anions (O$^{2-}$) forms an in depth cubic crystal structure, and the remaining interstices are occupied by the metal ions the in an unusual two-lattice arrangement. The drug release mechanism and hyperthermia is favored by the switching property of ferrites. The dimensions of the particles for biological applications needs to be within the vary of 30 to 50 nm and the coating thickness is to extend to the size of 70 to 80 nm. The magnetically soft Cobalt ferrite (CoFe$_2$O$_4$) nanoparticles finds its applications as carriers for targeted drug delivery but their toxicity proves to be a limitation. Because of their high coercivity, high magneto crystalline anisotropy and their moderate saturation magnetization [6], these nanoparticles finds itself to be an area of interest. Cobalt ferrites finds its applications in electrical equipments and electronic devices and are employed in high-frequency applications. Telecommunications, quality filter circuits, high frequency transformers, wide band transformers, adjustable inductors, delay lines, and other high frequency electronic circuits, magnetic circuits for both
low level and power applications [7, 8] are some other fields wherein Cobalt ferrites are employed. As the chemical composition and microstructural characteristics decides the properties, suitable fabrication and synthesis processes is adopted to have required physical and chemical properties. The preparations of cobalt ferrite nanoparticles include ceramic method by firing [9], co-precipitation [10], hydrothermal methods [11], sol-gel [12] and laser ablation [13]. In the present work, we've got tried to ascertain an ecofriendly, economical as well as an easily reproducible method to synthesize cobalt ferrite nanoparticle using yeast.

2. Experimental

2.1. Synthesis of CoFe₂O₄ Nanoparticles

Yeast is allowed to grown as a suspension culture in 250 mL of distilled water within the presence of carbon (2 g glucose) and nitrogen (0.2 g glycine) for forty eight hours, which is being treated as a source culture. About 25mL this was filtered and diluted fourfold by adding Et-OH containing 1 g glucose and 0.1 g glycine as nutrients. After being allowed to incubate for 24 h. This diluted culture turned a light straw color. The incubation mixture is heated up to 60°C before being charged, leading to the nutrients being completely dissolved and turned a golden yellow colour. The solution is maintained at a pH of 6. A 20 ml volume of 0.15 M cobalt nitrate solution is taken and is mixed with 0.2 M of ferrous nitrate, which is then heated about 5-10 mins until it turned a light brown color. This solution is later charged to the culture solution and a magnetic stirrer was used to heat the solution at a temperature of 50 °C until the deposition started to appear at the bottom of the flask, which indicates the initiation of transformation. After being cooled, the culture solution is allowed to incubate at room temperature in the laboratory overnight. Then it is heated in the furnace at 800 °C for 40 minutes and grinded into a fine powder. The same procedure is repeated for the different concentration of cobalt nitrate (0.20M and 0.25M) and the concentration of the ferric nitrate (0.2M) is kept constant.

2.2. Characterization

The prepared sample was subjected to X-ray diffraction analysis using Shimadzu XRD 6000 diffractometer with CuKα radiation wavelength of 1.541 Å. The functional group were analysed by FTIR using Perkin-Elmer spectrometer using the range of 4000-400 cm⁻¹ with the help of KBr pellet technique. The morphology and compositional analysis of the prepared samples was assessed by Scanning Electron microscopy with EDAX using JEOL (JSM 6390). Magnetic properties of the samples were analyzed by VSM by maintaining a room temperature (Lakshore).

3. Results and Discussion

3.1. Structural Analysis

Figure 1 shows the PXRD pattern of Cobalt ferrite nanoparticles synthesized by sol-gel technique. The prepared samples show amorphous nature and the samples are annealed for one hour at 600°C to improve the crystallinity. After annealing, the peaks become sharper and narrower which implies the higher degree of crystallinity of cobalt ferrite nanoparticles. The broadening line in the XRD indicates the grains are very fine [14]. The observed peak corresponding to the plane (220), (311), (400), (511) and (440) matches well with the cubic phase of the cobalt ferrite nanoparticle (PDF 04-007-8945). Microstructural parameters calculated for the prominent peak (311) are shown the Table 1. The average size of the crystallite was calculated using the formula of Scherrer [15]

\[ D = \frac{0.89\lambda}{\beta \cos \theta} \] (1)

Here \( \lambda \) is the wavelength of the incident Cu-Kα line of X-ray (\( \lambda \cdot 1.5418 \) Å), \( \beta \) represents the value of full width at half maximum in the maximum intensity peak and the unit is radians. The \( \theta \) is the angle at
which the maximum peak occurs. The crystallite size is found to be 44nm size and this higher value is due to the formation of crystallite clusters and coalesce of these cluster with each other under favorable energetic conditions which leads to the increase of crystallite size. A very slight increase in the crystallite size is observed when the concentration of cobalt nitrate is increased from 0.15 to 0.25 M.

Table 1. Micro structural parameters of Cobalt ferrite nanoparticle

| Samples   | Plane   | Grain Size (nm) | Dislocation Density 10^{14} (l/m^2) | Microstrain 10^{-6} | Calculated d (Å) | a (Å) | X-ray density (g/cm^3) |
|-----------|---------|-----------------|-------------------------------------|---------------------|------------------|-------|-----------------------|
| Sample 1  | 311     | 44.30           | 5.094                               | 0.0002617           | 2.526            | 8.378 | 5.300                 |
| Sample 2  | 311     | 44.32           | 5.091                               | 0.0002625           | 2.519            | 8.355 | 5.344                 |
| Sample 3  | 311     | 44.33           | 5.088                               | 0.0002633           | 2.511            | 8.330 | 5.392                 |

The strain and dislocation density is found to be varied according to the crystallite size. The lattice constant is calculated by d-spacing using the following [16]

\[
a = d_{hkl} \left( h^2 + k^2 + l^2 \right)^{\frac{1}{2}}
\]  

(2)
Here \((h, k, l)\) are the Miller indices. The lattice constant found here is close to the bulk value of the nanoparticles of cobalt ferrite, 8.373Å. The calculated volume of the cell is less compared to the bulk [590.99 Å] which is due to the nano sizing effect in n-cobalt ferrite [17]. The X-ray density \((\rho_x)\) is calculated by the formula considering that there are 8 ions [18] in the basic unit cell of the cubic spinel structure.

\[
\rho_x = \frac{8M}{Na^3} \quad (3)
\]

Where \(M\) is the molecular mass of the compound, \(N\) is the Avogadro number \((6.0225 \times 10^{23} \text{ particles/mole})\) and \(a\) is the lattice parameter. X-ray density is dependent on the lattice constant and molecular weight of the compound and in the present case the X-ray density is found to be in the range of 5.300-5.392 g/cm³. In the present case, X-ray density increases as the lattice constant decreases. Similar types of observations are noted by Pandit et.al. for Mg-Zn ferrite system prepared at different molar concentrations [17]. Also X-ray density is found to be higher than their bulk counterpart which may be the reason for the formation of pores during the synthesis process [19] and also due to the ionic radii [20]. With the help of X-ray diffraction values the calculations are done for the tetrahedral and octahedral ionic radii \((r_A, r_B)\) and bond lengths at tetrahedral \((A-O)\) and octahedral \((B-O)\) sites of cubic spinel structure [21].

\[
\begin{align*}
    r_A &= \left( u - \frac{1}{4} \right) a \sqrt{3} - r (O^{-2}) \, \text{Å} \quad (4) \\
    r_B &= \left( \frac{5}{8} - u \right) a - r(O^{-2}) \, \text{Å} \quad (5) \\
    A - O &= \left( u - \frac{1}{4} \right) a \sqrt{3} \, \text{Å} \quad (6) \\
    B - O &= \left( \frac{5}{8} - u \right) a \, \text{Å} \quad (7)
\end{align*}
\]

Where ‘\(a\)’ is the lattice constant; ‘\(u\)’ gives the oxygen ion parameter and an ideal spinel ferrite has \(u=3/8\). \(r (O^{-2})\) is the radius of oxygen ion \((1.35 \, \text{Å})\). The following formulas given below are used to calculate the Hopping lengths at tetrahedral sites \((L_A)\) and at octahedral sites \((L_B)\) [21].

\[
\begin{align*}
    L_A &= a \left( \frac{\sqrt{3}}{4} \right) \, \text{Å} \quad (8) \\
    L_B &= a \left( \frac{\sqrt{2}}{4} \right) \, \text{Å} \quad (9)
\end{align*}
\]

The radius of the cations in the tetrahedral sites \((r_A)\) and the octahedral sites \((r_B)\) hopping length at the tetrahedral LA and octahedral sites \(L_B\) are listed in the table 1. The mean ionic radius at tetrahedral site \((r_A)\) is found to decrease with octahedral site B \((r_B)\) and the increase in \(r_A\) with \(r_B\) is noted by other investigators for their Co-Zn system [22]. The hopping lengths of both tetrahedral and octahedral sites is found to decrease gradually when the concentration of cobalt nitrate is increased. The calculated bond length A-O and B-O found to decrease which reflects the decline in the lattice constant.

3.2. Compositional Analysis

EDS (figure 2) shows the presence of Co, Fe and O elements in the sample. As the concentration of cobalt nitrate increases the atomic weight percentage increase. It is noted that no organic chelating agents remained in the system. Atomic percentage of the prepared samples are tabulated (table 2).
3.3. Functional Group Analysis

Fourier transform infrared (FT-IR) spectroscopy technique provides information about the nature and structure of ferrites. FT-IR spectra of pure cobalt ferrite NPs synthesized is shown in the figure 3. Cobalt ferrite nanoparticles are characterized by the intrinsic stretching vibrations around 600 and 450 cm\(^{-1}\) which corresponds to M\(_{tetra}\) - O and M\(_{octa}\) - O vibrations in the tetrahedral and octahedral sites. [23, 24]. In the present case the M-O vibrations observed at 876 cm\(^{-1}\). The other important peaks around 3400 and 1640 cm\(^{-1}\) is attributed to H-O-H stretching and bending vibrations of the absorbed water molecules on the surface of cobalt ferrite NPs respectively [25]. The additional peaks observed at 2977 and 2899 cm\(^{-1}\) correspond to (C-H) stretching band. The peak at 1400 cm\(^{-1}\) assigned to C=O stretching vibrations and the C-N stretching vibrations are observed at 1240 cm\(^{-1}\).

![FTIR Spectrum of CoFe\(_2\)O\(_4\) nanoparticles by biological synthesis method](image)

**Table 2.** Atomic % of CoFe2O4 nanoparticles by biological synthesis method

| Samples  | Atomic (%) |
|----------|------------|
|          | Co  | Fe   | O  |
| Sample 1 | 311 | 44.30| 5.094|
| Sample 2 | 311 | 44.32| 5.091|
| Sample 3 | 311 | 44.33| 5.088|

![FTIR Spectrum of CoFe\(_2\)O\(_4\) nanoparticles by biological synthesis method](image)

**Figure 3.** FTIR Spectrum of CoFe\(_2\)O\(_4\) nanoparticles by biological synthesis method
3.4. Morphological Analysis
The imaging of the as-synthesized samples with different concentration of cobalt nitrate is shown in the figure 4. It is observed that similar type of shapes reflected in all the samples. It is noted that flake like structure with large clusters at some regions are observed which is due to the heating during the synthesis process [26].

![Figure 4. SEM Images of CoFe$_2$O$_4$ nanoparticles by biological synthesis method](image)

3.5. VSM Analysis

![Figure 5. VSM plots of CoFe$_2$O$_4$ nanoparticles by biological synthesis method](image)

| Table 3. Magnetic Parameters of CoFe$_2$O$_4$ nanoparticles by biological synthesis method |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Samples                        | Coercivity (Oe) | Retentivity (emu) | Saturation Magnetization (emu) | M$_r$/M$_s$ |
| Sample 1                       | 288.8           | 0.0002           | 0.0097          | 0.206          |
| Sample 2                       | 400.0           | 0.2369           | 0.5454          | 0.4343         |
| Sample 3                       | 1044.4          | 0.4639           | 1.1032          | 0.4205         |
Figure 5 shows the ferromagnetic behavior of the cobalt ferrite nanoparticle prepared at three different concentration of cobalt nitrate (0.15, 0.2 and 0.25M) keeping concentration of ferric nitrate (0.2M) as constant. In spinel ferrites, there is a super exchange interaction happening between the magnetic ion in the tetrahedral and octahedral sites decides the ordering of the spinel ferrites [27]. The anisotropy constant is calculated using the formula below [28].

$$H_c = \frac{(0.96K)}{M_s}$$

(9)

The magnetic parameters are listed in the table 3. From the observations it is noted that the coercivity increases from 288 to 1044 Oe with the increase in the cobalt nitrate concentration. The increase in the coercivity may be attributed to increase of the stress anisotropy and the increase in the density of structural defects that reflects in the increase of the centers of domains wall pinning [29, 30]. The saturation magnetization is found to increase from 0.0097 to 1.1032 emu when the concentration of cobalt nitrate increases from 0.15 to 0.25 M. Magnetization depends on various factors which includes particle size, shape and the replacement of cation with smaller radius cation. In the present work the saturation magnetization increases with the increase in the crystallite size even though the increase in the crystallite size is not much appreciable. The increase in saturation magnetization is attributed to intrinsic factors such as preferential occupation of cation and extrinsic factors such as microstructural and bulk density of the ferrites. In cobalt ferrite, an inverse spinel ferrite, the divalent cations occupy the octahedral sites and the trivalent cations occupy both the tetrahedral and octahedral sites equally. The increase in the saturation magnetization with the crystallite size and the concentration of cobalt nitrate is attributed to the increase in the exchange of interactions between tetrahedral and octahedral sites. The direction of magnetization to the nearest easy axis of magnetization direction after the magnetic field switch is given by ratio of Mr/Ms which indicated the anisotropic nature of the cobalt ferrite nanoparticle [31]. In the present study, all the samples show the ferromagnetic behavior of cobalt ferrite nanoparticles.

4. Conclusion

Cobalt ferrite nanoparticles are prepared by biological method using yeast, ferric nitrate and cobalt nitrate. The concentration of ferric nitrate is kept constant (0.2M) and the concentration of cobalt nitrate varied from 0.15 to 0.25M. Structural analysis shows the cubic phase of the cobalt ferrite nanoparticles and from the microstructural analysis calculated for the prominent shows the crystallite size is 44nm. When the concentration of the cobalt ferrite increases from 0.15 to 0.25M there is no appreciable change in the crystallite size. The decrease in the lattice constant compared to the bulk shows the nano sizing effect of the synthesized particle. The calculated X-ray density, increases with the concentration of the cobalt nitrate. Also the observed X-ray density is greater than the X-ray density for bulk which is attributed to the formation of pores during the synthesis process. FT-IR analysis shows C=H stretching around 2900cm⁻¹, H-O-H stretching around 3400 and 1600cm⁻¹ and C=O stretching around 1400 cm⁻¹. The M-O stretching is observed at 876 cm⁻¹. SEM analysis shows the flake like structure of the synthesized nanoparticles and VSM analysis reveals the ferromagnetic nature of the cobalt ferrite nanoparticle. The increase in coercivity with the increase in the concentration of cobalt nitrate attributed to the increase in stress isotropy increase of the centers of domains wall pinning. The increase in the saturation magnetization with the crystallite size and the concentration of cobalt nitrate the shows exchange of interactions between tetrahedral and octahedral sites.

5. References

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