Synthesis and characterization of Co$_{0.8}$Fe$_{2.2}$O$_4$ nano ferrite

S Raghuvanshi*, S N Kane*, N P Lalla and V R Reddy

*Magnetic Materials Laboratory, School of Physics, Devi Ahilya University, Khandwa Road Campus, Indore-452001, India
*UGC-DAE CSR, University Campus, Khandwa Road, Indore-452001, India

Abstract. Co$_{0.8}$Fe$_{2.2}$O$_4$ nano ferrite has been synthesized by sol gel auto-combustion method. X-ray diffraction (XRD) and Mössbauer spectroscopy were used to characterize the synthesized as burnt and thermally annealed (600 °C for 3 hours) samples. Both XRD and Mössbauer measurements confirm the formation of spinel phase with Scherrer’s grain diameter ($D_s$) ≈ 37 nm. Presence of α-Fe and Fe$_2$O$_3$ was also observed. Thermal annealing induced decrease of $\rho_{\text{xrd}}$ (from 5267.9 to 5262.7 Kg/m$^3$) for the annealed samples is ascribable to the fact that, increase of unit cell volume overtakes the increase in mass of the unit cell. Comparison of dry gel and thermally annealed sample shows that in dry gel, B site is more populated with Fe ions, whereas thermal annealing leads to migration of Co from A to B site with simultaneous migration of Fe from B to A site, thus dropping the Néel magnetic moment. Bond angle values clearly reveal that thermal annealing leads to strengthening of B-O-B interaction with simultaneous weakening of A-O-B, and, A-O-A interaction.

1. Introduction

Nanosized spinel ferrites have been a topic of intense research owing to broad possibilities of their use in various technological applications e.g., high density data storage [1], biomedical applications [2] etc. and, fundamental understanding of these materials. Spinel ferrites exhibit face centred cubic (fcc) structure belongs to Fd$_{3}$m space group. The lattice consists of 32 divalent oxygen ions forming a closed pack face centred cubic arrangement with 64 tetrahedral interstitial sites (A sites) and 32 octahedral interstitial sites (B sites). Out of these, only 8 tetrahedral (A sites) and 16 octahedral (B sites) sites are occupied by the divalent and, trivalent cations and, rest remain empty. Thus, large fraction of empty interstitial sites, makes the crystal structure rather unfilled, encouraging migration of cations. It is well-known fact that the properties of ferrites are strongly influenced by their composition, microstructure and, are also sensitive to the preparation methodology used in their synthesis [3].

Phase transition is an important subject of study in magnetic materials and, temperature is one of the important parameters known to influence properties of magnetic materials [4]. In magnetic materials, the applied magnetic field also has been shown to be a variable parameter [4,5], highlighting the need of structural studies in presence of magnetic field, i.e. doing x-ray diffraction (XRD) measurements in the presence of magnetic field, (usually available only at synchrotron sources [6]), to be able to study magneto-structural phase transition. For ease in the experiments, at the same time keeping the quality of the information on magneto-structural phase transition in magnetic materials, there is a need for a laboratory source based XRD setup, capable of performing measurements at high...
magnetic fields as well as at low temperatures. This need is fulfilled by the recent development of low
temperature and high magnetic field (LTHM) powder x-ray diffraction (XRD) [7] and, now is being
used for LTHM XRD measurements to study magneto-structural phase transition.

Co ferrite has emerged as quite promising material for the development of rare-earth free
hard magnets, with high coercivity (~16.7 kOe), reasonable magnetization (~ 89.1 emu/g) and, rather
high magneto-crystalline anisotropy (~ 11.6×10^6 erg/cc), which can be controlled by grain diameter
[8]. It also shows remarkable chemical stability and, mechanical hardness [9]. CoFe2O4 has face
centered cubic (fcc) structure belonging to Fd3m space group and has two inter-penetrating sub-lattices
A (tetrahedral) and B (octahedral) and, displays inverse spinal structure shown as : (Fe^{3+})^A [Co^{2+}
Fe^{3+}]B O_4^2- [10]. Co-ferrite is also magnetostrictive, shows magnetostrictive constant \( \lambda_s \approx 400 \) ppm)[11], so application of high magnetic field would lead to changes in the sample dimension (i.e.
generating deformation in the sample), which is expected to be reflected in changes in the line
intensities of the XRD pattern [12,13], indicating changes in cation distribution. Recently [11] via
magnetic measurements, anisotropy driven transition (caused by rotation of the magnetization vector
jumping over an energy barrier) is reported in single crystal Co-ferrite - Co_{0.8}Fe_{2.2}O_4, although
structural studies were not reported. XRD measurements under applied magnetic field (where changes
in the intensity of XRD peaks can be observed) can yield information on magneto-structural phase
transition, as was also reported in earlier studies in TbVO_4 system [12].

Consequently, as a first step to study magnetic field induced phase transition in poly-
crystalline Co nano-ferrite, in the present work report the synthesis of poly-crystalline Co_{0.8}Fe_{2.2}O_4,
spinel ferrite by sol-gel auto combustion method and, its preliminary characterization using XRD and
Mössbauer measurements. In the second step of our studies, we intend to perform low temperaturer
XRD measurements under applied magnetic field, which will be a subject of separate paper.

2. Experimental Details
2.1 Material synthesis and, characterization
Co_{0.8}Fe_{2.2}O_4 specimen was synthesized by sol–gel auto-combustion technique by utilizing nitrate-
Citrate precursors: [Co(NO_3)_2.6H_2O – Cobalt Nitrate and Fe(NO_3)_3.9H_2O - Ferric Nitrate]. All the
precursors were taken in stoichiometric ratio, were dissolved in de-ionized water and citric acid was
used as fuel, taking metal salt to fuel mass ratio as 1:1. Solution pH was maintained to 7 by adding
Ammonia solution (NH_4OH). Afterwards the solution was heated at 110 °C to obtain fluffy powder
(dry gel). Obtained dry gel powder was annealed at 600 °C for 3 hours. Both dry gel and annealed
samples were used for x-ray diffraction and, Mössbauer studies. Schematic diagram of the synthesis
process is shown in figure 1.

Room temperature x-ray diffraction (XRD) measurements (θ - 2θ configuration) were done
by 18 kW rotating anode source (Rigaku) utilizing CuKα (λ = 0.1540562 nm) radiation. X-ray tube is
focused, made parallel by using a parabolic mirror (Xenox). Scattered x-rays were detected by NaI
detector. Room temperature Mössbauer spectra were recorded in transmission geometry using a
^{57}Co:Rh source and, the spectra were computer fitted to obtain hyperfine parameters.

Figure 1: Schematic diagram of the synthesis of Co_{0.8}Fe_{2.2}O_4 by sol-gel auto combustion method.
2.2 Data analysis
Lattice parameter (a<sub>xrd</sub>) corresponding to [311] reflection was obtained by: 
\[ a_{xrd} = d \left( h^2+k^2+l^2 \right)^{1/2}, \]
where d - inter-planer spacing and (h, k, l) – Miller indices. a<sub>xrd</sub> was used to obtain the x-ray density (ρ<sub>xrd</sub>) of the prepared samples using the equation 
\[ \rho_{xrd} = 8M_w/N(a_{xrd})^3, \]
where M<sub>w</sub> – Molecular weight, N – Avagadro’s number. Grain diameter was calculated by the line width of [311] reflection, using Scherrer’s formula: 
\[ D = \frac{0.9\lambda}{\beta \cos \theta}, \]
Where \( \lambda \) - wavelength of the x-ray used, \( \beta \) - line width, \( \theta \) peak position (in 20 scale). Cation distribution of the studied samples was estimated using XRD peak intensities. The calculated and, observed intensity ratios were compared for several combinations of cations distribution at (A) and [B] sites [14]. The best cation distribution amongst the tetrahedral and octahedral sites for which theoretical and experimental ratios agree clearly, is taken to be the correct one. Ionic radii of tetrahedral (r<sub>t</sub>), octahedral sites (r<sub>o</sub>), theoretical lattice parameter (a<sub>th</sub>), oxygen positional parameter (u), inter-ionic distances between cations (Me-Me) (b, c, d, e, f), bond angle between cations (θ<sub>1</sub>, θ<sub>2</sub>, θ<sub>3</sub>, θ<sub>4</sub>, θ<sub>5</sub>) and cation-anion (Me-O) (p, q, r, s) were calculated as described elsewhere [15,16].

Néel magnetic moment (n<sub>N</sub>) was calculated by using expression: 
\[ n_N = M_B - M_A, \]
where M<sub>B</sub> and M<sub>A</sub> respectively are magnetic moments at B and A site. Both M<sub>A</sub> and M<sub>B</sub> were obtained from cationic distribution. Full profile Rietveld analysis of XRD pattern is done by MAUD (Materials Analysis Using Diffraction) software [17]. The program continues the refinement till convergence is obtained with the values of the quality factor GOF (goodness of fit) is close to 1, confirming the goodness of refinement.

2. Results and Discussion
Fig. 2 depicts Rietveld refined XRD plot of (a) Co<sub>0.8</sub>Fe<sub>2.2</sub>O<sub>4</sub> (Dry gel), (b) Co<sub>0.8</sub>Fe<sub>2.2</sub>O<sub>4</sub> (ann. at 600°C/3hours.). XRD confirms the formation of nano-crystalline cubic spinel structure. XRD analysis provides - lattice parameter, grain diameter etc., theoretical lattice parameter (a<sub>th</sub>), oxygen positional parameter (u), interionicic distances between cation and anion (Me-O) (p, q, r, s), interionic distance between cations (Me-Me)(b, c, d, e, f), bond angle between cation and anion (θ<sub>1</sub>, θ<sub>2</sub>, θ<sub>3</sub>, θ<sub>4</sub>, θ<sub>5</sub>). Néel magnetic moment (n<sub>N</sub>) were calculated from cation distribution.

Table 1 shows the calculated values of experimental and, theoretical lattice parameters, (a<sub>xrd</sub>, a<sub>th</sub>), average Scherrer’s grain diameter (D), x-ray density (ρ<sub>ord</sub>), and specific surface area (S) for dry gel and annealed samples. Lattice constant does not change appreciable for the studied samples. The average Scherrer’s grain diameter (D<sub>av</sub>) increases from 37.3 to 37.6 nm. Observed minor change in D can be ascribed to thermal annealing induced grain growth. Thermal annealing induced decrease of ρ<sub>ord</sub> (from 5267.9 to 5262.7 Kg/m<sup>3</sup>) for the annealed samples is ascribable to the fact that, increase of unit cell volume overtakes the increase in mass of the unit cell.

Table 2 gives cation distribution and, Néel magnetic moment of the studied samples. Perusal of table 2 shows that thermal annealing leads to migration of Co from A to B site with simultaneous migration of Fe from B to A site. In case of dry gel sample, more population of Fe ions on B site leads to higher Néel magnetic moment.

Table 3 illustrates the variation of ionic radii of A-site (r<sub>A</sub>) and B-site (r<sub>B</sub>), oxygen positional parameter (u), inter-ionic distances between cations (Me-Me) (b, c, d, e, f) and cations anions (Me-O)

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**Figure 2:** Rietveld refined plot of (a) Co<sub>0.8</sub>Fe<sub>2.2</sub>O<sub>4</sub> - Dry gel, (b) Co<sub>0.8</sub>Fe<sub>2.2</sub>O<sub>4</sub> - Ann. at 600 °C / 3hours.
values for ferrite component indicates that iron present in ferrite component is Fe
in XRD measurements) and, in annealed sample, formation of
Perusal of table 4 shows that in dry gel apart from ferrite presence of
and, the magnetic nature of the samples, as reflected in Mössbauer parameters shown in table 4.
whereas
radii (\(r\)) bond angles (\(\theta_1, \theta_2, \theta_3, \theta_4, \theta_5\)) for effective magnetic interactions (A-O-A, A-O-B, B-O-B).
It is worth noting that strength of the magnetic interactions (A-O-B, B-O-B and, A-O-A) strongly
depend on bond length and bond angles between the cations and, cation-anion and is directly
proportional to the bond angle, but inversely proportional to the bond length [13]. Bond angle values
(shown in table 3) clearly show that thermal annealing leads to strengthening of B-O-B interaction
with simultaneous wreaking of A-O-B, and, A-O-A interaction, which is reflected in bond length and
Néel magnetic moment. Oxygen positional parameter (\(u\)) is a measure of distortion in the structure
and, its reduction after thermal annealing suggests reduction of structural disorder. Variation of ionic
radii (\(r_a, r_b\)) in the studied samples can be explained as follows : due to presence of more Co on B site
(shown in table 2), in thermally annealed sample shows higher \(r_b\) in comparison to dry gel sample,
whereas \(r_a\) shows opposite behaviour as that of \(r_b\).
Mössbauer measurements (spectra not shown here) also depict the formation of spinel phase
and, the magnetic nature of the samples, as reflected in Mössbauer parameters shown in table 4.
Perusal of table 4 shows that in dry gel apart from ferrite presence of \(\alpha\)-Fe is also seen (also observed
in XRD measurements) and, in annealed sample, formation of FeO is observed. Obtained isomer shift
values for ferrite component indicates that iron present in ferrite component is Fe\(^{3+}\).

### Table 3. Variation of ionic radii of A site (\(r_a\)) and B site (\(r_b\)), oxygen positional parameter (\(u\)), inter-ionic
distance between cations (\(Me-\ Me\)) (\(b, c, d, e, f\)), between cation and anion (\(Me-\ O\)) (\(p, q, r, s\) and
bond angles (\(\Omega_1, \Omega_2, \Omega_3, \Omega_4, \Omega_5\))

| Parameters          | \(Co_{0.8}Fe_{2.2}O_4\) (Dry gel) | \(Co_{0.8}Fe_{2.2}O_4\) (Ann.600°C/3h) |
|---------------------|-----------------------------------|--------------------------------------|
| \(r_a\) (nm)        | 0.0495                            | 0.0490                               |
| \(r_b\) (nm)        | 0.0682                            | 0.0685                               |
| \(u\)               | 0.3791                            | 0.3787                               |
| \(p\) (nm)          | 0.2062                            | 0.2067                               |
| \(q\) (nm)          | 0.1875                            | 0.1870                               |
| \(r\) (nm)          | 0.3591                            | 0.3581                               |
| \(s\) (nm)          | 0.3652                            | 0.3651                               |
| \(b\) (nm)          | 0.2965                            | 0.2966                               |
| \(c\) (nm)          | 0.3477                            | 0.3478                               |
| \(d\) (nm)          | 0.3632                            | 0.3633                               |
| \(e\) (nm)          | 0.5448                            | 0.5450                               |
| \(f\) (nm)          | 0.5136                            | 0.5138                               |
| \(A-O-B\) \(\theta_1\) (°) | 123.94                           | 124.08                               |
| \(A-O-B\) \(\theta_2\) (°) | 147.76                           | 148.41                               |
| \(B-O-B\) \(\theta_1\) (°) | 91.92                            | 91.72                                |
| \(B-O-B\) \(\theta_2\) (°) | 125.71                           | 125.66                               |
| \(A-O-A\) \(\theta_1\) (°) | 76.16                            | 76.53                                |
Table 4. Isomer shift (I.S.), Average hyperfine field (B_{hf}) and, components present in the studied samples.

| Sample                  | I. S. (mm/s) | B_{hf} (T) | Component |
|-------------------------|--------------|------------|-----------|
| Co_{0.8}Fe_{2.2}O_{4}  | 0.485 ± 0.036| 33.33 ±0.10| α-Fe     |
| (Dry gel)               | 0.335 ± 0.0004| 51.13 ±0.08| Ferrite* |
|                         | 0.306 ± 0.002| 49.65 ±0.06| Ferrite# |
| Co_{0.8}Fe_{2.2}O_{4}  | 0.432 ± 0.031| 51.98 ±0.15| Fe_{2}O_{3}|
| (Ann 600°C/3h)          | 0.266 ± 0.022| 51.84 ±0.09| Ferrite* |
|                         | 0.289 ± 0.007| 49.07 ±0.09| Ferrite# |

*Octahedral (B) site, #Tetrahedral (A) site

Based on the hyperfine field values, magnetic sextets are assigned to Fe ions located on tetrahedral (A) and octahedral(B) sites.

To summarize, XRD, Mössbauer study dry gel and thermally annealed (600 °C for 3 hours) Co_{0.8}Fe_{2.2}O_{4} nano ferrite (grain diameter ~ 37 nm) prepared by sol gel auto-combustion method is reported. Studies reveal the formation spinel phase and, also the presence of α-Fe and, Fe_{2}O_{3} phase. Thermal annealing leads to : i) minor changes in x-ray density, ii) migration of Co from A to B site with simultaneous migration of Fe from B to A site, resulting in reduction of Néel magnetic moment and, iii) illustrate strengthening of B-O-B interaction with simultaneous wreaking of A-O-B, and, A-O-A interaction.

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