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# Structural and Magnetic properties of Ultrafine $CoFe_2O_4$ Nanoparticles

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**Abstract**

Nanosized Cobalt ferrite ($CoFe_2O_4$) particles are prepared through the sol-gel method using polyvinyl alcohol (PVA) as a chelating agent. The powder as prepared is annealed at three different temperatures (400ºC, 500ºC and 1000ºC) for one hour. The X-ray diffraction patterns confirm the spinel structure of the samples. The XRD patterns of the samples indicate broad peaks and the full width at half maximum decreased with increasing annealing temperature. Infrared (IR) spectra of the samples confirm the presence of metal - oxygen complexes within the spinel lattice. The average particle size obtained from TEM micrographs demonstrates ultrafine particles having spherical morphology. The particle size of the annealed samples is in between 4.5-6.8 nm. The saturation magnetization ($M_s$) and remnant magnetization ($M_r$) of the samples show dependence on particle size and crystallinity of the samples. The highest saturation magnetization (78.1 emu/g) is achieved for the sample annealed at $1000^0$C having average particle size of 6.8 nm. The high saturation magnetization of the samples suggests the present method is suitable for obtaining nanocrystalline magnetic ferrites which is desirable for practical applications.



*Keywords:*Nanoferrites;sol-gel method;saturation magnetisation;

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## 1. Introduction

Synthesis of magnetic nanoparticles with desired magnetic properties have been attracted much attention in the last few years.

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The properties of ferrite nanoparticles are influenced by composition and microstructure, which are sensitive to distribution of cations among tetrahedral (A) and octahedral sites (B) of the spinel lattice which in turn, depend on synthesis method. Among various spinel ferrites, $CoFe_2O_4$ has received special attraction due to the unique physical properties such as high Curie temperature, large magneto crystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, excellent chemical stability and mechanical hardness (Rajath et al. (2008) and Jing Wang et al. (2006)). These properties could make the cobalt ferrite technologically important and has been used in high density magnetic recording media (Khandekar et al. (2011)), Ferro fluid technology, magnetic resonance imaging enhancement, biosensors, magnetic hyperthermia,(Dong-Hyun Kim et al.(2008) and Morais (2009) ) and gas sensors( Deraz (2010)).

In general cobalt ferrite exists partially inverse spinel structure in which both sites (A and B) contain a fraction of $Co^{2+}$ and $Fe^{3+}$cations, however it is generally accepted that a large fraction of $Co^{2+}$ions are at B-site and the remaining are at A-site. The cation distribution is given by

$$\left(Co_{1-\delta}^{2+}Fe_{\delta}^{3+}\right)_A\left[Co_{\delta}^{2+}Fe_{2-\delta}^{3+}\right]_B O_4^{2-}$$

where δ is a fraction of tetrahedral sites occupied by $Fe^{3+}$ ions, which is known as degree of inversion. The degree of inversion is sensitive to the thermal history of the sample, microstructure and synthesis parameters. Normally annealing temperatures or annealing times are used to control the magnetic properties of cobalt ferrite. However, a direct correlation between microstructure and magnetic response is not obtained due to the variation of cation redistribution. Since magnetic properties of cobalt ferrite depends on heat treatment conditions and synthesis, the capability to optimize and to understand magnetic properties is desirable.

Recently, great efforts have been made by various groups to achieve a fine-tuning of size of ferrite nanoparticles by employing different synthesis techniques and varying experimental parameters such as heating rate, and quantity of chelating agent (surfactants).S.C.Goh et al. (2010) prepared cobalt ferrite nanocrystals directly with no further heat treatment through a simple hydrothermal method. It is observed that with increasing hydrothermal temperature from 120ºC to 300ºC, the average crystallite size improved from 14.53 nm to 26.79 nm respectively. Yue Zhang et al. (2014) synthesized cobalt ferrite nano-particles using combustion method. The particle size varies from 30 nm to > 1μm as a function of annealing temperature. Khandekar et al. (2011) for the first time made an attempt to prepare cobalt ferrite nanocrystallites by combustion method using hexamethylenetetramine (hexamine) as a fuel and the crystallite size is in the range of 19 nm - 21 nm. Shun Hua Xiao et al. (2007) prepared cobalt ferrite nano-particles by low temperature, auto combustion method. With these synthesis techniques, cobalt ferrite of desired size and microstructures can be achieved, but their mass production involves complicated procedures, high reaction temperatures, long reaction times and they are not cost effective. Furthermore, the toxic reagents used in the preparation and the end products will harm the environment. Among synthesis methods, sol-gel method has advantages like mixing of multiple components at an atomic level at low temperatures. The method of preparation results in homogenous precursors and there are no by product effluents. This process is economic, environmental friendly and provides high purity ceramic powder.

In the present work, $CoFe_2O_4$ nanoparticles are prepared through sol-gel method using polyvinyl alcohol (PVA) as a chelating agent. The structural and magnetic properties of the $CoFe_2O_4$ nanoparticles are investigated using X-ray Diffractometer (XRD), FT-IR spectrometer, Transmission Electron Microscope (TEM) and Vibrating sample magnetometer (VSM).

## 2. Experimental Details

### *2.1. Synthesis of cobalt ferrite nanoparticles*

In order to prepare $CoFe_2O_4$ ferrite nanoparticles, analytical grade iron nitrate Fe $(NO_3)_3.9H_2O$ and Cobalt nitrate Co $(NO_3)_2.6H_2O$ are weighed according to the required stoichiometric proportions and dissolved in a minimum

amount of de - ionized water. The cationic solutions are mixed and stirred for 2 hours to improve homogeneity, the resulting solution is known as precursor. The molar ratio of total metal ions to vinyl alcohol monomer units of PVA is maintained at 1:3. The PVA solution (10% W/V) is prepared by dissolving PVA powder in de- ionized water. The PVA solution is prepared by slowly sprinkling PVA powder under constant stirring and this step should be followed to avoid clumping of powder in the water. The clear PVA solution is added to the precursor and dehydrated around 100ºC with a constant stirring rate of 700 rpm. The gelation continued step by step till a slightly red gel type product is formed with the release of reddish brown gas around 100 ºC, where the gel further gets converted into fluffy ferrite mass. The beaker containing fluffy mass is dried in hot air oven for 10 hours. The dried powder is annealed at 400ºC, 500ºC and 1000ºC for 1 hour with a heating rate of 5 ºC/minute in a programmable muffle furnace.

### *2.2. Characterization*

The $CoFe_2O_4$ nanoparticles are characterized using sophisticated techniques to know the structure, particle size and distribution and also to explore other parameters of interest. The crystal structure of the annealed samples is analyzed using X-ray diffractometer of PAN analytical X'pert PRO system with CuKα (λ= 1.5406Aº) radiation as a source. Crystallite size and lattice constant are calculated by considering peak width and peak position of the reflections collected from diffractometer in the 2θ range from 5º to 85º with a step scan of $0.02^o s^{-1}$. The working voltage is 40 KV and the current is 40 mA. The particle size and morphology of the samples is investigated by Transmission electron microscope (TEM) model Tecnai-12, FEI, Netherlands with acceleration voltage 120 KV. A small amount of powder is dispersed into de ionized water and is subjected to an ultrasonification for 10 minutes. A drop of the suspension is placed on a carbon coated copper grid and then dried for about 30 minutes. The average particle size and standard deviation of the particles is obtained by considering nearly 175 particles. Fourier transform infrared spectroscopic study is carried out using Shimadzu FTIR-8400 system in the wave number range of 400 - 4000 $cm^{-1}$ with a resolution of 1-5 $cm^{-1}$. Vibrating sample magnetometer (EV-7 VSM) is used to measure room temperature specific saturation magnetization ($M_s$), coercive force ($H_c$) and remanence ($M_r$) in an applied magnetic field of 15 KOe.

## 3. Results and discussion

### *3.1. X-ray diffraction analysis*

Fig.1 (a-c) shows X-ray diffraction patterns of $CoFe_2O_4$ samples annealed at 400ºC, 500ºC and 1000ºC. The formation of spinel phase is confirmed by comparing XRD patterns with the standard JCPDS card 22-1086. There are no additional peaks related to secondary phase found in the XRD patterns, ensuring phase purity. The samples present broad peaks indicating nanocrystalline nature. The average crystallite size is calculated using Debye Scherrer formula

$$D = \frac{0.9 * \lambda}{\beta \cos\theta}$$

Where λ is the wavelength of X-rays, β is the full width at half maximum after applying correction due to instrumental broadening $\sqrt{\left(\beta_{meas}^2 - \beta_o^2\right)}$ and θ is the Bragg's diffraction angle.

As the annealing temperature increases, the peaks become sharp reflects improved crystallite size and crystallinity (inset Fig.1.). Lattice parameter (a) has been calculated for each peak using equation $a = d\sqrt{h^2 + k^2 + l^2}$. The values of the lattice parameter for each reflected plane are plotted against Nelson-Riley function $F(\theta) = \frac{1}{2}\left[\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right]$ (Mahesh Kumar et al. (2010)).

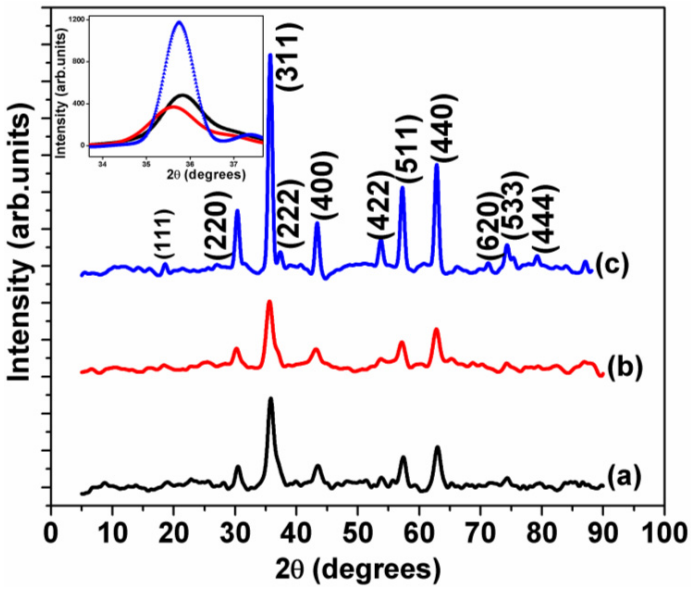


Fig.1 (a) - (c) X-ray diffraction patterns of samples annealed at 400ºC, 500 ºC and 1000 ºC

The lattice constant can be obtained by extrapolating straight line to F (θ) = 0 or θ = 90º.The average crystallite size and lattice constant of the samples is listed in Table 1.The lattice constant for the sample annealed at 400ºC has been found to be 8.3891Aº and is in good agreement with the reported values (Vaidyanathan et al. (2008) and Sonal Singhal et al. (2012)).There is a slight shift of (311) peak towards lower angle side with increasing annealing temperature (Inset of Fig.1). This may be attributed to the fact that on increasing the annealing temperature, a certain number of $Co^{2+}$ ions migrate from octahedral to the tetrahedral sites, accompanied by opposite transfer of equivalent number of $Fe^{3+}$ ions from tetrahedral to octahedral sites in order to relax the compressive strain.

Table.1: Crystallite size, Strain, Particle size and Lattice constant for samples annealed at temperatures such as 400ºC, 500ºC and 1000ºC.

| Annealing Temperature (ºC) | Crystallite Size (nm) | Strain | Particle size (nm) (TEM) | Lattice Constant (Aº) |
|---|---|---|---|---|
| 400 | 5 | 0.0673 | 4.3 | 8.3891 |
| 500 | 5.7 | 0.0424 | 5.8 | 8.3936 |
| 1000 | 7.5 | 0.0323 | 6.4 | 8.3999 |

### *3.2. Tem analysis*

Fig.2 shows TEM microstructures of the samples and least square fit of the log normal distribution to the measured points obtained from the TEM micrographs. From these results the average particle size and standard deviation in measuring average particle size is found. For this purpose nearly 175 particles are taken in to consideration. From TEM microstructures, it has been observed that the majority of particles are spherical and they are monodispersed. Particle size varied in the range of 2 - 8 nm for the sample annealed at 400ºC and 2 - 11 nm for the sample annealed at 1000ºC. The average particle size of the samples matches well with the crystallite size obtained from XRD.

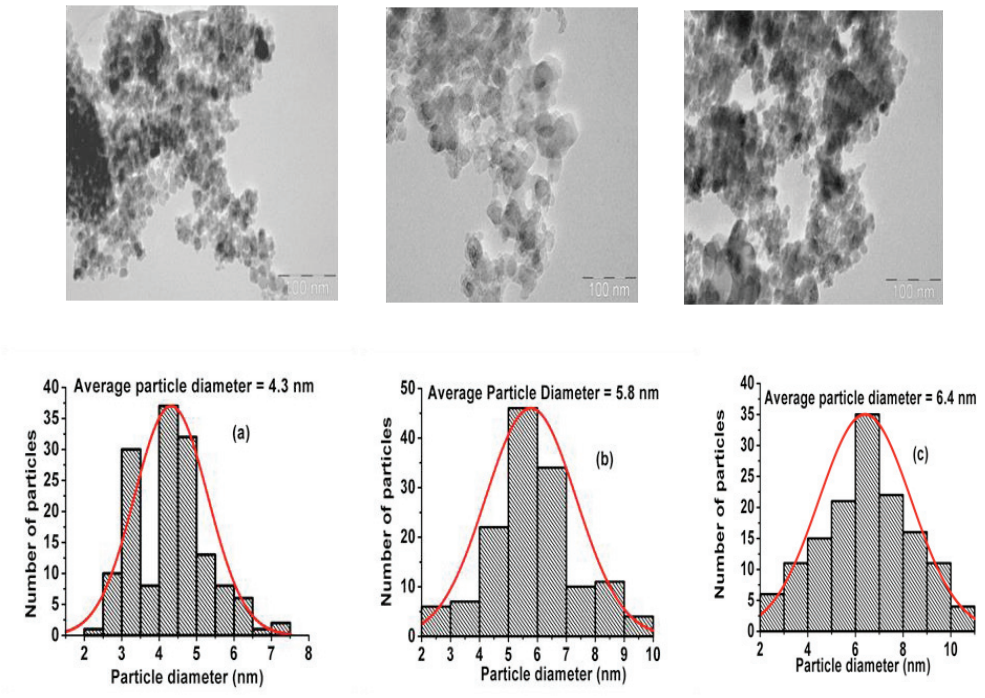


Fig.2.TEM microstructure and corresponding log normal distribution curves of samples annealed at (a) 400°C (b), 500 °C and (c) 1000 °C

### *3.3. FTIR spectroscopic analysis*

The FT-IR spectroscopic technique is useful to know the structure formation. FT-IR spectra can offer information about redistribution of cations between octahedral and tetrahedral sites of the inverse spinel structure in $CoFe_2O_4$. It is also useful to determine the local symmetry in crystalline solids, ordering phenomenon in spinels and presence/absence of $Fe^{2+}$ ions (Rajesh Iyer et al. (2009)). Fig.3 shows FT-IR spectra of $CoFe_2O_4$ nanoparticles annealed at 400°C, 500°C and 1000°C. Two prominent metal-oxygen bands $\nu_1$ and $\nu_2$ have been observed in spinel ferrites. The higher frequency band $\nu_1$ is assigned to the vibrations of the bond between the oxygen ion and the tetrahedral metal ion $M_{tetra} \leftrightarrow O$. The lower frequency band $\nu_2$ is assigned to vibrations of the bond between Oxygen ion and octahedral metal ion $M_{octa} \leftrightarrow O$ (Abdülhadi Baykal et al. (2008)).

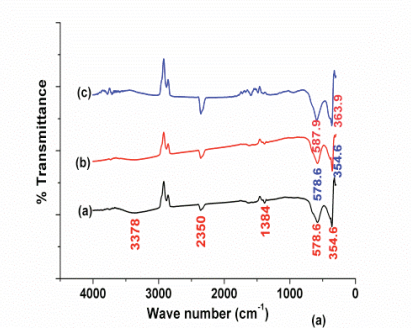


Fig.3.FTIR spectra of samples annealed at 400°C, 500 °C and 1000 °C

Waldron (1955) assigned the high-frequency band to the tetrahedral group (575 $cm^{-1}$region) and the low frequency band to octahedral group (374 $cm^{-1}$). The low frequency band in the range of 370-380 $cm^{-1}$ is related to the divalent octahedral metal complexes (Hemeda (2004)).The absorption bands at 355 $cm^{-1}$ and 579 $cm^{-1}$ corresponds to vibrations of Co↔O and Fe↔O respectively. The absorption bands observed within this limit reveal formation of spinel structure. For the sample annealed at 1000ºC, the absorption bands corresponding to Co↔O and Fe↔O bonds are shifted to 364 $cm^{-1}$ and 588 $cm^{-1}$ respectively. The broad band at about 3378$cm^{-1}$ is ascribed to stretching mode of O-H group in the free and absorbed water and PVA (Mozaffari et al. (2010)). The peak observed at 1384 $cm^{-1}$ for the samples annealed at 400ºC, 500ºC corresponds to asymmetric stretching vibration of $COO^-$ group. This peak confirms coordination of metal ions by carboxylate groups and its intensity decreases with increasing annealing temperature (Mehrnaz Gharagozlou (2009)). The functional groups O-H, $COO^-$ disappear for the sample annealed at 1000ºC due to loss of water and decomposition of poly (vinyl alcohol) at high temperature heat treatment. The absence of organic bands in the FTIR spectrum annealed at 1000ºC could be ascribed to the decomposition of organic compounds and formation $CoFe_2O_4$ ferrite.

### *3.4. Magnetic properties*

Fig.4 shows room temperature hysteresis loops for the samples annealed at 400ºC, 500ºC and 1000ºC respectively. The magnetic parameters such as saturation magnetization ($M_s$), coercivity ($H_c$), and remanent magnetization ($M_r$) from the hysteresis loops are listed in Table 2. It has been observed (From Table 2) that the saturation magnetization ($M_s$) increases with increasing annealing temperature due to increase of particle size (Chauhan et al. (2004)).The value of saturation magnetization ($M_s$) increased from 42.42 emu/g to 78.06 emu/g with increasing annealing temperature. This is due to gradual increase of crystallinity and particle size. The observed saturation magnetization ($M_s$) for the sample annealed at 1000ºC is in good agreement with the reported values (Sonal Singhal et al. (2006)).

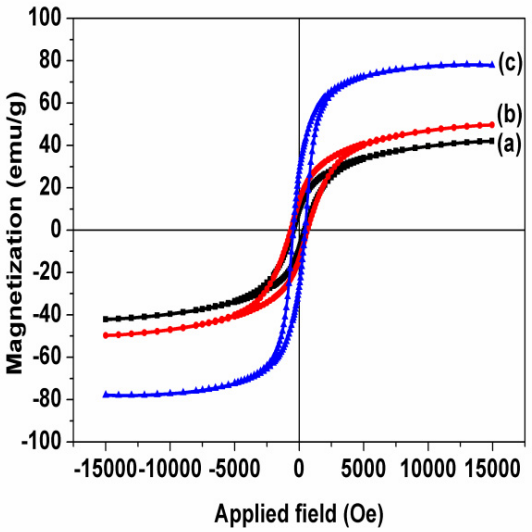


Fig.4 Hysteresis curves of samples annealed at (a) 400ºC (b), 500 ºC and (c) 1000 ºC

The variation of saturation magnetization with annealing temperatures is possibly due to the rearrangement of the cation distribution, i.e., the exchange of $Co^{2+}$ and $Fe^{3+}$ ions from octahedral and tetrahedral sites and vice versa Mohamed et al. (2010).The low values of $M_s$ for the samples annealed at 400ºC and 500ºC could be attributed to surface distortion which destabilizes the collinear spin arrangement and producing various canted spin structures at the surface. This effect is especially prominent for ultrafine particles due to their large surface to volume ratio (Chiu et al. (2008)). The other reason for low values of magnetization is due to, the magneto crystalline anisotropy of the

particles, which depends on the degree of crystallinity of the nanoparticles. As can be observed in the XRD pattern, the samples annealed at 400ºC, 500ºC are partially crystalline. Hence, a large proportion of crystal defects, dislocations and lattice strain can occur within the lattice. This will cause a significant reduction of magnetic moment within the particles. This surface effect becomes less significant if the annealing temperature is above 700ºC (Maaz et al. (2007)).

Table 2: Saturation magnetization, Remanent magnetization and Coercivity for the samples annealed at temperatures such as 400ºC, 500ºC and 1000ºC.

| Annealing temperature ($^{O}$C) | Saturation Magnetization $M_S$ (emu/g) | Remnant magnetization $M_r$ (emu/g) | Coercivity $H_C$ (Oe) |
|---|---|---|---|
| 400 | 42.42 | 8.94 | 434.08 |
| 500 | 49.72 | 13.72 | 650.63 |
| 1000 | 78.06 | 27.4 | 461.33 |

The coercivity of samples is studied as a function of annealing temperature. It has been observed that coercivity increases with annealing temperature then decreases, which is in good agreement with the literature (El-Okr et al. (2011)).The reversal of the magnetization in a single domain particle occurs via coherent rotation of magnetization, where there is no domain wall motion. Since the domain wall motion is easier than the rotation of the magnetization, the coercivity is expected to be larger in the nano range. Thus increase in particle size on heating, will increase the anisotropy energy, which in turns results in increase in coercivity. The decrease in coercivity for the sample annealed at $1000^0$C could be attributed to either of two reasons. Firstly, it may be due to the expected crossover from single domain to multidomain behaviour with increasing particle size. Secondly, such an effect can arise from combination of surface anisotropy and thermal energies (Maaz et al. (2007)).

Table 3: Magnetic properties of $CoFe_2O_4$ reported in literature

| Synthesis technique | Average particle size(nm) | Saturation magnetization ($M_S$) (emu/g) | Coercivity ($H_C$) (Oe) | References |
|---|---|---|---|---|
| Sol-gel, PVA as chelating agent | 6.4 | 78.06 | 461.3 | Present work |
| Solution combustion | 11 | 39 | 1369 | Jnaneshwara et al. (2013) |
| Hydrolysis reaction in a micelle system | 36.2 | 72 | 670 | Chiu et al. (2008) |
| Sol-gel auto- combustion | 26 | 63.5 | 2478 | Aghav et al. (2011) |
| Reverse micelle process | 25 | 72 | 45 | TahminehSodaee et al. (2013) |
| Co-precipitation | 16.4 | 69.67 | 775.27 | Vadivel et al. (2014) |

## 4. Conclusions

Ultra-fine Cobalt ferrite nanoparticles have been synthesized by a simple sol-gel method using PVA as chelating agent. It is cost effective, uses relatively low reaction temperatures and is environmentally friendly. The influence of annealing temperature on the magnetic properties and crystallite size of the samples is investigated with the aim of tuning magnetic properties and greatly expanding the range of applications. The results show the present method

facilitates magnetic tunability of the cobalt ferrite nanoparticles by using proper thermal treatment. The cobalt ferrite samples obtained by this method have the single phase spinel structure with good magnetic properties. Particle size of the samples increased with increasing annealing temperature. The magnetic properties of the samples are strongly affected by the annealing temperature as a consequence there is a gradual increase in the crystallinity and particle size. The sample annealed at 1000ºC manifests high saturation magnetization, narrow hysteresis loop and low coercivity and is suitable for RF heating in hyperthermia treatment.

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