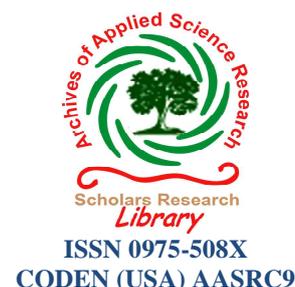




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Synthesis and Characterization of Highly Monodisperse CoFe_2O_4 Magnetic Nanoparticles by Hydrothermal Chemical Route

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ABSTRACT

Cobalt ferrite (CoFe_2O_4) nanoparticles were prepared by hydrothermal-chemical route and annealing treatment. It was found that the characteristics of the products depend on annealing temperature and coexistence of the capping molecules in the reactant solutions. The formations of highly monodisperse spherical nanoparticles were confirmed by X-ray diffraction and scanning electron microscope. The functional groups of the magnetic materials were determined by FTIR spectrum. Energy dispersive X-ray results confirmed the ratio of the transition metal atoms in each material according to the nominal stoichiometry. The VSM studies showed that the coercivity and saturation magnetization of CoFe_2O_4 were found to be maximum for the reported samples. The magnetic hysteresis obtained at room temperature revealed smaller effective magnetic anisotropy. In order to investigate the effect of degree of crystallinity on the mean crystalline size of CoFe_2O_4 nanocrystals and on the magnetic properties, a series of CoFe_2O_4 sample with different degree of crystallinity and size were prepared by varying the synthesis and subsequent calcination temperatures.

Keywords: CoFe_2O_4 , Magnetic nanoparticles, SEM, VSM.

INTRODUCTION

Ferrite nano-particles have shown a growing interest in recent years due to their specific magnetic and electrical properties. They have potential applications in high-density magnetic recording devices especially those with high coercivity in electronic devices and in medicine [1-3]. One of the most recent applications studied is the complete decomposition of CO_2 [4]. This decomposition has been significantly improved by developing ultra fine ferrite particles with high surface area as a catalyst [5]. Among spinel ferrites, CoFe_2O_4 has cubic spinel structure. CoFe_2O_4 has been extensively studied because of its interesting magnetic properties. It has remarkable chemical stability and mechanical hardness as well as high coercivity (5400 Oe) and

moderate saturation magnetization (≈ 80 emu/g) [6]. The physical and chemical properties of spinel nano-particles are greatly affected by the synthesis route. Therefore a large number of research reports are available concerning the preparation techniques.

In order to investigate the effect of degree of crystallinity and mean crystallite size of CoFe_2O_4 nanocrystals on the magnetic properties, a series of CoFe_2O_4 samples with different degree of crystallinity and mean crystallite size were produced by varying the synthesis and subsequent calcination temperatures. These CoFe_2O_4 nanocrystals were synthesized by a wet chemical co-precipitation approach [8]. The chemical co-precipitation is the most widely used method due to its high yield and simplicity in producing ultrafine magnetic nanocrystals. To date, there are two different chemical co-precipitation methods that have been used to produce CoFe_2O_4 nanocrystals, i.e., with and without oxidizing agent. Previous studies reported the precipitation of CoFe_2O_4 nanocrystals by mixing Fe^{2+} , Co^{2+} and NaOH in the presence of oxidizing agent such as H_2O_2 [7] and KNO_3 [8,4]. The oxidizing agent is required for the formation of Fe^{3+} from Fe^{2+} as precursor of the formation of CoFe_2O_4 . However, the coexistence of Fe^{2+} and Fe^{3+} ions resulted in the formation of magnetite (Fe_3O_4) and CoFe_2O_4 which will subsequently affect the purity of the products. In order to avoid this adverse effect, precipitation has been carried out without using oxidizing agent [9]. Previous reports indicate that the synthesis temperature plays an important role in controlling the size of the CoFe_2O_4 which will significantly influence the magnetic properties of the products. Besides a number of attempts have also been made to improve the magnetic properties of the CoFe_2O_4 nanocrystals by subsequently calcinations of the as-precipitated CoFe_2O_4 naocrystals [7]

The magnetic properties of CoFe_2O_4 nano-particles are more complicated than those of the bulk materials and show size dependence. For example, saturation magnetization(M_s) was found to be smaller than that of the bulk one and decrease with the decrease in particle size due to the disorder canting spins on the surfaces [11]; H_c was observed to reach a maximum value as the crystallite size is near the single-domain size [8]. However, it is noteworthy that besides the crystallite size, the magnetic properties of CoFe_2O_4 nano-particles also show much dependence on the synthesis methods and reaction conditions. For instance, as for the CoFe_2O_4 nano-particles synthesized by the co-precipitation method, the H_c above 4000 Oe, a value much larger than that of the CoFe_2O_4 nano-particles fabricated by other methods [9,12] and the (M_s) was found to decrease with the increase in particle sizes by prolonging digestion time or by increasing the concentrations of NaOH solutions. Even though significant discoveries on the size-dependent magnetic properties for CoFe_2O_4 nano-particles synthesized by the wet chemical methods have been reported, the corresponding mechanism is still in debate. Till recently, the decreased M_s and the enhanced H_c were thought to be related with the formation of some impure phase, such as the paramagnetic β -FeOOH in the final products synthesized using the NaOH solutions with higher concentrations. However, some- times the situation is contrary. There are other reports in the hydrothermal synthesis of CoFe_2O_4 nano-particles, using the KOH solutions with high concentrations seem to inhibit the formation of β -FeOOH and favor the synthesis of single-phase CoFe_2O_4 [13]. Furthermore, some micro cosmic factors, such as the microstructure and composition, may also have greater impact on the magnetic properties; however they have not been studied in detail yet. Thus, efforts to ascertain the mechanism on this surprising process-dependence of the magnetic properties are far more difficult. In the present work, the cobalt ferrite nanoparticles were synthesized by hydrothermal co-precipitation method and the prepared

samples were subsequently annealed at different temperatures. In this work an attempt has been made to study the mechanism for the size dependence of magnetic properties.

MATERIALS AND METHODS

Experimental Procedure

2.1 Synthesis

The materials used in the synthesis of CoFe_2O_4 nanoparticles were of analytical grade. The chemicals were procured from Merck 98 % purity and were used without any further purification. The cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 60% aqueous milli-Q solution of ethylene glycolic acid ($\text{C}_2\text{H}_6\text{O}_2$) were used in the preparation of nanocrystalline CoFe_2O_4 .

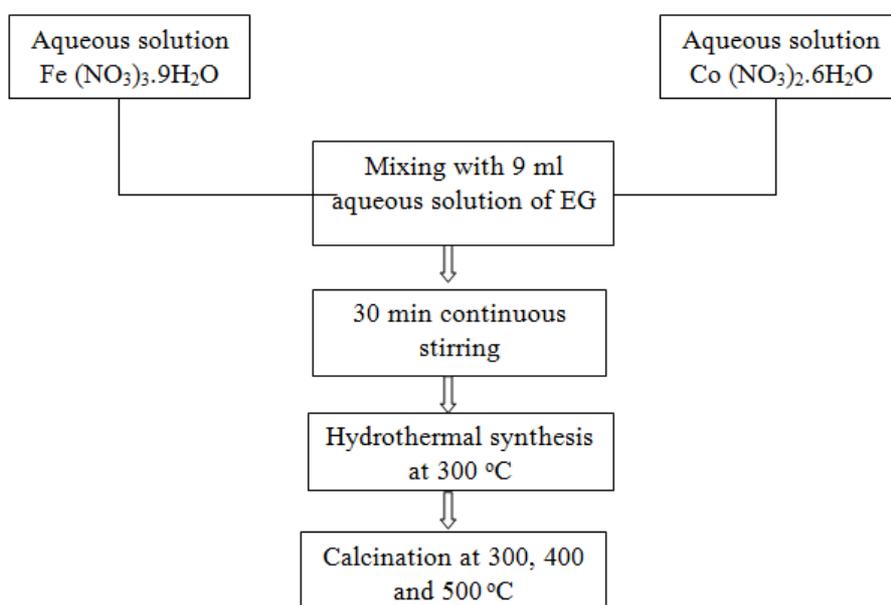


Figure1. Flow chart showing the EG assisted hydrothermal synthesis of CoFe_2O_4

A step wise description of synthesis procedure of CoFe_2O_4 powder is shown in figure 1. In a typical synthesis 2.91 g of cobalt nitrate was dissolved in 40 ml of milli-Q water and ferric nitrate 0.8 g was dissolved in 40 ml of water. Both solutions were mixed together and further 9 ml of Ethylene Glycolic acid (EG) was added drop by drop of the above solution with continuous stirring. The prepared EG mixed solution was transferred in to a Teflon coated autoclave and heat treated in the furnace at 300 °C for 5hrs. After the hydrothermal reaction time the autoclave was cooled at room temperature naturally. Finally a dark powder was obtained. It was annealed at three different temperatures 300, 400 and 500 °C. According to the present experimental results, the following reactions may be involved in the synthesis process of CoFe_2O_4 in water. Dissolution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water



CoFe₂O₄ was synthesized from the reaction of Fe(NO₃)₃·9H₂O and Co₃O₄ obtained by the reaction of Co(NO₃)₂·6H₂O in water.

RESULTS AND DISCUSSION

3.1 X-ray Diffraction Analysis

XRD diffraction patterns of the as-prepared and calcined CoFe₂O₄ nanocrystals are presented in figure 4.11a, b, and c. These patterns confirm the formation of cubic spinel type lattice of CoFe₂O₄, which matches well with the standard XRD pattern (JCPDS No: 22-1086). All samples were analyzed using a X-ray diffractometry (Model-Rich Schiffer) with CuK_α radiation ($\lambda=1.5406 \text{ \AA}$). The samples were continuously scanned at a scanning rate $0.02^\circ \text{ S}^{-1}$ in the 2θ range of $10\text{--}80^\circ$. Further the XRD pattern consists of fairly broad but still resolved peaks superimposed on a smoothly varying intensity. All peaks correspond to a cubic spinel type lattice (space group Fd3m) with parameter $a=0.821 \text{ nm}$. There are no other detectable traces of extra crystalline or amorphous phases. The considerable broadening of all diffraction peaks, amounting up to 1° full width at half maximum (FWHM) for the strongest peaks at 35° phase (311) indicates that the investigated samples consists of high crystalline and quite small crystallites in size. These results match well with the previous report [13]. The presence of strains and stacking faults can also be exempted. This is to be expected considering the low-temperature sample preparation technique employed.

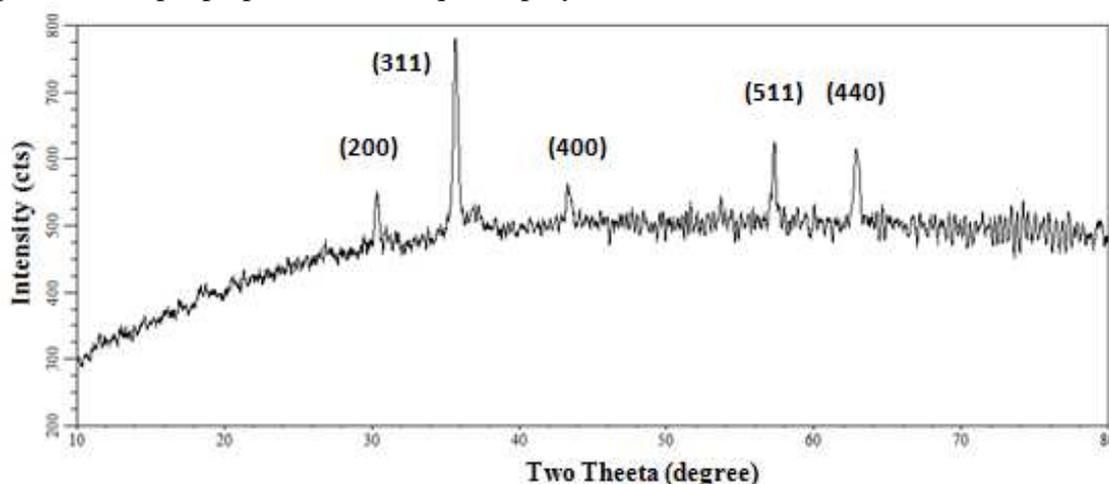
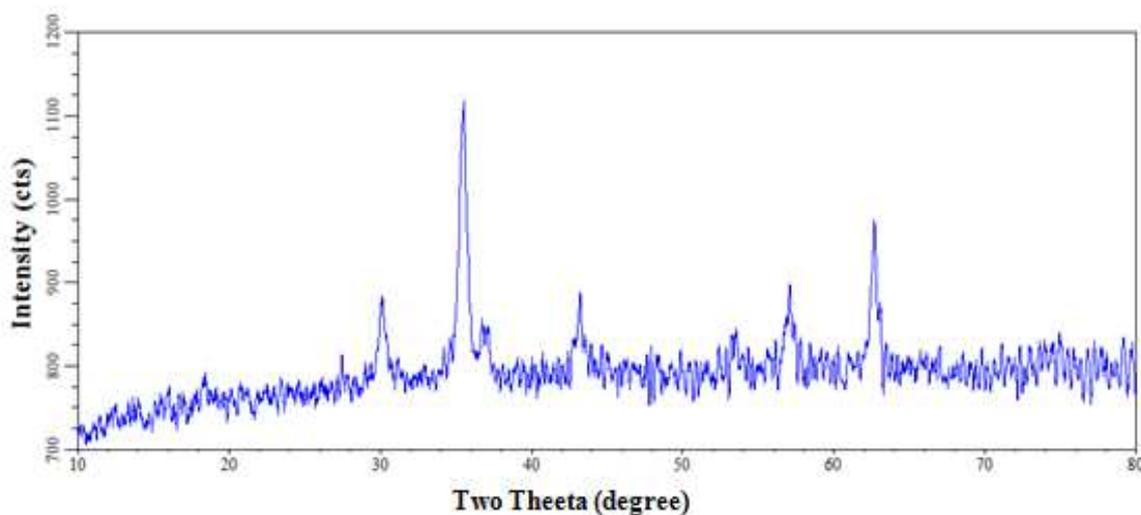
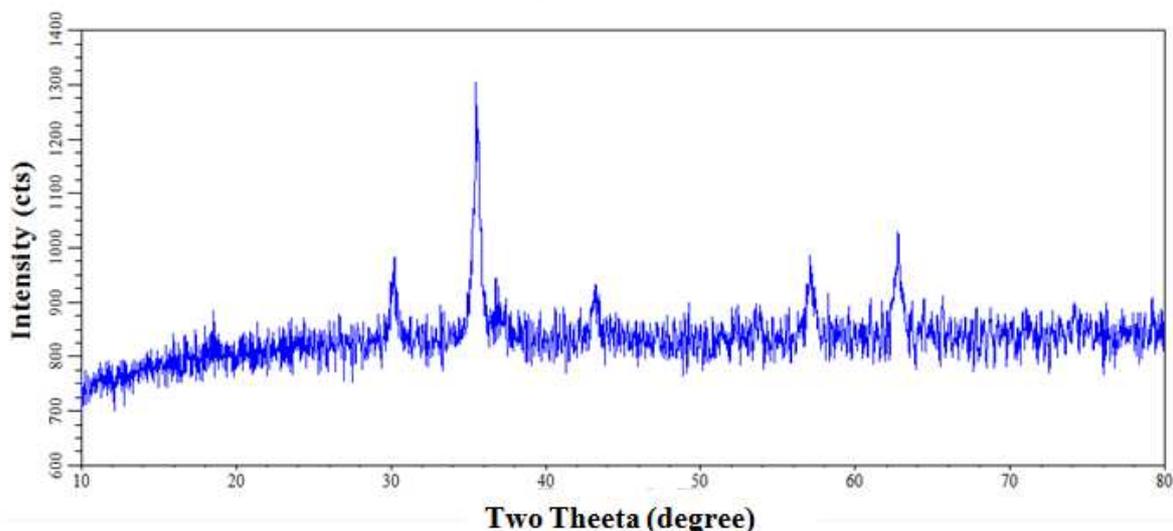


Figure 1a. X-ray diffraction pattern of CoFe₂O₄ sample at 300 °C

The average particle size was calculated from line broadening using the Debye-Scherrer equation

$$d = \frac{0.9\lambda}{\beta \cos \theta}$$

Where, d is the particle diameter and β is the full width at half maximum of the diffraction line. For this calculation the plane (220), (311), (400), (511) and (440) peaks were deconvoluted to Lawrence curves using nonlinear curve fitting by Autox software and the average diameter were estimated at three different temperatures 300 °C, 400 °C, 500 °C as 22 nm, 19 nm and 17 nm respectively. The crystalline size is also in good agreement with the SEM analysis.

Figure 1b. X-ray diffraction pattern of CoFe₂O₄ sample at 400 °CFigure 1c. X-ray diffraction pattern of CoFe₂O₄ sample at 500 °C

3.2 FT-IR spectroscopy analysis of as prepared CoFe₂O₄

The fourier transform infrared spectra analyses were carried out in an FT-MIR Nicdet Magna-IR550 series II spectrometer, capable of measuring at 4 cm⁻¹ resolution in the spectral range covering 4000-400 cm⁻¹ a range commonly used in a first determination step. The sample pellets were prepared using 100 mg of dry KBr and 2 mg of the obtained CoFe₂O₄ nanopowder. The FTIR spectra of the CoFe₂O₄ materials are shown in figure 4.2 a,b,c in the three different temperature range. The pattern confirms the presence of cobalt ferric and hydroxides. The bands at ~ 3414 cm⁻¹ have been assigned to antisymmetric and symmetric OH stretching vibration of lattice water. Adsorbed water is featured by the bands at 1622-1383 cm⁻¹ assigned to the $\delta_{\text{H-O-H}}$ bonding mode. The bands at 2924-2335 cm⁻¹ are assigned to C-O stretching vibration. These peaks are the characteristic absorption bands assigned of Ethylene Glycolic (EG) acid. The difference in the absorption position in octahedral and tetrahedral complexes of CoFe₂O₄ crystal

is due to the difference in distance between $\text{Fe}^{3+}\text{-O}^{2-}$ in the octahedral and tetrahedral sites. The XRD results and FTIR results confirms the presence of impurity free nanocrystalline CoFe_2O_4 .

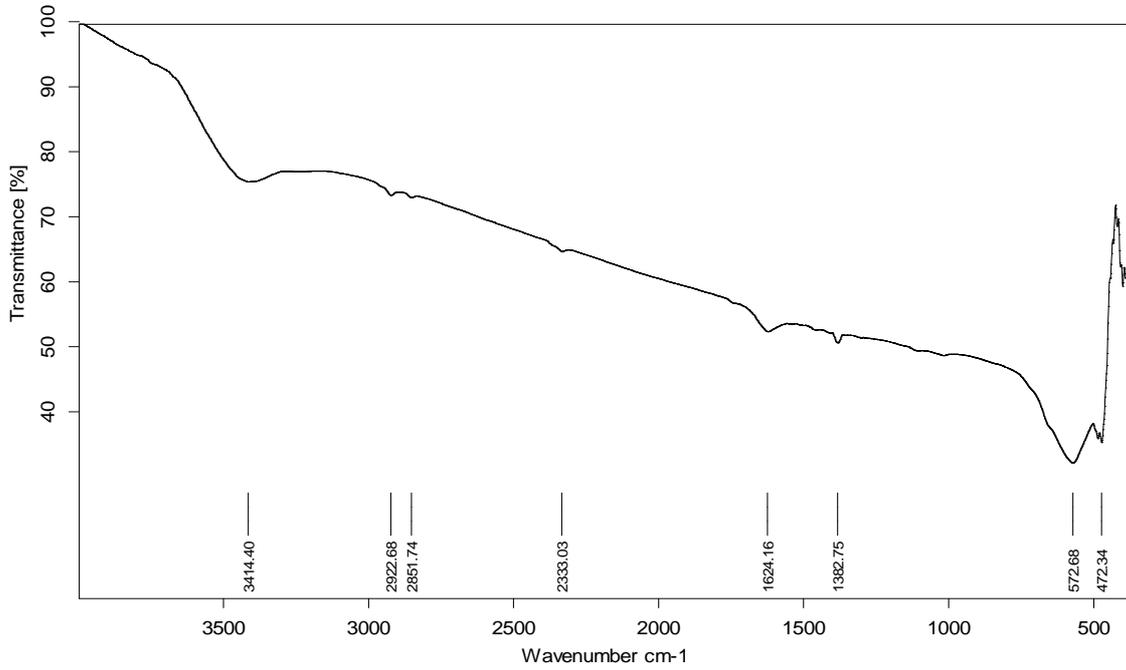


Figure 2a. FTIR Spectrum of CoFe_2O_4 sample at 300 °C

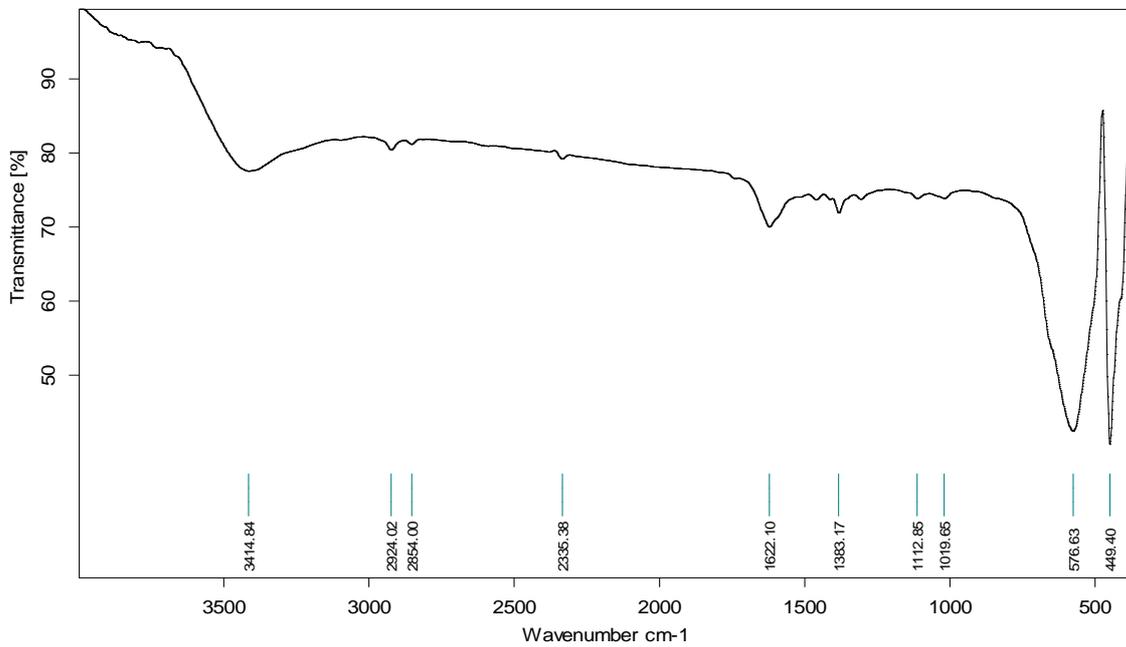


Figure 2b. FTIR Spectrum of CoFe_2O_4 sample at 400 °C

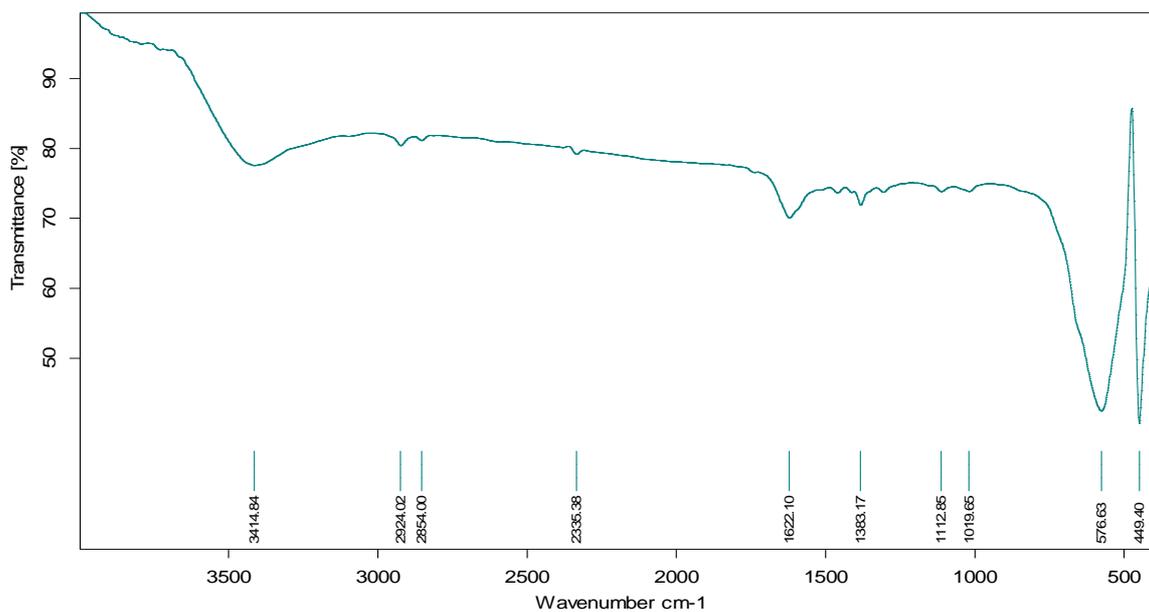


Figure 2b. FTIR Spectrum of CoFe_2O_4 sample at $500\text{ }^\circ\text{C}$

3.3. Morphological behavior of CoFe_2O_4

The structural morphology of nanoparticles was investigated through SEM. Figure a-c shows the SEM images of CoFe_2O_4 nanoparticles. The SEM images show that the CoFe_2O_4 nanoparticles prepared by hydrothermal method have uniform, monodispersive spherical structure morphology with a narrow size distribution of particles. The morphology of the crystals, particles size and the energy dispersion X-ray analysis (EDX) are studied by a scanning electron microscopy (model Joel Jem 3010).

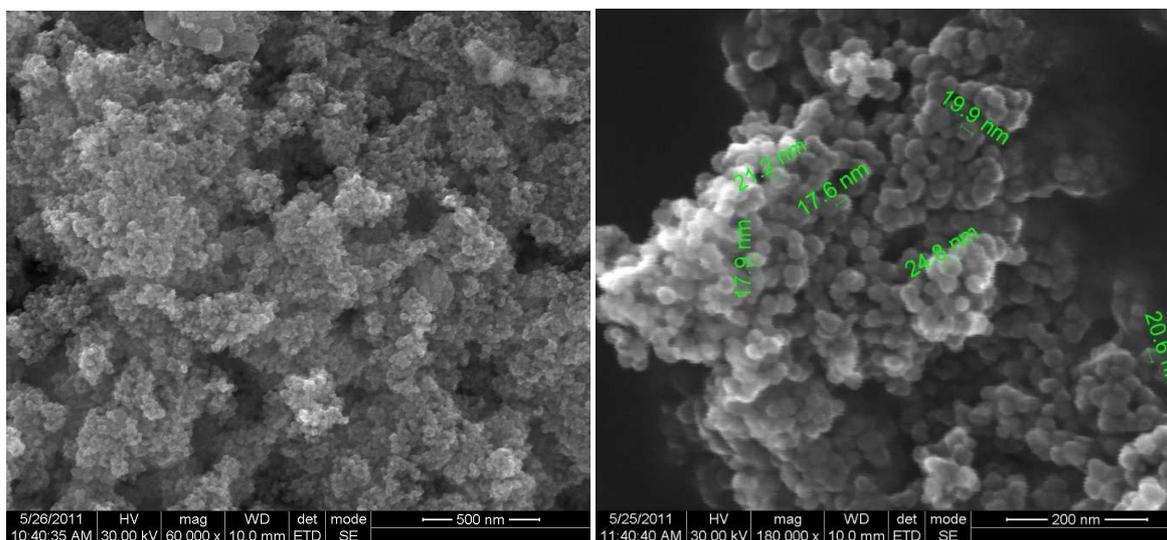


Figure 3a. SEM photograph of CoFe_2O_4 nanoparticles at $300\text{ }^\circ\text{C}$

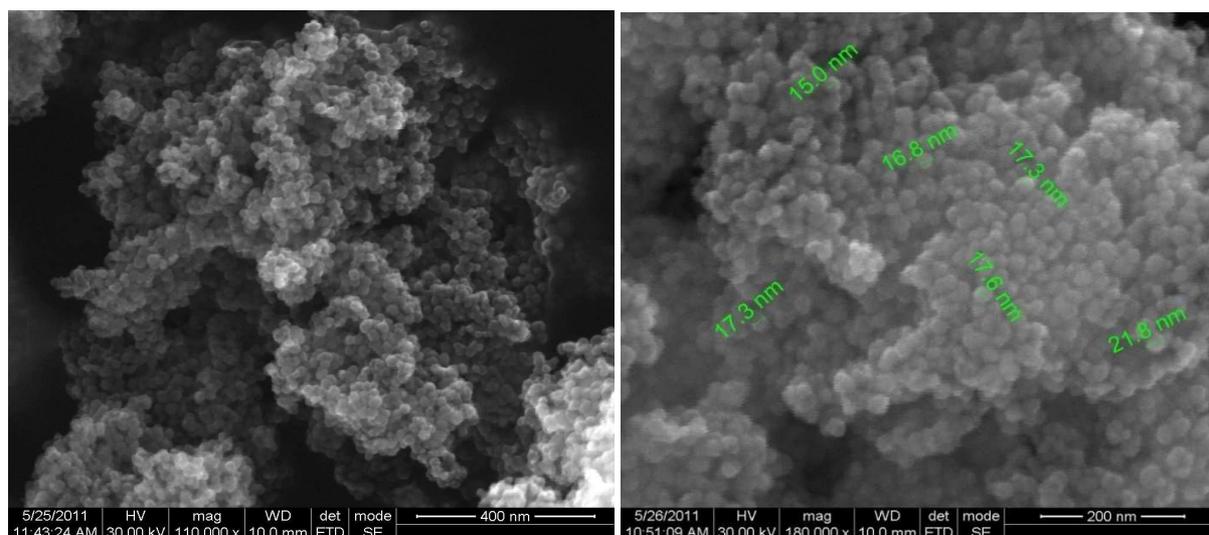


Figure 3b. SEM photograph of CoFe_2O_4 nanoparticles at 400 °C

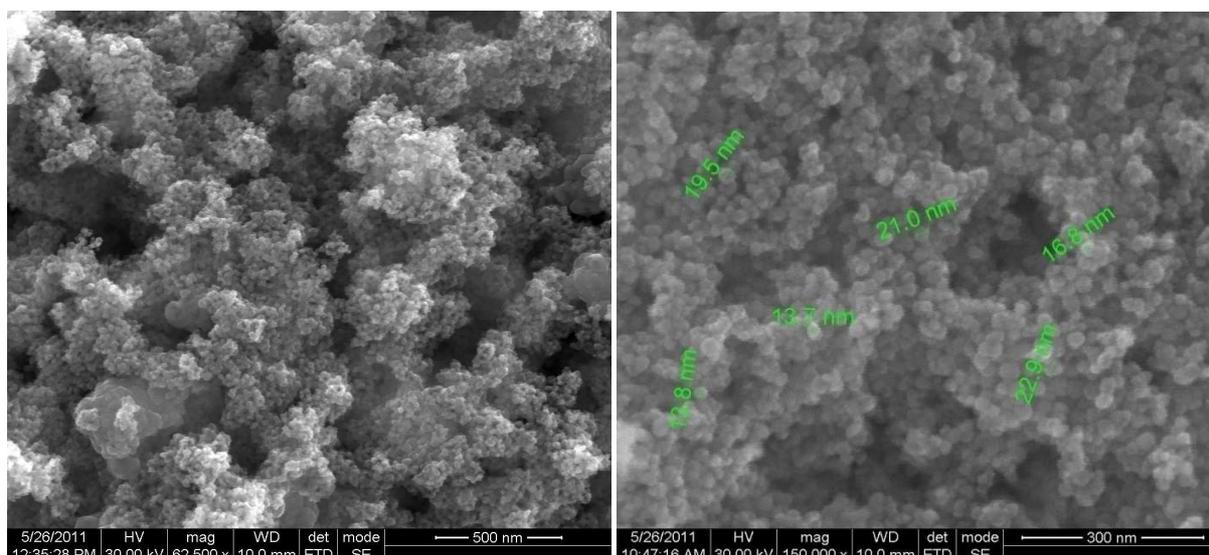


Figure 3c. SEM photograph of CoFe_2O_4 nanoparticles at 500 °C

The uniform spherical morphology of nanoparticles obtained in the temperature range of 300-500 °C is shown in figure (a,b,c). The product appeared highly monodisperse spherical morphology and size is 22 nm, 19 nm, 17 nm at 300 °C, 400 °C and 500 °C respectively. The annealing temperature increases and the particles size decreases simultaneously. From the morphology it is interesting to note that when temperature increases the shape does not change but affects only the radius of the nanoparticles. In this experiment, the Ethylene Glycolic (EG) acid was used for getting spherical shape nanoparticles. The temperature and EG plays an important role in getting spherical shapes morphology for the nanoparticles and reduction in the particle size. This result is exactly matching with the XRD Debye-scherrer equation.

The obtained results at various temperatures agree with the nucleation theory. At subcritical conditions, reaction takes place to produce monomers during the heating period. Subsequently, the reaction gradually proceed to increases the concentration of monomer in the reaction and nucleation occurred when the monomer concentration went beyond the saturation point [6,7]. As a result, the crystals grow with increasing temperature and the solubility of metal oxides gradually decreases and drops to an extremely low level at the critical temperature. Particles formed at lower temperature could dissolve again to re-crystallize at constant temperature (390 °C).

3.3.1 EDAX Spectrum

Energy dispersive X-ray results confirmed the ratio of the transition metal atoms in each material according to the nominal stoichiometry. The atomic ratio of Fe:Co for the entire calcined sample (Figure 4) is maintained at ~ 2:1. These results revealed the sustained spinel structure of the CoFe_2O_4 crystal at low calcinations temperature.

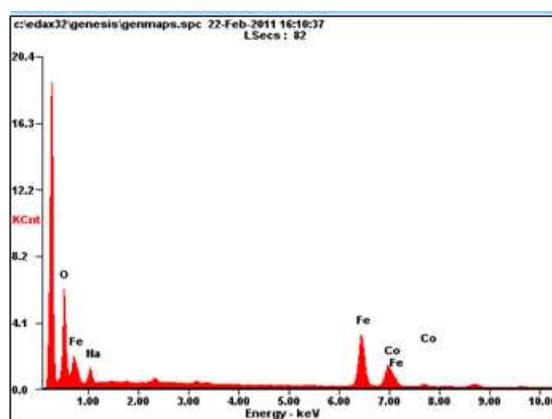


Figure 4. EDAX line scanning spectrum of CoFe_2O_4

3.4 Magnetic properties of the products

The magnetic properties of the CoFe_2O_4 nanoparticles were measured through vibrating sample magnetometer (VSM) at a maximum applied field of 20,000 Oe at room temperature. The hysteresis loops of as prepared samples at different temperature 300 °C, 400 °C and 500 °C the sample code are sample 1, sample 2 and sample 3 respectively are shown in figure 5. The saturation magnetization (M_s) of the sample 1, sample 2 and sample 3 are 58, 62 and 65 emu/g respectively. The coercivity (H_c) are 253, 245 and 233 Oe for the sample annealed at 300 °C, 400 °C and 500 °C respectively, which is higher than that of bulk CoFe_2O_4 nanoparticles[14]. It is generally expected as the particle size decreases, H_c increases. This may be due to the low temperature in the synthesis procedure. The difference in M_s may be due to the difference in size of the nanoparticles. As for the CoFe_2O_4 synthesized by co-precipitation method, the decrease in M_s was ascribed to the existence of impure phase such as $\beta\text{-FeOOH}$ as reported by [12]. But here the small M_s cannot be simply ascribed to the formation of impure phase. It was also reported that in CoFe_2O_4 nano-particles the decreased M_s and the enhanced H_c are related with the disorder canting spins (spin-glass-like) on the surfaces due to the coordination- number imperfection; however, the CoFe_2O_4 nanoparticles with similar sizes synthesized by other methods generally have much larger M_s and drastically smaller H_c [13].

Therefore, it can be concluded that the magnetization in these samples is contributed from two parts: one is the rotation of spins in the inner crystals under the small fields (the technical magnetization) and the other is the flip of the spins distributed on the surfaces and in the outer layers in high fields (the paramagnetic magnetization). The spins in the inner crystals also have the ferromagnetic magnetization, which, however, is much smaller due to the stronger exchange interactions in the intact lattice. In the present case the annealing temperatures show great impact on the magnetic properties, which are associated with the changed valance of the cobalt ions, size and the morphologies of the nanoparticles. It is very well reported in literature that the magnetic properties of nanosize particles depend on the preparation method and the particle size.

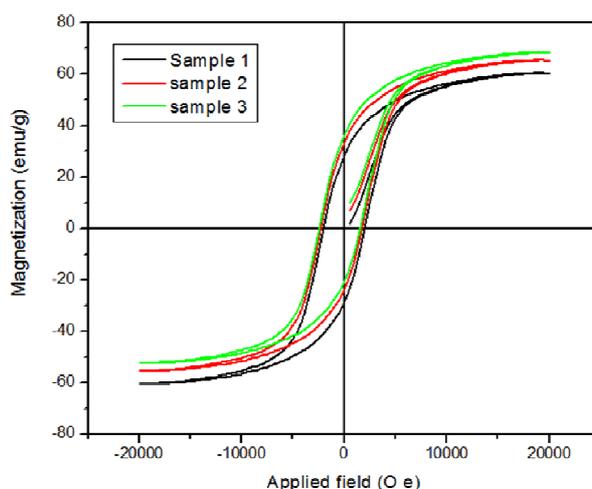


Figure 5. Hysteresis loop of CoFe_2O_4 nanoparticles prepared by hydrothermal method

CONCLUSION

The lower synthesis and subsequent calcinations temperature have resulted in greater degree of crystallinity with lesser mean crystalline size of CoFe_2O_4 nanocrystals. FT-IR and XRD results confirm the preparation of impurity free nanocrystalline material. The SEM images shows that the CoFe_2O_4 nanoparticles prepared by hydrothermal method have uniform; monodisperse spherical structure morphology with a narrow size distribution of particles. The annealing temperature increases abusively the particles size decreases simultaneously. Further the SEM results reveals that EG plays an important role in getting spherical shape morphology nanoparticles and reduction in particles size. The VSM results indicate saturation magnetization of (M_s) 58, 62 and 65 emu/g and the coercivity of sample is decreases with annealing temperature of 300 °C, 400 °C and 500 °C respectively. The synthesized nanoparticles can be used in several technological applications such as soft magnets, low loss materials at higher frequencies and magnetic fluids.

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