

Synthesis and characterization of low temperature superparamagnetic cobalt ferrite nanoparticles

Kamlesh V. Chandekar*, K. Mohan Kant

Department of Applied Physics, Visvesvararya National Institute of Technology, Nagpur 440010, India

*Corresponding author, Tel: (+91) 8275866144; E-mail: k.mohankant@gmail.com

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Abstract

Cobalt ferrite (CoFe_2O_4) nanoparticles were synthesized by co-precipitation route at 80 °C. X-ray diffraction pattern (XRD) confirmed cubic inverse spinel structure of CoFe_2O_4 nanoparticles. The average crystallite size of CoFe_2O_4 nanoparticles estimated by X-ray line profile fitting was 12 ± 2 nm for high intensity peak (311). The particle size, distribution and surface morphology was estimated using Transmission electron microscopy (TEM) with average particle size of 16 ± 2 nm. Raman spectra of CoFe_2O_4 nanoparticles exhibits phonon modes corresponding to tetrahedral sites (679 cm^{-1}) and octahedral sites (465 cm^{-1}) respectively. The saturation magnetization M_s for CoFe_2O_4 sample is found to be 63 and 82 emu/g at 300 K and 10 K respectively. The cubic magnetic anisotropy constant K_1 and saturation magnetization M_s are obtained by fitting M versus H isotherm to the saturation approach law. By fitting, K_1 and M_s is $2.16 \times 10^5 \text{ J/m}^3$ and 66 emu/g respectively at 300 K. The cubic magnetic anisotropy constant $K_1 = 5.49 \times 10^5 \text{ J/m}^3$ is evaluated at blocking temperature of 144 K. The particle size and L - S coupling is responsible for superparamagnetic behaviour of CoFe_2O_4 nanoparticles. Fitting of FC curve provides Curie temperature at $T_c = 823 \text{ K}$ using modified Bloch's law for CoFe_2O_4 nanoparticles. Tunable particle sizes by controlling the magnetic anisotropy and L - S coupling will tailor magnetic properties and usage in bio-medical applications. Copyright © 2017 VBRI Press.

Keywords: CoFe_2O_4 ; co-precipitation; L - S coupling; superparamagnetism; anisotropic constant.

Introduction

Metal oxides (MFe_2O_4 , $\text{M} = \text{Fe, Co}$) are magnetic materials with cubic spinel structure which have been used extensively for various applications due to their prominent magnetic properties. Among the transition metal oxides, Cobalt ferrite (CoFe_2O_4) is well known hard magnetic material with high magneto-crystalline anisotropy, high coercivity, moderate saturation magnetization and Curie temperature about 790K [1]. These magnetic properties, along with interesting physical properties and chemical stability, enables cobalt ferrite nanoparticles suitable for magnetic recording applications such as audio and videotape and high-density digital recording disks [2-3]. The cobalt ferrite nanoparticles are being used for various biomedical applications such as magnetic resonance imaging, magnetic hyperthermia and targeted drugs delivery [4].

CoFe_2O_4 is an inverse spinel structure with Fe^{3+} ions equally shared among the tetrahedral sites (A) and octahedral sites (B), while Co^{2+} ions occupy the octahedral sites only. The magnetic properties of CoFe_2O_4 is depends upon types of cations (Co^{2+} , Fe^{3+}) and their distribution among the A-sites and B-sites. The spin

moment of all Fe^{3+} ions among the A and B-sites in an inverse spinel structure of CoFe_2O_4 are cancelled to one another (direction of Fe^{3+} ions on A-sites is antiparallel to B-sites) whereas all Co^{2+} ions are aligned in same direction, which results in net magnetic moment of CoFe_2O_4 nanoparticles.

The CoFe_2O_4 at nanoscale form makes considerable interest in magnetism; include surface effects, finite size effect and interparticle interactions. At low dimension below critical size, surface spin plays the dominant role. The randomly oriented surface spins are primarily responsible for reduction in saturation magnetization and enhancement in coercivity.

The particle size is related to the relative interdependence between the nucleation and growth steps. For powdered CoFe_2O_4 nanoparticles of 40 nm at room temperature, the highest coercivity is reported as 4.65 kOe [5]. The large concentration of nuclei with smaller particle size of cobalt ferrite nanoparticles prepared by co-precipitation method, by rapid increased in pH to 12, with rapid addition of precipitating agent into mixed solution of precursors. In recent years, several synthesis methods have been employed to prepare cobalt ferrite magnetic

materials, which includes hydrothermal [6], redox process [7], co-precipitation [8], combustion [9], thermal decomposition [10], solvothermal [11]. Among these methods, co-precipitation is efficient and versatile method for preparation of CoFe_2O_4 nanoparticles in large quantity and narrow particles size distribution. The co-precipitation method consists of nucleation rate followed by growth rate are strongly affected by precipitation parameters as pH, temperature and concentration of precursors [12].

The influence of cations distribution (Co^{2+} , Fe^{3+}) among A and B-sites in the crystal lattice and its effect on magnetic properties of CoFe_2O_4 nanoparticles is reported in this article. The contribution of spin orbit ($L-S$) coupling, the Co^{2+} ions from B-sites are responsible for higher magnetic anisotropy. The relationship between particle size and $L-S$ coupling resulting in superparamagnetic property of CoFe_2O_4 nanoparticles. As prepared CoFe_2O_4 nanoparticles of average particle size $16 \pm 2 \text{ nm}$ exhibits superparamagnetic property above blocking temperature of 144 K. Hence, superparamagnetic property of CoFe_2O_4 magnetic nanoparticles is determined by magneto-crystalline anisotropy.

According to Stoner-Walferth domain theory [13], the magneto-crystalline anisotropy of single domain nanocrystal, $E_A = KV \sin^2 \theta$ where K is the magneto-crystalline anisotropy constant, V is the volume of nanocrystal, and θ is the angle between the easy axis of nanocrystal and the direction of field induced magnetization. The magneto-crystalline anisotropy serves as magnetic barrier which blocks the magnetic moment of particles, which changes from ferromagnetic state to superparamagnetic state. The height of E_A determines the blocking temperature at which thermal activation energy overcomes the barrier E_A , which is controlled by anisotropic constant and volume of nanocrystal. The magnitude of K is closely related to the strength of $L-S$ coupling. As a result, the superparamagnetic property of nanocrystal is directly correlated with the variation of $L-S$ coupling strength. As synthesized CoFe_2O_4 nanoparticles exhibits the superparamagnetic property above blocking temperature, which is dependent on the size of nanoparticle.

The magnetic nanoparticles in the range of 20-400 nm in size show better permeability and retention effect [14, 15]. In this article, we report synthesis, structural and magnetic properties of CoFe_2O_4 nanoparticles with average particle size of 16 nm, with emphasis on superparamagnetic behaviour and interplay between $L-S$ coupling and particle size.

Investigations on the influence of cation distribution (Co^{2+} , Fe^{3+}) among A and B-sites in the crystal lattice and its effect on magnetic properties of CoFe_2O_4 nanoparticles is carried out and reported in this article. The contribution of spin orbit $L-S$ coupling, the Co^{2+} ions from B-sites responsible for higher magnetic anisotropy. The relationship between particle size and $L-S$ coupling resulting in superparamagnetic property of CoFe_2O_4 nanoparticles. As prepared CoFe_2O_4 nanoparticles of

average particle size $16 \pm 2 \text{ nm}$ exhibits superparamagnetic property above blocking temperature of 144 K. Hence, superparamagnetic property of CoFe_2O_4 magnetic nanoparticles is determined by magneto-crystalline anisotropy and $L-S$ coupling.

Experimental

Materials

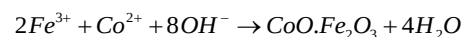
Ferric nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity $\geq 98\%$ Alfa Aesar, Germany), Cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (purity $\geq 98\%$ of Alfa Aesar, Germany), Sodium hydroxide pellets NaOH (purity $\geq 97\%$ of Merck India Ltd, manufactured at Mumbai) and double distilled water used as solvent.

Method

The aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4M) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2M) were taken in 2:1 molar ratio as precursors in each 25 ml double distilled water. The aqueous solution of precursors was refluxed separately at 60°C for half an hour with magnetic stirring and then mixed. The mixed solution again refluxed for half an hour. The particle size and size distribution was controlled by controlling the nucleation rate and growth rate during reaction. The rapid addition of precipitating agent NaOH (25ml, 4M) into mixed cationic solution directly; pH level of solution was increased to 12 and solution turn dark brown with rigorous stirring.

The large pH value of 12 was used to control the nucleation rate greater than that growth rate with smaller particles size [16]. The resultant dark brown solution heated to 80°C under constant stirring for 3 hrs. The solution contains precipitates of cobalt ferrite nanoparticles. The precipitated nanoparticles centrifuged (10000 rpm, 5 mins), washed several times with deionized water and ethanol until pH becomes neutral to remove the possible by-products. The black precipitate of cobalt ferrite dried at 50°C in order to obtain cobalt ferrite nanoparticles.

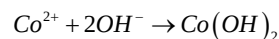
Cobalt ferrite nanoparticles synthesized by fast co-precipitation method, by rapid addition of aqueous solution of sodium hydroxide into mixture of divalent (Co^{2+}) and trivalent (Fe^{3+}) salts. The small sizes of CoFe_2O_4 nanoparticles are influenced by the alkaline medium and addition of velocity, which result nucleation and growth process. The pH of mixed salts increased to 12 by rapid addition of precipitating agent into salts which enables fast nucleation process forms high concentration of nuclei of smaller particles. The chemical reaction takes place during the synthesis of cobalt ferrite nanoparticles.



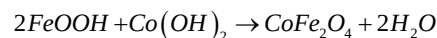
The Fe^{3+} hydrolyses and hydroxide species, corresponds to formation of trivalent iron oxide-hydroxide by chemical reaction.



The divalent cobalt cation in solution (Co^{2+}) reacts to form divalent cobalt oxide in presence of hydroxyl ions OH^- .



The trivalent iron oxide-hydroxide (FeOOH) and divalent cobalt oxide $\text{Co}(\text{OH})_2$ reacted together at pH value at 10 to 11 and forming Cobalt ferrite.



X-ray diffraction pattern (XRD) was recorded using Brucker X-ray diffractometer with $\text{Cu-K}\alpha$ radiation at $\lambda = 1.54060 \text{ \AA}$ in 2θ ranging from 10 to 70° . The surface morphology and particle size is determined by Philips (Model: CM 200) Transmission electron microscopy (TEM) with operating voltage of 200 kV and resolution $2.4 \text{ \AA}$. Infrared spectra of CoFe_2O_4 nanoparticles in range of wavenumber $400\text{--}4000 \text{ cm}^{-1}$ was carried out by FTIR spectrometer (Thermo Scientific Nicolet iS5). Raman spectra were measured in the range of wavenumber $200\text{--}2000 \text{ cm}^{-1}$ using Witech Raman spectrometer with excitation wavelength of 532 nm (Nd-YAG Laser). The magnetic properties of CoFe_2O_4 nanoparticles were studied by using (Quantum Design MPMS 3 EverCool system) Superconducting Quantum Interference Device (SQUID) magnetometer with applied magnetic field of $\pm 7 \text{ T}$. Zero-field cooled (ZFC) and field cooled (FC) was studied with SQUID magnetometer in range of $10\text{--}300 \text{ K}$ at applied field of 1.5 T .

Results and discussion

Fig.1 (a) shows the X-ray diffraction pattern of as prepared CoFe_2O_4 magnetic nanoparticles by co-precipitation method. XRD pattern of cobalt ferrite nanoparticles are crystalline in nature and all indexed peaks correspond to expected inverse spinel structure of JCPDS data card (22-1086) and space group $\text{Fd}3\text{m}$ (227). The cubic crystal lattice of CoFe_2O_4 was $a_c = 8.391 \text{ \AA}$ with $\alpha = \beta = \gamma = 90^\circ$ according to PDF (22-1086). The average crystallite size of CoFe_2O_4 estimated by X-ray line profile fitting has been calculated $12 \pm 2 \text{ nm}$ by Scherer's equation for most intensity peak (311).

$$D = \frac{0.9\lambda}{\beta_D \cos \theta} \quad (1)$$

where, β_D is full-width at half maximum (FWHM) due to crystallite size and θ is Bragg's angle of diffraction. In XRD investigation, the d -spacing of unit cell is measured by Bragg's equation.

$$d = \frac{\lambda}{2 \sin \theta} \quad (2)$$

The lattice parameter $a_c = d\sqrt{h^2 + k^2 + l^2}$ of particular indexed plane is calculated as showed in **Table 1**, indicates the difference between observed (o) and corrected values (c). This is due to shifting XRD peak position toward higher value compared to PDF, thereby decreasing d -spacing of corresponding peaks, resulting decrease in lattice parameter of the corresponding peaks. Hence, lattice shrinkage is observed in the sample. The indexing of CoFe_2O_4 nanoparticles is indicated in **Table 1**.

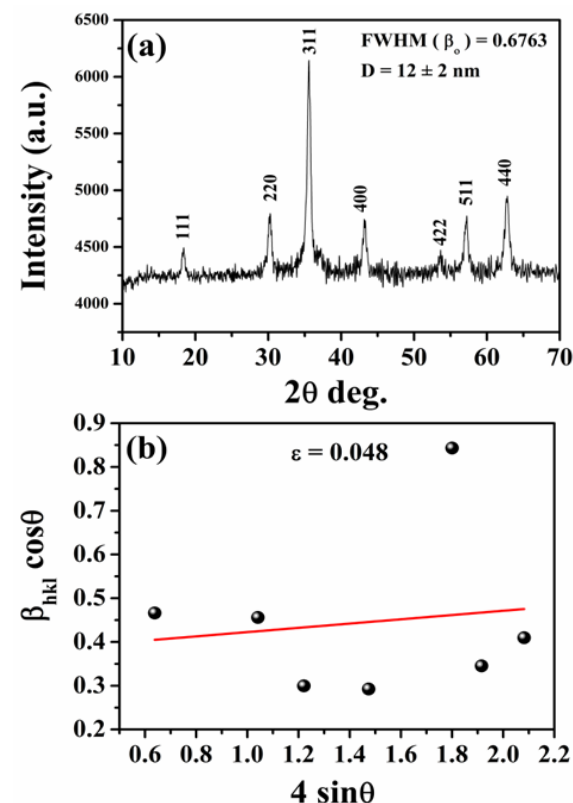


Fig. 1. (a) XRD pattern of CoFe_2O_4 nanoparticles, average crystallite size is calculated by X-ray profile fitting to data; (b) Williamson-Hall analysis of CoFe_2O_4 nanoparticles. Fit to the data, strain is measured from the slope of the fit.

Table 1. Pattern indexing of CoFe_2O_4 nanoparticles: Observed (o) and Corrected (c).

Observed		JCPDS		Lattice parameter			
2θ (o)	d (Å) (o)	2θ (c)	d (Å) (c)	d_{TEM} (Å)	(hkl)	a (Å) (o)	a (Å) (c)
18.36	4.828	18.28	4.847	4.85	(111)	8.362	8.395
30.18	2.958	30.08	2.968	2.97	(220)	8.368	8.394
35.55	2.523	35.43	2.531	2.53	(311)	8.368	8.394
43.25	2.090	43.05	2.099	2.09	(400)	8.360	8.396
53.50	1.711	53.44	1.713	1.72	(422)	8.383	8.391
57.23	1.608	56.97	1.615	1.61	(511)	8.356	8.391
62.74	1.479	62.58	1.483	1.47	(440)	8.370	8.389

The lattice strain of cobalt ferrite sample is calculated by Williamson-Hall Eq. (3), depending on different of angle of diffraction (θ) [17].

$$\beta_{hkl} = \sqrt{\beta_o^2 - \beta_{std}^2}$$

$$\beta_{hkl} = \beta_D + \beta_S$$

$$\beta_{hkl} \cos \theta = \frac{0.9\lambda}{D} + 4\epsilon \sin \theta \quad (3)$$

where, β_{hkl} is full width at half maximum due to crystallite size and stain, β_S is full width half maximum due to strain, β_o is full width at half maximum of XRD peak and β_{std} is full width at half maximum due to instrumentation line broadening and ϵ is the lattice strain. Williamson-Hall analysis used Lorentzian function in calculation of this parameter. Williamson-Hall Eq. (3) indicates the straight line in **Fig. 1(b)** with slope resulting in lattice strain induced during the co-precipitation process. A lattice strain of 4.8×10^{-2} is observed in CoFe_2O_4 sample. This may be accompanied with the migration of Co^{2+} ions from the tetrahedral to the octahedral lattice. This process of migration decreases the induced lattice strain, thereby stabilizing the crystal structure [18]. The average lattice constant for CoFe_2O_4 system is 8.369 Å and density 5.316 g/cm^3 from X-ray diffraction pattern which is less than that of PDF.

The surface morphology and particle size distributions of CoFe_2O_4 magnetic nanoparticles was investigated by transmission electron microscopy (TEM) as shown in **Fig. 2 (a and b)**. The images show that CoFe_2O_4 nanoparticles appears to be agglomerated and in spherical shape. The particle size distribution is estimated by measuring the size of particles, sorting the particle size in histogram. The histogram in inset of **Fig. 2 (a)** shows the average particle size of 16 nm is estimated by fitting to log-normal distribution function. The occurrence of agglomeration of individual nanoparticles is due to Ostwald ripening at low temperature. Ostwald ripening is one of the causes of agglomeration, while nanoparticles have appreciable solubility is dispersed in solvent. The combining of particles together to form large particles through sintering or Ostwald ripening, and agglomeration. The particles are agglomerated by reducing overall surface free energy. In agglomeration, many particles are associated with one another by chemical bonds and physical forces such as Vander wall attraction force and electric potential.

The average particles size from TEM and XRD is $16 \pm 2 \text{ nm}$ and $12 \pm 2 \text{ nm}$ respectively. X-ray intensity is proportional to average particle volume, while particle size obtained from TEM. TEM images are representing the average particle diameter and particles size distribution is restricted to the primary particles and TEM excludes the secondary particles by epitaxial attachments. Secondary particles are formed from integer multiples of primary particles and lead to significant influence on the volume distribution, at relatively low concentration [19].

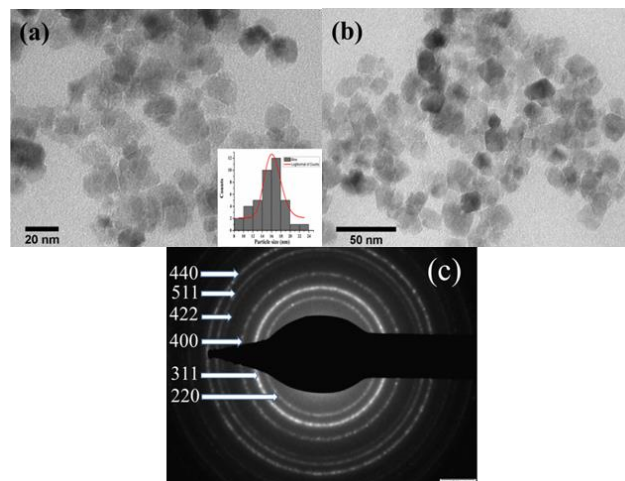


Fig. 2. (a, b) TEM images of CoFe_2O_4 nanoparticles synthesized at 80 °C, and (c) Selected area electron diffraction (SAED) pattern of CoFe_2O_4 nanoparticles.

Fig.2 (c) show selected area electron diffraction (SAED) pattern of cobalt ferrite magnetic nanoparticles. The SAED pattern provides the high intensity ring corresponds to (311) peak and less intensity diffuse rings correspond to (220), (400), (422), (511), (440) and (533) plane reflections on increasing radius of rings. SAED ring pattern conclude that sample is in polycrystalline nature. The accelerating voltage of 200kV is used to characterize the sample (CoFe_2O_4) with camera constant (λL). The d_{TEM} spacing of diffused rings are calculated by inverting the calibrated value (p) which is shown on each individual diffused rings in **Table 1**. The d_{TEM} spacing of unit cell is calculated for each diffused ring and matched with PDF (22-1086) and d -spacing from XRD. This confirmed that the formation of cobalt ferrite as presented in **Table 1**.

Cobalt ferrite has an inverse spinel structure with space group O_h^7 ($Fd3m$), which gives 39 normal modes.

$$\Gamma = A_{1g}(R) + E_g(R) + T_{1g}(in) + 3T_{2g}(R) + A_{2u}(in) + 2E_u(in) + 4T_{1u}(IR) + 2T_{2u}(in)$$

where, Raman active modes ($A_{1g} + E_g + 3T_{2g}$), Infrared active modes ($4T_{1u}$) and remaining are inactive modes [20]. Here the notation A is for one, E for two and T for three dimensional representations respectively. The symbol g and u denotes the symmetry and antisymmetry with respect to the center of inversion. The presence of an inversion center in the centrosymmetrical space group $Fd3m$ implies mutual exclusion of Raman and infrared activities for the same vibrational modes.

Raman peak at 465 cm^{-1} is corresponds to octahedral mode that reflects the local lattice effect in octahedral sub-lattice. The higher frequency peak at 679 cm^{-1} related to tetrahedral mode that reflects the local lattice effect in tetrahedral sub-lattice. The higher phonon mode reflects at 679 cm^{-1} is due to A_{1g} the symmetry stretching of oxygen anion with Fe^{3+} ions at A-sites while the lower phonon number reflects at 465 cm^{-1} is due to metal ions involved in

B-sites (E_g and $3T_{2g}$). These modes correspond to the symmetric and anti-symmetric bending of oxygen anion in $M-O$ bond at B-sites [21].

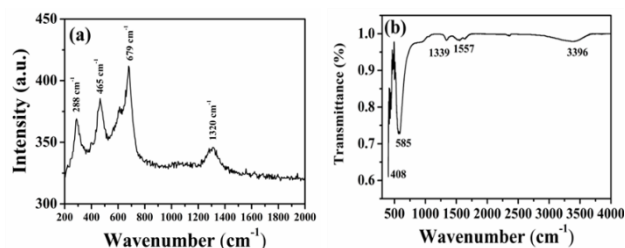


Fig.3. (a) Raman spectra, and (b) FTIR spectra of CoFe_2O_4 nanoparticles.

The high wavenumber represents the vibration of $\text{Fe}^{3+}-\text{O}^{2-}$ in the sub-lattice A-sites, while the lower wavenumber band represents the trivalent metal-oxygen vibration at the octahedral B-sites [22]. The peak at A-sites has higher intensity than that of B-sites, due to higher surface to volume ratio of nanoparticles in the sample. All the observed peaks are shifted to lower wavenumber because mass of Co ion is higher than that of Fe . The peaks at $\sim 288 \text{ cm}^{-1}$ illustrate the E_g mode [23] and there exists one peak at 1320 cm^{-1} corresponding to the ferrihydrite phase [24]. Janney *et al.* have reported that the band at 1320 cm^{-1} is due to the magnetite-like modification of ferrihydrite [25]. It has also been reported in the literature that the band at 1320 cm^{-1} correspond to maghemite ($\gamma\text{-Fe}_2\text{O}_3$) [26]. The small amount of ferrihydrite phase, which is nonmagnetic in nature, is formed during the synthesis of CoFe_2O_4 nanoparticles and it is untraceable by XRD because most intense peaks of both phases are identical. The $\gamma\text{-Fe}_2\text{O}_3$ is responsible for reduction in saturation magnetization of as-synthesized CoFe_2O_4 nanoparticles sample as compared to bulk CoFe_2O_4 .

Fig. 3 (b) shows FTIR spectra of CoFe_2O_4 , where A-sites correspond to 585 cm^{-1} and B-sites corresponds to 408 cm^{-1} . The difference in the ν_1 and ν_2 bands position is expected because of the difference in the $\text{Fe}^{3+}-\text{O}^{2-}$ distance for the octahedral and the tetrahedral sites [27]. The observed peak at 3396 cm^{-1} is due to hydroxyl group (O-H) stretching vibration. Medium weak peaks are observed at $1400-1600 \text{ cm}^{-1}$ that presents symmetric and asymmetric stretching vibration of (Co-O) groups respectively. The ratio of the line position of FTIR bands can be determined by [28].

$$\frac{\nu_1}{\nu_2} = \sqrt{2} \frac{K_t}{K_o}$$

where, K_t and K_o are the force constants for the $M-O$ bonds in A-sites and B-sites respectively. The ratio of K_t to K_o is found to be 1.013, that provides forces acting on B-sites are nearly equal to forces acting on A-sites even as A-sites has four coordination number while B-sites has six coordination number.

Magnetic characterization of CoFe_2O_4 nanoparticles performed at two different temperatures 300 K and 10 K showed in **Fig. 4 (a)** with applied magnetic field of $\pm 7 \text{ T}$. For average particle size of $16 \pm 2 \text{ nm}$, the coercivity H_C of pure CoFe_2O_4 sample increases from 441 to 9896 Oe, as decreasing temperature from 300 to 10 K respectively. At 300 K, these nanoparticles exhibit hysteresis loops with coercivity, remanent magnetization and saturation magnetization of 441 Oe, 16 emu/g and 63 emu/g respectively. At 10 K, magnetic hysteresis loop is seen typical of ferromagnetism, with coercivity H_C of 9.8 kOe, remanent magnetization M_r of 58 emu/g and saturation magnetization M_S of 82 emu/g, deduced from the **Fig.4 (a)** as showed in **Table 2**.

The increase values of H_C , M_r and M_S at 10 K may be due to proper ordering of magnetic moment in direction of field and randomised at 300 K due to thermal activation. At 10 K, irreversibility remains even as applied magnetic field of 7 T. The irreversibility and unsaturated magnetization at lower temperature of 10 K and higher magnetic field of 7 T is generally related to frozen spin glass layer (SGL) state on the surface of magnetic nanoparticles [29]. The temperature dependence of dM/dH in magnetization curves from 4 T to 7 T, which is plotted in **Fig. 4 (c)**, shows drastically increasing the value of dM/dH by decreasing temperature from 300 K to 10 K. This is due to SGL freezing, which causes increase in magnetic anisotropy at 10 K [30].

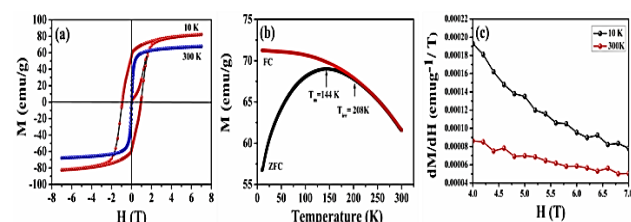


Fig. 4. (a) $M-H$ curve of CoFe_2O_4 sample at 10 K and 300 K; (b) ZFC/FC curve of CoFe_2O_4 sample at maximum field of 1.5 T and (c) The temperature dependence of dM/dH magnetization curves in field from 4 T to 7 T.

Spinel ferrite structure contains two interstitial sites occupied by metals ions, with A-site and B-site. The net magnetization is proportional to difference between $|M_A - M_B|$ sub-lattice magnetizations. Thus, saturation magnetization depends upon cations distribution

Table 2. H_c , M_r , M_r/M_s , K_1 and H_k of CoFe_2O_4 nanoparticles.

Temp. (K)	H_c (Oe)	M_r (emu/g)	M_S (emu/g)	M_r/M_S	M_S (emu/g) by LA	K_1 (J/m ³) by fitting	H_k (T)
10 K	9896	58	82	0.70	83	1.243×10^6	5.582
300 K	441	16	63	0.25	66	2.160×10^5	0.804

(inversion degree) which are related to surface spin-canting and finite size effect. The reduction in saturation magnetization of as-synthesized CoFe_2O_4 nanoparticles as compared to bulk at room temperature with particle size is attributed to surface spin canting yields magnetic disorder at particle surface [31-33]. This is due to nonmagnetic ferrihydrite present on the surface of CoFe_2O_4 nanoparticles, which causes to decrease in saturation magnetization.

The squareness ratio, $M_r/M_s = 0.25$ at 300 K, which is smaller than the expected value of randomly oriented isolated particles with uniaxial anisotropy (0.5) and particle with cubic anisotropy (0.8) respectively. CoFe_2O_4 sample shows $M_r/M_s = 0.7$ at 10 K, which suggests a tendency towards cubic anisotropy. The enhancement in squareness ratio at 10 K leads to increase in anisotropic energy barrier of CoFe_2O_4 nanoparticles.

Fig. 4 (b) shows the temperature dependence zero-field-cooled (ZFC) curve in the absence of magnetic field and field-cooled (FC) curve of as prepared CoFe_2O_4 sample measured at temperatures between 10 K and 300 K with applied magnetic field of 1.5 T. The magnetization direction of each particle is frozen in the direction of field in FC. As the temperature enhances from 10 to 300 K, ZFC magnetization first increases to reach the wide maximum point. ZFC magnetization exhibits a maximum at blocking temperature T_B^m at which the relaxation time equals the time scale of magnetization measurements (100s). For CoFe_2O_4 sample of 16 nm average particle size, the blocking temperature is $T_B^m = 144$ K and both curves tend to superimpose at above $T_{irr} = 208 \pm 5$ K, as superparamagnetic (SPM) region was reached. The difference between T_B^m and T_{irr} corresponds to the width of the blocking temperature distribution. The lowest T_B^m and highest T_{irr} value with respect to those for dispersed particles are due to inter particle interaction, since particles are close in contact.

The temperature below which ZFC and FC curves show an irreversible behaviour T_{irr} is associated with blocking of the biggest particles [34]. **Fig. 4(b)** shows that, the FC curve tends to saturate below T_B^m , in comparison with non-interacting small particles system, suggested the existence of magnetic dipole interaction between the nanoparticles. Thus, T_B^m is reflected as blocking process. The superparamagnetic state is reached at $T_B^m = 144$ K. After blocking temperature, ZFC curve decreases on increasing temperature upto 300 K. When the measurement temperature for magnetization is less than T_B^m , the grains showed the ferromagnetic state. Above T_B^m , thermal activation energy $k_B T$ overcomes the magnetic anisotropy energy E_A and each nanoparticle fluctuates between two directions of the easy axis. Thus, CoFe_2O_4 nanoparticles relax from blocked state to superparamagnetic state.

Under an applied magnetic field at room temperature, the magnetization direction of all magnetic vectors aligns in the direction of magnetic field. As the temperature decreases to 10 K, the directions of all magnetic vectors align along field direction even in the absence of magnetic field. The magnetization of each magnetic

vector still unaltered. The magnetic anisotropy acts as the energy barrier blocks the overall magnetization direction switching towards the easy axis. As the particles size increases, blocking temperature also increases [35]. This reflects the size dependence of the anisotropic energy (E_A). Below blocking temperature T_B^m , the magnetic moment of as-synthesized CoFe_2O_4 nanoparticles with energy $E_A > 25k_B T$ are blocked and there are no magnetic fluctuations. The magneto-crystalline cubic anisotropy constant is estimated by

$$K_1 = \frac{25k_B T_B^m}{V} \quad (4)$$

where, V is volume of particle and k_B is Boltzmann's constant. $K_1 = 5.49 \times 10^5 \text{ J/m}^3$, is obtained at blocking temperature of $T_B^m = 144$ K. Above T_B^m , all of the nanoparticles are in same relaxation state as in ZFC process leading to overlapping in FC and ZFC curves. The magnitude of K_1 is closely related to the strength of $L-S$ coupling. As a result, the superparamagnetic property of nanocrystal can be directly correlated with the variation of $L-S$ coupling strength. The magnetic anisotropy is accumulative contribution of cations in A-sites and B-sites. Therefore, magnetic $L-S$ coupling at lattice sites is directly related to the magnetic property such as superparamagnetism. Since, ligand (crystal) field is weak in spinel ferrite and all cations assumed with high spin state.

The electronic configuration $3d^5$ of Fe^{3+} on A and B-site usually have its orbital angular momentum quenched in a weak ligand field. Therefore, the contribution to the magnetic anisotropy should only come from Co^{2+} cation in inverse spinel structure of CoFe_2O_4 . The $L-S$ coupling associated with the Co^{2+} determines relative magnitude of magnetic anisotropy energy. As a result, the variation of $L-S$ coupling strength is directly determining the superparamagnetic property of nanocrystals. A Co^{2+} cation with $3d^7$ electronic configuration at B-site in CoFe_2O_4 has a triplet $4T_{1g}$ ground state with non-zero orbital angular momentum ($e_g^2 t_{2g}^5$), has a whole state on t_{2g} orbital [36]. The whole on t_{2g} orbital rotate about an axis, which may generate the orbital momentum. In cubic crystal field of octahedral symmetry indicates the fivefold degeneracy of d electrons presents in Co^{2+} ions by splitting the energy levels and forming higher doubly degenerate of e_g (d_{z^2} and $d_{x^2-y^2}$) whose electronic configuration points toward six neighbouring sites, take on different energy relative to lower triply degenerate of t_{2g} (d_{xy} , d_{yz} , d_{zx}) orbitals, which are directed between neighbouring sites. Even though the trigonal field is introduced with the T_{1g} ground state further splitting into A_2 and E states, the Co^{2+} cation with a degenerated ground state of E is still considered to have a strong $L-S$ coupling, and therefore contributes greatly to the magnetic anisotropy of CoFe_2O_4 [37]. The strong coupling of Co^{2+} in lattice sites provides the large anisotropic energy barriers in CoFe_2O_4 nanocrystal. Since, anisotropic field is directly

related to magnetic anisotropy. From the graphs in **Fig. 4(a)**, the anisotropic field H_k is found where the magnetizing and demagnetizing curves are merged for 10K and 300K respectively. The anisotropic constant is obtained by Eq. (5), is 1.216×10^6 (J/m³) at 10 K and 2.0×10^5 (J/m³) at 300 K, very well matched with anisotropic constant estimated from the Eq.(8).

$$H_k = \frac{2K_1}{M_s} \quad (5)$$

At 10 K of temperature, the required magnetic field for overcoming anisotropy to flip the magnetic spin increases with increasing anisotropy energy barrier. This is due to strong $L-S$ couplings in Co^{2+} cations result in much higher coercivity in $CoFe_2O_4$ at 10 K.

If the resultant magnetization decreases with increase in temperature, the magnetization of one sub-lattice decreases more rapidly than other sub-lattice. The saturation magnetization (M_s) value was estimated by fitting the high magnetic field part ($H > H_C$) of magnetization curves M_H [38].

$$M_H = M_s \times \left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + cH \quad (6)$$

where, a is related to structural defect on nonmagnetic inclusion, b is determined by fitting procedure, M_H is magnetization along field direction in magnetic field, cH is caused by an increase of the spontaneous magnetization itself and H is applied magnetic field. Assumed the crystallites are randomly oriented on averaging. The temperature dependent magneto-crystalline anisotropy constant and temperature dependent saturation magnetization M_s is explained by “Law of Approach” (LA). The cubic anisotropy constant K_1 and saturation magnetization M_s for polycrystalline $CoFe_2O_4$ sample were determined by a “LA” to saturation that explained the field dependent magnetization for magnetic field much higher than the coercive field H_C . The magnetization near M_s for randomly oriented polycrystalline sample with cubic anisotropy [39].

$$M = M_s \times \left(1 - \frac{8K_1^2}{105M_s^2H^2}\right) + cH \quad (7)$$

where, M is magnetization and c is linear constant term. The phenomenological linear term cH is very small at high magnetic field and it is due to forced magnetization. The cubic anisotropic constant is calculated K_1 from Eq.(6) and (7) as

$$K_1 = M_s \sqrt{\frac{105b}{8}} \quad (8)$$

The temperature dependence K_1 and M_s are obtained by fitting the Eq. (6) to the values of magnetization corresponding to high magnetic field part of the curve from 1 to 7 T, above which hysteresis loop is completely closed. For $CoFe_2O_4$, M_s decreases from 83 to 66 emu/g and K_1 reduced from 1.243×10^6 to 2.16×10^5 J/m³ on increasing temperature from 10 to 300 K respectively.

The K_1 value obtained from fitting, which is compatible with the value of $CoFe_2O_4$ bulk [40] and higher than that of value obtained from [41] at 10 K and 300 K respectively. The fitted curves of M_s to LA at 10 K and 300 K for $CoFe_2O_4$ sample is showed in **Fig. 5 (a and b)**. For $CoFe_2O_4$ sample, M_s is $3.48 \mu_B/f.u.$ and $2.77 \mu_B/f.u.$ at 10 K and 300 K calculated respectively for obtained M_s by fitting Eq. (6).

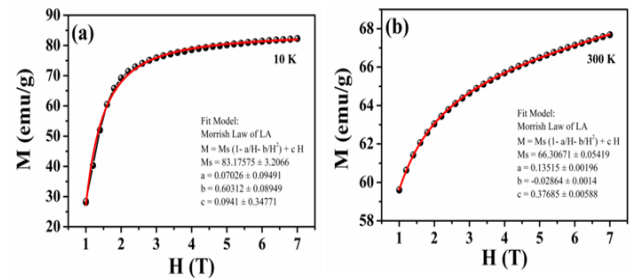


Fig. 5. (a and b) Fitted data of M_s to LA saturation for $CoFe_2O_4$ at 10 K and 300 K respectively.

The FC curve in **Fig. 6** represents the variation of magnetization with temperature at 1.5 T. On the other hand, it is reported in case of cobalt ferrite, the temperature dependence of saturation magnetization follow a T^2 law for nanoparticles instead of $T^{3/2}$ [42].

$$M_s(T) = M_s(0) [1 - BT^2] \quad (9)$$

where, $M_s(0)$ is saturation magnetization as T tends to zero, and B is Bloch's constant. From the **Fig. 6**, it is evident that magnetization increases with decreasing temperature of the sample. For the bulk ferromagnetic material, the magnetization below Curie temperature T_C follows the Bloch' law as [43].

$$M(T) = M(0) \left[1 - \left(\frac{T}{T_C}\right)^\alpha\right] \quad (10)$$

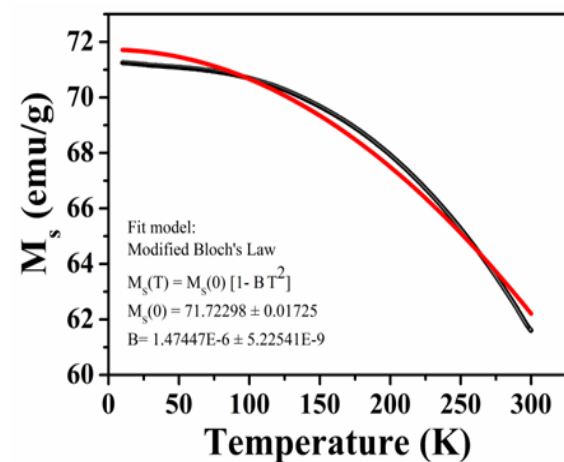


Fig. 6. Fitted data of FC magnetization curve with temperature of $CoFe_2O_4$ nanoparticles in range of 10 -300 K to provide the Curie temperature.

where, Bloch constant $B = (1/T_C)^\alpha$ and α is Bloch's exponent with value 3/2. The Eq. (10) is generally useful

for bulk material in high temperature range. However, at the nanoscale, due to the finite size effects, the thermal dependence of magnetization deviates from Bloch's law as the magnons with wavelength larger than the particle dimensions cannot be excited and a threshold of thermal energy is required to generate spin waves in these small scaled particles. Thus for nanoparticles, the spin-wave structure is modified in the form of a power law T^α with Bloch's exponent larger than its bulk value of 3/2. This is known as the modified Bloch's law [44]. The T_C is estimated by fitting the values of temperature dependence saturation magnetization $M_S(T)$ in the temperature range of 10-300K is fulfilled using modified Bloch's law with $\alpha = 2$ (shown by red line) provides $T_C = 823\text{ K}$ for CoFe_2O_4 sample showing paramagnetic state as shown in Fig. 6, which is compatible with value for bulk cobalt ferrite of about 793 K.

Conclusion

The cobalt ferrite nanoparticles of 16 nm particle size are prepared by co-precipitation method. Nonmagnetic ferrihydrite and $\gamma\text{-Fe}_2\text{O}_3$ formation from Fe^{3+} solution during precipitation is confirmed by Raman spectroscopy. The presence of nonmagnetic ferrihydrite, $\gamma\text{-Fe}_2\text{O}_3$ and bigger particles due to the Ostwald ripening process leads to a progressive decrease in saturation magnetization. The anisotropic constant for as-synthesized CoFe_2O_4 nanoparticles which is higher than that of value of bulk at 300 K. The characteristics of superparamagnetic nanoparticles, FC and ZFC magnetization measurements show a divergence below blocking temperature 144 K of CoFe_2O_4 sample. The magnetic anisotropy is directly related to the superparamagnetic relaxation. For average particle size of $16 \pm 2\text{ nm}$, the cubic anisotropy constant K_1 and saturation magnetization M_S increased at lower temperature than at room temperature. This is due to the magnetic field is no longer enough to align all magnetic spin at low temperature. As synthesized CoFe_2O_4 nanoparticles follows the modified Bloch law as T^2 instead of $T^{3/2}$ for bulk material, which provides Curie temperature at 823 K by fitting of temperature dependence saturation magnetization with temperature.

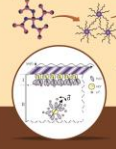
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