



# Tuning of ferrites ( $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ) nanoparticles by co-precipitation technique

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## Abstract

The synthesis of cobalt ferrites ( $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ) materials with sympathetic size and tunable magnetic properties is used for the promising industrial and biomedical applications. Such cobalt ferrites nanoparticles have been employed by co-precipitation technique. XRD analysis revealed that the average crystallite size of synthesized powder is 9 nm using (311) peaks, and it has exhibited polycrystalline structure. FTIR spectroscopy showed the formation of ferrite phase with high- and low-frequency bands at  $573\text{ cm}^{-1}$  and  $455\text{ cm}^{-1}$ , respectively. The TEM images exposed that the materials have been well agglomerated along with spherical-shaped nanoparticles. EDX study confirmed the presence Co, O, Fe and C with stoichiometric composition and no more impurity detected in the spectrum. The VSM analysis revealed that the sample exhibits the hard magnetic materials. In addition, the magnetic anisotropy increases ( $19.05 \rightarrow 344.84\text{ erg/g}$ ) when Co is added with  $\text{Fe}_3\text{O}_4$ . EPR spectroscopy confirmed the ferromagnetic behavior of composites.

**Keywords** Cobalt ferrites · Co-precipitation · Spherical shape · Polycrystalline · Magnetic anisotropy · EPR spectroscopy

## 1 Introduction

Nowadays, nonpolluting vehicles have been constructed using advanced magnetic spinel materials. The cobalt ferrites were formed by face-centered cubic structure through oxygen ions filled together with the divalent and trivalent metal ions in the tetrahedral and octahedral voids, respectively. Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) nanocomposites are broadly used in a variety of applications, such as transformer cores, magnetic sensors, stress and biomedical sensors, catalytic insulators, information and energy storage media, solar energy conversion, coatings, recording heads, antenna rods, loading coils, microwave devices, ferrofluids, magnetic refrigeration, drug delivery, gas detectors, cellular therapy, tissue repair and hyperthermia treatment. Cobalt ferrite spinel is a promising material for various commercial applications [1, 2]. For materials calcined at  $900\text{ }^\circ\text{C}$ , there is

a slight move of the 311 peak toward lower edges, credited to the migration of  $\text{Co}^{2+}$  cations from octahedral to tetrahedral voids and to a contrary exchange of a proportional number of  $\text{Fe}^{3+}$  particles so as to loosen up the compressive strain. It demonstrates the variety of crystallite sizes and lattice parameters with  $\text{CoFe}_2\text{O}_4$  content (X %). By calcining temperature, at  $700\text{ }^\circ\text{C}$ , the evaluated lattice parameters of  $\text{CoFe}_2\text{O}_4$  are underneath the theoretical value ( $8.39\text{ \AA}$ ) as per JCPDS NO. 22-1086, because of the progressions of  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  cations circulation among tetrahedral and octahedral destinations. In cobalt ferrite structure,  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  can possess both tetrahedral and octahedral sites [3, 4]. The exchange of cations framework is said to be a spinel structure. Normally, cobalt ferrites ( $\text{CoFe}_2\text{O}_4$ ) exist in the spinel oxide family and every unit cell containing  $32\text{O}^{2-}$ ,  $8\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  ions. The cobalt ferrite molecule framed the  $\text{Fe}^{3+} [\text{Co}^{2+}\text{Fe}^{3+}] \text{O}_4^{2-}$ ; here,  $\text{Fe}^{3+}$  cations occupy half of the

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octahedral fashion and tetrahedral fashion.  $\text{CoFe}_2\text{O}_4$  is an example of an inverse spinel structure [5–9]. In view of its high magnetocrystalline anisotropy, saturation magnetization, high coercivity, substance soundness, mechanical hardness and chemical stability, cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) spinel is a promising material for different business applications. Its magnetic properties are for the most part dictated by the  $\text{Co}^{2+}$ , and along these lines, the tuning of its magnetic characters by modifying the Co/Fe proportion ends up conceivably. By warm treatment, the  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  is gradually changed in two iron-rich and cobalt-rich spinel stages [10]. For the gel that contains a high abundance of Co, the hysteresis loop demonstrates expansive coercive field, yet the magnetic subsidiary outline exhibits sharp peaks, conceivable as a result of the existence of  $\text{CoFe}_2\text{O}_4$  as a single magnetic phase. In favor of samples calcined at  $700^\circ\text{C}$ , the saturation magnetization declines, and the decline pattern of the saturation magnetization could be a result of the diverse cation distribution [11]. The exchange of the different cations in the spinel matrix is responsible for the fascinating magnetic performance of the different ferrites [12]. These magnetic cations were exchanged between the voids in various experimental methods, and also an exchange of cations depends on doping materials, annealing temperature and duration of time [13]. Magnetic cobalt ferrites have been synthesized by a variety of methods, such as mechanical milling, co-precipitation, hydrothermal methods and sol-gel techniques. Among this, co-precipitation is the most convenient technique when compared to others by controlling the size of the nano particles [14]. The polyvinylpyrrolidone (PVP) is added with  $\text{CoFe}_2\text{O}_4$  as a stabilizer [15]. These ferrite materials have been widely used in various technical applications in magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anticancer drugs, magnetic resonance imaging contrast enhancement, magnetic cell separator, magnetic devices, switching devices, permanent magnets, hard disk, recording media, read-write heads, active component of ferrofluids, color imaging, gas-sensitive materials, etc. [16–19]. In the present work, a novel co-precipitation technique is utilized for the arrangement of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  nanoferrites. The reactants utilized are modest, nonlethal and eco-accommodating. The grain sizes of the arranged ferrites are in the request of a couple of nanosizes. The combined ferrites are checked for their virtue and organization. The nanoferrites are found to have high caliber and great stoichiometric piece which purifies the inclination of this technique.

## 2 Experimental section

### 2.1 Materials

Ferric sulfate monohydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ , assay: 99%), cobalt (II) sulfate heptahydrate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), ethanol, ammonia, polyvinyl pyrrolidone (PVP,  $(\text{C}_6\text{H}_9\text{NO})_n$ , assay: 98%) were purchased from Sigma-Aldrich Chemical company. All chemicals are used without any further purification.

### 2.2 Synthesis of PVP-coated $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ nanoparticles

Nanoscale particles were prepared by chemical co-precipitation method. The number of moles of all reagents of sample and the corresponding chemical formula are shown in Table 1. In an experiment, aqueous solutions of 100 ml containing the ferric sulfate, cobalt (II) sulfate heptahydrate ( $x: 0.00 \leq x \leq 0.04$ ), respectively, and polyvinyl pyrrolidone ( $\text{PVP} = 0.0025\text{M} = 1\text{ g}$ ) were mixed with 250-ml conical flask with stoichiometric proportion. The stoichiometric mixtures were stirred for 45 min to obtain a homogeneous solution, and the ammonia (0.25 M) was dissolved in 50 ml of distilled water and added slowly to the mixtures for maintaining the pH level at 11 of materials. Under vigorous mechanical stirring for 3 h at room temperature, the solution appears in black color; this is the required condition for precipitation of the nanoparticles. The precipitates were then magnetically alienated using a magnet bar. The alienated materials were dissolved in methanol and then again alienated with magnet bar. This process was continuously done for four times in order to eliminate the excess amine molecules. Finally, we got a black powder of  $\text{CoFe}_2\text{O}_4$  after drying the precipitate at room temperature for 6 h. The dried powder was kept at muffle furnace and annealed at  $600^\circ\text{C}$  for 4 h in order to obtain pure-phase high-crystallinity  $\text{CoFe}_2\text{O}_4$  ferrites. Therefore, annealing operation removes all structural imperfections by complete recrystallization.

**Table 1** The number of moles of all reagents of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  nanoparticles with  $x: 0.00\text{M} \leq x \leq 0.04\text{M}$

S. no	Reagent ( $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ )	Mole
1	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	3 M
2	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	$x: 0.00\text{M} \leq x \leq 0.04\text{M}$
3	$\text{NH}_3$	0.25M
4	PVP	$0.0025\text{M} = 1\text{ g}$

### 3 Results and discussion

#### 3.1 XRD analysis

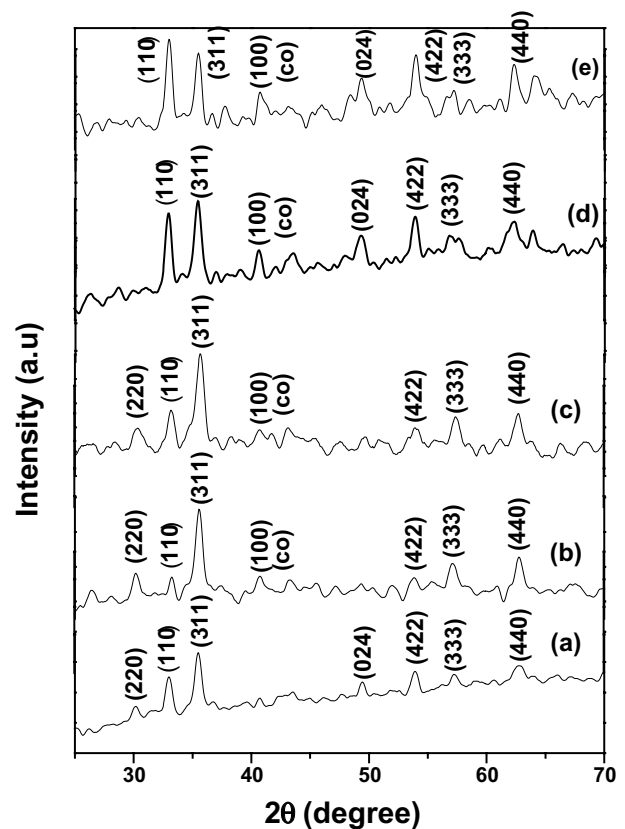
We used the officially announced [20] XRD spectrum  $\text{Fe}_3\text{O}_4$  for correlation in the succeeding employment. The chemical composition, nanosize, lattice constant, X-ray density, volume of unit cell and micro-strain are summarized in Table 2. The XRD patterns of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  (where  $x: 0.00 \leq x \leq 0.04$ ) are shown in Fig. 1. From the XRD graph, it is confirmed that no extra peaks of impurity are present in the crystalline microstructure. On adding 'Co' with  $\text{Fe}_3\text{O}_4$ , it affects domain structure and improves its crystal parameters. Because cobalt cations promote the crystalline forms a spherical shape with peaks. The  $\text{Co}^{2+}$  (70 pm) ions at the tetrahedral sites are being replaced by  $\text{Fe}^{3+}$  ions (60 pm) with significant ionic radius [21, 22]. The crystallite size decreases ( $19.2 \rightarrow 5.53$  nm) significantly when the annealing temperature is  $600^\circ\text{C}$  with different doping ratios of  $\text{Co}^{2+}$  while the  $\text{Fe}^{3+}$  cations are shared in both voids. Now the sample performs as the inverse spinel structure [23]. All the observed peaks were indexed to cubic spinel structure using JCPDS data (Card No: 89–4307), and their reflections (220), (110), (311), (024), (422), (333) and (440) showed the construction of single-phase cubic inverse spinel structure. The crystallite size of  $\text{CoFe}_2\text{O}_4$  nanoparticles is calculated by using Debye–Scherrer's formula [15, 24, 25]:

$$D = K \lambda / \beta \cos \theta$$

where  $K$  is the shape factor (0.9),  $\lambda$  is the wavelength of the X-ray ( $1.5406 \text{ \AA}$ ),  $\beta$  is the full width at half maximum and  $\theta$  is the Bragg angle. The average crystallite size of the sample is 9 nm using the (311) peak. The lattice constant was determined from XRD data by the following formula [26]:

$$a = d (h^2 + K^2 + l^2)^{1/2} \text{ \AA}$$

where ' $a$ ' is the lattice constant, ' $d$ ' is the interplanar spacing and (h k l) are Miller indices. The lattice constant shows the single phase and has the same value ( $8.35 \text{ \AA}$ ) for their entire sample. The lattice constant of  $\text{Fe}_3\text{M}\text{O}_4$  is  $8.357 \text{ \AA}$  while increasing the mole ratio of  $\text{Co}^{2+}$  ions by



**Fig. 1** X-ray diffraction of cobalt ferrite nanoparticles. **a**  $\text{Fe}_3\text{M}\text{O}_4$ , **b**  $\text{Co}_{0.01\text{M}}\text{Fe}_{2.99\text{M}}\text{O}_4$ , **c**  $\text{Co}_{0.02\text{M}}\text{Fe}_{2.98\text{M}}\text{O}_4$ , **d**  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$ , **e**  $\text{Co}_{0.04\text{M}}\text{Fe}_{2.96\text{M}}\text{O}_4$

0.01M, 0.02M, 0.03M the lattice constant remains the same. The strain produced beyond 0.03M the lattice constant is slightly increased by  $0.034 \text{ \AA}$  due to stress and strain on the surface of the materials are induced by PVP matrix [27]. As the  $\text{Co}^{2+}$  concentration rises, the structure will be more nearby to inverse spinel type that in turn reduces the contribution of hopping and decreases the size [9]. The X-ray density ( $D_x$ ) was computed from the values of lattice parameter ( $a$ ) using the following formula [28–31]:

$$D_x = 8M/\text{Na}^3\text{g}/\text{cm}^3.$$

**Table 2** Structural properties of ferrite nanoparticles (XRD)

Materials	Crystalline size (nm)	Lattice constant (a) $\text{ \AA}$	Lattice strain ( $\epsilon$ )	Volume $\text{ \AA}^3$	X-ray density ( $\text{g}/\text{cm}^3$ )
$\text{Fe}_3\text{M}\text{O}_4$	13.2	8.357	0.009	583.6	5.34
$\text{Co}_{0.01\text{M}}\text{Fe}_{2.99\text{M}}\text{O}_4$	19.2	8.357	0.006	583.6	5.34
$\text{Co}_{0.02\text{M}}\text{Fe}_{2.98\text{M}}\text{O}_4$	5.8	8.357	0.020	583.6	5.34
$\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$	5.8	8.357	0.020	583.6	5.34
$\text{Co}_{0.04\text{M}}\text{Fe}_{2.96\text{M}}\text{O}_4$	5.7	8.391	0.020	590.8	5.27

where '8' represents the number of molecules in a unit cell of spinel lattice, 'M' is the molecular weight of composition, 'N' is the Avogadro's number and 'a' is the lattice parameter. It can be seen from Table 2, the X-ray density ( $D_x$ ) increases with the increasing Co substitution in Ni Ferrites and it shows the densification of the material. The X-ray density is found to depend on the lattice parameter and molecular weight of the samples. Hence, the substituted  $\text{Co}^{2+}$  increases, the lattice parameter decreases and X-ray density increases. The volume of the unit cell is [28]

$$V = a^3 (\text{\AA})^3.$$

The volume of the unit cell decreases with increasing Co substitution in  $\text{Fe}_3\text{O}_4$ , because the lattice parameter decreases by increasing the Co concentration. The strain induced in the grown nanoparticles has been calculated using the following formula [31]:

$$\varepsilon = (\beta \cos \theta) / 4$$

where  $\beta$  is full width at half maximum measured in radians and  $\theta$  in degrees. A micro-strain (lattice strain) means that the distance of the relevant crystal planes is not identical which is possibly due to the presence of defects and stress. Furthermore, the overall decrease of the lattice parameters occurred when the bigger ion ( $\text{Co}^{2+} \rightarrow 70 \text{ nm}$ ) is partially substituted by the smaller one ( $\text{Fe}^{3+} \rightarrow 60 \text{ nm}$ ).

### 3.2 FTIR analysis

To legitimize the presence of  $\text{Co}^{2+}$  particles in our tail compound, we think about the effectively detailed FTIR spectrum of pure  $\text{Fe}_3\text{O}_4$  [20] for comparison as appeared in Fig. 2. FTIR spectroscopy is used to study the surface chemistry and different bonds existing in the nanoparticles [32]. The Fourier-transform infrared spectra of  $\text{CoFe}_2\text{O}_4$  nanoparticles were recorded in the frequency range in between 400 and 4000  $\text{cm}^{-1}$ . The subject of the absorption spectrum reveals that positions of the cations in the crystal through the vibration mode. The strong peaks about 573–538  $\text{cm}^{-1}$  wave number were due to the stretching vibrations of the metal at the tetrahedral voids (Fe–O–Co) with the high-frequency bands, and the stretching vibrations of the metal complex (Fe–O–Fe) at the octahedral voids appear lower with frequency bands at 468–455  $\text{cm}^{-1}$  which confirms the phase of  $\text{CoFe}_2\text{O}_4$  [24, 32]. It helps to improve their magnetic property to have inverse spinel structures. The stretching of C–O bond at 1136  $\text{cm}^{-1}$  [33] and 867  $\text{cm}^{-1}$  was assigned to deformation of Fe–OH groups [34]. The peaks at 1594  $\text{cm}^{-1}$  were assigned to stretching and bending vibrations of absorption water on surfaces of nanostructures [35]. The vibrational frequencies associated

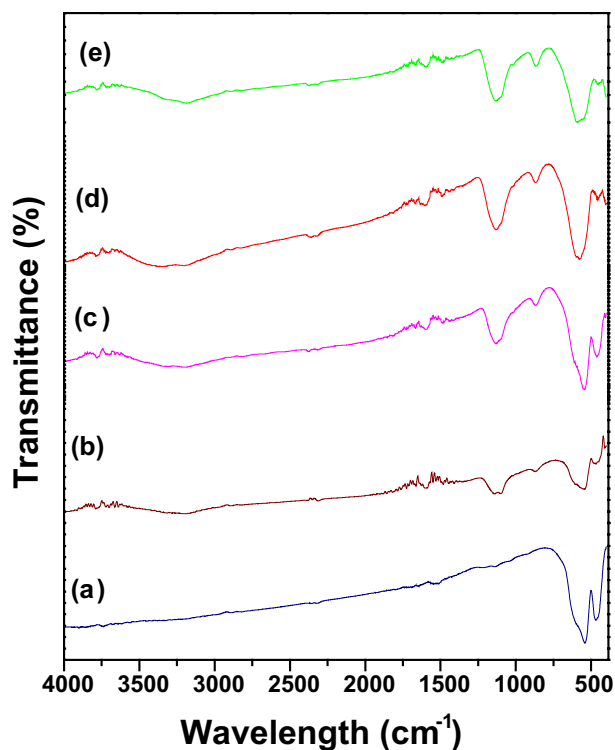


Fig. 2 FTIR spectra of cobalt ferrite nanoparticles. **a**  $\text{Fe}_3\text{M}_0\text{O}_4$ , **b**  $\text{Co}_{0.01M_x}\text{Fe}_{2.99M_x}\text{O}_4$ , **c**  $\text{Co}_{0.02M_x}\text{Fe}_{2.98M_x}\text{O}_4$ , **d**  $\text{Co}_{0.03M_x}\text{Fe}_{2.97M_x}\text{O}_4$ , **e**  $\text{Co}_{0.04M_x}\text{Fe}_{2.96M_x}\text{O}_4$

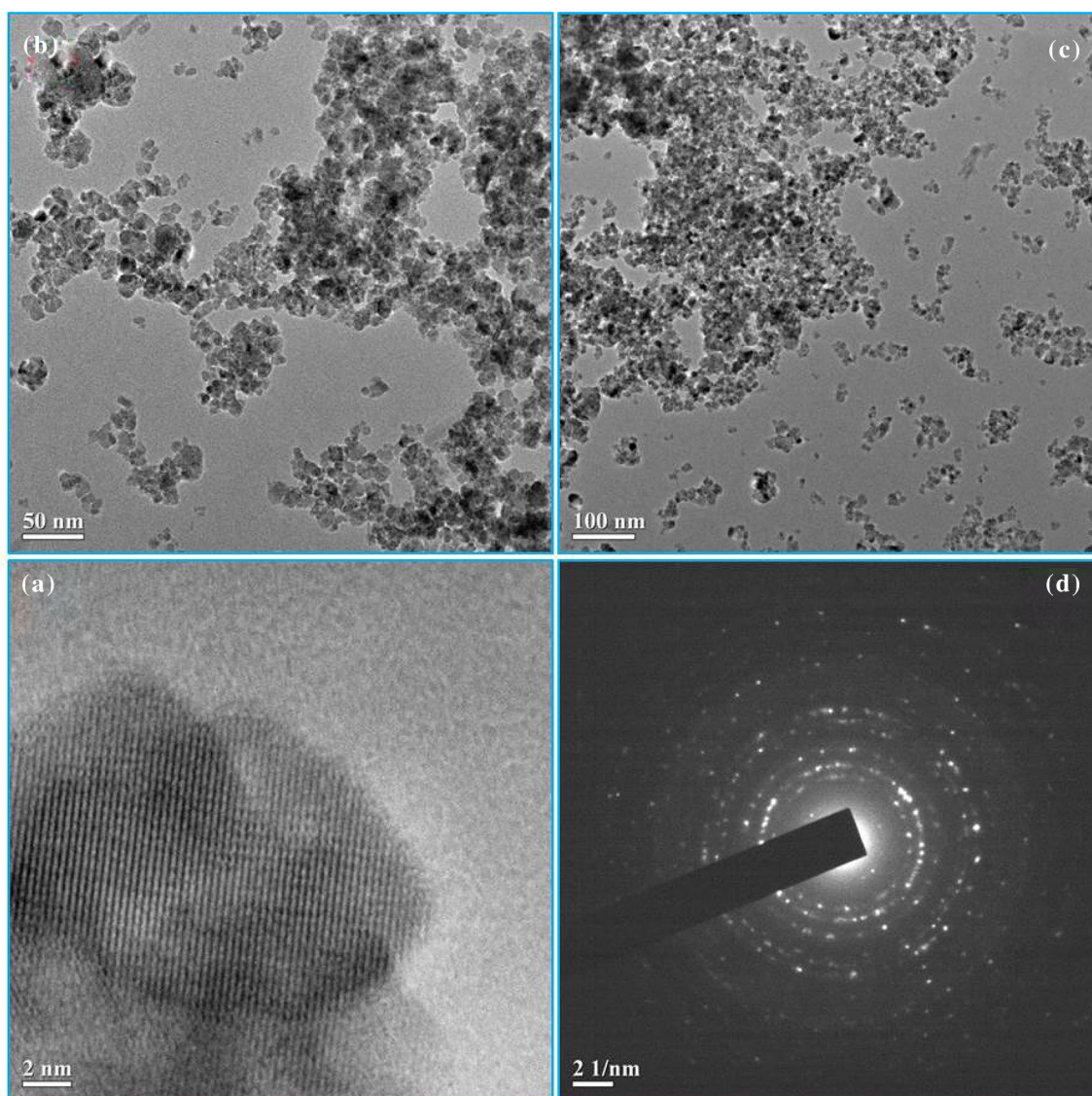
with cobalt ferrite material centered at 3191  $\text{cm}^{-1}$  are due to O–H stretching. The infrared absorption frequencies and the corresponding vibrational assignments of  $\text{CoFe}_2\text{O}_4$  nanoparticles are shown in Table 3.

### 3.3 TEM analysis

Figure 3a–c shows the morphology of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  ( $x=0.03 \text{ M}$ ) which was observed by a picture of TEM, correspondingly. The particle size is varied from 2 to 50 nm which is evident from our work reported [20] for  $\text{Fe}_3\text{O}_4$  nanoparticles. The domain wall morphology has positively oriented domains that grow up, and the negatively oriented ones shrink. The nature of  $\text{CoFe}_2\text{O}_4$  particles becomes regular, and the allotment of particles is uniform. The  $\text{Co}^{2+}$  cation is doped with  $\text{Fe}_3\text{O}_4$  pure ferrites, and the nanoparticles achieved spherical shape and good agglomeration. Hence, the estimated particle size decreases from 100 to 2 nm. It reveals that the particles exhibited the super-ferromagnetic nature [16]. These nanosized particles form nanocluster in order to reduce the interfacial energy connecting the personage nanocrystals with the desired size of particles and are used in drug delivery applications [17]. The patterns of selective area electron diffraction (SAED) of the samples are shown in Fig. 3d. The

**Table 3** Tentative vibrational assignments of ferrite nanostructures

Frequencies ( $\text{cm}^{-1}$ )					Tentative vibrational assignments
$\text{Fe}_3\text{M}\text{O}_4$	$\text{Co}_{0.01\text{M}}\text{Fe}_{2.99\text{M}}\text{O}_4$	$\text{Co}_{0.02\text{M}}\text{Fe}_{2.98\text{M}}\text{O}_4$	$\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$	$\text{Co}_{0.04\text{M}}\text{Fe}_{2.96\text{M}}\text{O}_4$	
–	–	–	–	3191	O–H stretching
–	–	–	1594	1594	Stretching and bending vibrations of absorption water on surfaces nanostructures
–	1126	1136	1126	1126	Stretching of C–O bond
–	–	867	867	867	Fe–OH groups
538	538	538	573	573	Tetrahedral clusters intrinsic stretching vibrations of the metal at the tetrahedral site ( $\text{C}_\text{o} \leftrightarrow \text{Fe}$ ) high-frequency bonds
468	468	455	455	468	Octahedral clusters assigned to octahedral-metal stretching ( $\text{Fe} \leftrightarrow \text{Fe}$ ) low-frequency bonds

**Fig. 3** TEM images (a–c) and SAED pattern (d) of  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  nanoparticles

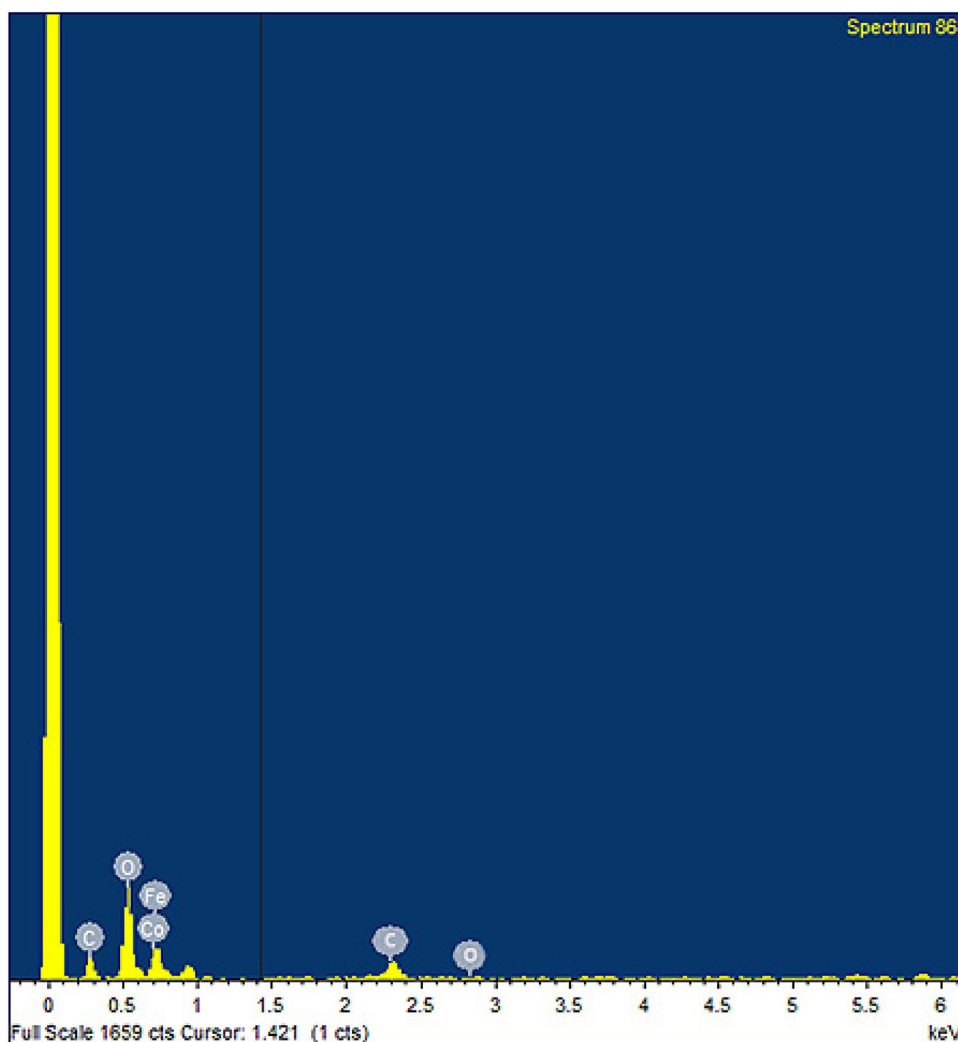
polycrystalline nature of a pure  $\text{CoFe}_2\text{O}_4$  with high crystallinity is revealed. And the bright spot is also obtained with Debye ring pattern which represents polycrystalline nature of the samples. Chemical purity along with stoichiometry of the  $\text{CoFe}_2\text{O}_4$  nanoparticles was examined by EDX spectroscopy. We found that Co, Fe, C, O elements alone are present in the sample as shown in Fig. 4. The EDX study also confirmed that the precursors used in the synthesis have entirely undergone the chemical effect to form the single-phase nanocrystalline cobalt ferrite.

### 3.4 VSM analysis

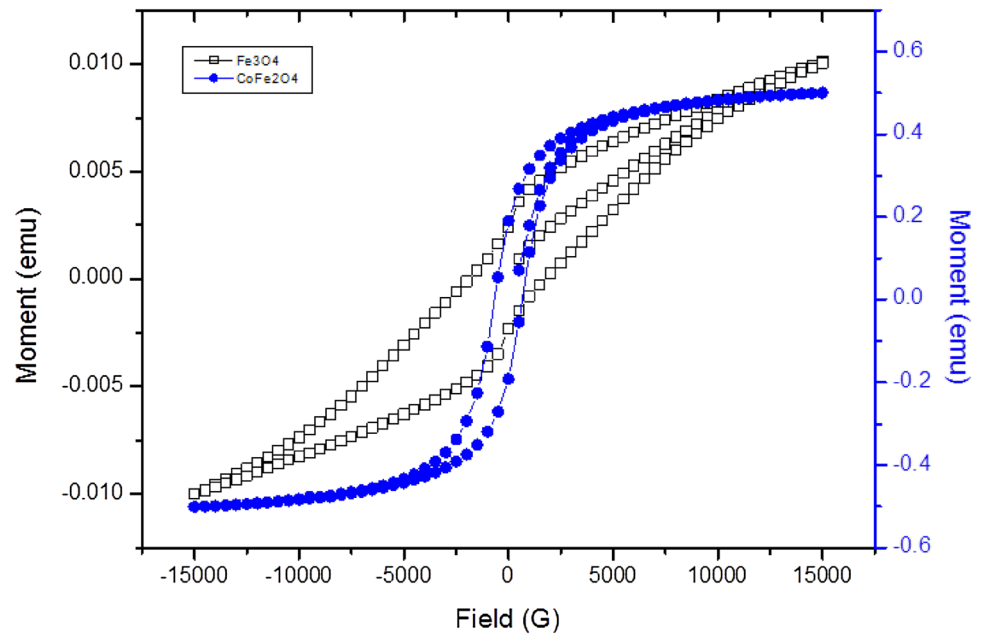
The VSM analysis of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  (where  $x=0.03$  M) is shown in Fig. 5. The sample of  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  shows the enormous changes in magnetic specifications, when compared to  $\text{Fe}_3\text{O}_4$  nanoparticles [20] which are synthesized by precipitation method. The hysteresis loops were identified and characterized to clarify the parameters of ferromagnetic materials, such as the saturation magnetization ( $M_s$ ), retentivity ( $M_r$ )

and coercivity ( $H_{ci}$ ). The magnetic factors for the materials are prepared by co-precipitation methods as summarized in Table 4. For the site occupancy of magnetic cations at the tetrahedral along with octahedral sites define magnetization ( $M_s$ ) [16]. The magnetic ability of spinel ferrites is actively dependent on the share of the various cations among (A) and (B) sites [17]. The  $\text{Co}^{2+}-\text{O}^{2-}-\text{Fe}^{3+}$  exchange interaction is very strong. So, these pairs of metal ions (radical's production: two or more atoms bound together as a single unit and form part of a domain) were contributing magnetic energy, whereas the  $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$  interaction is very weak because  $\text{Fe}^{3+}$  ions were antiferromagnetically ( $\uparrow\downarrow$ ) coupled. Hence, these pair of metal ions cannot contribute magnetic energy in the sample [36]. This involves that the hysteresis loop of the materials was exaggerated evidently by doped elements at the room temperature, The saturation magnetization was decreased from  $10.064\text{E}-3$  to  $0.5008$  emu/g, but the residual magnetization and coercivity of ferrite were endorsed of the cobalt ferrite [21]. The ionic radius of  $\text{Co}^{2+}$  (70 pm) is greater than  $\text{Fe}^{3+}$  (60 pm) cation. Hence,  $\text{Fe}^{3+}$  cations are shared

**Fig. 4** Energy-dispersive analysis of X-ray spectrum (EDAX) of  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  nanoparticles



**Fig. 5** VSM images of  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  nanoparticles at room temperature



**Table 4** VSM analysis of  $\text{Fe}_3\text{O}_4$  and  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  samples

Sample	$M_s$ (emu/g)	$M_r$ (emu/g)	$H_{ci}$ (G)	Magnetic moment ( $\mu\text{B}$ )	$R = M_r/M_s$	Anisotropy constant (K) erg/g
$\text{Fe}_3\text{O}_4$	10.064E-3	2.3715E-3	1817.7	$4.34 \times 10^{-4}$	0.2356	19.05
$\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$	0.5008	0.1908	661.04	0.0210	0.3809	344.84

among tetrahedral and octahedral voids which defines the antiparallel magnetic spin enclosed by the tetrahedral along with octahedral sites. It causes inverse spinel ferromagnetic structure. The following reduction in saturation magnetization is a way of decreasing the particle size. The highest coercive field up to 661.04 G is accredited to the sample synthesized at pH ~ 11 [37]. The sharing of cations among the lattice sites is provisional on methodologies of preparation. The average particle size is very small (9 nm) and approaches the simple dimension of a simple saturated magnetic domain. The setback of magnetization can occur only by complete rotation of domain within a particle. From Table 4, the coercivity is decreased when  $\text{Co}^{2+}$  is increased and then the magnetic specifications considerably increased. Because  $\text{Fe}^{3+}$  ions are parallel to one direction and remaining half of the  $\text{Fe}^{3+}$  ions parallel to opposite direction, and hence they cancel each other. Therefore, the net magnetic moment is only due to  $\text{Fe}^{3+}$  ions alone. The magnetic moment ( $\mu\text{B}$ ) per atom in Bohr magneton for each sample is calculated using the following equation and included in Table 4:

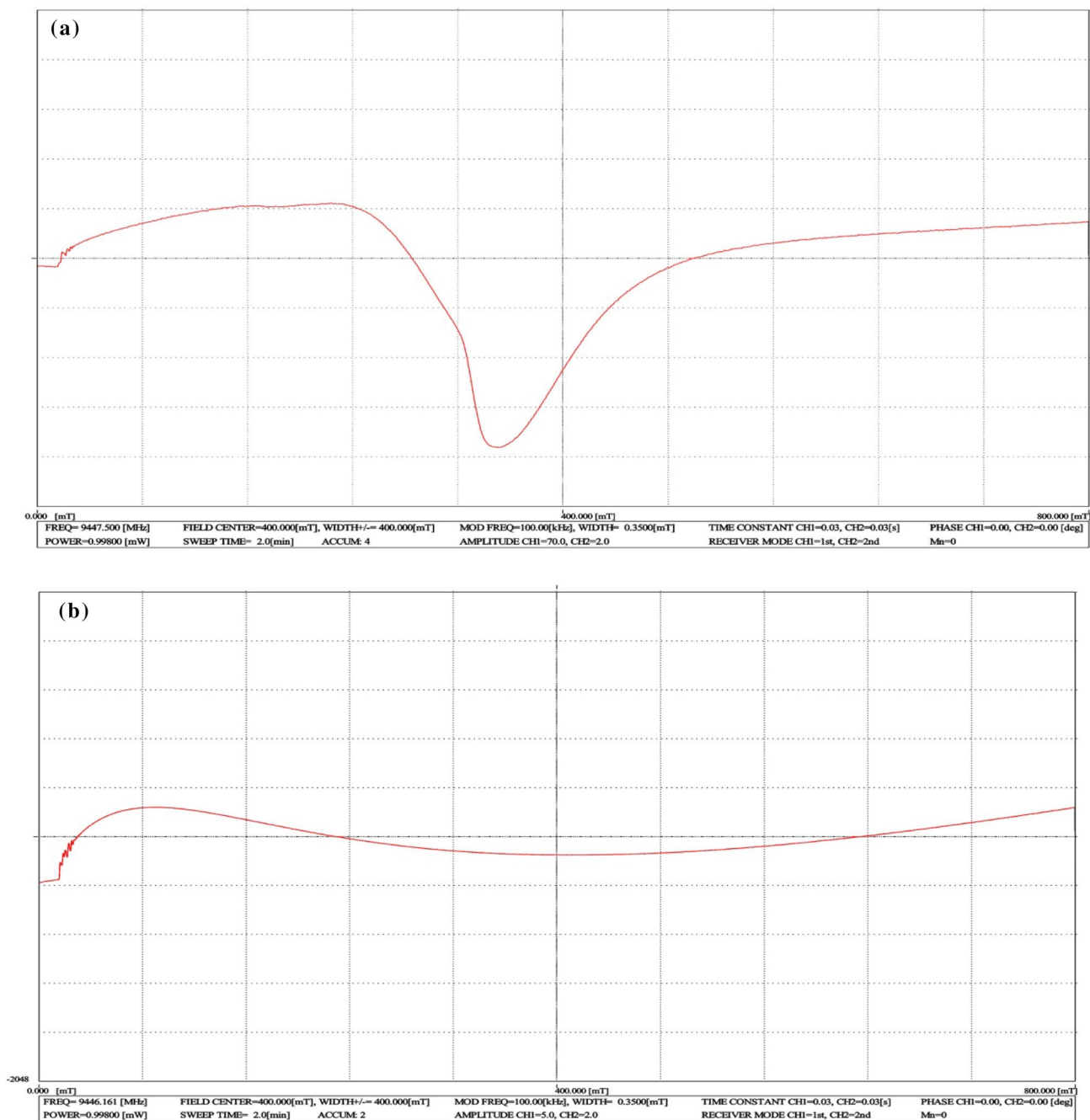
$$\mu\text{B} = M \times [M_s/5585]$$

where ' $M$ ' is the molecular weight of  $\text{CoFe}_2\text{O}_4$  [38]. For lower value of magnetic moment was obtained of all

sample exhibits to minimize energy loss. The remnant ratio is a property of magnetic materials results high value, the lower value of remnant to help us to analyze different materials response and accordingly determine where the materials to be applied. The lesser remnant ratio was used as the sensitivity, whereas higher values of remnant ratio designate different materials response of magnetic recording and memory devices. Also the magnetic anisotropy ( $K$ ) is calculated as [39]

$$K = (H_{ci} \times M_s)/0.96 \text{ erg/g}$$

Magnetic anisotropy depends upon the magnetic properties. It gives some valuable information about the orientation of the field with respect to the crystal lattice. From Table 4, magnetic anisotropy increases (19.05  $\rightarrow$  344.84 erg/g) when Co is added with  $\text{Fe}_3\text{O}_4$ . This is due to the fact that  $H_c$  decreases with increase in magnetocrystalline anisotropy [39]. The hysteresis loop is very narrow, so the loop area is less. Hence, hysteresis loss is minimum where as coercivity and retentivity are small, having low eddy current loss results all samples are exhibited to soft magnetic materials. This is the important consideration when the materials can be used for microwave frequency applications.



**Fig. 6** EPR images of **a**  $\text{Fe}_3\text{M O}_4$  and **b**  $\text{Co}_{0.03\text{M}}\text{Fe}_{2.97\text{M}}\text{O}_4$  nanoparticles at room temperature

### 3.5 EPR analysis

Electron spin resonance (ESR) spectra also called electron paramagnetic resonance (EPR) spectra had confined to the evaluation of molecules or ions having more unpaired electrons. Still, the technique is used for investigating the character of aspect in paramagnetic systems. It is same as the frequency split-up among two voids. This forms the basis of resonance phenomenon.

It has been used to study of radical atoms with at least one unpaired electron formed in the materials. Since the radicals characteristically yield an unpaired spin on the ferrite particles from which electron is uninvolved. On the other hand, the materials normally have an oxygen molecule  $\text{O}^{2-}$  that missed an electron and will steady it by thieving an electron from an adjacent molecule ( $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$ ). It is particularly fruitful that the radicals have been produced in the materials. The study of radicals gives



selective information about the locations of cations and magnetic specifications. The  $g$  factor was calculated using the following equation [38, 40]:

$$g = h\nu/H\beta$$

where ( $h$ ) is the Planck's constant,  $\nu$  is the frequency;  $H$  is the resonance magnetic field and  $\beta$  is the Bohr magneton. The EPR spectra of  $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$  (where  $x=0.03$  M) are shown in Fig. 6. The strong dipole interactions give  $g$  value and a huge resonance line width, while strong super-exchange interactions produce a small line width and  $g$  value ( $g=2.40$ ). This suggests that the magnetic particle spins interact with  $\text{O}^{2-}$ . Hence, magnetic materials exhibit to ferromagnetism as the result of unpaired electrons spins can be induced between tetrahedral and octahedral sites. Generally, the magnetic dipolar interactions and super-exchange interactions between the magnetic ions through oxygen ions are the two important factors that determine the  $g$  values and the resonance line width ( $H$ ). The super-exchange interactions generally increase, when the distance between the magnetic ions and oxygen ions decreases. From the EPR spectra, all the samples display a sharp symmetrical signal and a broad asymmetrical signal with a slight shift from the free electron position ( $g=2.0023$ ). The ferromagnetic behavior of the samples is confirmed through the  $g$  values ( $g=2.812$ ). The line width and the  $g$  values obtained for the samples may be attributed to the ferromagnetic resonance due to  $\text{Co}^{2+}$  ions [41].

## 4 Conclusions

The PVP-coated cubic inverse spinel cobalt ferrite nanoparticles were acquired by chemical co-precipitation technique. XRD results show that the particle sizes fall in the range from 19 to 5 nm. The FT-IR spectroscopy expresses the relative occupancy between half of  $\text{Co}^{2+}$  ions in the tetrahedral along with octahedral fashion through their lower and higher vibration modes. So these materials behaved as ferromagnetic materials about the inverse spinel structure of the cobalt ferrite. The TEM is exposed to a good formation of agglomerated spherical nanosphere. EDX confirmed the occurrence of Co, Fe, C, O elements alone in the sample. The VSM results reveal that the hysteresis loop of the samples was disturbed by doped  $\text{Co}^{2+}$  at the room temperature, resulting in the increase of exchange interaction connecting two sites. The EPR spectra at room temperature confirm the occurrence of ferromagnetism from the  $g$  value of Co-doped  $\text{Fe}_3\text{O}_4$  nanoparticles.

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## Compliance with ethical standards

**Conflicts of interest** There are no conflicts to declare.

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