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Effect of Cobalt Ion Concentration and Thermal Annealing Temperature on Structural and Magnetic Properties of CoFe 2 0 4 nanoparticles

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Abstract

Exploring physical properties of magnetic nanoferrites for applications in data storage media and biomedicine is a crucial step, providing new insights into the physics of nanostructured materials. Here, the focus is on studying the effect of cobalt ion concentration and thermal annealing temperature on structural and magnetic properties of cobalt ferrite (CoFe₂O₄) nanoparticles (NPs) synthesized using a co-precipitation method. To this end, $Co_{1-x}(Fe_2O_4)_x$ (x = 0.25, 0.5, and 0.75) NPs are initially prepared and then thermally annealed at different temperatures (T = 400 °C-800 °C). X-ray diffraction patterns along with field-emission scanning electron microscopic images indicate the formation of inverse cubic spinel structure with different crystallite sizes and NP size distributions when changing the cobalt ion concentration. Based on hysteresis loop measurements, magnetic parameters such as saturation magnetization (M_s) and coercivity (H_c) show increasing trends from 5.641 emu/g and 146.246 Oe to 8.936 emu/g and 1789.555 Oe when decreasing the cobalt ion concentration. By performing the annealing process, magnetic properties are significantly enhanced in the case of x = 0.25 and 0.5 at T = 400 °C and 600 °C, achieving M_s = 129.954 emu/g and H_c = 1137.697 Oe. Meanwhile, first-order reversal curve (FORC) diagrams are employed to map magnetostatic interactions and coercivity distributions as a function of cobalt ion concentration for NPs annealed at T = 400 °C, manifesting magnetically soft and hard phases. It is found the maximum FORC distribution shifts to higher H_c values with decreasing the cobalt ion concentration.

1. Introduction

Magnetic plasmonic nanoparticles are of tremendous interest in biomedicine due to their numerous potential uses [1], including as in drug delivery, magnetic hyperthermia, photo thermal treatment, and molecular imaging [2]. Metallic-nonmetallic structures are the most common type of magnetic-plasmonic heterodimer due to their superior qualities, particularly magnetic properties and chemical/biological stability. Where it is considered CoFe₂O₄ Nps, one of the types nonmetallic magnetic transition metal oxides used to form magnetic-plasmonic nanoparticles[3].

Cobalt ferrite (CoFe₂O₄) is one of hard magnetic materials and have recently been of interest due to its high coercivity (H_c= 5400 Oe) at room temperature, moderate saturation magnetization (M_s= 80 emu/g), and good mechanical and chemical stability [4, 5]. Also, cobalt ferrite possesses high hardness, electrical insulation, photomagnetism, magnetocrystalline anisotropy, wear resistance, and electromagnetic performance [6–8]. In turn, these features make CoFe₂O₄ a promising candidate for various applications in magnetic devices such as high-density recording media and spintronics [9, 12], as well as in magnetic fluids for biomedical purposes [13].

 $CoFe_2O_4$ is considered a member of the family of inverse spinel structures, where cobalt ions (Co⁺²) occupy half of octahedral sites of the lattice structure. The other half of octahedral sites as well as all the tetrahedral sites are occupied by iron ions (Fe⁺³). Accordingly, the ferrimagnetic structure is created by

the two anti-parallel sub lattices, being coupled by superexchange interactions through oxygen ions (0^{-2}) [14, 15].

Basically, magnetic properties of $CoFe_2O_4$ nanoparticles (NPs) strongly depend on annealing temperature, heating rate, and NP size and shape [16]. The morphological properties of NPs are directly related to the method of preparation. There are a number of reports on the chemical synthesis of $CoFe_2O_4$ NPs using different methods such as co-precipitation [17], hydrothermal [18], micro-emulsion [19], citrategel precursor [20], and sol-gel [21]. However, several of these methods cannot be used for large scale synthesis purposes because they require costly and often toxic reagents, high reaction temperatures, cumbersome synthetic steps, and lengthy reaction times [22]. Among the aforementioned methods, the co-precipitation is taken into account as one of the best and attractive approaches due to its simple and cost-effective experimental steps, while also providing small NP sizes at low annealing temperatures [23]. However, the effect of Co^{+2} ion concentration and thermal annealing temperature on structural properties and magnetic behavior of $CoFe_2O_4$ NPs needs to be better studied and understood.

As an important task, it is crucial to understand magnetic characteristics of ferrite NPs so as to develop their applicability in different research fields. In this respect, first-order reversal curve (FORC) diagram technique can be utilized as a powerful approach to investigating magnetic properties in detail [24]. In other words, FORC diagram technique can reveal different magnetic phases, in addition to determining magnetic states (e.g., single domain, superparamagnetic, and multi-domain states) of materials. This technique also enables the determination of magnetostatic interactions and coercive field distributions, providing extra data compared to hysteresis loop measurements. Thus far, FORC diagram technique has been employed to study magnetic characteristics of various nanomaterials, including nanowires, NPs, and nanorods [25].

In this paper, a co-precipitation method is utilized to synthesize cobalt ferrite NPs with varied cobalt ion concentrations, followed by thermal annealing at different temperatures. Various characterization techniques are used to study structural, morphological, and compositional properties of the resulting NPs. In particular, magnetic behavior of as-synthesized and annealed $Co_{1-x}(Fe_2O_4)_x$ (x = 0.25, 0.5, and 0.75) NPs is studied based on magnetic parameters extracted from hysteresis loop and FORC diagram measurements, indicating their dependence on the physical and chemical features.

2. Experimental details

2.1. Materials

All the chemical reagents, including iron (III) chloride (FeCl₃, Thomas Baker, 99%), sodium hydroxide (NaOH, Thomas Baker, 99%), and cobalt (II) chloride hexahydrate (CoCl₂.6H₂O, Oxford Lab Chem., 99%) were of analytical grade and utilized without performing further purification. Also, deionized water was used as a solvent.

2.2. Synthesis of CoFe₂O₄ NPs

A co-precipitation method was used to synthesized $Co_{1-x}(Fe_2O_4)_x$ NPs with varied values of x (0.25, 0.5, and 0.75). The molarity and weight of the precursors used are presented in Table 1.

Table 1

The molarity and weight of precursors used in the co-precipitation synthesis of $Co_{1-x}(Fe_2O_4)_x$ NPs.											
x	FeCl ₃		CoCl ₂ .6H ₂ O		NPs						
	Molarity	Weight	Molarity	Weight							
0.25	0.06 M	4.05 g	0.09 M	8.91 g	Co _{0.75} (Fe ₂ O ₄) _{0.25}						
0.5	0.12 M	8.1 g	0.06 M	5.94 g	Co _{0.5} (Fe ₂ O ₄) _{0.5}						
0.75	0.18 M	12.15 g	0.03 M	2.97 g	Co _{0.25} (Fe ₂ O ₄) _{0.75}						

In order to prepare the NPs, FeCl₃ and CoCl₂.6H₂O precursors were weighed (according to stoichiometric proportions with molarity listed in Table 1) and dissolved in 400 ml of deionized water. The resulting mixed solution was stirred at the temperature of ~ 75 °C for 30 min in order to improve its homogeneity. Afterwards, NaOH solution (6 M in 100 ml of deionized water) was dropwise added to the previous solution using a burette until reaching pH = 13. During the reaction process, the solution color changed from brown to dark brown, which indicated the formation of ferrite NPs. The precipitate was collected using a permanent magnetic and then rinsed several times with distilled water and ethanol. Finally, the rinsed precipitate was heated in an oven at 100 °C for 6 h, followed by crushing it to powder. Figure 1 schematically depicts the co-precipitation synthesis process of CoFe₂O₄ NPs. On the other hand, the effect of thermal annealing temperature on the properties of the CoFe₂O₄ NPs was studied by placing them in a furnace at temperatures of 400 °C, 600 °C, and 800 °C under mixed argon and hydrogen atmosphere (85% Ar and 15% H₂).

2.3. Characterizations

To study crystal structure of CoFe₂O₄ NPs synthesized with different cobalt ion concentrations, X-ray diffraction (XRD, Philips X'Pert Pro) analysis with Ni-filtered Cu Kα radiation was performed. Morphological and compositional characteristics were determined using field-emission scanning electron microscopy (FE-SEM, MIRA3 TESCAN) equipped with energy dispersive spectroscopy (EDS).

Room-temperature magnetic properties of $CoFe_2O_4$ NPs were investigated using hysteresis loop analysis via a vibrating sample magnetometer (VSM, MDK, Iran) equipped with FORC software. To carry out FORC diagram technique, a strong external magnetic field (*H*) was applied to magnetically saturate the NPs. Afterwards, *H* decreased to a reversal field (*H*_r), while also performing the measurement of magnetization

 $M(H, H_r)$. Thereby, sets of FORCs were acquired. To obtain the distribution of FORC, $\rho(H, H_r)$, the equation given below was used [26]:

$$ho_{(H,H_r)=-rac{1}{2}rac{\partial^2 M_{(H,H_r)}}{\partial H\partial H_r}}$$

1

The FORC diagram was plotted, having colors ranging from blue (minimum of ρ) to red (maximum of ρ). Also, the coordinates {*H*, *H*_{*r*}} changed to interaction field (*H*_{*u*}) and coercive field (*H*_{*c*}) axes as follows [27]:

$$H_u=rac{H+H_r}{2}, H_c=rac{H-H_r}{2},$$

2

3. Results and discussion

3.1. Structural properties

Figure 2 shows XRD patterns obtained from $Co_{1-x}(Fe_2O_4)_x$ NPs (x = 0.25, 0.5, and 0.75). The observed peaks of (111), (220), (311), (222), (400), (205), (442), (511), (440), (531), (553) and (622) in the XRD patterns are well matched with standard JCPDS card no. (00-022-1086) [28], indicating the formation of inverse cubic spinel structure with Fd-3m space group. Also, no impurities are present in the NPs synthesized with different cobalt ion concentrations.

The average crystallite size was estimated using Scherrer's equation [29], taking into account the highly intense peak of (311) orientation. The lattice constant (*a*) was also calculated using the following equation: $a = d\sqrt{h^2 + k^2 + l^2}$ [30, 31], where *d* is the interplanar distance and (hkl) are the Miller indices. The results obtained are presented in Table 2. As observed, the crystallite size considerably increases from 7.077 to 23.559 nm with decreasing the cobalt ion concentration from $Co_{0.75}(Fe_2O_4)_{0.25}$ to $Co_{0.25}(Fe_2O_4)_{0.75}$ NPs. Meanwhile, the lattice parameter slightly changes from 8.247 to 8.349 Å.

synthesized with different cobalt ion concentrations.								
NPs	Average crystallite size	Lattice parameter						
	(nm)	(Å)						
Co _{0.75} (Fe ₂ O ₄) _{0.25}	7.077	8.247						
Co _{0.5} (Fe ₂ O ₄) _{0.5}	11.786	8.304						
Co _{0.25} (Fe ₂ O ₄) _{0.75}	23.559	8.349						

Table 2

3.2. Morphological and compositional properties

Figure 3(a)–(c) shows FE-SEM images of $Co_{1-x}(Fe_2O_4)_x$ NPs synthesized using different cobalt ion concentrations (x = 0.25, 0.5, and 0.75). The NP size distributions were determined using Digimizer software, and the corresponding histograms are shown in Fig. 4. As observed, the NPs have spherical-like morphology with size distribution ranging from 7 to 30 nm. While the NPs possess homogeneous sizes, the agglomeration increases with decreasing the size. In other words, the mean diameter of the synthesized NPs increases with decreasing the concentration of Co²⁺ ions, thereby reducing their agglomeration.

The mean diameter of $Co_{0.75}(Fe_2O_4)_{0.25}$, $Co_{0.5}(Fe_2O_4)_{0.5}$, and $Co_{0.25}(Fe_2O_4)_{0.75}$ NPs is found to be 9.89, 12.27, and 24.03 nm, respectively, as shown in Fig. 4(a)-(c). It is worth noting that the mean diameter of the NPs matches well with the crystallite size obtained from the XRD analysis (see Table 2). The EDS spectra shown in Fig. 5 also confirm the formation of $Co_{1-x}(Fe_2O_4)_x$ NPs with the stoichiometric ratio.

3.3. Magnetic properties

3.3.1. Hysteresis loop measurements

The room-temperature hysteresis loop measurements of as-synthesized and annealed $Co_{1-x}(Fe_2O_4)_x$ NPs (x = 0.25, 0.5, and 0.75) are shown in Fig. 6. Based on these measurements, the values of M_s , H_c , remnant magnetization (M_r) and remanence ratio (M_r/M_s) of the NPs were extracted, and the results are presented in Table 3.

From Fig. 6(a) and Table 3, magnetic properties of the as-synthesized NPs are noticeably observed to increase with decreasing the Co^{+2} ion concentration. In general, an increase in M_s can be justified based on the exchange interaction taking place between tetrahedral and octahedral sub-lattices and site occupation. The Neel model specifies three types of magnetic interactions between tetrahedral and octahedral sites for the spinel ferrite system, including both ions at the tetrahedral A site (i.e., A-A interaction), both ions at the octahedral B site (i.e., B-B interaction), and one ion at the tetrahedral A site

and the other at the octahedral B site (i.e., A–B interaction). The strength of the (A–B) interaction is considerably higher than that of the other two magnetic interactions [31]. Moreover, the increase in M_s (from 5.641 to 8.936 emu/g) with the reduction in Co⁺² concentration may arise from the replacement of Co⁺² ions (having a magnetic moment of 3 μ_B) by stronger magnetic Fe⁺³ ions (magnetic moment = 5 μ_B) in the octahedral B sites.

Alternatively, H_c value is observed to increase by replacing Co⁺² ion in Fe⁺³ octahedral site of CoFe₂O₄ NPs. Essentially, H_c of magnetic NPs is affected by several factors such as magnetocrystalline anisotropy, shape anisotropy, NP morphology, NP size distribution, and M_s [32]. In fact, it has been well documented that H_c of ferrite NPs can be correlated with their size, so that single domain particles with larger sizes will possess a larger magnetic anisotropy [33]. Herein, the increase in H_c (from 146.246 to 1789.555 Oe) with the reduction in Co⁺² concentration may be related to the increase in the mean diameter (from 9.89 to 24.03 nm), according to the FE-SEM results shown in Figs. 3 and 4.

Figure 4(b)–(d) shows room-temperature hysteresis loops of $Co_{1-x}(Fe_2O_4)_x$ NPs (x = 0.25, 0.5, and 0.75) annealed at T = 400 °C, 600 °C, and 800 °C. As can be seen, the hysteresis loop shape varies depending on the thermal annealing temperature. In the case of $Co_{0.25}(Fe_2O_4)_{0.75}$ NPs, M_s increases with increasing the annealing temperature, whereas the corresponding H_c is reduced. For $Co_{0.75}(Fe_2O_4)_{0.25}$ and $Co_{0.5}(Fe_2O_4)_{0.5}$ NPs, the maximum values of M_s (49.385 and 129.954 emu/g) are achieved at T = 600 °C.

Table 3 Magnetic properties of as-synthesized and annealed $Co_{1-x}(Fe_2O_4)_x$ NPs with x = 0.25, 0.5 and 0.75 extracted from hysteresis loop measurements.

NPs			Magnetic parameter				
			M _s (emu/g)	M _r (emu/g)	H _c (Oe)	M _r /M _s	
$Co_{0.75}(Fe_2O_4)_{0.25}$	As-synthesized NPs		5.641	1.051	146.264	0.186	
Annealed NPs		T = 400 °C	34.174	14.221	1093.088	0.416	
		T = 600 °C	49.385	14.601	924.476	0.408	
		T = 800 °C	35.781	6.561	575.679	0.132	
$Co_{0.5}(Fe_2O_4)_{0.5}$	As-synthesized NPs		6.933	1.504	208.291	0.216	
	Annealed NPs	T = 400 °C	68.079	27.225	1137.697	0.399	
		T = 600 °C	129.954	10.548	111.85	0.081	
		T = 800 °C	94.660	27.595	369.137	0.291	
$Co_{0.25}(Fe_2O_4)_{0.75}$	As-synthesized NPs		8.936	3.562	1789.555	0.398	
	Annealed NPs	T = 400 °C	67.049	32.577	1067.903	0.485	
		T = 600 °C	86.959	12.399	150.805	0.142	
		T = 800 °C	91.123	14.554	136.836	0.159	

Regarding the variation behavior of H_c , an increase in size of annealed NPs may enhance the anisotropy energy, which in turn results in an increase in H_c . The further increase in the thermal annealing temperature decreases H_c , which could be related to one of the following two reasons. Firstly, it may be due to a transition from single domain to pseudo-single domain or multidomain state with increasing NP size. Secondly, a combination of surface anisotropy and thermal energies may occur due to the increased temperature[34]. It is possible to acquire information about exchange interactions and magnetocrystalline anisotropy of ferrite nanomaterials based on M_r/M_s ratio [34]. In this respect, non-interacting uniaxial single domain NPs are expected to have M_r/M_s of 0.5, as theoretically described by Stoner-Wohlfarth model [36]. In the present study, M_r/M_s of annealed CoFe₂O₄ NPs is found to be in the range of 0.485– 0.081, indicating their magnetically interacting nature that can be evaluated using FORC diagram technique.

3.3.2. FORC diagrams

The FORC diagram technique was employed to acquire detailed and comprehensive information about magnetic behavior of the NPs [24]. The FORC diagrams of $Co_{1-x}(Fe_2O_4)_x$ NPs (x = 0.25, 0.5, and 0.75) annealed at T = 400 °C are shown in Fig. 7(a)–(c). From Fig. 7(a), a tear-drop configuration is observed in

the FORC diagram, having broad coercive field distributions with two peaks. The first distribution is located around the origin of the diagram, featuring the contribution of magnetically soft NPs with almost zero FORC coercivity value ($H_C^{FORC} \sim 0$ Oe). The second distribution is elongated along the H_c axis, arising from magnetically hard NPs with H_C^{FORC} = 1185 Oe. From the hysteresis loop measurements, H_c of $Co_{0.75}(Fe_2O_4)_{0.25}$ NPs was found to be about 1095 Oe, which is near to the corresponding H_C^{FORC} value. This indicates the dominant contribution of single domain NPs in determining the magnetic properties. In the case of $Co_{0.5}(Fe_2O_4)_{0.5}$ NPs, H_C^{FORC} shifts to a higher value (~ 1450 Oe) (see Fig. 7(b)), which is however accompanied with a slight increase in the hysteresis loop H_c to about 1135 Oe. The reason for this variation can be ascribed to the narrower coercive field distribution along the H_c axis after annealing the NPs with the reduced cobalt ion concertation.

By further reducing the cobalt ion concentration for the annealed $Co_{0.25}(Fe_2O_4)_{0.75}$ NPs, Fig. 7(c) demonstrates distinct magnetic soft and hard phases. In this case, H_C^{FORC} of the hard phase is similar to that of annealed $Co_{0.5}(Fe_2O_4)_{0.5}$ NPs. Moreover, the coercive field distribution is reduced along the H_c axis, leading a decrease in hysteresis loop H_c to about 1065 Oe. Concerning the magnetostatic interactions, while FORC diagrams of $Co_{0.75}(Fe_2O_4)_{0.25}$ and $Co_{0.5}(Fe_2O_4)_{0.5}$ NPs show similar distributions along H_u axis, the interaction field distribution of $Co_{0.25}(Fe_2O_4)_{0.75}$ NPs (Fig. 7(c)) is reduced, likely due to the separation of the magnetic phases.

4. Conclusions

 $Co_{1-x}(Fe_2O_4)_x$ NPs (x = 0.25, 0.5, and 0.75) have been synthesized by a co-precipitation method, followed by thermal annealing at T = 400 °C, 600 °C and 800 °C. Various characterization techniques such as XRD, FE-SEM, EDS and VSM were utilized to investigate structural, morphological, compositional, and magnetic properties of the resulting NPs. Based on XRD patterns and FE-SEM images, crystallite size and mean diameter of spherical-like NPs showed increasing trends in the range of 7.077–23.559 and 9.89– 24.03 nm, respectively, when decreasing the cobalt ion concertation (from x = 0.25 to 0.75). The VSM results comprised hysteresis loop and FORC diagram measurements of as-synthesized and annealed NPs. From the former measurement, a significant enhancement was observed in H_c value up to 1789.555 Oe, which was ascribed to the increase in the mean diameter of NPs. From the latter measurement, decreasing the cobalt ion concentration at T = 400 °C was found to separate soft and hard phases with reduced magnetostatic interactions. Also, the FORC diagrams indicated dominant role of single domain NPs in determining the magnetic properties after performing the annealing process.

Declarations

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24 g NaOH in 100 ml deionized water CoCl₂.6H₂O It is added 1:2M after $pH = \pm 13$ FeCl₃ Constantly stirred 1h hot-plate/magnetic T= 70-80 C° stirrer Washing with deionized water and ethanol bycentrifugation dry by oven CoFe₂O₄ and $Co_{1-x}(Fe_2O_4)_x$ Placed on heaters for nanoparticles 30 min 100 °C for 6 h

Figures

Figure 1

Schematic representation of the co-precipitation synthesis process of CoFe₂O₄ NPs.



XRD patterns of $Co_{1-x}(Fe_2O_4)_x$ NPs (x=0.25, 0.5, and 0.75).



FE-SEM images of $Co_{1-x}(Fe_2O_4)_x$ NPs: (a) x= 0.25, (b) x= 0.5, and (c) x=0.75.



Size distribution histograms of $Co_{1-x}(Fe_2O_4)_x$ NPs: (a) x=0.25, (b) x= 0.5, and (c) x=0.75.



Figure 5

EDS spectra of $Co_{1-x}(Fe_2O_4)_x$ NPs: (a) x= 0.25, (b) x= 0.5, and (c) x= 0.75.



Hysteresis loop measurements of $Co_{1-x}(Fe_2O_4)_x$ NPs: (a) as-synthesized NPs, and (b)–(d) annealed (T=400–600 °C) NPs with x=0.25, 0.5 and 0.75. The bottom-right insets show details of the loops.



Room-temperature FORC diagrams of $Co_{1-x}(Fe_2O_4)_x$ NPs annealed at T = 400 °C: (a) x = 0.25, (b) x = 0.5, and (c) x = 0.75. Note: magnitude of *H* is different in part (c).