Effect of pH Value on Synthesis and Properties of Zinc Cobalt Ferrite Nano Powders Prepared via Co-Precipitation Method

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Effect of pH Value on Synthesis and Properties of Zinc Cobalt Ferrite Nano Powders Prepared via Co-Precipitation Method

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Abstract

The effect of pH value on the synthesis of zinc cobalt ferrite nano powder via co-precipitation method was investigated. Zinc cobalt ferrite ($\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$) precipitated using a solution of nitrate raw materials under different pHs (pH=8, 10, 11, 12 and 14) and calcined at 750 °C for 2 hours. The obtained nano-powders were characterized by X-ray diffraction (XRD), Williamson-Hall relations and Extrapolate functions, field emission scanning electron microscopy (FESEM) and vibrating sample magnetometer (VSM) measurements.

The amount of pH had a significant effect on the structural and magnetic properties of the synthesized powders. At pHs 8 and 10, a tensile strain and above that a compressive strain was created in the system. By changing the tensile strain to compression the crystallite diameter increased, so that the crystallite diameter increased from 19.3 nm at pH 8 to 47.8 nm for pH=11. The H_c of the all samples was in the range of 140-150 Oe. The saturation magnetization, anisotropy and Bohr magneton constants were 100.38 emu/gr, 15357.70 erg/Oe and 4.27, respectively for the synthesized sample at pH=11, which were higher than the other samples. These changes are due to the effect that pH has on the parameters of the crystallite diameter, particle size and also on the cation distribution of the ions in tetrahedral/octahedral spaces.

Keywords: Cobalt ferrite; Coprecipitation; Cation distribution; Magnetic propertie

1. Introduction

Spinel ferrites with general formula MFe_2O_4 or $\text{MO}.\text{Fe}_2\text{O}_3$ (M: Fe, Co, Ni, Zn, etc.) are composed of a unit cell with 32 oxygen atoms in cubic close packed positions, with 8 tetrahedral spaces and 16 occupied octahedral sites. These ferrites are divided into two groups of normal and inverse. In normal spinel, all 8 divalent elements are in tetrahedral positions and all 16 trivalent elements are in octahedral spaces. Whereas in the inverse spinel, half of the 3-valent elements sit in tetrahedral spaces and the other half placed in the octahedral positions, and the 2-valence elements also occupy the octahedral spaces [1-3].

Cation distribution can effect electron mutation, magnetic exchange interactions, modify magnetic properties, and consequently the use of ferrites [4-7]. Due to this and achieving

various properties such as magnetic permeability, coercive force, anisotropy constant, saturation magnetization (M_s), mechanical stiffness, physical and chemical stability, the range of use of these materials is varied. Accordingly, much research has been done on the doping effect of different 2/3 valent elements inside the ferrite structures on the synthesis and magnetic properties [5–15]. Among them, cobalt ferrite is interested due to properties such as high magnetic permeability, high coercive force (H_c) (≥ 50 KOe), good saturation magnetization (M_s) (80 emu/gr), mechanical hardness and excellent physical and chemical stability. Hence, it is a good candidate for high-density magnetic recording, ferrofluid technology, drug delivery, magnetic resonance imaging (MRI), magnetic hyperthermia (MH) for cancerous tissues and radar absorption materials (RAM) [13].

Cobalt ferrite (CoFe_2O_4) has an inverse spinel structure. This means that 2-valent cobalt ions are in the octahedral (B) positions and half of the 3-valent iron ions are in the tetrahedral (A) spaces and the other half are in the octahedral sites [14,15]. On the other hand, the zinc element is a low-cost material and it's doping into cobalt ferrite to achieve the desired magnetic properties, especially for hyperthermia applications, is of interest to many researchers. Zinc ferrite is a normal spinel with 2-valent ions in the tetrahedral positions and all 3-valent ions in the octahedral spaces [2]. As a result, zinc doped cobalt ferrite may have a modified spinel structure $(\text{Zn}^{2+}_x\text{Fe}^{3+}_{1-x})^A [\text{Co}^{2+}_{1-x}\text{Fe}^{3+}_{1+x}]^B\text{O}_4$ [16].

Therefore, the synthesis of zinc cobalt ferrite is of great interest due to its potential application in multiple domains including magnetic hyperthermia. The properties of synthesized ferrites depend on the particles size, morphology and composition [17]. There are a number of methods for preparing magnetic nanoparticles (gaseous, solidous and liquidous phase synthesis). Although uniform nanoparticles have been synthesized using some of these methods, precise control of their size, shape and surface is generally challenging [8, 18, 19]. Among the various methods, Coprecipitation method is an easy and conventional way for the synthesis of magnetic nanoparticles from aqueous salt solutions. Ferrites are usually synthesized in an aqueous medium by chemical reaction according to following equations [17, 19]:

And as a result:

Where M can be Fe^{2+} , Mn^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Zn^{2+} , Ni^{2+} .

In powder synthesis by coprecipitation method, it is first necessary to precipitate various elements as hydroxide in the reaction system (Equations 1-2 and 1-4), then react with each other to form the desired product phase after calcination [17]. The pH value required for the formation of different elements as hydroxide varies. This means that the iron ion may precipitate at a pH value. This number is another value for the cobalt precipitate and for the zinc ion on another [7]. In general, complete precipitation at pHs between 8 and 14 is expected [7,19]. The size, morphology and composition of magnetic nanoparticles largely depend on the parameters affecting the synthesis process such as the type of salt used (eg chlorides, sulfates, nitrates), type of elements, M^{2+}/Fe^{3+} ratio, reaction temperature and pH value [19]. Therefore, in order to achieve the optimum properties, it is important to investigate the effective parameters on the formation of synthesized particles and how they affect them.

Although the pH parameter is one of the most effective factors in precipitation, and in particular the final properties of the powders, but so far, little research has been done on how it affects microstructure and magnetic properties of cobalt ferrite. However, Xiaogu Huang [7] has studied the effect of this factor on the properties of electromagnetic loss. Therefore, in this work, the link between pH parameter and cationic distribution, strain created in the structure, morphology and size of the crystallites have been investigated. Then, the role of these changes on magnetic properties of synthesized nanopowders has been discussed.

2. Experimental

2.1. Materials

In order to synthesis of zinc cobalt ferrite via co-precipitation method iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) ($M = 404 \text{ gr/mol}$, $\rho = 1.68 \text{ gr/cm}^3$, Merck), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) ($M = 290.93 \text{ gr/mol}$, $\rho = 1.87 \text{ gr/cm}^3$, Merck), zinc nitrate ($Zn(NO_3)_2 \cdot 4H_2O$) ($M = 261.39 \text{ gr/mol}$, $\rho = 1 \text{ gr/cm}^3$ Merck) and sodium hydroxide (NaOH) (Merck) were used as raw materials.

2.2. Synthesis method

To determine the effect of pH value on the process of zinc cobalt ferrite synthesis, at a constant molar ratio of zinc ($x_{zn} = 0.4$), ($Co_{0.6}Zn_{0.4}Fe_2O_4$), 0.5 M solutions of each of the

starting materials were first prepared on a heater stirrer at 400 rpm and 50 °C for 10 minutes. The prepared solutions were then mixed with each other and the pH of the resulting system was adjusted to 8, 10, 11, 12 and 14 with NaOH solution. After the solution was brought to the desired pH, the resulting solution was stirred at 80 °C for 5 hours at 700 rpm. The precipitates were poured onto filter paper and washed several times with deionized water. It is noteworthy that with the increase of the first NaOH droplets, the sheet-shaped precipitates were formed in the solution and with the further increase of NaOH the volume of the precipitates increased and the color of the solution changed from brown-cherry to dark brown. The obtained precipitates were dried for 24 hr at 110 °C. The dried powders were calcined for 2 h. From now on, specimens at different pHs are introduced as Z4P (8-14). The number 4 after Z denotes 0.4 mole zinc, and the numbers 8 through 14 after the letter P indicate the pH of the solution prepared.

2.3. Analysis techniques

Thermogravimetric analysis (TA Instruments, D-32609 Hullhorst, STA 504, Bahr Co. Germany) was taken to determine the calcination temperature. Phase compositions, strain analysis and lattice parameters of samples were analyzed by X-ray diffraction (XRD) (D8 ADVANCE, BRUKER, Germany) analysis. FESEM analysis (Mira 3-XMU) was performed to investigate the microstructural changes, size and morphology of the nanoparticles. The magnetic properties of the samples were also evaluated by VSM (Danesh Pajouh Co. Iran) technique.

3. Results and discussion

3.1. Thermogravimetric analysis

To determine the calcination temperature, thermogravimetric analysis was taken from the Z4P11 sample which is shown in Figure 1.

Figure 1- (a) TG/difTG analysis and, (b) rel. Mass analysis of sample containing 0.4 mol of zinc element prepared at pH=11

By examining the TG/dTG diagram (Fig. 1-a), it is observed an endothermic peak at a temperature of about 750 °C, which represents about 18.28% of the weight loss (Fig. 1-b), hence this temperature was selected as calcination temperature for prepared precipitates. The appearance of endothermic peaks around 100 °C and in the range of 220 to 460 °C are attributed to the evaporation of water present in the system as well as the nitrate and NaOH compounds, respectively [13]. The reaction system of the raw materials can be written as follows:

Also the weight changes of the calcined sample at 750 °C for 2 hours (20.94% weight loss) showed good agreement with the TG analysis. Higher weight loss in calcination is probably due to longer time.

3.2. XRD analysis

The XRD patterns of the synthesized samples at 750 °C for 2 hours are shown in Figure 2:

Figure 2- X-ray diffraction patterns of the synthesized powders at 750 °C for 2 h from samples prepared at different pH conditions

Appearance of crystal planes (111), (220), (311), (222), (400), (422), (511), (440), (533) and (622) based on JCPDS Card 00-022-1086 confirms the formation of spinel cubic nanocrystalline structure with $Fd\bar{3}m$ space group in all synthesized sample. This result is different from the work of Xiaogu et al [8] who reported that at pH=8 and at pHs above 11, some Fe_2O_3 and $Zn(OH)_2$ impurities are present in the product, respectively. However, the appearance of higher backgrounds at pHs 8 and 14 than other samples may be attributed to the presence of glass or crystalline phases that were not observed by XRD analysis.

It is well known that the intensity of X-rays scattered from the planes is related to their atomic density. In addition, it has been reported that in solid solutions, including spinel ferrites the intensities depend on the cationic distribution of the elements in different positions [3]. Therefore, for each XRD spectrum, the peak intensity ratio of plane (440) to plane (220) $I_{(440)} / I_{(220)}$ is calculated for each prepared sample that will be listed in Table 1. The corresponding diagram is given in Figure 3.

Figure 3-The peak intensity of plane (440) to peak intensity of plane (220), ($I_{(440)}/I_{(220)}$), for each sample at different pHs

It can be seen in Fig. 3 that the peak intensity ratio ($I_{(440)} / I_{(220)}$) increases with increasing pH from 8 to 10 and then decreases to pH 11. It then rises slightly again by changing the pH to 12 and then decreasing to pH=14. Since the composition and calcination conditions (temperature and time) are constant in all the samples above, it is concluded that the pH changes in the sample preparation process have caused changes in the cation movement and distribution in the structure. Hence, there have been changes in the peak intensity ratio. Although zinc ions have a large radius (0.74 Å) and naturally prefer to be in a larger space (B site), they sit in tetrahedral position (A site) due to great power of Zn-O bonds and crystal field stabilization energy (CFSE) of zinc ions in this space [20, 21]. Thus, by doping zinc into the cobalt ferrite structure, the Zn^{2+} ions are in the tetrahedron position [21]. This placement of ions means the force applied to the 3 valent iron ions in the tetrahedral space to move to the octahedral position. Assuming, that distribution of elements within the structure of zinc cobalt ferrite can be considered as $(Zn^{2+}_x Fe^{3+}_{1-x})^A [Co^{2+}_{1-x} Fe^{3+}_{1+x}]^B$ [3 , 14, 20,21].

The Williamson-Hall relation was also used to determine the exact crystalline diameter as well as the strain within them:

$$B \cdot \cos(\theta) = (0.9 \cdot \lambda / D) + 4\varepsilon \sin(\theta) \quad (3-5)$$

In this equation, D is the grain size on an angstrom scale, λ is the wavelength of $Cu_{K\alpha}$ (1.54056 Å), B is the broadening line at half the peak height in radians, ε is the lattice strain

and θ is the bragg angle of the scattered peak. The line slope is the lattice strain and the point that the line intersects the y axis is equal to $0.9\lambda/ D$ [22].

The results of the Williamson-Hall equation for synthesized powders prepared at different pHs are given in Table 1 and Figure 4.

Table 1- Strain and crystallite diameter of samples prepared at different pH and calcinated at 750 °C for 2 hours

samples	Z4P8	Z4P10	Z4P11	Z4P12	Z4P14
$2\Theta_1(^{\circ})$	35.38	35.54	35.37	35.46	35.52
$2\Theta_2(^{\circ})$	62.42	62.65	62.46	62.60	62.66
$2\Theta_3(^{\circ})$	56.83	57.05	56.88	57.00	57.07
$2\Theta_4(^{\circ})$	30.00	30.20	30.04	30.11	30.17
$B_1(^{\circ})$	0.39	0.26	0.26	0.32	0.27
$B_2(^{\circ})$	0.38	0.32	0.32	0.35	0.33
$B_3(^{\circ})$	0.39	0.28	0.34	0.37	0.28
$B_4(^{\circ})$	0.38	0.25	0.22	0.31	0.20
ε	$-7*10^{-4}$	$-3.5*10^{-4}$	$10*10^{-4}$	$1.5*10^{-4}$	$10*10^{-4}$
$D(\text{\AA})$	193	301	478	272	514
$I_{(440)}/I_{(220)}$	1.84	2.15	1.63	1.76	1.33

Figure 4- Williamson-Hall diagram of samples synthesized at 750 °C for 2 h; (a) Z4P8, (b) Z4P10, (c) Z4P11, (d) Z4P12, and (e) Z4P14

So the trend of changing the crystallite diameters by pH is shown in Figure 5:

Figure 5- Diagram of the crystallites diameter of the synthesized powders at 750 °C for 2 h from zinc doped cobalt ferrites (0.4 mole Zn) prepared at different pH conditions

Interestingly, the calculations and results of the Williamson-Hall equations show how the slope changes, which represents the type of strain (Figure 4, Table 1). Such that, at pHs 8 and 10, the slope is negative, indicating the type of tensile strain in the system, and the strain slope has decreased from -7×10^{-4} to -3.5×10^{-4} . That is, the strain decreased with increasing pH from 8 to 10. The crystallite diameter has shown an increasing trend in the pH range from 19.2 nm to 30.1 nm (Table 1, Fig. 5). As the pH increases to 11 and higher, the slope of the line changes, meaning that the type of strain in the system is changed to pressure (Fig. 4).

It is necessary to explain that in this state the amount of compressive strain in the system decreases with increasing pH from 11 to 12 and then, it increases again with increasing further pH to 14. This trend of strain change is also observed in the amount of crystallite diameters. That is, at pH=11 the crystallite diameter from 47.8 nm decreased to 27.2 nm, then increased to 51.4 nm (Figures 4 and 5, Table 1). In other words, the change in the tensile strain to compressive strain increases the diameter of the crystallites, and the more this strain increases, the larger the crystallite diameter and vice versa.

Another point to consider is that the strain values in the different planes also differ for a sample. This behavioral difference is also seen in the intensity of the scattered peaks in these centers. As noted, the $I_{(440)}/I_{(200)}$ ratio, that is, the intensity of the peak scattered on a plane passing through the tetrahedron site with respect to the peak intensity obtained from the plane

in octahedral space, has changed for different samples (Fig. 3). The presence of lattice strain and these differences in the structure are due to the effect that pH has on the movement of ions in network spaces [22].

To determine the lattice parameter various methods can be used. The most accurate way is to plot the curve of the lattice parameter in terms of the extrapolate function $\cos^2\theta/\sin\theta$ [23]. Therefore, the graph of extrapolate functions for the synthesized powders was drawn (Figure 6). Theoretical density (X-ray density) and specific surface area of the powders were also calculated using the following equations [10,24]:

$$\rho_x = 8M/Na^3 \quad (3-6)$$

Which, ρ_x is theoretical density (gr/cm^3), M is molecular weight of the sample (gr/mole), N is the Avogadro number, a is lattice parameter and 8 denotes the number of unit cells.

$$S = 6000/D\rho_x \quad (3-7)$$

D is crystallite diameter (nm), ρ_x is theoretical density (gr/cm^3) and S is specific surface area (m^2/gr).

Therefore, the results of the extrapolate functions for the lattice parameter, as well as the theoretical density and specific surface area of the powders are presented in Table 2.

Figure 6- Diagram of extrapolation functions for samples synthesized at 750 °C for 2 h; (a) Z4P8, (b) Z4P10, (c) Z4P11, (d) Z4P12, and (e) Z4P14

Table 2- lattice parameters, specific surface area and x-ray density of synthesized samples at 750 °C for 2 hours

samples	Z4P8	Z4P10	Z4P11	Z4P12	Z4P14
$2\Theta_1(^{\circ})$	35.38	35.54	35.37	35.46	35.52
$2\Theta_2(^{\circ})$	62.42	62.65	62.46	62.60	62.66
$2\Theta_3(^{\circ})$	56.83	57.05	56.88	57.00	57.07
$d_1(\text{\AA})$	2.535	2.524	2.536	2.530	2.526
$d_2(\text{\AA})$	1.487	1.482	1.486	1.483	1.482
$d_3(\text{\AA})$	1.619	1.613	1.617	1.614	1.613
$a(\text{\AA})$	8.412	8.391	8.400	8.386	8.384
s	$\pm 16 \cdot 10^{-4}$	$\pm 82 \cdot 10^{-4}$	$\pm 30 \cdot 10^{-4}$	$\pm 12 \cdot 10^{-4}$	$\pm 36 \cdot 10^{-4}$
$\rho_x(\text{gr/cm}^3)$	5.303	5.342	5.325	5.352	5.356
$S(\text{m}^2/\text{gr})$	58.76	37.26	23.57	41.24	21.82

• (plane order): (311), (440), (511)

Figure 7- X-ray density graph and lattice parameter of synthesized zinc doped cobalt ferrites (0.4 mole Zn) at 750 °C for 2 h at different pHs

The effect of pH on the lattice parameter of synthesized powders is also illustrated in Figure 7. Although in all the powders mentioned, the composition and other synthesis conditions were constant except pH, but the lattice parameter was changed with pH alteration. However, these changes are very small. This is attributed to changes in the distribution of ions within the structure by the pH value, just as the amount of strain within the structure also altered (Figure 4). In fact, the relationship between the transition metals and the lattice parameter is justified by the Vegard's law. This rule applies to solid solutions of cobalt ferrite nanoparticles substituted with transition metals [13, 15, 25]. On the other hand, according to Bragg's law ($2d \sin\theta = n\lambda$) and Equation $\{d = a (h^2 + k^2 + l^2)^{0.5}\}$ [23], a decrease in the diffraction angle means that the planar distance increases, and thereby the lattice parameter increases. Changing the position of the peaks at various angles (Table 2) for different samples is consistent with this statement. The theoretical density of the samples is also inversely correlated with the lattice parameter according to Equation 3-6, which means that as the lattice parameter increases, the density decreases and vice versa.

3.3. FESEM/EDX analysis

FESEM analysis was performed to compare the microstructure of powders prepared under pH 8, 11 and 14 (Fig. 8).

Figure 8- FESEM and EDS analysis of synthesized powders at 750 °C for 2 h; (a) Z4P8, (b) Z4P11, (c) Z4P14, (d) EDS of Z4P11 specimen

The micrographs of the synthesized powders show that in all samples the particle size range is less than 60 nm and is relatively uniform. This uniformity is most evident in synthesized powders at pH=11 (Fig. 8-b). The particle size in the samples prepared at pH=11 is somewhat greater than the other samples. In the powders prepared at pH 8 and especially 11, the cubic shape of the formed particles is quite evident. By increasing the pH to 14 (Fig. 8-c) the particles appear to be finer, and although the particle size distribution is uniform, the shape of the particles is slightly out of cubic state and look partially spherical. The particles are also axial and the agglomeration of the particles is seen in this sample. Particle agglomeration is due to the higher surface-to-volume ratio of the nanoparticles, which causes high interfacial tension and the particles adhere to each other. In addition, magnetic nanoparticles tend to cluster and stick together due to the interaction of magnetic dipoles [26].

It seems that by increasing the pH and increasing the concentration of OH^- ions in the system up to $\text{pH}=11$, a supersaturated lattice is created in the medium and slows down the nucleation. As a result, the rate of grain growth is greater than that of nucleation in this range, which results in the growth of grains and particles, according to Xiaogu Huang et al. [7]. As the pH increased, especially at $\text{pH}=14$, the particles became smaller (Fig. 8-c). This means that the rate of nucleation is higher than the grain growth rate and the reverse effect of hydroxide concentration on the system, as growth has occurred less, particle's surfaces have increased and agglomeration has taken place. In addition, quantitative EDS analysis for Z4P11 specimen can be seen in Figure 8-d. Z4P11 is approximately the same composition as $\text{Co}_{0.2}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$. However, very minor amounts of sulfur and aluminum are present (less than 1%), which are very likely to be related to the raw materials consumed.

3.4. Magnetic properties

To investigate the effect of pH value on the magnetic properties of the prepared samples, vibrating sample magnetometer (VSM) analysis of synthesized powders were performed which are given in Figure 9. The extracted results from these graphs are also presented in Table 3.

Figure 9- VSM diagram of zinc doped cobalt ferrite (0.4 mole Zn) samples prepared at different pHs and synthesized at 750 °C for 2 h; (a) $\text{pH}=8$, (b) $\text{pH}=10$, (c) $\text{pH}=11$, (d) $\text{pH}=12$, and (e) $\text{pH}=14$

Table 3- Ms Value of samples synthesized at 750 °C for 2 h at different pHs

Magnetic properties	Z4P8	Z4P10	Z4P11	Z4P12	Z4P14
M (emu/g) at (3000 Oe)	88.39	89.49	91.54	77.21	73.67
M (emu/g) at (4000 Oe)	90.80	91.86	94.16	79.72	75.98
M (emu/g) at (5500 Oe)	92.60	93.94	96.48	81.91	78.07
M (emu/g) at (7000 Oe)	94.02	130.51	98.01	83.46	79.61
M (emu/g) at (8500 Oe)	94.77	99.028	99.18	84.57	80.81
Ms (emu/g) at (10000 Oe)	95.48	65.14	100.38	85.68	81.98
Hc (Oe)	150	140	150	140	140
Mr (emu/g)	8.79	8.50	12.16	8.72	8.89
Mr / Ms	0.09	0.13	0.12	0.10	0.10

The amount of pH value had a significant effect on the saturation magnetization as it can be seen in Figure 10. As soon as pH changed from 8 to 11, Ms increased from 95.48 emu/gr to 100.38 emu/gr, and then decreased at pHs 12 and 14 to 85.68 emu/gr and 81.98 emu/gr, respectively. Since the composition is the same in these samples, the changes in Ms are attributed to the two factors of crystallite diameter and particle size, as well as to the different presence of elements in tetrahedral/octahedral sites. Larger grains tend to have larger magnetic domains. It is easy to move the domain wall, magnetize or non-magnetize with greater grains [15, 27]. In this way, specimens with larger grains have less H_C and higher M_S .

On the other hand, FESEM analysis (Fig. 8) and Fig. 5 showed that as the pH changed to 11, the particle size and crystallite diameter increased. Since the existence spins at the particles surfaces are highly disordered, they have decreased with increasing particle size [27, 28]. As a result, the amount of Ms in the Z4P11 sample increased. This increase in M_S , as previously mentioned, is attributed to the migration of Fe^{3+} ions from the tetrahedral to the octahedral space and the change in interaction by intermediating oxygen ions, known as superexchange interactions, between sublattices A and B [3, 26 and 29]. As the pH increases above 11, the crystallite diameter first decreases and then increases (Table 1). Therefore, the saturation magnetization is expected to decrease and then increase. However, this trend only decreases with increasing pH (Fig. 10). The micrograph image of the synthesized particles shows that at pH=14 (Fig. 8-c), the synthesized powders have become agglomerated because of small size. So, it is expected that the magnetization of the sample reduced by the same extent. Also, the amount of coercive force for samples was 140-150 Oe (Fig. 10). These values show significant decrease compared to that obtained from the synthesis of zinc cobalt ferrite by Mohammad Sajjad Hossain *et al.* [16] ($H_C=726.13$ Oe). This reduction is attributed to the movement of Co^{2+} ions to the tetrahedral position [3].

Figure 10– Saturation magnetization and coercive force of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ samples prepared at different pHs and synthesized at $750\text{ }^\circ\text{C}$ for 2 h

In addition, the residual ratio ($R=M_r/M_s$) in the synthesized powders was about 0.1, which means easy change of magnetization path to nearest easy axis of magnetic path after removal of external magnetic field.

For comparison, the amount of saturation magnetization obtained by other researchers synthesizing ferrite nanoparticles is presented in Table 4:

Table 4- Ms Value of different ferrite compositions investigated in different references

Composition	Synthesis method	Ms (emu/g)	Reference
Zn-Ni ferrites	Mechanical alloying	63	Ghayour et al. [3]
$\text{Co}_{0.2}\text{Fe}_{0.8}\text{Fe}_2\text{O}_4$	Coprecipitation	53	Linh et al. [6]
Zn-Mn ferrites	Coprecipitation-Hydrothermal	90	Pilati et al. [11]
Zn-Co	Coprecipitation-Hydrothermal	75	Pilati et al. [11]
CoFe_2O_4	Pechini	64.92	Motavallian et al.[15]
$\text{Cd}_{0.1}\text{Co}_{0.9}\text{Zr}_{0.05}\text{Fe}_{1.95}$	Pechini	67.71	Motavallian et al.[15]
Fe_3O_4	in situ and semi-two-step co-precipitation	50.70	Shaterabadi et al. [26]
$\text{Mg}_{x-y}\text{Fe}_2\text{O}_3$	Coprecipitation	70	Jang et al. [29]
$\text{Co}_{0.5}\text{Ni}_{0.37}\text{Cu}_{0.13}\text{Fe}_2\text{O}_4$	sol-gel auto combustion	65.29	Ramakrishna et al. [30]
$\text{Co}_{0.5}\text{Zn}_{0.37}\text{Cu}_{0.13}\text{Fe}_2\text{O}_4$	sol-gel auto combustion	50.35	Ramakrishna et al. [30]
CoFe_2O_4	Mechanical Alloying	78	Mahdikhah et al. [31]
Fe_3O_4	Coprecipitation	15.92	Salavati-Niasari et al. [32]
Ni-Zn ferrites	Coprecipitation	52	Ahmad et al. [33]

$\text{Cu}_{0.3}\text{Zn}_{0.2}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$	Coprecipitation	52	Ansari et al. [34]
CoFe_2O_4	solvothetmal	98	Lavorato et al. [35]
cobalt	solvothetmal	158	Kotoulas et al. [36]
$\text{Ce}_x\text{Fe}_{3-x}\text{O}_4$	Coprecipitation	62	Shaw et al. [37]
$\text{Zn}_{0.2}\text{Co}_{0.8}\text{Fe}_2\text{O}_4$	hydrothetmal method	76.6	Topkaya et al. [38]

The saturation magnetization of the present work (100.38 emu/gr) is almost greater than the M_s of most ferrite nanoparticles synthesized by others (Table 4). In addition, according to Wuhlfarth's theory, anisotropic constant (K) and magnetic moment (n_B) for the formula unit are obtained by Equations (3-8) and (3-9) [4,16,39]:

$$H_c = 0.98K/M_s \quad (3-8)$$

$$n_B = (M_w.M_s)/5585 \quad (3-9)$$

Where M_w is molecular weight. Therefore, the values of K and n_B are given in Table 5, and their changes vs. pH parameter are shown in Figure 11.

Table 5- Magnetic moment and anisotropic constant of samples prepared at different pH and synthesized at 750 °C for 2 hours

Magnetic properties	Z4P8	Z4P10	Z4P11	Z4P12	Z4P14
K (erg/oe)	14614.33	9305.63	15357.70	12239.34	11711.98
n_B (μ_B /f.u)	4.06	2.77	4.27	3.64	3.49

Figure 11– Anisotropic constant and Bohr magneton of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ samples prepared at different pHs and synthesized at 750 °C for 2 h

Bohr magneton and anisotropic constant of the prepared samples behaved alike similar to what observed for saturation magnetization. The value of magnetic moment in the structure of the nanoparticles depends on momentum differences between octahedral and tetrahedral

spaces. Therefore, based on the changes seen in Figure 11, it can be deduced as pH amount rises, some Fe^{3+} ions moves to B sites from A sites, while Co^{2+} would be forced to go tetrahedral positions. This means reduction of cobalt ion concentration in octahedral space, and consequently decreases in anisotropic constant which enhances magnetic moment.

4. Conclusions

Single phase zinc-doped cobalt ferrite nanoparticles prepared under various pHs via co-precipitation method. The pH value had a significant influence in the structural and magnetic properties of the synthesized ferrites. FESEM micrographs showed relatively uniform distribution of spherical-like grains in the range of less than 60 nm. The crystallite size of the spherical nanoparticles changed at different pHs. These changes are attributed to the concentration of OH^- ions in the system and its effect on the nucleation rate and grain growth. Saturation magnetization, Bohr magneton and anisotropic constant of the prepared samples behaved alike, approximately as observed for crystallite sizes at various pHs. The H_c was in the range of 140-150 Oe for the all synthesized powders. These variations can be attributed to the change in crystallite diameter, particle size, and cation distribution in tetrahedral/octahedral positions.

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6. References

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Figures

Figure 1

(a) TG/difTG analysis and, (b) rel. Mass analysis of sample containing 0.4 mol of zinc element prepared at pH=11

Figure 2

X-ray diffraction patterns of the synthesized powders at 750 °C for 2 h from samples prepared at different pH conditio

Figure 3

The peak intensity of plane (440) to peak intensity of plane (220), ($I(440)/I(220)$), for each sample at different pHs

Figure 4

Williamson-Hall diagram of samples synthesized at 750 °C for 2 h; (a) Z4P8, (b) Z4P10, (c) Z4P11, (d) Z4P12, and (e) Z4P14

Figure 5

Diagram of the crystallites diameter of the synthesized powders at 750 °C for 2 h from zinc doped cobalt ferrites (0.4 mole Zn) prepared at different pH condition

Figure 6

Diagram of extrapolation functions for samples synthesized at 750 °C for 2 h; (a) Z4P8, (b) Z4P10, (c) Z4P11, (d) Z4P12, and (e) Z4P14

Figure 7

X-ray density graph and lattice parameter of synthesized zinc doped cobalt ferrites (0.4 mole Zn) at 750 °C for 2 h at different pHs

Figure 8

FESEM and EDS analysis of synthesized powders at 750 °C for 2 h; (a) Z4P8, (b) Z4P11, (c) Z4P14, (d) EDS of Z4P11 specimen

Figure 9

VSM diagram of zinc doped cobalt ferrite (0.4 mole Zn) samples prepared at different pHs and synthesized at 750 °C for 2 h; (a) pH=8, (b) pH=10, (c) pH=11, (d) pH=12, and (e) pH=14

Figure 10

Saturation magnetization and coercive force of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ samples prepared at different pHs and synthesized at $750\text{ }^\circ\text{C}$ for 2 h

Figure 11

Anisotropic constant and Bohr magneton of $\text{Co}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ samples prepared at different pHs and synthesized at $750\text{ }^\circ\text{C}$ for 2 h