A Study on Structural Properties of Cobalt Ferrite Nanoparticle

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Abstract

The present paper intends to study the effect of adding zinc to the structure of cobalt ferrite, to determine how it influences the heat resulted from magnetic losses, and to find nanoparticles with proper magnetic properties in this field. Different compounds of cobalt-zinc ferrite nanoparticles have been synthesized by chemical techniques of normal micelle, reverse micelle, and co-precipitation. In order to study magnetic properties and the superparamagnetic behavior, VSM has been applied; while, the structural properties have been studied via analysis of XRD and FTIR. Moreover, TEM is applied to study the size and shape of the particles. Considering different compounds of cobalt-zinc ferrite nanoparticles, it has been determined that $Co_{0.22}Zn_{0.78}Fe_2O_4$ is the best choice for medical applications.

Keywords: Cobalt Ferrite, Magnetic Properties of Nanoparticles, Zinc, Curie Temperature

Introduction

Since 1990, an interest in the field of nanotechnology concentrating on nano-sized particles with the size ranging from one to hundreds nm increased. Decades of study showed that the very high surface to volume ratio of nano-sized particles had provided different physical and chemical properties comparing with the properties of materials with larger scales[1]. Magnetic properties have a noticeable influence on the living organisms. Hemoglobin which exists in the human blood is one of the compounds of iron that naturally has the magnetic property. Therefore, it is true to declare that all of the living organisms including animals and humans have magnetic particles and they act like magnets. Therefore, it is confirmed that magnetism and magnetic materials play an important role in healthcare and biologic applications[2].

Superparamagnetic behavior of magnetic nanoparticles was studied by Franklin and Dorfman (1930) and then by Kale as a property associated with single-domain state of ferromagnetism or anti-ferromagnetism at very low dimensions. For such nanoparticles within the single domain, many of the magnetic moments were homogeneously locked in one direction and they formed the super moment[3]. Furthermore, when the superparamagnetic nanoparticles were coated by a proper layer, they could be dispersed in the water-based solutions and keep their stability in order to form ferrofluid. In order to take advantage of ferrofluids in in-vivo and in-vitro applications, different parameters such as particles distribution, toxicity, chemical properties of the surface, biocompatibility, and so forth should be considered[4]. Therefore, surface modification of the functional groups could be a strategic approach in order to solve the problem and make

the nanoparticles non-toxic, biocompatible, and traceable. The present paper has studied the magnetic nanoparticles. It intends to study the effect of adding zinc to the structure of cobalt ferrite and how it affects the heat resulted from the magnetic losses; moreover, it finds nanoparticles with the proper magnetic properties in this field.

Magnetic properties of nanoparticles

In a nutshell, material has dipole (small magnetic domains). If a magnet is divided into two parts, two magnets will be formed. If dividing the magnet is continued, each of the smaller magnets will also have north and south poles and theoretically, they will reach the size of a dipole. In the mass of a material, the dipoles have random orientations toward each other, however, when the material is influenced by a strong magnetic field, the dipoles could linearly be formed as N-S, N-S, N-S, N-S, N-S. If the field is removed, the linearity of dipoles is maintained in some materials and it makes a permanent magnet with the north and south poles at two ends of it. Such materials that maintain the linearity after removing the magnetic field are called hard magnetic materials. However, the materials that do not maintain the linearity after removing the magnetic field are called soft magnetic materials. In other words, in contrast with the soft magnetic materials, hard magnetic materials have high H_c[5]. The change of magnetic properties such as H_c, M_s, and Curie temperature of the magnetic nanoparticles is influenced by different factors such as surface effects, cation stoichiometry, and filling the atomic spaces. If the diameter of the magnetic particles decreases to a lower level of the critical value, the particles cannot have more than a magnetic domain, therefore, they will be known as single-domain particles[7]. The critical diameter is determined by the following equation (1).

$$D_c = 2A^{1/2}/M_s \quad (1)$$

In equation 1, A stands for the exchange constant, and M_s stands for the moment value in the unit size. The value of critical diameter of the particles for the single-domain state in different magnetic materials is between 10 to 100 nm.

Curie temperature

All of the ferromagnetic materials have a certain transition temperature. At this temperature, the ferromagnetism disappears and the material is changed into the paramagnetic state. The mentioned transition temperature is called Curie temperature or Curie point[8]. Many of the materials lose their magnetic property after exceeding the Curie temperature, and then being cooled. If the materials are located within a strong magnetic field, some of them will regain their state of permanent magnet; while some others will need a thermal processing in a strong field[9]. Below the Curie temperature, the ferromagnetism is regular; however, above the Curie temperature it is irregular. At the Curie temperature, saturation magnetization goes toward zero. Figure 1 indicates the curve for cobalt-zinc ferrite regarding magnetization and temperature.
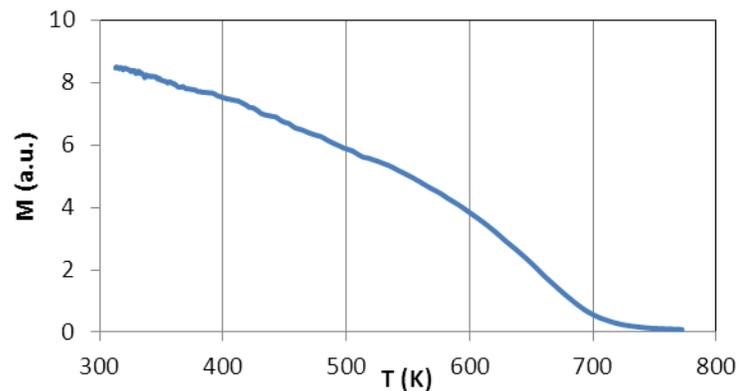

Figure 1: magnetization curve based on the temperature indicating the Curie temperature

Effect of particle size

The increase of the surface to volume ratio related to nano-materials leads to the change of magnetic properties. The formation of a dead layer on the surface, the distortion of SPIONs of the particles surface, desaturation resulted from random distribution of particle size, deviation of normal cation distribution, and presence of absorbed water result from the small size of the particles[10]. Figure 2 indicates the effect of the particle size reduction on the hysteresis field. The figure shows that the decrease of particle size increases the hysteresis field up to the time that particles reach the single-domain state[11]. When the particles reach the superparamagnetic size, the value of hysteresis field goes toward zero. The nanoparticles that have a superparamagnetic behavior maintain their magnetic property after being influenced by the magnetic field, moreover, they have advantages such as decreasing the adhesion of the particles influenced by the magnetic field. The high surface to volume ratio of the particles and their superparamagnetic behavior are the causes to consider the particles in biological discussions as well[12].
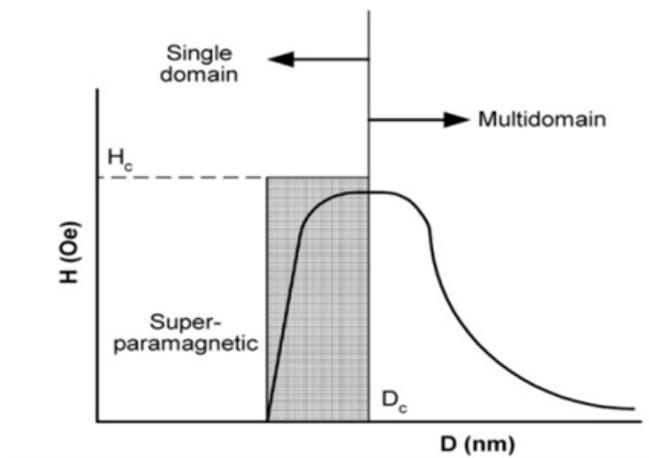
Figure 2: the effect of particle size on the hysteresis field

Superparamagnetic behavior is severely influenced by the magnetocrystalline anisotropy[13]. Therefore, the change of value of the magnetocrystalline anisotropy leads to the change of the decreasing value of the required particle size for reaching the superparamagnetic behavior[14]. Since substituting an ion with higher anisotropy at the ferrite structure increases the magnetic anisotropic behavior of the material, more particle size reduction is needed to reach the superparamagnetic behavior[15]. Therefore, in comparison with the thermal energy, the anisotropic energy reaches a smaller scale as a result of the decrease of particles size; moreover, the thermal energy is enough to change the SPION direction. Such magnetic turbulence resulted from the thermal energy leads the total magnetization to zero and it manifests the concept of superparamagnetization[16].

Table 1 indicates the magnetic properties and the critical particle size needed to reach the superparamagnetic behavior. As it has been mentioned, the type of the substituting ion affects the properties and critical particle size in order to reach the superpaoramagnetic behavior. Table 1 shows that higher anisotropic energy of the cobalt ferrite leads to the decrease of the critical size of the superparamagnetic behavior.


Table 1: magnetic properties, single-domain critical size (D_c), and critical size of the superparamagnetic behavior (D_{sp})

D_{SP} (nm)	D_C(nm)	$K_1(\times10^5)$ (erg/cm^3)	T_C (K)	M_S emu/g	Ferrite type
14	70	+18، +30	790	80–94	$CoFe_2O_4$
28	100	−0/68	860–870	56	$NiFe_2O_4$
25	128	−1/2	860	90–100	Fe_3O_4
25	128	−0/25	550–620	80	$MnFe_2O_4$

Figure 3: hysteresis curve for three samples of ferrites MFe2O4(M=Mn, Co, Ni) with the size particle of 7 nm

The effect of chemical composition

The chemical properties of the ferrites directly depend on the chemical composition and action distribution at the tetrahedral and octahedral sites[17]. Since the magnetic moments per ion in the subnet and between two subnets are parallel, the difference of magnetic moments between two subsets indicates the value of the crystal ferrite magnetic moment. Figure 3 shows hysteresis loops for three samples of ferrites MFe_2O_4(M=Mn, Co, Ni) with the particle size of 7 nm. Comparing the magnetizations of the mentioned ferrites indicate that cobalt ferrite has a higher magnetization than the other two ferittes[18].
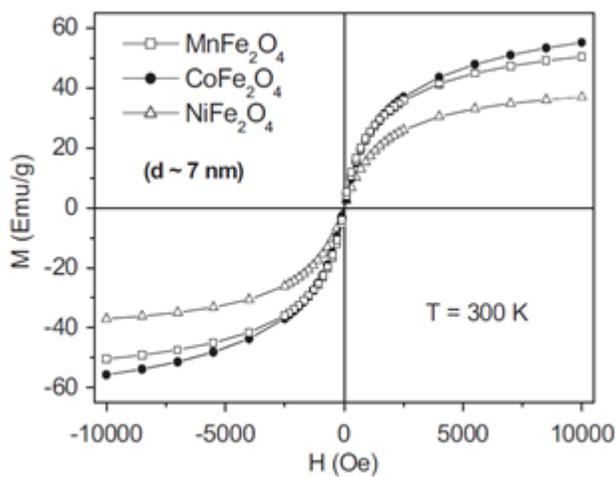
The effect of zinc

Temperature sensitivity in the ferrites could be changed by substituting zinc in their structure. Zinc has considerable effects on the magnetic properties of the ferrites. The Curie temperature of the material is the most important property changed as a result of zinc substitution[19]. Zinc ion could be applied in the smart hyperthermia. The non-magnetic zinc ion is preferentially located in the tetrahedral site, therefore, exchange interaction between tetrahedral and octahedral sites decreases[20]. As a result, the increase of zinc percentage causes different magnetic properties. For instance, the increase of zinc percentage exceeding 10 percent in the cobalt ferrite instead of cobalt decreases the value of saturation magnetization.

Methodology

In this section, different magnetic nanoparticles synthesized in the present project would be studied. Zinc would be added to the cobalt ferrite via co-precipitation method.

Synthesis of cobalt-zinc ferrite nanoparticles

Required materials

The materials needed for synthesis includes iron chloride ($FeCl_3$), zinc sulfate ($ZnSO_4$), Cobalt chloride ($CoCl_2$) and sodium hydroxide ($NaOH$) related to Merck Company.

Synthesis of cobalt-zinc ferrite nanoparticles

The co-precipitation method is used to synthesize cobalt-zinc ferrite nanoparticles ($Co_{(1-x)}Zn_xFe_2O_4$, x=0.1, $0.5 < x < 0.8$). According to this method, aqueous solutions of iron (III) chloride, zinc sulfate (II), and cobalt (II) chloride are prepared. For instance, when x=0.5; it shows that in the compound of $Co_{0.5}Zn_{0.5}Fe_2O_4$, at first, 5 ml of a 1 M solution of cobalt chloride, 5 ml of a 1M solution of zinc sulfate, and 10 ml of a 2M solution of iron chloride have been prepared. After combining the solutions, the obtained solution is exposed to heat up to 60 °C. The obtained compound is immediately added to a 120 ml of a 0.63 M solution of sodium hydroxide influenced by the magnetic stirrer. Ferrite nanoparticles are formed by converting metal salt to hydroxide, and then hydroxide groups to ferrite.

$$(1-x)Co^{2+} + xZn^{2+} + 2Fe^{3+} + 8OH^- \rightarrow$$
$$(1-x)Co(OH)_2 \times xZn(OH)_2 \times 2Fe(OH)_3. \downarrow$$
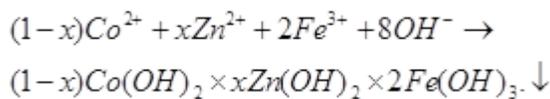
Later, the solution is kept at the temperature of 85 °C for an hour. The considered time is enough to convert all hydroxyl groups to the structure of spinel ferrite. After the formation of sediments, the 5000 rpm centrifuge is used for 15 min in order to separate sediments from the solution. In the next step, the distilled water is used through several continuous cycles in order to wash the sediments. The particles are washed by acetone, and then they are dried at the room temperature in order to get prepared for different analyses.

Findings

The results of X-ray diffraction related to the produced cobalt-zinc ferrite samples based on the co-precipitation method have confirmed the single-phase formation with the spinel nature. Moreover, the results of analysis have been presented in table 2. The final product in all of the samples consists of the inverse spinel structure without any impurity. Moreover, after substituting 70 percent of the cobalt ions with the zinc ions in the total structure, the cobalt ferrite structure is converted to zinc ferrite. Symmetrically, the unit cell is located in the space group of $fd\bar{3}m$. Moreover, the filling amount of tetrahedral and octahedral sites, the constant value of the network, and crystallite size of the samples have been determined via analyzing the sample X-ray diffraction pattern based on the Rietveld method.

Table 2: the structural study of nanoparticles via X-ray diffraction

χ^2 (%)	R_p (%)	R_{wp} (%)	E (kcal/mol)	Filling amount of position			Crystallite size (nm)	Net parameter (nm)	Samples
				Co/Zn	Fe	O			

1/78	5/63	7/14	837.58	/8630	/9330	/0001	10/7	/839090	$Co_{0.90}Zn_{0.10}Fe_2O_4$
1/05	5/20	7/00	/16 1109	/8780	/8990	/0001	9/8	/841290	$Co_{0.50}Zn_{0.50}Fe_2O_4$
1/88	5/48	7/10	/92 1106	/8650	/9040	/0001	9/2	/841290	$Co_{0.45}Zn_{0.55}Fe_2O_4$
1/22	5/83	7/24	1104.27	/8650	/9800	/0001	7/8	/814440	$Co_{0.40}Zn_{0.60}Fe_2O_4$
1/33	6/32	7/84	/44 1102	/8630	/9620	/0001	7/2	/841550	$Co_{0.35}Zn_{0.65}Fe_2O_4$
1/08	5/50	7/01	/23 1100	/8630	/9540	/0001	6/9	/841690	$Co_{0.30}Zn_{0.70}Fe_2O_4$
1/11	6/00	7/68	/91 1093	/8390	/9800	/0001	6/6	/842030	$Co_{0.25}Zn_{0.75}Fe_2O_4$

Analysis of infrared spectroscopy

Figures 4 to 8 indicate the absorption bands of cobalt-zinc ferrite formed based on the co-precipitation method for different values of zinc at the range of wave number of 4000-400 cm^{-1}. At these spectra, two bands are observed at the range of 600-400^1 cm, and the bands confirm the formation of spinel phase. There are two tetrahedral and octahedral subsets in the structure of cobalt-zinc spinel ferrite and they consist of two absorption bands in the infrared spectrum at the range of 600 cm^{-1} and 425 cm^{-1}. These bands were located in the structure of cobalt ferrite in the bands of 595 cm^{-1} and 416 cm^{-1}, and the formation of the spinel structure were confirmed regarding these bands. With the increase of zinc in the compound of$Co_{0.90}Zn_{0.10}Fe_2O_4$, the position of the tetrahedral band toward the cobalt ferrite is changed. In other words, the frequency band higher than $v1$ is transferred from 594 cm^{-1} to 586 cm^{-1}, however, the position of the bands is constant in other analyzed compounds. Moreover, $v1$ band is located at the frequency of 570/9 cm-1 and $v2$ is located at the frequency of 416/6 cm-1 and they indicate the spinel phase formation. The observed change of bands position in the cobalt-zinc ferrites in comparison with the cobalt ferrite has resulted from the change of distance between ions of Fe $^{3+}$ and O^{2+}.
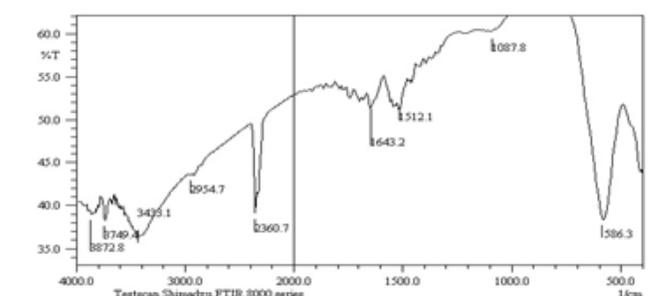

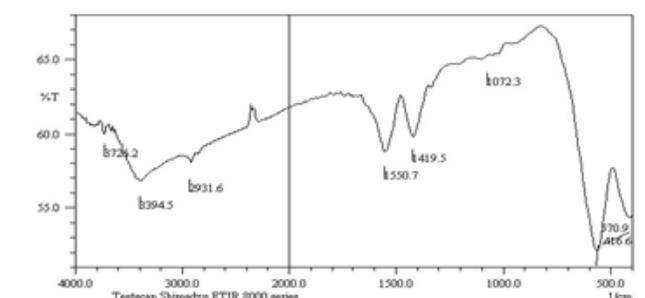Figure 4: IR spectrum of the sample of cobalt-zinc ferrite $Co_{0.90}Zn_{0.10}Fe_2O_4$

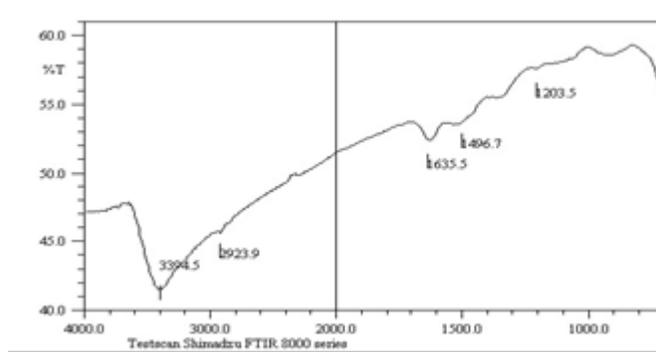Figure 5: IR spectrum of the sample of cobalt-zinc ferrite $Co_{0.50}Zn_{0.50}Fe_2O_4$

Figure 6: IR spectrum of the sample of cobalt-zinc ferrite $Co_{0.40}Zn_{0.60}Fe_2O_4$
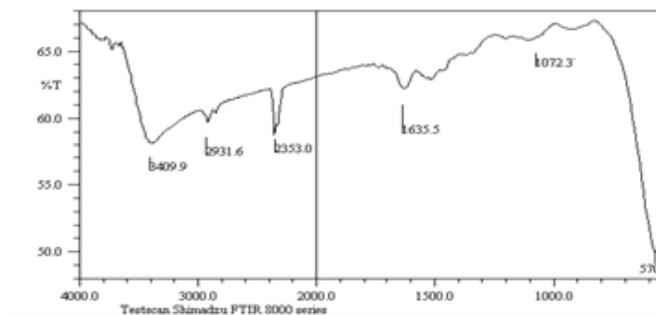

Figure 7: IR spectrum of the sample of cobalt-zinc ferrite $Co_{0.35}Zn_{0.65}Fe_2O_4$
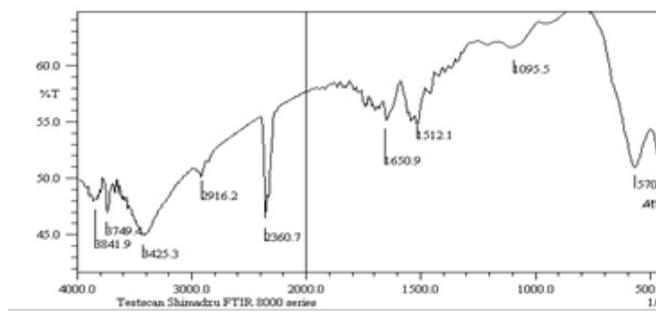

Figure 8: IR spectrum of the sample of cobalt-zinc ferrite $Co_{0.25}Zn_{0.75}Fe_2O_4$

Magnetic analysis

Recently, cobalt-zinc ferrite nanoparticles are increasingly considered. The adjustability of the Curie temperature is one of the characteristics that make the nanoparticles noticeable. In fact, adding zinc to cobalt ferrite decreases the Curie temperature; therefore, the Curie temperature of 42-43°C is achieved to reach smart hyperthermia. Bulk cobalt ferrite has the Curie temperature of 517 °C and saturation magnetization of about 95 AM^2kg^{-1} at the temperature of 20°C, however, when the crystalline size decreases, the magnetic order is more likely to be omitted. As a result, saturation magnetization and Curie temperature decrease, therefore, in the nanoparticles synthesized by the co-precipitation method along with the heat treatment with dimensions of about 15 nm, the saturation magnetization decreases to 58 AM^2kg^{-1} and Curie temperature decreases to 462°C.

If cobalt cations are substituted by the non-magnetic zinc cations which have a tendency to be in the tetrahedral position, the magnetic properties will change. The general formula of $(Zn^{2+}Fe^{3+}_{(1-x)})A[Co^{2+}_{(1-x)}Fe^{3+}_{(1-x)}]_BO_4$ could be applied to express the substitution mechanism in cobalt-zinc ferrite. In low concentrations of Zn^{2+}, $0<x<0.5$ leads to the increase of magnetic moment, however, the decrease of concentration of magnetic ions will decrease the exchange interaction between A and B. Consequently, the SPIONs order will be disturbed and it will lead to instability of magnetic order. This issue affects the shape anisotropy and magnetocrystalline anisotropy, decreases hysteresis field, and affects hysteresis loss. Therefore, considering these losses helps to have a suitable choice of the compound at the range of $0.5<x<0.7$, moreover, the control mechanism of temperature would also be observed. Since time loss could also affect the superparamagnetic particles and since the size change of particles could affect the Curie temperature, the range of $0.5<x<0.8$ and

x=0.1 have been selected. In fact, Vaidianatan et al. noticed that the maximum saturation magnetism in Zn equaled 0.1.
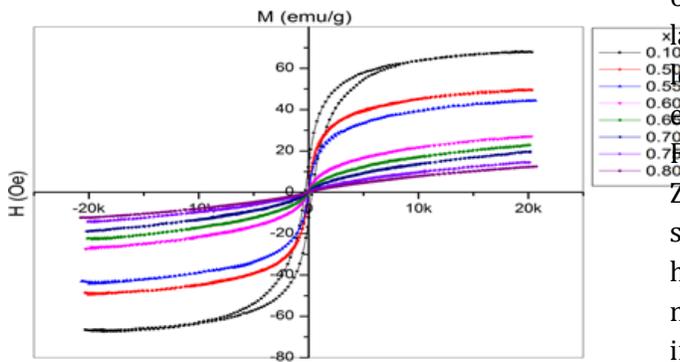

Figure 9: hysteresis curve of the samples of cobalt-zinc ferrite

Figure 9 indicates the hysteresis curve of the samples of cobalt-zinc ferrite. According to figure 9 and tables 4 to 8, it is clarified that adding 10 percent zinc instead of cobalt would increase M_s of the material from 58emu/g to 66/62emu/g. In fact, it is the position of the larger ion of Zn^{2+} in the tetrahedral site that leads to the mentioned increase; therefore, the exchange interaction of the ions would change. Furthermore, adding more than 50 percent of Zn^{2+} instead of cobalt would decrease the saturation magnetization, hysteresis, and hysteresis field as a result of the entrance of non-magnetic ion and affecting the exchange interaction (figure 10). In comparison with the sample of cobalt ferrite with the same synthesized method, the aforementioned samples have less saturation magnetization; however, their hysteresis field has decreased. As a result, in the zinc value of x=0.75, the value of hysteresis value has reached 1.27 Oe.

Table 3: magnetic properties of the samples of cobalt-zinc ferrite

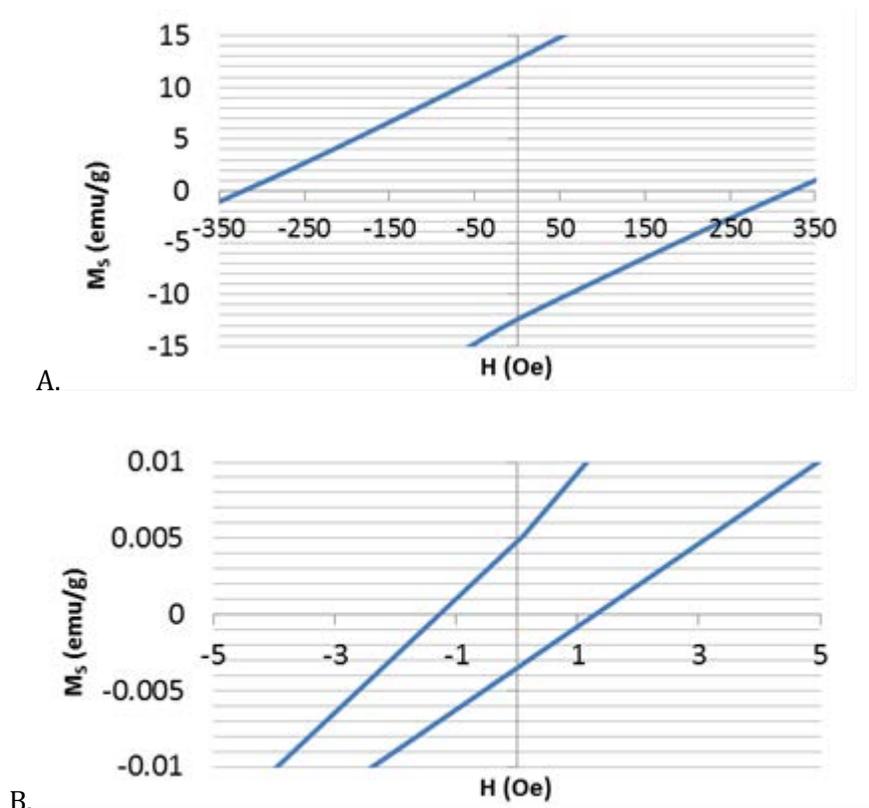| Hysteresis field (Oe)	Hysteresis magnetization (emu/g)	Saturation magnetization (emu/g)	Crystallite (nm) size	Material
323/46	12/78	66/62	10/5	$Co_{0.90}Zn_{0.10}Fe_2O_4$
17/17	0/87	49/55	9/8	$Co_{0.50}Zn_{0.50}Fe_2O_4$
20/51	0/84	44/28	8/9	$Co_{0.45}Zn_{0.55}Fe_2O_4$
20/08	0/29	27/40	8/3	$Co_{0.40}Zn_{0.60}Fe_2O_4$
25/57	0/27	22/75	7/1	$Co_{0.35}Zn_{0.65}Fe_2O_4$
5/32	0/05	18/88	7/0	$Co_{0.30}Zn_{0.70}Fe_2O_4$
1/27	0/00~	14/35	6/9	$Co_{0.25}Zn_{0.75}Fe_2O_4$

Figure 10: a study on changes of the values of hysteresis field and hysteresis magnetism A: Co0.90Zn0.10Fe2O 4 B: Co0.25Zn0.75Fe2O4

Table 3 presents the values of hysteresis field, and magnetism of the hysteresis along with the maximum magnetism (up to the magnetic field of 20 kOe) for all the samples. The mentioned information is achieved via direct observation of VSM device. What is observed on the curves at values higher than $x \geq 0.5$ shows desaturation of samples even at high magnetic fields. This could be resulted from the formation of an amount of superparamagnetic particles in the material and this issue is more manifested in the state of

$x \geq 0.65$. The table also shows that the increase of zinc percentage will decrease hysteresis magnetization and it confirms the formation of more superparamagnetic particles in the samples.

Another magnetic study has calculated the magnetic Curie temperature of the material by taking advantage of cooling curves related to the magnetic sample observed in the VSM device. The results of the study have been presented in figure 11. According to the mentioned curve, the increase of zinc from 10 percent to 80 percent will

decrease the Curie temperature of the material from 432℃ to 38℃. By considering the following curve equation, if the value of ~0.785 is considered instead of the zinc concentration, the Curie temperature about 43℃ which is optimal in this research will be achieved.
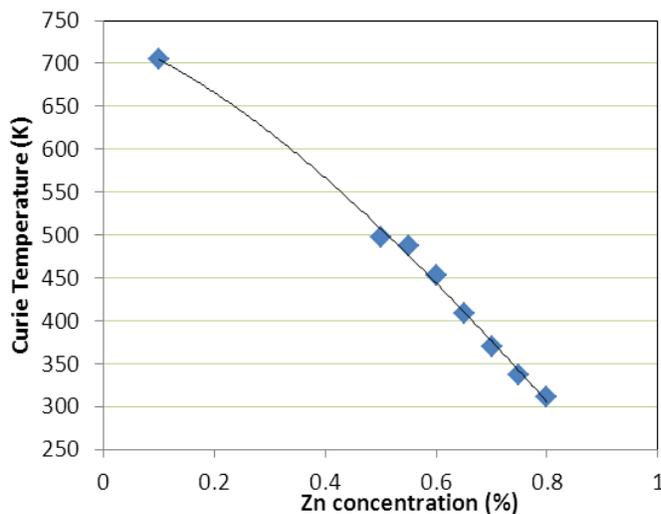
$$y = 165.8x^3 - 490.49x^2 - 249.3x + 734.45$$

Figure 11: the curve of Curie temperature changes based on the percentage of zinc concentration

Conclusion

In this study, cobalt-zinc ferrite nanoparticles have been synthesized with the homogeneous chemical composition by three techniques of normal micelle, reverse micelle and co-precipitation. According to the structural and magnetic analysis of different samples, the following points have been clarified:

1. Magnetic properties of the particles are severely dependent on the size of particles, moreover, the cation distribution is highly important in this field.

2. Nanoparticles obtained via the method of co-precipitation have the largest particle size. Therefore, in comparison with the micelle method, the saturation magnetization and hysteresis field are much higher in this method.

3. Nano-crystalline materials of cobalt ferrite show absorption bands at the range of 400 cm-1 and 600 cm^{-1}. Frequency band higher than 600 cm^{-1} are related to the tetrahedral complexes, while frequency band of 400 cm^{-1} is related to the octahedral complexes.

4. The magnetic properties of the samples are severely dependent on the size of nanoparticles. The present paper shows that the cation distribution highly affects magnetic properties; however, the particle size is more effective than the cation distribution.

5. Among different compounds of cobalt-zinc ferrite nanoparticles, the compound of $Co_{0.22}Zn_{0.78}Fe_2O_4$ is the best choice for medical applications.

Suggestions

1. Since the controlled increase of PH during the test could change the particle size, the increasing of PH could change the particle size, therefore, it will disturb the effect of particle size on the magnetic properties through the studies.

2. With regard to the electrical properties of the cobalt ferrite nanoparticles, the dielectric properties and other properties could also be studied as a result of increasing different ions.

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