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Magnetic Properties of Cobalt Ferrite synthesized by Hydrothermal and Co-precipitation Methods: A Comparative Study

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Abstract

The magnetic properties of calcined cobalt ferrite formed by nano-crystalline powders have been compared by two different methods (co-precipitation and hydrothermal). The structural properties of the produced powders were investigated by X-ray Diffraction (XRD), scanning electron microscopy (SEM). The results show that the formation of cobalt ferrite spinel structures is effected by changing methods. Both techniques were effective and led to the production of spinel phase and crystalline nano-powders. Magnetic hysteresis was measured by using a vibrating sample magnetometer (VSM) in a maximum field of 10 kOe. The saturation magnetization (Ms), remanence (Mr) and coercivity (Hc) were derived from the hysteresis loops. The results revealed that the magnetic properties of nano-particles depend on the structure, composition and size of particle.

Keywords: *Magnetic properties, Hysteresis loop, Co-precipitation, Hydrothermal, Nano-particles.*

Introduction

The present research investigated the magnetic nanoparticles because of their potential applications in high density magnetic recording and magnetic fluids [1]. Many investigations have been done so far, they focused on the controlled synthesis of ferrite nano-particles and also the relationship between their magnetic properties and the particulate properties and/or the synthetic conditions [2]. The physical and chemical properties of spinel nano-particles are greatly affected by the synthesis route [3]. Bahem and Joy reported that $CoFe_2O_4$ were prepared under different conditions which indicated different conducting behaviors [4]. As magnetic particles are too small for multi-domain formation, the domain wall response is excluded and the material can act frequently.

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The recent technological advances in electronics need more compact cores to work frequently [5]. Spinel ferrites have the general formula of AFe_2O_4 (where A^{2+}: Co, Ni, Zn, etc.) and unit cell contains 32 oxygen atoms in cubic close packing with 8 tetrahedral (T_d) and 16 octahedral (O_h) occupied sites [6]. AFe_2O_4 has high coercivity and moderate magnetization [7]. By changing type of the divalent Cation, it is possible to obtain significantly different physical and magnetic properties in these ferrites [6]. Cobalt ferrite nano-particles are of interest because of their unique optical, electronic and magnetic properties. Also $CoFe_2O_4$ have an excellent chemical stability, mechanical hardness and high saturation magnetization; therefore it is a promising choice for high density magnetic recording, Ferro fluids technology, bio-molecule separation, biomedical drug delivery, catalysis, magnetic resonance imaging, biocompatible magnetic nano-particles for cancer treatment and magneto-optical devices [8]. With regard to above mentioned applications, the particles need to have suitable magnetic properties such as diminished size and uniform shape [5]. Various methods of breaking up have been developed to obtain nano ferrite particles, such as mechanical [9], thermal decomposition [10], hydrothermal [11], sol-gel auto-combustion [12], and co-precipitation [13] methods. Wet chemical methods are highly interesting for their versatility, low temperature for preparation, and substantial potential for high rate of production [14]. Among these techniques, chemical co-precipitation is reported to be the most economical one [15] and hydrothermal synthesis is an attractive method for the high rate of production and simplicity [16]. Despite the great number of papers, preparing ferrite nano-particles which is suitable for new advanced applications is still a challenge [5].In this manuscript, we reported the effect of structural properties on magnetic properties of Cobalt ferrite samples, prepared by hydrothermal and co-precipitation processes.

Experimental

Materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 .6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 .9H_2O$), and sodium hydroxide (NaOH), were used as precursors and deionized water as solvent. All chemical materials which were applied have an alytical grade and supplied by Merck Company.

Synthesis with co-precipitation route

The nitrates of cobalt and iron were dissolved in deionized water at the determined molar ratio (Fe/Co = 2). Aqueous solution of 4 M NaOH was used as the precipitating agent. The metal nitrate solutions at a fixed temperature were immediately added to the boiling solution of 4M NaOH which was at the same temperature. The acquired solution was stirred and maintained at a fixed temperature for 9 hours. The size and size distribution were controlled by checking the nucleation and growth rates during the reaction. Smaller particles were obtained if the nucleation rate was higher than growth rate [17]. Large pH values (above 11.5) were used because it controls the process of nucleation rate and reduces the particles sizes. This precursor is called (B) and used for hydrothermal synthesis. For co-precipitation, the mixture was stirred strongly for 8 hours at 80 ºC. This precursor obtained after this time is called (A).

Synthesis with hydrothermal route

The pH adjusted mixture described in co-precipitation route was stirred strongly for 4 hours at 80 ºC. The prepared mixed solution (B) was transferred in to a 50 ml Teflon-lined stainless autoclave. The autoclave was sealed and treated at 180 ºC for 15 hours. The pressure in the sealed autoclave was lower than the equilibrium vapor tension of water at the same temperature because the solution contained NaOH [4]. After the hydrothermal reaction time, the autoclave was taken out and the autoclave was cooled at room temperature naturally. The obtained solid product was filtered and washed by water and absolute alcohol several times. Finally a dark powder was obtained. Drying at 80 ºC for 4 hours, powders were collected for calcinations.

Nanocrystals Characterization

The final powders were calcined at 600˚C for 2 hours with a heating rate of 10˚C min^{-1} and collected for characterization.

The samples prepared by co-precipitation and hydrothermal methods were denoted as (A) and (B), respectively. The produced powders were further characterized by the powder X-ray Diffraction (Cukα for (A) and Cokα for (B)). X-ray diffraction (XRD) patterns were measured by a “Philips X’pert”. A Philips XL-30 scanning electron microscope was used to characterize the morphologies and microstructure of the samples. The elemental analysis of the samples was carried out by using energy dispersive analysis of X-ray spectrometer. The magnetic properties of the ferrites were measured at room temperature using a VSM-7300 vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co., Kashan, Iran) in a maximum applied field of 10 kOe. From the obtained hysteresis loops, the saturation magnetization, M_s, remnant magnetization, M_r and coercivity H_c were determined.

Result and discussion

X-ray diffraction pattern of $CoFe_2O_4$ samples prepared using both hydrothermal and co-precipitation methods are shown in Figure 1., we have estimated the crystallite size D of the samples from peak at $2\theta = 35.5^o$ with miller indices by (311) using Scherrer equation [18]:

$$D = (0.9)\lambda/\beta \cos\theta \qquad (1)$$

In which D is the grain diameter, β is half-intensity width of the relevant diffraction,

λ is X-ray wavelength and θ the diffraction angle. The lattice parameter was calculated according to the Eq. (2):

$$a = d_{hkl} (h^2+k^2+l^2)^{1/2} \quad (2)$$

The reflection plan (311) was used to calculate the crystallite size and lattice constant since this crystallographic plane exhibited the maximum diffraction intensity. The crystallite size and lattice constant of the cobalt ferrite nanoparticles have been summarized in Table 1.

Table 1. The crystallite size and lattice constant of the synthesized cobalt ferrite prepared with different methods.

Sample	Synthesis method	Lattice parameter (Å)	Crystallite size (nm)
A	Co-precipitation	8.39	33
B	hydrothermal	8.35	15

As shown the lattice parameter estimated from the strongest diffraction peak of (311) is 8.36 and 8.43 Å. These values are close to the known bulk of $CoFe_2O_4$ (8.39570.005) [19].

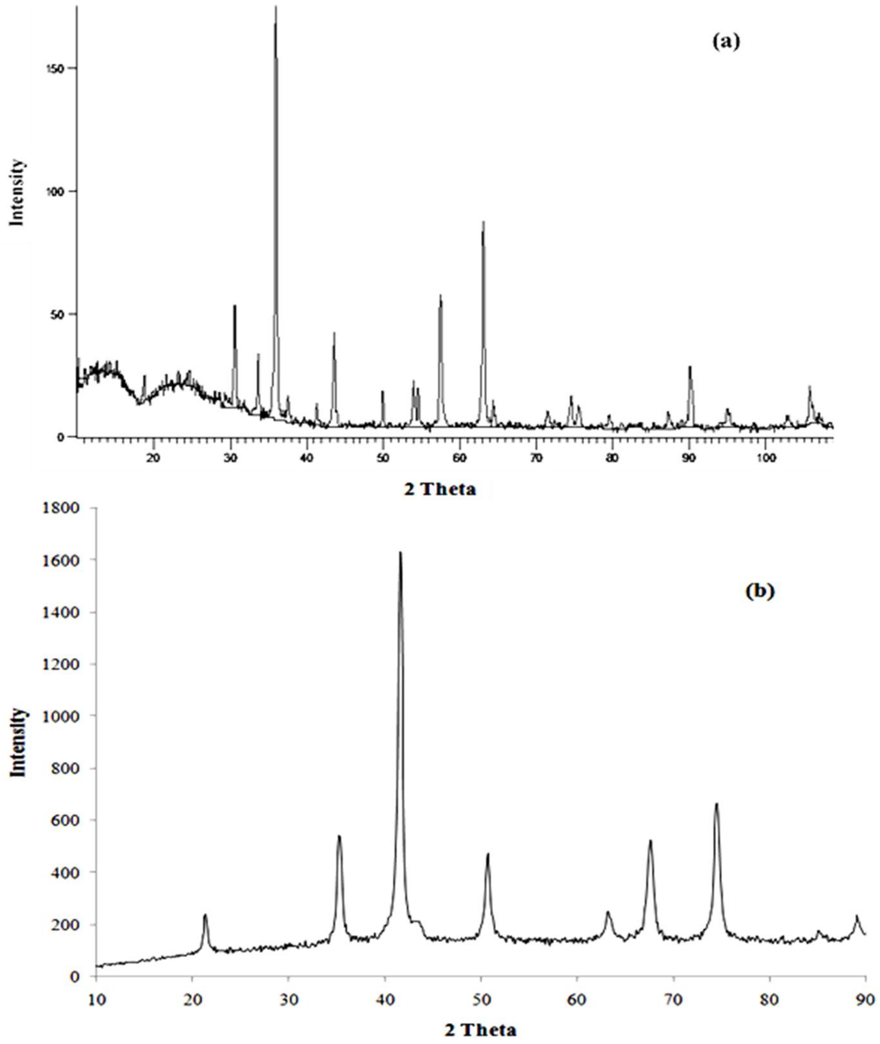

Figure 1. XRD patterns of the products synthesized by different methods (a) co-precipitation, (b) hydrothermal.

The average crystallite sizes were 14 nm and 15 nm for nano-particles which were produced by hydrothermal and co-precipitation methods, respectively. According to the Figure 1.a and Figure 1.b, the XRD patterns confirm the formation of ferrite structure. All samples exhibit similar diffraction peaks which correspond to the cubic spinel lattice of $CoFe_2O_4$ (JCPDS Card No. 22-1086). The sharp diffraction peaks indicate the transparence of the nano-crystals. Further the XRD pattern consists of fairly broad but still resolved peaks which were superimposed on a slightly various intensity. All peaks correspond to a cubic spinel lattice (space group Fd3m) with parameter a=0.821 nm. There are no other detectable traces of extra crystalline or amorphous phases. The considerable extension of all diffraction peaks, which were more than 1° full width at half maximum (FWHM) for the strongest peaks at 35° phase (311) indicates that the investigated samples consist of high crystalline and quite small crystallites. These results are highly compatible with the previous report. The presence of strains and stacking faults can also be excluded. [16].

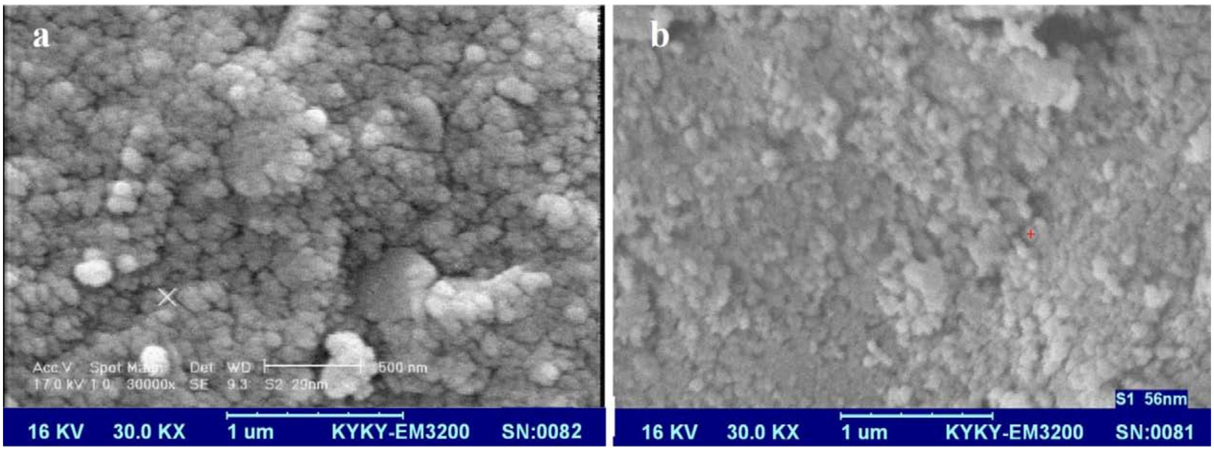

Figure 2. SEM of annealed sample in 600 ºC for 2 h prepared with (a) co-precipitation, (b) hydrothermal methods.

Figure 2 (a, b) indicates the SEM images of samples which were obtained by different methods. The average sizes of nano-particles were about 29 and 56 nm for samples prepared by hydrothermal and co-precipitation methods, respectively. This result is exactly matching with our calculations by the XRD Scherer equation. The products contained spherical particles but some extent aggregations were observed in both samples. $CoFe_2O_4$ nanoparticles prepared by hydrothermal method have uniform, mono dispersive spherical structure with a narrow size distribution of particles (Figure 2b).

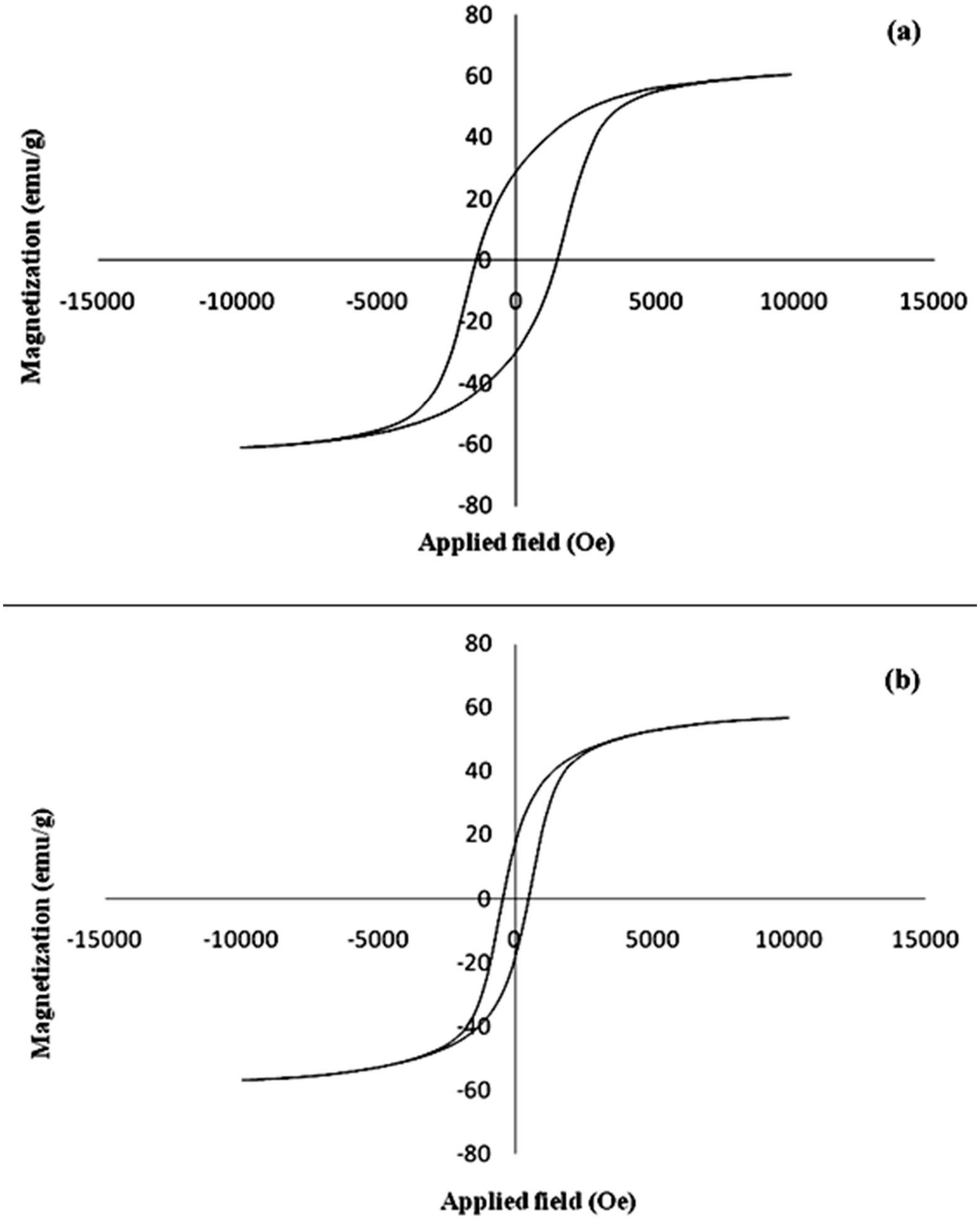

Figure 3. Hysteresis loops of prepared by (a) co-precipitation and (b) hydrothermal methods.

Magnetization versus the applied field plots at room temperature for samples obtained by two above methods are shown in Figure 3(a, b). It is demonstrated that the magnetic properties of samples which were treated by hydrothermal route were less than the samples which were prepared by co-precipitation method. A sample which was synthesized by hydrothermal route suggested a saturation magnetization, Ms, 56.88 emu g^{-1} and remnant magnetization, Mr, 21.44 emu g^{-1}. The saturation and remnant magnetization for the sample which was prepared by co-precipitation route were 60.85 and 29.34 emu g^{-1}. Ms Values for the samples are less than what was reported for the bulk of $CoFe_2O_4$ and this is devoted to particle size which is less than the actual size and it is estimated to be 70 nm [3]. A coercive force, Hc, was 507.7 and 1492.6 Oe for hydrothermal and co-precipitation methods, respectively. It was found in previous studies that the coercivity increases as the particle size decreases, but in this paper in agreement with A.M. Ibrahim et al. [3], it is observed that the coercivity increases as the crystallite size increases. M.M. El-Okr et al. [20] investigated the relationship between coercivity and particle size and reported that coercivity was reported to increase along with particle size attaining a maximum value at 29 nm (about 650 Oe) and then decreases. This trend agrees with what reported in table 2.

Table 2. Magnetic properties of samples synthesized with different method.

Sample name	Average Particle size (nm)	Ms (emu g^{-1})	Mr (emu g-1)	Hc (Oe)
A	33	60.85	29.34	1492.6
B	14	56.88	21.44	507.7

For the hydrothermal sample, a scan be seen in the coercivity value of $CoFe_2O_4$ with average particle size around 14 nm and in contrast to the amount of average particle size 33 nm in the co-precipitation sample, about twice the value was reported by El-Okr. This unexpected expansion in hysteresis loop may refer to highly dependent, magnetic properties of $CoFe_2O_4$ on the distribution of the iron and cobalt ions in the A and B sites in spinel structure. Even small changes in substantial changes of magnetic moments and the magnetic anisotropy is a rule [21]. The value of the total magnetic moment was calculated by (M=MB-MA) [16]. Therefore, the content of Fe^{3+} ions on B-site for hydrothermal sample was larger than that of co-precipitate sample. The results were derived from the different preparation methods. It is generally expected that by decreasing the particle size, H_c increases. This may be due to the low temperature and type of synthesis procedure. The difference in M_s may result from the difference in size of the nanoparticles. As $CoFe_2O_4$ was synthesized by co-precipitation method, the decrease of M_s has recognized the existence of impure phase such as β-FeOOH [22]. But in the present study, the small Ms cannot be simply attributed to the formation of impure phase. It was also reported that in $CoFe_2O_4$ nano-particles, the decreased M_s and the enhanced H_c are related to disorder canting spins (spin-glass-like) on the surfaces due to the imperfection of coordination; however, the $CoFe_2O_4$ nanoparticles with similar sizes synthesized by other methods generally have much larger M_s and drastically smaller H_c [16].

Conclusion

In summary, cobalt ferrite nano-particles have been successfully synthesized by the hydrothermal and co-precipitation methods. Results indicate that the size and shape of the acquired products are sensitive to method of preparation. It was demonstrated that using the hydrothermal method considerably accelerates the formation of the $CoFe_2O_4$ ferrite as compared to co-precipitation method, this work showed that the hydrothermal route leads to obtaining smaller particles compared to co-precipitation method. The hydrothermal technique yields fine particles because the rates of hydrolysis and dehydration of the metal salts in high temperature water are enhanced. It was found that the nano-particles which were obtained by hydrothermal method were shaped irregularly and spherically and were uniformly distributed. As we expected for single domain nano-particles, the hysteresis loops of both samples, shows their super-paramagnetic behavior, Coercive force of sample which was synthesized by co-precipitate route was higher than that of other samples due to Fe^{3+} distribution in spinel structure resulting from the difference between applied synthesis methods.

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