

Evaluating of structural and magnetic properties of Cobalt ferrite synthesized by Pechini sol-gel method

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Abstract

Structural and magnetic properties of Cobalt ferrite nanoparticles (CoFe_2O_4) synthesized by sol-gel Pechini has studied. X-ray diffraction pattern (XRD) confirmed the formation of cubic crystalline phase in synthesized nanoparticles. X-ray diffraction and field emission scanning electron microscope (FESEM) were used for characterization of the crystallite size and structural properties of this type of ferrite. It was observed that the particle size is in the nanometer range. The lattice constant and crystallite size were also in nanometer range. To evaluate the thermal properties, thermal analysis (DTA/TG) and FTIR analysis that is a proper method for identifying functional groups and molecular structure were performed. Magnetic properties were studied via vibrating sample magnetometer (VSM). The greatest amount of saturation magnetization (Ms) for cobalt ferrite sample was 34/75emu/g.

Keywords: Nanoparticle, Cobalt ferrite, Structural and magnetic properties.

Introduction:

In the past two decades, study over the effects of reduction of particle size on the magnetic properties has drawn the massive attention. It's impossible to reduce a magnetic particle size and still have the same magnetic properties. The main stimulus for producing and study of magnetic materials in nanometer scale occur dramatic changes in the magnetic properties. magnetic nanoparticles is subject of interest in terms of the principles and applications. Also because of unique features from theoretical perspective and even for laboratory and industrial point of view they are a subject of interest for both scientists and engineers (Dorman, Fiorani, 1992). Cobalt ferrite is a compound having inverse spinel structure with the formula of CoFe_2O_4 of mixed metal oxides category. Spinel structure is both in normal and reverse spinel form. In spinel structure oxygen anions based on compact arrangement and cations placed in tetrahedral and octahedral voids. Cations depend on the aspect ratio and according to the principle of minimization the total energy of a crystal, occupy the pores as justification. Due to the structural characteristics, spinels accept a wide range of cations with different aspect ratio of tetrahedrals and octahedrals into their voids. Spinel family is introduced with the general formula of AB_2O_4 which A is a bivalent cation and B is a trivalent cations and spinel structure is based on the spatial group of $\text{Fd}3\text{m}$ (Adam, Davis and Dionne, 2002). Because of the structure and electrical and magnetic properties, spinel ferrite (CoFe_2O_4) is a subject of interest to many researchers.

These features along with good physical and chemical stability, make cobalt ferrite nanoparticles proper for various applications, such as magnetic recording, drug delivery and so on. Spinel ferrites have excellent magnetic and electrical properties and especially emphasized on CoFe_2O_4 because of structural, magnetic and electric conductivity. CoFe_2O_4 has a reverse structure to some degrees and inversion value depends on the preparation and heat treatment (Yang et al, 2006). Among the various spinel ferrites, cobalt ferrite due to excellent chemical stability, good mechanical hardness, high Curie temperature, suitable saturation magnetization, high coercivity field and the positive constant of anisotropy is an important ferrite. Due to the properties of cobalt ferrite, it is widely used in high frequency applications (Sutka, Mezinskis, Pludons, 2010). For preparation of Cobalt ferrite mostly use the wet chemical methods.

Experimental:

Cobalt spinel ferrite nanocrystals were synthesized by sol-gel Pecini method. All chemical compounds which used in this research had laboratory purity. This method is based on forming a homogeneous and stable solution. In this research chemical reactants were in a stoichiometric amount of cobalt nitrate 6 hydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron nitrate 9 hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$). For all the specimens, metal nitrates were dissolved in distilled water by means of stirrer magnet which is a hydrolysis reaction. At the temperature of 60°C , citric acid was added to the solution. Then at the temperature of 80°C ethylene glycol was added to the solution. The solution was heated up to the temperature range of $80\text{-}90^\circ\text{C}$ until a wet gel of metal nitrates achieved. After that the wet gel in the temperature of 185°C was dried in an oven for 24 hours. Subsequently, the dry gel was placed in an oven for an hour at 700°C and the calcination process was occurred. Finally ferrite nanopowders were formed. To characterize the samples used X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), thermal analysis (DTA/TG), vibrating sample magnetometer analysis (VSM) and FTIR.

Results and discussion:

XRD Analysis

Fig.1 show the XRD pattern of CoFe_2O_4 . This pattern show the structure of single phase spinel with cubic symmetry. The synthesis product was a black powder which its X-ray diffraction pattern is showed in fig.1.

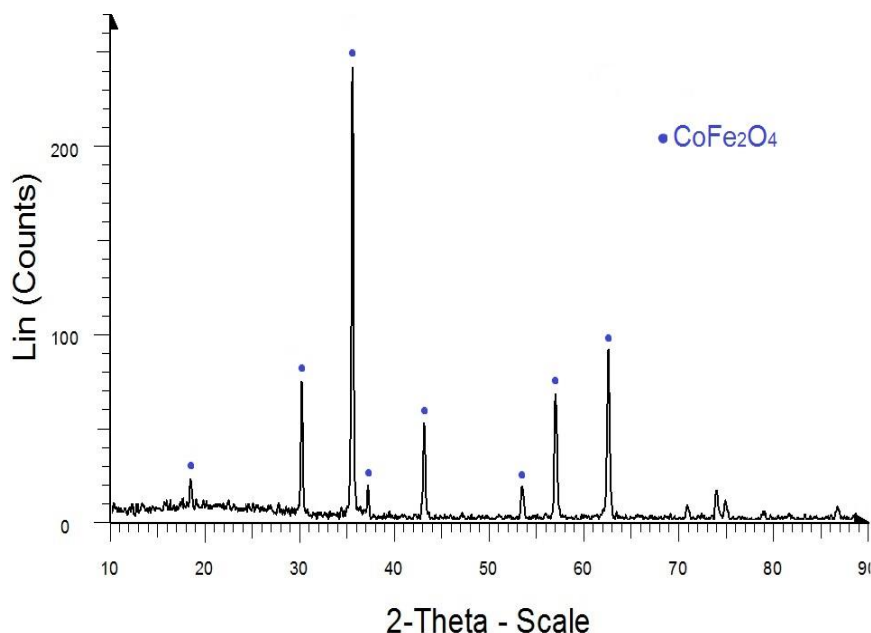


Fig1: XRD pattern of CoFe_2O_4 sample

The peaks position of spinel structure observed in Fig.1 along with the relative intensities and full width at half maximum (FWHM) of this sample is shown in Table 1. As it's obvious from Fig.1 and Table 1, the peaks are at angles close to 18/335, 30/113, 35/362, 37/165, 43/108, 53/486, 56/040, 62/629 degrees and the tallest peak is the third peak at angle of 35/485 degrees, which is based on the others work (Sajjia et al, 2014).

The calcined nanocrystal powder grain size is calculated by the formula 1:

$$D = \frac{k \lambda}{\beta \cos \theta} \quad (1)$$

Which D is grain size, λ is wavelength of X-ray ($\lambda = 1/5406 \text{ \AA}^0$), θ is the Bragg angle, β is full width at half maximum (FWHM), K is constant (0/94). Lattice parameter "a" also for the important peak of (311) is calculated by Bragg equation which d is the distance between the two plates:

$$a = d \times \sqrt{h^2 + k^2 + l^2} \quad (2)$$

True density of X-ray, ρ_x is calculated by the following formula:

$$\rho = \frac{8M}{Na^3} \quad (3)$$

Which M is the molecular weight, N is Avogadro's number and "a" is the lattice parameter.

Table1: peaks position of spinel structure with full width at half maximum and relative intensity in CoFe₂O₄ sample

FWHM (2θ)	Intensity (%)	Miller index	Position (2θ)	Peak numbers
0/214	13/284	(111)	18/335	1
0/227	29/889	(220)	30/113	2
0/245	100	(311)	35/362	3
0/191	7/380	(222)	37/165	4
0/251	18/450	(400)	43/108	5
0/255	7/380	(422)	53/486	6
0/333	27/306	(511)	57/040	7
0/296	36/162	(440)	62/629	8

Also physical and theoretical properties of produced ferrite through mathematical equations and using XRD results were calculated. This information is given in Table 2.

Table2: lattice parameter, crystallite size and the density of ferrite nanoparticles CoFe₂O₄

composition	Lattice (Å)parameter	crystallite size (nm)	density(g/cm ³)
CoFe ₂ O ₄	7/848	34/552	5/357

FESEM Analysis

Electron microscopy was used For study the morphology and particle size. For better detecting of particle size, FESEM resolution is higher than SEM. So to prove nano-particles and particle size distribution FESEM images has used. The particle size of the images was calculated by the ImageJ software. Fig.2 shows the FESEM image of the sample CoFe₂O₄. As it's seen in this picture, particles are in spherical shape and particle size is in nanometer scale.

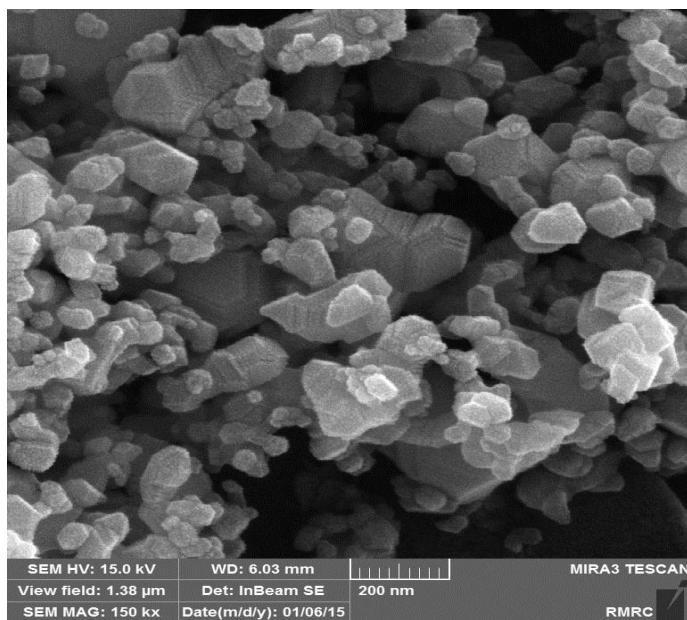


Fig2: FESEM image of CoFe₂O₄ sample

The graph in Fig.3 shows the distribution of particles size of CoFe₂O₄ samples which is obtained from electron microscope. According to the graph, the most distribution of particle size is between 20 and 60 nm which is corresponded to X-ray diffraction pattern results in Table 2 that calculated by Scherrer equation (formula1).

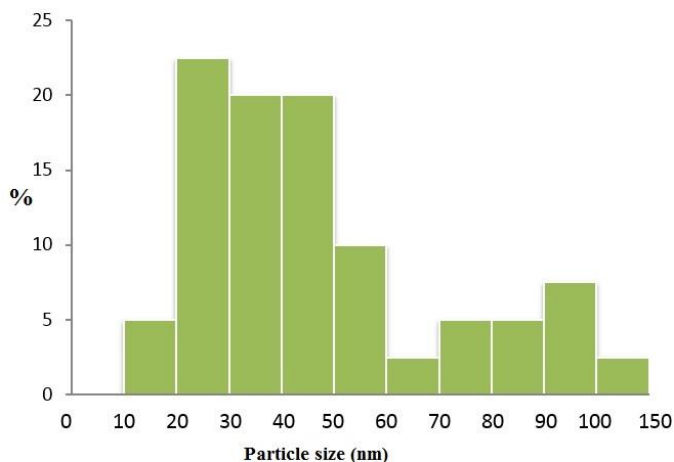


Fig3: Distribution of particle size of CoFe₂O₄

FTIR Analysis

Figures 4 and 5 show infrared Fourier transform spectra before and after the calcination of the sample CoFe₂O₄, respectively. Fig.4 shows a peak near the band of 1400cm⁻¹, that according to other researches

this peak implies on vibration of the bond group -CH- (Kumar, Manoranjan, 2014). Also the peak near 1700cm^{-1} band is related to C=O bond (carbonyl group) in the molecule. The peak near the 2500cm^{-1} band is related to C≡N bond. A peak near the band 2900cm^{-1} is probably related to the C-H bond and the last peak in the band 3440cm^{-1} existed due to the stretching vibration of hydroxyl groups (OH) or H-O-H bonds(T.S. Halil, 2007).

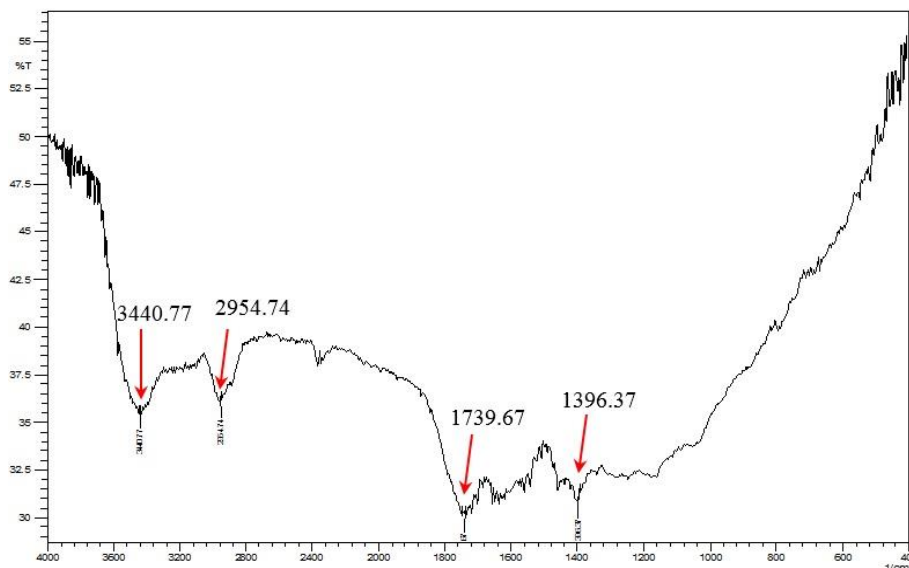


Fig4: Absorbed infrared waves curvature for CoFe₂O₄ sample before calcination

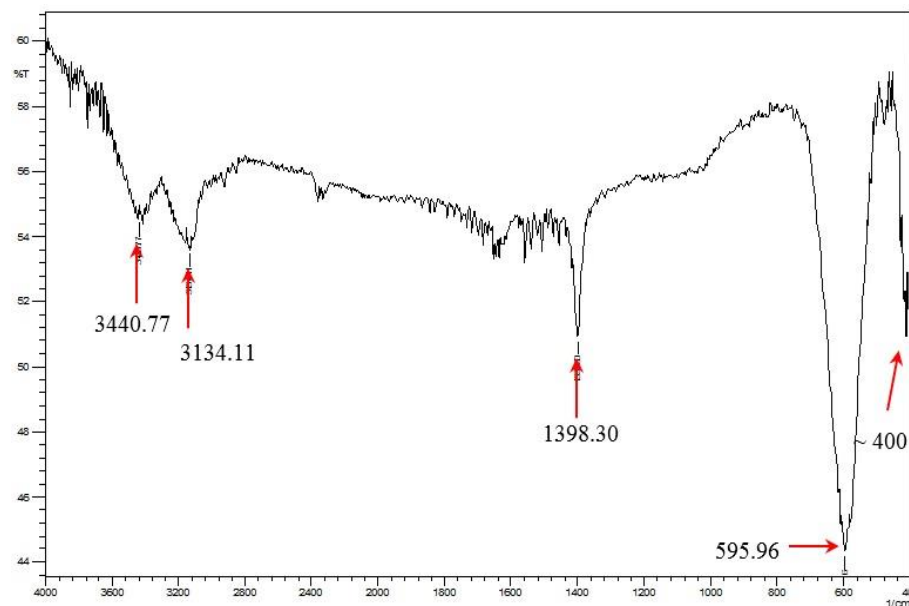


Fig5: Absorbed infrared waves curvature for CoFe₂O₄ sample after calcination

In Fig.5, which the sample is calcined, a band has removed and other bands have been moved up due to evaporation of some organic materials or participating the organic materials in the reaction. Between zones of $300-600\text{cm}^{-1}$ FTIR bands are attributed to metal ions(Kontad, Sukon Phanichphant, 2012).in zones of $400-600\text{cm}^{-1}$ Two new bands has seen. One with high wave number that corresponds to the natural stretching vibration of metal in the tetrahedral and other with lower wave number related to natural stretching vibration of metal in the octahedral sites. The stretching vibration of tetrahedral is more than octahedral which is related to the short M-O bond in tetrahedral in comparison to octahedral (Jauhar, Singhaln, 2011). So we can conclude that the cations placed in octahedral and tetrahedral sites.

DTA/TG thermal analysis

Fig.6 show the diagrams of thermal analysis of the sample CoFe_2O_4 . As it is seen in fig.6 at a temperature close to 300°C the TG curve starts to decrease that shows the sample weight loss while increasing heat. At the same temperature (about 320°C), a small peak appeared in the DTA curve which indicates an exothermic reaction and decomposition (Sozeri, Durmus, Baykal, 2012), followed by oxidation of some organic materials such as ethylene glycol and maybe in other words evaporate organic solvents and water (Deligo et al, 2012) and partially coming out the composition of material and during these reactions, the weight began to decrease.

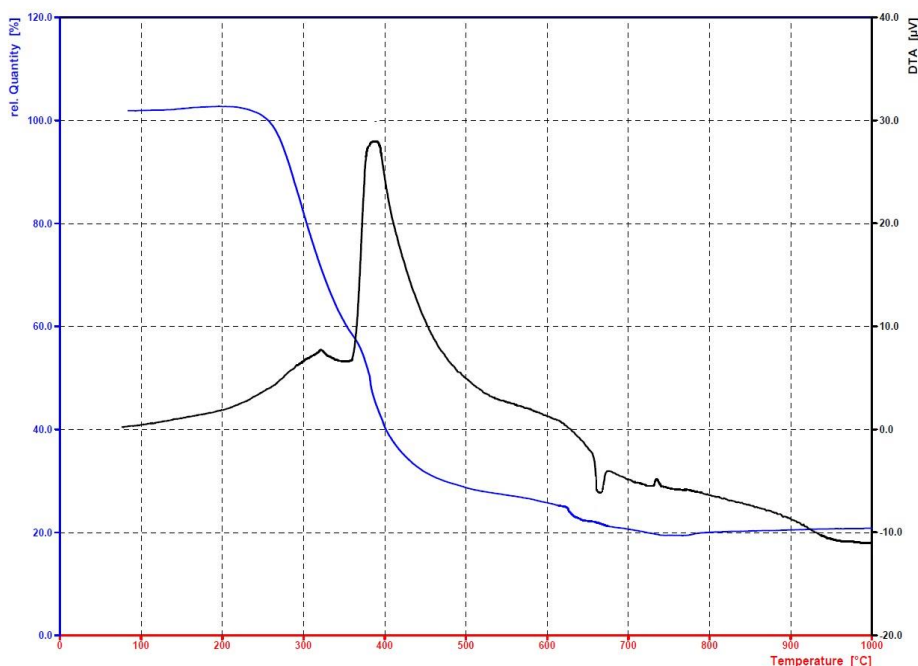


Fig6: DTA/TG curve of CoFe_2O_4 sample

In the dry gel there are hydroxyl group, carboxyl group and NO_3^- ions (Aghav et al, 2011). At a temperature about 390°C in DTA curve observed a high peak which indicates a exothermic reaction and reduction reaction of anionic ato catalyst between nitrate and citrate systems in the material (Hankare et al, 2013). Within this peak carboxyl groups, NO_3^- ions and other organic ions in the material decompose.

At this temperature almost all the organic material oxidized and went out in gas state. So the weight loss increased and in the mentioned temperature we could see the almost 60 percent weight loss. With the continuing rise in temperature up to 640°C the TG curve decreases more. An endothermic peak in the temperature of 670 °C can be seen that at this stage the remaining ingredients react together and the final composition of ferrite crystallites formed.

VSM Analysis

Ferrite properties depend on size, shape, chemical composition, particle distribution which all of them are related production method. Exchange interaction between A-O-A, B-O-B and A-O-B bonds in tetrahedral or octahedral places becomes weak with increasing the concentrations of diamagnetic ions. This leads to significant changes in the properties of ferritic materials (Dlamini, Msomi, Moyo, 2015). To measure the magnetic properties of samples including saturation magnetization, the coercivity field and residual magnetization used VSM analysis. The results of this experiment are hysteresis curves. Hysteresis curves of CoFe_2O_4 sample is shown in Fig.7.

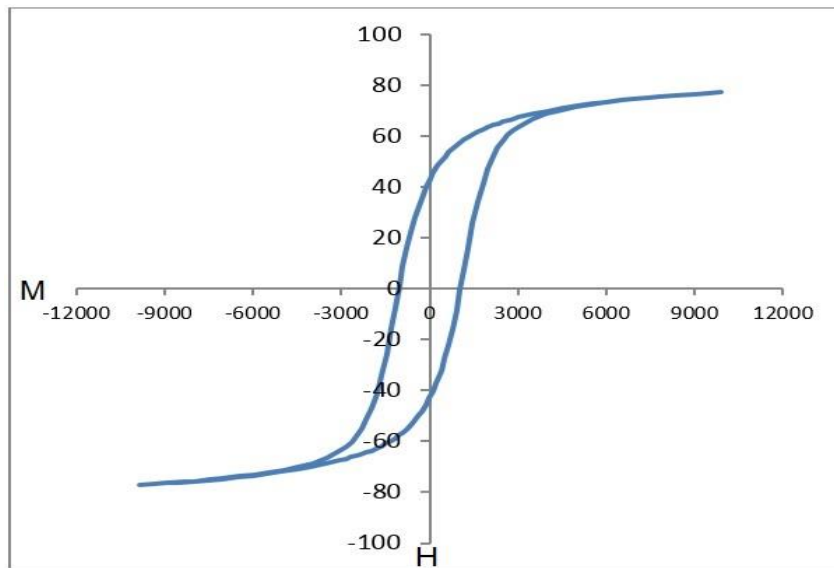


Fig7: Hysteresis curve of CoFe_2O_4 sample

The amount of saturation magnetization, the coercivity field and residual magnetization generated by hysteresis curve for this sample are shown in Table 3.

Table3: saturation magnetization (M_s), the coercivity field (H_c) and residual magnetization(M_r) for CoFe_2O_4 sample

composition	M_s (emu/g)	H_c (Oe)	M_r (emu/g)
CoFe_2O_4	75/34	1054/78	40/92

Conclusion:

Cobalt ferrite nanoparticles (CoFe_2O_4) were successfully synthesized by using sol-gel Pechini method. X-ray density and the lattice constant values are in the similar reported limits. Particle size obtained from Scherrer formula and average grain size in the nanometer range were calculated. The average grain size resulting from FESEM image of the particles is between 20-60 nm and also these particles agglomerated which is due to the magnetization of ferrites. With using of FTIR analysis proved that nanoparticles of cobalt ferrite had spinel structure and cations placed in octahedral and tetrahedral sites. DTA/TG thermal analysis proved the ferrite crystallites formation in the final composition. CoFe_2O_4 nanoparticles showed ferromagnetic behavior and values of 75/34 emu/g and 1054/78 Oe are for saturation magnetization (M_s) and the coercivity field (H_c), respectively. High amounts of M_s and H_c , proved the nature of nanocrystalline ferrite spinel of formed CoFe_2O_4 .

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