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Preparation and characterization of the cobalt ferrite nano-particles by reverse coprecipitation



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ABSTRACT

In this paper, cobalt ferrite nano-particles were rapidly prepared using a reverse coprecipitation method. The effects of pH value, aging time, aging temperature and calcination temperature were studied by VSM, XRD and TEM. The results presented that the conditions to obtain the cobalt ferrite nano-particles with a perfect cubic spinel ferrite type structure are the pH value of 12.00, aging time of 60 min, aging temperature of 92 °C and calcination temperature of 800 °C. The crystallite size of cobalt ferrite increased with increasing the aging and calcination temperature. The saturation magnetization of cobalt ferrite increased with increasing the aging and calcination temperature. The VSM analysis demonstrated that the optimum sample has a high saturation magnetization and proper coercivity, 72.95 emu/g and 717 Oe, respectively. Furthermore, the particle size estimated from the TEM was seen to be larger than that observed from the XRD analysis.

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1. Introduction

The magnetic nano-particles have aroused widespread interest among researchers due to the high surface to volume ratio of these nano-crystallites which was expected to result in some exceptional magnetic properties and unique functional applications in the fields of imaging and therapy [1,2]. Among these magnetic nano-particles, cobalt ferrite, a cubic spinel ferrite [3], has gained its prominence due to its high corecivity (Hc), moderate saturation magnetization (Ms) [4,5], good chemical stability and high mechanical hardness [6]. These properties make it a promising material for high-density magnetic recording [7], permanent magnets, magnetic fluids, catalysis, photo-magnetic material [8,9], and in developing new cell thawing agents [10].

Various synthetic approaches have been employed to prepare cobalt ferrite nano-particles, such as the sol-gel method [11], chemical coprecipitation [12–14], forced hydrolysis in a polyol medium [15], synthesis in oil-in-water micells [16], and in reverse micells [17], or thermal decomposition of a mixed Co^{2+} – Fe^{3+} oleate complex [18]. The coprecipitation process has been proved to be an efficient method to prepare ultra-fine particles dispersed in different matrices [19]. However, the particle diameter and shape of the nano-particles prepared by traditional coprecipitation method are ununiform and difficult to control. Recently, an improved chemical coprecipitation method called reverse coprecipitation has been applied to obtain cobalt ferrite nano-particles. Different from the traditional coprecipitation method, precursor ions were added

into the precipitant solution, which ensures the precipitant in a supersaturated state, so that the precursor ions precipitate completely and generate nano-particles more evenly and smaller than that generated by traditional coprecipitation method. Using this method, cobalt ferrite nano-particles with controlled surface morphology, structure and chemical composition can be attained by carefully monitoring the preparation parameters.

In the present work, the cobalt ferrite nano-particles were synthesized by reverse coprecipitation method through changing the concentration of NaOH solution, aging temperature and aging time, as well as the temperature in subsequent calcination treatment. The mechanism for composition and size dependence of magnetic properties was studied in detail.

2. Experimental

2.1. Materials

All reagents were analytical grade and used without further purification. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are the cobalt and iron precursors while NaOH (pellets, 98%, Alfa Aesar) acts as precipitant. All solutions were prepared with distilled water.

2.2. Synthesis of CoFe_2O_4 nano-particles

The CoFe_2O_4 nano-particles were prepared using the reverse coprecipitation method. In a typical synthesis, 200 ml $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 M) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (1.0 M) mixture solution was dropped into a 100 ml NaOH solution with desired pH value. During the precipitation process, the reaction solution was vigorously stirred and

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0.1 M NaOH solution was added to keep pH value as the initial stage. The precipitate was aged for a period at a desired temperature. It was then filtered out and washed with distilled water several times. And then, the precipitate was dried at 110 °C for 12 h.

The powders was then calcined at 600–1000 °C for 1 h in static air and cooled to room temperature to get CoFe_2O_4 nano-particles.

2.3. Characterization

The phase of sintered materials was confirmed by X-ray diffraction (XRD) technique using an X-ray diffractometer (Panalytical X' Pert PRO) equipped with $\text{CuK}\alpha$ as a radiation source ($\lambda=0.15406$ Å). Each sample was scanned for 2θ range (15–75°) with a step size of 0.02°. The X-ray tube was excited at 40 kV and 150 mA. The diffraction maxima can be compared to known diffraction patterns through the Joint Committee on Powder Diffraction Standards (JCPDS) database collected. The crystallite size was estimated from the width of the diffraction line, which corresponds to a particular reflection using the Scherrer equation. The analysis of size, shape and particle distribution of the samples was carried out using a transmission electron microscope (Tecnai G2 F30) at 100 kV. For this purpose, dispersions of nano-particles were pipetted onto carbon-coated copper grids. A vibrating sample magnetometer (VSM, model Lake Shore, new 7304 series) was used to investigate the magnetic properties of the samples at room temperature. The maximum applied external field was 15 kOe. By applying this technique, parameters like specific saturation magnetization (Ms) and coercive force (Hc) can be deduced.

3. Results and discussion

3.1. Effect of synthesis conditions on the magnetic and structural properties

Cobalt ferrite nano-particles were synthesized by reverse coprecipitation method. The effects of pH value, aging time, aging temperature and calcination temperature on the magnetic properties, crystal structure and crystallite size have been systematically studied.

3.2. 1 pH value

A series of experiments have been carried out by changing the pH value from 10.00 to 13.00 under the following operating conditions: 1 h aging time, 92 °C aging temperature, 800 °C calcination temperature. The samples were examined by a vibrating sample magnetometer and the obtained results are listed in Table 1.

The results revealed that the value of saturation magnetization reached a maximum 72.95 emu/g at pH 12.00. The Hc attained high value of 717 Oe. This behavior is probably due to a more completely aging reaction which increases the integrality of crystalline structure at pH 12.00. The proper supersaturation of precipitant at pH 12.00 suppressed the crystallization rate effectively, which affected the crystalline structure significantly: the reactant ions precipitated of a reasonable rate, ensured sufficient time for the ions to form a crystalline structure, the magnetic properties increased.

Table 1
Magnetic properties versus different pH values.

Serial number	pH value	Saturation magnetization (emu/g)
1	10.00	2.92
2	12.00	72.95
3	13.00	12.58

3.2.1. Aging time

This section is dedicated to understanding the effect of aging time on the properties of as-formed nano-crystalline cobalt ferrite powders. To achieve that, a series of experiments were conducted at different aging times ranging from 30 to 120 min at a constant pH value of 12.00, aging temperature of 92 °C and calcination temperature of 800 °C. The samples were examined by a vibrating sample magnetometer and the obtained results are listed in Table 2.

Table 2 shows that increasing the aging time increased the value of saturation magnetization. As can be realized, the values of saturation magnetization 72.95 and 75.18 emu/g were obtained when aging time reached 60 min and 120 min respectively. On the other hand, the increase of the aging time was beneficial to the diffusion and deposition of the ions, and the formation of well crystallized cobalt ferrite [3]. Furthermore, saturation magnetization had no obvious enhancement by increasing the aging time to 120 min. It was possible that the cobalt ferrite nano-crystal had formed completely when the aging time reached 60 min, and the increase of the aging time had no significant effect on crystalline structure.

3.2.2. Aging temperature

Before the heat treatment to the precursor, a series of experiments have been carried out by changing aging temperature from 60 °C to 92 °C under the following operating conditions: pH 12.00, 1 h aging time, 800 °C calcination temperature. The samples were examined by vibrating sample magnetometer and X-ray diffractometer, the obtained results are shown in Fig. 1 and Table 3.

Fig. 1 shows the XRD patterns of the cobalt ferrite powders synthesized at various temperatures. The diffraction peaks appearing at $2\theta=30.06^\circ$, 35.44° , 43.08° , 53.48° , 57.00° and 62.62° which corresponded to [220], [311], [400], [422], [511] and [440], respectively, planes of cobalt spinel ferrite (JCPDS No. 22-1086) with a

Table 2
Magnetic properties versus different aging times.

Serial number	Aging time (min)	Saturation magnetization (emu/g)
1	30	12.27
2	45	13.17
3	60	72.95
4	120	75.18

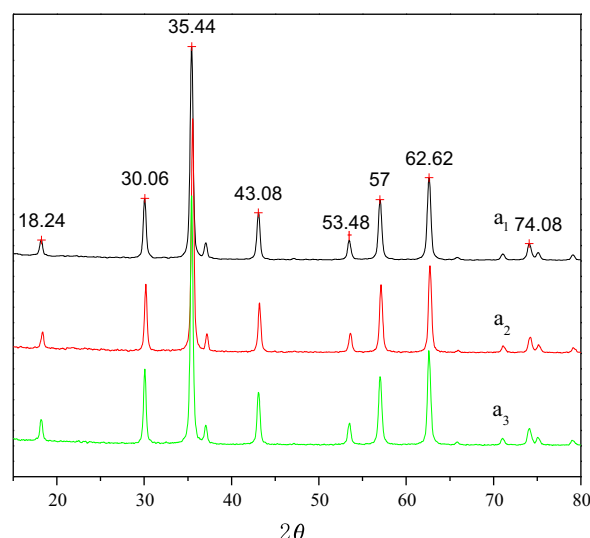


Fig. 1. XRD patterns of CoFe_2O_4 with different aging temperatures (a1, a2 and a3 correspond to the 92 °C, 75 °C and 60 °C, respectively).

cubic spinel type lattice were ascribed. The average crystalline sizes were determined through the strongest [311] peaks using the well-known Scherrer formula. The results are listed in Table 3.

From Table 3, it was clear that the value of saturation magnetization increased significantly by increasing the aging temperature, and it came out to be 72.95 emu/g at 92 °C. The possible reason was that dissolution was an endothermic process, it was accelerated when the temperature increased. The diffusion and crystal growth were intensified as the temperature rose, therefore, the complete crystal can be acquired. Moreover, examination of these diffractograms revealed that the crystalline size increased with the aging temperature. However, the effect of the aging temperature was not obvious.

3.2.3. Calcination temperature

This final section is devoted to clarifying the effect of different calcination temperatures from 600 to 1000 °C. These series of experiments were performed at pH 12.00, keeping the aging temperature of 92 °C, aging time of 1 h. The ferrite powders were examined by a vibrating sample magnetometer and X-ray

diffractometer, the obtained results are shown in Table 4 and following graphs.

XRD patterns of the cobalt ferrite powders calcinated from 600 to 1000 °C are shown in Fig. 2 and relevant data are collected in Table 4. All peaks correspond to the characteristic peaks of CoFe_2O_4 in the JCPDS Card (No. 22-1086) which has a cubic, spinel type lattice [20]. Examination of these diffractograms showed the sharpness of the XRD peaks increased by increasing the calcination temperature, which is the result of enhanced crystallization. Furthermore, with the increase of calcination temperature from 600 °C, cubic spinel structure was formed as a major phase with a minor impurity of hematite. A well crystallized single phase of cobalt ferrite was detected when the precursor was calcinated at 800 °C. The crystallinity of the sample was found to increase with higher calcination temperature from 600 to 1000 °C. This means that a gradual increase in crystallite size as a function of calcination was expected [9]. The crystallite size for the most intense peak ([311] plane) was calculated from the XRD data using the Scherrer formula and found to increase from 19.7 nm at 600 °C to 29.3 nm at 1000 °C.

Magnetic measurements for different calcination temperatures were performed using the VSM technique and the results of magnetic hysteresis loops are shown in Fig. 3. Saturation magnetization as well as coercivity (H_c), Grain size from XRD and Particle size from TEM for different calcination temperatures is computed and listed in Table 4. The saturation magnetization was found to show almost linear increase on increasing the annealing

Table 3
Magnetic properties and grain size versus different aging temperatures.

Serial number	Aging temperature (°C)	Saturation magnetization (emu/g)	Grain size from XRD (nm)
1	60	1.51	22.51
2	75	19.41	24.36
3	92	72.95	26.57

Table 4
Magnetic properties, grain size and particle size versus different calcination temperatures

Serial number	Calcination temperature (°C)	Saturation magnetization (emu/g)	Coercivity (Oe)	Grain size from XRD (nm)	Particle size from TEM (nm)
1	600	68.85	865	19.7	18–25
2	800	72.95	717	26.6	30–60
3	1000	74.87	478	29.3	60–100

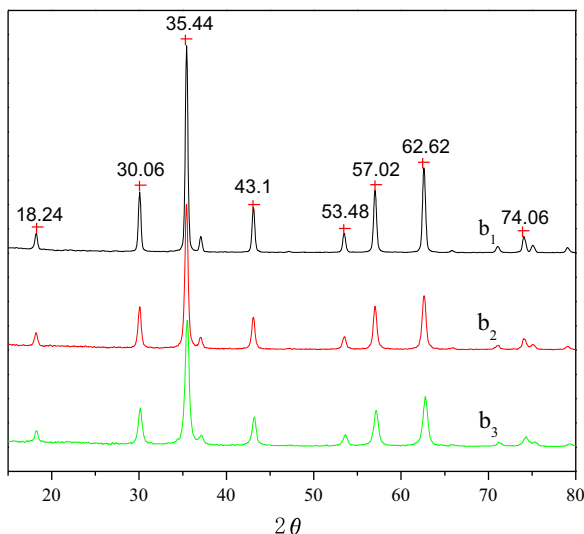


Fig. 2. XRD patterns of CoFe_2O_4 with different calcination temperatures (a_1 , a_2 and a_3 correspond to the 1000 °C, 800 °C and 600 °C, respectively).

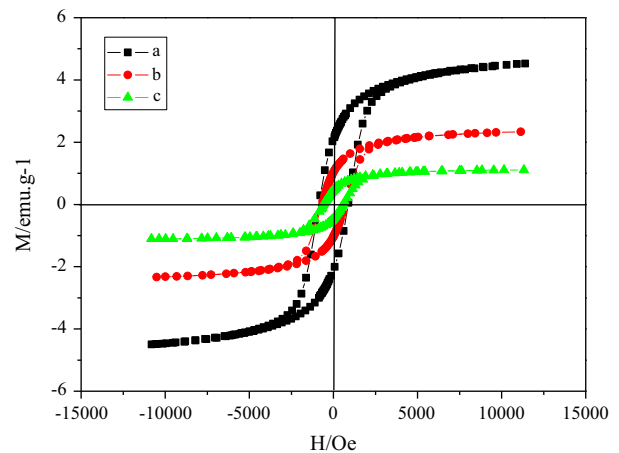


Fig. 3. Magnetic hysteresis loops of CoFe_2O_4 with different calcination temperatures (a , b and c correspond to the 600 °C, 800 °C and 1000 °C, respectively).

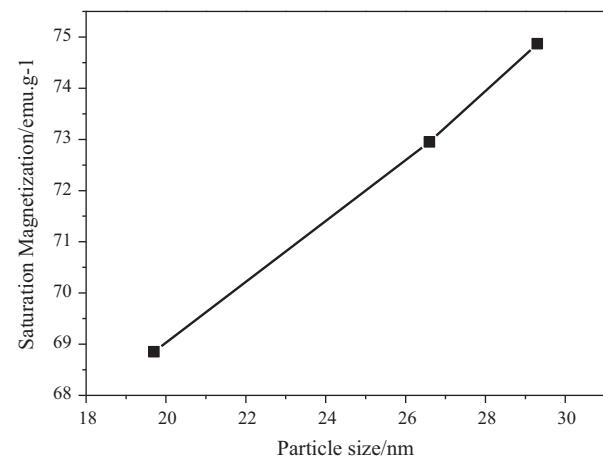


Fig. 4. Dependence of saturation magnetization (M_s) on particle size.

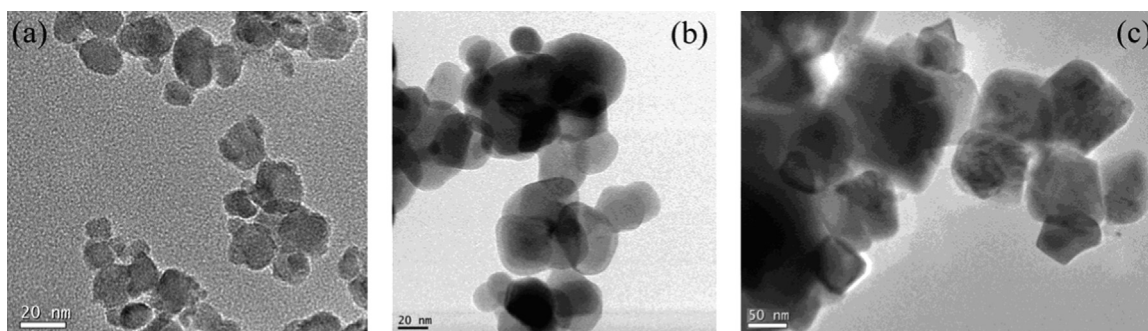


Fig. 5. TEM image of CoFe_2O_4 with different calcination temperatures (a, b and c correspond to the 600 °C, 800 °C and 1000 °C, respectively).

temperature as shown in Fig. 4, and it came out to be 72.95 emu/g at calcination temperature 800 °C. This may be due to the increase of calcination temperature, which was beneficial to the formation of well crystallized single phase of cobalt ferrite, the disordered structure and lattice defects disappeared gradually. But the H_c decreased obviously when calcination temperature reached 1000 °C. This may be because disordered structure and lattice defects induced by O–H bonds had important influence on nano-particles magnetization reversal, nano-particles had high M_s and proper H_c when the calcination temperature was 800 °C. The high saturation magnetization and proper coercivity of the sample can improve the noise problem when it is used as a magnetic recording media [4].

Fig. 5 illustrates the TEM images of samples 600, 800 and 1000. From the TEM micrograph, it can be seen the particles were nano-sized, the sample calcinated at 800 °C (Fig. 5b) revealed approximately spherical shape. Furthermore, the particle size estimated from the TEM was seen to be larger than that observed from the XRD analysis. This may be because the crystallite size was fine, the strong surface effect easily gathered them into the larger aggregates with weakly bonded interfaces, lowering these surface energy and magnetostatic energy.

In conclusion, the optimum sample with high M_s and proper H_c , 72.95 emu/g and 717 Oe, respectively, can be obtained at pH value of 12.00, aging temperature of 92 °C for 60 min and calcination temperature of 800 °C.

4. Conclusions

In summary, single phase cobalt ferrite nano-particles were successfully synthesized by the reverse coprecipitation method and subsequently heat treatment. Structural properties have been studied by XRD while magnetic properties have been studied by vibrating sample magnetometer (VSM) and morphology and microstructure have been studied by TEM. The results obtained permitted to draw the following conclusions:

1. Cobalt ferrite nano-particles were successfully synthesized using the reverse precipitation method.
2. A well crystalline single cubic structure of cobalt ferrite phase was synthesized with the mixed solutions of Co^{2+} and Fe^{3+} ions added into the NaOH solutions with a pH value of 12.00 at 92 °C for 60 min and calcinated at 800 °C for 1 h.
3. The crystallite size and lattice parameters were found to be dependent on both aging and calcination temperature.
4. The crystallite size of cobalt ferrite increased with increasing the aging and calcination temperature.
5. The saturation magnetization of cobalt ferrite increased with increasing the aging and calcination temperature.

6. The optimum sample has a high saturation magnetization and proper coercivity, 72.95 emu/g and 717 Oe, respectively.
7. The particle size estimated from the TEM was seen to be larger than that observed from the XRD analysis.

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