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Synthesis and characterization $CoFe_2O_4$ nanoparticles prepared by the hydrothermal method

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Nano-crystalline particles of $CoFe_2O_4$ with a spinel structure were prepared by hydrothermal method. The synthesized nanoparticles were characterized by XRD, SEM, and AFM techniques. XRD analysis revealed a high degree of crystallinity and also indicated that the diffraction peaks correspond to the cubic spinel structure. The morphology of the obtained powders was studied by SEM technique; the obtained SEM images evidenced the presence of spherical nanometric scale ferrite particles. The AFM data for $CoFe_2O_4$ showed an uniform surface; the average grain size estimated from AFM data was ~ 40 nm. The $CoFe_2O_4$ nanopowder obtained via this simple hydrothermal method and without further calcination, presented a ferromagnetic behavior, with a high saturation magnetization (Ms) and coercivity field (Hc).

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1. Introduction

Several studies have been reported recently regarding the utilization of $CoFe_2O_4$ nanocrystals in various applications, such as lithium ion batteries [1], magnetic catalysis [2], sensors and actuators [3, 4], hyperthermia treatment [5] and antitumor applications [6].

Spinel ferrite can be prepared by a number of methods that have been developed in order to obtain nanosize ferrite particles, such as solid state reaction [7], chemical-wet methods [8], coprecipitation and oxidation [9-11], high-energy ball-milling [12], sol-gel processing [13-15], spray drying method [16], microemulsion processes [17, 18], mechanical alloying [19, 20] and hydrothermal methods [21-25]. The hydrothermal synthesis method requires neither sophisticated processing nor high processing temperature. For example, $CoFe_2O_4$ nanoparticles can be prepared in the temperature range of 150–200 ^{0}C by a microwave hydrothermal process, where as the solid-state method required a temperature of about 800 ^{0}C [26].

In the present paper CoFe2O4 nanoparticles has been synthesized by hydrothermal method and have been investigated the structure and magnetic properties of such powders.

2. Experimental procedure

Powder with the normal formula of $CoFe_2O_4$ was prepared by hydrothermal method. Synthesis of high-dispersion oxide powders from aqueous solutions nitrate and acetylacetonate was carried out in a stainless steel autoclave with tefflon cell hermetically sealed. This mixture consisted in cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$) (99.99%, Merck), and ferric acetylacetonate ($Fe(C_{15}H_{21}O_6)$) (99.99%, Merck). The proportion of each reagent was defined according to its respective molar ratio Co:Fe of 1:2. These two salts were mixed and dissolved in an 1% (mass percent) aqueous solution of citric acid. $CoFe_2O_4$ was precipitated with 5M NaOH solution in drop until the reaction mass reached the pH = 9.

The resulting suspension was transferred into a Teflon-lined stainless steel autoclave and was introduced in an oven at 200 ^{0}C for 5 h. The brown precipitate resulted was filtrated, and then washed 5 times with distilled water and finally 3 times with ethanol. In the next stage, the precipitate was dried in an oven at 105°C for 4 hours.

After drying, the obtained powder was characterized by X-ray diffraction (XRD) performed with X'pert Pro MPD X-ray diffractometer, with monochromatic Cu Kα (λ = 1.54 Å) incident radiation. The morphology of the powder, the particle size and chemical composition of the ferrite particles were determined by field emission-scanning electron microscopy – SEM, energy dispersive spectroscopy – EDAX (Model INSPECT S), and atomic force microscopy – AFM (Model Nanosurf® EasyScan 2 Advanced Research). The magnetic properties of the ferrite powder were examined on 3 cm long samples subjected to AC magnetic field up to 160 KAm^{-1}, by means of a conventional induction method [27].

3. Results and discussion

3.1. Characterization

The structure of the obtained $CoFe_2O_4$ powders was studied by means of the X-ray powder diffraction technique. Fig. 1 shows the representative pattern obtained at room temperature for the as synthesized powder. The XRD spectra exhibit broadened diffraction peaks indicating the nanocrystalline nature of the powder. All the

peaks correspond to crystalline $CoFe_2O_4$ phase (JCPDS, card No. 03-0867): ~18.24^0 (111), ~30.06^0 (220), ~35.45^0 (311), ~37.28^0 (222), ~43.47^0 (400), ~53.89^0 (422), ~57.16^0 (511), ~62.73^0 (440), ~65.70^0 (531), ~70.79^0 (620), ~74.00^0 (533), ~75.37^0 (622) and ~79.08^0 (444). The (311) peak had the highest intensity in the XRD patterns. The diffraction peaks in the patterns are indexed to spinel (space group Fd3m) phases. The intensity of the peaks relative to the background signal demonstrates high purity and good quality of the samples. Thus, the X-ray patterns confirmed that the powder prepared by hydrothermal method consists of single spinel phase $CoFe_2O_4$.

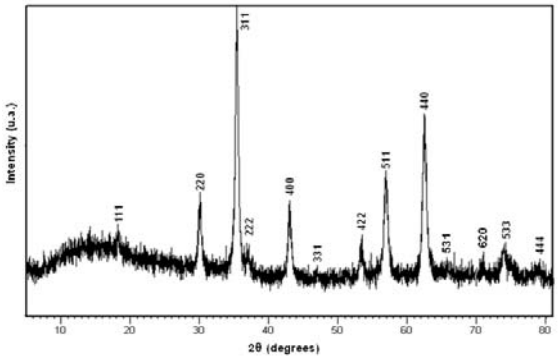

Fig. 1. XRD pattern of $CoFe_2O_4$ powder.

The average crystallite size (d) of the cobalt ferrite powder was calculated using Scherrer's formula [28]:

$$d = \frac{K\lambda}{(\beta^2 - \beta_0^2)^{1/2}} \cos\theta \tag{1}$$

where β is the half-width of the diffraction peak in radians, β_0 corresponds to the instrumental broadening, K = 180/π, λ is the X-ray wavelength, and θ is the Bragg diffraction angle. The as caculated average crystallite size was 37 nm.

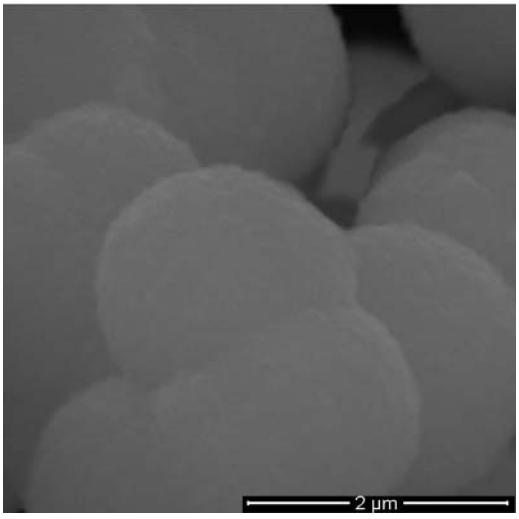

Fig. 2. SEM image of the $CoFe_2O_4$ powder.

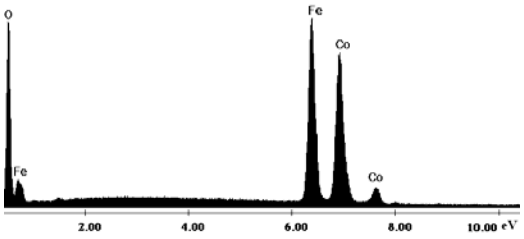

Fig. 3. The qualitative EDAX analysis for $CoFe_2O_4$ powder.

The morphological aspect of the obtained powder was examined by SEM, as shown in Fig. 2 obtained at room temperature. These measurements of surface topography evidenced the formation of micrometric aggregates consisting of nanometric spherical ferrite particles.

The EDAX analysis is considered a semi-quantitative analysis. A typical EDAX spectrum obtained from the analyzed samples is presented in Fig. 3 where the lines corresponding to Co, Fe and O have been identified.

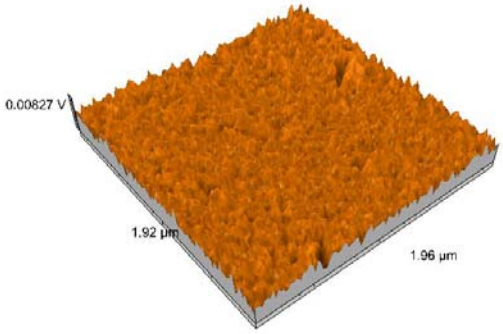

Fig. 4. AFM image: the 3D view of the cobalt spinel ferrite.

Fig. 4 shows the AFM images of surface morphology for the $CoFe_2O_4$. The AFM studies revealed uniform surface without any valleys, due to the homogenously distribution of the ferrite particles. The average particle size for $CoFe_2O_4$ is about ~40 nm. The roughness of the cobalt ferrite can be quantitatively estimated by the root mean-squared roughness (rms) (R_{rms}). R_{rms} is given by the standard deviation of the data from the AFM image, and determined using the standard definition as follows:

$$R_{rms} = \sqrt{\frac{\sum_{n=1}^{N}\left(z_n - \bar{z}\right)^2}{N-1}} \tag{2}$$

where z_n represents the height of the *n*th data, $\bar{z}$ is equal to the mean height of Z_n in AFM topography, and N is the number of the data. For an area of 4.87pm^2 the roughness average is 0.29 nm.

3.2. Magnetic properties

The magnetic properties of $CoFe_2O_4$ nanocrystals obtained by hydrothermal synthesis were investigated with a vibrating sample magnetometer. Fig. 5 shows the magnetization curve measured at the room temperature for the obtained $CoFe_2O_4$ powder. The saturation magnetization (Ms), the remanent magnetization (Mr) and the coercivity (Hc) are about 1000 Am^{-1}, 300 Am^{-1} and 2200 Am^{-1}. The cobalt ferrite shows an obvious ferromagnetic behavior, indicating the presence of a magnetic structure which can exist in the spinel systems.

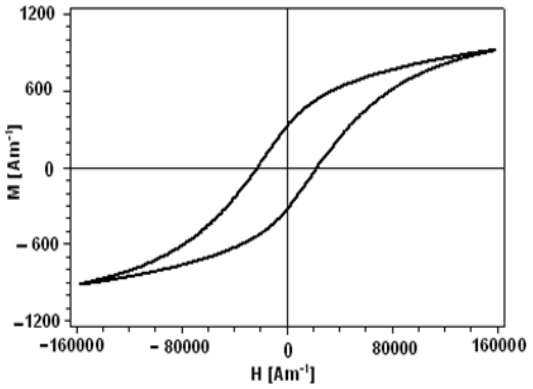

Fig. 5. Hysteresis loop of the $CoFe_2O_4$ powder.

4. Conclusions

$CoFe_2O_4$ powder was obtained by the hydrothermal method using as reactants ($Co(NO_3)_2 \cdot 6H_2O$), ($Fe(C_{15}H_{21}O_6)$) in the presence of citric acid. The experimental results obtained by X-ray diffraction, scanning electron microscopy and atomic force microscopy indicated that the material has spinel structure and it is formed by spherical particles with the average size of about ~40 nm. The conventional hydrothermal method can be used to obtain $CoFe_2O_4$ nanocrystals with high Ms (magnetization) and Hc (coercitivity) properties.

These results suggest the applicability of this hydrothermal method for the obtaining of monodomenial cobalt ferrite nanocrystals. This method does not require subsequent calcination processes, which makes it suitable for producing magnetic nanocrystals with high crystallinity and narrow size distribution.

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