

Cobalt Ferrite Nanoparticles in a Mesoporous Silicon Dioxide Matrix

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Abstract—We have studied magnetic nanoparticles of cobalt ferrite obtained by the extraction–pyrolysis method in a mesoporous silicon dioxide (MSM-41) molecular sieve matrix. The X-ray diffraction data show evidence for the formation of CoFe_2O_4 particles with a coherent scattering domain size of ~ 40 nm. Measurements of the magnetization curves showed that powders consisting of these nanoparticles are magnetically hard materials with a coercive field of $H_c(4.2 \text{ K}) = 9.0$ kOe and $H_c(300 \text{ K}) = 1.8$ kOe and a reduced remanent magnetization of $M_r/M_s(4.2 \text{ K}) = 0.83$ and $M_r/M_s(300 \text{ K}) = 0.49$. The shape of the low-temperature (4.2 K) magnetization curves is adequately described in terms of the Stoner–Wohlfarth model for randomly oriented single-domain particles with a cubic magnetic anisotropy.

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Nanoparticles of cobalt ferrite (CoFe_2O_4) are promising as a material for isotropic permanent magnets, magnetic data recording media, and magnetic fluids [1, 2]. Cobalt ferrite is characterized by very high cubic magnetocrystalline anisotropy and saturation magnetization: $M_s(5 \text{ K}) = 93.9$ emu/g and $M_s(300 \text{ K}) = 80.8$ emu/g. The room-temperature critical domain size of CoFe_2O_4 is about 70 nm, while the critical superparamagnetic single-domain grain size is about 10 nm [3, 4]. Theoretical limits of the coercive field (H_c) and reduced remanent magnetization M_r/M_s for a system of randomly oriented spherical cobalt ferrite particles are as follows: $H_c(5 \text{ K}) = 25.2$ kOe, $H_c(300 \text{ K}) = 5.3$ kOe, and $M_r/M_s = 0.83$ [5].

Experimental values of the coercive field and reduced remanent magnetization depend on the particle size [1]. The maximum room-temperature coercive fields ($H_c = 1.7$ – 2.1 kOe) were observed for cobalt ferrite particles with average sizes within 30–50 nm, for which $M_r/M_s = 0.35$ [1]. A decrease in the average particle size below 30–50 nm leads to a decrease in H_c as a result of the transition to a superparamagnetic state [6, 7]. Particles of greater size exhibit lower coercivity as a result of the transition to a multidomain state.

An analysis of the available published data also indicates that the magnetic properties of cobalt ferrite particles depend on the methods of preparing samples [1, 6]. One possible reason for this dependence is the different content of single-domain particles in the syn-

thesized powders. In particular, single-domain particles are frequently obtained using various substrates and matrices with inhomogeneities of preset dimensions, which serve as nuclei for the growth of desired particles. In the present study, we used mesoporous silicon dioxide (MSM-41) as a matrix for the synthesis of cobalt ferrite nanoparticles. This powdered material consists of particles, in which pores are ordered in a hexagonal honeycomb-type structure with 0.6- to 0.8-nm-thick walls and calibrated channel diameter that can be controlled in a range of 3–10 nm.

This Letter presents the results of an investigation of the magnetic properties of cobalt ferrite nanoparticles obtained by the extraction–pyrolysis method in a mesoporous silicon dioxide (MSM-41) molecular sieve matrix.

The nanoparticles of cobalt ferrite have been synthesized using a solution technology, which ensures the formation of numerous crystallization centers and provides soft conditions for the synthesis of desired compounds and phases. The process was carried out using organic solutions of metal carboxylates, which offer an additional advantage of self-organization leading to the formation of homogeneous particles. The powders and films of cobalt ferrite were obtained using organic extracts of iron and cobalt as precursors, which were preliminarily prepared by extracting metals from inorganic solutions of iron and cobalt chlorides of various purities into an organic extractant phase representing a mixture of carboxylic acids. This

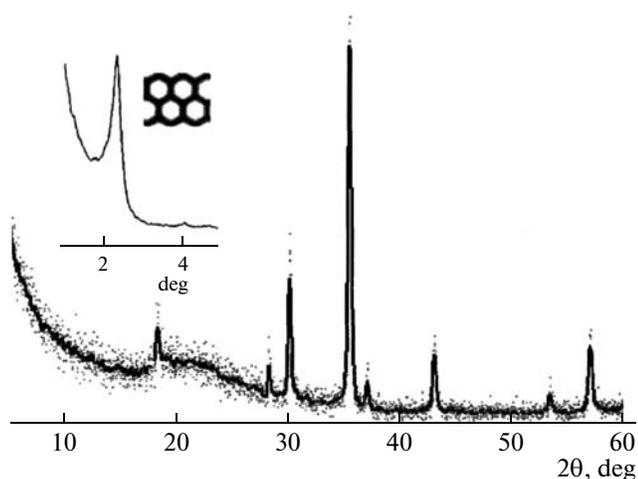


Fig. 1. Typical powder X-ray diffractogram of CoFe_2O_4 cobalt ferrite particles synthesized using the MSM-41 molecular sieve matrix. The inset shows a diffraction peak in the region of small angles, which shows that the hexagonal mesostructure of MSM-41 is retained during the synthesis.

was accompanied by the purification of components from impurities and the formation of stock solutions of organic metal salts with preset concentrations, which could be stored and used for a long time.

A mixture of the organic extracts of iron and cobalt with a preset stoichiometry was used to impregnate the MSM-41 molecular sieve powder. The optimum time of impregnating the molecular sieve with a metal extract solution was 10 min. The subsequent pyrolysis at 400°C led to removal of the organic component and to the formation of a CoFe_2O_4 mixed oxide without destruction of the molecular sieve framework. The impregnation and pyrolysis stages were repeated several times, which led to an increase in the total content of cobalt ferrite powder up to 28%. In order to obtain pure cobalt ferrite powder, the MSM-41 molecular sieve matrix can be readily dissolved in an alkaline solution (4 M NaOH) with subsequent neutralization by 1 M HCl solution and washing with distilled water.

The structure of obtained powders was studied by X-ray diffraction (XRD) measurements on a DRON-4 diffractometer using $\text{CuK}\alpha$ radiation. The magnetization curves were measured on a vibrating-sample magnetometer with a superconducting coil. These measurements were performed using magnetic fields up to 60 kOe in a 4.2–300 K temperature range.

Figure 1 presents the XRD pattern of the synthesized powder, in which all peaks correspond to the reflections of CoFe_2O_4 cobalt ferrite with a spinel structure. The inset in Fig. 1 shows the characteristic diffraction peak in the region of small angles, which shows evidence for the retained hexagonal mesostructure of MSM-41. The coherent scattering domain size (evaluated from the diffraction peak width) amounts to 40 nm. This value is significantly greater than the

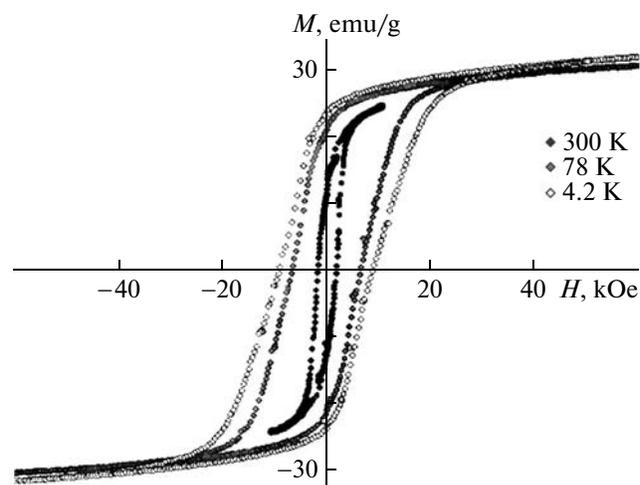


Fig. 2. Magnetization curves measured at 4.2, 78, and 300 K for a CoFe_2O_4 cobalt ferrite powder synthesized using the MSM-41 molecular sieve matrix.

inner diameter of pores in the MSM-41 matrix, which implies that the particles of cobalt ferrite are situated outside the pores.

Figure 2 presents the magnetization curves of a cobalt ferrite powder measured at 4.2, 78, and 300 K, which were used to determine the saturation magnetization M_s (see table) by assuming that the magnetization approaches the saturation level as described by relation (1) (see below). Using these values and taking into account that the saturation magnetization of pure CoFe_2O_4 is $M_s(5\text{ K}) = 93.9$ emu/g, the mass fraction of cobalt ferrite in the synthesized powder can be estimated at 34%.

The observed hysteresis loops exhibit a rather rectangular shape as characterized by the M_r/M_s ratio (see table). It should be emphasized that this shape was obtained for a macroscopically isotropic cobalt ferrite powder. While the values of M_s slightly decrease in the 4.2–300 K range, the reduced remanent magnetization (M_r/M_s) and the coercive field (H_c) exhibit quite significant changes with the temperature. The local magnetic anisotropy field (i.e., the magnetic anisotropy field of an individual particle) H_a was also calculated using experimental curves of the magnetization

Parameters of the magnetization curves of cobalt ferrite particles synthesized in the MSM-41 molecular sieve matrix

| T , K | M_s , emu/g | M_r/M_s | H_c , kOe | H_a , kOe |
|---------|---------------|-----------|-------------|-------------|
| 4.2 | 31.9 | 0.83 | 9.0 | 32 |
| 78 | 30.5 | 0.75 | 6.7 | 30 |
| 300 | 25.6 | 0.49 | 1.8 | 16 |

approach to the saturation level, which could be well described by the following approximate expression:

$$M(H) = M_s \left[1 - \frac{2}{105} \left(\frac{H_a}{H} \right)^2 \right] + \chi H. \quad (1)$$

Here, the first term describes the magnetization approaching saturation in a system of randomly oriented particles with a cubic anisotropy, which is determined by the Akulov–Kirensky law [8]. The second term corresponds to a linear response that can be related both to the susceptibility of a ferromagnet in the region of high fields and to the contribution of superparamagnetic particles to the total magnetic response. The values of H_a determined from this description of the magnetization approach to saturation are given in the table.

It should be noted that the room-temperature coercive field in the obtained powders was close to the maximum H_c values reported in the literature, while the remanent magnetization even exceeds the analogous values reported for cobalt ferrite powders. We believe that the high M_r/M_s values in our samples are related to the use of the MSM-42 molecular sieve (ordered on a mesoscopic level) as a matrix for the deposition and, hence, to a monodisperse character of the synthesized nanopowder. Indeed, the obtained H_c values are typical of cobalt ferrite particles in a single-domain state with dimensions of 30–50 nm [1], which agree with the estimates of particle size from the XRD data. The local room-temperature magnetic anisotropy field H_a satisfactorily agrees with the magnetocrystalline anisotropy of single-crystalline cobalt ferrite [4], while the H_a values at 78 and 4.2 K well agree with the recent data of Ranvah et al. [2].

According to the Stoner–Wohlfarth model, the coercive field H_c in a system of randomly oriented single-domain particles with a cubic magnetic anisotropy is related to the anisotropy field of a particle as $H_c \approx 0.32H_a$ and the reduced remanent magnetization is $M_r/M_s = 0.83$ [9]. The experimental value of H_c (4.2 K) presented in the table is close to the estimate based on the Stoner–Wohlfarth model ($32 \text{ kOe} \times 0.32 =$

10.2 kOe), while the value of remanent magnetization at 4.2 K exactly coincides with that predicted by the model. However, the model estimates of H_c and M_r/M_s significantly exceed the experimental values. This decrease in the magnetic parameters of cobalt ferrite powders at 78 and 300 K can be related to the influence of thermal fluctuations of the magnetization of individual particles (see, e.g., [10]).

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