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High coercivity induced by mechanical milling in cobalt ferrite powders

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ABSTRACT

In this work we report a study of the magnetic behavior of ferrimagnetic oxide $CoFe_2O_4$ treated by mechanical milling with different grinding balls. The cobalt ferrite nanoparticles were prepared using a simple hydrothermal method and annealed at 500 °C. The non-milled sample presented coercivity of about 1.9 kOe, saturation magnetization of 69.5 emu/g, and a remanence ratio of 0.42. After milling, two samples attained coercivity of 4.2 and 4.1 kOe, and saturation magnetization of 67.0 and 71.4 emu/g respectively. The remanence ratio M_R/M_S for these samples increase to 0.49 and 0.51, respectively. To investigate the influence of the microstructure on the magnetic behavior of these samples, we used X-ray powder diffraction (XPD), transmission electron microscopy, and vibrating sample magnetometry. The XPD analysis by the Williamson–Hall plot was used to estimate the average crystallite size and strain induced by mechanical milling in the samples.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a promising compound with potential biomedical applications [1,2], as well as use in high density magnetic storage [3], permanent magnets [4], and electronic devices. This is due to several properties, such as electrical insulation, chemical stability, high magnetic-elastic effect [5], moderate saturation magnetization, and high coercivity (H_C).

Particularly in permanent magnet applications, high H_C is a fundamental characteristic mainly because H_C is an important parameter to the maximum energy product $(BH)_{max}$, the figure of merit for permanent magnets. Many authors report tuning the H_C through thermal annealing [6], capping [7] and mechanical milling treatment [8] of the grains. Limaye et al. [7] obtained cobalt ferrite nanoparticles with very high coercivity (9.5 kOe) by capping it with oleic acid; however, the saturation magnetization decreased to 7.1 emu/g – that is, about 10 times less than that obtained from uncapped nanoparticles. This small value of saturation magnetization (M_S) is an undesirable property in hard magnetic applications. In another interesting article, Liu et al. [9] increased the H_C of cobalt ferrite, from 1.23 to 5.1 kOe, with a relatively small decrease in M_S. They used a brief (1.5 h) mechanical milling process on relatively large particles (average grain size of 240 nm). However, for nanoparticles with an average grain size of 12 nm, no improvement in magnetic parameters was obtained.

Application of mechanical milling to nanoparticles (diameter < 100 nm) seeking to increase H_C has not yet been successful. However, few important phenomena happen only at the nanoscale. Exchange spring (exchange coupled) is an example. High H_C cobalt ferrite make possible an expressive increase in the $(BH)_{max}$ in exchange coupled nanocomposite $CoFe_2O_4/CoFe_2$ [10,11]. The importance of studying the magnetic behavior of this nanocomposite, aiming to improve its magnetic properties, is what led to this work.

In order to increase the H_C of cobalt ferrite nanoparticles, we processed them with thermal annealing at moderate temperature (500 °C) and brief mechanical milling. Using a shake miller and several different milling parameters, we increased the H_C of all treated samples. The result of this processing was an increase of about 150% in coercivity. Also, the M_R/M_S ratio improved from 0.42 to 0.49 and 0.51 for the two best samples, and the $(BH)_{max}$ was amplified almost 100%. This substantial enhancement in magnetic parameters justifies the publication of this study. Samples were analyzed by X-ray powder diffraction (XPD), transmission electron microscopy (TEM), and magnetic hysteresis curves, all at room temperature.

2. Experimental procedure

The cobalt ferrite nanoparticles were synthesized using a simple hydrothermal method described in a previous work [10]. The morphology and particle size distribution of the samples were examined by direct observation via transmission electron microscopy (TEM) using JEOL-2100 apparatus installed at LNNano/

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Table 1
Details of mechanical milling process.

Sample	Ball material (mass density) (g/cm^3)	Ball diameter (mm)	Proportion ball/sample	Milling time (h)
CF1	Stainless steel 7.8	6.5	1:4	1.5
CF2	Zirconia 6.1	6.0 and 1.2–1.4[a]	1:7:3	1.5
CF3	Zirconia 6.1	6.0	1:7	1.5
CF4	Tungsten carbide 15	5.0	1:9	1.5

[a] The sample CF2 was milled by balls of both indicated sizes.

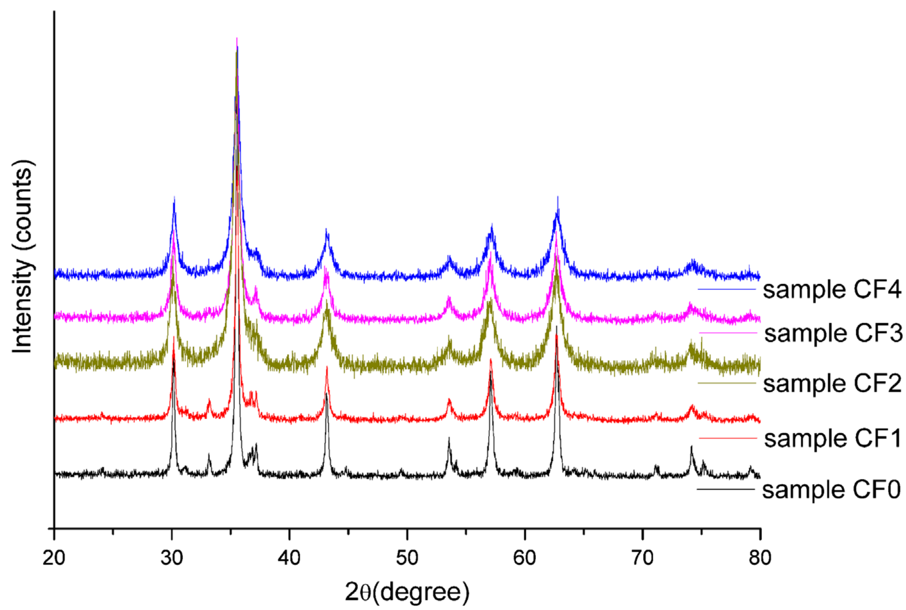

Fig. 1. XPD patterns of Co ferrite.

LNLS–Campinas–Brazil, working at 200 kV, was used for this purpose.

The pristine sample (with neither thermal nor mechanical milling treatments) was annealed at 500 °C for 6 h and separated into 5 amounts called CF0, CF1, CF2, CF3 and CF4. The sample CF0 was not milled while the other samples were milled for 1.5 h using different milling parameters. The milling process used was the high-energy mechanical ball milling in a Spex 8000 miller. Details of the different milling processes for each sample are described in Table 1.

The crystalline phases of the cobalt ferrite nanoparticles were identified by X-ray powder diffraction (XPD) patterns, obtained on a Shimadzu XRD-6000 diffractometer installed at the "*Laboratório Multiusuário de Técnicas Analíticas*" (LAMUTA/ UFMT–Cuiabá-MT–Brazil). It was equipped with graphite monochromator and conventional Cu tube (0.154178 nm), and working at 1.2 kW (40 kV, 30 mA), using the Bragg-Brentano geometry.

Magnetic measurements were carried out using a vibrating sample magnetometer (VSM) model VersaLab Quantum Design, installed at CBPF, Rio de Janeiro-RJ—Brazil. Experiments were done at room temperature and using magnetic field up to 2.5*T*.

3. Results and discussion

The XPD patterns obtained from samples CF0, CF1, CF2, CF3 and CF4 (see Fig. 1) confirming that all samples are $CoFe_2O_4$ with the expected inverse spinel structure. These measurements indicate the absence of any other phases or contamination before and after milling processing.

TEM images of the pristine cobalt ferrite nanoparticles revelead an extremely polydisperse system with several forms (see Fig. 2a). The particle size distribution indicates that cobalt ferrite particles have a mean diameter of 22.6 nm; hovewer TEM images also revealed the presence of particles larger than 100 nm. TEM measurements also indicate that nanoparticles increased after thermal treatment, changing the mean diameter to 44.7 nm. As occurred for the pristine sample, some big particles were observed to sample CF0 (Fig. 2b). These results indicate that, despite the relatively low annealing temperature, there was coalescence of nanoparticles causing the increase of mean size.

For samples CF3 and CF4 the TEM images revealed similar particles with shear bands (see the Fig. 3a and b). We observed both regular and irregular shear bands in good agreement with the microstructural evolution described by Liu et al. [9]. These observations suggest that the shear bands are moiré fringes (see Fig. 3c).

To evaluate the influence of mechanical milling on the magnetic behavior of our samples, we measured the magnetic hysteresis loop. These measurements are shown in Fig. 4. Three interesting characteristics can be noted from the hysteresis loops obtained from milled samples: the increase in H_C, the changes in M_S, and the increase of M_R to all milled samples. These characteristics are discussed in detail below.

Samples CF3 and CF4 presented the highest H_C values found in this work, 4.1 and 4.2 kOe, respectively. This enhancement in H_C,