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Structure and magnetic properties of nanostructured Ni-ferrite

A.S. Albuquerque[a,*], J.D. Ardisson[a], W.A.A. Macedo[a], J.L. López[b], R. Paniago[b], A.I.C. Persiano[b]

[a]Centro de Desenvolvimento da Tecnologia Nuclear, CP 941, 30123-970, Belo Horizonte, Brazil

[b]Departamento de Física, Universidade Federal de Minas Gerais, 30123-970, Belo Horizonte, Brazil

Abstract

The structural and magnetic properties of $NiFe_2O_4$ ultrafine powders synthesized by coprecipitation, a nonconventional method of preparation, were investigated. The samples were obtained by annealing at relatively low temperatures (300–600°C) and characterized by X-ray diffraction, Mössbauer spectroscopy, and vibrating sample magnetometry. The average particle diameter ranges from 4 to 15 nm, as determined by X-ray diffraction. All nanometric powder samples presented strong superparamagnetic relaxation at room temperature and reduced magnetic hyperfine fields at -193°C. Magnetometry measurements indicated different magnetic behavior related with crystallinity of samples, coercivity as high as 168 Oe at 27°C, value that is nearly two times higher than coercivity of bulk Ni-ferrite. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrites spinel; Nanoparticles; Mössbauer spectroscopy; Magnetic measurements

Nickel ferrite, $NiFe_2O_4$, is an inverse spinel in which the tetrahedral sites (*A*) are occupied by Fe^{2+} ions and the octahedral sites (*B*) by Fe^{2+} and Ni^{2+} ions [1]. This material is largely used in electric and electronic devices and in catalysis. In order to improve sinterability and magnetic properties, the investigation of alternative, nonconventional methods to obtain Ni-ferrite and other ferrites in the form of nanostructured powders is a current subject [2,3].

In this work, we investigated the synthesis of the nanostructured $NiFe_2O_4$ powders by coprecipitation, followed of annealing at relatively low temperatures (300–600°C) and determined the structural and magnetic properties of the obtained samples by X-ray diffraction, ^{57}Fe Mössbauer spectroscopy, and vibrating sample magnetometry. Ni-ferrite powder was synthesized by dissolving Fe and Ni nitrates in deionized water in the required mole proportion. After 1 h stirring, the precipitating agent NaOH (2.5 M) was added to the solution and the resultant precipitate was washed with deionized water and ethanol. Ultrathin powder was obtained after drying at 70°C for 20 h. Samples with different average particle size were prepared by annealing the precipitate at temperatures between 300°C and 600°C, for 2 h, under ordinary atmosphere. A well-crystallized reference sample was prepared by heat treatment at 1100°C. The precipitation of Ni-ferrite occurred according to the following reaction:

$$1Ni(NO_3)_2 \cdot 6H_2O + 2Fe(NO_3)_3 \cdot 9H_2O + 8NaOH \rightarrow 1NiFe_2O_4 + 8Na(NO_3) + 28H_2O \quad (1)$$

Fig. 1 illustrates the evolution of crystallinity of the stoichiometric Ni-ferrite with increasing annealing temperature, as determined by X-ray diffraction. The powders present average particle diameter of 4, 5, 6, 8 and 15 (2) nm for samples as-obtained and annealed at 300, 400, 500 and 600°C, respectively, as estimated by using Scherrer's equation.

Fig. 2 shows Mössbauer spectra of the different samples, together with the reference one, measured at room temperature and at -193°C. The spectrum of the reference sample, obtained at room temperature, was fitted to two magnetic sextets referring to the A and B sites, with

* Corresponding author. Fax: +55-31-499-3390.

E-mail address: asa@urano.cdtn.br (A.S. Albuquerque).

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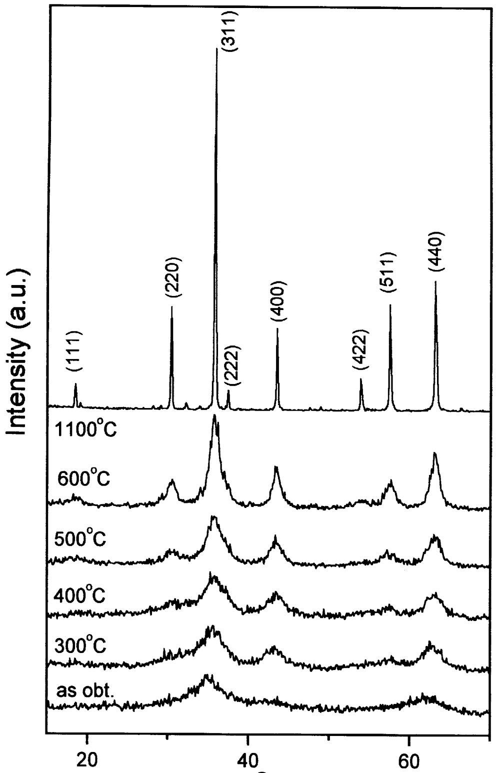

Fig. 1. X-ray diffraction patterns of Ni-ferrite samples annealed at different temperatures.

magnetic hyperfine fields $B_{HF}(A) = 49.2$ (5) T and $B_{HF}(B) = 52.9$ (5) T, values that are comparable with those reported by De Marco et al. [4] for solid-state reacted Ni-ferrite. All nanometric samples presented a strong superparamagnetic relaxation at room temperature. As can be observed, at -193°C all the powders annealed at temperatures higher than 400°C are characterized by resolved ferrimagnetic sextets, although with reduced magnetic hyperfine fields. As determined by Mössbauer measurements, the as-obtained sample showed the magnetic transition between -248°C and -238°C, while bulk Ni-ferrite are characterized by a transition temperature of 585°C [5].

Vibrating sample magnetometry indicated the different magnetic behavior related to the crystallinity of the material. The nanometric samples presented magnetization, under 10 kOe, 5–24 emu/g at 27°C, and from 16 to 28 emu/g at -268.8°C, as the average particle diameter increases from 4 to 15 nm. The maximum coercivity at 27°C was observed for the material annealed at 400°C (168 Oe), while at -268.8°C it was observed for the powder annealed at 300°C (945 Oe), indicating that this material presents critical magnetic behavior for average particle diameter near 5 nm. Plots of magnetization (M) as a function of applied magnetic field per temperature (H/T) are shown in Fig. 3 for the samples heat treated at 300°C and 400°C. The superposition of the M versus H/T curves obtained at 27°C and at -193°C is a clear evidence of superparamagnetic behavior of the first sample [5,6]. On the other hand, for annealing at 400°C or

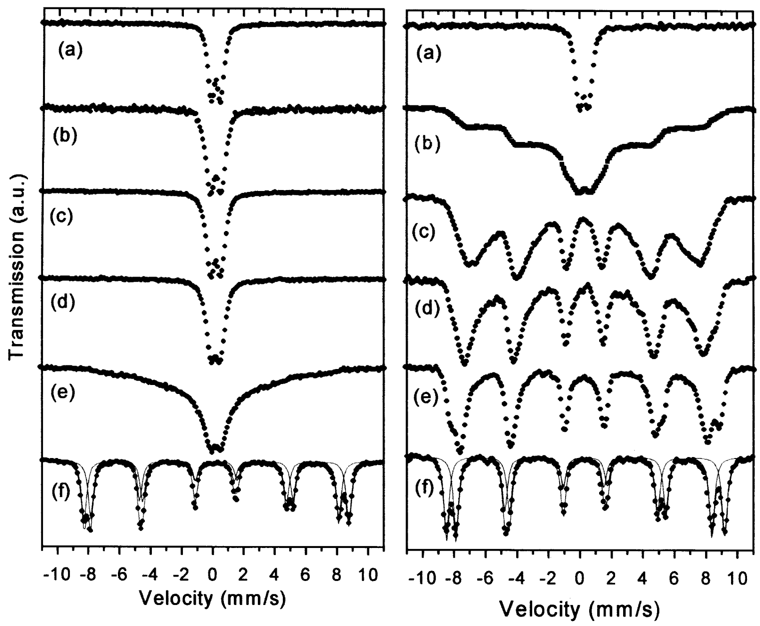

Fig. 2. Mössbauer spectra of the Ni-ferrite samples, at room temperature (left) and at -193°C (right), (a) as obtained and annealed at (b) 300°C, (c) 400°C, (d) 500°C, (e) 600°C and (f) 1100°C.

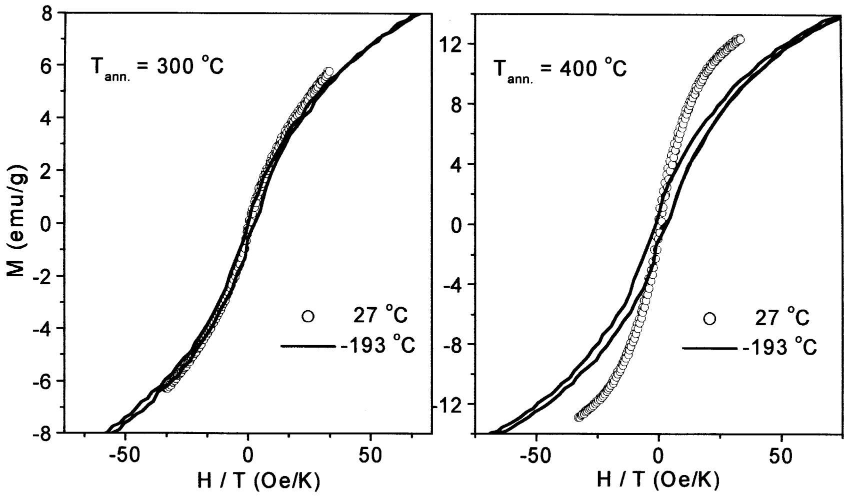

Fig. 3. Magnetization as a function of H/T for Ni-ferrite samples annealed at 300°C and 400°C, and measured at 27°C and -193°C.

higher temperatures, these curves are not superposed due to the decrease of superparamagnetic relaxation of larger particles.

In summary, ultrafine powders of Ni-ferrite with particle diameter ranging from 4 to 15 nm were successfully synthesized by coprecipitation followed by annealing at temperatures between 300°C and 600°C. The results of Mössbauer spectroscopy and vibrating sample magnetometry at 27°C and -193°C indicated that the obtained Ni-ferrite nanoparticles exhibit superparamagnetic relaxation and coercivity as high as 168 Oe, that is nearly two times the coercivity of bulk Ni-ferrite.

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