Synthesis of magnetite nanoparticles by high energy ball milling

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ABSTRACT

We report on the preparation of magnetite nanoparticles, with size ranging from 12 nm to 20 nm, by high energy ball milling. The synthesis is made using stoichiometric amounts of distilled water and metallic iron powder. The milled powder samples were analyzed by Mossbauer spectroscopy (MS), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). Our results indicate that the milling time is a key parameter of the synthesis. By increasing the milling time one achieves high purity magnetite samples. Also, the particle size decreases with the milling time. The sample milled during 10 h contained a fraction of 56 nm metallic Fe particles and 20 nm magnetite particles. By increasing the milling time to 96 h we have obtained a sample that is mainly composed of 12 nm magnetite particles. MS performed at room temperature showed a spectrum consisting of two sextets with hyperfine parameters related to iron ions occupying octahedral (A) and tetrahedral (B) sites. We have used a self-consistent method to investigate the impact of the dipolar interaction to drive the system to a magnetically blocked regime.

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1. Introduction

Mechanical milling, is one of the widely used techniques to produce nanoparticles [1,2]. It is feasible for large-scale nanoparticle production. Yet it is a simple and low cost technique. It is a complex process and requires optimization of a few parameters to obtain the required phase, absence of residues and control of particle size. These features are relevant for current biomedical applications of magnetic nanoparticles, most of which requires biocompatible magnetic nanoparticle ferrofluid with small particle size.

Mutlu et al. [3] recently reported the synthesis of magnetite using a planetary ball milling, they used a molar ratio between Fe and water of 0.147, this value is almost twice the expected value of 0.75 for preparing stoichiometric magnetite. Their samples had the crystallite size increasing from 23.5 nm to 33 nm when the milling time increased from 6 to 48 h.

In this work we report on the preparation of superparamagnetic magnetite nanoparticles, with size ranging from 12 nm to 20 nm, by high energy ball milling. The particles were made using stoichiometric amounts of distilled water and metallic iron powder. The pristine iron and the milled samples were analyzed by Mössbauer spectroscopy (ME), X-ray diffraction (XRD) and vibrating sample magnetometry (VSM). Our results indicate that by proper choice of the milling time one may control the nanoparticle size as well as the composition of the powder.

2. Experimental

The samples were prepared in normal atmosphere using a milling planetary (Fritsch Pulverisette 7 – Premium line) with angular velocity of 300 rpm. XRD measurements were performed with Cu Kα radiation in a Rigaku-Miniflex II diffractometer. VSM magnetic measurements were done at 300 K in a home-made magnetometer. ^{57}Fe Mössbauer spectra were recorded at room temperature using a spectrometer from Wiessel with a ^{57}Co:Rh source and activity of 25 mCi.

The starting material to prepare the magnetite particles was iron powder (99.9% purity) from Sigma–Aldrich. The samples were prepared by ball milling in a hardened steel vial. The ball to powder mass ratio was of 20:1 and the rotation speed of 200 rpm. The powder was milled for period up to 96 h. Small amounts of milled powder were taken at intervals of 10 h, 40 h, 60 h and 96 h to characterize the samples. These samples are called as Fe10h, Fe40h, Fe60h and Fe96h.

The chemical reaction between water and Fe powder follows the reaction equation: $3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$. Accordingly, we have used 1.4156 g and 0.6089 g of Fe and water, respectively. The Fe and water masses gave the number of moles of 0.02532 and 0.03383, respectively, with a ratio of 0.748 very close to the expected value of 3/4.

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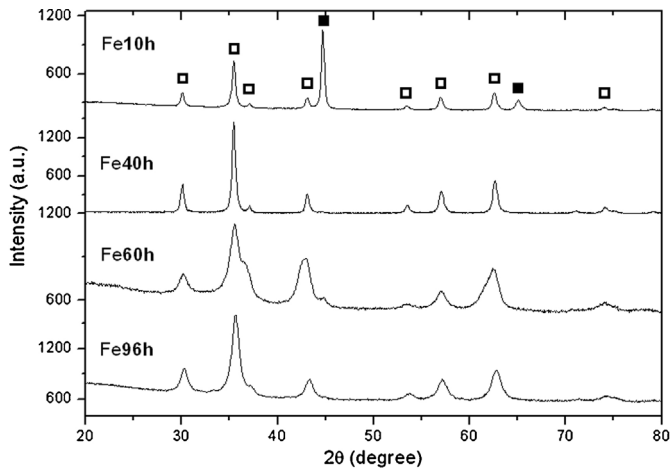E-mail address: marco.moralestorres@gmail.com (M.A. Morales).

Fig. 1. XRD patterns for the Fe milled powder. Filled and empty squares in the Fe10h sample indicate the α-Fe and magnetite diffraction peaks, respectively.

Table 1
Lattice parameters and relatives intensities of the different phases found in the XRD analysis.

Sample	wt%		Cell parameter (Å)		Size (nm)	
	Fe	Fe$_3$O$_4$	Fe	Fe$_3$O$_4$	Fe	Fe$_3$O$_4$
Fe10h	28	72	2.866	8.398	56	20
Fe40h	–	100		8.401		20
Fe60h	–	100		8.366		15
Fe96h	–	100		8.351		12

3. Results and discussion

In the XRD analysis, we have found that by increasing the milling time one achieves high purity magnetite samples as well as reduced particle size (Fig. 1). Sample Fe10h contains a fraction of 55% of 56 nm α-Fe particles and 45% of 20 nm size magnetite particles. By increasing the milling time up to 96 h we have obtained samples made of mainly magnetite with 12 nm of crystallite size.

Figs. 1 and 2 show the evolution of XRD patterns for all the samples and their crystal parameters, respectively. From the fits it is clear that the size of the iron oxide particle decreases with the milling time, reaching the minimum value of 12 nm for the sample Fe96h. The α-Fe nanoparticles found in the Fe10h had 56 nm of particle size and the amount of this component becomes smaller for the sample Fe40h. These results are opposed to the ones showed in reference [3] for magnetite prepared with ball to sample ratio of 36:1, in that work the magnetite particle size increases up to 33 nm for milling times up to 48 h. In the present work, the samples Fe10h and Fe40h showed magnetite nanoparticles with approximately the same particle size, and with lattice parameters ranging from 8.398 to 8.401 Å, these values are very close to the reported for pure magnetite [4]. The samples milled longer than 40 h showed a steady decrease in particle size and lattice parameter. For the sample Fe96h the lattice parameter was of 8.351 Å, this small value may be due to the
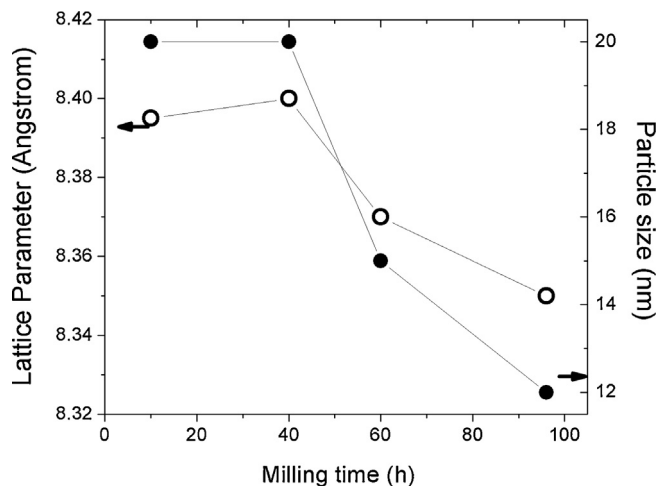
partial oxidation of Fe^{2+} in the magnetite structure, this sample can be consider as non stoichiometric magnetite. The degree of oxidation can be calculated assuming a general chemical form for magnetite: $Fe_{3-\delta}O_4$, where the molar ratio between Fe^{2+} and Fe^{3+} is given by $x = Fe^{2+}/Fe^{3+} = (1-3\delta)/(2+2\delta)$, for pure magnetite $\delta = 0$ (which means $x = 0.5$) and when magnetite is completely oxidized: $\delta = 1/3$. When $x = 0$ the mineral transforms to maghemite (γ-Fe$_2$O$_3$). Gorski et al. [5] found in magnetite samples with varying stoichiometries a linear relationship between the lattice parameter and the relative concentration of Fe^{2+}/Fe^{3+}. The authors proved that the lattice parameter is useful to discuss the stoichiometry of magnetite. Following this result, we have determined the stoichiometry of sample Fe96h, and it is given by $Fe_{2.73}O_4$, this finding is related to a value of $x = Fe^{2+}/Fe^{3+} = 0.083$. Table 1 shows the calculated lattice parameters and the relative intensities of the several phases present in the samples.

The Mössbauer spectra for the samples are shown in Fig. 3. The spectra for all the samples showed a sextet with hyperfine parameters typical of the α-Fe phase. Table 2 shows the hyperfine parameters found in the analysis. Magnetite has the cubic spinel structure and besides oxygen its structure is composed by Fe^{3+} and Fe^{2+} ions. The ferric ions are distributed equally between the tetrahedral (Tetra) and octahedral (Octa) crystal sites, and the number of ferrous and ferric ions are equal in the Octa sites. For stoichiometric magnetite is expected a molar ratio of $[Fe^{3+}+Fe^{2+}](Octa)/[Fe^{3+}](Tetra)$ equal to 2.0. Above the Verwey transition ($T_V = 120$ K), a very fast electron exchange occurs between the octahedral ferrous and ferric ions. Since the exchange time is smaller than the ME measuring time, the spectrum for this site was related to the $Fe^{2.5+}$ ion [4]. For sample Fe10h, the ratio of the RAA between Fe octahedral and Fe tetrahedral is equal to 2.0 and this value decreases for samples Fe60h and Fe96h. This finding is in agreement with the XRD results which show smaller lattice parameters for these samples, this result is attributed to oxidation of some of the divalent iron ions. The samples Fe10h and Fe40h
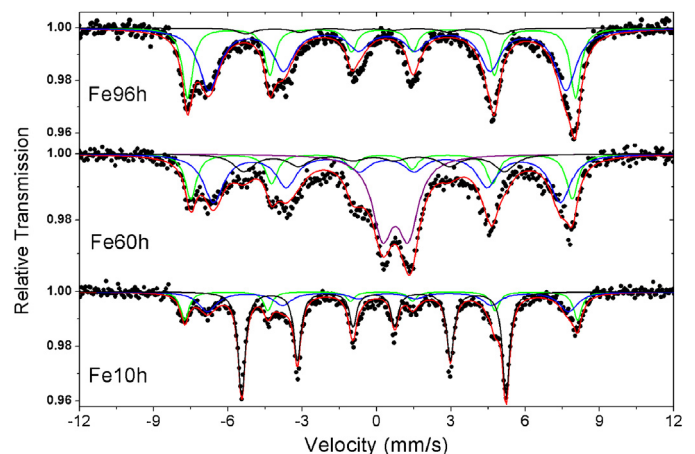

Fig. 2. Lattice parameters and crystallite size as a function of milling time.

Fig. 3. Mössbauer spectra for some of the milled samples.