Synthesis of magnetite nanoparticles by high energy ball milling

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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 Mössbauer 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. 57Fe Mössbauer spectra were recorded at room temperature using a spectrometer with a 57Co: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 + 4H2O → Fe3O4 + 4H2. 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.
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$_{3-x}$O$_4$, where the molar ratio between Fe$^{2+}$ and Fe$^{3+}$ is given by $x = \text{Fe}^{2+}/\text{Fe}^{3+} = (1 - 3\delta)/(2 + 2\delta)$, 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 $x = \text{Fe}^{2+}/\text{Fe}^{3+} = 0.083$. 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$^{2+}$ and Fe$^{3+}$ 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. 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.](image1)

![Fig. 2. Lattice parameters and crystallite size as a function of milling time.](image2)

![Fig. 3. Mössbauer spectra for some of the milled samples.](image3)

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt%</th>
<th>Cell parameter (Å)</th>
<th>Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe10h</td>
<td>28</td>
<td>2.866</td>
<td>56</td>
</tr>
<tr>
<td>Fe40h</td>
<td>100</td>
<td>8.401</td>
<td>20</td>
</tr>
<tr>
<td>Fe60h</td>
<td>100</td>
<td>8.366</td>
<td>15</td>
</tr>
<tr>
<td>Fe96h</td>
<td>100</td>
<td>8.351</td>
<td>12</td>
</tr>
</tbody>
</table>
have a magnetite component with lattice parameters very close to stoichiometric magnetite.

The spectrum of the sample Fe10h showed 55% and 45% of RAA of α-Fe and magnetite particles, respectively. The spectrum of sample Fe60h contains 14% and 57% of RAA of α-Fe and magnetite particles, respectively. The remaining RAA of 29% is related to a Fe\(^{2+}\) paramagnetic component. The spectrum of sample Fe96h showed blocked magnetite nanoparticles with RAA of 95% and a very small absorption due to α-Fe. The Fe\(^{2+}\) paramagnetic component in sample Fe60h, may be related to oxidation of Fe atoms located on the surface of very fine α-Fe particles. Although the α-Fe is present in all the Mössbauer spectra somehow it only appears in the XRD pattern of sample Fe10h. The reason for that may be their smaller particle size as compared with the magnetite nanoparticles. Furthermore the α-Fe and magnetite relative abundances for sample Fe10h show an opposite trend in the MS and XRD analysis, as noted in Tables 1 and 2. That may be due to the different values of the atomic scattering factors, multiplicity, and to the different values of the Lamb-Mössbauer factors for these phases at room temperature.

The hysteresis curves are shown in Fig. 4. The hysteresis of sample Fe96h shows magnetization values very close to the bulk values [4]. The large magnetization value found in the sample Fe10h is related to the presence of α-Fe. The coercive fields were of 11 mT and 22 mT for samples Fe10h and Fe96h, respectively. Although the sample Fe96h has a particle size of 12 nm as determined by the X-ray diffractogram, we have found that this sample has a broad distribution of particle diameters, extending from around 4 nm up to 20 nm.

One key feature of the hysteresis curves shown in Fig. 4 is the existence of coercivity. We have chosen the sample Fe96h for the discussion of this point. As shown in Fig. 4 for an applied field of 1 T the magnetization is larger than that of bulk magnetite (92 emu/g) at room temperature. We have attributed this to the contribution of α-Fe particles. We have assumed a 14% fraction of the sample mass consists of superparamagnetic 5 nm α-Fe particles. In Fig. 5(c) we show the measured hysteresis and the magnetization of superparamagnetic α-Fe 5 nm diameter particles, calculated using a Langevin function and a saturation magnetization of 217 emu/g. As shown in Fig. 5(c), at an applied field of 1 T the magnetization of 14% α-Fe particles amounts to nearly 30 emu/g. Thus the magnetite contribution for an applied field of 1 Tesla, as shown in Fig. 5(a), turns out to be around 73 emu/g.

As shown in the inset in Fig. 5(b), sample Fe96h consists of magnetite particles with a broad distribution of diameters, extending from 4 nm up to 20 nm. The peak in the distribution function \(f(d)\) occurs for \(d = 6.8 \text{ nm}\) and the average diameter of the magnetite particles is 7.7 nm. Notice from the percentual cumulative distribution function, shown in the inset in Fig. 5(b), that 99.8% of the particles have diameter smaller than 18 nm. Therefore, except for a negligible fraction of the nanoparticles, they should all be superparamagnetic, with no coercivity.

The origin of coercivity is the dipolar interaction between the particles assembled together in the VSM sample holder. The basic phenomenology is based on the fact that each superparamagnetic particle produces its own dipolar field. Therefore each one of the particles is under the action of the applied field and the effective dipolar field produced by all the other particles. The effective dipolar field, for a given value of the applied field, depends on the relative position of the particles in the VSM sample holder. Furthermore, for a given particle, it also depends on the diameters of the particles distributed in the first, second, third shells of particles around it. We adopted a simplifying assumption. We represent this dipolar field effect by an effective dipolar field proportional to the dipolar field produced by a magnetite particle with diameter equal to the mean diameter of the system of particles.

We use a self-consistent method to investigate the impact of the dipolar interaction in the hysteresis. The thermal average value of the magnetization is given by \(M = \int \mu(z) f(z) \, dz\), where \(f(z)\) is the number of particles with diameter \(z\) per unit mass. The thermal average value of the magnetic moment of a particle with diameter \(z\) is \(\mu(z) = \mu(0) M(z) / |z|\), where \(\mu(0)\) is the Langevin function, \(k\) is the Boltzmann constant and \(M(z)\) is the saturation value of the magnetic moment. The effective field includes the applied field and an effective dipolar field \(H_{\text{eff}} = H + H_d\), where the dipolar field \(H_d\) is determined self-consistently.

We assumed that the dipolar field acting on a given nanoparticle is proportional to the thermal average dipolar field produced

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### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>RAA (%)</th>
<th>IS (mm/s)</th>
<th>Δε (mm/s)</th>
<th>Bhf (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe10h</td>
<td>Fe(^{3+}) (Tetra)</td>
<td>15</td>
<td>0.28</td>
<td>−0.015</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Fe(^{3+}) Fe(^{2+}) (Octa)</td>
<td>30</td>
<td>0.54</td>
<td>0.04</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>α-Fe blocked</td>
<td>50</td>
<td>0.01</td>
<td>−</td>
<td>33</td>
</tr>
<tr>
<td>Fe60h</td>
<td>Fe(^{3+}) (Tetra)</td>
<td>20</td>
<td>0.29</td>
<td>−0.019</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Fe(^{3+}) Fe(^{2+}) (Octa)</td>
<td>37</td>
<td>0.52</td>
<td>0.01</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>α-Fe paramag.</td>
<td>29</td>
<td>0.75</td>
<td>1.03</td>
<td>−</td>
</tr>
<tr>
<td></td>
<td>α-Fe blocked</td>
<td>14</td>
<td>−0.01</td>
<td>−</td>
<td>33</td>
</tr>
<tr>
<td>Fe96h</td>
<td>Fe(^{3+}) (Tetra)</td>
<td>35</td>
<td>0.30</td>
<td>−0.002</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>Fe(^{3+}) Fe(^{2+}) (Octa)</td>
<td>60</td>
<td>0.53</td>
<td>0.02</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>α-Fe blocked</td>
<td>5</td>
<td>−0.01</td>
<td>−</td>
<td>33</td>
</tr>
</tbody>
</table>

OBS: Isomer shift (IS) values are related to α-Fe. Δε is the quadrupolar shift and Bhf is the hyperfine magnetic field, RAA is the relative absorption area.
by a nanoparticle with the average particle diameter \( d_0 = 7.7 \text{ nm} \) at its surface \( H_d = \alpha (8 \mu_0 / d_0^3) \). \( \mu_0 \) is the thermal average moment of the 7.7 nm nanoparticle, \( f(z) \) is a log-normal distribution function, and \( \alpha \) is a fitting parameter. \( \alpha \) and the distribution function were adjusted to fit the experimental data shown in Fig. 5(a).

The log-normal distribution function which describes the particle size distribution is given by \( f(z) = (A / \sigma \sqrt{2 \pi}) \exp \left[ - \frac{(\ln(z/z_m))^2}{2 \sigma^2} \right] \), where \( A \) is a normalization constant, \( z_m \) is the median diameter and \( \sigma \) is the standard deviation parameter.

For a given value of the applied field \( H (\mu_0) \), is calculated from the equations: \( H_d = \alpha (8 \mu_0 / d_0^3) \), \( (\mu_0) = \mu_0 0 \left[ (\mu_0 / k_B T) (H + H_d) \right] \), and \( d_0 = \int f(z) dz \), where \( L \) is the Langevin function.

In order to fit the experimental results shown in Fig. 5(a) we have \( z_m = 7.4 \text{ nm} \), \( \sigma = 0.3 \), and \( \alpha = 0.46 \).

Notice from Fig. 5(a) that the theoretical model reproduces quite well the experimental results. We have found a coercivity of 22 mT, as found in the VSM data. We have also reproduced the large field limit of the magnetization curve, except for a small asymmetry found in the VSM data.

4. Conclusions

By using water and iron powder we have prepared magnetite nanoparticles with diameters of 12 nm by high energy ball milling. The magnetite particles were magnetically blocked at room temperature due to the dipolar magnetic interaction. We have used a self-consistent method to determine the coercivity field, finding good agreement with the experimental magnetization and XRD data. The method can yield a large amount of magnetite nanoparticles that could be used in biomedical applications.

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