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Magnetite nanoparticles obtained from the system Fe(III)/Fe(II) - glycine

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Magnetite nanoparticles were synthesized from Fe^{3+}/Fe^{2+} salts in the presence of glycine (2:1:8; 2:1:3 ratio metal ions/glycine) using NH_4OH 25% as precipitating agent. The parameters which influence the synthesis are discussed. The magnetite powders were characterized by XRD, IR spectra, magnetic measurements and Mössbauer spectra. The average diameter of crystallites is in the range 10 – 13 nm. The magnetization value is ~ 43 emu/g.

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1. Introduction

Magnetite (Fe_3O_4) is a very important iron oxide with many potential applications in medicine and pharmaceutics [1,2], such as magnetic resonance imaging [3,4], hyperthermic tumor treatment [5], controlled drug delivery [6].

All the medical applications require very fine particles with sizes smaller than 20 nm and narrow particle size distribution. For this reason the fabrication of monodispersed magnetic particles which can be controlled in size, distribution, shape, crystalline and alignment focused the interest of researchers.

Fe_3O_4 nanoparticles are commonly produced by several methods, e.g. coprecipitation from the solution of ferrous/ferric salts, in alkaline medium followed by aging and digestion in the temperature range 90-150 °C [7,8], chemical synthesis [7,9,10], hydrothermal/solvothermal reactions [8,11], thermal decomposition of different type precursors: $FeCup_3$, $Fe(acac)_3$, $Fe(CO)_5$ [12-14], etc.

The nature of the precursors play a very important role in the synthesis of nanoparticles. Synthesis routes, in which polynuclear coordination compounds with two or more metal ions are formed as precursors are preferred because these compounds are capable of giving mixed oxides by thermal decomposition [15].

It is well known that the presence of several organic anions such as carboxylate or hydroxycarboxylate ions in solution of Fe^{2+}/Fe^{3+} mixed salts influences the formation of iron oxides [16].

Organic ions are known to affect the formation of these oxides through the following proccesses:

- the chelation of these ions with metal ions preventing nucleation;
- the adsorption of these ions on the nuclei produced by hydrolysis inhibiting the growth of the nuclei [17].

The citrate ions are known to interfere with the formation and growth of the oxides [17-19]. In the absence of citrate ions, the size of the maghemite particles (γ-Fe_2O_3) is ~ 8 nm; with citrate ions, the size can be small than ~ 2 nm. The presence of citrate ions affects not only the size of the particles but, also, their chemical properties. These particles become more stable from pH = 3.5-11 [16].

Many years ago, we have demonstrated the influence of formate/acetate anions on the formation of Fe_3O_4. In this case the precursors of Fe_3O_4 were formate/acetate polynuclear complex compounds [20].

The purpose of this paper is to investigate the formation of magnetite in the presence of glycine ($CH_2(NH_2)$-COOH). In the reaction medium, the precursors – aminoacid complex compounds decomposed with the formation of Fe_3O_4. Due to this reason, the bearing mixed oxide has a high level of homogeneity. The parameters which influence the synthesis are discussed. The structure and magnetic behavior of the magnetite nanoparticles are studied.

2. Experimental

All chemicals: $FeCl_3 \cdot 6H_2O$; $FeCl_2 \cdot 4H_2O$ and $CH_2(NH_2)COOH$ were of reagent quality (Merck).

System **I**

1.6 g $FeCl_3 \cdot 6H_2O$ and 0.6 g $FeCl_2 \cdot 4H_2O$ in the 2:1 ratio of cations were dissolved in 50 ml water and mixed with an aqueous solution of glycine (1.8g) in a 2 : 1 : 8 ratio cations/glycine, under continuous stirring. When the pH was raised to 10-11, by adding 25 % NH_4OH solution, a deep brown compound was separated. After 10 h at 80°C, this compound decomposed in the solution medium and a black crystalline magnetic powder separated. This powder was filtered, washed very well with water (until the pH ~ 7) and dried on P_4O_{10}.

System **II**

In order to study the influence of the glycine concentration on the morphology of the magnetic particles, another experiment was performed in which a 2:1:3 ratio cations/glycine has been used. The procedure was the same.

The phase content was examined using a DRON X-ray powder diffractometer linked to a data acquisition and processing facility; CuK$_\alpha$ radiation (λ = 1.540598 Å) and a graphite monochromator were used.

The IR spectra (KBr pellets) of the magnetic powders were recorded on a Bio-Rad spectrophotometer in the range 400 - 4000 cm^{-1}.

The saturation magnetizations of the magnetites, at the room temperature, were determined with a Faraday balance, using Ni powder as calibrant.

Mössbauer spectra were recorded with Promeda type Mössbauer spectrometer linked to a data acquisition and processing facility.

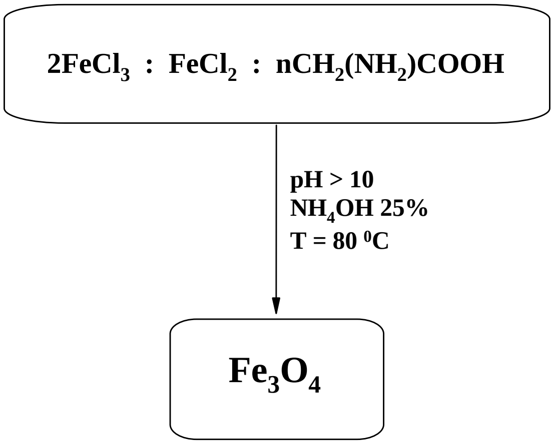
3. Results

Twenty years ago, S. Hamada et al.[21] have extensively studied the system Fe(III) chloride-glycine in aqueous and 2-propanol/water media, in order to obtain monodispersed α-Fe_2O_3 (hematite) particles.

They have been established that the glycinato-iron complex formed in these media was a permanent reservoir of hydroxocomplexes (pH = 1.2 - 2.8): $[Fe(OH)]^{2+}$, $[Fe(OH)_2]^{+}$, $[Fe_2(OH)_2]^{4+}$.

We performed the synthesis of magnetite nanoparticles salts in the presence of glycine (2:1:8; 2:1:3 ratio metal ions/glycine), with a 25 % NH_4OH solution (pH>10). The magnetic powders obtained, after 10 h at 80°C have the structural characteristics of magnetite (Scheme 1).

Scheme 1



4. Discussion

Fig. 1 (a, b) shows a typical X-ray pattern which reveals the formation of Fe_3O_4 phase in all these samples. No characteristic peaks of impurities are observed.

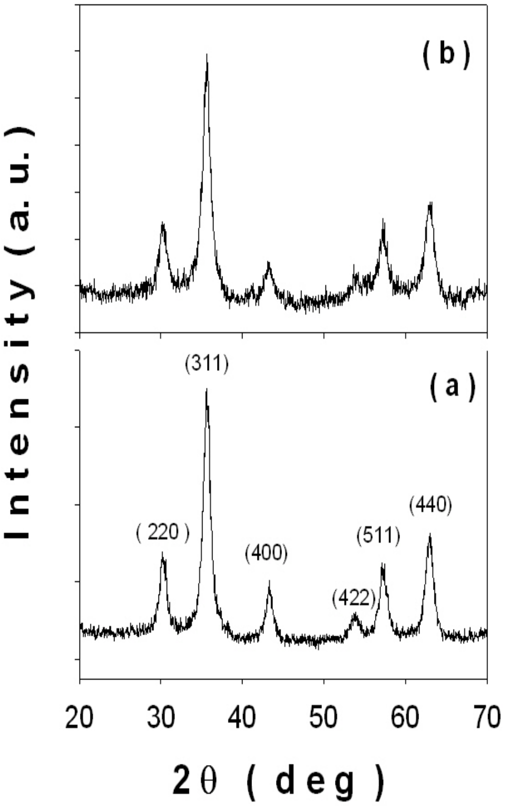


*Fig. 1. X-ray diffraction for the magnetite obtained from: a) system **I**; b) system **II**.*

The large line widths can be explained in terms of nanoscaled particles representing the investigated samples. Sherrer formula gives a mean particle dimension in the range of 10 - 13 nm for the investigated magnetite samples.

The average diameter of particles is 10 nm for the magnetite obtained from the system **I** and 13 nm for the system **II**. The size of magnetite is affected by the glycine concentration. It means that for the ratio 2 : 1 : 8 (metal ions/glycine) the obtained magnetite has the smaller size of particles (10 nm).

The IR spectra recorded for the magnetite samples, in the range 400 - 4000 cm^{-1}, showed bands at ~ 580 and 470 cm^{-1} (Fig.2 a, b) associated with the stretching and torsional vibration modes of the magnetite Fe-O bonds in tetrahedral and octahedral sites, respectively. The assignments are in accordance with Keiser et al. [22] and Poling [23] who described two broad bands at 580 and 400 cm^{-1}associated with magnetite.

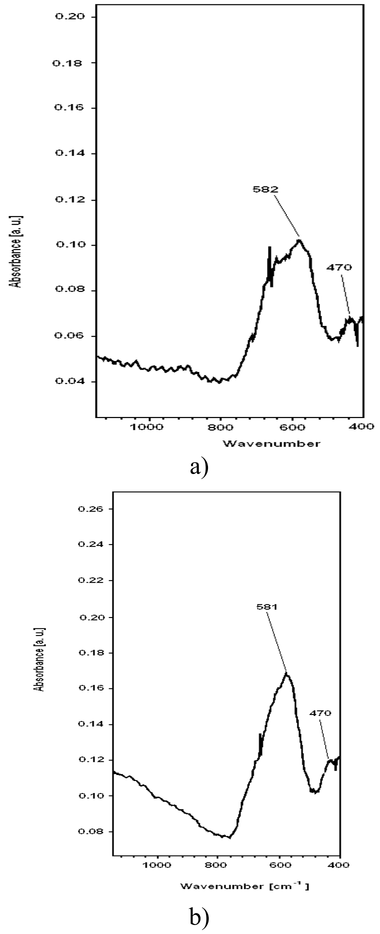


*Fig. 2. IR spectra for the magnetite obtained from: a) system **I**; b) system **II**.*

The ^{57}Fe Mössbauer spectra were recorded at room temperature using a ^{57}Co (Rh) source and a constant acceleration spectrometer. The representative room temperature Mössbauer spectra are shown in Fig. 3.

Mössbauer spectra of magnetite in bulk form consist in a superposition of magnetic sextets corresponding to tetrahedral A and octahedral B coordinations of iron ions [24]. As the particle dimension decreases the Mössbauer spectrum collapse due to the superparamagnetic relaxation processes. The critical quantity that determines the mechanism of magnetic relaxation is the magnetic anisotropy energy KV were K holds for magnetic anisotropy and V is the particle volume. When $KV \ll k_B T$, the relaxation time becomes comparable with the nuclear life time of Mössbauer nucleus and consequently the spectrum collapses.

The Mössbauer spectra in the Fig. 3. are representative Mössbauer relaxation spectra. The relaxation time associated with the spectrum (a) is clearly higher than for spectrum (b) which is more collapsed. The order of magnitude of relaxation times is 6.5×10^{-6} s.

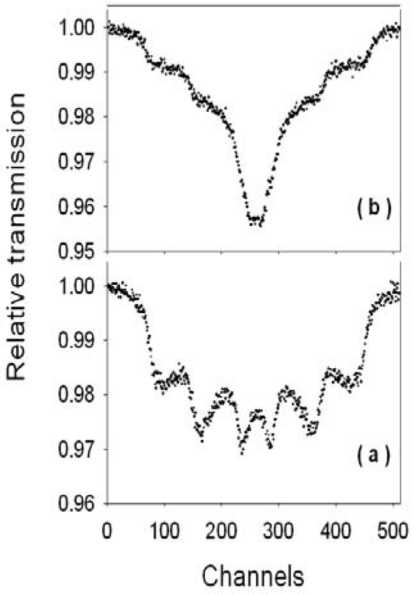


*Fig. 3. Mossbauer spectra for the magnetite obtained from: a) system **II**; b) system **I**.*

The magnetic behavior of these magnetite (M versus H/T) at the room temperature is presented in Fig. 4. The lower values of the magnetization compared with the magnetization value of the bulk magnetite (92 emu/g) [25] are due to the nanostructural character of the powders.

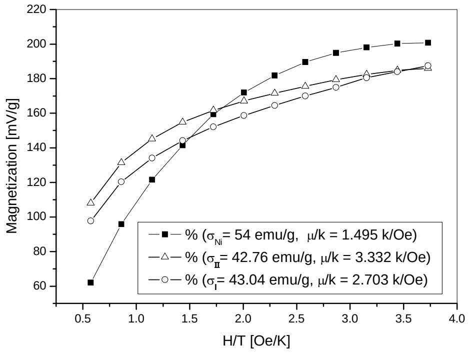


*Fig 3. Magnetization curves for the magnetite obtained from system **I** and system **II**.*

5. Conclusions

A variant of precipitation method is reported in this paper, which is extremely simple and promising for the obtaining of magnetite nanoparticles. The magnetite powders were characterized by XRD, IR spectra and magnetic measurements.

The average size of the magnetite particles is in the range 10-13 nm.

The concentration of glycine influences the size of magnetite nanoparticles.

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