

MAGNETIC BEHAVIOUR OF MAGHEMITE NANOPARTICLES STUDIED BY MÖSSBAUER SPECTROSCOPY

D.Predoi, V.Kuncser, and G.Filoti

National Institute for Physics of Materials, Ro-76900 Bucharest-Magurele, Romania

Abstract: Two systems of nanoparticles with different surface states have been prepared by sol-gel methods and analysed by X-ray diffractometry, transmission electron microscopy, thermal analysis and temperature dependent Mossbauer spectroscopy. Surface states and phase content, particle mean size and the magnetic anisotropy energy constant were evaluated.

1. Introduction

The dependence of the physical properties of the magnetic materials on the particle grain size is a well-known phenomenon. The interest in this field is increased on the account of the observation that materials with nanometer-size particles (3-10 nm in diameter) exhibit novel electronic, optical, magnetic, chemical and bio-medical properties [1].

Maghemite, $\gamma\text{-Fe}_2\text{O}_3$, is a technologically important compound widely used for the production of magnetic materials and catalysts. Unfortunately, pure maghemite transforms into $\alpha\text{-Fe}_2\text{O}_3$ (hematite) at rather low temperature ($\sim 300^\circ\text{C}$). In order to avoid the sintering process and to stabilise the magnetic phase, maghemite based nanocomposites are more suitable materials for applications. A great deal of interest in nano-composite containing maghemite nano-particles dispersed in polymeric, glassy or ceramic a matrix has been therefore evidenced in the recent years. However, the magnetic behaviour of the composite is mainly imposed by the behaviour of the maghemite nano-constituent [2].

In this paper we report on the preparation of $\gamma\text{-Fe}_2\text{O}_3$ nano-particles with a mean size of order of 10 nm and with different hydration and surfactant degrees. The particles were prepared by sol gel method and their structural and magnetic characteristics were analysed by X-ray diffractometry (XRD), transmission electron microscopy (TEM), thermal analysis and Mossbauer spectroscopy (MS).

2. Experimental

Based on Massart's methods [3], aqueous mixture of ferric and ferrous salts with NaOH, as an alkali source has been prepared as stock solutions. The synthesis of maghemite nanoparticles has been carried out via a controlled coprecipitation approach.

The fractions stock solutions (30ml) have been obtained in two ways: (i) by neutralizing the surface electrostatic charge at a pH ~ 8 and, (ii) by rapidly adding 100–150 ml of H₂SO₄ 1 M. The precipitate were separated by centrifugation and then dried at room temperature, producing thus samples GN (case i) and GS (case ii), respectively.

Spherical nano-particles were observed in electron micrographs obtained with an JEOL 100 CX microscope, for both samples. The particle size and structure were

additionally analysed by using an X-ray diffractometer (Philips PW 1830), operating in the reflexion mode, with $\text{Cu}_{K\alpha}$ radiation. Thermal analysis of the samples was simultaneously performed by DTA/TG (differential thermal analysis and thermogravimetry) techniques. The experiments were realised under oxygen atmosphere with a heating speed of 50C/min, on a NETZSCH STA 409 instrument. Magnetic relaxation phenomena were studied by Mössbauer spectroscopy. The Mössbauer spectra were acquired at different temperatures with sample inserted in a nitrogen bath-cryostat and using a constant acceleration spectrometer with symmetrical waveform and a $^{57}\text{Co}(\text{Rh})$ source.

3. Experimental results and discussion

The XRD patterns of sample GN are presented in Fig.1. Peak positions and relative intensity correspond to those of the reference date for $\gamma\text{-Fe}_2\text{O}_3$ [4]. The lattice parameter of $\gamma\text{-Fe}_2\text{O}_3$ crystalline structure, as obtained from the peak positions in Fig.1 is $a = 0.834$ nm.

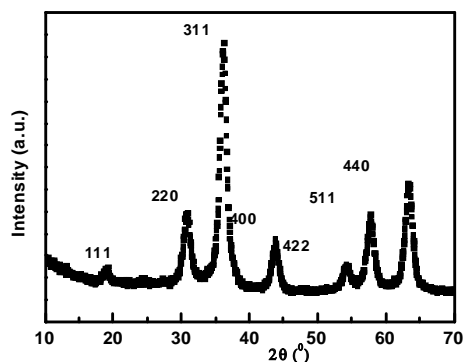


Fig. 1- X-ray diffraction pattern of the GN sample ($\text{Cu } K_{\alpha}$). A mean coherence length of 10,5 (5) nm was derived by using Scherrer's formula.

An average grain size of 10,5(5) nm was deduced from the full width at half maximum (FWHM) by using Scherrer's formula. FWHM of the diffraction peaks were evaluated from profile fit analyse performed with Philips PC-APD software and assuming Gaussian profiles. This mean grain size obtained via X-ray

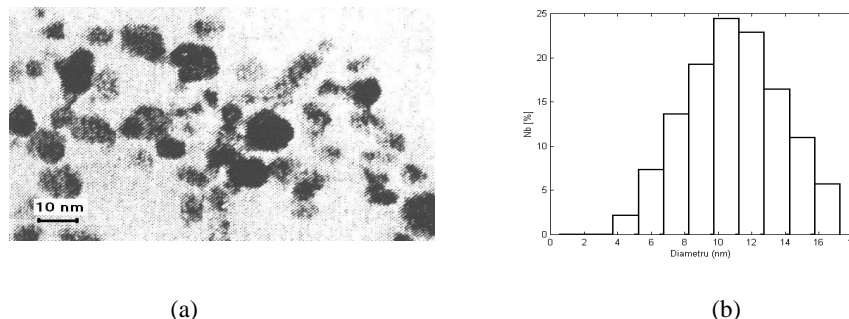


Fig. 2 - A micrograph for sample GN (a) and the corresponding size distribution (b). A mean particle diameter of 10,5 (5) nm was derived from this distribution.

diffraction is consistent with the mean size deduced from TEM observations (Fig.2). Similar results were obtained for sample GS, which show within the error range almost the same particle mean, size as GN.

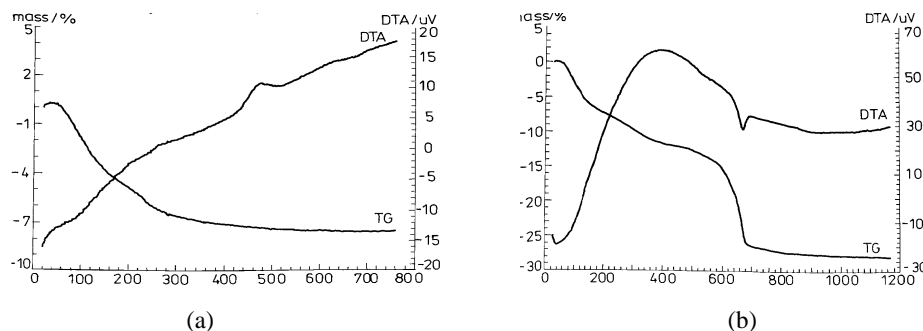


Figure 3 -Typical DTA/TG curves relative to the sample GN (a) and GS (b).

Figure 3 shows typical DTA/TG curves relative to the sample GN (Fig. 3a) and GS (Fig 3b). The TG data indicates a loss of water up to the transformation $\gamma\text{-Fe}_2\text{O}_3$ into $\alpha\text{-Fe}_2\text{O}_3$, at about 500°C (sample GN) and 700°C (sample GS) respectively, as evidenced by corresponding exothermic picks in DTA curves For sample GN there is a total weight loss of around $\cong 2.15\%$ (Fig.3a) taking place approximately in three steps: (i) from room temperature up to 150°C, (ii) between 150°C and 250°C and (iii) above 250°C. The first weight loss corresponds to the elimination of hydroxyl groups weakly bonded to the particles (physisorbed water). The second weight loss corresponds to the removal of the perchlorate content. Above 250°C, the weight loss results from the removal of strongly adsorbed water (e.g. the dehydration of surface hydroxo ligands). For sample GS, the successive weight losses represent in all around 8.5 % (Fig. 3b) and take place approximately in four steps: (i) from room temperature up to 180°C, (ii) from 180 to 400°C, (iii) from 400 to 600°C and (iv) above 600°C, the last one being due to the elimination of SO_2 gas (evidenced by a sharp local minimum -endothermic pick- in DTA curve).

The particles hydration obtained by thermal analysis, neglecting residual perchlorate, is given in Table 1. From these results it can be deduced that for sample GN, the surface Fe atoms, Fe_{surf} , are contained in an outer layer of about 0.3 nm thick and in average one H_2O molecule corresponds to a surface Fe atom. For samples GS, the S content estimated by chemical and thermal analysis are in very good agreement. In addition, the thermal analysis data for sample GS suggest adsorbed species with net composition SO_2 , $2H_2O$, and one sulphur atom corresponding to one surface iron.

Table 1
Thermal analysis characteristics for the considered samples.

Sample	D (nm)	Fe_2O_3 (wt%)	H_2O/Fe (mol/mol)	A/Fe (mol/mol)	Fe_{surf}/Fe
GN	10.5	97.85	0.11	-	0.09
GS	10.5	92,5	0.19	0.09	0.08

Note: A stands for SO_2 in samples

The Mössbauer spectra (MS) collected at different temperatures on samples GN and GS are presented in Fig.4 a and b, respectively. The spectrum of sample GN at 80K consists in a large sextet. This broadens significantly at higher temperatures. Moreover, the intensity ratio between both the first and the third and the second and the third line respectively are changing with temperature, the spectra collected above 150 K presenting clear evidence for magnetic relaxational effects. The general trend of the collected spectra stand for a superparamagnetic transition-taking place above 300 K and therefore the spectrum collected at 80 K may be still considered as corresponding to a magnetic static regime. For intermediate temperatures in the range between 80 K and 300 K, the nano-particle magnetic moments (and consequently the individual spins) behave in the regime of collective excitations [5]. However, even at lower temperatures the typical sextets are still broad and therefore, all the temperature dependent Mössbauer spectra were fitted by a distribution of hyperfine fields, following the Hesse-Rubartsch algorithm. Excepting the broad sextet, sample GS show at 80 K a central paramagnetic doublet with an isomer shift of about 0.9 mm/s and QS of 1.2 mm/s, inferring the presence of paramagnetic iron in an oxidation state lower than 3, most probable connected with the sulphur atoms in the particle surface shell. At 80K, the most probable hyperfine magnetic field for both GN and GS samples is about 50 T, which is a typical value of nanocrystalline maghemite [6]. For a particle of volume V , the hyperfine magnetic field at a temperature T is expressed as [5]:

$$H_{ef}(T, V) = H_0 \left(1 - kT/2KV\right), \quad (1)$$

where H_0 is the magnetic hyperfine field in the absence of magnetic fluctuations, k is the Boltzmann's constant and K is the magnetic anisotropy energy constant.

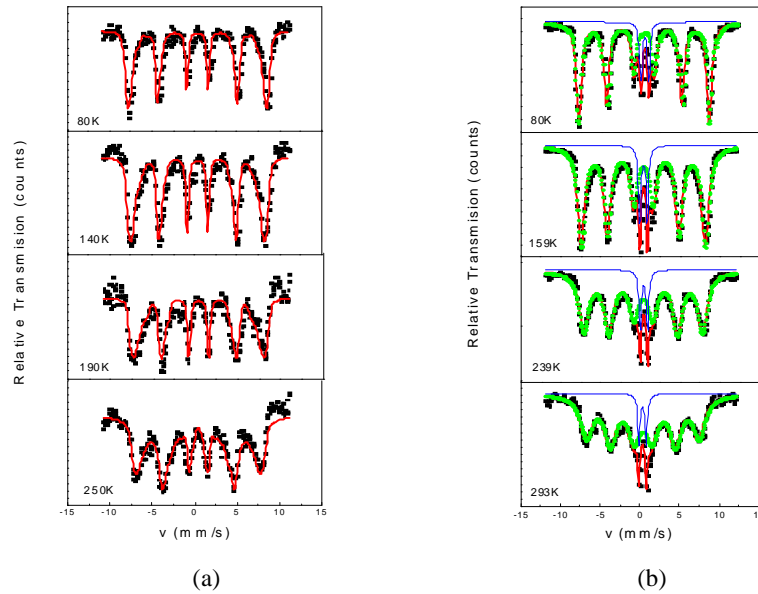


Figure 4 - Mössbauer spectra of sample GN (a) and GS (b), collected at different temperatures.

A linear decrease of the hyperfine field vs. the temperature has to be mentioned for this regime, with the slope dependent on both the anisotropy energy constant and the mean particle size.

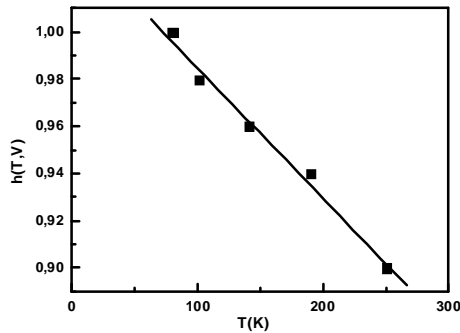


Figure 5 - Magnetic hyperfine field $h(T,V)=H_{ef}(T,V)/H_0$ vs. temperature. The solid line indicates the best linear fit to the experimental results.

The value of $h(T,V)=H_{ef}(T,V)/H_0$ as a function of temperature is shown in Fig.5 for the sample GN. Most probable values for the hyperfine fields were considered, according to the hyperfine field distributions. The most probable value from the 80 K distribution (corresponding to the static regime) was considered for H_0 . It is seen from Fig.5 that the results are in agreement with a linear temperature dependence of $h(T,V)$. The

value of K , obtained from the slope of the best-fitted linear dependence and considering 10.5(5) as a mean particle diameter, is $(2,1 \pm 0.3) \cdot 10^5 \text{ erg/cm}^3$.

3. Conclusions

The performed investigations show that particle surface states and phase composition may be controlled by sol-gel preparation methods. Two systems of nanoparticles with different surface states and with a particle mean size of about 10.5 nm were obtained.

The magnetic behaviour and the local interactions were analysed by Mossbauer spectroscopy at variable temperature. The X-ray and Mossbauer patterns provide evidence for only defected maghemite nano-particles in sample obtained without the addition of the sulphuric acid and an additional paramagnetic surface state in sample obtained by adding sulphuric acid. An anisotropy constant of about $2 \cdot 10^5 \text{ erg/cm}^3$ was derived via the Mossbauer data for the sample containing pure maghemite nano-particles, by assuming the magnetic regime of the collective excitations.

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