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MAGNETIC IRON OXIDE NANOPARTICLES SYNTHESIZED VIA MICROEMULSIONS

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Abstract

We have prepared magnetic iron oxide nanoparticles with sizes between 2-3 nm using stable microemulsions at 65 °C. The as-obtained particles present diffraction patterns with broad peaks, characteristic of small particle size. This simple method eliminates some complications of the typical microemulsion routes and further treatments in order to get a good crystallization.

Keywords: Microemulsions, magnetic nanoparticles, magnetitc iron oxides.

Introduction

Small magnetic iron oxide particles (magnetite, maghemite) have been obtained by different synthesis ways, being the most common coprecipitation in water. In this method, Fe^{2+}/Fe^{3+} salts are precipitated adding another aqueous solution containing an alkaline agent (NH_4OH, NaOH, etc.) [1]. Several factors act on this precipitation, like addition rates, concentration of the agents, etc. [2]. The synthesis in presence of other reactives like PVA has also been studied [3]. Some authors have achieved the same coprecipitation reaction using microemulsions [4]. A microemulsion is an isotropic and thermodinamically stable single phase formed by at least three components, two of them are non-miscible and a third, called surfactant, has an amphiphilic behaviour [5]. This method is similar to the previous ones, as two stable microemulsions are prepared, one containing the salts and other the alkaline medium. Up to date, the microemulsion method has been carried out at room temperature [6], but a poor crystallization is obtained and a further thermal treatment is needed [7]. The addition of large amounts of Fe^{2+} or a work under inert atmosphere have been used to avoid these problems [4]. In this paper we report the possibility of using the microemulsion route at higher temperatures. We find significant advances in the crystallization of the as-obtained particles, which allow to save further steps in the synthesis. We study also the effect of mechanical stirring on the synthesis procedure.

Sample preparation and experimental details

Double distilled water, $FeCl_3{\cdot}6H_2O$, cyclohexane and $FeSO_4{\cdot}7H_2O$ 99% pure from Aldrich and brij-97 (polyoxiethylene-10-oleyl-ether) from Sigma were used in the synthesis. Two microemulsions of cyclohexane, brij-97 and an aqueous solution in the volume ratio 89/7/4 were used: one of them containing an aqueous solution 1M in Fe^{3+}, 0.5 M in Fe^{2+} and 0.5 M in HCl (the acid medium is used in order to avoid oxidation of Fe^{2+} to Fe^{3+}); the other one containing a 35 ammonia water solution. 100 ml of each were introduced in a thermostatic bath at 65 °C, havin transparent single phase indicating the formation of stable microemulsions. Once this temperature w reached, the microemulsion containing the iron salts was added on the other one while stirring. Thr mechanical stirring rates of 100, 150 and 200 r.p.m were used to see the effect of this variable on t synthesis procedure. The resulting mixtures were aged at 65°C during 15 minutes; after this peri they were taken out of the bath and allowed to reach room temperature. The obtained precipita were floculated with acetone and decanted with the aid of a magnet. After this they were wash several times in large amounts of acetone and water and dried at room temperature, resulting th final samples labeled as T100, T150 and T200.

X-ray diffraction data were taken with a Philips PW-1710 diffractometer. TEM microgra were taken in a 200 kV ultrahigh resolution analytical electron microscope JEOL, JEM-2010. DMS-1660 vibrating sample magnetometer was used to obtain magnetization versus field curves fr 77 to 300 K in fields up to 10 kOe; a Quantum Design SQUID was used to record magnetization temperature loops at 5 Oe between 4-300 K and magnetization vs. field data up to 55 kOe.

Sample characterization

X-ray diffractograms of the three samples show wide peaks characteristic of small partic as shown in Fig. 1. In sample T100 the peaks correspond to a typical spinel phase of magnetite maghemite. In sample T200 only two broad peaks appear, while T150 presents an intermedi diffractogram. This evolution could be interpreted as a gradual broadening and overlapping of t peaks when lowering particle size, until the x-ray pattern is undistinguishable from that of 2-li ferrihydrite [8].

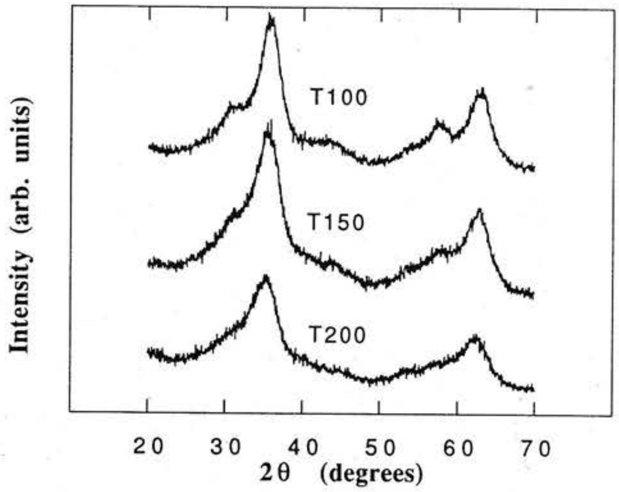

Figure 1: x-ray diffractograms of the samples

Fits of the diffractograms with the profile fitting procedure of the PC-APD software (ver. 3.5b) based on a Marquard-non-linear least square algorithm have been done. From the position and width of the most intense peak the plane spacing (d) and crystal size using Debye-Scherrer formula were calculated. The results of the fits are shown in Table I.

Sample	**particle size (Å)**	**d (Å)**
T100	29	2.510
T150	26	2.518
T200	25	2.544

Table I: Structural parameters of the studied samples from x-ray diffractograms.

TEM micrographs were taken after solving small amounts of the samples in ethanol and deposited in a TEM grid after ultrasonical dispersion. A typical one can be seen in Fig. 2. Particle aggregates of about 2-3 nm can be observed, in agreement with x-ray data.

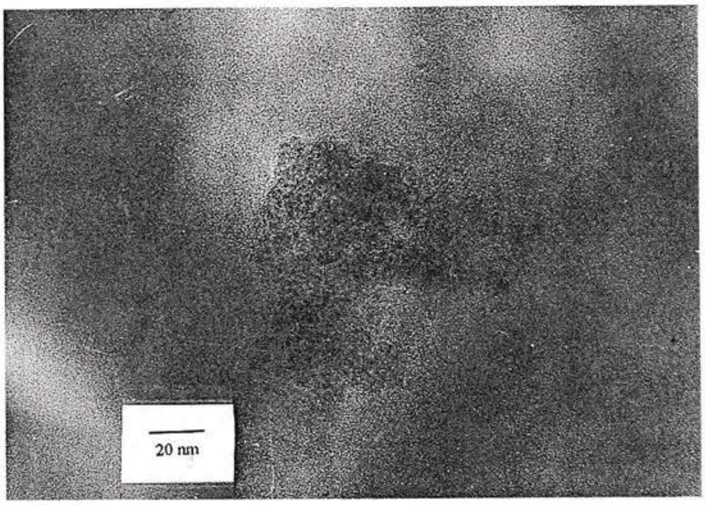

Figure 2: TEM micrograph of sample T150.

Magnetic results

In Fig. 3 we show magnetization versus field curves at 77 K for the three samples. It can be seen that the maximum magnetization values decrease with the stirring rate; the curvature of the magnetization also decreases, indicating a slight decrease of the mean particle size. Small coer fields between 2 and 5 Oe were measured at 77 K, which increased up to 4 - 11 Oe when measu at room temperature.

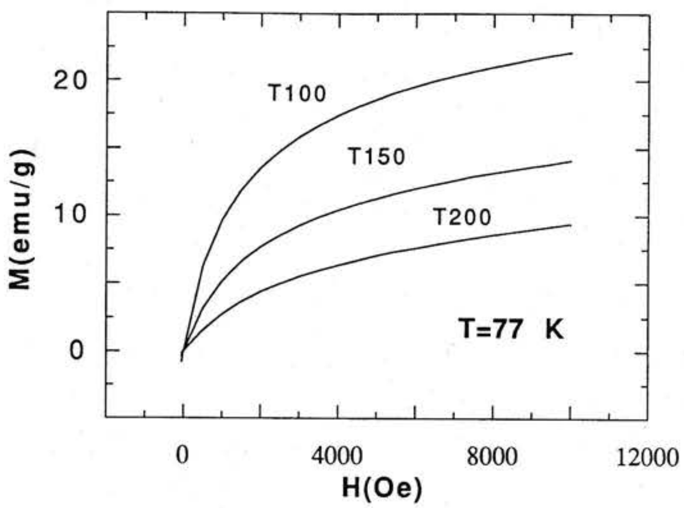

Figure 3: Magnetization vs. magnetic field in the superparamagnetic state for all samples.

In order to try to saturate the samples, magnetization vs. field data were taken at 5 K for fi up to 55 kOe (Fig. 4).

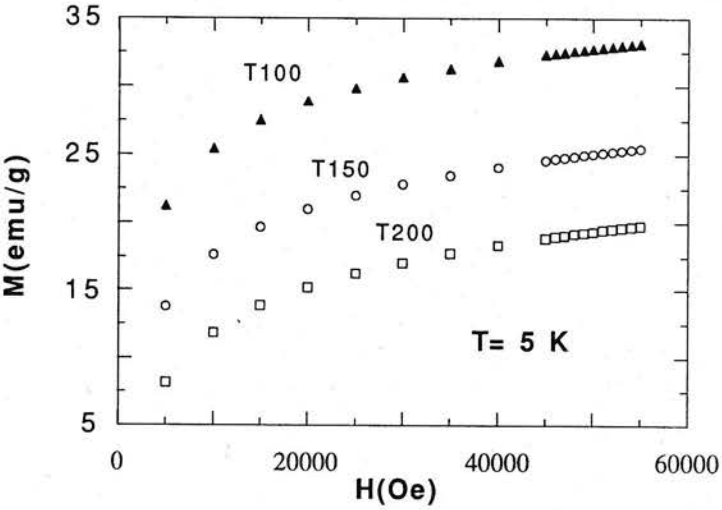

Figure 4: Magnetization versus magnetic field at low temperatures for all samples.

The maximum magnetization values followed the same trend as in Fig.3, diminishing with the stirring rate, moreover, saturation magnetization values corresponding to bulk γ-Fe_2O_3 (70 emu/g) were not achieved. From magnetization vs. temperature curves taken at 5 Oe (Fig. 5) we obtained a superparamagnetic behaviour above basically constant blocking temperatures between 35-40 K. Nevertheless, the shape of the ZFC curve widens when increasing the stirring rate.

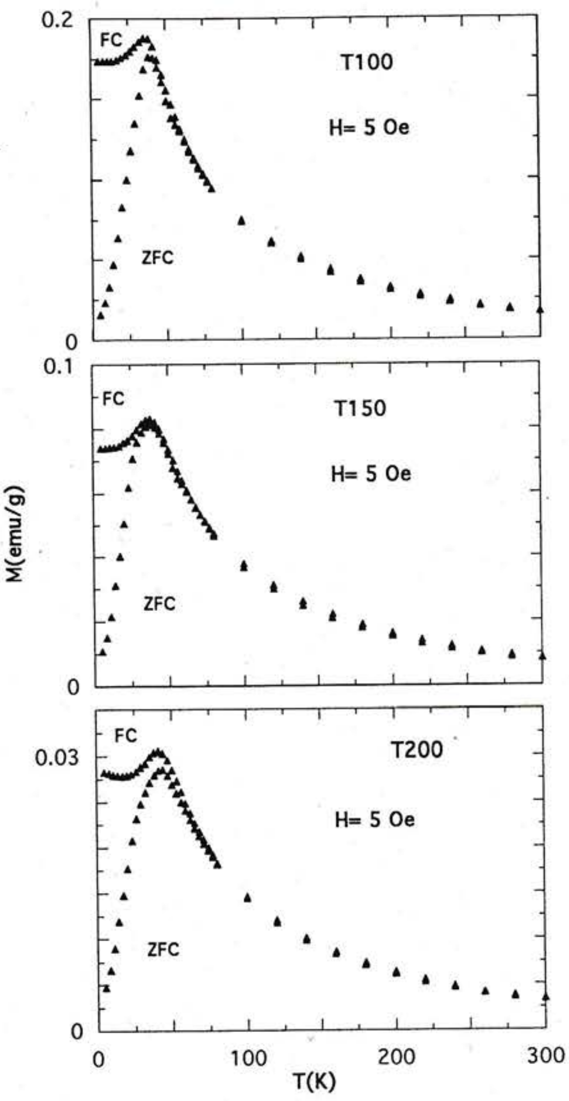

Figure 5: FC and ZFC dc magnetization curves for the three samples.

Discussion

A slight decrease of particle size is observed when increasing the stirring rate, as expected, provided that a more intense agitation generates the creation of more initial crystalline nuclei. Although magnetite is first obtained in the microemulsion, the fact of working in open air and at 65 °C with very small particle sizes makes a rapid oxidation to maghemite to occur [9].The obtained plane spacing (d) values for samples T100 and T150 are very similar to d=2.52 Å, typical of maghemite, while T200 experiences a little increse, approaching d=2.5 Å characteristic of a 2-line ferrihydrite [8].

The progressive decrease in the curvature of M vs. H curves at the superparamagnetic state (Fig. 3) indicates a certain volume reduction of the magnetic species when going from T100 to T200. The broadening of the ZFC cusp to lower temperatures in M vs. T curves (Fig. 5) agrees also with this, as it reveals the increase of size polydispersity for sample T200 with the presence of smaller particle sizes.

When reducing particle size, the obtaining of pure oxides is very difficult and the formation of oxyhydroxides like ferrihydrite is more likely, in fact the typical mean crystal size for 2-line ferrihydrite is 20 Å [8], very close to the calculated values. This gradual phase change from maghemite to ferrihydrite could explain the decrease in the magnetization values in Fig. 5 when increasing the stirring rate.

In summary, the advantage offered by this method is a good crystallization of the as obtained nanoparticles without any other further steps, which means a qualitative improvement with respect to other previous methods.

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