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► **To cite this version:**

N. Feltin, M. Pileni. New Technique to Make Ferrite Nanosized Particles. Journal de Physique IV Proceedings, 1997, 07 (C1), pp.C1-609-C1-610. 10.1051/jp4:19971252 . jpa-00254960

**HAL Id: jpa-00254960**

**<https://hal.science/jpa-00254960>**

Submitted on 4 Feb 2008

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## New Technique to Make Ferrite Nanosized Particles

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**Abstract.** Preparation of magnetite/maghemite nanometric particles is reported from the precipitation of ferrous dodecyl sulfate micellar solution with methylamine. The size of nanocrystals is controlled by the micellar concentration and by temperature. It varies from 3.3nm to 11nm. Magnetic properties are studied for various sizes of maghemite particles.

### 1. INTRODUCTION

Synthesis of magnetite,  $\text{Fe}_3\text{O}_4$ , has been extensively studied these last few years. Generally, maghemite,  $\gamma\text{Fe}_2\text{O}_3$ , is directly obtained by oxidation from magnetite. Two iron oxides, magnetite and maghemite are the most commonly used material for the preparation of magnetic fluids. They are made of ultrafine ( $D=10\text{nm}$ ), single domain ferri- or ferromagnetic particles dispersed in a suitable liquid carrier, such as kerosene, diester, water etc...A superparamagnetic regime is obtained.

Commonly, magnetite (and maghemite) magnetic fluids are obtained by coprecipitation technique. Fe(III) and Fe(II) salt concentrations are high (more than 0,1M) and a basis is added to the solution. An immediate precipitation of hydroxide derivatives is observed. The particles are washed in a given solvent and magnetite magnetic fluid is obtained. Very shortly magnetic fluid formation, magnetite nanosized particles are oxidized in maghemite,  $\gamma\text{Fe}_2\text{O}_3$ , by heating at  $100^\circ\text{C}$  and by acid treatment. The particle size is controlled by the ionic strength, the pH and reactants concentrations. Furthermore it has been shown that the presence of Fe(III) and Fe(II) salts are needed to make ferrite oxides [1]. Magnetite has been previously observed from synthesis performed in the absence of Fe(III) and in the presence of Fe(II) [2,3]. Immediately after basis addition, crystal made of  $\text{Fe}(\text{OH})_2$  is formed. Progressively, magnetite,  $\text{Fe}_3\text{O}_4$ , arises by crystallization from this ferrous hydroxide gel. This process involves dissolution-oxidation-nucleation sequences on  $\text{Fe}(\text{OH})_2$  platelets. In such experimental conditions, very well defined and very large particles are obtained. As matter of fact, the average sizes are in the range of 500nm to  $1\mu\text{m}$ .

In the present paper, it is proposed a new synthetic mode which does not involve any Fe(III) at the starting point of the chemical reaction and induces formation of very small ferrite particles (from 3.3nm to 11nm). The reactant concentration is almost two orders of magnitude lower than that usually used. The chemical reaction can be performed at room temperature. The coprecipitation reaction is performed by using iron dodecylsulfate,  $\text{Fe}(\text{DS})_2$  oil in water micelles. Surfactant concentration used is very low ( $2.5 \cdot 10^{-3}\text{M} < [\text{Fe}(\text{DS})_2] < 10^{-2}\text{M}$ ). The control in the size is obtained by either increasing  $\text{Fe}(\text{DS})_2$  concentration or at fixed  $\text{Fe}(\text{DS})_2$  concentration by increasing temperature.

### 2. SYNTHESIS AND CHARACTERIZATION OF FERRITE NANOSIZE PARTICLES

Sodium dodecylsulfate,  $[\text{NaDS}] = 0.1\text{M}$ , solubilized in aqueous solution is mixed with an iron chloride,  $[\text{Fe}^{2+}] = 0.1\text{M}$ , solution. A precipitate of iron dodecylsulfate,  $\text{Fe}(\text{DS})_2$ , appears. After washing several times, it is dissolved again in an aqueous solution. Above the critical micellar concentration, c.m.c = 1.3.10<sup>-3</sup>M, iron dodecyl sulfate,  $\text{Fe}(\text{DS})_2$  forms oil in water micelles. Methylamine,  $\text{CH}_3\text{NH}_2$ , is added to a  $\text{Fe}(\text{DS})_2$  micellar solution. The solution is stirred during three hours at different temperatures ( $25^\circ\text{C}$ - $50^\circ\text{C}$ - $80^\circ\text{C}$ ). Nine samples (table 1) have been synthesized with three different surfactant concentrations (0.0025M-0.005M-0.01M) and at three temperatures ( $25^\circ\text{C}$ - $50^\circ\text{C}$ - $80^\circ\text{C}$ ). The particle size and morphology (Figure 1) are characterized by Transmission Electron Microscopy (TEM) measurements, (Phillips model CM 20, 200 kV). The average particle diameter varies from 3.3nm to 11.5nm. X-ray diffraction analysis (Stoe Stadi goniometer with Siemen Kristoflex-X-Ray generator with a cobalt cathode) exhibits spinel structure.

Immediately after synthesis the X Ray diffraction shows a peak characteristic of magnetite,  $\text{Fe}_3\text{O}_4$ . After one month, X Ray diffraction shows a peak due to formation of maghemite,  $\gamma\text{Fe}_2\text{O}_3$ . This is confirmed by  $^{57}\text{Fe}$  Mossbauer spectroscopy with a disappearance of Fe(II) in the invert spinel structure.

Table 1

$D_{mp}$ (nm)	3.3	5	6.3	5.3	6.4	7	6.2	7.7	11.05
$\sigma_{mp}$ (%)	0.33	0.34	0.33	0.34	0.26	0.24	0.25	0.28	0.22
$D_{mm}$ (nm)	2.3	3.2	4.1		8.4	9.6	7	8.7	9.4
$\sigma_{mm}$ (%)	0.35	0.36	0.55	-	0.29	0.25	0.38	0.33	0.35
$M_s$ (emu/g)	5	6	11	-	33	46	30	33	55
$H_c$ (Oe)T=200K	-	-	50	-	-	250	-	110	215

### 3. MAGNETIC PROPERTIES

Magnetization measurements of aqueous ferrofluid were made at 200K and room temperature (Vibrating Sample Magnetometer Digital Measurement systems Inc., model VSM 1660). In the case of ferrite powder a commercial alternative gradient magnetometer (princeton measurements corporation micromag model 2900) operating at room temperature in a field up to 2T is used. Particle having an average diameter in the range between 3.3 to 7nm, no coercivity is observed. The magnetic diameters ( $D_{mm}$ ) are deduced from Langevin curve (Table 1) and show a good agreement with the size ( $D_{mp}$ ) determined from T.E.M. In both cases, the size distributions ( $\sigma_{mm}$ ,  $\sigma_{mp}$ ) of the particles are closed to 35%. The variation of magnetization versus  $H/T$  (field over temperature) is unchanged with temperature. This confirms a superparamagnetic behavior. Magnetic fluids made of particles having an average diameter in the range of 7 to 10nm, a coercivity ( $H_c$ ) appears, at 200K. This could be attributed to the fact that the larger particles present in each sample are blocked at 200K [4]. Saturation magnetization ( $M_s$ ) is measured for various particle sizes. The Figure 2 shows a decrease in the saturation magnetization with increasing the specific surface. Even for the larger particles (11nm), the saturation magnetization is less than the bulk value.

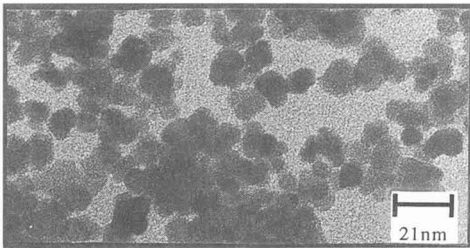
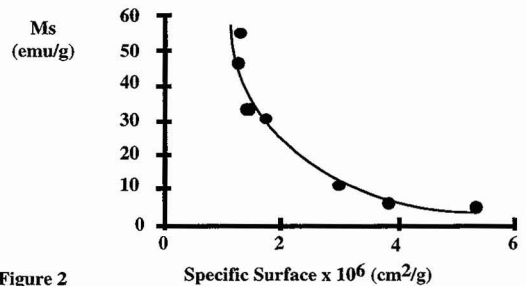
Figure 1 : Morphology of nanoparticles ( $D_p=9$  nm)

Figure 2

### 4. CONCLUSION

In this paper we describe a new synthesis of ferrite nanosized particles which induces formation of maghemite and magnetite particles in the size range between 3.3nm to 11nm with a relatively low polydispersity. The control of the particle size from 3.3nm to 11nm is obtained either by increasing the concentration of reactant (in a very low range  $2.5 \cdot 10^{-3} \text{M} < [\text{Fe}(\text{DS})_2] < 10^{-2} \text{M}$ ), or by increasing temperature. This technique is suitable to obtain particles having various sizes and similar surface. As a matter of fact the change in the particles size is obtained by a very small change in the micellar concentration. Presence of hydroxide or polymers is avoid. The remaining surfactant present in the ferrofluid is negligible (less than  $10^{-6} \text{M}$ ). It has been demonstrated that the magnetization properties depend, as expected, to the particle size.

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