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Ionic magnetic fluid based on cobalt ferrite nanoparticles: Influence of hydrothermal treatment on the nanoparticle size

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ABSTRACT

Magnetic fluid based on cobalt ferrite nanoparticles was obtained using a hydrothermal treatment added to the Massart procedure. This treatment increases the average size of the nanoparticles from 11.9 to 18.7 nm and also improves the dispersity and crystallinity of the cobalt ferrite particles. The nanoparticles obtained after the hydrothermal treatment were dispersed in aqueous solvent by the classical procedure for ionic magnetic fluids. The ferrofluid thus obtained is stable at pH 7 and may be useful for hyperthermia applications.

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1. Introduction

There is continuing interest in magnetic nanoparticles, especially because of their applications in the fields of imaging and therapy [1]. Among these applications, the treatment of tumors by hyperthermia has been recognized as very promising, and the efficiency of cobalt ferrite, CoFe_2O_4 , nanoparticles has been established [2–4]. For such an application, control of the particle size and shape is very important. It is therefore of interest to propose synthesis procedures allowing easy control of the particle size without introducing any chemicals that could be left in the final formulation. The synthesis of cobalt ferrite nanoparticles has been intensively investigated in the past because of the potential applications of these nanoparticles for high-density magnetic recording [5]. Several processes have been proposed, such as the sol–gel method [6], chemical coprecipitation [7–9], spraying coprecipitation [10], forced hydrolysis in a polyol medium [11], synthesis in oil-in-water micelles [12], synthesis in reverse micelles [13] or thermal decomposition of a mixed Co^{2+} – Fe^{3+} oleate complex [14].

The hydrothermal preparation (i.e., synthesis in an autoclave at temperatures around 200 °C) of ultrafine ferrite was described long time ago [15]; however, the particles were obtained by a sintering step at high temperature and the particle size increased from the nano- to the micrometer range. Hydrothermal synthesis has also been described for ferrite nanoparticles: barium ferrite nanoparticles [16], manganese ferrite [17], magnetite [18], maghemite [19], Zn-doped nickel ferrite [20] or cobalt ferrite nanocrystals [21]. For

these, the synthesis is achieved in the presence of a surfactant (cetyltrimethylammonium bromide) and the particle size was of the order of 40 nm.

We report here the hydrothermal synthesis of cobalt ferrite ferrofluid based on nanoparticles with an average diameter in the order of 11.9 and 18.7 nm by varying the temperature and the incubation time. We also describe the dispersion of such particles in water at pH 7 to obtain an ionic magnetic fluid.

2. Experiment

2.1. Synthesis

In a typical experimental procedure, stoichiometric aqueous mixtures of cobalt(II) nitrate ($\text{Co}(\text{NO}_3)_2$) and iron(III) nitrate ($\text{Fe}(\text{NO}_3)_3$) were prepared with a total concentration of $10^{-1} \text{ mol L}^{-1}$. Sodium hydroxide (NaOH , 10 mol L^{-1}) was added to increase the pH to 13 under vigorous stirring [22]. The mixture was stirred for 1 h at room temperature and then transferred in the Teflon vessel of an autoclave (also called a “bomb”, purchased from Parr Instrument Co.). The autoclave was then introduced to an oven at 100 or 200 °C. The oven was heated during variable incubation times ranging from 2 to 120 h. The precipitate obtained after the temperature of the suspension naturally fell to room temperature was isolated, then dispersed in an aqueous solution of hydrochloric acid (10 min, $(\text{HCl})=0.2 \text{ mol L}^{-1}$). Citrate ions were then added as described in a previous study [23]. At the end of this process, the precipitate was washed several times with acetone and ether and finally dispersed in distilled water, producing a colloidal dispersion of nanoparticles stable at pH 7.

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2.2. Characterization

Information on all the samples is presented in Table 1. They were characterized by X-ray diffraction (XRD) using a Appareil with monochromatic high-intensity Cu K_{α} radiation ($\lambda=1.5418 \text{ \AA}$), transmission electronic microscopy (TEM) and magnetization measurements. The average particle size D_{RX} was determined by Scherrer's formula using the halfwidth of the (3 1 1) XRD line. Particle size was also determined from TEM images obtained in a JEOL 100 CX2 apparatus.

TEM images of the cobalt ferrite particles obtained using the process described by Massart et al. (alkaline coprecipitation of a

stoichiometric mixture of Fe(III) and Co(II)) was compared with the particles obtained by the hydrothermal process as a function of temperature and maturation time (Fig. 1).

3. Results and discussion

3.1. Particle morphology

When the temperature of the oven was set close to the temperature used in Massart's synthesis (100 °C, sample B), the

Table 1
Characteristic size of cobalt ferrite nanoparticles.

Hydrothermal step	D_{rx} (nm)	D_{tem} (nm)	σ_{tem}	d_{LF} (nm)	D_0 (nm)	σ
Sample A	9.2	11.9	0.26	15	7.01	0.41
Sample B	10.0	12.9	0.22	13.3	6.79	0.39
Sample C	200 °C, 2 h	14.4	0.19	–	–	–
Sample D	200 °C, 24 h	11.2	17.6	0.18	–	–
Sample E	200 °C, 120 h	13.3	18.7	–	–	–
Sample F	200 °C, 24 h, with citrate ions	12.6	15.2	0.24	–	–

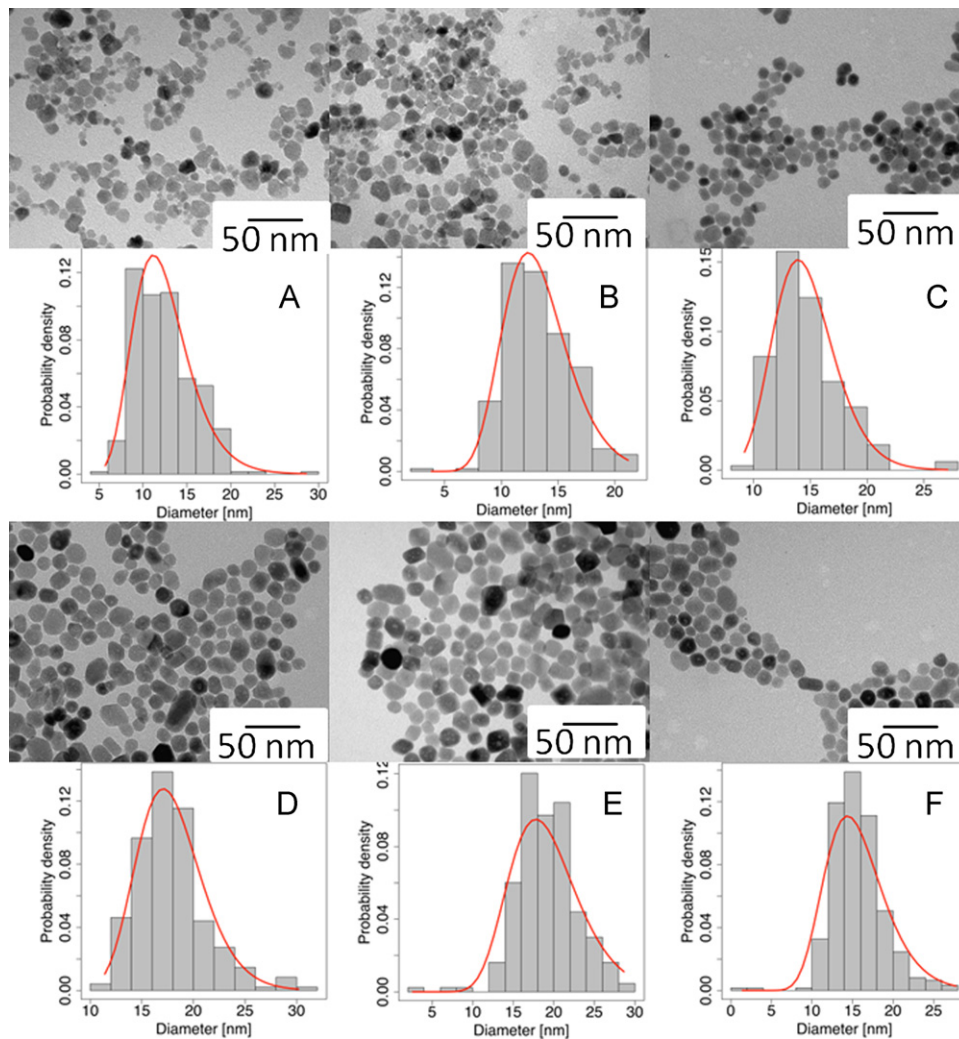


Fig. 1. TEM pictures and corresponding histograms. (A) Sample A: classical heating at 100 °C for 1 h; (B) sample B: hydrothermal treatment at 100 °C for 1 h; (C) sample C: hydrothermal treatment at 200 °C for 1 h; (D) sample D: hydrothermal treatment at 200 °C for 24 h; (E) sample E: hydrothermal treatment at 200 °C for 120 h and (F) sample F: hydrothermal treatment at 200 °C for 24 h in the presence of citrate ions (5%).

particle morphology did not seem to change compared to the classical particles (sample A). However the size increased and polydispersity was slightly improved by the hydrothermal process. When the temperature of the oven was increased to 200 °C, the polydispersity decreased, especially for short maturation times, as can be seen in Fig. 1 (sample C). The nanoparticles obtained with the autoclave treatment are more spherical than the nanoparticles obtained without the hydrothermal treatment, which are usually described as rock like (Fig. 1, sample A). The mean size of the particles obtained after the hydrothermal treatment was around 17 nm, which is slightly larger than the mean diameter of the particles obtained with the usual coprecipitation process. This behaviour is probably due to the Oswald ripening process [24].

When the hydrothermal step is longer (120 h, sample E), the cobalt ferrite particles become more and more cubic. This shape is the most stable product, as Bao et al. [25] discussed.

The crystal structure of the cobalt ferrite nanoparticles was characterized by powder XRD (Fig. 2). All the peaks can be indexed to the spinel structure of CoFe_2O_4 (JCPDS N° 22–1086). The X-ray powder diffraction patterns of the samples proved their crystalline nature [26].

The presence of species such as citrate ions in the synthesis mixture decreases the particle size, as observed in Massart's procedure (Fig. 1F) [21].

3.2. Magnetic properties

The magnetic properties of the cobalt ferrite magnetic fluid were measured either by a SQUID system or by a vibrating sample magnetometer at room temperature (Figs. 3 and 4).

The room temperature magnetization vs. field curves, measured up to $\mu_0 H \sim 1$ T and normalized by the sample volume fraction magnetization, are shown in Fig. 3 for samples A, B and D. They are reversible (no hysteresis), as expected for superparamagnetic nanoparticles, except for sample D, which shows a slight hysteretic behavior limited to the moderate field region ($500 \text{ G} < \mu_0 H < 4000 \text{ G}$)

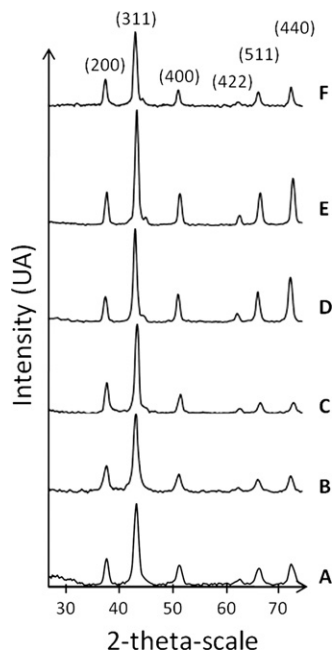


Fig. 2. XRD pattern of the cobalt ferrite nanoparticles. (A) Sample A: classical heating at 100 °C for 1 h; (B) sample B: hydrothermal treatment at 100 °C for 1 h; (C) sample C: hydrothermal treatment at 200 °C for 1 h; (D) sample D: hydrothermal treatment at 200 °C for 24 h; (E) sample E: hydrothermal treatment at 200 °C for 58 h and (F) sample F: hydrothermal treatment at 200 °C for 120 h.

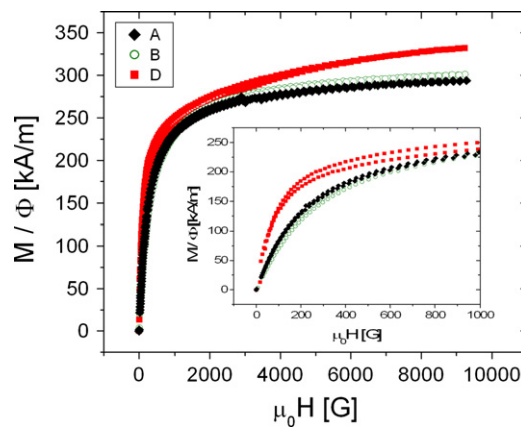


Fig. 3. Magnetization vs. magnetic field curves measured at room temperature for cobalt ferrite nanoparticles prepared at 100 °C (samples A and B) and obtained after hydrothermal treatment at 200 °C for 24 h (sample D).

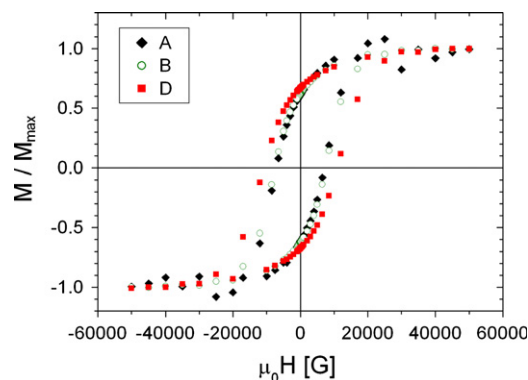


Fig. 4. Hysteresis loops measured at 5 K for cobalt ferrite nanoparticles prepared at 100 °C (samples A and B) and obtained after hydrothermal treatment at 200 °C for 24 h (sample D).

attributed to a probable reversible field-induced texturing (chaining) [27]. Moreover, for cobalt ferrite nanoparticles obtained after hydrothermal treatment at 200 °C (sample D), the magnetization reaches its maximum sooner than for particles prepared at 100 °C, in agreement with an increase in the particle size. In order to extract quantitative information about the particles size from the magnetization curves, we tried to fit our data with a size distribution weighted magnetization using a log-normal size distribution function [28]. This analysis gave good results for samples A and B ($d_0 \sim 7$ nm, $\sigma \sim 0.4$) but failed for sample D, the quality of the fitting being pretty bad especially in the shoulder region. To overcome this difficulty we limited our analysis to the low field region ($\mu_0 H < 60$ G) and extracted an averaged low field diameter $d_{LF} = (\langle d^6 \rangle / \langle d^3 \rangle)^{1/3}$ from the slope of the magnetization curves. The values are listed in Table 1 and indeed confirm a larger size for sample D compared to samples A and B.

To investigate the coercivity of our particles, we performed hysteresis loop $M(H)$ measurements on a commercial Quantum Design MPMS55 SQUID at 5 K. The results (normalized by maximum magnetization) are shown in Fig. 4 for the same three samples as discussed before. A slight increase in the coercive field ($H_c = 10.5$ kOe compared with 7 kOe) may be due to an interplay between a size enhanced magnetic anisotropy energy and a modification of the crystallinity is observed for cobalt ferrite nanoparticles obtained after hydrothermal treatment at 200 °C [29].

Finally, as ferrite nanoparticles are interesting for their magneto-optical properties, we investigated their birefringence

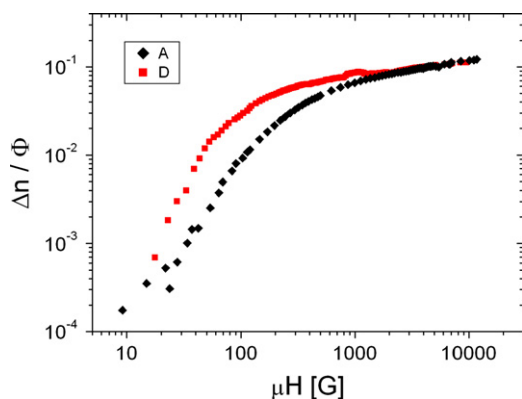


Fig. 5. Birefringence vs. magnetic field curves measured at room temperature for cobalt ferrite nanoparticles prepared at 100 °C (samples A and B) and obtained after hydrothermal treatment at 200 °C for 24 h (sample D).

properties using a home-made setup [30]. The results (birefringence normalized by the maximum birefringence) are shown in Fig. 5. As in the case of magnetization measurements, the birefringence of sample D reaches saturation sooner than that of sample A. This is certainly due to an enhanced coupling of the sample D particles with the magnetic field either because of their larger size or because of a possible chaining of the particles indeed expected for large particles [31].

4. Conclusions

In conclusion, adding a hydrothermal treatment to Massart's procedure enables cobalt ferrite-based ionic magnetic fluid to be obtained with nanoparticles characterized by an increased size and an improved dispersity. The increase in the particle size is smaller for the cobalt ferrite nanoparticles than for the maghemite particles. In all cases, the nanoparticles obtained after hydrothermal treatment may be dispersed in aqueous solvent by the classical procedure for ionic magnetic fluids.

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