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Comparative study of magnetite and cobalt ferrite submicron particles

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Colloidal magnetic particles based on magnetite and cobalt ferrite were prepared and characterized aiming to reveal their suitability for several applications, especially in the biomedical field and biotechnology. Sodium oleate ($C_{17}H_{33}COONa$) shell was intended to stabilize the magnetic particles into the aqueous suspensions in order to get stable ferrofluids by preventing the agglomeration in gravitational but especially in magnetic field gradients. The application of usual physical methods (X-ray powder diffraction, vibrating sample magnetometry and scanning electron microscopy (SEM)) allowed the assessing of some material features. The Bragg reflection curves showed the pattern characteristic of the cubic spinel structure and the specific size for both ferrophase samples. The magnetization curves and ferrophase volume fraction were comparatively discussed. The SEM image analysis evidenced the good granularity of both magnetite and cobalt ferrite.

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1. Introduction

Submicron magnetic particles elicited a growing interest in last decades due of their wide application in the domain of nanostructured material technologies [1].

The first aqueous magnetic fluid based on magnetite was synthesized in 1938 by Elmore [2], but extensive research on magnetic fluids started around 1960 with Rosensweig [3] and Papell [4] that prepared the ferrophase by size reduction, and further coating either with oleic acid- for oily final products- or with perchloric acid or tetramethylammonium hydroxide- for aqueous products.

Various reports stated that stable ferrofluids requires suspended particle size in the range of 10-30 nm. The supermagnetic behavior [5-6] was found to underlie the possibility of magnetic control and monitoring of ferrofluids intended for most technical and biomedical applications. Surface properties of magnetic particles should be controlled according to the main goal of the designed utilization considering possible interactions with specific environment whether vacuum, gas, liquid or biological tissues [5-7]. Interparticle magnetic interactions are critical factors governing ferrofluid behavior in different situations. With proper surface coating, the magnetic nanoparticle suspensions that can be used in medicine and medical research represent biocompatible ferrofluids [8-9]. Among the first biomedical utilizations of aqueous ferrofluids one can find the positioning tamponade for retinal detachment repair in eye surgery [10-11] and the improved magnetic resonance imagery (MRI) for diagnostic with iron based contrast agents [12]. In the last decades it has also been reported that ferrofluids can assist cancer therapy when combined with an external AC magnetic field application [13-14].

This paper present the preparation and characterization of two ferrofluids based on magnetite and cobalt ferrite co-precipitated in accord with Massart method [15-17], further peptization using an appropriate particle surface treatment whith sodium oleate being carried out at high temperature.

2. Experimental

2.1 Ferrofluid preparation

Magnetite and cobalt ferrite have been prepared by chemical co-precipitation from hydrated $FeCl_3$, $FeCl_2$ and respectively $FeCl_3$ and $CoSO_4$ solutions in their respective stoichiometry.

$$xM_{aq}^{2+} + (1-x)Fe_{aq}^{3+} \xrightarrow{OH} MFe_2O_4.$$

where M is either Fe or Co.

Experimental conditions of this reaction, such as temperature, molar ratio x of divalent metal, pH of the reaction medium, nature and concentration of the cations [18-19], are the parameters determining the synthesis efficiency and the particles-size distribution.

During mixing and heating of metal salt solutions at 80^0C, boiling solution of NaOH was poured slowly. The temperature of 80^0C maintained for 1h duration is believed to represent an essential factor for the precipitation of iron oxides into spinel ferrite structure. The particles were washed several times with distilled water and dried at room temperature. Ferrophase coating with surfactant – sodium oleate - was carried out at a temperature of about 80^0 C, colloidal submicron particles being further dispersed in water**.** The samples remained stable for two months.

2.2 X-ray analysis

Spinel structure of precipitates is identified by X-ray powder diffraction. XRD investigation was accomplished using Shimadzu XRD 6000 device with CuKα radiation.

2.3 Magnetization measurement

Magnetization measurements were performed using a vibrating sample magnetometer ***Quantum Design, model 6000*** on native ferrofluid samples. Using magnetization data, the average sizes of magnetic diameter was calculated following Langevin's equation. The size of large particles, which are influenced by low magnetic field, assuming a spherical particle shape, can be calculated with the formula:

$$d_m{}^3 = \frac{18K_BT}{\pi\mu_0 M_S M_\infty}\left(\frac{dM}{dH}\right)_{H\to 0} \qquad (1)$$

where d_m is the magnetic particle diameter, k_B is Boltzmann's constant, T is the absolute temperature, Ms is the saturation magnetization of the sample, μ_0 is the permeability of vacuum, and for the M_∞ value of bulk magnetite was utilized $0.48{\cdot}10^6$ A/m [20].

2.4 SEM analysis

The scanning electron microscopy (SEM) was used to characterize the shape and average size of submicron magnetic particle powders.

2. Results and discussion

The magnetic fluid samples prepared as described above were dark brown materials that exhibited obvious magnetic behavior in the presence of a permanent magnet.

As the particle size plays a fundamental role in both magnetic and magneto-optical behavior, it is very important to perform a careful characterization of powder granularity. Investigations of the submicron particles by X-rays diffraction [21] constitute an additional method in order to confirm the crystalline structure. X-ray diffraction measurements were carried out on powder samples obtained through the evaporation of the liquid reaction medium.

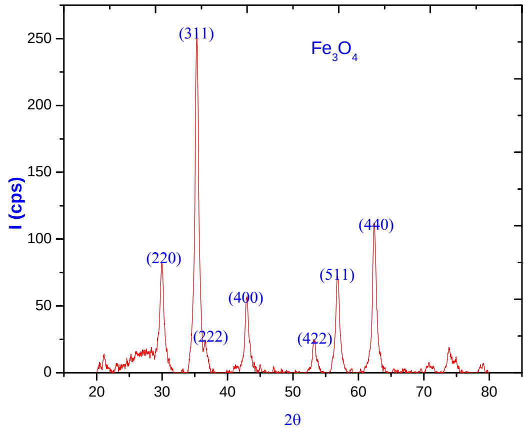


Fig. 1. XRD patterns of Fe_3O_4.

Figs. 1 and 2 show XRD patterns for Fe_3O_4 and $CoFe_2O_3$ samples. As one can see they both exhibit several diffraction lines corresponding to the characteristic interplanar spacing [220], [311], [400], [511] and [440] of the spinel structure.

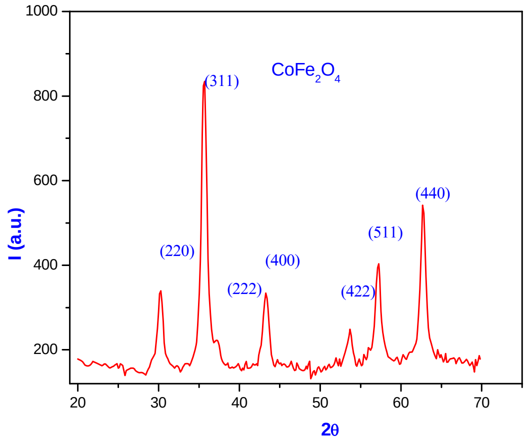


Fig. 2. XRD patterns of $CoFe_2O_3$.

The broadening of the peaks which arises from the finite dimension of the crystal is essentially due to the roughly spherical particle diameter, being assessed according to the Debye- Scherrer equation:

$$D_x = \frac{K\lambda}{\Delta\cos\theta} \qquad (2),$$

where K= 0.9 is a correction factor to account for particle shapes, θ is the Bragg angle and Δ is the observed breadth at half the maximum peak intensity.

The crystallite diameter, D_x, of the samples was found equal to:

$$D_{Fe_3O_4} = 8 \text{ nm}$$
$$D_{CoFe_2O_3} = 5 \text{ nm}.$$

The VSM is based upon Faraday's law according to which an electromagnetic field is induced in a conductor by a time-varying magnetic flux.

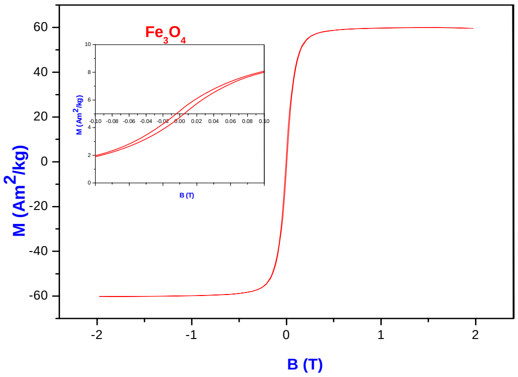


Fig. 3. Hysteresis loop for Fe_3O_4 at 5 K. The inset shows the field scan from −2 to +2 T with the corresponding specific magnetization values.

In VSM, a sample magnetized by a homogenous magnetic field is let to vibrate sinusoidally at small fixed amplitude with respect to stationary pick-up coils. The recorded voltage is thus a measure of the magnetic moment of the sample. In this study, the VSM was used to record hysteresis plots of the magnetic powders. Typical hysteresis plots obtained from VSM are shown in Figs. 3 and 4.

Saturation magnetization is considerably higher in the case of magnetite (60 Am^2/kg) in comparison to cobalt ferrite (0.1 Am^2/kg) which is in concordance with the powder structure and composition.

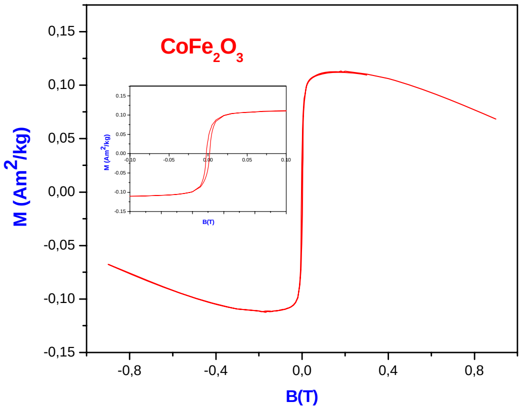
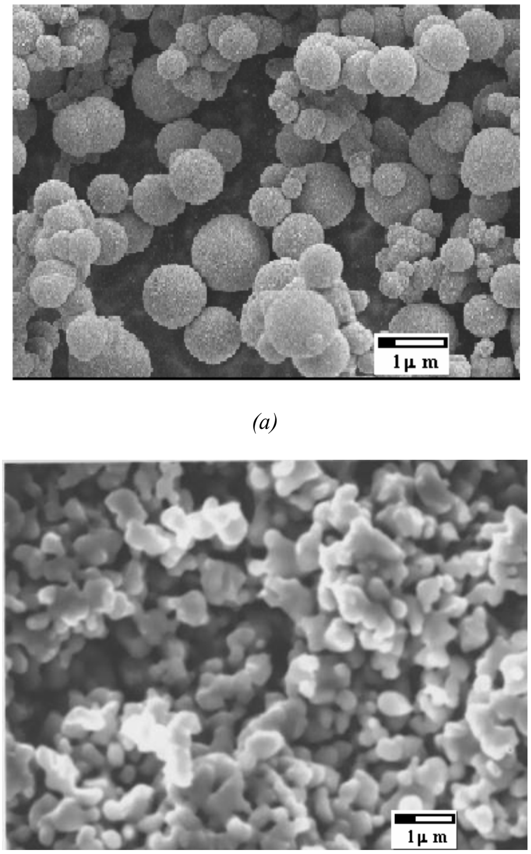


Fig. 4. Hysteresis loop for $CoFe_2O_3$ at 5 K. The inset shows the field scan from −0.15 to +0.08 T with the corresponding specific magnetization values.



(a)

(b)

Fig. 5. (a) SEM images of magnetite and (b) cobalt ferrite (down) powders.

The volume fraction Φ of ferromagnetic phase particles in the magnetic fluid samples was determined from mass density measurement according to the equation:

$$\phi = \frac{\rho_F - \rho_L}{\rho_S - \rho_L}, \tag{3}$$

where ρ_F is the density of the magnetic fluid, ρ_L is the density of the carrier liquid, and ρ_S is the density of the solid particles.

Ferophase volume fraction for $CoFe_2O_3$ was found equal to 0.11 while for Fe_3O_4 it was equal to 0.13.

The SEM micrographs presented in Fig. 5 revealed that the investigated particles are mostly spherical. Magnetite particles diameter ranged between 0.2 μm and 1.1 μm while cobalt ferrite particles are characterized by physical diameters between 0.1 μm and 0.7 μm. Rare particle agglomerations could be seen in the first situation involving mainly small particles. In the second case also short particle chains could be seen within the investigated samples. From magnetization curves the average magnetic diameter was calculated according to Langevin's formula, the values obtained for magnetite and cobalt ferrite being of about 31.9 nm and respectively 13.9 nm.

3. Conclusions

Both magnetic powder samples are characterized by submicron physical diameters with finest granulation for cobalt ferrite material. The crystallite diameter was found at nanometric size by XRD analysis while the magnetic diameter was evidenced to be one order of magnetite higher but smaller than the physical one. In both cases the submicron sizes and magnetic properties as well as the stability in environmental field gradients allow to assume that the colloidal nanostructures such as magnetite nanoparticles coated in sodium oleate can be used in various technical or bio-medical applications.

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