

# Characterization of Magnetite Nanoparticles Obtained by Chemical Coprecipitation

Dragoș-Viorel Brezoi, Gheorghe Ioniță, Rodica-Mariana Ion

Universitatea Valahia din Târgoviște, Bulevardul Unirii Nr.18-20, Târgoviște, România  
e-mail: dragosh\_brezoi@yahoo.com

## Abstract

*This work aims to analyze the properties of nano-sized magnetite obtained by chemical coprecipitation: morphology and phase, average size of particles, and magnetic properties. For future biomedical applications like magnetic biofunctional material vectors to target tissues, the magnetite particles obtained have to be spherical with 10 nm average diameter. Magnetic properties obtained (saturation magnetization  $M_s$  and coercitivity field  $H_c$ ) are proper for superparamagnetic character of these nanoparticles.*

**Keywords:** magnetite, coprecipitation, nanoparticles

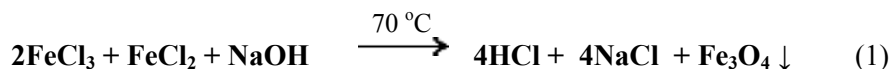
## Introduction

Magnetite is a material which shows no magnetic degradation. Thus, ferrofluids made of magnetite nanoparticles are magnetically stable and are proper to be used for bio-applications. Is very attractive to use magnetic nanoparticles in medicine because its exhibit dimensions similar to those of biomolecules, such as proteins (enzymes, antigens, and antibodies) or DNA. This offer the possibility to be in contact with a biological entity. Magnetite nanoparticles can be manipulating by application a magnetic external field and thus, these can be used to transport anti-tumor substances (transport agent for chemotherapy) to a target zone in organism like tumor tissues [17].

A more convenient process to produce magnetite nanoparticles is chemical coprecipitation. In 1925, Welo and Baudisch has studied phase transformation of iron oxide with temperature [12]. The original process has been established by Khalafalla and Reimers in 1973. The most common iron salts used in chemical coprecipitation are  $\text{FeCl}_2$  and  $\text{FeCl}_3$ , but we have used ferric nitrate in place of  $\text{FeCl}_3$  in other work [1]. Reaction temperatures range from room temperature to 100 °C with reported nanoparticle's diameter ranging from 2 nm to 50 nm [1-6, 9-11, 13-16]. D.K. Kim, M. Mikhaylova, Y. Zhang, and M. Muhammed reported that temperature is a major factor in controlling particle size [12], but some studies on hydrolysis of ferric and ferrous salts indicated that both pH and temperature had a simultaneous effects [4, 15].

## Experimental

A wet chemical method was adopted to prepare the nanosized magnetite. We have used: ferrous chloride tetrahydrate  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , ferric chloride anhydrous  $\text{FeCl}_3$ , sodium hydroxide anhydrous  $\text{Na}(\text{OH})$ , poly(vinyl alcohol)  $(\text{CH}_2\text{CHOH})_n$ , and oleic acid  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , all were purchased from Aldrich and Merck. In all experiments it has been used distilled water. The experimental conditions have selected based on literature [3-6, 9-16]: temperature was kept constant at  $70^\circ\text{C}$ , stirring 15 minutes, and  $[\text{Fe}^{2+}] = 1.8\text{ M}$  with  $[\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 1$ . The synthesis is based on classic reaction of coprecipitation (1), by mixing ferric (2.650 g) and ferrous chloride (4.474 g) in 25 ml distilled water with 5 g  $\text{NaOH}$  dissolved into 250 ml distilled water (precipitation agent):



Then, it was added few drops of oleic acid (OA) like surfactant into the magnetite suspension already prepared, and sonicated at 50 % amplitude for 30 s. Due to the presence of the surfactant, the particles will be covered by a protection layer during the mixing process and minimize the agglomeration tendency of magnetite nanoparticles. The precipitate was decanted with a permanent magnet and washed with distilled and deoxygenated water. The magnetite was dried in an oven at  $90^\circ\text{C}$  till it's formed a fine powder of constant weight ensuring the absence of water or oleic acid.

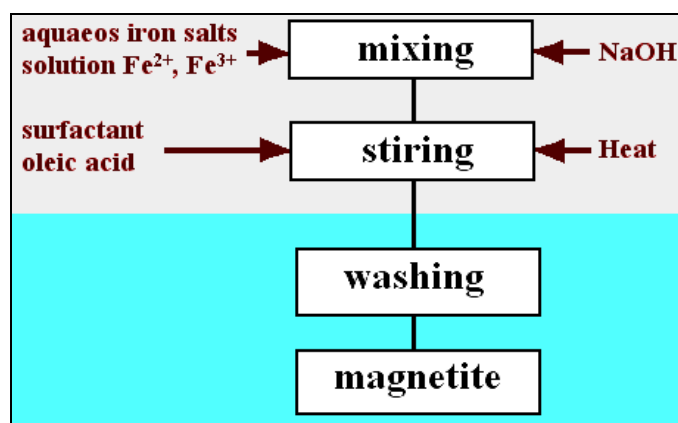


Fig. 1. Synthesis of magnetite nanoparticles by chemical coprecipitation

Some analytical techniques as: X-ray diffraction (XRD), atomic force microscopy (AFM), vibrating sample magnetometer (VSM) and UV/Vis absorbance spectroscopy have been used to characterize the magnetite powder obtained.

## Results and Discussion

### Properties of nanoparticles

#### Morphology and phase

XRD spectra from samples 1 and 2 are shown in Fig. 2, which are representative data of magnetite only. We have used Scherrer's equation applied on (311) peak to calculate average size for the magnetite particles [15]:

$$d = k\lambda [L_{1/2} \cos \Theta]^{-1} \quad (2)$$

where  $d$  = particle's average diameter,  $k = 0.9$ ,  $\lambda = 1.5418 \text{ \AA}$  (for  $\text{CuK}\alpha$  X-Ray source at 35 kV),  $\Theta$  = peak position and  $L_{1/2}$  = effective full width half maximum of peak (311).

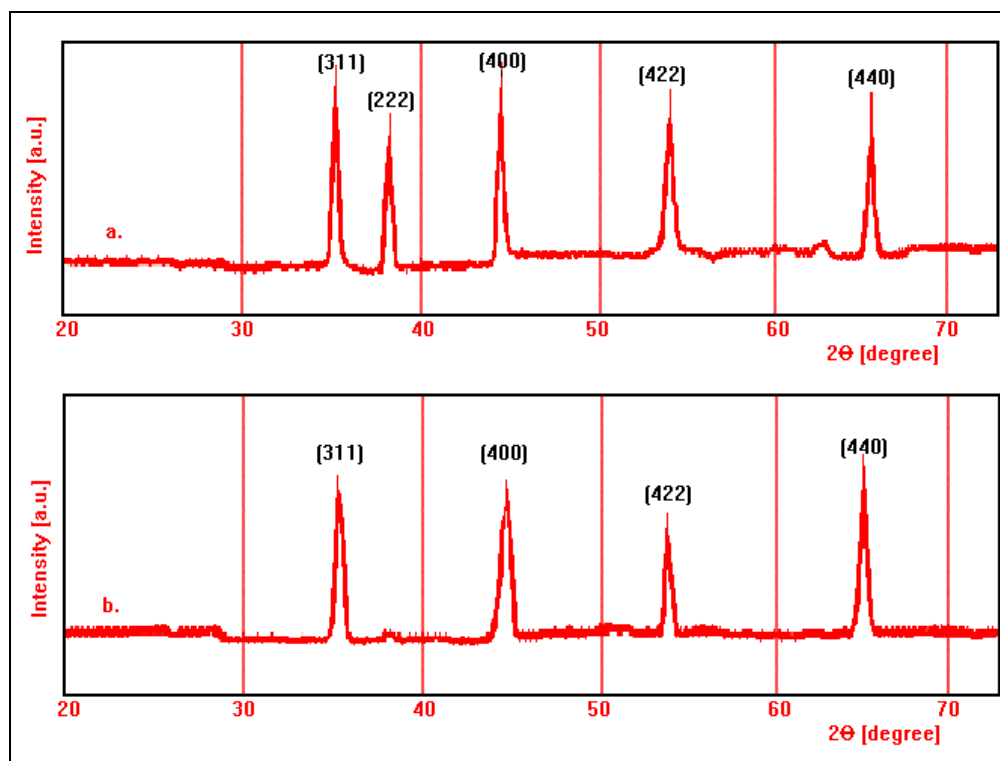
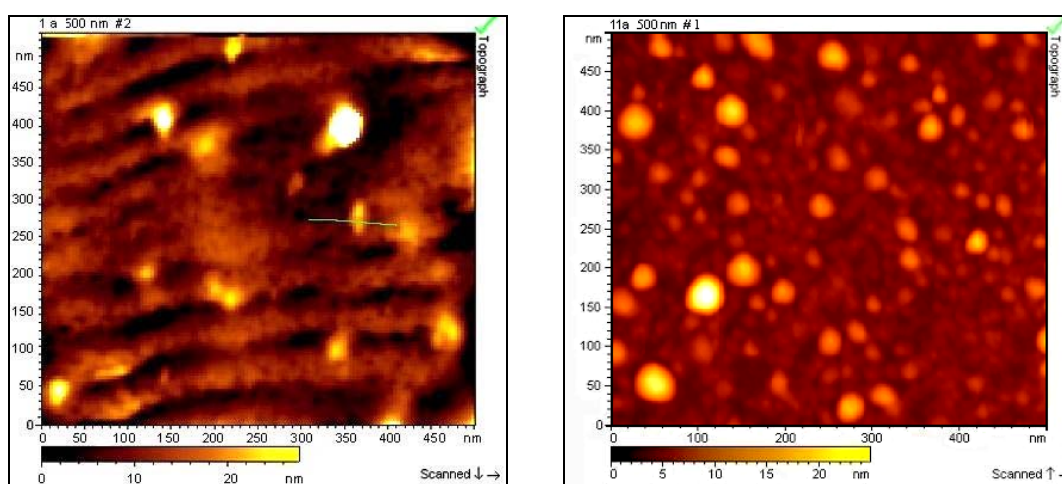


Fig. 2. XRD spectra of the samples: (a) 1 and (b) 2

We have realized AFM imaging to validate the results regarding average size of particles. It has been deposited the magnetite powder on a glass slice (1.5 cm length, 1.5 mm thick, and 1 cm width). We have used the vibrating mode with cantilever oscillating at its resonance frequency, which minimize the damage on the sample surface. The measurement has been taken in the low amplitude mode.



a) sample 1, "vibrating mode"

b) sample 2, "vibrating mode"

Fig. 3. AFM images,  $500 \times 500 \text{ nm}$

All AFM images of this work are presented directly as we were taken and were not manipulated by using filters or other mathematical transforms. The AFM images for: (3 a) sample 1 (dried magnetite into exicator, at room temperature); (3 b) sample 2 (magnetite with oleic acid, dried into drying ovens) show spherical particles aleatory deposited on surface, without tendency to agglomerate. With help of X'Pert Software, it was calculated the average diameters of particles and this was 11 nm.

### UV-Vis absorption diffuse-reflectance spectroscopy

Magnetite powder sample needs a special preparation because is black. We have used white MgO powder and mixed with magnetite black powder. Magnetite spectrum (Fig. 4.) show absorption band in UV region at 208, 220, 233 nm due  $\text{Fe}^{3+}$  tetrahedral coordinated and 278 nm due  $\text{Fe}^{3+}$  ions octahedral coordinated. The bands from 242 and 333 nm are generated by the intervalence charge transfer transitions due the electronic delocalization between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions from magnetite [7].

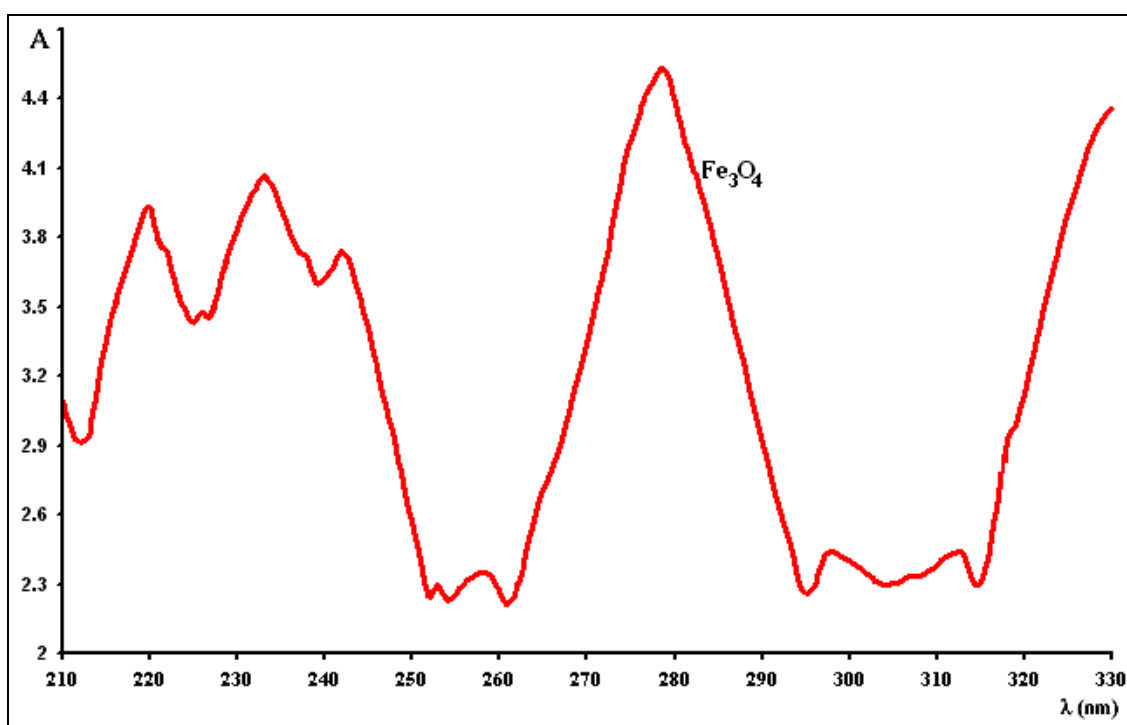


Fig. 4. UV absorption spectrum of magnetite (sample 1)

### Magnetic properties

We have determined the magnetic properties (saturation magnetization,  $M_s$ , and coercivity field,  $H_c$ ) on the solid sample of magnetite (powder dried in an oven for AO elimination) mixed with PVA and pressed into pellets. All VSM measurement was made at room temperature.

A bulk magnetite is ferromagnetic but a nanoparticle is superparamagnetic if the average size (diameter) is around 10 nm. In the figure 5a (sample 1) it is no histerezis: remnant magnetization was  $M_r = 56$  emu/g and coercivity field was  $H_c = 0.75$  Oe can be approximated at zero. Therefore, at room temperature, magnetite nanoparticles were superparamagnetic.

For the sample 2 (figure 5b), magnetic properties were  $M_r = 53$  emu/g and  $H_c = 1.26$  Oe, due the anisotropy: magnetite nanoparticles was separated by OA surfactant and even thermal elimination affected superparamagnetic character.

The AFM images clearly show that the nanoparticles are polydisperse and average size of diameter is 11 nm, and this is the second condition for superparamagnetism character.

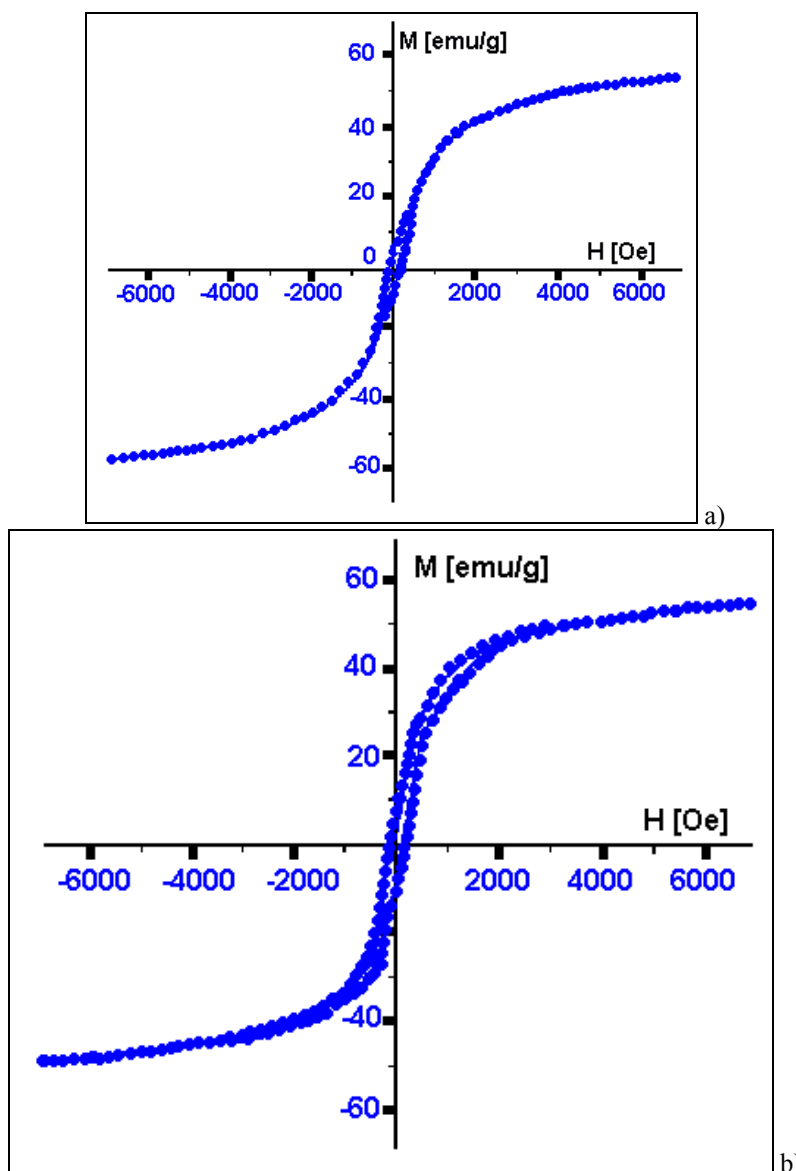


Fig. 5. Magnetization curves for: (a) sample 1; (b) sample 2

## Conclusions

It was obtained magnetite nanoparticles by chemical coprecipitation using mixed ferric and ferrous salts at low temperature. Magnetic properties obtained (saturation magnetization,  $M_s$  and coercivity field,  $H_c$ ) are proper for superparamagnetic character of these nanoparticles. For all samples, the measured values of properties (average diameter and magnetic properties,  $M_s$  and  $H_c$ ) are shown in Table 1.

Table 1. The measured properties of all samples

Sample	d [nm]	$M_s$ [emu/g]	$H_c$ [Oe]
1	10.8	56	0.75
2	10.3	53	1.25

## Acknowledgments

The authors wish to acknowledge the technical support of LOT Oriel Darmstadt and ICECHIM Bucharest.

## References

1. D.V. Brezoi, R.M. Ion, *Sensors and Actuators B: Chemicals*, vol.109-1, pp. 171, 2005;
2. D.V. Brezoi, R.M. Ion, *Proc. ROMAT*, pp. 235, 2004;
3. R.M. Cornell and U. Schwertmann, *The Iron Oxides*, 2nd ed. Weinheim: Wiley-VCH Verlag GmbH & Co., 2003;
4. R. Massart, *IEEE Transactions on Magnetics*, vol. 17, pp. 1247, 1981;
5. Y.S. Kang, S. Risbud, J.F. Rabolt, P. Stroeve, *Chemistry of Materials*, vol. 8, pp. 2209, 1996;
6. S.H. Gee, Y.K. Hong, D.W. Erickson, M.H. Park, J.C. Sur, *Journal of Applied Physics*, vol. 93, pp. 7560, 2003;
7. A.B.P. Lever, *Inorganic electronic spectroscopy*, Amsterdam: Elsevier, pp. 862, 1984;
8. S. Qu, H. Yang, D. Ren, S. Kan, G. Zou, D. Li and M. Li, *Journal of Colloid and Interface Science*, vol. 215, pp. 190, 1999;
9. C.-Y. Hong, I. J. Jang, H. E. Horng, C. J. Hsu, Y. D. Dao and H. C. Yang, *Journal of Applied Physics*, vol. 81, pp. 4275, 1997;
10. L. Vayssieres, C. Chaneac, E. Tronc and J. P. Jolivet, *Journal of Colloid and Interface Science*, vol. 205, pp. 205, 1998;
11. L.A. Welo and O. Baudisch, *Philosophical Magazine*, vol. 50, pp. 399, 1925;
12. Z.L. Liu, Y. J. Liu, K. L. Yao, Y. H. Ding, J. Tao and X. Wang, *Journal of Materials Synthesis and Processing*, vol. 10, pp. 83, 2002;
13. D.K. Kim, M. Mikhaylova, Y. Zhang and M. Muhammed, *Chemistry of Materials*, vol. 15, pp.1617, 2003;
14. R.M. Cornell, U. Schwertmann, *The Iron Oxides*, Weinheim:VCH Verlagsgesellschaft, 1996;
15. J.E. Otterstedt, D.A. Brandredth, *Small Particles Technology*. New York: Plenum Press, 1998;
16. B. D. Cullity, *Elements of X-Ray Diffraction*, 2nd ed. Reading: Addison-Wesley Publishing Co., 1978;
17. Y. Zhu and Q. Wu, *Journal of Nanoparticle Research*, vol. 1, pp. 393, 1999;
18. Ion, R.M., *Nanocrystalline Materials*, Ed.FMR, Bucharest, 2003.

## Caracterizarea nanoparticulelor de magnetită obținute prin coprecipitare chimică

### Rezumat

Scopul acestei lucrări este de a analiza proprietățile magnetitei nanodimensionate obținute prin coprecipitare chimică: morfologie, fază, dimensiunea medie a particulelor și proprietățile magnetice. Pentru viitoare aplicații biomedicale, cum ar fi materialele magnetice biofuncționale care să vectorizeze medicamente către țesuturile bolnave, nanoparticulele de magnetită obținute trebuie să fie sferice cu diametrul mediu în jur de 10 nm. Proprietățile magnetice obținute (magnetizația de saturație,  $M_s$ , și câmpul coercitiv,  $H_c$ ) denotă caracterul superparamagnetic al acestor nanoparticule.