

Soft Magnetic Materials in the Form of Nanosized Metal Oxides in Stable Suspension

D.E. CREANGA, M. OPRISAN, C. NADEJDE, V.NICA M. RACUCIU,

University Alexandru Ioan Cuza, Physics Department, 11 Blvd. Carol I, Iasi, Romania, e-mail:mdor@uaic.ro

University Lucian Blaga, Science Faculty, Sibiu, Romania

Abstract — The study presented in this paper is focused on the stabilization of metal oxide nanoparticles in aqueous suspensions in the form of soft magnetic materials, i.e. water based ferrofluids. Magnetic nanoparticles of Fe₃O₄, CoFe₂O₃, ZnFe₂O₄ and Mn_{0.5}Zn_{0.5}Fe₂O₄ were prepared by chemical coprecipitation in alkali medium. Fine granularity and spinel crystallinity properties were evidenced in all samples by Atomic Force Microscopy and X-ray diffractometry while superparamagnetic properties were investigated by means of vibrating sample magnetometry; significant coercitivity field was found only for cobalt ferrite nanoparticles. The stabilization of various types of magnetic grains in water was possible due to the sodium oleate coating shell – an organic molecule with biocompatibility features – enabling the producer to ensure the hydrophobic repulsion balance with magnetic attraction among nanoparticles. Various levels of saturation magnetization for the nanoparticles prepared by the same basic protocol sustain the possibility of producing diverse ferrofluids for various biomedical applications: magnetically targeted drug delivery, contrast agent in magnetic resonance imaging, cancer experimental thermotherapy.

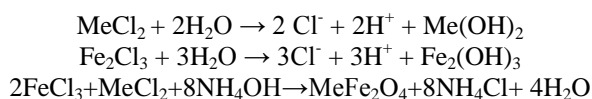
1. INTRODUCTION

Stable suspensions of nanoparticles (NP) with magnetic properties represent soft magnetic materials known also as ferrofluids. First the magnetite fine particles suspended in hydrocarbons were used in technical applications related to loudspeakers for heat removing, to magnetic control of spacecraft's attitude, to friction reducing in magnet gliding or as liquid seals around the spinning drive shafts in computer hard disks [1]. Later, aqueous ferrofluids were considered for biomedical applications as contrast agents in magnetic resonance imaging, for experimental cancer treatment by magnetic hyperthermia and also for magnetic targeting in controlled drug delivery [2]. One of most common preparation method is the chemical coprecipitation, still widely spread due to its availability and low cost; various changes in the physico-chemical parameters of the basic method developed by Massart [3] have resulted in derived preparation protocols that enable the producer to get low average size of magnetic particles and consequently high stability of the magnetic suspensions. Unlike the oily ferrofluids where ferrophase grains can be relatively successful stabilized in hydrocarbons using mainly the oleic acid, known for its strong interactions with iron ions [4, 5] the magnetic NP incorporation in water is more difficult, resulting usually in ferrofluids with lower NP volume fraction. Some results reported by us were focused on magnetite cores dispersed by coating with organic shells consisting in citric acid [6], tetramethyl ammonium hydroxide [7], tartaric acid [8], perchloric acid [9], beta-cyclodextrin [10] and others. In this paper we present comparatively the ferrofluids prepared in our laboratories as soft magnetic materials based on mixed metal oxides like Fe₃O₄, CoFe₂O₄, ZnFe₂O₄, Mn_{0.5}Zn_{0.5}Fe₂O₄ suspended as colloidal nanoparticles in deionized water.

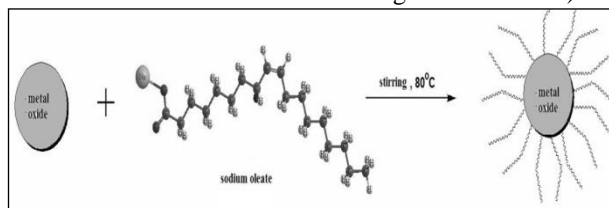
2. EXPERIMENTAL

2.1. Ferrophase preparation.

Pure crystallized metal salts, of Fe₂Cl₃·6H₂O, FeCl₂·6H₂O, CoCl₂·6H₂O, ZnCl₂·4H₂O, MnCl₂·5H₂O (purchased from Merck) were solved in deionized water in their respective stoichiometry (Me²⁺:Fe³⁺ =2:1). Then hot NH₄OH (25%) was poured as precipitating agent of magnetite nanoparticles under constant non-magnetic stirring at 80 °C for about for 1 h; this duration was considered sufficient for the transformation of hydroxides into spinel ferrite nanoparticles [11]. Magnetic NP were generated by conversion of metal salts into hydroxides and further transformation of hydroxides into mixed metal iron oxides:



The metal oxide nanosized powders precipitated as shown above were washed several times with up to 1.5 l deionized water to remove secondary reaction products. Finally the powders were decanted and separated on paper filter. Colloidal metal oxide nanoparticles (NPs) were yielded by using sodium oleate (1.7 g of C₁₈H₃₃NaO₂ in 15 ml deionized water for about 4.5 g of metal oxide).



Scheme 1. NP coating with sodium oleate shell

Sodium oleate was used for NP stabilization in water suspension (Scheme 1) as the best hydrosoluble substitute of oleic acid (soluble in hydrocarbons but insoluble in water) that is known as developing the strongest interactions with metal oxide NPs [4]; in the same time the biocompatibility of sodium oleate was also considered taking into account possible biomedical applications of coated nanosized metal oxides [12].

2.2. Microstructural and magnetic characterization

Dimensional and topological NP characterization was accomplished by Atomic Force Microscopy device (AFM) provided with commercial standard silicon nitride cantilevers (NSC21), having a force constant of 17.5 Nm^{-1} , 210 kHz resonance frequency and tip with radius of about 20 nm (intermittent contact, tapping mode cantilevers). The AFM images recorded in 2-dimensional (2-D) and phase modes, have dimensions of $1 \times 1 \mu\text{m}$. The NP suspension samples (5 ml diluted in 195 ml of deionized water) were deposited on glass substrate (microscope slides) and dried before scanning. Crystallinity features were studied by means of X-ray diffractograms (XRD) recorded by using a Shimadzu XRD 6000 device with $\text{Cu-K}\alpha$ radiation at 0.15418 nm between 20 and 80 degrees ($I = 25 \text{ mA}$, $U = 35 \text{ kV}$, 0.004 deg/step, 1.2 sec step duration) in Bragg–Brentano arrangement. XRD patterns were analyzed and indexed using Powder X software, commercially available. The crystallite size of nanocrystalline samples was measured from the X-ray line broadening analyses using Debye–Scherrer formula. Magnetometry investigations were carried out with a Quantum Design 600 vibrating sample magnetometer (VSM) at room temperature ($22.0 \pm 0.1^\circ\text{C}$). Magnetic core diameter was estimated from Langevin's theory.

3. RESULTS AND DISCUSSION

AFM scanning provided images (Fig. 1 a, b) on the NPs topology revealing mostly cvasi-spherical structures with rare agglomerations in the form of short chains of NPs. The AFM investigation was repeated on different sites of the studied sample, keeping the same conditions of room temperature and ambient atmosphere. The dominance of relatively low size nanoparticles (average values of about 20 nm) was evidenced though little number of aggregates (no more than 90 nm diameter size) was also noticed.

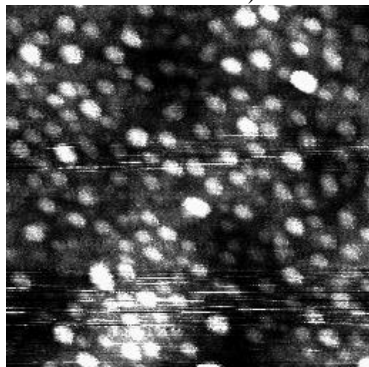


Figure 1 a. AFM 2-D image of cobalt ferrite NP

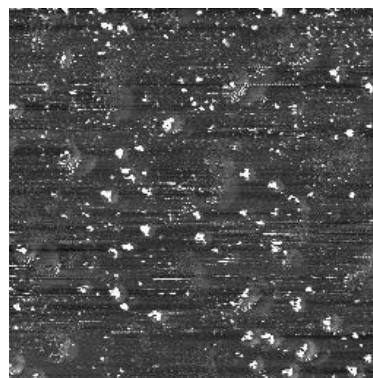


Figure 1 b. AFM phase recording image of magnetite NP

The limitation imposed by the radius of the AFM device scanning tip resulted in the missing of image capturing for NPs smaller than 20 nm. Largest NP size was noticed for cobalt ferrite probably because of lower efficacy of sodium oleate coating ability in the presence cobalt ions though there were not undoubtable proves for such hypothesis. Crystalline structure of the colloidal metal oxide NP was investigated by XRD technique the results being presented in Figure 2 a-d. The experimentally recorded XRD peaks were matched with the theoretically generated ones with no peak being left unindexed, evidencing the spinel structure within the various types of ferrite grains analyzed inhere. In the case of manganese-zinc ferrite some higher recording noise can be observed (Fig. 2d) affecting the apparent baseline. Applying the Debye-Scherrer theory the crystallite average size is given by:

$$D_{hkl} = \frac{0.94 \cdot \lambda}{B \cos \theta} \quad (1)$$

where λ is the X-ray wavelength θ is the Bragg angle and B is effective full width at half maximum of the XRD diffraction line with hkl indexes. In Table 1 the crystallite size, the NP diameter estimated by AFM and the magnetic core diameter from the magnetization data are given. The values of crystallite size resulted from XRD measurement are given by D_{XRD} which is ranging between 11.4 nm, for zinc ferrite and 13.6 nm for magnetite. Comparatively the AFM data provided larger values, i.e. D_{AFM} between 20.5 nm in the case of magnetite NP and 45.0 nm for cobalt ferrite grains.

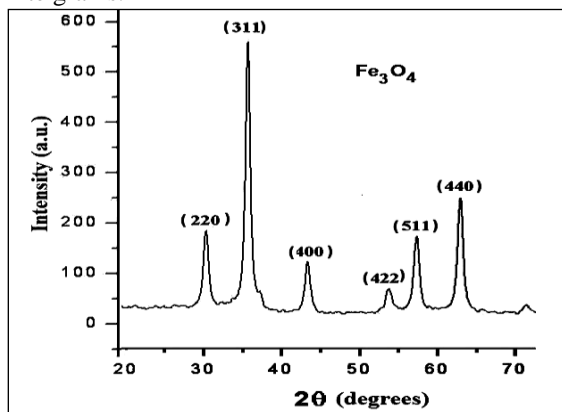


Figure 2 a. XRD diagram for colloidal magnetite NP

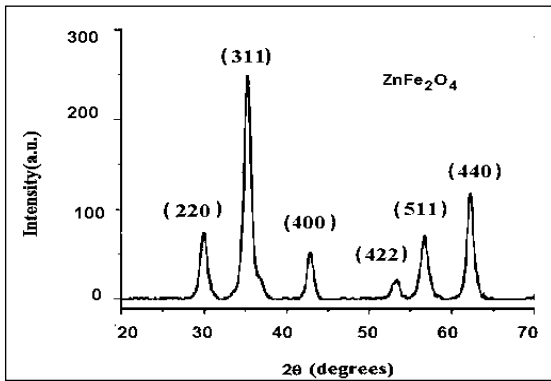


Figure 2 b. XRD diagram for colloidal cobalt ferrite NP

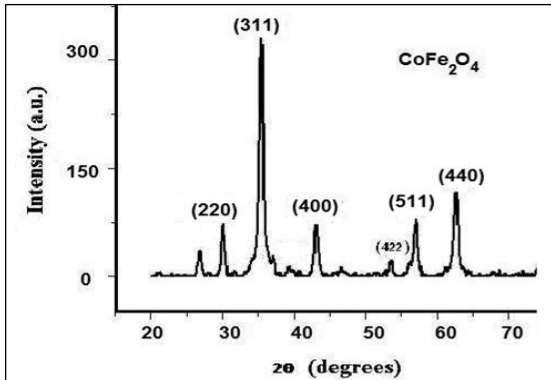


Figure 2 c. XRD diagram for colloidal zinc ferrite NP

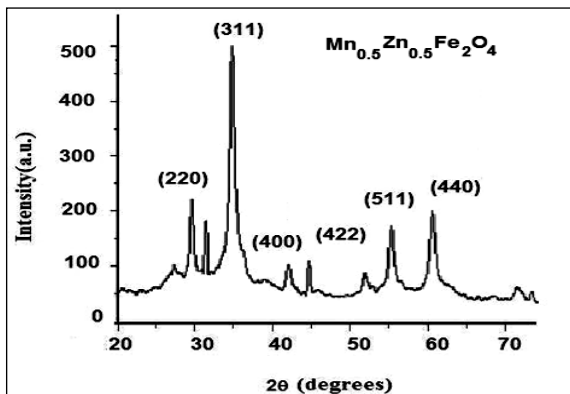


Figure 2 d. XRD diagram for manganese-zinc ferrite NP

Table 1. Dimensional data resulted from AFM, XRD and VSM investigations

SAMPLE	D _{AFM} (NM)	D _{XRD} (NM)	D _{VSM} (NM)
Fe ₃ O ₄	20.5	13.6	9.3
CoFe ₂ O ₄	45.0	13.0	8.9
ZnFe ₂ O ₄	20.0	11.4	9.8
Mn _{0.5} Zn _{0.5} Fe ₂ O ₄	20.3	12.2	9.7

The magnetization recordings (Fig. 3 a-d) shown mostly superparamagnetic behavior; coercivity magnetic field was zero for magnetite and zinc ferrite (Fig. 3 a, c) and almost zeroed for manganese zinc ferrite (Fig. 3 d) while for cobalt ferrite the coercivity field was significant (Fig. 3 b) – which could be probably associated with the higher size of grain average diameter. This suggests that the NP larger size (possible lower interaction of oleate ions with

metal cations) is reflected also in the magnetic features of the cobalt ferrite NP. Magnetization curves saturated at the highest value of mass density magnetization for magnetite colloidal NP (about 60 emu/g) - while for zinc ferrite and cobalt ferrite colloidal NP the corresponding values were respectively of about 26 emu/g and 20 emu/g. As known, in the cubic system of ferromagnetic spinels, the magnetic order is mainly due to a superexchange interaction mechanism occurring between the metal ions in the A and B sublattices. The substitution of nonmagnetic ion, which has as preferential A site occupancy results in the reduction of the exchange interaction between A and B sites – this resulting in the magnetic properties variation. From the magnetization curves the slope in the graph origin was assessed ((dM/dH)_{H→0}) and the largest magnetic diameter D_M was calculated following Langevin's equation:

$$D_M^3 = \frac{18 \cdot k_B T}{\pi \mu_0 \cdot M_S \cdot m_S} \left(\frac{dM}{dH} \right)_{H \rightarrow 0} \quad (2)$$

with D_M - magnetic diameter (D_{VSM}), k_B - Boltzmann's constant, T - absolute temperature, μ₀ - vacuum magnetic permeability, M_S - saturation magnetization of sample, m_S - saturation magnetization of the bulk ferrite [4].

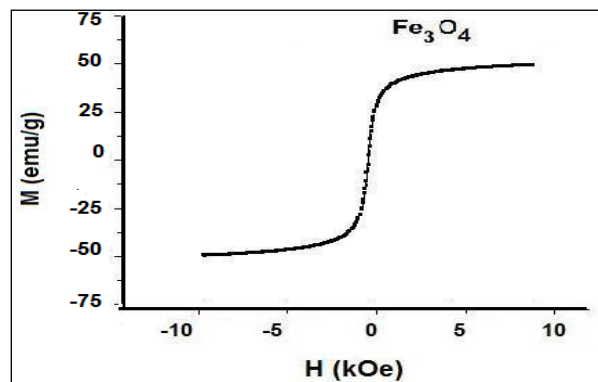


Figure 3 a. Magnetization curve for magnetite NP

Nevertheless, the issue of the non-magnetic shell yielded following the organic shell combination with the metal oxide core could be derived from the above mentioned results.

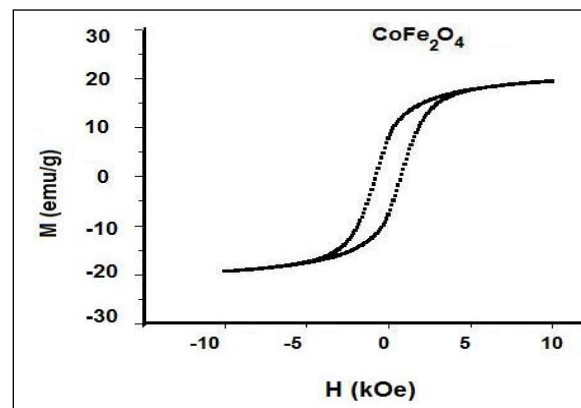


Figure 3 b. Magnetization curve for cobalt ferrite NP

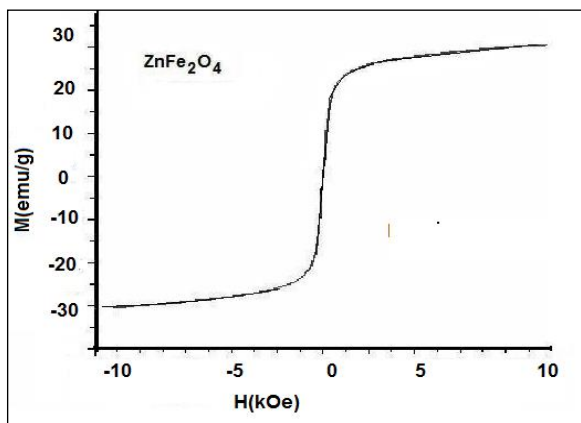


Figure 3 c. Magnetization curve for zinc ferrite NP

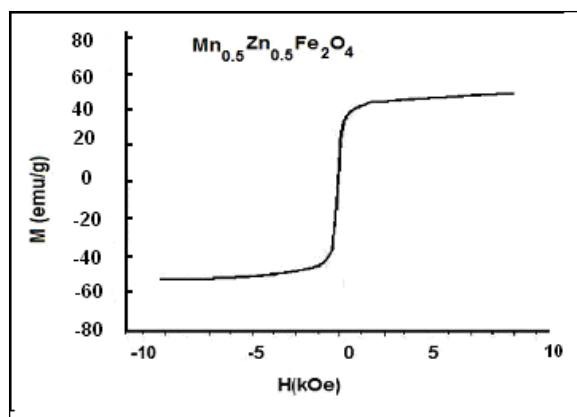


Figure 3 d. Magnetization curve for manganese-zinc ferrite NP

4. CONCLUSIONS

Small size of ferrite powder crystallite (11.4 nm – 13.6 nm) was obtained in all prepared samples and also, relatively low values of the magnetic core diameter (8.9 nm – 9.8 nm). Saturation magnetization was the highest in pure magnetite (60 emu/g); also relatively high value was noticed for manganese-zinc ferrite (55 emu/g) while lower saturation magnetization was obtained in the other ferrofluid samples, where the reduced magnetic properties of the second metal ion might be the cause. Cobalt ferrite sample exhibit peculiar behavior with larger size particles (40 nm) and significant non-zeroed coercivity field which denoted exception from superparamagnetism. The manganese-zinc ferrite NP, well known for their thermal conduction properties recommend such combined ferrite suspension for heat transfer applications. Further studies are planned for the in vitro testing of such soft magnetic materials with biocompatibility properties from the viewpoint of their interaction with living cells in the presence of external magnetic fields.

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