

MAGNETIC RESONANCE STUDY OF ZnO-Fe₂O₃-ZnFe₂O₄ SYSTEM

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Received: December 10, 2009

Abstract. Nanocrystalline particles composed of ZnO doped with a different content of Fe₂O₃ (in the range 50-95 wt. %) were prepared by the wet chemistry method. According to the XRD analysis, the samples with 95%, 90%, 80% of iron oxide contained γ -Fe₂O₃ and ZnFe₂O₄ phases, while other samples contained ZnFe₂O₄ and ZnO phases. The mean crystalline size of ZnFe₂O₄ varied from 8 nm to 30 nm. A magnetic resonance study performed with an electron paramagnetic resonance spectrometer was carried out at room temperature for the obtained samples. A very intense magnetic resonance line with asymmetry depending on the iron oxide concentration was recorded for all samples. For samples containing less than 60% Fe₂O₃ the resonance line is centred at $g = 2.005(2)$ and its integrated intensity increases with the ferrite content, reaching a maximum for a sample with a 70% content of iron oxide. For samples with more than 70% of Fe₂O₃ the g -factor and the integrated intensity of the resonance signal strongly depend on the ratio of iron in form of γ -Fe₂O₃ to that in form of ZnFe₂O₄, decreasing with that ratio. The magnetic resonance study has shown that the resonance line originates from isolated iron(III) ions in zinc ferrite in case of a small iron oxide content and from γ -Fe₂O₃ magnetic nanoparticles (ferromagnetic resonance lines) for higher concentrations.

1. INTRODUCTION

Semiconducting nanocrystals, especially nanostructures made of ZnO have attracted much interest due to their potential applications in low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films, and spintronic devices [1,2]. ZnO has been recognized as a promising host material exhibiting ferromagnetism when doped with transition metal ions [3]. It has been also shown that ferromagnetism can be induced by inclusion of nanoscale oxides of transition metals or nanoparticles with a high content of magnetic ions [4].

The cubic structure nanoparticles of MFe₂O₄ (M=Fe(II), Mn(II), Co(II), Ni(II) and Zn(II)) materials

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exhibit interesting magnetic properties, high mechanical hardness, high electrical resistivity, and chemical stability [5-9]. These materials attract great research interest due to their potential application in such areas as information storage media, electronic devices, sensors, medical diagnostics agents, drug delivery, magnetic resonance imaging (MRI) contrast materials, ferrofluids etc. [10,11]. In a spinel structure with a general formula AB₂O₄, where A corresponds to bivalent and B to trivalent metal, the oxygen ions form a flat centered cubic lattice of the densest packaging in which tetrahedral (A) and octahedral (B) interstitial sites are occupied by cations. Zinc ferrite belongs to a class of normal spinels which presumably have a cation distribution of

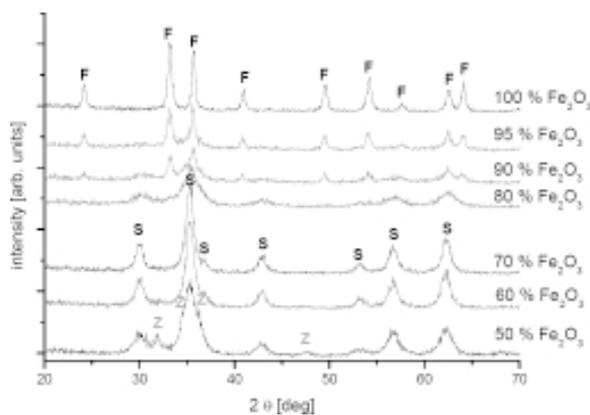


Fig. 1. The XRD patterns for the investigated samples: the peaks attributed to Fe₂O₃ are marked as F, the peaks attributed to ZnFe₂O₄ are marked as S, and the peaks attributed to ZnO are marked as Z.

(Zn²⁺)A((Fe³⁺)₂)B(O)₄. The ZnFe₂O₄ spinel exhibits a variety of magnetic phenomena including formation of small (sized below 3 nm) short-range magnetic ordered regions far above T_N with the fluctuation rate in the GHz range [6]. The room temperature magnetization of zinc ferrite displays a strong dependence on annealing processes and is not saturated up to 7 kOe while above that value it shows ferrimagnetic behaviour with coercivity (0.117 kOe) and remenace (8.13 emu/g) values and saturation 62 emu/g [9]. It could be a result of a strong interaction between iron(III) ions of octahedral and tetrahedral sites after redistribution processes of cations [9]. The electron paramagnetic resonance (EPR) spectrum of zinc ferrite at room temperature presents a very intense and single broad line centered at $g_{\text{eff}}=2.006$ [8]. The EPR spectra strongly depend on the calcination temperature and particle sizes. Magnetic resonance spectra from magnetic agglomerates of ZnFe₂O₄ have not been reported yet.

The aim of this paper is to report preparation of a series of fine particle (magnetic nanoparticles) samples composed of ZnO doped with Fe₂O₃ in the 50-95 wt.% range and their study by the magnetic resonance spectroscopy in the microwave range. An increase in the iron oxide concentration above some critical level could provide for formation of magnetic nanoparticles in which a transition from paramagnetic state of the zinc ferrite (EPR spectra) to a ferromagnetic state of iron oxide (ferromagnetic resonance (FMR) spectra) could be observed. The role of the magnetic dipole interactions will be assessed.

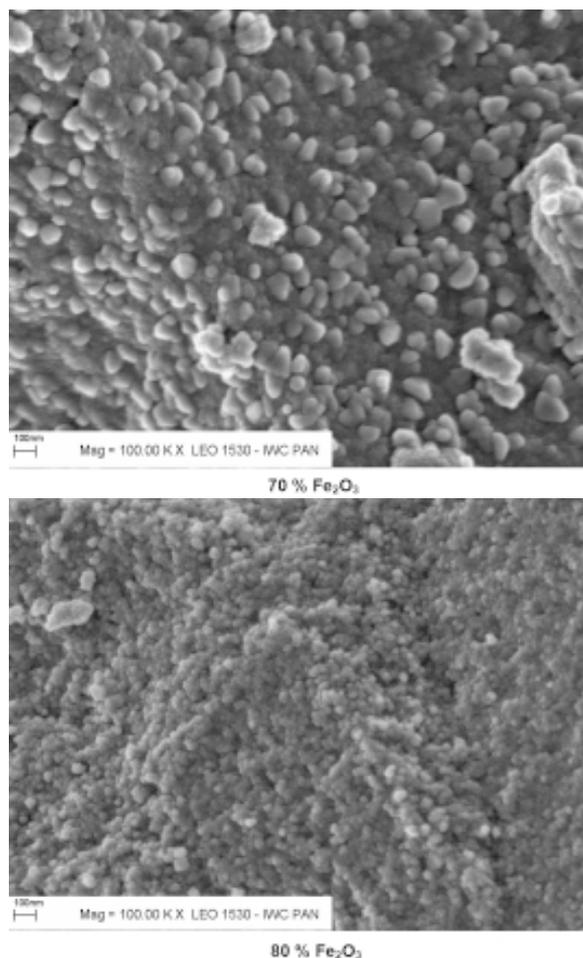


Fig. 2. SEM images for two nanosize samples of ZnO doped with different concentrations of Fe₂O₃.

2. EXPERIMENTAL

A mixture of iron and zinc hydroxides was obtained by addition of an ammonia solution to a 20% solution of a proper amount of Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·4H₂O in water. The obtained hydroxides were filtered, dried and calcined at 300 °C during 1 hour. A series of samples containing 50 to 95 wt.% of Fe₂O₃ was obtained.

The phase composition of the samples was determined using XRD (CoK_α radiation, X'Pert Philips). The mean crystallite size of these phases was determined using Scherrer's formula. The morphology of the samples was investigated using scanning electron microscopy (LEO 1530).

The specific surface area of the nanopowders was determined by the BET method (nitrogen adsorption) using Gemini 2360 manufactured by Micromeritics. The helium pycnometer AccuPyc

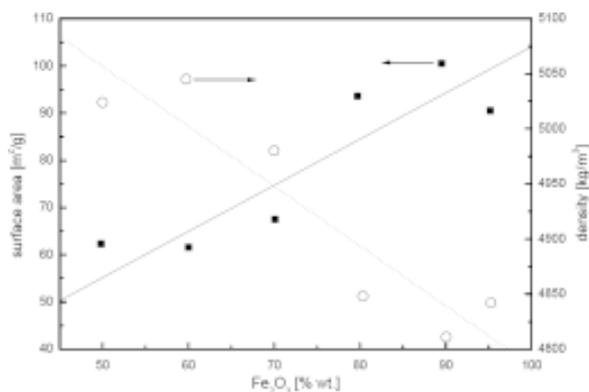


Fig. 3. Dependence of the surface area (left axis, solid squares) and density (right axis, open circles) on the Fe₂O₃ content in the investigated samples. The straight lines (solid and dotted) are the best fits to the experimental points.

1330 of Micromeritics was applied to determine the density of powders.

The composition of the calcined samples was determined using the ICP – AES method to verify whether the chemical composition of the prepared samples is in accordance with the assumed one. A small amount of powder (about 0.05 g) was diluted in 5 ml of hot 37% HCl. The obtained solution was diluted with deionised water up to 100 ml. The determined chemical composition of the samples was almost the same as that calculated on the basis of the initial amount of salts.

The measurements of magnetic resonance spectra were performed on a conventional X-band ($\nu = 9.4$ GHz) Bruker E500 EPR spectrometer with 100 kHz magnetic field modulation. Samples containing around 20 mg sample powder were placed in 4 mm diameter quartz tubes. The measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of ZnO doped with γ -Fe₂O₃ where the phases of ZnFe₂O₄ spinel, iron oxide and zinc oxide are present in the system. The peaks attributed to Fe₂O₃ are marked by letter F, these attributed to ZnFe₂O₄ are designated as S, and peaks attributed to ZnO are marked by letter Z. As expected, the ZnO phase content is decreasing with the increasing γ -Fe₂O₃ concentration and disappears in samples containing more than 66 wt.% of magnetic oxide iron. The intensity of spinel lines increases with the increasing γ -Fe₂O₃ phase con-

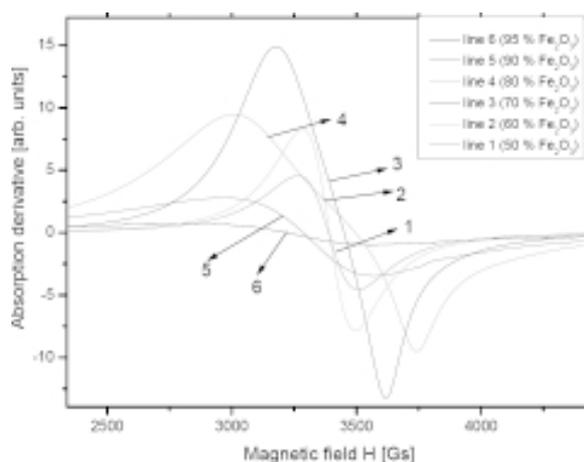


Fig. 4. Magnetic resonance spectra for all the investigated samples with different Fe₂O₃ content registered at room temperature.

centration reaching a maximum at 66 wt.% concentration of iron oxide. The ZnFe₂O₄ spinel phase composition was determined after fitting the spectra to the ICDD patterns and on the basis of calculated crystal lattice parameters for a spinel. The obtained crystal lattice parameter is in the range of 8.438 – 8.444 Å, which indicates ZnFe₂O₄ spinel formation. The XRD method was applied also to determine a mean crystallite size in the prepared samples, using the Scherrer's formula. It was found that the mean crystallite size of ZnFe₂O₄ varied from 8 to 13 nm, depending on the content of Fe₂O₃.

Fig. 2 shows two SEM images of two samples of ZnO doped with different amounts of Fe₂O₃ (70 and 80 wt.%). Spherical and elongated nanograins are seen, they are smaller in the right picture. The agglomeration degree depends on the amount of Fe₂O₃ and is the smallest in the sample with 80 wt.% of iron oxide. The whole zinc oxide has been used for the two presented samples to form the spinel ZnFe₂O₄ phase that has a cubic structure and is indistinguishable from the iron oxide rhombohedral phase in the above pictures.

The relation between the iron oxide content in a sample and the specific surface area is shown in Fig. 3. Samples with a high content of Fe₂O₃ have a considerably larger specific surface area because the amount of agglomerated ZnO particles is small in these samples. On the contrary, the density of powders decreases with the increasing content of iron oxide because the density of iron oxide (III) is smaller than the density of zinc oxide (the theoretic-

Table 1. Magnetic resonance parameters (*g*-factor, linewidth, integrated intensity) for samples with different compositions.

Sample composition (wt.% of Fe ₂ O ₃)	Effective <i>g</i> -factor <i>g</i> _{eff}	Linewidth ΔH_{pp} [Gs]	Integrated intensity ratio $I_{\%}/I_{70\%}$
50%	2.000(2)	255(2)	0.28
60%	2.000(2)	225(2)	0.32
70%	2.000(2)	440(4)	1.00
80%	2.000(3)	250(10)	0.50
	2.011(3)	735(7)	1.60
90%	2.066(3)	740(5)	0.85
95%	2.111(3)	745(5)	0.36

cal density is: 5600 kg/m³ for ZnO and 5240 kg/m³ for Fe₂O₃).

Fig. 4 presents the magnetic resonance spectra of a series of ZnO-Fe₂O₃-ZnFe₂O₄ samples containing from 50 to 95 wt.% of Fe₂O₃. The magnetic resonance spectra are dominated by a slightly asymmetrical and very intense broad line. The resonance line centered at about *g*_{eff} ~2 with a linewidth below 300 Gs for samples containing below 70 wt.% of Fe₂O₃ (Table 1) is characteristic for the EPR spectra of isolated iron(III) ions in a ZnFe₂O₄ compound [8]. The dependence of magnetic resonance spectral parameters (*g*-factor, integrated intensity, linewidth) on the Fe₂O₃ content in the investigated samples is presented in Table 1. The integrated intensity increases essentially with an increase in the concentration and it could be suggested that the ZnFe₂O₄ phase dominates in samples containing up to 70 wt.% of Fe₂O₃. Above this concentration, another line appears which is about three times broader and essentially shifted in the magnetic field in comparison to the first line. This new resonance line is similar to the ferromagnetic resonance spectrum of magnetic γ -Fe₂O₃ nanoparticles in an agglomerated state [12]. The XRD characterization has shown that two phases - ZnO and ZnFe₂O₄ dominate in samples containing up to 70 wt.% of Fe₂O₃. The EPR line of iron(III) ions is very intense producing a large value of the integrated intensity which evidences a large concentration of the spinel phase. At the 80 wt.% Fe₂O₃ content, a the spectrum being a superposition of two magnetic centers has appeared, one from iron(III) ions and the other from magnetic agglomerates of iron oxides. The *g*_{eff} parameter and the integrated intensity suggests that the concentration of iron(III) ions is very low [13-15]. The *g*_{eff} is increasing and the integrated intensity is decreasing with

the increasing concentration of the iron oxide which suggests that the magnetic dipole interaction plays a very important role. The increase in the *g*_{eff} parameter reflects an increase in the internal magnetic field that changes the resonance condition: $h\nu = g_{\text{eff}} \mu_B (H_0 \pm H_{\text{int}})$, where h is the Planck constant, ν is the microwave frequency, μ_B is the Bohr magneton, H_0 is an external applied magnetic field and H_{int} is an internal magnetic field produced by interacting magnetic agglomerates.

Preliminary results of AC magnetic susceptibility measurements of samples from the ZnO-Fe₂O₃-ZnFe₂O₄ system have been published recently [16]. Different types of magnetic behavior have been observed depending on the iron oxide content. Ferromagnetic ordering has been registered at room temperature for samples with a high Fe₂O₃ content (77-90 wt.%). Superparamagnetic behavior has been observed with the blocking temperature depending on the magnetic dopant content for samples with a low iron oxide content [16]. These results are in good agreement with the magnetic resonance results and seem to confirm our interpretation of the registered spectra.

4. CONCLUSIONS

The XRD study of the prepared fine particles (magnetic nanoparticles) samples of ZnO doped with different content of Fe₂O₃ (in the range 50-95 wt.%) has evidenced that the investigated samples are dominated by a zinc ferrite phase with a small addition of ZnO phase for iron oxide concentration smaller than 70 wt.% while it is mainly an iron oxide phase that has been detected with only a small traces of zinc oxide for concentration of iron oxides greater than 80 wt.%. Samples with a high Fe₂O₃

content have a higher specific surface area and lower density. The degree of agglomeration for these samples is lower than that for samples dominated by ZnO. The magnetic resonance measurements have confirmed that the maximum zinc ferrite concentration value has emerged for a sample with 70 wt.% of iron oxide and a strong dipole-dipole interaction has been registered in that sample. The superposition of two kinds of magnetic centres has been observed - trivalent iron ions and agglomerates of magnetic iron oxide for a sample with 80 wt.% of iron oxide and higher. The internal magnetic field increases and the integrated intensity of magnetic resonance spectra strongly decreases with the increasing concentration of magnetic nanoparticles.

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