



EPR/FMR study of ZnO-Fe₂O₃-ZnFe₂O₄ system



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Abstract

Fine particles composed of $n(\text{Fe}_2\text{O}_3)/(1-n)\text{ZnO}$ ($n=0.5$ to 0.95) were prepared by wet chemistry method. According to XRD analysis the samples with $n=0.95, 0.90, 0.80$ contained $\gamma\text{-Fe}_2\text{O}_3$ and ZnFe_2O_4 phases, other samples contained ZnFe_2O_4 and ZnO phases. The mean crystalline size of ZnFe_2O_4 varied from 8 nm to 30 nm. The electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) investigations of the obtained samples have been carried out at room temperature. The almost symmetrical and very intense magnetic resonance line was recorded for all samples. For samples with $n<0.60$ the resonance line is centred at $g=2.005(2)$ and its integrated intensity increases with ferrite content, reaching the maximum for $n=0.70$. For samples with $n>0.70$ the g parameter and integrated intensity strongly depend on the ratio of iron in form of $\gamma\text{-Fe}_2\text{O}_3$ to that in form of ZnFe_2O_4 , decreasing with that ratio. For samples with $n<0.70$ the magnetic resonance study showed that the magnetic resonance line originates from isolated iron(III) ions in zinc ferrite while for higher concentrations from magnetic nanoparticles $\gamma\text{-Fe}_2\text{O}_3$ (FMR lines).

Sample composition (wt.% of Fe ₂ O ₃)	Effective g-factor g_{eff}	Linewidth ΔH_{pp} [Gs]	Intensity ratio $I_0/I_{70\%}$
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) 2.011(3)	250(10) 735(7)	0.50 1.60
90%	2.0066(3)	740(5)	0.85
95%	2.111(3)	745(5)	0.36

Table 1 The values of EPR/FMR spectra parameters.

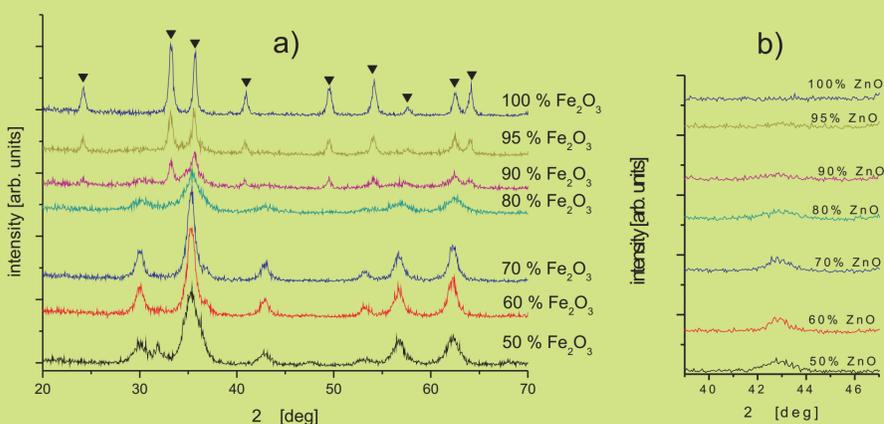


Fig. 1 The XRD patterns of Fe₂O₃ doped ZnO. Peaks attributed to Fe₂O₃ are marked by \blacktriangledown . Non marked peaks are attributed to ZnFe₂O₄ (a) and the XRD patterns of ZnO (b).

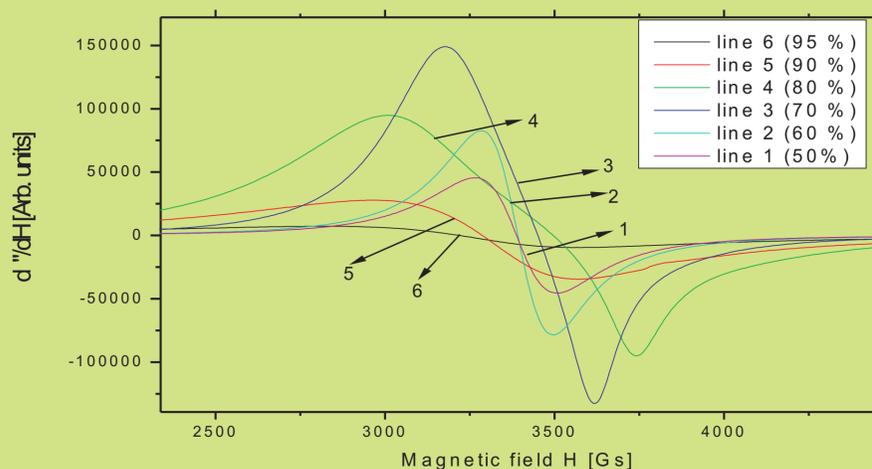


Fig. 2 The EPR/FMR spectra for all series of fine particles composed of $n(\text{Fe}_2\text{O}_3)/(1-n)\text{ZnO}$ ($n=0.5$ to 0.95) registered at room temperature.

Conclusions

The XRD study of prepared fine particles (magnetic nanoparticles) samples composed of $n(\text{Fe}_2\text{O}_3)/(1-n)\text{ZnO}$ ($n=0.5$ to 0.95) evidenced that for $n<0.70$ samples are dominated by zinc ferrite phase with small concentration of ZnO phase and for $n>0.80$ mainly iron oxide phase was formed with small amount of zinc oxide. The magnetic resonance measurements have shown that the maximum value of the concentration zinc ferrite is appeared for $n=0.70$ with the strong dipole-dipole interaction while for $n=0.80$ the superposition of two kinds of magnetic centres was observed - trivalent iron ions and agglomerates of magnetic iron oxide. With increasing concentration of magnetic nanoparticles the internal magnetic field increases and the integrated intensity of magnetic resonance spectra strongly decreases.

Introduction

The cubic structure nanoparticles of $M\text{Fe}_2\text{O}_4$ ($M=\text{Fe(II)}, \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}$ and Zn(II)) materials exhibit interesting magnetic properties, high mechanical hardness, high electrical resistivity, and chemical stability [1-5]. These materials attract great research interest due to their potential application such as information storage media, electronic devices, sensors, medical diagnostics agents, drug delivery, magnetic resonance imaging (MRI) contrast materials, ferrofluids etc. [6-15]. The spinel structure is described by a general formula AB_2O_4 , where A corresponds to bivalent and B - to trivalent metal, respectively. Depending on cations position the normal and inverse spinels can be distinguished. In a spinel structure 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. In the inverse spinel structure some Fe^{3+} ions may occupy tetrahedral, as well as octahedral sites. Zinc ferrite belongs to the class of normal spinels which presumably have a cation distribution of $(\text{Zn}^{2+})_A(\text{Fe}^{3+})_2\text{B}(\text{O})_4$. The spinel ZnFe_2O_4 exhibits a variety of magnetic phenomena including formation a small (sized below 3 nm) short-range magnetic ordered regions far above T_N (superantiferromagnetic state) with the fluctuation rate in the GHz range (microwave region) [2]. 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 shows ferrimagnetic behaviour with coercivity (0.117 kOe) and remanence (8.13 emu/g) values and saturation 62 emu/g [5]. It could be the result of a strong interaction between iron(II) ions of octahedral and tetrahedral sites after redistribution processes of cations [9]. The electron paramagnetic resonance (EPR) spectrum of zinc ferrite at room temperature present a very intense and single broad line centered at $g_{\text{eff}}=2.006$ [4]. The EPR spectra strongly depend on the calcination temperature and the particle sizes. Magnetic resonance spectra from magnetic agglomerates have not recorded yet.

The aim of this paper is to report preparation of a series of fine particle (magnetic nanoparticles) samples composed of $n(\text{Fe}_2\text{O}_3)/(1-n)\text{ZnO}$ ($n=0.5$ to 0.95) powders and their study by the magnetic resonance spectroscopy in the microwave range. The increase concentration above some critical level of iron oxide component could provide for formation of magnetic nanoparticles in which a transition from paramagnetic state of the zinc ferrite (EPR spectra) to ferrimagnetic state of iron oxide (FMR spectra) could be observed. The role of the magnetic dipole interactions will be assessed.

Experimental

The mixture of iron and zinc hydroxides was obtained by addition of an ammonia solution to 20% solution of proper amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ 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 ($\text{CoK}\alpha$ radiation, X'Pert Philips). The mean crystallite size of these phases was determined using Scherrer's formula. The morphology of samples was investigated using scanning electron microscopy (LEO 1530). The real chemical composition of samples was determined using ICP AES (inductively coupled plasma atomic emission spectroscopy) method (Yvon-Jobin, France).

The specific surface area of the nanopowders was determined by BET method (nitrogen adsorption) using the equipment Gemini 2360 of Micromeritics. The helium pycnometer AccuPyc 1330 of Micromeritics was applied to determine the density of powders.

To verify whether the chemical composition of the prepared samples is in accordance with the assumed one, the composition of the calcined samples was determined using ICP - AES method. 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 is almost the same that this calculated on the basis of initial amount of salts.

The measurements of magnetic resonance spectra were performed on 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.

Results and discussion

Figure 1 shows the XRD patterns of ZnO doped with $\gamma\text{-Fe}_2\text{O}_3$, where the phases of spinel, iron oxide and zinc oxide are present in the system. The peaks attributed to Fe₂O₃ are marked by sign \blacktriangledown while non marked peaks are attributed to ZnFe₂O₄. The concentration dependence of ZnO is presented in Fig. 1b. With increasing $\gamma\text{-Fe}_2\text{O}_3$ concentration the content of ZnO phase is decreasing and disappears in sample with 100% of magnetic oxide iron. The intensity of spinel lines increase with increasing concentration of ZnO phase. For samples with Fe:Zn ratio lower than 2:1 the lines corresponding to pure ZnO appear (60% of $\gamma\text{-Fe}_2\text{O}_3$). The phase composition of spinel was determined after fitting of 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 on spinel ZnFe₂O₄ formation. XRD method was applied as well to determine a mean crystallite size in 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.

Figure 2 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 $g_{\text{eff}}=2$ with a linewidth below 300 Gs for samples containing below 70 wt.% Fe₂O₃ (Table 1) is characteristic for the EPR spectra of isolated iron(III) ions in ZnFe₂O₄ compound [4]. The integrated intensity increases essentially with increase of concentration and it could be suggested that the ZnFe₂O₄ phase is dominating in samples containing up to 70 wt.% of Fe₂O₃. Above this concentration another line appears that is about three times broader and essentially shifted in the magnetic field in comparison to the first line. This new resonance line is similar as for the FMR spectrum of magnetic $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in an agglomerated state [16]. The XRD characterization has shown that in samples containing up to 70 wt.% of Fe₂O₃, two phases ZnO and ZnFe₂O₄ dominate. The EPR line of iron(III) ions is very intense producing a large value of the integrated intensity which evidences the greater concentration of the spinel phase. At 80% content of Fe₂O₃ the spectrum being superposition of two magnetic centers has appeared, one from iron(III) ions and the other from magnetic agglomerates of iron oxides (in ferrimagnetic state above room temperatures). The value of the g_{eff} parameter and integrated intensity suggests that the concentration of iron(III) ions is very low [17,18]. With increasing concentration of the iron oxide the g_{eff} is increasing and the integrated intensity is decreasing what suggests that the magnetic dipole interaction plays a very important role. The increase of the g_{eff} parameter reflects the increase of 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 Planck constant, ν is the microwave frequency, μ_B is Bohr magneton, H_0 is an external applied magnetic field and H_{int} is an internal magnetic field produced by interacting magnetic agglomerates.

The internal magnetic field acting on agglomerates is usually very low in value is given for the localized magnetic moments because the average magnetic field on the paramagnetic state is approaching zero value [19].