The preparation and EPR study of nanocrystalline ZnFe₂O₄

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Abstract. Nanocrystalline zinc oxide doped with different concentrations of Fe₂O₃ (from 5 to 50 wt.%) has been prepared by means of coprecipitation and calcination processes. Depending on the chemical composition, phases of hexagonal ZnO, and/or cubic ZnFe₂O₄ were identified. The mean crystallite size of the latter phase, determined using the Scherrer’s formula, varied from 8 to 12 nm. The EPR spectra for six different concentrations of Fe₂O₃ were recorded. A symmetrical, very intense and broad EPR resonance line has been obtained for all the samples where the intensity strongly depended on the ratio of ZnO/Fe₂O₃ in the samples. The resonance field slightly shifted in the direction of lower magnetic field and the integrated intensities increased with increasing concentration of magnetic nanoparticles of ZnFe₂O₄, where the linewidth showed an extraordinary behaviour. The dipole-dipole interaction depended essentially on the concentration of magnetic nanoparticles.

1. Introduction
Nanoscale inorganic materials, in particular semiconductor nanocrystals have been of much interest for over two decades because of their unique physical properties resulting from modification of the electronic states due to the confinement effect.

The nanomaterials described by the formula MFe₂O₄ (M=Fe(II), Mn(II), Co(II), Ni(II) and Zn(II)) exhibit interesting magnetic properties, high mechanical hardness, high electrical resistivity, and chemical stability [1-5].

Nanomaterials on the basis of ZnO have attracted significant attention owing to their proposed applications in low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films, and spintronic devices [6, 7]. Zinc oxide has also been identified as a promising host semiconductor material, exhibiting ferromagnetism when doped with most of the transition metals - V, Cr, Fe, Co, Ni [8]. In this paper the EPR studies of the zinc oxide samples doted with iron are presented.

2. Experimental
A mixture of iron and zinc hydroxides was obtained by addition of an ammonia solution to 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 for 1 hour. A series of samples containing 5 to 95 wt.% of Fe₂O₃ was obtained.

The phase composition of the samples was determined using XRD (CoKα radiation, X’Pert Philips). The mean crystallite size of these phases was determined using the Scherrer’s formula. The morphology of the samples was investigated using scanning electron microscopy (LEO 1530). The real chemical composition of the samples was determined using the ICP AES (inductively coupled plasma atomic emission spectroscopy) method (Yvon-Jobin, France).

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

3. Results

Figure 1 presents FMR spectra of zinc oxide samples doted with iron oxide (5 to 50 wt.%), which corresponds to the concentration of ZnFe$_2$O$_4$ from 7.5 to 75 wt.%.

A very intense, broad and almost symmetrical EPR line is observed for all the concentration of Fe$_2$O$_3$. The EPR lines were fitted by Lorentzian function and in Table 1 the obtained EPR parameters are given. The $g_{\text{eff}}$ is almost constant for all the analyzed samples and is comparable with that for iron oxide compounds [9]. The linewidth is slightly changing, and an essential increase of integrated intensity with increasing concentration is recorded. For the first three samples it almost agrees with nominal values.

**Table 1.** The EPR parameters of different concentration of ZnFe$_2$O$_4$

| Sample n° | Content of Fe$_2$O$_3$, wt.% | Content of ZnFe$_2$O$_4$, wt.% | $g_{\text{eff}}$ | $\Delta H_{\text{pp}}$ [Gs] | $I_{\text{integr}}$ |
|-----------|-----------------------------|-------------------------------|-----------------|------------------|---------------|
| 1         | 5                           | 7.5                           | 2.003(1)        | 273(2)           | 1             |
| 2         | 10                          | 15.1                          | 2.000(1)        | 256(2)           | 1.4 (2)       |
| 3         | 20                          | 30.1                          | 2.001(1)        | 248(2)           | 5.3 (4)       |
| 4         | 30                          | 45.2                          | 2.001(1)        | 258(2)           | 11.4 (6)      |
| 5         | 40                          | 60.4                          | 2.001(1)        | 284(2)           | 14.4 (8)      |
| 6         | 50                          | 75.3                          | 2.000(1)        | 247(2)           | 18.0 (10)     |

Figure 1. The EPR spectra of different concentration of Fe$_2$O$_3$ in the samples.

The XRD spectra of some selected samples are shown in Figure 2. Two phases are present: zinc oxide and spinel (zinc ferrite). The intensity of peaks attributed to spinel decreases with increasing ZnO content. It corresponds to the drop of the intensity of EPR spectra. The lines attributed to iron oxide are not visible as all iron oxide is bound in the spinel phase ZnFe$_2$O$_4$. The mean crystallite size of ZnFe$_2$O$_4$, calculated using the Scherrer’s formula, varies from 8 to 12 nm.
Figure 2. The XRD patterns of ZnO doped Fe$_2$O$_3$. Peaks attributed to ZnO are marked as Z, Peaks attributed to ZnFe$_2$O$_4$ are marked as S.

To verify the real composition of the samples, they were analysed using the ICP-AES method (Figures 3 and 4). A good fitting can be observed, because the real content of zinc and iron oxides in the samples is, in fact as theoretically predicted.

Figure 3. Dependence between the theoretical and real content of iron oxide.
The analysis of the morphology of the samples using a Scanning Electron Microscope confirms the presence of two phases (Figure 5).

The powders containing more iron oxide are less agglomerated than the samples with a lower content of Fe$_2$O$_3$. In Figure 5B the agglomerates of zinc oxide (hexagonal structures) are well visible, while smaller spherical structures correspond to the cubic spinel phase.

**Conclusions**

The samples of zinc oxide doted with iron oxide (5 to 50 wt.%) contain two phases: zinc oxide and spinel of zinc ferrite. The mean crystallite size of ZnFe$_2$O$_4$, calculated using the Scherrer’s formula, varies from 8 to 12 nm. The powders containing more iron oxide are less agglomerated than the samples with a lower content of Fe$_2$O$_3$. A very intense and broad EPR line centered at effective g near 2 was recorded. The resonance field and linewidth do not depend significantly on the concentration of Fe$_2$O$_3$, while the intensity strongly increases with increasing concentrations of Fe$_2$O$_3$. 

**Figure 4.** Dependence between the theoretical and real content of zinc oxide.

**Figure 5.** SEM image of ZnO doped powders. A- 50% Fe$_2$O$_3$, B- 20% Fe$_2$O$_3$
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