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Nanocrystalline ZnO Doped with Fe_2O_3 — Magnetic and Structural Properties

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We have studied the magnetic properties of ZnO nanocrystals doped with Fe_2O_3 in the magnetic dopant range from 5 to 70 wt%. The nanocrystals were synthesized by wet chemical method. The detailed structural characterization was performed by means of X-ray diffraction and micro-Raman spectroscopy measurements. The results of systematic measurements of magnetic AC susceptibility as a function of temperature and frequency are presented. We observed different types of magnetic behavior. For ZnO samples doped with low content of Fe_2O_3, the results of low-field AC susceptibility are satisfactorily explained by superparamagnetic model including inter-particle interactions. With the increase of magnetic Fe_2O_3 content, the spin-glass-like behavior is observed.

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1. Introduction

In recent years, great progress has been made in the synthesis and properties of nanoscale inorganic materials. Magnetic nanoparticles are of great interest for researchers mainly due to the perspectives of their use in data storage, enhanced hard magnets, soft magnetic materials with lower energy losses and rapid magnetic response at variable magnetic fields, magnetic microsensors, magnetic resonance imaging, catalysis, environmental remediation (see e.g. [1, 2] and references therein). Recently it was shown that superparamagnetic nanoparticles based on a core consisting iron oxides are very promising for *in vivo* applications (e.g. hyperthermia and radiotherapy *in vivo*) [3].

Currently, nanostructures made of a wide-gap II–VI semiconductor ZnO bear important potential application in low-voltage and short-wavelength electro-optical devices, transparent ultraviolet protection films, and spintronic devices (see eg. [4] and references therein).

In the context of spintronics, doped ZnO nanoparticles are of particular interest. In the present paper we have studied magnetic properties of nanosized ZnO powders doped with Fe_2O_3 in a wide range of magnetic dopant. The dynamic magnetic responses, i.e. the frequency dependence of the linear AC susceptibility were studied. The detailed structural studies, systematic micro-Raman spectroscopy as well as X-ray diffraction (XRD) measurements were performed.

2. Experimental results

2.1. Structural characterization

The samples were synthesized by use of wet chemical method. First, the mixture of iron and zinc hydroxides was obtained by addition of an ammonia solution to the 20% solution of proper amount of $Zn(NO_3)\cdot 6H_2O$ and $Fe(NO_3)_3\cdot 4H_2O$ in water. Next, the obtained hydroxides were filtered, dried and calcined at 300 °C during 1 h. A series of samples containing from 5 to 70 wt% of Fe_2O_3 was obtained. The structural properties of the samples were studied by means of XRD and systematic micro-Raman spectroscopy measurements. The results of detailed XRD studies are shown elsewhere [5].

The XRD measurements revealed the presence of hexagonal ZnO and cubic $ZnFe_2O_4$ crystal phases. The mean crystallite size of these phases varied from 8 to 51 nm. For high content of magnetic dopant the XRD studies did not reveal the presence of ZnO crystalline phase.

The micro-Raman spectra were taken in the backscattering configuration and analyzed using a Jobin Yvon T64000 spectrometer, equipped with nitrogen cooled charge-coupled-device detector. As an excitation source we used the 514.5 nm line of an Ar-ion laser. The measurements were performed at different laser powers.

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The advantage of micro-Raman technique is the very accurate chemical phases determination. The Raman spectroscopy has already proven to be a unique tool for probing nanophases dispersed in a matrix (see eg. [1]).

The selected Raman spectra are shown in Fig. 1. The main characteristics of experimental Raman spectrum in 200 to 1600 cm^{-1} spectral region are sharp peak at 436 cm^{-1} and broad two-phonon structure at $\approx$ 1150 cm^{-1}, typical for ZnO; broad structure below 700 cm^{-1} is attributed to $ZnFe_2O_4$ nanoparticles.

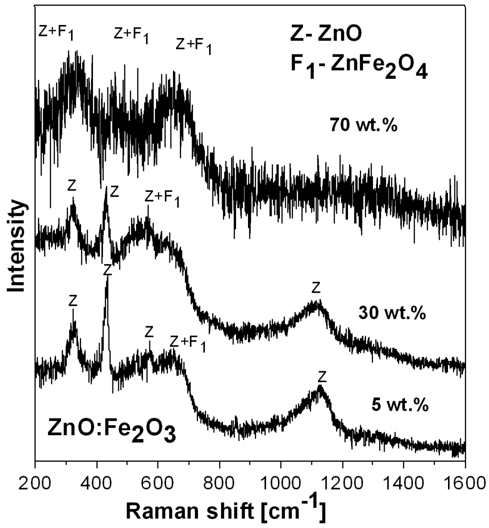

Fig. 1. The selected Raman spectra for nanocrystalline samples $ZnO:Fe_2O_3$.

The Raman spectroscopy measurements allowed to determine the detailed structural characterization. In particular, XRD analysis did not reveal the presence of ZnO phase in samples doped with high content of magnetic dopants. Despite of fact that XRD does not evident ZnO, sharp peaks at 436 cm^{-1} is clearly $E_2^{(2)}$ mode of ZnO. This peak is typical for undoped ZnO nanoparticles [6]. The Raman spectroscopy studies revealed the presence of two phases: ZnO and $ZnFe_2O_4$ in the entire content range.

2.2. Magnetic properties

The dynamic magnetic properties were studied by means of AC susceptibility χ. The real, Re(χ), as well as imaginary, Im(χ) parts of magnetic susceptibility were measured using a mutual inductance method in an AC magnetic field of frequency range 7–10 kHz and amplitude not exceeding 5 Oe. Figure 2 shows the temperature dependence of the real part of the AC susceptibility for selected $ZnO:Fe_2O_3$ samples in the wide range of magnetic dopant. The Re(χ) curves show pronounced maxima (the positions of maxima T_f derived at $f = 625$ Hz are summarized in Table).

We have observed the pronounced changes in the positions of temperature maxima T_f with the nominal concentration of Fe_2O_3. The measurements of AC susceptibility were performed at the small AC magnetic field with amplitude not exceeding 5 Oe and different frequency values (from 7 Hz to 9970 Hz). We observed that the positions of the maxima shift towards higher values with increasing driving frequency (Fig. 3). The above-described experimental features are expected in the superparamagnetic system [7]. A useful criterion for classifying the observed freezing/blocking process is the empirical parameter Φ [8, 9] that is a quantitative measure of the frequency shift and is given by the relative shift of the peak temperature per decade shift in frequency

$$\Phi = \Delta T_f / T_f \Delta \log_{10}(f), \qquad (1)$$

where ΔT_f is the difference between the peak temperature measured in the $\Delta \log_{10}(f)$, and f is the AC magnetic field frequency.

We obtained values in the range from 0.04 for the sample with 70 wt% of Fe_2O_3 up to 0.06 for the sample with 5 wt% of Fe_2O_3 (the determined values of parameter Φ are gathered in Table). For the superparamagnetic sys-

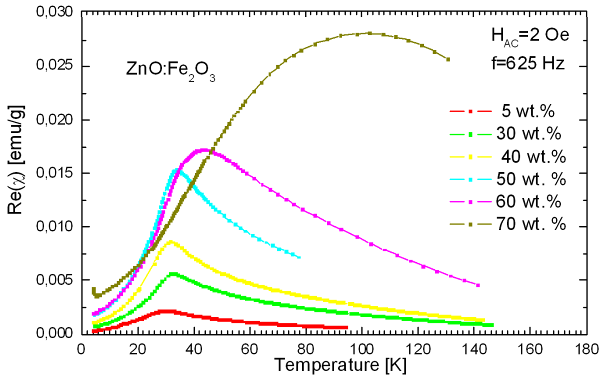

Fig. 2. The temperature dependence of the in-phase component Re(χ) of the magnetic susceptibility for several ZnO: Fe_2O_3 nanocrystalline samples in the wide range of magnetic dopant. The data were taken in external magnetic field $H_{AC} = 2$ Oe and frequency $f = 625$ Hz.

TABLE

The positions of maxima T_f derived at $f = 625$ Hz and determined values of parameter Φ for $ZnO:Fe_2O_3$.

Nominal concentration	T_f [K] (625 Hz)	Φ
5 wt%	30.2	0.06
30 wt%	33	0.03
40 wt%	31.8	0.04
50 wt%	34	0.04
60 wt%	43.3	0.04
70 wt%	34	0.04

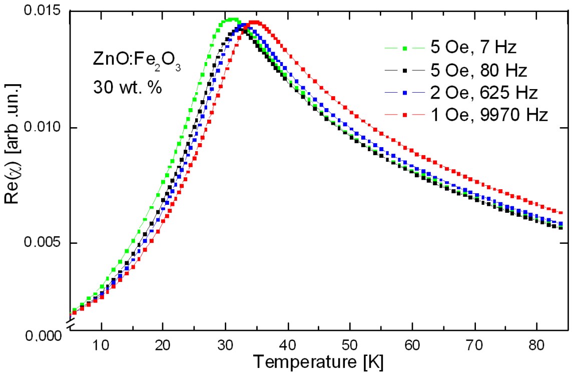

Fig. 3. The frequency dependence of the in-phase component Re(χ) of the magnetic susceptibility for selected ZnO:Fe_2O_3 nanocrystalline sample with $x = 30$ wt%.

tem of noninteracting nanoparticles, the frequency dependent peaks in linear AC susceptibilities are characterized by the so-called blocking temperature (T_b), and the relative variation of $T_f = T_b$ with frequency is between 0.10 and 0.13 [7]. For interacting nanoparticles, superparamagnetic systems exhibit values of Φ between 0.05 and 0.10, in spin-glass systems $\Phi < 0.05$ [7, 8].

3. Conclusions

We have studied the dynamic magnetic properties of ZnO:Fe_2O_3 by carrying out the frequency-dependent AC susceptibility measurements. We analyzed the observed frequency dependence of the peak temperature in the AC susceptibility curve using the empirical parameter Φ [8, 9]. For ZnO doped with 5 wt% of Fe_2O_3, the results of low-field AC susceptibility are satisfactorily explained by superparamagnetic model including inter-particle interactions. For higher content of magnetic Fe_2O_3, we have observed the spin-glass-like behavior.

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