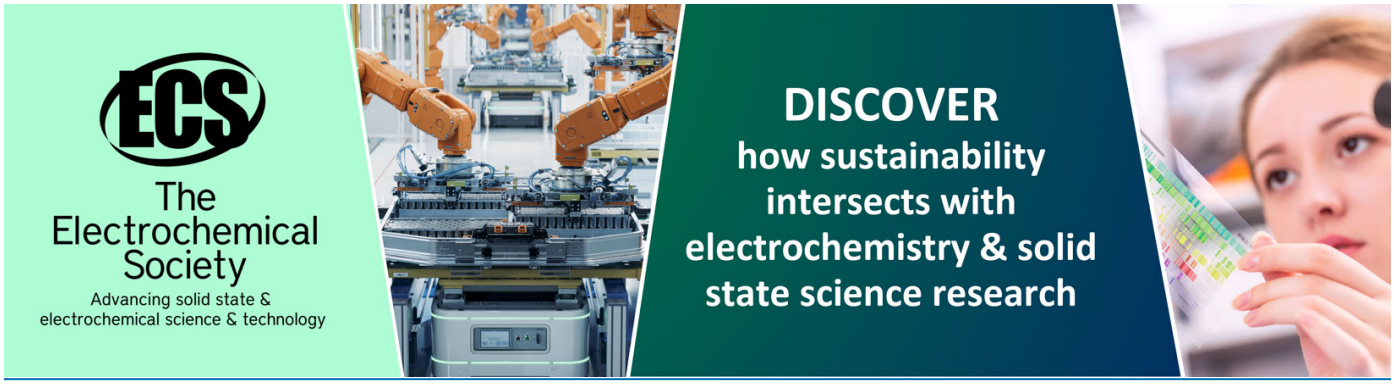
Magnetic properties of nanocrystalline ZnO doped with MnO and CoO



Journal of Physics: Conference Series **200** (2010) 072058 doi:10.1088/1742-6596/200/7/072058

Magnetic properties of nanocrystalline ZnO doped with MnO and CoO

I. Kuryliszyn-Kudelska[1], W. D. Dobrowolski[1], Ł. Kilański[1], B. Hadžić[2], N. Romčević[2], D. Sibera[3], U. Narkiewicz[3], P.Dziawa[1]

[1]Institute of Physics, Polish Academy of Sciences, Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland
[2]Institute of Physics, Belgrade University, Pregrevica 118, 11080 Belgrade, Serbia
[3]Szczecin University of Technology, Institute of Chemical and Environment Engineering, Pulaskiego 10, 70-322 Szczecin, Poland

E-mail: kuryl@ifpan.edu.pl

Abstract. We have studied the magnetic properties of ZnO nanocrystals doped with MnO and CoO in the wide range of magnetic dopant (from 5 to 95 wt. %), synthetized by wet chemical method. The samples were characterized by means of XRD and micro-Raman spectroscopy. The results of systematic measurements of magnetic susceptibility as a function of temperature and frequency as well as SQUID magnetization are presented. We observed different types of magnetic behavior. ZnO nanocrystals doped with CoO demonstrate Curie-Weiss behavior at higher temperatures. For samples doped with MnO, we observed the superparamagnetism above the blocking temperature.

1. Introducion

In the past few years, great progress has been made in the synthesis and properties of nanoscale inorganic matrerials. Recently, nanoparticulated magnetic systems attracted significant attention owing to their proposed use to obtain enhanced hard magnets, soft magnetic materials with lower energy losses and rapid magnetic response at variable magnetic fields, magnetic microsensors and other applications in medical diagnosis, catalysis, magnetic liquids for drug delivery, pigments for painting and ceramics [1]. Currently, nanostructures made of a wide-gap II-VI semiconductor 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 [2, 3]. ZnO has been identified as a promising host semiconductor material, exhibiting ferromagnetism when doped with most of the transition metal elements – V, Cr, Fe, Co, Ni [4]. However, the origin of ferromagnetic behavior is not very well known in these compounds. Recently, it was shown that the ferromagnetism in these materials can be induced by inclusions of nanoscale oxides of transition metals [4] and/or nanoparticles containing a large concentration of magnetic ions [5].

The aim of this work was to synthetize and study magnetic properties of nanosized ZnO powders doped with MnO and CoO. The samples were characterized by means of X-ray diffraction and micro-Raman spectroscopy. The systematic magnetic measurements including AC susceptibility and SQUID magnetization were carried out.

2. Experimental

The samples were synthetized by use of wet chemical method. First, the mixture of manganese hydroxides and zinc hydroxides / cobalt hydroxides and zinc hydroxides from an aqueous solution of nitrites were obtained. Next, the obtained hydroxides were filtered, dried at the temperatue of 70^0C and calcined at 300^0C during 1 hour. Two series of samples containing from 5 to 95 wt.% of MnO and from 5 to 95 wt.% of CoO were obtained.

The phase composition of the samples was determined by use of X-ray diffraction ($Co_{K\alpha}$ radiation, X'Pert Philips). For ZnO doped with MnO, the crystalline phases of hexagonal ZnO, and/or cubic $ZnMnO_3$, and/or cubic Mn_3O_4, and/or cubic $ZnMn_2O_4$ were identified. For ZnO doped wih CoO, the crystalline phases of hexagonal ZnO and cubic Co_3O_4 were identified. XRD data allowed to determine a mean crystallite size *d* in prepared samples by use of Scherrer's formula [6]. The mean crystallite size of these phases varied from 9 to 100 nm for ZnO doped with MnO and from 17 to 156 nm for ZnO doped with CoO. The results of XRD measurements, i.e. the phase compositions as well as the mean crystallite size are gathered in Table 1 and Table 2.

	d [nm] ZnO phase	*d* [nm] $ZnMnO_3$ phase	*d* [nm] Zn_2MnO_4 phase	*d* [nm] Mn_3O_4 phase
5 wt.%	+	13	-	-
10 wt.%	+	9	-	-
20 wt.%	+	10	-	-
30 wt.%	100	9	-	-
40 wt.%	100	+	-	-
50 wt.%	100	+	+	-
60 wt.%	-	-	+	24
70 wt.%	-	-	-	37
80 wt.%	-	-	-	45
90 wt.%	-	-	-	47
95 wt.%	-	-	-	43

Table 1. The results of X-ray diffraction measurements for ZnO doped with MnO. The identified crystalline phases as well as mean crystallite size *d* determined by use of Scherrer's formula are gathered.

	d [nm] ZnO phase	*d* [nm] Co_3O_4 phase
5 wt.%	156	55
10 wt.%	118	50
20 wt.%	57	21
30 wt.%	101	30
40 wt.%	80	17
50 wt.%	43	21
60 wt.%	-	14
70 wt.%	-	15
80 wt.%	-	21
90 wt.%	-	25
95 wt.%	-	20

Table 2. The results of X-ray diffraction measurements for ZnO doped with CoO. The identified crystalline phases as well as mean crystallite size *d* determined by use of Scherrer's formula are gathered.

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. With increase of laser power, the peaks shift to lower frequencies and broaden. For all samples Raman peak at 436 cm^{-1} was observed. This peak is typical for undoped ZnO nanoparticles [7]. For the samples of ZnO doped with MnO, Raman peak at 660 cm^{-1} is observed. This peak is typical for spinel structure. In these samples, especially in the case of high doping level, bands from $ZnMnO_3$ and Mn_3O_4 crystal structures were identified at about 315 and 525 cm^{-1}. For the samples of ZnO doped with CoO, the Raman spectrum showed a band at ~ 691 cm^{-1}. The presence of this band is typical for Co_3O_4. We also observed bands at ~ 194, 482, 521 and 618 cm^{-1}. These bands are also typical for Co_3O_4.

The systematic magnetic measurements were performed. The AC magnetic susceptibility χ studies in the temperature range 4.2 – 150 K using a mutual inductance method were carried out. The real, Re(χ), as well as imaginary, *Im*(χ) parts of magnetic susceptibility were determined in an ac magnetic

field of frequency range 7-10 000 Hz and amplitude not exceeding 5 Oe. Magnetization measurements were performed by use of SQUID magnetometer.

Inverse magnetic susceptibility for selected ZnO doped with CoO nanocrystalline samples is shown in Figure 1. For all the investigated samples the high temperature behavior of the inverse low-field susceptibility χ^{-1} was nearly linear. Such behavior is characteristic of TM-doped ZnO samples. We did not observed peak in AC magnetic susceptibility, typical for antiferromagnetic Co_3O_4 nanoparticles [8]. Generally, in the range of high temperatures, II-VI semimagneic semiconductors are Curie-Weiss paramagnets with the temperature dependence of the magnetic susceptibility described by the Curie-Weiss law:

$$\chi(T) = C/(T - \theta) \qquad (1)$$

,where $C = g^2\mu_B^2 S(S+1)N_m$ is the Curie constant and $k_B\theta = (1/3)S(S+1)x\Sigma z_i I(R_i)$ is the paramagnetic Curie temperature (Curie-Weiss temperature). Here, N_M is the concentration of magnetic ions, z_i the number of magnetic neighbours on the ith crystallographic shell, $I(R_i)$ the exchange integral between the central ion and its ith magnetic neighbours, S the spin of the magnetic ion, g the spin splitting g-factor, k_B the Boltzman constant, and μ_B is the Bohr magneton.

The diamagnetic ac susceptibility of $-0.33\cdot10^{-6}$ emu/g for ZnO [9] was substructed from the measured magnetic susceptibility. The results of the fitting procedure are shown in Figure 1. The obtained negative values of the paramagnetic Curie-Weiss temperature indicate that an antiferromagnetic superexchange interaction is a dominant mechanism of interaction. At lower temperatures, inverse ac susceptibility deviates from the linear dependence toward a temperature close to zero. This is the result of additional antiferromagnetic interactions between the next nearest neighbour magnetic ions. The Curie-Weiss behavior at higher temperatures, with antiferromagnetic interactions, was observed for polycrystalline $Zn_{1-x}Co_xO$ samples prepared using a standard solid-state reaction technique [10]. The authors determined material parameters that are in good agreement with the literature values for $Zn_{1-x}Co_xO$. The determined in our work Curie-Weiss temperature values are lower than reported in Ref. [10]. However, one should realize that in our case the content of magnetic ions incorporated into ZnO lattice is different and probably much lower than the nominal, technological concentration of magnetic dopant. We have estimated the concentration of magnetic ions assuming that material parameters are similar to reported in literature for $Zn_{1-x}Co_xO$ (see eg. [10] and references therein). The Curie-Weiss temperature θ can be described by formula $\theta = x\theta_0$, where θ_0 is constant related to the exhange integral between the nearest Co neighbours J_{eff}.

$$2J_{eff}/k_B = 3\theta_0/zS(S+1) \qquad (2)$$

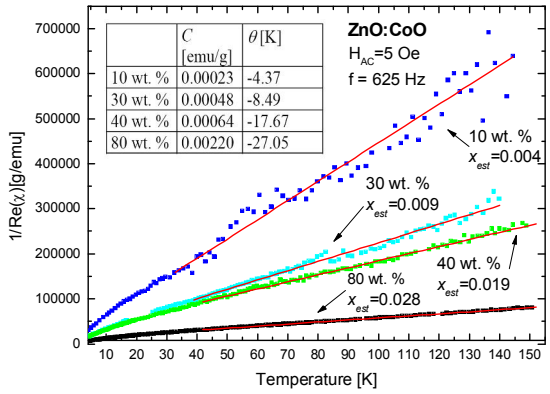
,where $z = 12$ is the number of nearest neighbours in the wurzite structure of $Zn_{1-x}TM_xO$. If one will assume that the value of θ_0 is equal to -951 K, as was shown in Ref. [10], the concentration of magnetic ions x_{est} can be estimated. The results of such a procedure, the determined values of x_{est} are shown in Figure 1.

The results of magnetic AC susceptibility for ZnO doped with MnO are shown in Figure 2. For the samples with low content of MnO (up to 50 wt. %) we observed superparamagnetic behavior above the blocking temperature. The inset in Fig. 2 shows typical SQUID magnetization for sample with low content of magnetic dopant. A clear bifurcation of the FC and ZFC plots is visible. For samples with higher content of magnetic dopant we observe peak at around 43 K, characteristic of a Mn_3O_4 ferrimagnet.

3. Conclusions

We have studied structural and magnetic properties of nanocrystalline ZnO doped with transition metal osides. For ZnO doped with CoO structural measurements showed the presence of Co_3O_4 nanoparticles and ZnO nanoparticles. The AC susceptibility measurements revealed the Curie-Weiss behavior at higher temperatures, with antifferomagntic interactions. For ZnO doped with MnO (up to 50 wt. %) samples the magnetic measurements showed the superparamagnetism above the blocking

temperature. For samples, with higher magnetic dopant, the presence of ferrimagnetic Mn_3O_4 is clearly visible. The structural measurements revealed the presence of Mn_3O_4 crystal structure for samples with MnO content above 50 wt. %.



	C [emu/g]	θ [K]
10 wt. %	0.00023	-4.37
30 wt. %	0.00048	-8.49
40 wt. %	0.00064	-17.67
80 wt. %	0.00220	-27.05

Figure 1. Inverse magnetic susceptibility for ZnO:CoO nanocrystalline samples.The results of the fitting procedure are gathered in the table.

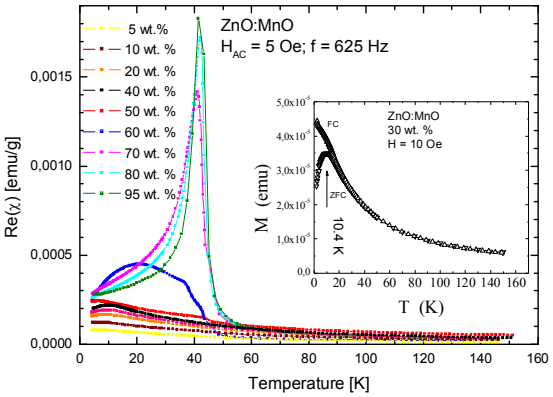


Figure 2. Magnetic AC susceptibility for ZnO:MnO nanocrystalline samples. The inset shows SQUID magnetization for sample with 30 wt. % of MnO.

References

[1] M. Knobel, W. C. Nunes, L. M. Socolovsky, E. De Niasi, J. M. Vargas, and J. C. Denardin, Journal of Nanoscience and Nanotechnology, **8**, 2836-2857, 2008 and references therein
[2] Y. Chen, D. M. Bagnall, H. Koh, K. Park, K. Hiraga, Z. Zhu, T. Yao, J. Appl. Phys., **84**, 3912, 1998
[3] J. Nemeth, G. Rodriguez-Gattorno, A. Vazquez-Olmos, D. Diaz , I. Dekany, Langmuir, **20**, 2855, 2004
[4] J. M. D. Coey, M. Venkatesan, and C. B. Fitzgerald, Nat. Mater., **4**, 173, 2005
[5] T. Dietl, Acta Physica Polonica A, **111**, 1, 27, 2007
[6] A. L. Patterson, Phys. Rev., **56**, 978, 1939
[7] R. Y. Sato-Berru, A. Vázquez-Olmos, A. L. Fernández-Osorio and S. Sortes-Martinez, J. Raman Spectrosc., **38**; 1073-1076, 2007
[8] P. Dutta, M. S. Seehra, S. Thota and K. Kumar, J. Phys.: Condens. Matter **20**, 015218, 2008
[9] CRC Handbook of Chemistry and Physics, 80th edn, 1999-2000, p.4-136. (CRC Press LLC, Boca Raton,London, New York, Washington, D. C. 1999)
[10] S. Kolesnik, B. Dabrowski, J. Mais, phys. Stat. sol. (c), **1**, 4, 900-903, 2004