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MAGNETIC PROPERTIES OF ZINC-OXIDE COMPOSITE DOPED WITH TRANSITION METAL IONS (Mn, Co, Cr)

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We have studied magnetic properties of zinc-oxide composite doped with transition metal (TM) ions (TM = Mn, Cr, Co) with relatively high concentration (4%) of TM ions. EPR measurements were carried out and temperature dependence of the EPR spectra was obtained. Analysis of the temperature dependences of the integral intensity of EPR spectra was carried out using Curie-Weiss law for ZnO;Mn sample.

INTRODUCTION

Diluted magnetic semiconductors (DMS) are of interest for study mainly due to the spin-spin exchange interaction between the localised magnetic moments and the band electrons (Dobrowolski, Kossut & Story, 2003). This property of DMS has potential applications in the spin-dependent semiconductor electronics (Awshalom, Loss & Samarth, 2002).

The ferromagnetism in DMS has been investigated theoretically using a model Hamiltonian (Dietl, Ohno, Matsukura, Cibert & Ferrand, 2000; Dietl, 2002; Jungwirth, König, Sinova, Kučera & MacDonald, 2002). Dietl *et al.* proposed the Zener p-d exchange interaction to describe the magnetism (Dietl *et al.*, 2000; Dietl, 2002).

Zinc-oxide have attracted intense attention due to the search for high Curie temperature (T_C) ferromagnetic DMS materials, since Dietl *et al.* predicted that GaN- and ZnO-based DMS could exhibit ferromagnetism above room temperature upon doping with transition elements, such as Mn (in the concentration of the order of 5% or more) in p-type materials (Dietl *et al.*, 2000). According to these calculations, the p-type $Zn_{1-x}Mn_xO$ is a promising candidate for a room temperature ferromagnet. *Ab initio* band calculations (Sato & Katayama-Yoshida, 2000) predict ferromagnetism to be stable in the p-type $Zn_{1-x}Mn_xO$, whereas antiferromagnetism in the n-type$Zn_{1-x}Mn_xO$. On the other hand, a ferromagnetic phase has been predicted for the n-type ZnO substituted with Fe, Co, or Ni (Sato *et al.*, 2000). Various substitutions (B, Al, Ga, In, Si, and F) in the parent compound ZnO can increase its natural n-type conduction caused by oxygen vacancies and Zn interstitials (Minegishi, Koiwai, Kikuchi, Yano, Kasuga & Shimizu, 1997). The ferromagnetic state with T_C above room temperature is predicted to be favourable for transition metals (TM), e.g. V, Cr, Fe, Co, and Ni in ZnO, while Mn-doped ZnO is predicted to be antiferromagnetic. These predictions largely boosted intensive experimental activities on TM doped ZnO. A large number of research groups have reported the experimental observation of ferromagnetism in TM doped ZnO fabricated by various methods including ion implantation (Johnson, Thurber, Anghel, Sabetian, Engelhard, Tenne, Hanna & Punnoose, 2010; Liu, Hsu, Venkataiah, Qi, Lin, Lee, Liang & Huang, 2010; Wang, Yuan, Song, Liu, Tian, Li, Zhou, Li & Yin, 2007; Heo, Ivill, Ip, Norton, Pearton, Kelly, Rairigh Hebard & Steiner, 2004; Hong, Brize & Sakai, 2005; Ip, Frazier, Heo, Norton, Abernathy, Pearton, Kelly, Rairigh, Hebard, Zavada & Wilson, 2003; Polyakov, Govorkov, Smirnov, Pashkova, Pearton, Ip, Frazier, Abernathy, Norton, Zavada & Wilson, 2004). For a comprehensive review, see Ref. (Zhou, Potzger, Xu, Talut, Lorenz, Skorupa, Helm, Fassbender, Grundmann & Schmidt, 2008; Özgür, Alivov, Liu, Teke, Reshchikov, Doğan, Avrutin, Cho & Morkoç, 2005; Liu, Yun & Morkoç, 2005; Jagadish & Pearton, 2006). However, the reported magnetic properties obtained using the same magnetic dopant vary considerably, e.g. for Mn doped ZnO the saturation moment varies from 0.075 to 0.17 μB/Mn (Hong *et al.*, 2005), whereas T_C from 400 K to 30-45 K (Jung, An, Yi, Jung, Lee & Cho, 2002). In contrast, other groups reported (i) the observation of antiferromagnetism (Bouloudenine, Viart, Colis, Kortus

& Dinia, 2005; Sati, Deparis, Morhain, Schafer & Stepanov, 2007), (ii) spin-glass behavior (Fukumura, Jin, Kawasaki, Shono, Hasegawa, Koshihara & Koinuma, 2001; Kolesnik, Dabrowski & Mais, 2002; Jin, Fukumura, Kawasaki, Ando, Saito, Sekiguchi, Yoo, Murakami, Matsumoto, Hasegawa & Koinuma, 2001), and (iii) paramagnetism (Rao & Deepak, 2005; Zhang, Chen, Lee, Xue., Sun, Chen, Chen & Chu, 2006; Zhou, Potzger, Reuther, Kuepper, Skorupa, Helm & Fassbender, 2007) in TM-doped ZnO.

We report here on the magnetic properties of zinc-oxide composite (ZnO) doped with Co, Cr and Mn. Electron paramagnetic resonance (EPR) spectra have been measured and analysed to extract information on the characteristics of the incorporation of the ions in the lattice.

EXPERIMENT

Hard solutions $Zn_{1-x}Mn_xO$, $Zn_{1-x}Co_xO$, and $Zn_{1-x}Cr_xO$ were obtained by the method of solid state reactions, which is widely applied in ceramic technology. Materials of special cleanness were used as initial components for preparation of charge. The powders of connections $MnCO_3$, $CoCO_3$, and $CrCO_3$ obtained by growing shallow to the size of particles 50–100 nm, and mixed up with powder ZnO and small ammount of water in the jasper drums of planetary mill SAND-1-1. Time of mixing and grating was determined by the degree of homogenization and was set to 16 h.

The mixture was drained for temperatures 120±5 ^oC. The previous annealing of mixture, which its activating was in the process of, was carried out in air at 700±5 ^oC for 4 hours. Press-purveyances by a diameter 11.5–15 mm thick formed 1–2.5 mm by applying pressure of 40–60 MPa on a hydraulic press PG-10 without the use of plastificators. Mixtures were annealed at temperatures near to 1000 ^oC. Hard solutions of $Zn_{1-x}Mn_xO$, $Zn_{1-x}Co_xO$, and $Zn_{1-x}Cr_xO$ with x=0.04 were obtained in this way. Standards were annealed in the chamber stove of periodic action VTP-06M1 in air (the accuracy of temperature control was ±5 ^oC) during 3 h. Maximal temperature of annealing, which reply the isothermal area of curve of heating–cooling, was 1110 ^oC.

Technology of preparation of ceramic materials on the basis of ZnO, as remarked earlier, utilizes solid states reactions. The reactions $MnCO_3 + ZnO > Zn_{1-x}Mn_xO$, $CoCO_3 + ZnO > Zn_{1-x}Co_xO$ and $CrCO_3 + ZnO > Zn_{1-x}Cr_xO$ yield powders of $Zn_{1-x}Mn_xO$, $Zn_{1-x}Co_xO$, and $Zn_{1-x}Cr_xO$.

EPR measurements were performed in the X-band. The temperature of the samples was controlled in the range of 92–370 K using the BRUKER liquid N gas flow cryostat.

RESULTS AND DISCUSSION

TEM images and EPR spectra of the investigated samples ZnO:TM are presented in Figs 1-3. TEM images (Figs 1a-3a) are included to show the morphology of samples at different magnification and present the material's structure. Figures 1b and 2b present room temperature EPR spectra of ZnO:Co and ZnO:Cr, respectively. Figure 3b presents temperature dependence of EPR spectra for the sample ZnO:Mn.

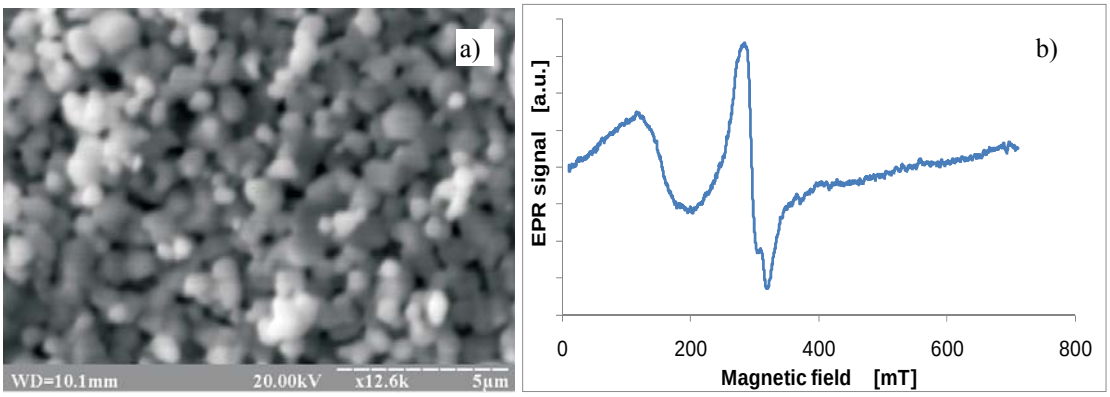

Fig.1. Characteristics of the sample ZnO:Co: a) TEM image, b) EPR spectra at room temperature.

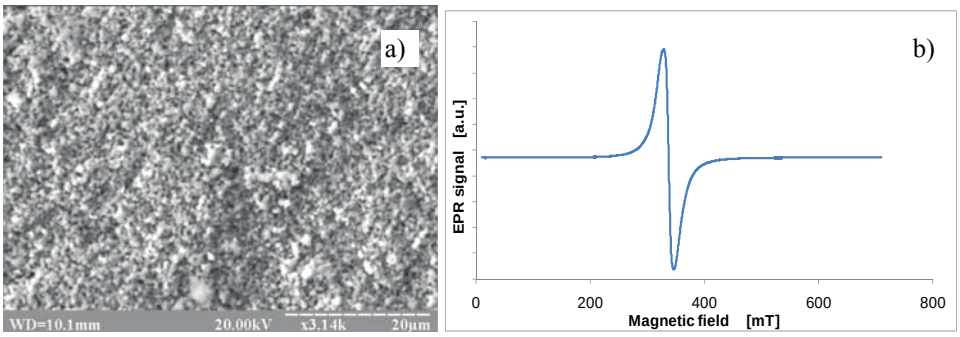

Fig. 2. Characteristics of the sample ZnO:Cr: a) TEM image, b) EPR spectra at room temperature.

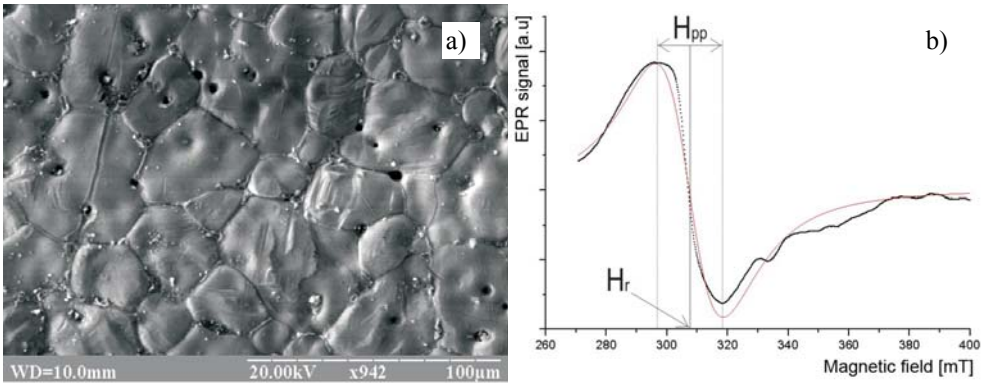

Fig.3. Characteristics of the sample ZnO:Mn: a) TEM image, b) EPR spectra at room temperature: experimental curve – black line, theoretical curve – red line.

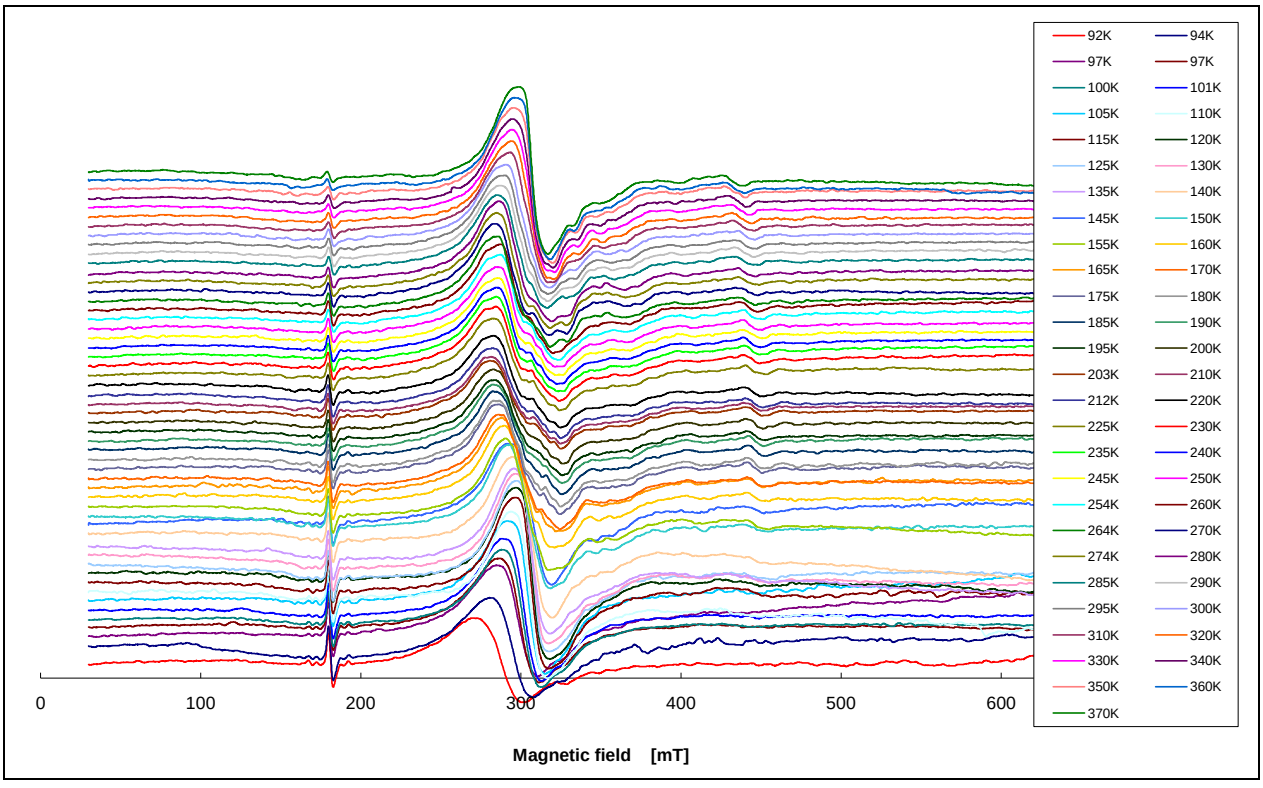

Fig. 4. EPR spectra of the sample ZnO:Mn in the temperature range 92-370 K.

Additonal analysis was carried out only for the sample ZnO Mn. The effective spectroscopic g-factor and the peak-to-peak linewidth of the resonance line H_{pp} were determined as illustrated in Figure 3b. Since the broad EPR line is asymmetric, the accuracy of parameters measured directly from the experimental spectrum is rather limited. Therefore, additionally the experimental line was fitted using the Lorenzian type curve, since such curves describe satisfactorily experimental EPR lines of DMS with manganium in high temperature range (see, Samarth & Furdyna, 1988, and references therein).

In this way we determined parameters for EPR lines such as the peak-to-peak line width (H_{pp}), the intensity (I) as well as the resonance field (H_r). Based on these data we obtained the temperature dependencies of $H_{pp}(T)$, $I(T)$, $H_r(T)$, and integral intensity as presented in Figure 5.

We used the Curie-Weiss law to analyse the temperature dependences of the integral intensity, which is directly proportional to the magnetic susceptibility χ. A linear increase of $\chi^{-1}(T)$ at higher temperatures can be fitted to the Curie-Weiss law

$$(\chi - \chi_0)^{-1}(T) = (T-\theta_{cw})/C \qquad (1)$$

where C is the Curie constant, θ_{cw} is the paramagnetic Curie temperature, and χ_0 is a temperature independent term to account for the diamagnetic host and any Pauli paramagnetism contribution.

Figure 5d displays the temperature dependence of the quantity $(\chi - \chi_0)^{-1}$. The lines are linear extrapolations illustrating the ferromagnetic (positive) Curie-Weiss temperatures.

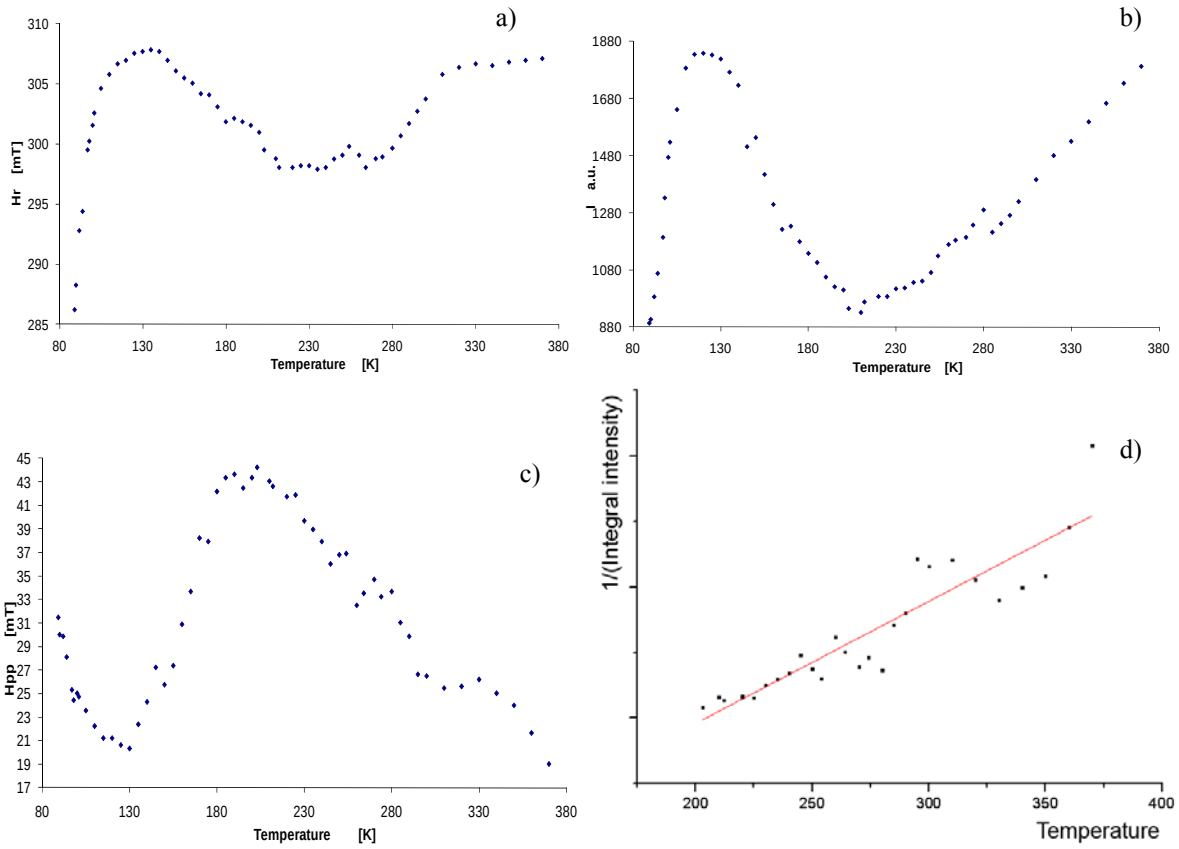

Fig.5. Temperature dependence of EPR spectra of the sample ZnO:Mn: a) Hr(T), b) I(T), c)Hpp(T), and d) inverse of integral intensity.

Fitting yields the following values: $\theta(x)$=97 K and $C(x)=1.13^{11}$.

The analysis of the dependencies in Figures 3-5 and the positive value of Curie temperature, 97 K, clearly indicate ferromagnetic interactions between Mn ions.

CONCLUSIONS

The materials prepared for this study exhibit different structure. The samples ZnO:Co and ZnO:Cr have porous structure of different grainity, whereas the sample ZnO:Mn is more homogenous as compared with the previous two samples.

In summary, we have reported the X-band EPR studies of ZnO:TM, TM=Co, Cr, Mn. We have determined from the EPR lines the for parameters: the peak-to-peak line width (H_{pp}), the intensity (I) as well as the resonance field (H_r).

The results of temperature dependence of EPR spectra for the sample ZnO:Mn and linear extrapolations to the Curie-Weiss law indicate the ferromagnetic interaction between Mn ions characterized by the Curie temperature 97 K.

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