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Structural and magnetic properties of Mn-doped ZnO powders

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A mixture of bi(acetylacetonato) zinc(II)hydrate and tris(acetylacetonato) manganese(III) complexes was thermally co-dissociated to synthesize Mn-doped ZnO powders. In order to examine the effect of oxygen vacancies on the ferromagnetic coupling of Mn ions, two preparation routes were used: in route (I) the preparation was done in an open environment, whereas in route (II) the preparation was done in a closed environment. The X-ray diffraction (XRD) and the X-ray fluorescence (XRF) measurements indicate that the Mn content in the three samples are 3.9% (I), 3.3% (II) and 4.2% (II). The XRD results showed that the Mn ions were incorporated in the ZnO crystal and that a $Zn_{1-x}Mn_xO$ solid solution has formed. The magnetic characterization indicated that only samples prepared via route (II) exhibited a room temperature ferromagnetic component of magnetization. Furthermore, magnetic analysis showed that the magnetic moment per dopant ion in the samples examined was in the range of 4.2–6.1 μ_B/Mn. The percentages of coupled Mn atoms to the total number of Mn atoms were found to be extremely small (less than 0.1%), which by itself cannot explain the observed RT hysteresis loops. Thus, in order to produce long-range ferromagnetic order in these samples, the FM coupling has to be mediated via defects. The observed FM in this study may be attributed to the presence of oxygen vacancies, which mediate the ferromagnetic exchange between the coupled Mn ions. This is consistent with the bound magnetic polarons (BMP) model where defects like oxygen vacancies cause the polarons to overlap and give rise to a long-range ferromagnetic order in dilute magnetic semiconductors (DMS).

1. Introduction

Zinc oxide (ZnO) is a degenerate semiconductor and has a wide bandgap (~3.3 eV), large excitonic binding energy (59 meV), and transparent properties in the visible range. Due to these properties, it has attracted considerable attention due to its wide applications in solar cells, flat panel displays, and other optoelectronic applications. It has been observed that the physical properties of ZnO can be greatly influenced by doping it with different types of metallic ions. Doping ZnO with metallic ions like Sn, Ga, In, Sn, Al, Sc, and Y, improves its *n*-type conductivity [1–3] whereas doping it with N or Sb make it a p-type semiconductor [4].

Doping ZnO with magnetic ions such as Fe, Cr, Co, and Ni adds a spin property to the host material, which gives the semiconductor a potential use in spintronics applications [5]. The magnetic behavior of Mn-doped ZnO (ZnO:Mn) has been studied extensively, and different magnetic behaviors, like spin glass [6], paramagnetism [7,8], antiferromagnetism [6], and ferromagnetism (FM) have been all reported [9–12]. These results show that the magnetization of ZnO:Mn is strongly dependent on the preparation method and procedure, and seems to be sensitive to the crystalline structure and the concentration of oxygen vacancies and defects.

The origin of room temperature ferromagnetism (RT FM) in dilute magnetic semiconductors (DMS) is still challenging our understanding of magnetic solids. In super or double exchange models, exchange interactions are mediated by charge carriers [13,14]. Coey et al. [15] have argued that carrier mediated exchange interactions cannot produce long-range magnetic order when the doping level of magnetic ions is a few percent. Instead, they have proposed the bound magnetic polarons (BMP) model in which the ferromagnetic exchange is mediated by shallow donor electrons. In the BMP model, the only option to obtain higher values for the Curie temperature (T_C) is to increase the donor electron density around the magnetic impurities. In ZnO, the nature of the vacancy defects responsible for shallow donors ore oxygen vacancies [16]. In a comprehensive study of TiO_2 doped with Co, oxygen vacancies were found to be responsible for the observed RT FM [17]. In that study, the samples that were annealed in open air were found to be paramagnetic, whereas those that were annealed in vacuum exhibited RT FM. In recent studies, the observed room temperature ferromagnetism in ZnO doped with Mn has been attributed to the presence of vacancy defects like zinc [11] or oxygen [12]. In other studies [18] of Ni-doped ZnO, the

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observed ferromagnetic behavior has also been attributed to the presence of defects like oxygen vacancies, and the results have been explained in terms of the BMP model.

For the magnetic moment per dopant atom, Coey et al. [15] have also argued that the observed high values for the magnetic moment per cation at low concentrations cannot be explained in terms of the possible known ferromagnetic phases. In ferromagnetically ordered superexchange systems, the average net moment per magnetic cation is rarely much more than one Bohr magneton (μ_B). For ZnO doped with 2% Mn, the reported values for the magnetic moment per Mn atom are 0.11 μ_B/Mn [11] and 0.16 μ_B/Mn [19]. In a recent study [12] of ZnO doped with 25% Mn, much lower values, 0.046 and 0.018 μ_B/Mn, were obtained when these values were extracted from the value of the samples saturation magnetization. However, these low values were boosted (1.5 and 3.5 μ_B/Mn) when the effective magnetic moment per cation was calculated. Similar results for ZnO doped with Gd were reported, where a low value of 0.01 μ_B/Gd was obtained from the value of the saturation magnetization and a much higher value of 9 μ_B/Gd was obtained when the uncorrelated spins were included in the calculations [20]. The obtained high values for the magnetic moment per magnetic cation support the BMP model.

The aim of this work is to examine RT FM in Mn-doped ZnO bulk samples prepared by the simple precipitation method using two routes: the first is in an open environment and the second is in a closed environment. Samples with different Mn concentrations were synthesized and characterized. The current study focuses on the effects of oxygen vacancies on the observed RT FM and gives some hints about the origin of ferromagnetism in the samples examined.

2. Experimental procedure

In our procedure, the starting materials are transition-metal complexes: bis(acetylacetonato) zinc(II)hydrate and tris(acetylacetonato) manganese(III). The chemicals that were used to prepare these complexes were Mn-chloride hexahydrate and zinc sulphate heptahydrate (Puriss-Fluka Chemica), sodium acetate trihydrate and sodium hydroxide (GPR-BDH), acetylacetone (98% assay Purum-Fluka Chemica), and methanol (Analar-BDH). In an earlier study, a detailed sample-preparation technique had been presented, in which appropriate amounts of fine powders of the two complexes had been totally mixed together in methanol until they dissolved [21]. In this study, the samples were prepared using two routes: in route (I), appropriate amounts of the starting powders are totally mixed and dissolve in methanol. The methanol was evaporated and the resulting mixture was placed in an open aluminum crucible and then flash-sintered at 400 °C for 2 h to allow for free dissolving in an open environment. In route (II), the resulting mixture was placed in a closed aluminum crucible for sintering at 400 °C for 2 h in order to allow for dissolving in a closed environment. The reason for this was to introduce partial oxygen deficiency in the samples and examine its effect on the formation of RT FM. Finally, the resulting powders were then grounded and pelletized using a pressure of 750 MPa and were then annealed in the same crucible conditions in order to crystallize at 600 °C for 2 h.

Elemental analyses for the samples were carried out using an energy dispersion X-ray fluorescence EDXRF spectroscopy method. The setup used consisted of a Philips PW-1710 X-ray tube with a Cu anode operated at 15 kV and 5 mA, and a sensitive Amptek XR-100CR detector. The Mn–Zn relative content in the examined samples was found to be 0% (undoped), 3.9% (I), 3.3% (II) and 4.2% (II). Structural analyses were made using a Philips PW-1710 θ–2θ X-ray diffraction (XRD) with Cu K radiation (0.15406 nm) and a step size of 0.02°.

Magnetic characterization was carried out using a vibrating sample magnetometer (Micro-Mag Model 3900) with a sensitivity of 0.5 emu for a 1 s averaging time scale. Magnetization curves were measured at room temperature ($T=294$ K) from $+1$ to -1 T using an averaging time of 1 s.

3. Results and discussion

3.1. Characterization by X-rays

Fig. 1 shows the EDXRF spectrum for one of the prepared samples. The spectrum shows Mn Kα (5.898 keV), Mn Kβ1 (6.490 keV), Zn Kα (8.638 keV),. Zn Kβ1 (9.572 keV) lines, and a signal from the Cu source of the X-ray tube. No other signals (including an aluminum signal) were detected. The relative fraction ratio of Mn to Zn in the samples was determined by measuring the ratio of the integral intensity of the Mn Kα-signal to that of the Zn Kα-signal. The reference samples were pure bis(acetylacetonato) zinc(II) hydrate and tris(acetylacetonato) manganese(III). The obtained relative weight ratios were 3.9% (I), 3.3% (II), and 4.2% (II), which were close to the values determined during preparation by weight.

Fig. 2 shows the XRD patterns for the prepared Mn-doped ZnO samples. For comparison, the XRD pattern for the undoped ZnO powder prepared using the same preparation procedure is also shown in the same figure. The XRD patterns show that all the investigated samples were polycrystalline with a hexagonal wurtzite structure (space group P63mc) of ZnO. Signals arising from Mn, Mn oxides, or any Mn related phases were not detected. The most expected secondary phase is Mn oxide, which usually crystallizes upon annealing the sample at 300 °C [22].

Table 1 shows the structural analysis results that were obtained for the prepared undoped and doped ZnO powders. The Bragg angle of intense (1 0 1) reflection showed a slight shift $\Delta(2\theta_{101})$ towards higher values relative to that of undoped ZnO, especially for samples prepared via route (II). This provides evidence for the creation of internal compressive micro-stress. This slight peak shift $\Delta(2\theta_{101})$ is a result of structural strain ($\varepsilon_s=-\Delta\theta_{(101)}\cot\theta_{(101)}$), which is of the order of 10^{-3}. This strain is caused by a compressive micro-stress (σ_{st}) that can be estimated by:$\sigma_{st}\approx(3\varepsilon_s)B$, where B is the average bulk modulus, which is usually about 143 GPa for ZnO [23]. Table 1 shows that the

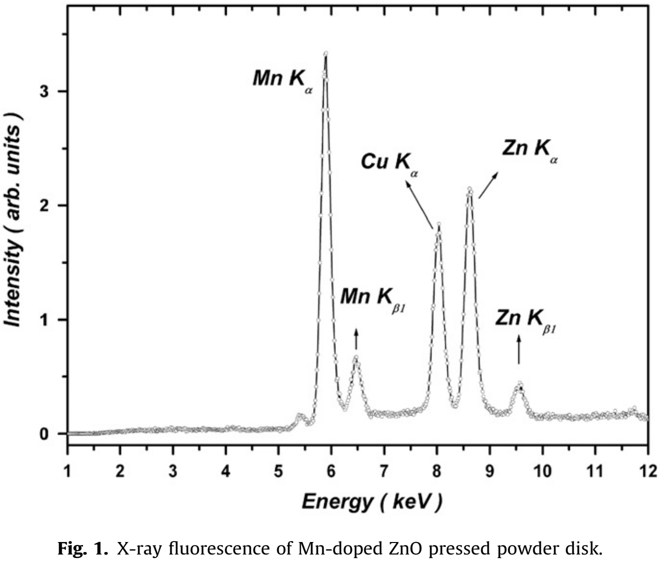

Fig. 1. X-ray fluorescence of Mn-doped ZnO pressed powder disk.