Magnetic Resonance Study of MnO/ZnO Nanopowders

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(Received May 18, 2011)

Fine particles $n$(MnO)/$(1 - n)$ZnO ($n = 0.05$ to $0.95$) were prepared by wet chemistry method. According to X-ray diffraction analysis the obtained samples with $n = 0.95$, $0.90$, $0.80$, $0.70$, $0.60$ contained Mn$_3$O$_4$ and ZnMn$_2$O$_4$ phases, while samples with $n = 0.05$, $0.10$, $0.20$, $0.30$, $0.40$ and $0.50$ contained ZnMnO$_3$ and ZnO phases. The mean crystalline size of ZnMnO$_3$ varied from 8 to 13 nm. The magnetic resonance investigations have been carried out at room temperature. Slightly asymmetric, broad and intense magnetic resonance line is recorded for all samples. The magnetic resonance spectra parameters showed marked differences depending on the composition index $n$. This could be explained by the variation of the magnetic susceptibility and a much slower evolution of spin relaxation, associated with the interaction of crystal field and superexchange interactions. Taking into account the values of magnetic resonance parameters, the investigated samples could be divided into two groups: these with the composition index $n < 0.50$ and those with $n > 0.50$. A detailed discussion of the magnetic properties of different phases in the $n$(MnO)/$(1 - n)$ZnO system is presented.

PACS: 75.50.Tt, 76.30.Fc, 76.50.+g

1. Introduction

In the recent years a lot of attention is devoted to theoretical and experimental study of a group of materials called diluted magnetic semiconductors (DMS) [1]. A serious obstacle in finding practical applications for these materials is the stabilization of their interesting physical properties at room temperature (thus their Curie temperature should be higher than 300 K). Despite initial promising results obtained for the compound ZnO:Mn [2], it is not clear at the present moment whether this material could be useful in technological applications. The main unsolved problem in DMS materials is the origin and nature of their magnetism [3]. In several cases magnetism was the result of segregation of metal agglomerates while in other cases the presence of transitional metals with different valences coupled by the double exchange mechanism was crucial [4, 5]. Recent research points to a very important role played by the defects [6]. For example, in ZnO:Mn in form of nanoparticles or thin films the ferromagnetism has appeared at room temperature only when the particle were capped by molecules introducing defects of the p-type [6]. Quite the opposite effect was observed for thin films of ZnO:Co in which ferromagnetism at high temperature was observed only in the presence of n-type defects [7]. It was found that the magnetic properties of ZnO:Co and ZnO:Mn strongly depended on thermal annealing in different atmospheres [8]. Moreover, doping of ZnO thin films with non-magnetic ions from the 3$d$ group (e.g. titanium or vanadium) can cause emergence of ferromagnetic properties [9]. All these results indicate on a critical role of electronic structure of a semiconductor (modified by the presence of magnetic ions) in appearance of ferromagnetic properties.

Another interesting property of ZnO nanoparticles, particularly in UV-A range, is the blocking of UV radiation. This allows employment of these nanoparticles in cosmetic industry as well as in fabrication of paints and fibers [10]. High catalytic activity of these nanoparticles in oxidative and photochemical reactions. However, it is possible to reduce it by modification of the surfaces of nanoparticles [11]. Applications of ZnO nanoparticles seem particularly promising in the area of optoelectronic devices. They find employment as blue light sources, in the form of nanotubes as radiation emitters of UV, also in biology and medicine as fluoro-
cence markers [12]. Recently, the electron paramagnetic resonance/ferromagnetic resonance (EPR/FMR) investigation of \( n(\text{FeO})/(1 - n)\text{ZnO} \) samples with \( n < 0.70 \) showed that the magnetic resonance line originates from the isolated iron(III) ions in zinc ferrite (EPR line) while for higher concentrations of iron oxide it could be attributed to the \( \gamma\text{-Fe}_2\text{O}_3 \) magnetic nanoparticles (FMR line) [13, 14].

The aim of this report is to study the EPR/FMR spectra of a series of \( n(\text{MnO})/(1 - n)\text{ZnO} \) \( (n = 0.05 \) to 0.95) nanopowders prepared by wet chemistry method. A wide compositional range of the used two metal oxides would allow to obtain a more complete picture of magnetic properties of the \( n(\text{MnO})/(1 - n)\text{ZnO} \) system.

2. Experimental

The mixture of manganium and zinc hydroxides was obtained by addition of ammonia solution to 20% solution of proper amount of \( \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) and \( \text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O} \) in water. The obtained hydroxides were filtered, dried and calcined at 300°C for 1 h. A series of samples containing \( n(\text{MnO})/(1 - n)\text{ZnO} \) \( (n = 0.05 \) to 0.95) was obtained.

The phase composition of samples was determined using XRD (Co \( K_\alpha \) radiation, X’Pert Philips). The mean crystallite size of these phases was determined using Scherrer’s formula. The morphology of samples was investigated using scanning electron microscopy (LEO 1530).

The specific surface area of the nanopowders was determined by the Brunauer–Emmett–Teller (BET) method (nitrogen adsorption) using the equipment Gemini 2360 of Micromeritics. The helium pycnometer AccuPyc 1330 of Micromeritics was applied to determine the density of powders.

The measurements of magnetic resonance spectra were performed on conventional X-band (\( \nu = 9.4 \) GHz) EPR Bruker E 500 spectrometer with 100 kHz magnetic field modulation. Samples containing around 20 mg of powder were placed in 4 mm diameter quartz tubes. The measurements were carried out at room temperature.

3. Results and discussion

Figure 1 presents the XRD patterns of ZnO doped MnO. (A) Peaks attributed to ZnO are marked as , peaks attributed to \( \text{ZnMnO}_3 \) are marked as •. (B) Peaks attributed to \( \text{Mn}_3\text{O}_4 \) are marked as ▼, peaks attributed to \( \text{ZnMn}_2\text{O}_4 \) are marked as vertical line.

![Fig. 1. The XRD patterns of ZnO doped MnO.](image)

Fig. 2. Deconvolution of a single XRD line for sample \( n(\text{MnO})/(1 - n)\text{ZnO} \) with \( n = 0.60 \).

![Fig. 2. Deconvolution of a single XRD line for sample \( n(\text{MnO})/(1 - n)\text{ZnO} \) with \( n = 0.60 \).](image)
The values of magnetic resonance spectra parameters ($H_r$ — resonance field, $g_{\text{eff}}$ — effective $g$-factor, $\Delta H_{pp}$ — peak-to-peak linewidth, $I_n$ — integrated intensity) for different values of composition index $n$ in $n$(MnO)/(1 $-$ n)ZnO nanopowders.

<table>
<thead>
<tr>
<th>Composition index $n$ in $n$(MnO)/(1 $-$ n)ZnO formula</th>
<th>$H_r$ [G]</th>
<th>$g_{\text{eff}}$-factor</th>
<th>Linewidth $\Delta H_{pp}$ [G]</th>
<th>Integrated intensity ratio $I_n/I_{0.05}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>3362(3)</td>
<td>2.000(2)</td>
<td>741(1)</td>
<td>1</td>
</tr>
<tr>
<td>0.10</td>
<td>3202(3)</td>
<td>3.329(2)</td>
<td>481(1)</td>
<td>4557</td>
</tr>
<tr>
<td>0.20</td>
<td>3350(3)</td>
<td>2.007(2)</td>
<td>2480(2)</td>
<td>4034</td>
</tr>
<tr>
<td>0.30</td>
<td>3340(2)</td>
<td>2.011(2)</td>
<td>2600(2)</td>
<td>6038</td>
</tr>
<tr>
<td>0.40</td>
<td>3360(2)</td>
<td>2.001(2)</td>
<td>2700(2)</td>
<td>10669</td>
</tr>
<tr>
<td>0.50</td>
<td>3610(3)</td>
<td>1.863(2)</td>
<td>3500(3)</td>
<td>13225</td>
</tr>
<tr>
<td>0.60</td>
<td>3500(3)</td>
<td>1.921(2)</td>
<td>2200(2)</td>
<td>11200</td>
</tr>
<tr>
<td>0.70</td>
<td>3530(3)</td>
<td>1.905(2)</td>
<td>2350(2)</td>
<td>15201</td>
</tr>
<tr>
<td>0.80</td>
<td>3570(3)</td>
<td>1.883(2)</td>
<td>2350(2)</td>
<td>11700</td>
</tr>
<tr>
<td>0.90</td>
<td>3560(3)</td>
<td>1.889(2)</td>
<td>2330(2)</td>
<td>14300</td>
</tr>
<tr>
<td>0.95</td>
<td>3560(3)</td>
<td>1.889(2)</td>
<td>2410(2)</td>
<td>15483</td>
</tr>
</tbody>
</table>

Figure 4 presents the results of specific surface area and density measurements. With the increase of ZnO content a drop of the specific surface area and an increase of density is registered. This is also illustrated by SEM images showing the morphology of specific samples (Fig. 5). The powders containing more manganese oxide are less agglomerated than samples with a lower content of MnO. Additionally, the agglomerates should be more stable, because the specific surface area drops from 14 m$^2$/g to 4 m$^2$/g.

Figure 6a–d presents the magnetic resonance spectra of a series of $n$(MnO)/(1 $-$ n)ZnO samples containing from 5 to 95 wt% of MnO. The magnetic resonance spectra are dominated by a slightly asymmetric, intense, and broad line. The resonance lines of manganese ions are basically centered at $g_{\text{eff}}$ ≈ 1.86–2.02 with peak-to-peak linewidths $\Delta H_{pp}$ in the range of 480–3500 G. In Table the values of magnetic resonance spectra parameters ($H_r$ — resonance field, $g_{\text{eff}}$ — effective $g$-factor, $\Delta H_{pp}$ — peak-to-peak linewidth, $I_n$ — integrated intensity) for different values of the composition index $n$ in $n$(MnO)/(1 $-$ n)ZnO nanopowders are given. The intensity of the observed spectra strongly depends on the concentration of magnetic ions.

Two spectral features are apparent in Fig. 6: a very broad and intense line and a six-line structure around $g$ ≈ 2. The broad line is typical for exchange coupled Mn ions, frequently observed in other Mn doped nanocrystals; while the six-line spectrum is usually attributed to Mn$^{2+}$ incorporated in the nanocrystals. Closer inspection of Fig. 6b reveals an additional set of six-line structure. It could be attributed to Mn$^{2+}$ ions in strongly distorted environment, e.g. on the surface of ZnO nanoparticles.
spectra of isolated Mn(II) ions is recorded for samples with small contents of the manganese oxides, while maximum concentration was registered for sample with 30% of MnO. The resonance line for sample with 10% MnO shows a marked anomaly — it is shifted drastically in the direction of small magnetic field. Additionally, the presence of a spurious phase attributed to isolated Mn(II) ions is observed (Fig. 6d). It is suggested that an intense magnetic agglomeration process was in action and in effect the FMR spectrum was recorded. The ZnMnO₃ compound could be in ferromagnetic phase above room temperature [1, 17–19]. Low concentration of magnetic nanoparticle agglomerates could shift essentially the resonance line in the direction of small magnetic fields [20]. For this sample only a small concentration of ZnMnO₃ phase is observed which could be detected by XRD method (Fig. 1). An additional resonance line is observed for sample with 80% concentration of MnO (Fig. 6 and Table) which is shifted strongly in the direction of smaller magnetic fields. It could be assumed that the magnetic agglomeration process could be responsible for this shift.

As it is seen in Fig. 7, from the point of view of magnetic resonance parameters, the investigated samples could be divided into two groups: those with the composition index $n < 0.5$ and those with $n > 0.5$. In samples with $n < 0.5$ the magnetic response comes from the magnetic ZnMnO₃ phase (Fig. 1) and the intensity of the registered signal is proportional to concentration of this phase (Fig. 8). The linewidth increases with the increase in concentration of the above phase due to stronger magnetic dipole–dipole interaction (Fig. 7). The broadening by the dipole–dipole interaction depends significantly on the concentration of the ZnMnO₃ phase.
The EPR signal changes essentially for samples with $n > 0.5$. The $g$-factor parameter and linewidth shift essentially towards smaller values (Fig. 7 and Table). XRD measurements have shown that in samples with $n > 0.5$ the Mn$_3$O$_4$ and ZnMn$_2$O$_4$ phases are dominating. The EPR measurements have shown that the integrated intensity is lower for samples with $n = 0.6$ and $n = 0.8$ while higher values are obtained for samples $n = 0.7$ and $n = 0.95$. The linewidth increases in samples with bigger composition index $n$ while $g$-factor shows an opposite tendency (Fig. 7). In sample $n = 0.80$ an additional resonance line has appeared from magnetically ordered phase that causes the dipole–dipole interaction to be stronger.

The magnetic resonance study of Mn$_3$O$_4$ and ZnMn$_2$O$_4$ nanoparticles was presented in Refs. [21, 22]. In Ref. [21] the structural and magnetic characteristics of the ZnMnO nanoclusters synthesized by the sol–gel method were investigated. A small quantity of ZnMn$_2$O$_4$ phase was also present in the studied samples. The EPR spectrum consisted of a broad line with $g \approx 1.9961$ and was attributed to Mn$^{2+}$ ions substituting Zn$^{2+}$. The paramagnetic centres were assumed to exist in the interior and near the surface of the crystals. The magnetization curve measured at room temperature showed a hysteresis loop arising probably due to the presence of the ZnMn$_2$O$_4$ phase [21]. Nanoparticles of Mn$_3$O$_4$ produced by a novel, environmentally friendly, room-temperature route using an ionic liquid have been studied by EPR method in Ref. [22]. The production technique created a broad-size distribution of Mn$_3$O$_4$ agglomerates in the range of 8–680 nm and having various morphologies. The broad EPR line observed at room temperature did not show hyperfine splitting for Mn$^{2+}$ and Mn$^{4+}$ ions and had the linewidth of 2787 G and the resonance field of 4026 G. This symmetric line showed the existence of strongly interacting Mn$^{2+}$ ions in Mn$_3$O$_4$ which was interpreted as the result of convolution of different resonance fields due to the distribution of local effective fields during dipolar interactions between particles [22].

4. Conclusions

The series of $n$(MnO)/(1 – $n$)ZnO ($n = 0.05$ to 0.95) nanopowders were prepared, characterized and investigated by magnetic resonance spectroscopy. The phases ZnO and ZnMnO$_3$ dominate for $n < 0.6$ while for $n > 0.6$ the phases Mn$_3$O$_4$ and ZnMn$_2$O$_4$ are recorded. The EPR measurements of samples with $n < 0.6$ (except sample with $n = 0.1$) have shown that the resonance line is centered above $g_{\text{eff}} = 2$ and is attributed to ZnMnO$_3$ phase. The integrated intensity increases with increasing $n$ and for $n = 0.6$ a very strong dipole–dipole interaction is observed. A strong magnetic spin correlated system is observed for sample $n = 0.10$ and it could be associated with the formation of a low amount of ZnMnO$_3$ phase. Above $n = 0.6$ the recorded EPR line is centered below $g_{\text{eff}} = 2$ and it could be attributed to ZnMn$_2$O$_4$ phase with the greatest content observed for samples $n = 0.7$ and $n = 0.95$. Additional resonance line is recorded for sample $n = 0.80$, probably due to the presence of small concentration of strongly correlated spins which essentially influence the broadening of the resonance line.

References