Optical and RES spectroscopy of the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$ nanocrystals in polyethyleneglycole films

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Abstract

We have studied at RT the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/polyethyleneglycole (PEG) composite film deposited on a quartz glass support, using optical and EPR spectral methods. The average dimension of Cd$_{0.75}$Mn$_{0.25}$Cl$_2$ nanoparticles was 30 nm. Optical spectrum of these nanocrystals in PEG films shows at room temperature an UV shift of the fundamental band edge. All the Mn$^{2+}$ ion absorption bands due to the ground configuration, observed with single crystals at low temperature and several supplementary bands attributed to double transitions are present on this spectrum. Results are discussed using ligand field theory and are compared with the results obtained on similar bulk single crystals.

Key words: nanocrystals, absorption and emission spectra, EPR spectra

Introduction

Optical properties of nanocrystals have extensively been studied in the last few years. Due to the quantum confinement, the large surface/volume ratio and the high density of surface states, the spectra of these materials differ from those of the bulk single crystals. Our studies are concerned with manganese doped systems. The crystal field theory applied to manganese ion usually mentions ten transitions. The number of the observed absorption bands attributed to the dopant depends on the fundamental band edge of the crystalline matrix. For Cd$_{1-x}$Mn$_x$S semiconductor one can observe just 5-6 bands [1-3]. The luminescence of this system is attributed to both CdS crystalline matrix and manganese dopant [4,5]. In the Cd$_{1-x}$Mn$_x$Cl$_2$ wide band gap of the bulk crystals one can observe ten absorption bands at liquid nitrogen temperatures and only six bands at room temperature (RT) [6,7] and an emission band due to the Mn$^{2+}$ ions, at about 640 nm.

In the present paper we are studying the optical properties of Cd$_{0.75}$Mn$_{0.25}$Cl$_2$ nanoparticles in PEG film.

Experimental

The Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film was obtained on a quartz glass by pouring a methanol solution containing CdCl$_2$, MnCl$_2$ and PEG followed by solvent evaporation at RT. The cadmium and manganese concentrations in the solution were 3.3x10$^{-2}$ M and 1.1x10$^{-2}$ M, respectively; the solution contains 10% PEG. Cadmium chloride and manganese (II) chloride are isomorphous and belong to space group D$^3_{3d}$ and they can form mixed crystals.
The average dimension of Cd$_{0.75}$Mn$_{0.25}$Cl$_2$ nanocrystals was 30 nm, estimated from transmission electron micrograph (Fig.1,a), obtained with a JEOL 200CX microscope; the electron diffraction diagram (Fig.1.b), of these nanoparticles shows a well defined ring diffraction which corresponds to the interplanar distance of 1.95 Å. The EPR measurements were performed on a JEOL JES-ME-3X spectrometer, interfaced to a PC, using 100 kHz field modulation, at RT. Optical absorption and excitation spectra have been recorded at RT with an SPM-2 monochromator equipped with a 100 W Xe lamp and filters (to separate the corresponding spectral domains). The detector was an EMI 6558 QB photomultiplier. The excitation spectra have been taken against a BaSO$_4$ neutral standard. The photoluminescence spectrum was obtained by irradiation in any of the absorption bands of the Mn$^{2+}$ ion.

**Results and Discussion**

![Fig.1. a) Transmission electron micrograph of Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film. b) Electron diffraction diagram of Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film.](image)

**Mn$^{2+}$ EPR spectra** for Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film deposited on fused quartz plates were recorded at RT. These spectra are shown in Fig.2. The principal signature for Mn$^{2+}$ in this system is the partially resolved sextet at $g_{ee}$ = 2.00, with a specific spacing and line width dependence of the hyperfine transitions. At least two types of such spectra, due to different crystal positions are supposed to exist. We didn't observe an EPR signal for MnCl$_2$/PEG composite film.

In the Fig.3 we present the excitation and absorption spectra of the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film deposited on a fused quartz plate. The absorption spectrum due to Mn$^{2+}$ complexes is very weak; it is especially used to reveal the structure and the position of the fundamental band edge for the studied systems.

Table 1 shows the experimental data obtained for this system in comparison with the literature data for a similar bulk single crystal [6,8]. In a separated experiment, we obtained the absorption spectrum of MnCl$_2$/PEG composite film (Fig.4), which shows some weak bands due to Mn$^{2+}$ ions transitions, also observed for the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film (Table1). The absorption spectra of the Cd$_1$,Mn$_x$Cl$_2$ bulk monocystal, for low manganese concentration ($x$=0.01) show at RT six bands under 330 nm [6], where the fundamental band edge of the crystalline matrix appears. At higher manganese concentration ($x$>0.05) a richer structure in the corresponding region of the absorption spectrum has been observed [7].
Fig. 2. Room temperature EPR spectra (second derivative) of Mn$^{2+}$ in Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film (a) and in methanol solution containing CdCl$_2$, MnCl$_2$ and PEG (b).

On the other hand, at low temperature (6.7 K) the fundamental band edge is moved towards the UV region and it is possible to observe supplementary manganese crystal field transitions [8].
For the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film (our case) the fundamental edge is shifted at about 200 nm and one can observe some new absorption bands due to Mn$^{2+}$ ion at RT. The intense maximum in the 352 nm region is attributed to $^6A_1\rightarrow^4E$ (D) transition (Table 1), based on the literature data [6]. Two absorption bands situated at 285 and 390 nm have an unknown origin.

To calculate the observed absorption structure (Table 1) we diagonalized Tanabe-Sugano $d^5$ energy matrices [9] using the following values of the crystal field parameters: B=633 cm$^{-1}$, C=3531 cm$^{-1}$ and $D_q$=800 cm$^{-1}$. These values were obtained after a fitting process using the experimental data. The corresponding values for bulk single crystal are B= 662 cm$^{-1}$, C= 3453 cm$^{-1}$ and $D_q$= 727 cm$^{-1}$ [10]. The $D_q$ value proposed for our nanocrystals is greater than the value for bulk monocrystals. This observation is in agreement with the Yamaki’s paper [11] that suggests an increase in Mn-Mn interaction in the thin films; as a result, the Mn-Cl distance (R) will decrease. The experimental band positions observed in the excitation spectrum are in good agreement with the calculated ones (Table 1). Taking the dependence $10D_q$=kR$^{-5.8}$, where k is a constant in the neighborhood of a given R [12] we estimate a 2% decreasing for R in our nanocrystals with respect to the bulk crystals.

Table 1. Position (in cm$^{-1}$) of the absorption and excitation peaks for Cd$_{1-x}$Mn$_x$Cl$_2$ systems.

<table>
<thead>
<tr>
<th>state</th>
<th>Cd$<em>{0.99}$Mn$</em>{0.01}$Cl$_2$ (bulk monocrystal)</th>
<th>Cd$<em>{0.96}$Mn$</em>{0.04}$Cl$_2$ (bulk monocrystal)</th>
<th>Cd$<em>{0.75}$Mn$</em>{0.25}$Cl$_2$ [our results]</th>
<th>Cd$<em>{0.75}$Mn$</em>{0.25}$Cl$_2$ [calculated]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4T_1$(G)</td>
<td>18940</td>
<td>18622 (537)</td>
<td>18522</td>
<td></td>
</tr>
<tr>
<td>$^4T_2$(G)</td>
<td>22500</td>
<td>22173 (451)</td>
<td>21620</td>
<td></td>
</tr>
<tr>
<td>$^4E,^4A_1$(G)</td>
<td>23690</td>
<td>23981 (417)</td>
<td>23980</td>
<td></td>
</tr>
<tr>
<td>$^4T_2$(D)</td>
<td>27100</td>
<td>26810 (373)</td>
<td>26735</td>
<td></td>
</tr>
<tr>
<td>$^4E$(D)</td>
<td>28170</td>
<td>28409 (352)</td>
<td>28409</td>
<td></td>
</tr>
<tr>
<td>$^4T_1$(P)</td>
<td>30120</td>
<td>30370</td>
<td>29940 (334)</td>
<td>33434</td>
</tr>
<tr>
<td>$^4A_2$(F)</td>
<td>36796</td>
<td>37175 (269)</td>
<td>37174</td>
<td></td>
</tr>
<tr>
<td>$^6A_1$ $^6A_1$ - $^4T_1$ $^4T_1$</td>
<td>37700</td>
<td>37244 (268)</td>
<td>37044</td>
<td></td>
</tr>
<tr>
<td>$^4T_1$(F)</td>
<td>38454</td>
<td>38610 (259)</td>
<td>39794</td>
<td></td>
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<td>$^4T_2$(F)</td>
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<td>40650 (246)</td>
<td>42664</td>
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<tr>
<td>$^6A_1$ $^6A_1$ - $^4T_2$ $^4T_2$</td>
<td>43290 (231)</td>
<td>43240</td>
<td></td>
<td></td>
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<tr>
<td>$^6A_1$ $^6A_1$ - $^4E$ $^4E$</td>
<td>44843 (223)</td>
<td>45862</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6A_1$ $^6A_1$ - $^4E$ $^4E$</td>
<td>47847 (209)</td>
<td>47960</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Excitation spectra at RT
b) Absorption spectra at 6.7 K
c) Excitation spectra at RT. In the parentheses are observed values in nm.
d) Obtained using $D_q$=800 cm$^{-1}$, B=633 cm$^{-1}$, C=3531 cm$^{-1}$.
The emission of the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film is due to manganese ions distributed in nanoparticles. The photoluminescence spectrum taken globally (Fig.5) of this system was excited in the $^4$E(D) band centered at 352 nm. The crystalline systems doped with Mn$^{2+}$ ions show only one emission band due to the $^4$T$_1$(G) $→$ $^6$A$_1$ transition [6]. The emission efficiency of these systems decreases with Cd$^{2+}$ content, reaching zero for pure MnCl$_2$ crystals. Our system desexcites on $^4$T$_1$(G) level and then emits in a wide band centered at 635 nm with a weak shoulder at about 657 nm. The emission maximum observed at 635 nm for the Cd$_{0.75}$Mn$_{0.25}$Cl$_2$/PEG composite film is due to the octahedral Mn$^{2+}$ complex in CdCl$_2$ lattice [10]. The weak shoulder at about 657 nm is attributed to manganese ion in modified surroundings: the manganese ions situated on nanocrystal surface can be surrounded both by chlorine ions and by oxygen atoms from the polymeric chain. This supposition is in agreement with EPR spectra, which show at least two
different positions for manganese ions. Because we didn't observe an emission spectrum for pure MnCl₂/PEG composite film, we consider that the photoluminescence of the Cd₀.₇₅Mn₀.₂₅Cl₂/PEG composite film is attributed to Mn²⁺ centers, in the phase that also contains Cd²⁺ ions.

Conclusions

We have studied Cd₀.₇₅Mn₀.₂₅Cl₂/PEG composite film deposited on fused quartz plates by electronic microscopy in transmission, EPR and optical spectroscopy (absorption and emission). Electronic microscopy data reveal the presence of nanocrystals in the PEG film. EPR and emission data indicate that the manganese ions are distributed in the nanoparticles, having two different surroundings. In the Cd₀.₇₅Mn₀.₂₅Cl₂/PEG composite film we observe a large UV displacement of the fundamental absorption edge at RT (from 270 for bulk crystals to about 200 nm). In this case all the absorption bands due to Mn²⁺ ions can be observed.

References