

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

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Abstract

We have studied at RT the $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2$ /polyethyleneglycole (PEG) composite film deposited on a quartz glass support, using optical and EPR spectral methods. The average dimension of $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2$ 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 $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ 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 $\text{Cd}_{1-x}\text{Mn}_x\text{Cl}_2$ 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 $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2$ nanoparticles in PEG film.

Experimental

The $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2$ /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 3.3×10^{-2} M and 1.1×10^{-2} M, respectively; the solution contains 10% PEG. Cadmium chloride and manganese (II) chloride are isomorphous and belong to space group D_{3d}^5 and they can form mixed crystals.

The average dimension of Cd_{0.75}Mn_{0.25}Cl₂ 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 BaSO₄ neutral standard. The photoluminescence spectrum was obtained by irradiation in any of the absorption bands of the Mn²⁺ ion.

Results and Discussion

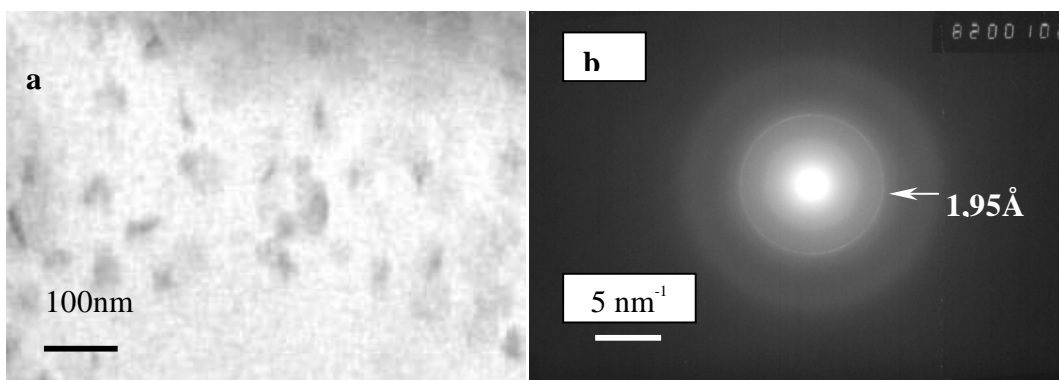


Fig.1. a) Transmission electron micrograph of Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film.
b) Electron diffraction diagram of Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film.

Mn²⁺ EPR spectra for Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film deposited on fused quartz plates were recorded at RT. These spectra are shown in Fig.2. The principal signature for Mn²⁺ in this system is the partially resolved sextet at $g_{ef} = 2.00$, 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 MnCl₂/PEG composite film.

In the Fig.3 we present the excitation and absorption spectra of the Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film deposited on a fused quartz plate. The absorption spectrum due to Mn²⁺ 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 MnCl₂/PEG composite film (Fig.4), which shows some weak bands due to Mn²⁺ ions transitions, also observed for the Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film (Table1). The absorption spectra of the Cd_{1-x}Mn_xCl₂ 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].

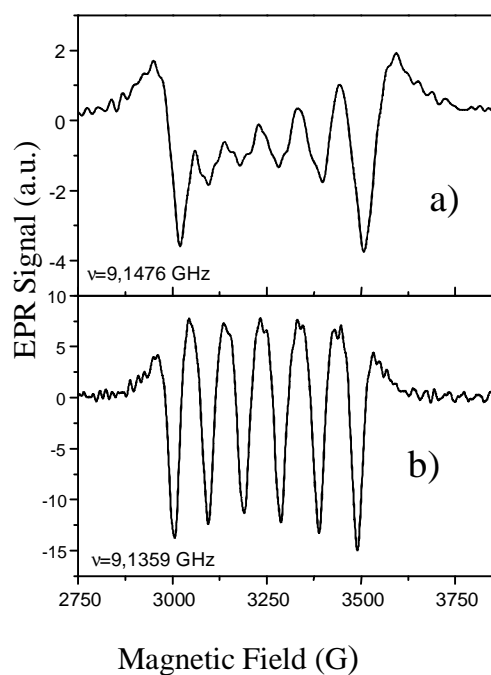


Fig.2. Room temperature EPR spectra (second derivative) of Mn^{2+} in $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ composite film (a) and in methanol solution containing CdCl_2 , MnCl_2 and PEG (b).

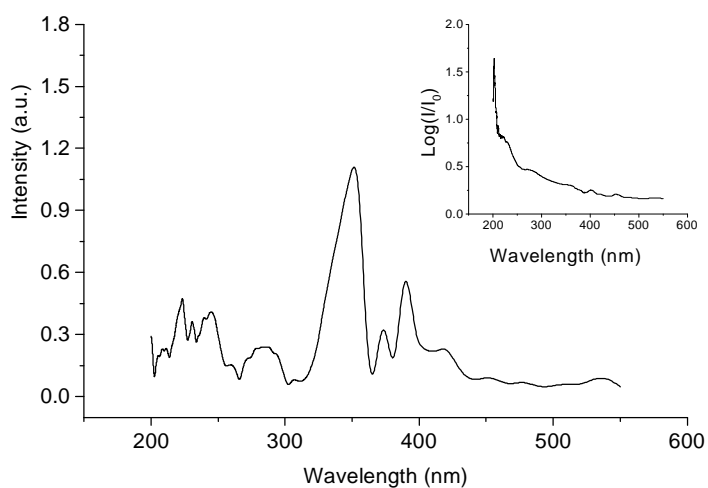


Fig.3. Excitation spectrum of $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ composite film, at RT.
 Inset: Absorption spectrum of $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ composite film, at RT.

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}Cl₂/PEG composite film (our case) the fundamental edge is shifted at about 200 nm and one can observe some new absorption bands due to Mn²⁺ ion at RT.

The intense maximum in the 352 nm region is attributed to ⁶A₁→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 d⁵ 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_xCl₂ systems.

state	Cd _{0.99} Mn _{0.01} Cl ₂ (bulk monocrystal) a) [6]	Cd _{0.96} Mn _{0.04} Cl ₂ (bulk monocrystal) b) [8]	Cd _{0.75} Mn _{0.25} Cl ₂ c) [our results]	Cd _{0.75} Mn _{0.25} Cl ₂ d) [calculated]
⁴ T ₁ (G)	18940		18622 (537)	18522
⁴ T ₂ (G)	22500		22173 (451)	21620
⁴ E, ⁴ A ₁ (G)	23690		23981 (417)	23980
⁴ T ₂ (D)	27100		26810 (373)	26735
⁴ E(D)	28170		28409 (352)	28409
⁴ T ₁ (P)	30120	30370	29940 (334)	33434
⁴ A ₂ (F)		36796	37175 (269)	37174
⁶ A ₁ ⁶ A ₁ - ⁴ T ₁ ⁴ T ₁		37700	37244 (268)	37044
⁴ T ₁ (F)		38454	38610 (259)	39794
⁴ T ₂ (F)		40500	40650 (246)	42664
⁶ A ₁ ⁶ A ₁ - ⁴ T ₂ ⁴ T ₂			43290 (231)	43240
⁶ A ₁ ⁶ A ₁ - ⁴ T ₂ ⁴ E			44843 (223)	45862
⁶ A ₁ ⁶ A ₁ - ⁴ E ⁴ E			47847 (209)	47960

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.

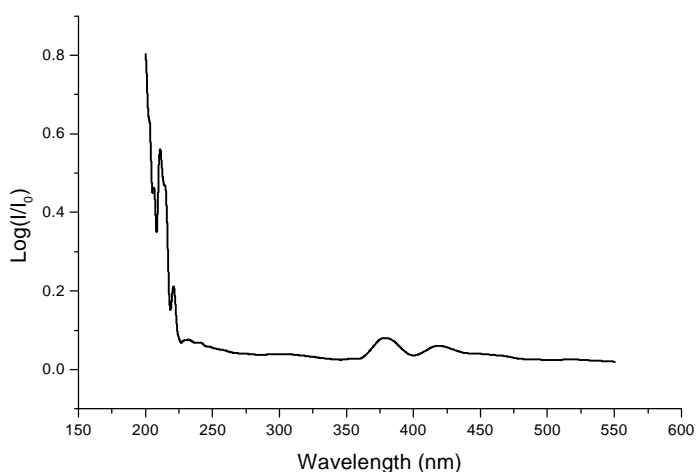


Fig.4. Absorption spectrum of MnCl_2/PEG composite film, at RT.

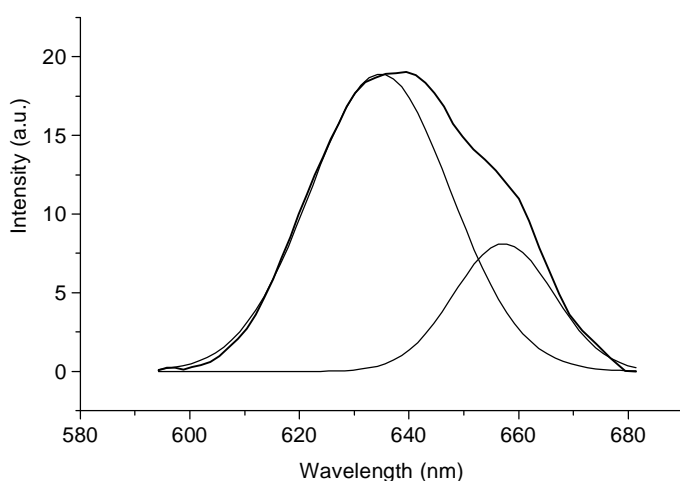


Fig.5. Photoluminescence spectrum of $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ composite film, at RT.

The emission of the $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ composite film is due to manganese ions distributed in nanoparticles. The photoluminescence spectrum taken globally (Fig.5) of this system was excited in the ${}^4\text{E}(\text{D})$ band centered at 352 nm. The crystalline systems doped with Mn^{2+} ions show only one emission band due to the ${}^4\text{T}_1(\text{G}) \rightarrow {}^6\text{A}_1$ transition [6]. The emission efficiency of these systems decreases with Cd^{2+} content, reaching zero for pure MnCl_2 crystals. Our system desexcites on ${}^4\text{T}_1(\text{G})$ 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 $\text{Cd}_{0.75}\text{Mn}_{0.25}\text{Cl}_2/\text{PEG}$ 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 Cd_{0.75}Mn_{0.25}Cl₂/PEG composite film is attributed to Mn²⁺ centers, in the phase that also contains Cd²⁺ ions.

Conclusions

We have studied Cd_{0.75}Mn_{0.25}Cl₂/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 Cd_{0.75}Mn_{0.25}Cl₂/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.

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