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Synthesis, Characterization and Optical Properties of Bulk and Doped Cadmium Sulphide Nanocrystals

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Abstract

The manganese doped cadmium sulphide nanocrystals were prepared by chemical route technique. The scanning electron microscope (SEM), X-ray diffraction and absorption spectra characterized these samples.

The Photoluminescence and optical absorption spectra of the CdS nanocrystals were studied for various concentrations of Mn. SEM estimated the crystallite sizes of the order of 40 nm. Optical absorption spectra of nanocrystals are blue shifted and show steps confirming the discrimination of energy levels due to quantum confinement. Two peaks are observed in the photoluminescence spectra of Mn doped nanocrystals, intensity of first peak increases and second peak shifts towards blue by increasing Mn concentrations.

Keywords: Nanocrystals, Photoluminescence, SEM, Optical absorption spectra.

Introduction

The synthesis and characterization of materials of the nanometer scale has provided not only new physics in reduced dimensions, but also the possibility of fabricating novel material. The studies of optical properties of semiconductor nanoparticles have become the topic of both theoretical and experimental interest because of their tailor able properties and wide applications [1]. Doped semiconductor nanoparticles are extensively investigated to obtain basic information on impurity states in quantum dots and to examine their potential application in novel display devices and light emitting diodes [2]. Recent results on ZnS: Mn nano particles [3] show that position of Mn is slightly shifted by changing the crystalline size and the life time of Mn^{2+} ions is also reduced. Essentially, doping luminescence centers creates favorable energy levels within the bandgap of nanocrystalline ZnS. CdS is another important semi conducting material used in various luminescence applications.

There are many methods to synthesize CdS nanoparticles. Nanda and his co-workers [4,5] have reported Photoluminescence (PL) of CdS nanoparticles. Artemyev et al. [6] have studied luminescence of doped CdS nanocrystals is sol-gel matrix.

In the present investigation, freely standing CdS Nanoparticles were prepared by chemical precipitation technique and characterized by Scanning Electron Microscopy (SEM). The Optical Absorption Spectra and Photoluminescence of nano particles have been studied for different Mn concentrations.

Experimental

Semiconductor nanoparticles of manganese doped Cadmium Sulphide has been prepared by chemical route [7-8]. For synthesis, 10^{-2} mole aqueous solutions of $CdCl_2$, mercaptoethanol (C_2H_5OSH) and Na_2S were taken. First mercaptoethanol solution was added drop wise to $CdCl_2$ (+$MnCl_2$) for doping) solution at the rate of I ml per minute, while stirring it continuously so that solution are properly mixed. Then Na_2S solution was also in similar manner. The chemical reaction gives CdS.

$$CdCl_2 + Na_2S \longrightarrow CdS + 2\,NaCl$$

CdS is precipitated, being insoluble in water. The presence of mercaptoethanol does not allow the particles size to grow. Four different samples were prepared with Mn concentrations 0.0%, 0.1%, 0.2% and 0.3%. The precipitate thus obtained was thoroughly washed in double distilled water, centrifuged and then air-dried.

In order to investigate the surface morphology and particle size, the samples were analyzed by scanning electron microscope (SEM) of Stereo Scan - 430 made by Leica Company. The experimental setup for measuring the size of CdS nanoparticles is shown in Fig. 1(d). Fractal features are observed, which under high magnification shows particles size. The SEM micrographs of bulk and CdS nanoparticles are shown in Fig.1. The Optical Absorption Spectra of samples were recorded with the help of Perkin Elimer Lamda –12 Spectrometer in the wave length 300 to 700 nm.

The Photoluminescence (PL) of nanoparticles bulk and doped with different Mn concentrations, were investigated using Grating Monochromator HM -104 and Photo multiplier Tube (PMT-RCA-931). The nanoparticles were placed on a glass slide using toluene and it was fixed onto the entrance slit of the monochromatic. Mercury lamp was used for PL excitation. The PL emission intensity in the range of 400-1100 nm was measure with the help of PMT placed at the other slit of monochromator.

Results and Discussion

The experimental set up for measuring the size of CdS nanocrystals is given in Fig. 1(d). In order to study the surface morphology, SEM analysis were carried out for different CdS samples and typical picture is shown in Fig. 1 (a) (b)& (c).

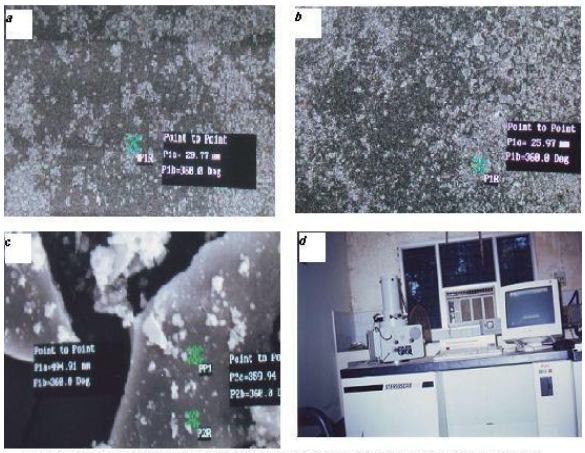

Fig.1. (a) (b)(c)&(d) SEM picture of CdS:Mn Doped nanocrystals and experimental setup.

Fig. 2(a) represents the absorption spectra of CdS nanocrystals. It is evident from the fig that the uniform absorption in the range of 700 to 560 nm and sudden rise in absorption is observed at 558 nm. After this there is slow decrease, and increases in absorption is observed in the range of 558 nm to 442.7 nm. At 429 nm step rise in absorption is observed. In this case, the absorption is found to be stepwise increase in absorption 394.4 nm. At 319 nm the maximum Peak is observed. It can be seen that the each peak in absorption spectra correspond to transition to different excited states of the conduction band. This is in good agreement with the observation of Ekimov et. al. [9] for CdS prepared on glass matrix.

Fig. 2 (b) shows the absorption spectrum of different samples having different crystallite size prepared by chemical technique. It is evident from the figure that the absorption edge shifts from 417 nm for nanocrystalline samples, which further shows, an absorption peak at 394.4 nm, which is expected to be due to 1S–1S quantum particle transition suggested by Brus [10], who gave an estimation of band gap as 3.14 eV. The bulk band gap of CdS is 2.4 eV. A blue shift of 0.7 eV has been achieved in the present case due to quantum size effect in CdS nanocrystals.

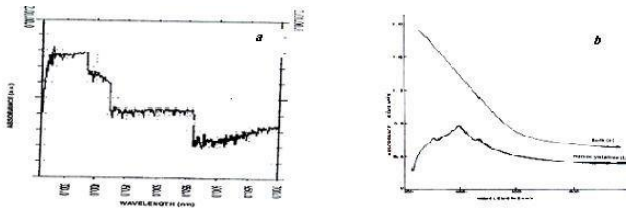

Fig.2. (a) & (b) Optical absorption spectra of CdS:Mn doped nanocrystals and bulk sample

The Photoluminescence (PL) measurement of CdS samples having different crystallize sizes varies with reaction time 60 minutes. Two intensity peaks A and B also observed at 695 nm and 940 nm for CdS samples with reaction time 60 minute. It is evident that the peak positions are observed by reconvicting the bands Nanda et al. [11]. It can be seen from the PL spectra that A and B bands shifts to lower energies as the crystalline size increases.

Fig.3 (a) (b) & (c) gives the Photoluminescence spectra of CdS: Mn nanocrystalline samples having 0%, 0.1%, 0.2% & 0.3% manganese doped concentrations at room temperature (300K). It is clear from the fig that the intensity peak is seen at 740 nm in case of 0% doping of Mn.

In this case, the emission energy mainly related to the election phonon- interaction. In the CdS: Mn nanoparticles the surface is even a little more significant than the confinement in determining the election phonon- interaction [12, 13].

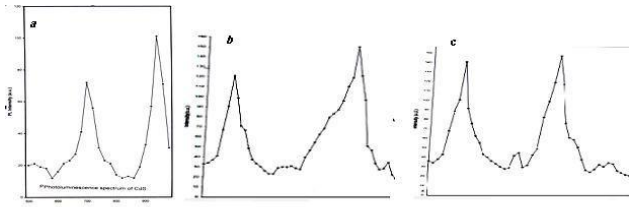

Fig.3 (a)(b)(c) photoluminescence spectrum of CdS nanocrystals for 0.1%, 0.2% and 0.3% Mn Concentration.

Conclusions

Photoluminescence of CdS: Mn shows two prominent peaks. The PL spectra for various concentrations of Mn are shown in Fig.3. The wavelength and the intensity corresponding to both the peaks of different samples are given in Table 1. It is seen that first peak (A) is obtained at 465 nm and the other peak (B) is found between 750 to 650 nm for different Mn concentrations. Both PL peaks exhibit significant Stoke's shift with respect to absorption edge (3 eV). Hence the luminescence band can be identified with transitions involving donors, acceptors and surface states; and photo excited electrons decay to these levels by some non irradiative processes.

An attempt is made to keep the size of CdS nanoparticles near about 20 nm and change only the Mn concentration while preparing the samples. At very low Mn concentration, some particles are doped and some are not. With increasing Mn concentration, more and more particles are doped increasing the photoluminescence intensity. This is similar to what has been observed earlier also in CdS: Mn samples viz, at higher concentration Poisson statistic applies with zero doping for some particles, one Mn for some and two or more Mn for some particles. At low concentration, of course, some particles are doped with one other without any Mn.

The present work indicates that emission band A is shifted by Mn doping but its intensity increases with Mn concentration. On the other hand emission band B shift towards lower wavelengths as Mn concentration is increased.

Table: 1 Crystallite Size and PL Peaks of CdS: Mn nanoparticles

Samples	**Mn %**	**D by SEM**	**PL Peak**					
			A			B		
			Int. a.u. a.u.	**nm**	**Photon energy**	**Int. a.u.**	**nm**	**Photon energy**
I	0.0%	36.35	122	460	2.69 eV	152	740	1.67 eV
II	0.1%	41.34	141	470	2.63 eV	150	680	1.82 eV
III	0.2%	46.74	150	460	2.69 eV	161	660	1.87 eV
IV	0.3%	44.91	175	460	2.69 eV	171	650	1.90 eV

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