

Photoluminescence in Nanocrystalline Films of $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S} : \text{Eu}$

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Abstract: Europium doped nanocrystalline films of $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ are prepared by chemical bath deposition method (using capping agents) on glass substrates at different temperatures (60°C, 80°C and 100°C). Their optical absorption spectra and photoluminescence (PL) emission spectra are studied and compared with that of the bulk film (prepared at 60°C without capping agents). Blue shift in the absorption edge is observed in the nanocrystalline film in comparison to that of bulk indicating quantum confinement effect. The values of optical band gap obtained from Tauc's plots have been found to be 2.41eV for the bulk film and in the range 2.81eV to 2.95eV for the different nanocrystalline films prepared at different temperatures. The value of band gap decreases with increasing bath temperature. The grain sizes obtained from these studies also lie in the nano range. Photoluminescence emission spectra show a shift in emission peak towards shorter wavelength suggesting particle size reduction. A less intense peak at around 615nm is also observed which may be due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in Eu^{3+} ions. Emission intensity is maximum for deposition at 60°C.

Keywords: Photoluminescence, chemical deposition, nanocrystalline property.

I. INTRODUCTION

Nanocrystalline materials have attracted many material researchers due to its enhanced thermal, electrical and optical properties when compared to that of bulk materials. These materials are becoming increasingly interesting for optoelectronics and photonics. The electronic and electrical properties of such materials show a remarkable change as the particle size approaches that of its excitonic Bohr radius and then electrons and holes are subject to quantum confinement effects [1, 2] due to their large surface to volume ratios resulting in high density of surface states. Nanoscale semiconductors show interesting electro-optical properties and catalytic behavior [3]. The II–VI semiconductor nanocrystals are interesting as their emission spectra are very narrow (spectrally pure) and the emission colour may be tuned by changing their size. As nanocrystal size increases, the energy of the first excited state decreases, qualitatively following a particle-in-a-box behaviour. This size dependence and the emergence of a discrete electronic structure from a continuum of levels in the valence and conduction bands of the bulk semiconductor result from quantum confinement [4]. $(\text{Cd-Zn})\text{S}$ nanocrystalline films find wide applications as window material for hetero junction solar cells and photoconductive devices [5]. The photoresponse of these materials could be

enhanced by doping with rare-earths. Rare-earths are well known as forming efficient luminescent centres and have drawn increasing attention as phosphor materials for use in optical display devices [6]. Their luminescence is caused by transitions within the 4f shell. This is shielded by the outer electron shells from the effect of the surroundings and therefore gives rise to a series of discrete energy levels [7]. These prepared photosensitive materials may find wide applications in light detectors, phosphors, LED's etc. The spectral distribution of Eu^{3+} ion is in the long wavelength region and the main emission lines occur between the $^5\text{D}_0$ levels and the $^7\text{F}_j$ multiplets [8]. These emission lines in the wavelength range 600-700 nm makes it suitable for use as a red phosphor. In the present work, results of optical absorption spectra and photoluminescence emission spectra are presented for chemically deposited nanocrystalline Eu^{3+} doped $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ films, not explored earlier and the corresponding results are discussed.

II. EXPERIMENTAL TECHNIQUES

2.1. Film preparation:

The films were prepared on cleaned substrates of microscopic glass slides of dimensions 24 mm x 75 mm by vertically dipping in a mixture of 1M Cadmium acetate + Zinc acetate in appropriate ratio, triethanolamine, 30% aqueous ammonia, thiourea and 0.01M Eu_2O_3 (since being insoluble in water was dissolved in dilute HCl). For reduction in particle sizes, mercaptoethanol and methanol in the ratio 1:1 were used as capping agents. All the chemicals were of analytical grade (minimum purity 99.9%). The solution was stirred using magnetic stirrer for 5 minutes (to facilitate uniform deposition) and kept in a water bath for 1 hour. The deposition of films is based on precipitation followed by condensation. The deposition was carried out at 3 different temperatures (60°C, 80°C and 100°C). After deposition, films were cleaned with distilled water and then dried by keeping the films in open atmosphere at room temperature.

2.2. Measuring Instruments:

For the study of optical absorption spectra, a Shimadzu (UV-VIS) Pharmaspec-1700 spectrophotometer was used. The PL excitation source was a 365 nm UV radiation. For detection of emitted light, a standard CdS photoresistor was used. The integrated light output in the form

of current was recorded using a digital NanoAmmeter (DNM-021).

III. RESULTS AND DISCUSSION

3.1. Optical absorption spectra:

Optical Absorption spectra of (Cd-Zn)S: Eu films

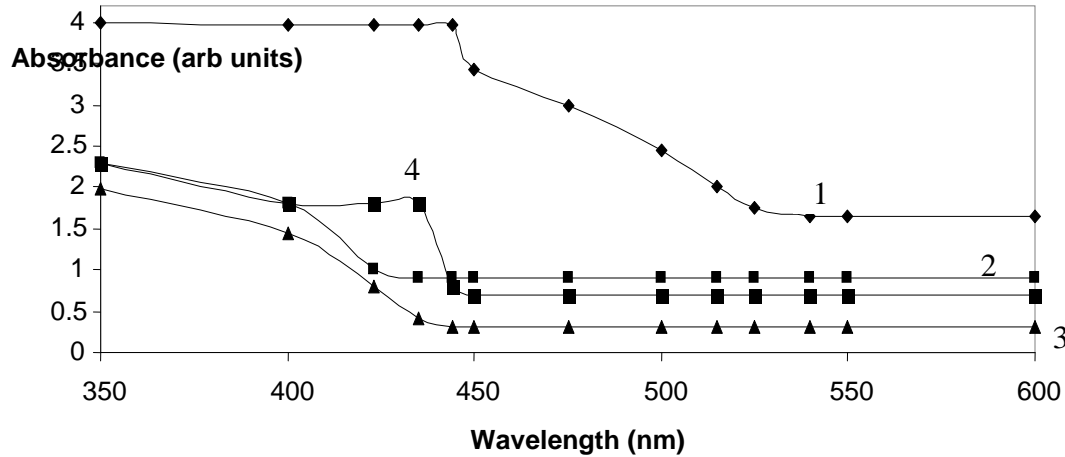


Fig 1: Optical absorption spectra of (Cd_{0.8}-Zn_{0.2}): Eu films; 1 – bulk; 2 – with capping agents (60°C); 3 - with capping agents (80°C); 4 - with capping agents (100°C);

The optical absorption spectra of different (Cd–Zn)S films prepared on glass substrates are shown in Figure 1. A shift in the absorption edge to shorter wavelength side is observed in all the nanocrystalline films prepared at different temperatures in comparison to that of the bulk film. This is due to quantum confinement effect in which the electrons, holes and excitons do not have sufficient space to move and their motion is possible only for discrete values of energies. This result in the quantisation of their energy spectrum and the continuum of states in conduction and valence bands are broken down into discrete states. Their energy spacing relative to band edges is approximately inversely proportional to the square of the particle size and reduced mass [9,10]. The highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively thereby resulting in the widening of band gap. This leads to the effective band gap larger than its bulk value and correspondingly a blue shift (to the shorter wavelength side) in the absorption spectra is observed. The optical absorption coefficient α and band gap E_g (for direct band gap materials) are represented by the equation

$$\alpha = c(\hbar\nu - E_g)^{1/2} / \hbar\nu \quad (1)$$

where E_g is the optical band gap and c is a constant. Thus a plot between $(\alpha \hbar\nu)^2$ vs $\hbar\nu$ (Tauc's plot) gives the band gap value E_g of the corresponding material. The values of optical band gap obtained from these plots have been found to be 2.41eV for the bulk film and in the range 2.81eV to 2.95eV

for the different nanocrystalline films prepared at different temperatures. The value of band gap was found to decrease with increasing bath temperature. The particle sizes were calculated using the Effective Mass Approximation (EMA) method and the following equation [10]

$$E_{gn} = E_{gb} + (\hbar^2 \pi^2 / 2 m^* R^2) \quad (2)$$

where E_{gn} & E_{gb} are the band gap of nanocrystallites, and bulk semiconductor respectively, R is the particle radius and m^* is the effective mass of electron. Substituting the values of E_{gb} determined from eq(1) and standard values of other parameters, the particle sizes were found to be in the range 3.43 nm to 4.32 nm. The particle sizes were thus found to lie in the nanocrystalline range. The values of band gap and the corresponding particle sizes are summarised in table 1.

Table 1: Band gap energies and particle sizes of different (Cd_{0.8}-Zn_{0.2}): Eu films prepared at different temperatures using capping agents.

Sample	Band gap (eV)	Particle Size (nm)
(Cd _{0.8} -Zn _{0.2}): Eu With capping agents (60°C)	2.95	3.43
(Cd _{0.8} -Zn _{0.2}): Eu With capping agents (80°C)	2.88	3.76
(Cd _{0.8} -Zn _{0.2}): Eu With capping agents (100°C)	2.81	4.32

3.2. PL spectra:

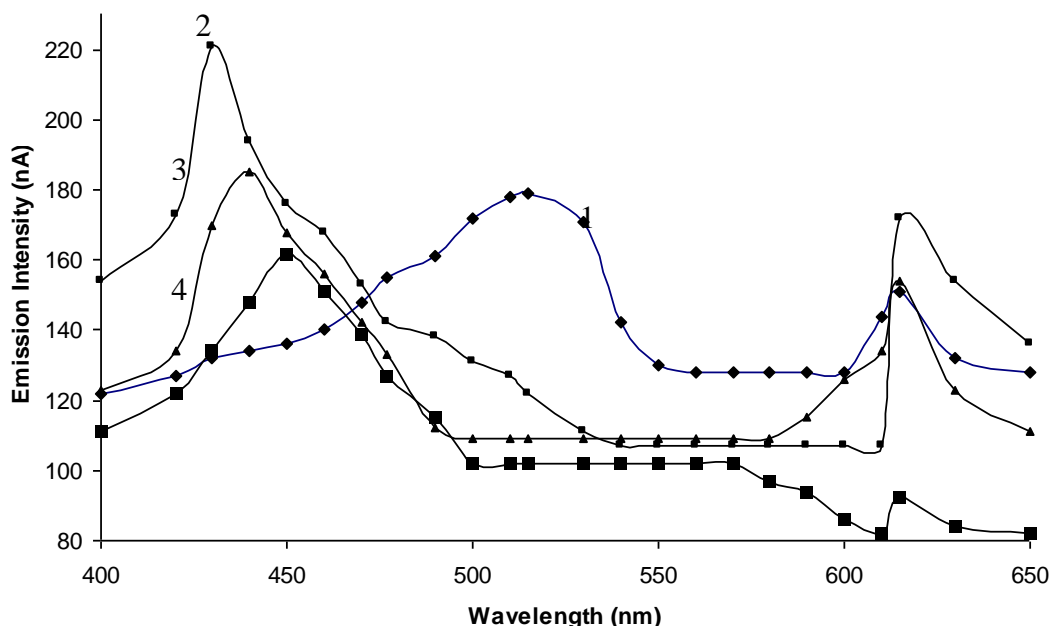


Fig 2: PL emission spectra of (Cd-Zn)S: Eu films; 1 – bulk; 2 – with capping agent (60°C); 3 - with capping agent (80°C); 4 - with capping agent (100°C);

The PL emission spectra of different $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ films prepared on glass substrates are shown in Figure 2. The more intense emission peak in Eu^{3+} doped bulk $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ film was found to be at 517 nm suggesting band to band transition and a less intense peak at around 615 nm is also observed which may be due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in Eu^{3+} ions [11]. The mechanism of lanthanide ion luminescence sensitization in II-VI semiconductor materials is rationalized in terms of an energy and charge transfer between trap sites and is based on a semi empirical model, proposed by Dorenbos and co-workers [12,13,14]. This model implies that Eu^{3+} acts as an electron trap. The higher intensity emission peaks in the Eu^{3+} doped nanocrystalline $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ films prepared at 60°C, 80°C and 100°C were at 423 nm, 435 nm and 444 nm respectively. The lower intensity peak at 615 nm was however not shifted in all the 3 cases. The shift in higher intensity emission peak towards shorter wavelength as compared with the bulk film indicates decrease in particle size. This again confirms the quantum confinement effect. Enhanced emission intensity was observed in nanocrystalline films with maximum intensity for deposition at 60°C. Emission intensity decreased for deposition at higher temperatures probably due to larger particle size.

IV. CONCLUSIONS

Optical absorption and PL emission spectral studies of Eu^{3+} doped $(\text{Cd}_{0.8}\text{-Zn}_{0.2})\text{S}$ films suggest a decrease in particle size on using capping agents. Absorption edge shifts to the lower wavelength region in the nanocrystalline films indicating quantum confinement effect. The band gap values decrease with increasing bath temperature. Two emission

peaks are observed in both bulk and nanocrystalline films. The higher intensity peaks shift to shorter wavelength side in the nanocrystalline films indicating decrease in particle size. The lower intensity peaks however remain unaffected. The less intense peak at around 615 nm may be due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in Eu^{3+} ions.

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