

## STUDIES ON NANO-CRYSTALLINE PROPERTIES OF CHEMICALLY DEPOSITED Pr DOPED CdS FILMS

KUSUMANJALI DESHMUKH\*, S. BHUSHAN, M. MUKHERJEE

*Shri Shankaracharya College of Eng. & Technology, Bhilai 490020, (C.G.), India*

Results of SEM, XRD, optical absorption spectra and photoluminescence(PL) emission spectra are presented for chemically deposited CdS:NaF,Pr nanocrystalline films at two volumes of thioglycerol with methanol(TGM) as capping agent. While the SEM studies show presence of needle type structure along with existence of microcrystals, XRD studies show change in FWHM. The average particle size determined from XRD studies, are corresponding to nano-range. It affirms that particle size decreases with increasing TGM volume. Blue shift in absorption edge with increase in TGM volume is seen from optical absorption studies which indicate increase in band gap. The particle sizes determined from such studies also lie in nano-range. PL spectra under 230nm excitation show enhancement in intensity in blue region which suggests that the host lattice of CdS absorbs energy from Pr and transfers it to visible radiation at 462nm. Thus, nanocrystalline CdS:NaF,Pr films can be used as effective UV filter.

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### 1. Introduction

Studies of nanocrystalline particles have become a subject of latest interest because of revolutionary changes in their physical and chemical properties particularly when their size remain closer or smaller than exciton Bohr radius [1]. Due to quantum confinement effect the band gaps change and the photoluminescence emission can be tuned in the whole visible region. CdS happens to be one of such prominent materials. The rare earth doped materials have drawn increasing attention as phosphor materials for use in optical display devices[2-6]. The electronic structure of rare earth ions differ from the other elements because of incompletely filled  $4f^n$  shells. The  $4f^n$  electrons are shielded by  $5s^2$  and  $5p^6$  electron orbitals. Excitation of materials doped with such ions results in sharp line emission due to intra  $4f^n$  shells transition of rare earth ion core [7,8] which lies in a wide range covering UV, VIS, IR regions of the spectrum. UV emission is equally important in device application and health sciences [8-10]. But the UV radiations cause damage to living beings and plants and there is a need to investigate methods of protection and safety from such radiations. Maqbool and Ahamed [10] reported recently that Pr doped GaN can be used as UV filter for radiation shielding and protection propose whereas AlN is transparent to UV radiation. The present paper concerns with the nanocrystalline effect on photoluminescence spectra of Pr doped CdS films prepared by chemical bath deposition (CBD) method using thioglycerol and methanol (TGM) as a capping agents. Results of different studies included in this paper are: XRD, SEM, optical absorption and photoluminescence spectral studies. Although many workers [11-14] have studied the role of capping agents on PL of CdS films but none have reported the effect for rare earth doped CdS films. Our studies on PL of CdS:NaF,Pr nanocrystalline films has shown blue shift in PL peak and a rapid increase in intensity as the volume of TGM is increased.

## 2. Experimental details

CdS nanocrystalline films were prepared on glass substrates by CBD technique. The microscopic glass slides of dimensions 24mm x 75mm were used as substrates. These slides were first cleaned with H<sub>2</sub>SO<sub>4</sub>, acetone, double distilled water and ultrasonic cleaner. Then the dried glass slides were dipped vertically into a mixture of solutions of 1M Cadmium Acetate, TEA, 30%Aq. Ammonia and 1M thiourea. 0.01M NaF and varied molar concentrations (0.001M, 0.005M, 0.01M, 0.05M) of Praseodymium Nitrate as an impurity were also added to the solution. All the solutions were prepared in double distilled water. TEA was used as a complexing agent to form [Cd(TEA)<sup>+2</sup>] complex for controlling the growth rate. Bhushan and Coworkers [15] reported that NaF acts as flux and helps in effective inclusion of rare earth impurities and in improving the crystallinity. The capping agents thioglycerol with methanol (TGM) in 1:1 ratio were then added to the above said mixture of solutions, since this gave better results. The films were then formed on glass substrate by dipping the substrate in the solution, kept in a constant temperature water bath, for 60 min. The deposition of films is based on precipitation followed by condensation. After deposition the films were then washed with double distilled water and dried at room temperature.

The structural parameter of Pr doped CdS films were characterized by using X-ray diffractometer (XRD, Rigaku Ruzhr, CuK $\alpha$  radiation) and JEOL (JSM-5600) scanning electron microscope respectively. The optical absorption spectral studies were done using Shimadzu (UV-VIS) Pharma Spec-1700 spectrophotometer and PL studies were made by RF 5301, Shimadzu fluoro spectrophotometer under 230nm excitation.

## 3. Results and discussion

### 3.1 SEM Studies

Fig 1(a), (b) and (c) show the SEM micrographs of CdS:NaF,Pr films for 0.2ml volume of capping agents at three magnifications. Similarly, Fig 2(a), (b) & (c) show micrographs of CdS:Pr films at higher concentration of capping agents (0.7 ml volume).

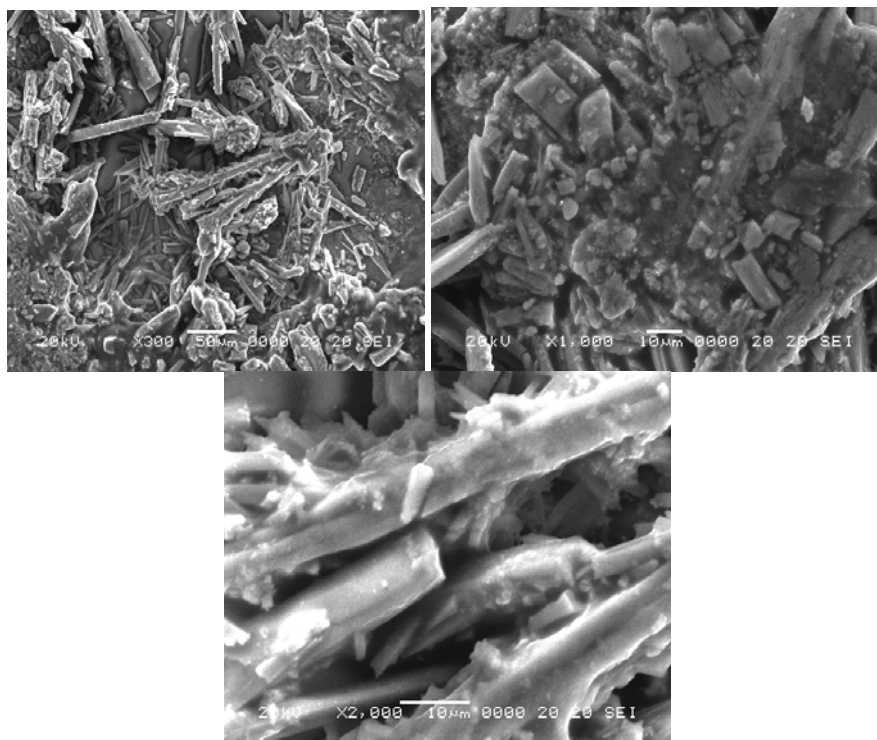


Fig1(a, b, c) : SEM micrographs of CdS:NaF,Pr films for 0.2ml volume of capping agents at three magnifications(x300,x1000, x2000 respectively).

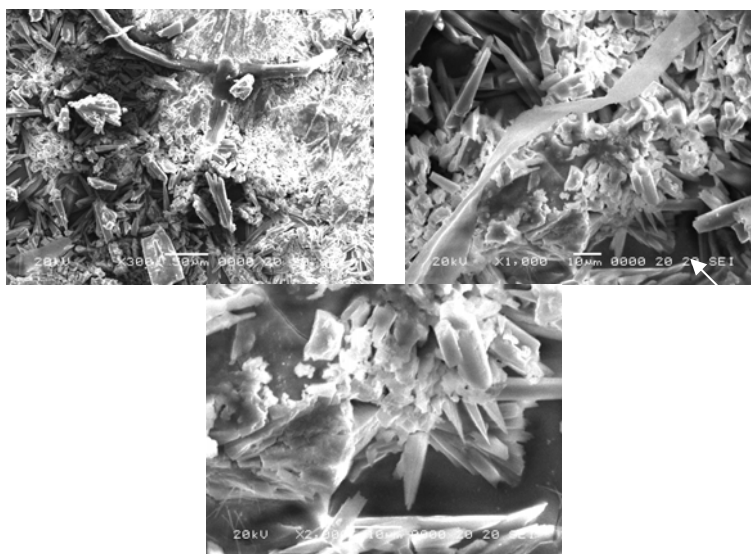


Fig. 2(a,b,c) : SEM micrographs of CdS:NaF,Pr films for 0.7ml volume of capping agents at three magnifications (x300,x1000, x2000 respectively).

From the figures it is observed that at lower magnification the presence of crystallites along with some platelet type structure appears. At higher magnification these platelets appear as needle type structure along with presence of some micro crystals. Role of capping agents is to avoid coalescenceness of particles and thus particle size reduces. As the concentration of capping agents increases particle size is expected to reduce further because of the more avoidance of coalescenceness of different particles in presence of capping agents and this obviously can be seen from the micrographs. Particularly in fig 2(a) the thickness of the rods seems to be quite closer to the nanorange. Along with rodtype structure some needle type growth is also observed in Fig 2(c). Such structures are indicative of nanocrystalline growth[16]. In our earlier communication [17] it has been reported that the micrograph of undoped CdS consists of combination of large number of smaller grain along with needle type structure and in presence of higher volume of capping agents more uniform and dense distribution of grains are observed.

### 3.2 XRD Studies

The XRD diffractograms of CdS:NaF,Pr films for two volumes of TGM are shown in Fig. 3. The XRD pattern shows a large number of peaks indicating that the films are crystalline in nature.

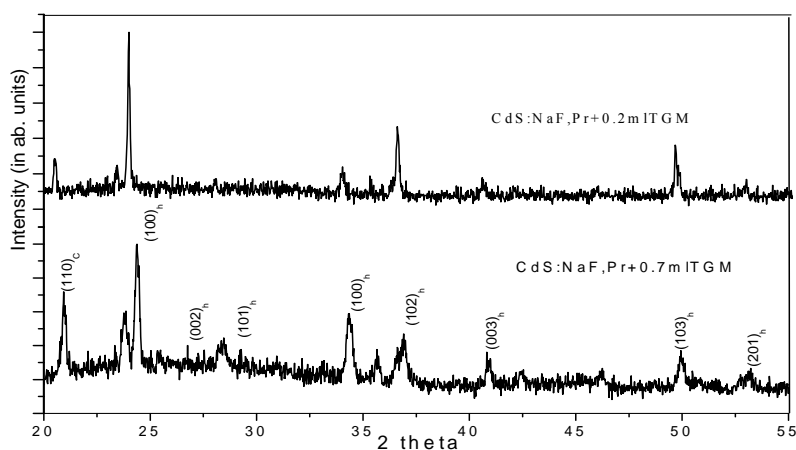


Fig. 3. The XRD diffractograms of CdS:NaF,Pr films for two volumes of TGM.

The assignment of peaks are made by comparing with ASTM data and calculation of lattice constants and their comparison with the reported values. Structural parameters like interplanar distances and lattice constants are listed in table1. The different assigned peaks are also mentioned in the figure 3. The prominent peaks in the diffractographs are of  $(100)_h$ ,  $(102)_h$ ,  $(200)_h$  and  $(210)_c$  of CdS. Hexagonal phase predominates over cubic phase. As shown in Fig.3, no peaks of Pr, PrS,  $Pr_2S_3$  were detected, which indicates that incorporation of  $Pr^{3+}$  ions does not affect the crystal structure of CdS film. This is also confirmed from bandgap calculations of Pr doped films. The average interplanar distance was calculated using the formula  $\lambda = 2d \sin \theta$ , where  $\lambda$  is the X-ray

Table 1. X-Ray Diffraction data for CdS:NaF,Pr for two volumes of TGM

d-values ( in Å°)		Relative intensities		h k l	Lattice constant ( in Å°)	
Observed values	Reported values	Observed values	Reported values		Observed values	Reported values
<b>CdS:NaF,Pr +0.2mlTGM</b>						
4.327	4.11	28	-	(110)c	a = 6.10	a =5.818
3.709	3.58			(100)h		
2.637	2.60	100	75	(210)c	a =4.28	a =4.135
2.458	2.450		32	(102)h	a = 5.88	
2.224	2.23	24	25	(003)h	a= 4.18, c=6.67	a=5.818
1.840	1.89		23	(103)h	c = 6.67	a = 4.135
1.731	1.729	47	42	(201)h	a = 4.24,	c= 6.71
		17	60		c=6.67	a=4.135
		37			a=4.139,	a=4.135
		17			c=6.67	
<b>CdS:NaF,Pr +0.7mlTGM</b>						
4.241	4.11	72	-	(110)c	a=5.99	a=5.818
3.649	3.58	100		(100)h	a=4.214	a=4.135
3.33	3.357	41	75	(002)h	c=6.661	c=6.67
3.135	3.16	45	59	(101)h	a=4.103, c=6.661	a=4.135
2.637	2.60	59	100	(210)c	a=5.83	a=5.818
2.458	2.450	47	32	(102)h	a=4.103, c=6.68	c=6.67
2.224	2.23	37	25	(003)h	c=6.63	c=6.67
1.840	1.89	37	23	(103)h	a=4.103, c=6.38	c=6.380
1.731	1.729	27	42	(201)h	a=4.125, c=6.63	a=4.135
			60			

wavelength ( $1.5406 \text{Å}^\circ$ ) and  $\theta$  is the Bragg angle. Increase in capping agent volume [Fig. 3, CdS:NaF,Pr+0.7mlTGM] has resulted in broadening of all the peaks and hence increased FWHM. Particle size is calculated using formula [18 ]

$$L = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \quad (1)$$

Where  $\beta$  is the full width at half maximum (FWHM) in radians. As shown in table 2, the grain size decreases with capping agent volume. This decrease in particle size may have caused lattice strain that resulted in the increase observed in the band gap of doped films grown at higher volume of TGM, as we mentioned earlier. Particle sizes are calculated for (110)<sub>c</sub>, (100)<sub>h</sub>, (210)<sub>c</sub>, (102)<sub>h</sub>, (003)<sub>h</sub>, (103)<sub>h</sub>, (201)<sub>h</sub> and is presented in the table 2.

Table 2. Particle sizes calculated for various peaks.

Peaks	CdS:NaF,Pr +0.2ml TGM		CdS:NaF,Pr +0.7ml TGM	
	FWHM (in degrees)	Particle size (in nm)	FWHM (in degrees)	Particle size (in nm)
(110) <sub>c</sub>	0.24	35.14	0.44	19.22
(100) <sub>h</sub>	0.24	60.65	0.32	26.51
(210) <sub>c</sub>	0.34	25.44	0.58	14.95
(102) <sub>h</sub>	0.20	43.67	1.2	7.278
(003) <sub>h</sub>	0.48	18.37	0.68	12.99
(103) <sub>h</sub>	0.36	25.363	0.68	13.45
(201) <sub>h</sub>	0.54	17.15	0.60	15.475

### 3.3 Optical absorption studies

The optical absorption spectra of CdS:NaF,Pr at two concentrations of capping agents are shown in Fig.4. A slight shift in absorption peaks is observed in the spectra near 310 nm which is indicative of quantum confinement effect in nanocrystalline materials in which the electrons, holes and excitons have limited space to move and their motion is possible for definite values of energies. Thus, their energy spectrum is quantized. As a result the continuum of states in conduction and valence bands are broken down into discrete states with an energy spacing relative to band edges which is approximately inversely proportional to the square of the particle size and reduced mass[19]. The highest occupied valence band and the lowest unoccupied conduction band are shifted to more negative and positive values respectively resulting in the widening of band gap which leads to the effective bandgap larger than its bulk value. Thus, there will be a blue shift in the absorption spectra with reduction in particle size as observed in the present case.

For direct band gap materials, the optical absorption coefficient ( $\alpha$ ) and the bandgap ( $E_g$ ) are related by [20]

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

where C is a constant. Thus, the extrapolation of nonlinear plot between  $(\alpha h\nu)^2$  vs  $(h\nu)$  gives the band gap of the corresponding material. Such plots for the films studied at two volumes of capping agents are shown in the Fig.5(a) and 5(b). The evaluated values of the band gaps are 3.75eV and 3.8eV at the two volumes. Thus, as expected the bandgap of materials increase with increasing concentration of capping agent, since the particle sizes then decreases.

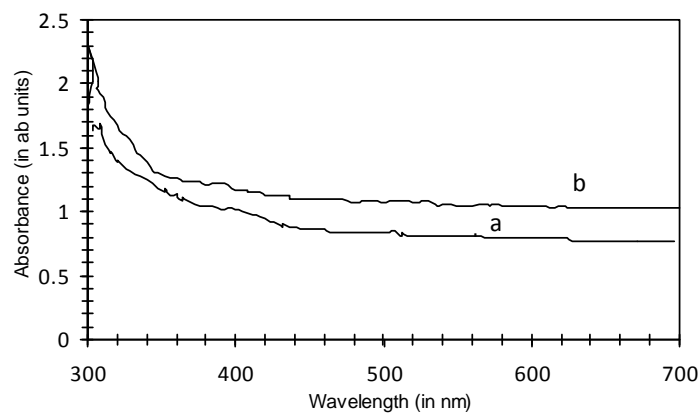


Fig.4.The optical absorption spectra of CdS:NaF,Pr at two concentrations of capping agents a. for 0.2ml of TGM ,b. for 0.7ml of TGM.

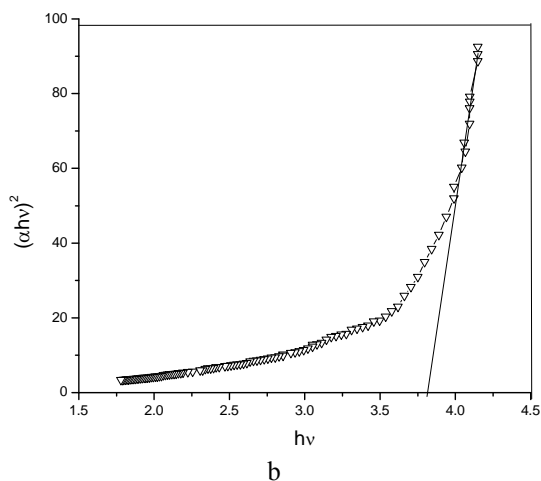
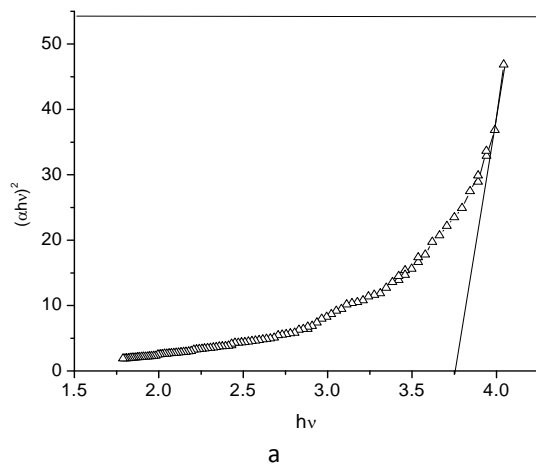


Fig.5(a) and 5(b).Tauc's plots for the films studied at two volumes of capping agents (a) for 0.2ml of TGM ,(b) for 0.7ml of TGM .

The particle sizes are calculated using the formula[ ]

$$E_{gn} = E_{gb} + \frac{\hbar^2 \pi^2}{2 \mu R^2} \quad (3)$$

where  $E_{gn}$  &  $E_{gb}$  are the band gap of nanocrystallites, and bulk semiconductor (2.42eV) respectively,  $R$  is the particle radius and  $m^*$  is the effective mass of electron. Substituting the values of  $E_{gn}$  determined from eq( 2) (3.75eV and 3.8eV) and standard values of other parameters, the particle sizes were found to be 1.18nm and 1.164nm. Thus, the particle sizes lie in the nanocrystalline range.

### 3.4. Photoluminescence studies

The photoluminescence emission spectra of CdS:NaF,Pr under the excitation of 230nm radiation at two volumes of capping agents are shown in the Fig.6(a) and 6(b). The results of CdS and CdS:NaF were reported in our earlier communication[17]. In CdS, the peak positions observed with 0.2ml TGM were at ~366 nm and 462 nm. With 0.7ml TGM more peaks were resolved with positions at 324nm, 353nm, 362 nm and 461nm. The strong peak at 462nm was considered due to band to band transition with increased band gap occurring due to nanocrystalline effect. This actually confirmed the quantum confinement effect also. As is known under nanocrystalline effect two prominent changes are observed: (i) change in band gap i.e. increase in band gap with reduced particle size and (ii) discreteness in the continuum of valence and conduction bands states. Thus, apart from the band emission, due to discreteness the transitions at higher levels may cause emission in the shorter wavelength side as observed in the present case. As also reported by Maleki et al [22], the peak at 363nm was attributed to higher level excitonic transition and its energy was calculated to be 3.38eV. Devi et al [23] also reported a peak in nanocrystalline CdS at 376nm with similar explanation. Maleki et al also observed a peak at 340nm under 220nm excitation which was related to higher level transitions. According to them this kind of band edge luminescence is caused by recombination of excitons and/ or shallowly trapped e-h pairs [22], it should be noted that PL edge emission in CdS was extensively investigated by a number of workers [24-26 ] and was associated with excitonic transitions or defect exciton complexes [27 ].

Similarly, in undoped CdS:NaF films ,with 0.2 ml TGM the intensities of two peaks at 366nm and 464nm were found to be improved as compared to uncapped films. Actually in presence of NaF better growth of films take place as it helps in crystallization and therefore, higher emission is observed. With 0.7ml TGM emission intensities of lower peak was found to be almost same but the intensity of peak at 462nm was improved. Also the two peaks observed at 353nm and 362nm were not found to be resolved in the presence of NaF. Since the peak at 462nm was associated to band –band transition due to increased band gap under nanocrystalline effect and hence it gets more affected because of quantum confinement in the presence of NaF.

The PL emission spectra of CdS:NaF,Pr are shown in Fig.6(a) and 6(b). It consists of two peaks, one at 363.97nm and 464.19nm for 0.2ml (lower) TGM volume and a little shifted peaks at 367.69nm and 460.5 for 0.7ml (higher) TGM volume.

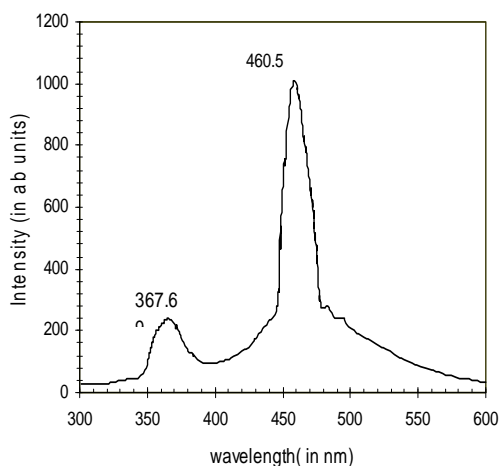
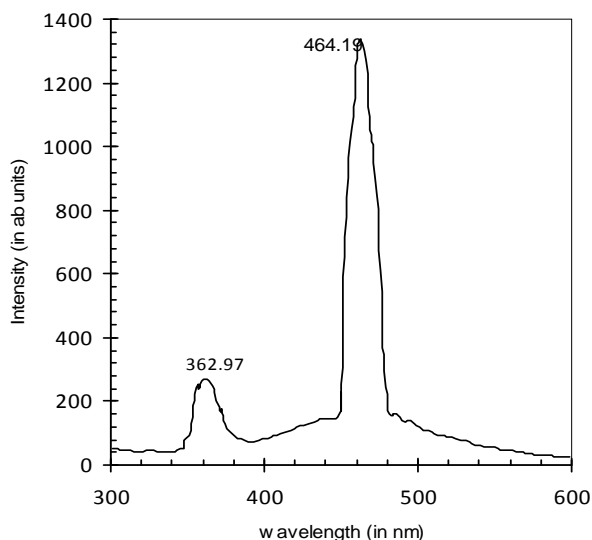


Fig.6(a) photoluminescence emission spectra of CdS:NaF,Pr at 0.2ml volumes of TGM under 230 nm excitation.



*Fig.6(b) photoluminescence emission spectra of CdS:NaF,Pr at 0.7ml volumes of TGM under 230 nm excitation.*

The intensity of first peak is not much affected, however, there is a major change in intensity of the second peak with incorporation of Pr as compared to that of undoped system. In view of the energy level scheme of  $\text{Pr}^{3+}$  [10], the different emissions expected from the transitions between energy levels of this ion are

$^1\text{S}_0 \rightarrow ^1\text{G}_4(295\text{nm})$ ,  $^1\text{S}_0 \rightarrow ^1\text{D}_2(335\text{nm})$  and  $^1\text{S}_0 \rightarrow \text{I}_6(385\text{nm})$ .

In present case, the observed peaks are not exactly same as expected for the transitions in this ion, however, the intensities are surely affected, particularly, of the peak at 462nm. This shows that the energy transfer takes place from levels of Pr to the host emitting centers. It is worth while to mention that UV radiations are very dangerous to human body and can cause skin cancer when exposed for a long time or with a higher dose. The Pr doped CdS can be considered as a suitable material to absorb UV radiation and convert it into mainly the 462 nm radiation which is in the visible region. It should be further noted that the intensity of peak at 362 nm is quite less compared to the emission at 462 nm.

#### **4. Conclusions**

From PL spectra of CdS:NaF,Pr films deposited on glass substrate, it is found that the emission intensity of blue peak ( $\sim 462\text{ nm}$ ) under 230 nm excitation is enhanced prominently and hence such system can be used for protection from UV. It can also be used as a window material as blue phosphors for display devices. Optical absorption spectra show shift due to decrease in particle size i.e. due to enlargement of band gap. Particle sizes determined from absorption and XRD studies lie in the nanocrystalline range. SEM studies also show existence of rod type structures with thicknesses in the nano-range.

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## References

- [1] L.E. Brus., J. Chem. Phys. **80**, 4403(1984).
- [2] M. Maqbool, I.Ahmad,H.H. Richardson, M.E. Kordesch, Appl. Phys. Lett. **91** 193511(2007)
- [3] M. Maqbool, H. H. Richardson, M. E. Kordesch, Mater. Res. Soc. Symp. Proc., Mater. Research Society 831(2005).
- [4] M. Maqbool, H. H. Richardson, P. G. Van Patten, M. E. Kordesch, Mater. Res. Soc. Symp. Proc., Mater. Research Society **798**, 8.5.1 (2004).
- [5] M. Maqbool, M.E. Kordesch, J.Mater.Sci.**42(14)**, 5657 (2007).
- [6] M.Maqbool, Eur.Phys.J.Appl.Phys. **34**, 31 (2006).
- [7] H. J. Lozykowski, W. M. Jadwisienkzak, I. Brown, J.Appl.Phys, **88(1)**, 102(2000).
- [8] S. Koti, K.R.Reddy,V.G.Kakani, D.Zhao,J.Exp.Bot. **56(412)**,725-736,(2005).
- [9] C. K.Bomford, Text book of Radiotherapy,Fifth ed.Churchill Livingstone Medical Division of Longman group United Kingdom limited, (1993).
- [10] M. Maqbool, I. Ahmad, Current Appl. Phy, **9**, 234(2009).
- [11] N.V.Hullavarad,S.S.Hullavarad,J.Vac.Sci.Techol.A, 26 (4)
- [12] M. J. Pawar, S. S. Chaure, Chalcogenide Letters **6(12)**,689(2009).
- [13] B. Saraswathi Amma , K. Ramakrishna, Manjunatha Pattabi ,J Mater Sci: Mater Electron **18**,11092007)
- [14] K. Suresh Babu,C.Vijayan,Prathap Haridoss,Mater.Letters **60**, 124(2006).
- [15] S.Bhusan, S.K Sharma, J.Mat.Sci[Mat. in electronics]1,165(1990).
- [16] S. G. Hussain, D. Liu, X. Huang, K. M. Sulieman, J. Liu, H. Liu, L. U. Rasool, J. Phys D: Appl. Phys. **40**, 7662 (2007).
- [17] S. Bhushan, Kusumanjali Deshmukh, M. Mukhejee, Bullet. of Mater. Sci, (Comm.)
- [18] H. Klung,L. Alaxander, X-Ray Diffraction Procedures, John Willey and Sons,Inc.NewYork, 491 (1962).
- [19] A. L. Afros, A. L. Afros, Sov.Phys.Semicond.**16**, 722 (1990).
- [20] A. L. Dawer, P. K. Shishodia, J. Chouhan, G. Kumar, A. Mathur, Mat.Sci.Lett. **9**, 547 (1990).
- [21] E. Caponitte, L. Peddone, D. Chillura Martino, V. Panto, V. T. Liveri, Material Sci Engineer.C. **23**, 531 (2003).
- [22] M. Maleki, M. Ghamsari, M. Sasani,S. H. Mirdamadi, R. Ghasemzadeh, Semicond. Phys. Quant. Elect.& Opto Ele. **10**, 30 (2007).
- [23] R. Devi, P. K. Kalita, P. Purkayastha, B. K. Sharma, Indian J. Phy. **82**, 707(2008).
- [24] R. E. Halsted, M. Aven, Phys. Rev. Lett. **14**, 64 (1965).
- [25] S. Iida, M. Toyoma, J.Phys.Soc. Jpn. **31**,190 (1971).
- [26] Y. Kokobun, T. Kaeriyama, J. Appl. Phys. Jpn. **14**, 1403(1975).
- [27]D. G. Thomas, J. Hopfield, J. Phys. Rev. **128**, 2135(1962).