# Photoluminescence Study of PbS and PbCdS Nanocrystalline Thin Films Fabricated by Chemical Bath Deposition Technique

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***Abstract:*** **Nanocrystalline lead sulphide (PbS) and Cd doped lead sulphide (PbCdS) thin films in Polyvinyl alcohol (PVA) matrix were deposited on glass substrate by chemical bath deposition (CBD) method. The nanocrystalline thin films were characterized by X-ray diffraction (XRD). XRD results show that the crystallite size varies from 58.39 nm to 67.76 nm for PbS and from 14.49 nm to 49.59 nm for PbCdS thin films. Photoluminescence study shows that the PL emission peak of PbS thin film was observed around 724 nm whereas the PL emission peak of PbCdS thin film was observed around 723 nm.**

***Keywords*: Chemical Bath Deposition, Nanostructure, PbS, PbCdS, Photoluminescence, XRD.**

## 1. INTRODUCTION.

Polymer capped inorganic nanoparticle composites have attracted much attention recently due to their enhanced optical and electronic properties. Lead sulfide (PbS) is a direct band gap compound semiconductor having energy of 0.4eV and belongs to IV-VI group. It is widely used as infrared sensor [1]. PbS possesses a large excitation Bohr radius i.e.18 nm [2]. This results in strong quantum confinement of both electrons and holes in nanostructure. Consequently, the value of the energy band gap can be controlled by the effective mass model with the modification of particle size [3]. Such semiconductor materials finds applications in radiation absorption [4], Selective sensors for $Pb^{2+}$ [5] and photography [6]. Besides these, PbS has been utilized as the temperature sensors, humidity, photo resistance, solar control, decorative coatings and diode lasers [7,8]. However, the nature of substrate and condition of crystal growth play an important role for acquiring all these properties. This in turns leads many researchers to employ different deposition technique in order to study such material. The most commonly employed techniques are microwave heating [9,10], electro deposition [11,12], chemical bath deposition [13-17] and spray pyrolysis [18]. However, the chemical bath deposition technique is employed for fabrication of PbS thin films because of its advantages such as low temperature requirement, low cost, suitable for large scale deposition areas, controllable properties of thin film through adjustable deposition parameters and the ability to deposit thin films on different types of substrates as compared to other methods [19]. The as fabricated PbS nanocrystalline thin film was characterized by XRD and Photoluminescence properties were studied in the present investigation.

## 2. EXPERIMENTAL DETAILS.

The PbS and Cd-doped PbS thin films in PVA matrix were deposited by Chemical Bath Deposition Technique on glass substrate. The glass substrates were first cleaned by liquid detergent and washed thoroughly in distilled water and then it was immersed in boiling water for a few minutes. They were then cleaned ultrasonically in acetone for 15 minutes and dried in an oven before deposition. The matrix solutions was prepared by adding lead acetate solution of 0.3M to an aqueous solution (1wt%) of PVA separately with constant stirring at 70C until a clear solution is obtained. The $P^H$ value of the solutions was maintained at around 8.5 by slowly adding ammonia solution drop by drop. Then the equimolecular solution of Thiourea was added to the matrix solutions. The same was stirred slowly until the color of the resulting solution was turned into dark brown slowly. Four ultrasonically cleaned glass substrates were immersed vertically in the solution using a suitable substrate holder for 3 h $30^0$C and then 16h at room temperature for deposition of PbS thin films. The as deposited PbS thin films on the glass substrate were taken out and washed thoroughly in distilled water several times and dried in air and then put in a dessicator. The Chemical reaction for deposition of PbS thin film is given by

Step I. $Pb(CH_3COO)_2.3H_2O = Pb^{2+} + 2CH_3COO- + 3H_2O$
Step II. $Pb^{2+} + 4NH_3 = Pb(NH_3)_4^{2+}$
Step III. $SC(NH_2)_2 + 2OH^- = S^{2-} + CH_2N_2 + 2H_2O$
Step IV. $Pb(NH_3)_4^{2+} + SC(NH_2)2 + 2OH^- = PbS + 4NH_3 + CH_2N_2 + 2H_2O.$

Similarly, the Cd-doped PbS thin films of 0.3 M were deposited on the glass substrate by adding an equimolar solution of cadmium acetate to the matrix solution of lead acetate and then thiourea solution maintaining the same pH value. The overall chemical reaction taking place is as follows.

$_{1-x}[Pb(CH_3COO)_2]+ {}_xCd^{2+} + CS(NH_2)_2 \rightarrow Pb_{1-x}Cd_xS + 2CH_3COOH + CH_2N_2$

## 3. RESULTS AND DISCUSSION.

### 3.1 XRD ANALYSIS

The structural characterization of PbS and Cd doped PbS (PbCdS) thin films were done by X-ray diffraction technique using Burker AXS D8 advance with Cu-kα line (λ = 1.5406 Aº). The XRD patterns of PbS and PbCdS thin films are shown in figure 1(a) and 1(b) and they possess face centered cubic structure as confirmed by JCPDS Data card file reference code: 05-0592 and the peaks correspond to (111), (200), (220), (311) corrected crystal planes for both PbS and PbCdS thin films. The sharp peaks in the XRD Pattern of PbS and CdPbS indicate that the materials have good crystallinity and they are preferentially oriented along the (111), (200), (220) and (311) directions. The XRD patterns reveal that a significant boardening occurs after doping of Cd for all orientations. This confirms that the phase transformation is produced due to doping of Cd into PbS lattice [20]. Further, it is also confirmed that the internal strain would arise when Cd2+ occupies more and more of $Pb^{2+}$ in the host lattice. As a result, the crystal structure of the PbCdS solid solution becomes unstable. This clearly implies that the ionic radius of $Cd^{2+}$ is less than that of $Pb^{2+}$ and $Cd^{2+}$ ions are well dissolved in the PbS lattice . The lattice d- spacing is calculated by using Bragg's Law,

**$n\lambda = 2d\sin\theta$ …….(1)**

The lattice constants is determined by using the relation,

**$a = d\,(h^2 + k^2 + l^2)^{1/2}$ ……..(2)**

The crystallite size of PbS and Cd doped PbS (PbCdS) hin films is calculated by using Scherrer's formula :

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{……(3)}$$

where K is a constant (= 0.94), β is the full width at half maximum (FWHM) in radian at 2θ.

The average stress in the sample was calculated by the relation [21] :

**$S = (a_0 - a)/a_0 \times Y/2\sigma$** ……(4)

where a and $a_0$ are the lattice parameters of the thin film samples and bulk one respectively, Y (= 70.2 GPa) and σ(= 0.28) are the Young's modulus and Poisson's ratio respectively. The microstrain was determined from the formula [21] :

**$\epsilon = (\beta\cos\theta) / 4$. ……(5)**

Their values are shown in table 1. The lattices constants '**a'** are found to be vary from 5.902 Aº to 5.948 Aº for PbS thin films and the average value is 5.927 Aº which is comparable with standard value **a** = 5.936 Aº. The lattice constant, '**a'** for PbCdS thin film are also found to vary from 5.876 Aº to 5.910 Aº and the average value is 5.892 Aº which is slightly lower than standard value **a** = 5.94 Aº. The results are also similar to earlier workers [22]. Further, the doping of Cd ions decreases the d spacing values which is in agreement with the literatures in which the similar results are reported [22]. Hence, this confirms the formation of PbCdS thin film. However, the microstrain and average stress are found to increase on doping of Cd ions. It is also found that the high intensity corresponds to larger crystallite size for both PbS and PbCdS thin films. The avearge crystallite size for PbS thin film is found to be 62.15 nm and that of 3 PbCdS thin film is found to be 8.10 nm. Thus, the doping of Cd ion also decreases the crystallite size.

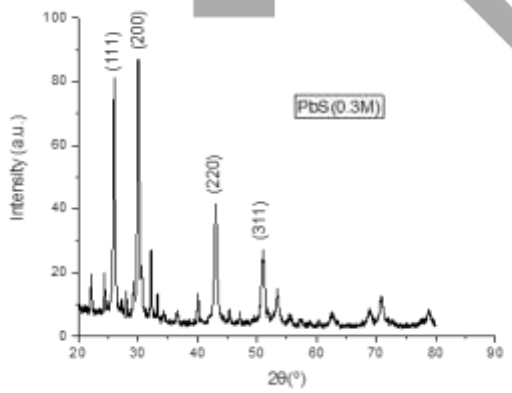


Figure. 1(a). XRD pattern of PbS thin film

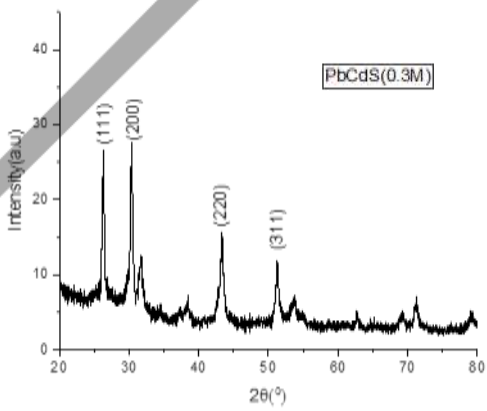


Figure. 1(b). XRD pattern of PbCdS thin film

**Table 1. Structural Parameters of PbS and PbCdS thin films.**

| Films | 2θ(º) | d (Aº) | Crystallite Size, D (nm) | Average D(nm) | (hkl) | a (Aº) Calculated | a(Aº) Average | Sx10$^9$(N/m$^2$) | Microstrain (ϵ) |
|---|---|---|---|---|---|---|---|---|---|
| PbS (0.3M) | 26.14 | 3.408 | 61.88 | 62.15 | (111) | 5.902 | 5.927 | 0.1900 | 5.85 X 10$^{-2}$ |
| | 30.14 | 2.963 | 67.76 | | (200) | 5.926 | | | 5.35 X 10$^{-2}$ |
| | 43.07 | 2.103 | 60.59 | | (220) | 5.948 | | | 5.97 X 10$^{-2}$ |
| | 51.02 | 1.789 | 58.39 | | (311) | 5.933 | | | 6.20 X 10$^{-2}$ |
| PbCdS (0.3M) | 26.27 | 3.393 | 49.59 | 38.10 | (111) | 5.876 | 5.892 | 1.0128 | 7.30 X 10$^{-2}$ |
| | 30.37 | 2.941 | 46.71 | | (200) | 5.882 | | | 7.75 X 10$^{-2}$ |
| | 43.33 | 2.087 | 41.61 | | (220) | 5.902 | | | 8.70 X 10$^{-2}$ |
| | 51.28 | 1.782 | 14.49 | | (311) | 5.910 | | | 24.97 X 10$^{-2}$ |

## 4. PHOTOLUMINESCENCE (PL) STUDIES.

When an electron is excited by a monochromatic photon beam of certain energy, it undergoes nonradiative or radiative recombination either at valance band or at traps/surface states. This process is called photoluminescence [23]. The nature of the PL emission also highly depends on chemical environment, morphology and crystallites size. The PbS and Cd doped PbS nanocrystalline thin films were excited at 355 nm using F-7000 FL Spectrophotometer. The PL spectra of the samples was measured in luminescence mode with canning speed 240 nm/min. The PL emission spectra of PbS and Cd doped PbS thin films are shown in Fig.2(a) and 2(b). The PL emission peak of PbS thin film is observed around 724 nm whereas the PL emission peak of PbCdS thin film is observed around 723 nm. This emission is due to the recombination of electron and hole pair. The emission wavelength slightly decreases due to doping of Cd ion. However, both emission peak lies in the visible region. The PL emission spectra reveals that the addition of metal ions like Cd increases the transition energy of electron. This in turn shows that the energy band gap of PbS thin film increase due to the addition of Cd which is also supported by the XRD results i.e the energy band gap of PbS thin film increase as the crystallite size decreases. This property makes it an excellent candidate for opto-electronic applications in many fields such as IR detectors, photography, light emitting devices, solar absorbers, and solar cells [24,25].

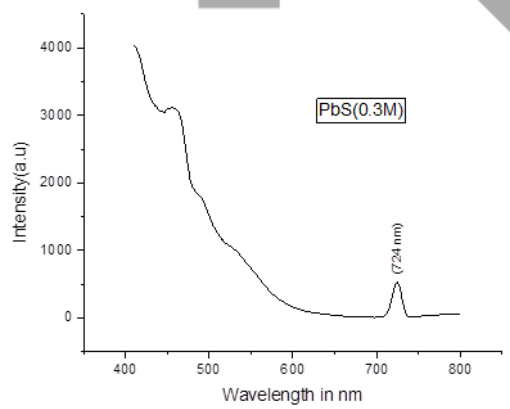


Figure. 2(a). PL emission spectra of PbS thin film

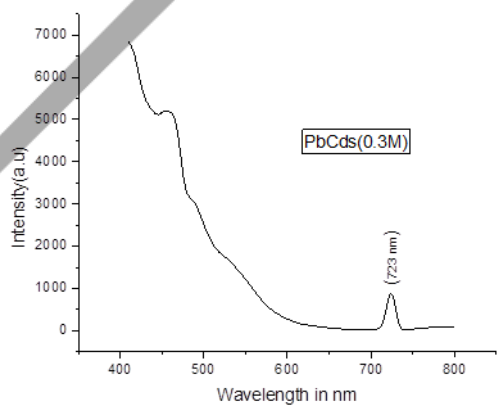


Figure. 2(b). PL emission spectra of PbCdS thin film

## 5. CONCLUSION.

Nanocrystalline PbS and Cd doped PbS (PbCdS) thin films in PVA matrix were fabricated by chemical bath deposition (CBD) method on glass substrates. The nanostructure was characterized by X-ray diffraction (XRD). The average crystallite size estimated from XRD peaks was found to be 62.15 nm for both PbS and to be 38.10 nm for PbCdS thin films. The photoluminescence study shows that the increase in energy band gap is correlated with decrease in crystallite size.

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