

## EFFECT OF DOPING CONCENTRATION ON THE OPTICAL PROPERTIES OF NANOCRYSTALLINE Zn DOPED PbS THIN FILMS DEPOSITED BY CBD METHOD

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Nanocrystalline PbS and Zn doped PbS thin films have been deposited on glass substrates by chemical bath deposition (CBD) method. The as deposited thin films were found to be crystalline having cubic phase structure. The optical properties of the undoped and Zn doped PbS thin film have been studied. The chemically prepared Zn doped and undoped nanocrystalline PbS films have high absorbance in the UV-visible region. The linear nature of  $(\alpha h\nu)^2$  vs  $(h\nu)$  plots of PbS thin films confirmed that the transition is direct and the optical band gap energy of PbS films is found to increase from 1.90 eV to 2.28 eV with decreasing crystallite size from 29 nm to 15 nm and these obtained band gap values are higher than the bulk value (0.40 eV). The increase in optical band gap supports the quantum confinement effect in the PbS thin films prepared by CBD technique. The optical band gap of Zn doped PbS films are found to increase with increase in dopant concentrations.

(Received August 21, 2020; Accepted November 26, 2020)

*Keywords:* Nanocrystalline, Thin film, Grain size, Optical band gap, Absorbance, CBD

### 1. Introduction

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. The study of optical properties of nanocrystalline solids have become the topic of great interest from the theoretical and experimental research point of view [1]. A bulk material should have constant physical properties regardless of its size, but at the nano-scale, size-dependent properties are often observed. It is known that nanocrystalline semiconductors exhibit the “quantum confinement effect” and possess many superior properties as compared to bulk counterparts. As a consequence of quantum confinement, the continuum of states in the conduction and valance band are broken down into discrete states with an energy spacing relative to the band edge, which is approximately inversely proportional to the square of the particle radius [2], resulting in widening of the band gap as compared to the bulk. This is normally observed by a blue shift in the optical absorption spectra. The absorption edge of lead sulphide (PbS) exhibits a large blue shift when the size of the crystallite size is reduced to nanometer scale [3-6]. The structural and optical properties of pure nanocrystalline PbS thin films have been widely reported in the literature. However, a few literatures on the detailed studies of optical properties of Zn doped PbS thin films have been reported. In this paper, a detailed study on the structural and optical properties of chemical bath deposited undoped and Zn doped PbS nanostructured thin films is reported. This study was aimed to gain into inside the material properties of the systems for their practical applications in electronic devices such as photovoltaic cells, light emitting devices, light detector etc.

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## 2. Experimental details

Nanocrystalline undoped PbS thin films were deposited onto chemically cleaned glass substrates by Chemical Bath Deposition (CBD) method using lead acetate and thiourea as  $\text{Pb}^{+2}$  and  $\text{S}^{-2}$  sources respectively while Zn doped PbS thin films were deposited by the same method using Zinc acetate, lead acetate and thiourea as  $\text{Zn}^{+2}$ ,  $\text{Pb}^{+2}$  and  $\text{S}^{-2}$  sources respectively. For this, pH value of freshly prepared 0.2 M solution of lead acetate was maintained at 11 by drop wise addition of  $\text{NH}_3$  solution. Another equal amount of 0.2 M solution of thiourea was added and the solution mixture was stirred well. Bare glass substrates were immersed vertically into the solution. The solutions mixture was heated at 313 K for 1 hour and then kept overnight at room temperature for further deposition. After deposition, the substrates coated PbS on both sides were taken out and thoroughly washed with distilled water and dried in air. In this way, undoped PbS thin films are prepared at constant molarity 0.2 M, pH value 11 and deposition temperature 313K. For preparation of Zn doped PbS thin films at three different Zn dopant concentrations, pH values of three sets of freshly prepared 0.2 M solution of lead acetate premixed with 2 wt. %, 3 wt. % and 4 wt. % Zinc acetate respectively are maintained at 11 by drop wise addition of  $\text{NH}_3$  solution into each set of solution. Another equal amount of 0.2 M solution of thiourea was added to each set of lead acetate and Zn acetate solution mixture and the final solution mixture was stirred well. Then proceeding in the same way of depositing undoped PbS thin films, Zn doped PbS thin films at different doping concentrations (2 wt%, 3 wt % and 4 wt% ) of Zn are deposited onto glass substrates at constant molarity 0.2 M, pH value 11 and deposition temperature 313 K to study their effects on structural, morphological and optical properties of the films. The films deposited on the glass substrates were used for XRD, EDX, SEM and TEM studies. The structure of the film was obtained using X-ray diffraction (XRD) XPERT-PRO Philips diffractometer. Surface morphology of the film was studied using JEOL-JSM 6360. Transmission electron microscopy (TEM) of the Zn doped PbS sample was carried out using JEM-2100 to estimate particle size. The optical properties of the samples were studied using UV-visible spectrophotometer CARRY 300.

## 3. Results and discussion

### 3.1. Structural properties

Fig.1 shows the XRD pattern of as-deposited PbS and Zn doped PbS films deposited at deposition temperature 313K, pH value 11 and concentration 0.2M at different dopant concentrations (2 wt%, 3 wt% and 4 wt%). In the case of as-deposited PbS films, we observe sharp peaks at  $2\theta = 25.9^\circ$ ,  $29.9^\circ$ ,  $43.0^\circ$ ,  $50.9^\circ$  and  $53.4^\circ$ . The observed peak positions are consistent with the fcc cubic phase structure of PbS [7,8]. With the addition of different dopant concentrations ( $\text{Zn}^{+2}$  source), the peak intensities decrease considerably. This can be attributed to doping induced structural disorder in the films [9].

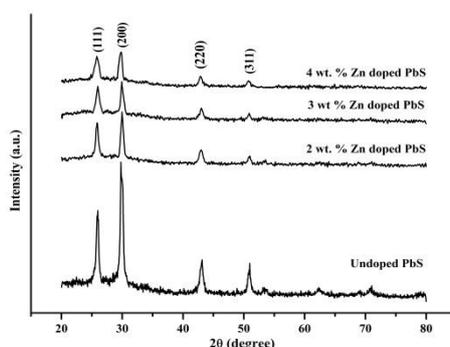


Fig. 1. XRD spectra of undoped and Zn doped PbS thin films prepared at different weight percent doping of  $\text{Zn}^{+2}$  source at constant reactant concentration 0.2 M, pH value 11 and deposition temperature 313K.

With increase in doping percentage of Zn, the increase in broadening of the peaks is quite obvious from Fig. 1. There are two main possible causes for the peak broadening. The first is the increase in heterogeneity of the films due to the occupation of Zn into the host lattice. A second cause could be the decrease in the particle size ( $D$ ). When  $Zn^{+2}$  occupies more and more sites of  $Pb^{+2}$  in the host lattice, internal strain would arise and the crystal structure of ZnPbS solid solution becomes unstable. In order to stabilize the crystal structure, there would be a spontaneous size reduction of the particles which might release the strain. As the Zn concentration is increased, the diffraction peaks become broader due to a reduction in the size [10]. The crystalline sizes of the films are calculated from the XRD spectra using the Scherer's relation [11] and are found to be 29 nm, 20 nm, 18 nm and 15 nm for undoped PbS film, 2 wt %, 3 wt % and 4 wt % Zn doped PbS films. There is decrease in crystallite size with increase in dopant concentration. The decrease in crystallite size of Zn doped PbS may be due to the replacement of some the larger size lead ions (Atomic radius = 1.21Å) by smaller size zinc ions (0.74Å). Similar results are reported for Mn-doped CdS films [12, 13].

### 3.2. Elemental analysis

To confirm the chemical composition of undoped PbS and Zn doped PbS thin films, the elemental analysis of the samples were performed by Energy Dispersive X-ray Spectrometer (EDX). Fig.(2-5) represent the EDAX spectra of the undoped PbS and Zn-doped PbS thin films at three different doping concentrations ( 2 wt%, 3 wt% and 4 wt% of  $Zn^{+2}$ ). EDAX Spectra of undoped PbS thin film shows the presence of Pb and S as shown in Fig. 2. Similarly, the presence of Zn atoms in the spectra shown in Fig. 3, 4 and 5 indicate that Zn atoms are also incorporated with the PbS film. It is also observed that atomic percentage of Zn atom increase with increase in Zn-doping concentration. The extra peaks observed in the EDAX spectra correspond to some impurity elements like Mg, Si, Na, Ca which are due to glass substrate or the substrate holder used in the EDAX instrument [14-16]. These might also be due to presence of C and O due to exposure of the film to the atmosphere [17]. There is no source of these elements in the chemicals used for the PbS film synthesis. We consider only the atomic % of Pb and S present in the spectra of doped sample neglecting the percentage of the other elements present in the spectra.

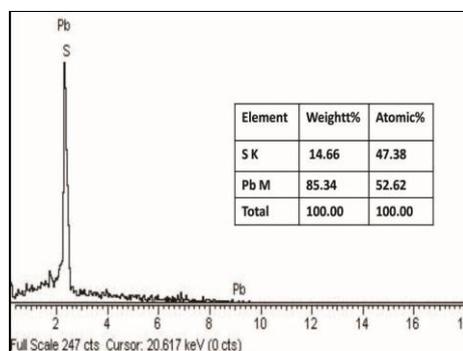


Fig. 2. EDAX Spectra of undoped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

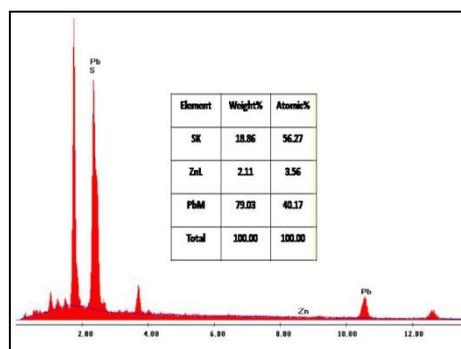


Fig. 3. EDAX Spectra of 2 wt.% of Zn doped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

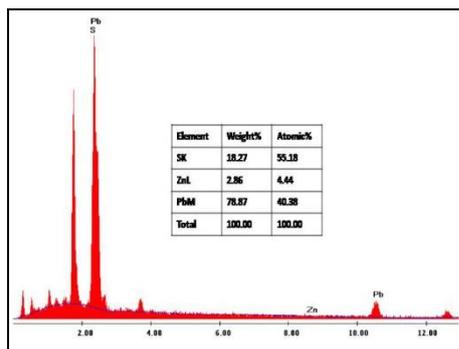


Fig. 4. EDAX Spectra of 3 wt% of Zn doped PbS thin film prepared at concentration 0.2 M, pH value 11 and deposition temperature 313K.

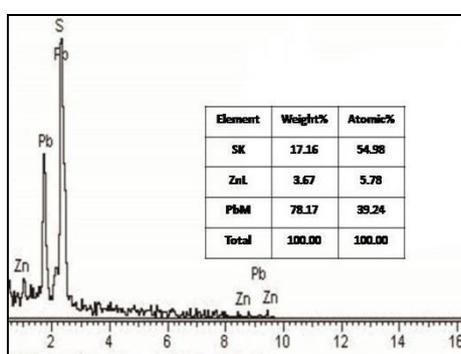


Fig. 5. EDAX Spectra of 4 wt. % of Zn doped PbS thin film prepared at 0.2 M, pH 11 and deposition temperature 313K.

### 3.3. SEM and TEM studies

Scanning electron microscopy (SEM) photographs are used for studying the surface morphology of the undoped PbS film and Zn doped PbS films. Fig. 6 (a-d) show 10000x magnification SEM images of the as-prepared undoped PbS film and the Zn-doped PbS thin films at different concentrations viz 2 wt%, 3 wt% and 4 wt%. It is observed that the films are continuous over the glass surface and are fairly uniform. The grains of the films have different shapes and sizes but almost compact. There are no macroscopic defects such as voids, peeling or cracks. From the photographs, it is observed that the grains are nearly spherical in shape. All the films are continuous, compact, homogenous and free from voids, cracks or holes.

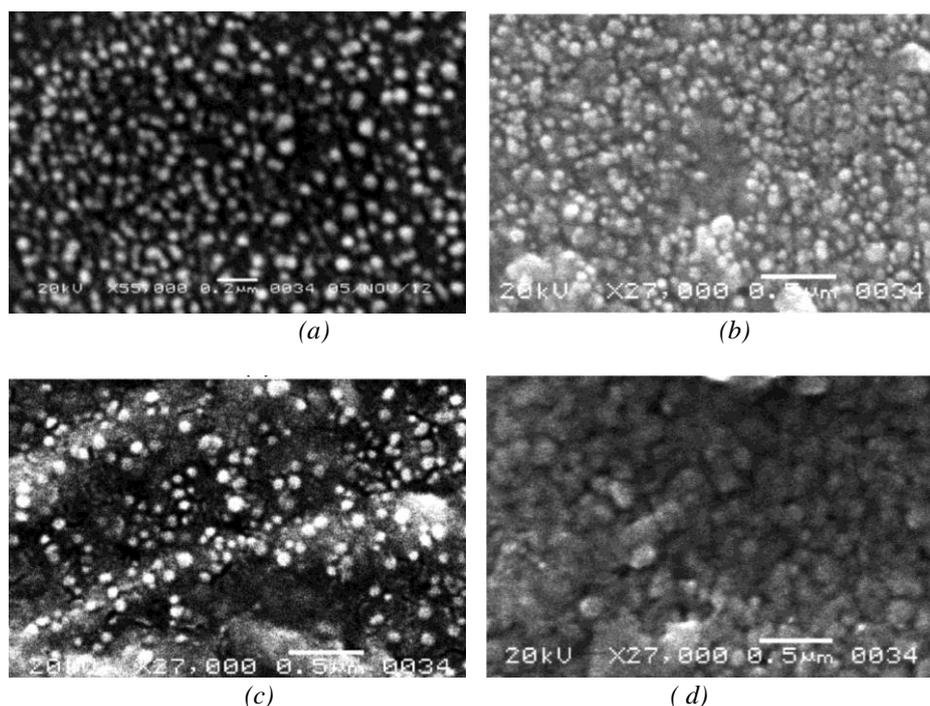


Fig. 6. SEM photographs of (a) PbS thin film and Zn doped PbS thin films deposited on glass substrates at different Zn concentration values of (b) 2 wt% (c) 3 wt% and (d) 4 wt% keeping constant pH value 11 and concentration 0.2 M and temperature 313 K.

TEM images of nanocrystalline undoped PbS thin film and 2 wt.% and 4 wt.% Zn doped PbS thin films as-prepared keeping constant concentration 0.2 M, pH value 11 and deposition temperature 313K respectively are shown in Fig. 7(a-c), Fig. 8(a-c) and Fig. 9(a-c) respectively. They also reveal that small grains attach together and produce large grains. The grains in dark colour shown in Fig. 7(a), Fig. 8(a) and Fig. 9(a) are those of nanocrystalline undoped PbS, 2 wt.% Zn doped PbS and 4 wt. % Zn doped PbS, the calculated average grain sizes are found to be in the ranges 32-46 nm, 12-15 nm and 8-10 nm respectively which are different from the X-ray diffraction results (15-29 nm). The discrepancy between the grain size obtained from the TEM and XRD measurements may be due to the difference in the thickness of these samples, since the TEM grid requires very thin layer deposition on the carbon coated grid, but for XRD characterization thicker film is deposited on the glass substrate [18]. HRTEM is used to study the structure as well as to observed lattice images showing different orientations of the nanocrystals of Zn doped PbS. The HRTEM image shown in Fig. 7(b) depicts lattice fringe with d-spacing of 0.30 nm corresponding to (200) plane which is in good agreement with the lattice constant for the PbS cubic structure and Fig. 8 (b) and Fig. 9(b) exhibit lattice fringes with d-spacing of 0.28nm to (200) plane of the Zn doped PbS cubic structure respectively. Also intersection of lattice fringes are observed which is an indication of the overlap of several Zn doped PbS nanoparticles with different orientations. Selected area electron diffraction (SAED) images shown in Fig.7(c), Fig.8(c) and Fig. 9(c) exhibit multiple diffractions rings with missing periodicity which is due to the random orientation of the polycrystalline particles. No significant difference is observed in both the images except the difference in grain sizes. In both cases nearly spherical Zn doped PbS nanoparticles are observed. From the TEM studies of undoped and doped PbS films, we observed that the d-value are slightly decreased for the Zn-doped PbS films.

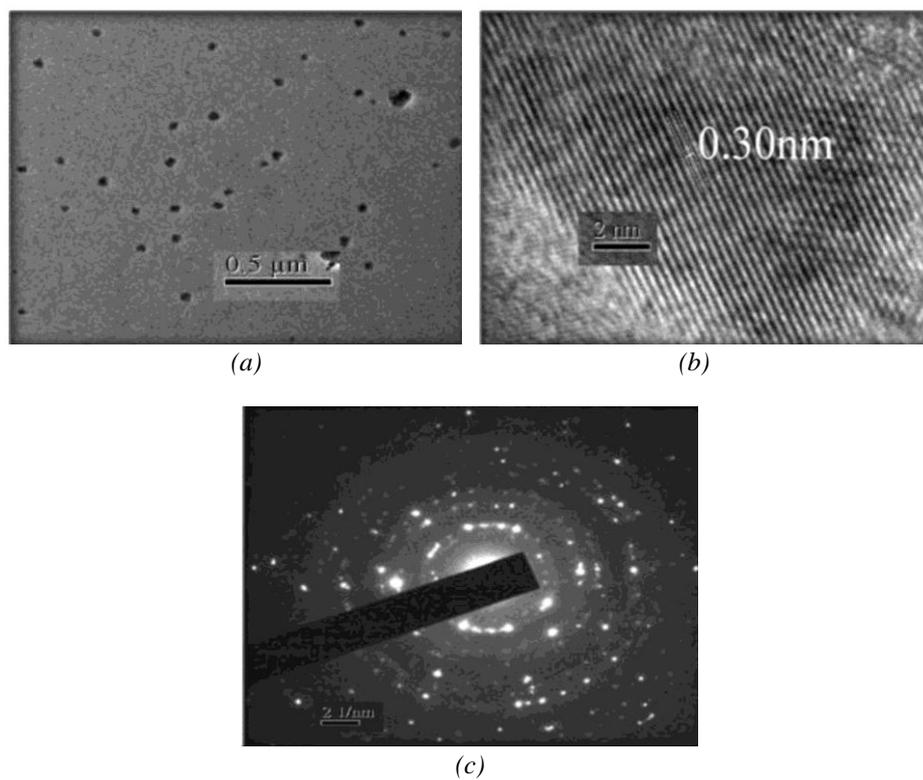


Fig. 7. (a) TEM image (b) HRTEM image and Interplanar spacing 'd' and (c) selected area electron Diffraction (SAED) images of nanocrystalline undoped PbS thin film prepared at concentration 0.2 M keeping constant pH value 11 and deposition temperature 313K.

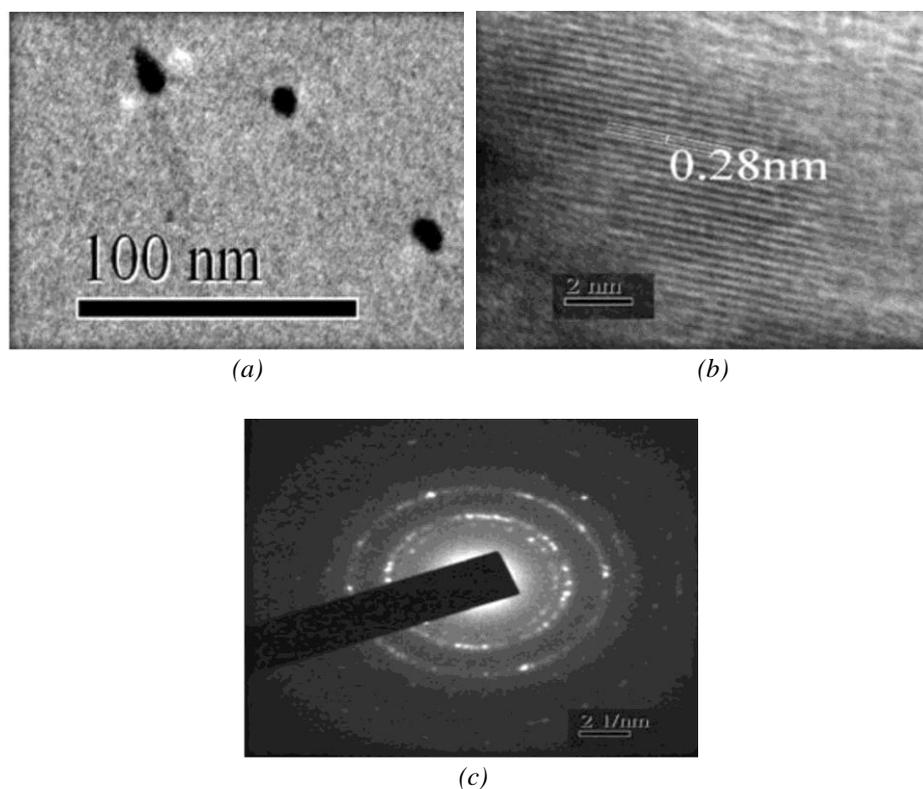


Fig. 8. (a) TEM image (b) HRTEM image and Interplanar spacing 'd' and (c) selected area electron diffraction(SAED) images of nanocrystalline 2 wt. % Zn doped PbS thin film prepared at concentration 0.2 M keeping constant pH value 11 and deposition 313K

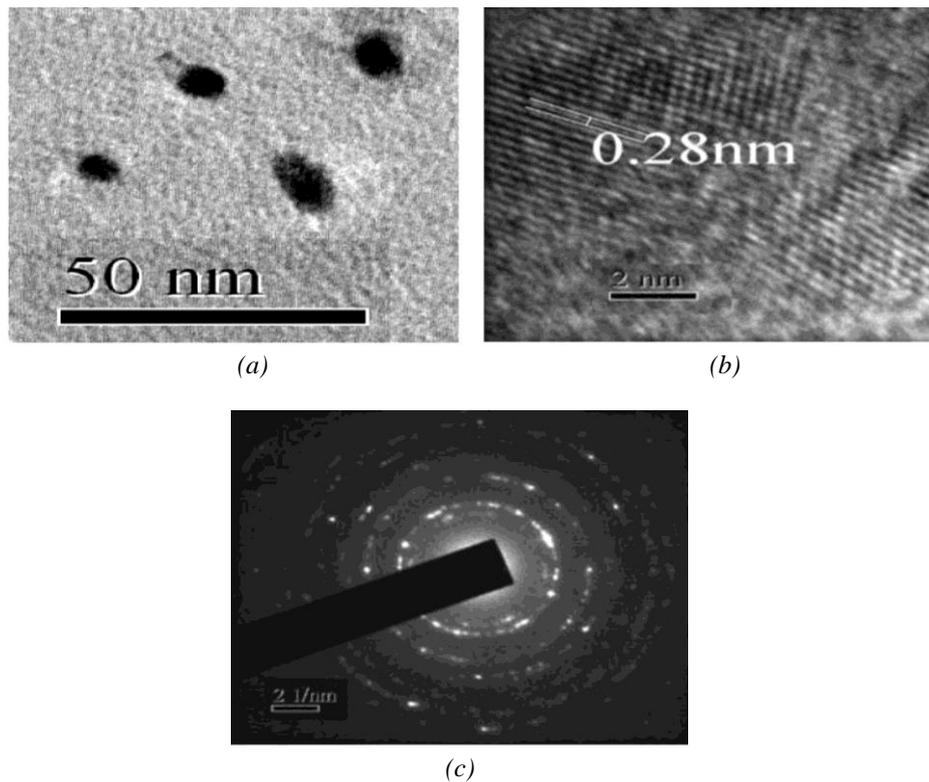


Fig. 9. (a) TEM image (b) HRTEM image and interplanar spacing 'd' and (c) selected area electron diffraction(SAED) images of nanocrystalline 4 wt. % Zn doped PbS thin film prepared at concentration 0.2 M keeping constant pH value 11 pH value and deposition 313K.

### 3.2. Optical Properties of Zn doped nanocrystalline PbS thin films

Fig.10 shows absorption spectra of undoped and Zn doped PbS thin films. It is evident from the figure that the absorbance decreases with increase in Zn doping concentration. Fig. 11 shows the  $(\alpha h\nu)^2$  vs  $(h\nu)$  plots for undoped and Zn doped PbS thin films respectively corresponding to different doping concentrations.

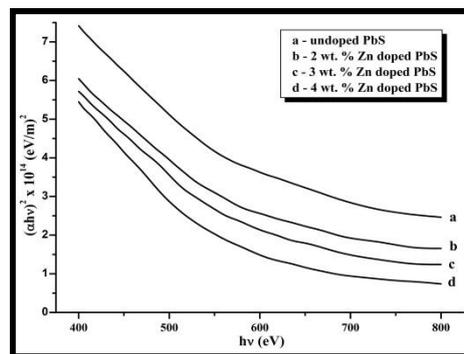


Fig. 10. Absorption spectra of undoped and Zn-doped PbS thin films prepared at three different wt. % of  $Zn^{+2}$  source keeping constant concentration 0.2 M, pH value 11 and deposition temperature 313K.

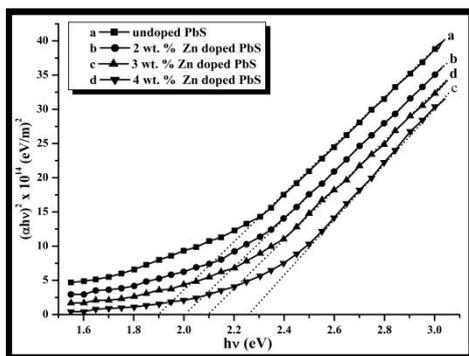


Fig. 11. Plot of  $(ahv)^2$  vs  $hv$  of PbS thin films of undoped PbS and Zn-doped PbS thin films prepared at three different wt. % of  $Zn^{+2}$  source keeping constant concentration 0.2 M, pH value 11 and deposition temperature 313K.

Extrapolation of the linear portions of the plots to the energy axis yield the direct band gap values for the Zn doped PbS thin films (Table 1). It is observed that band gap increases with increase in Zn doping concentration. Incorporation of Zn to PbS creates some structural changes and the optical band gap is strongly dependent on fractional concentration of Zn atoms. This may be due to the tendency of Zn atoms to introduce high degree of disorder and hence higher densities of localized states in the forbidden gap [19].

Table 1. Calculated values of crystallites size and optical band gap of PbS thin films prepared at different doping concentrations keeping fixed deposition parameters.

Deposition parameters	Sample of nanocrystalline PbS thin film with doping percentage of	Thickness (nm)	Crystallite Size (nm)	Optical band gap (eV)
Concentration = 0.2M pH value = 11 temperature = 313 K	0 wt% Zn (Undoped)	262	29	1.90
	2 wt% Zn	222	20	2.15
	3 wt% Zn	219	18	2.20
	4 wt% Zn	212	15	2.28

#### 4. Conclusion

The chemically prepared doped and undoped nanocrystalline PbS films have high absorbance in the UV-visible region. The linear nature of  $(ahv)^2$  vs  $hv$  plots of PbS thin films confirmed that the transition is direct and the optical band gap energy of PbS films is found to increase from 1.90 eV to 2.28 eV with decreasing crystallite size from 29 nm to 15 nm and these obtained band gap values are higher than the bulk value (0.40 eV). The increase in optical band gap supports the quantum confinement effect in the PbS thin films prepared by CBD technique. The optical band gap of Zn doped PbS films are found to increase with increase in dopant concentration.

#### Acknowledgments

One of the authors, L. Rajen Singh is thankful to IIT. Guwahati, India for EDX analysis, Department of Physics, Manipur University, Manipur, India, Department of Physics, Guwahati,

Department of instrumentation & USIC, Gauhati University, Guwahati, India for providing XRD, UV-Vis Spectrophotometer, SEM analysis and lastly SAIF, NEHU, Shillong, India for TEM analysis.

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