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ARTICLE

Effects of Thermal Annealing on Structural and Optical Properties of Nanocrystalline $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ Thin Films Prepared by CBD

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Abstract: $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films with ($x=0, 0.4$) were successfully deposited on glass substrates using chemical bath deposition (CBD) method. It was confirmed from the X-ray diffraction (XRD) analysis that all the films exhibited a polycrystalline nature with preferential orientation along (200) plane. The deposited films were thermally annealed in order to investigate the effect of thermal annealing on the structural and optical properties. From the XRD analysis, better crystallization was observed with increasing crystallite size as the annealing temperature was raised from (298 to 573) K, while optical absorption measurements showed that the allowed direct band gap of the annealed samples decreased from 1.59 to 1.55 eV and from 1.7 to 1.65 eV for PbS and $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$, respectively. The effect of thermal annealing on optical constants, such as extinction coefficient (k), refractive index (n), real and imaginary dielectric constants (ϵ_1, ϵ_2), was discussed. Each of the photo luminescence (PL) spectra revealed a single peak red emission around (680) nm for PbS and (670) nm for $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$.

Keywords: Optical properties; Thin films; CBD; Thermal annealing; XRD.

PACS: 79.60.Dp.

Introduction

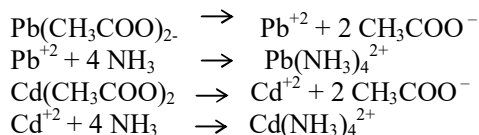
A considerable attention was paid to the deposition of ternary derivative semiconductors due to the possibility of controlling the energy gap and lattice constant [1]. Lead sulfide is a member of an important narrow-band IV-VI compound semiconductor group, and is widely used as infrared sensor (due to its 0.4 eV direct band gap) [2]. This material has also been utilized in many fields, such as photography [3]. There are several methods to prepare lead sulfide thin films, such as spray pyrolysis [4], photo-accelerated chemical deposition [5], microwave heating [6], electro deposition [7], photoelectrochemical deposition using olive oil [8] and chemical bath deposition [9,10]. The last method is an easy, inexpensive and most energy efficient method and has been traditionally used in chalcogenide semiconductor thin film preparation [11]. The narrow band gap of PbS semiconductor can be modified by adding a

molar ratio of a wide band gap compound, such as CdS (2.4) eV. Mixing thin films of PbS and CdS ($\text{Cd}_x\text{Pb}_{1-x}\text{S}$) has attracted special attention, since they are promising in many physical applications, such as photo-electronics, optical switches, solar cells and infrared photo - detectors [13,14]; as their band gap could be adjusted to match the ideal band gap (~1.5 eV) needed to produce most efficient solar cells. $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ has been employed in several techniques, such as chemical vapor deposition [15], successive ionic layer reaction [16] and sol-gel method [17]. Many studies highlighted the electrical and optical properties of CdPbS [18-20]. In this paper, we reported the influence of thermal treatment on structural and optical properties of $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ ($x = 0, 0.4$) prepared by CBD. The resulting films have been characterized in terms of structural and optical properties using XRD and UV-VIS-NIR spectrophotometer techniques, respectively.

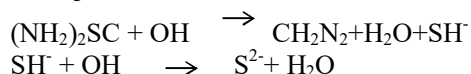
Experimental Process

Specimens of PbS and $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films were grown on ordinary glass slides (7.5x2.5 cm). Deposition was carried out in a reaction solution prepared in 100 ml beaker containing 0.1 M solution of lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$), 0.1 M of cadmium acetate ($\text{Cd}(\text{CH}_3\text{COO})_2$), ammonia (NH_3) and 0.1M of thiourea ($(\text{NH}_2)_2\text{SC}$). Lead acetate acts as the source of cation (Pb^{+2}) as cadmium acetate (Cd^{+2}) does and thiourea was the source of anion (S^{2-}). NH_3 was used to maximize growth by providing an alkaline medium. The deposition of $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films started with mixing lead acetate and cadmium acetate ($x=0$, $x=0.4$) with 1 ml NH_3 . The solution was completed to 50 ml with distilled water, then heated up to 323 K. The glass substrates were immersed vertically and then 10 ml of thiourea was added gradually (drop by drop) and heated to 333 K in a bath. This temperature was kept constant for about 90 minutes, then the substrates were taken out,

washed with distilled water and dried. The resulting films were homogeneous, well adhered to the substrate, with a mirror-like surface for PbS thin films and yellowish dark for $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ thin films. The average thickness of films estimated by weighing method was around 3000 ± 10 Å. The CBD depends on sequential reactions at the surface of substrate. The formation of $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ may involve the following steps [21]:



In alkaline medium, dissociation of $(\text{NH}_2)_2\text{SC}$ takes place.



The overall chemical reaction is as follows:



A change has been noticed in the reaction solution color after heating, marking a chemical reaction that resulted in deposition of homogenous $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ films, formed within optimum conditions. After complete drying, the films were annealed in atmosphere at 473 K and 573 K for one hour. The structure of the films was characterized by X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 1.54$ Å), where the average diameter (D) of grain size of $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ was calculated using Scherer formula [22]:

$$D = 0.9\lambda / \beta \cos \theta ;$$

where β is the experimentally observed diffraction peak width at full wave half maximum intensity (FWHM) and θ is Bragg angle. The strain ξ of the deposited films was obtained from the following relation [23]:

$$\cos \theta / \lambda = 1/D + \xi \sin \theta / \lambda \beta .$$

The grain size value can be used in the relation $\delta = 1/D^2$ to obtain the value of dislocation which shows the amount of defect in the crystal as it appears in Table 1 and Table 2.

TABLE 1. Values of energy gap, grain size, dislocation and strain of PbS thin films

T°C	Eg eV	D nm	$\text{nm}^{-2} \delta$	ξ
Without annealing	1.59	38	0.0006	0.018
200	1.57	45	0.0004	0.008
300	1.55	56	0.0003	0.007

TABLE 2. Values of energy gap, grain size, dislocation and strain of $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ thin films

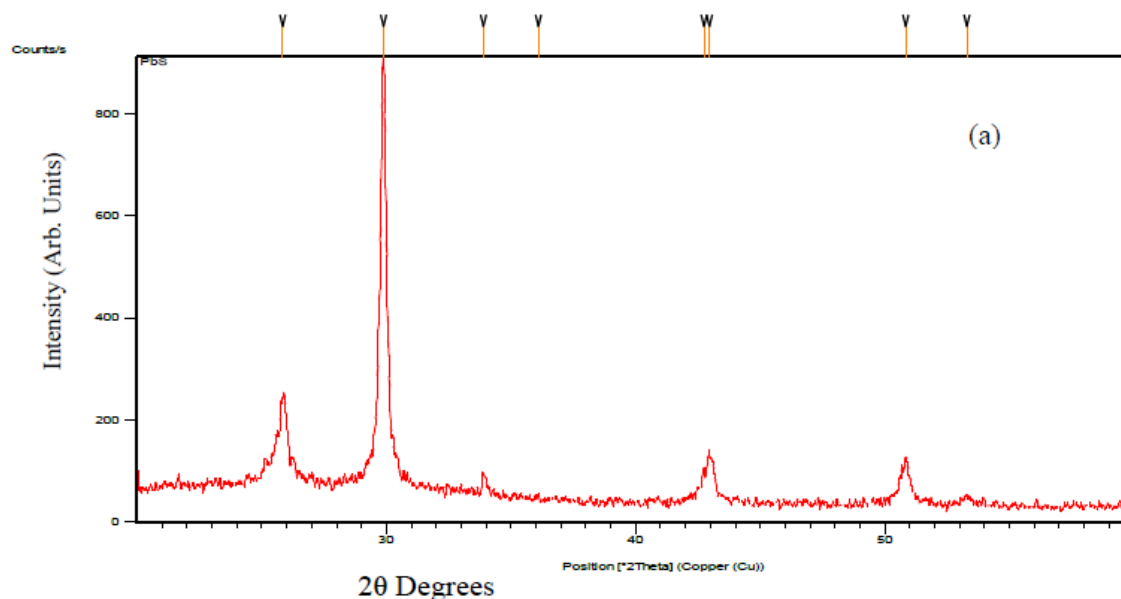
T°C	Eg eV	D nm	$\text{nm}^{-2} \delta$	ξ
Without annealing	1.7	22	0.008	0.0178
200	1.67	30	00011	0.0134
300	1.65	37	00007	0.028

Results and Discussion

Structural Properties

Fig. 1 and Fig. 2 indicate the XRD spectra of $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ ($x=0,0.4$) thin films annealed at (298, 473, 573)K. The main features of diffraction patterns are similar in case of ($x = 0$). Peak positions observed agree with the fcc structure of PbS and are represented by Miller indices of (111), (200), (220) and (311) planes of cubic observed at diffraction angles of 25° , 30° , 43° and 53° , respectively. The narrow peaks show that the material has good crystallinity. There is no clear thermal annealing effect on the crystal structure of the compound apart from becoming more accurate. Comparing the XRD patterns of PbS and $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ films clearly shows a decrease in peak intensities after adding Cd^{+2} ; a behavior that can be attributed to the increase in heterogeneity of the film, to host lattice occupation by Cd^{+2} and to decrease the crystalline size to nano-scale levels. Similar results have been found elsewhere [21,24]. In addition, a plane existed that does not belong to either PbS or CdS; thus there must be a solid formation, which is CdPbS in composition. The highest peaks in all deposited thin films were

those around (200), which indicates the preferential crystallite orientation. X-ray diffraction analysis showed that $\text{Cd}_x\text{Pb}_{1-x}\text{S}$ ($x=0,0.4$) thin films were polycrystalline in nature and exhibited better crystallization with increasing grain size as the annealing temperature was raised from as deposited to 573 K and no more intense diffraction peaks were observed for the annealed samples. Tables 1 and 2 show that film growth is influenced by adding Cd^{+2} to PbS which causes a reduction in crystalline size. Also, the average crystalline sizes increase with increasing thermal annealing due to decrement in strain and dislocation which are related to the lattice misfit. This tendency is caused by a variation in the crystal structure and inter planar distances of films, which in turn depends on the deposition conditions. Optical microscope Fig. 3(a, b) and Fig. 4(a, b) show a globular structure composite of nano-crystals. This reveals good homogeneity of material on substrate surface and average crystallite size that decreases with adding Cd^{+2} to the bath. Moreover, black color for PbS and brown yellowish color for CdPbS were seen.



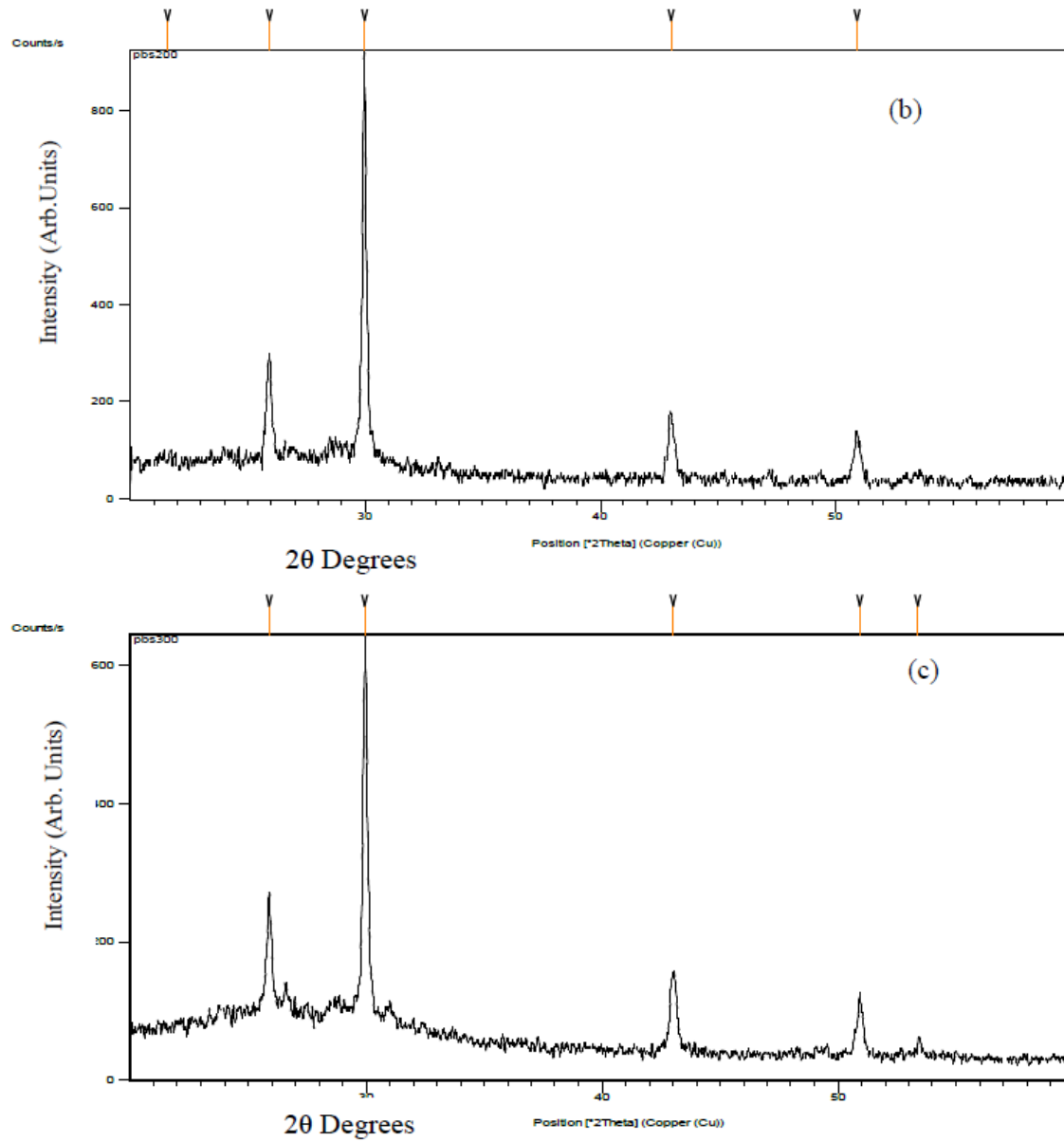


FIG. 1. X-ray diffraction of PbS thin films; (a) as deposited. (b) annealed at 473K. (c) annealed at 573 K.

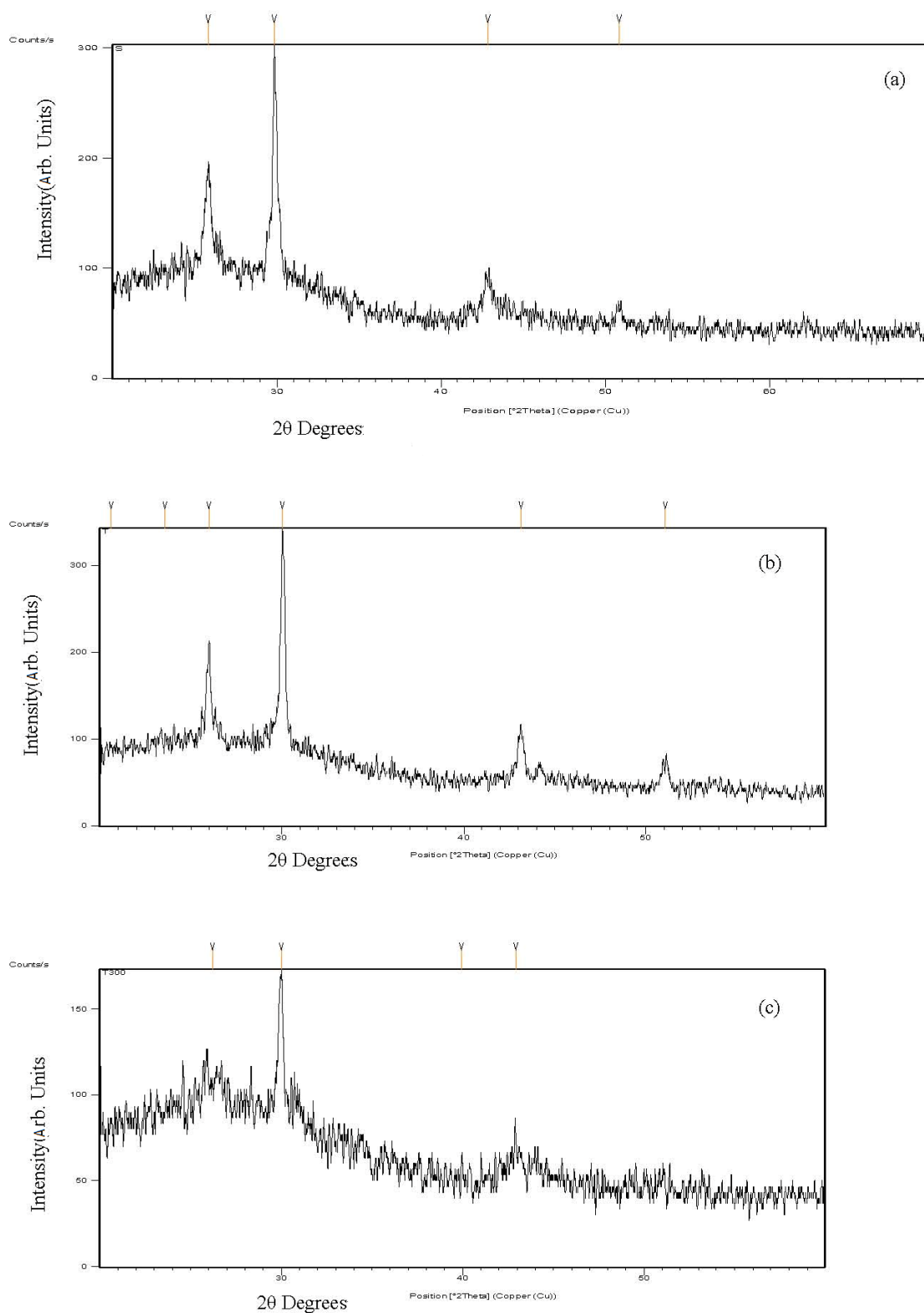


FIG. 2. X-ray diffraction of $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ thin films; (a) as deposited. (b) annealed at 473K. (c) annealed at 573 K.

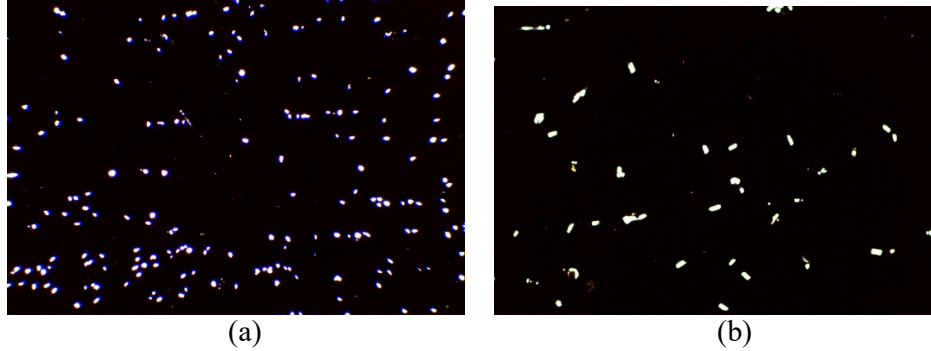


FIG. 3. Photo-microscope image of PbS thin films; (a) 100x. (b) 400x.

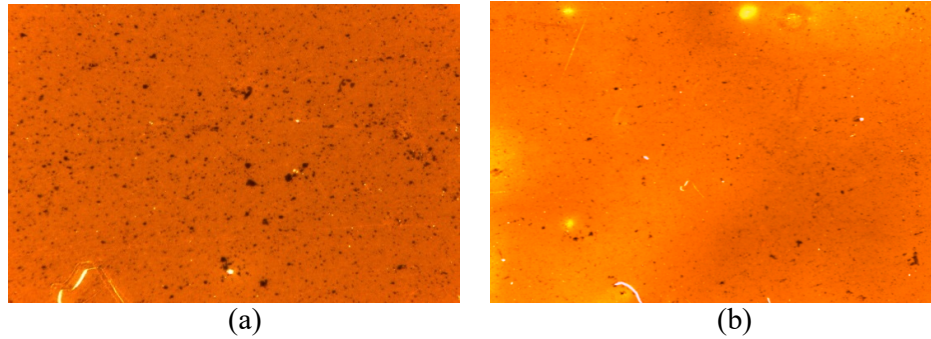


FIG. 4. Photo-microscope image of $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$; (a) 100x. (b) 400x.

Optical Properties

Optical absorbance and transmittance in the UV-VIS-NIR regions of the as deposited and annealed films are shown in Fig. 5(a, b) and Fig. 6(a, b), respectively. Fig. 5(a, b) demonstrates that absorbance is higher for the annealed film than for the as deposited one, while Fig. 6(a, b) reveals an increase in transmittance values for annealed films. This manner is because of some physical effects, such as defect density and structural surface irregularity. The band gap energy was obtained by plotting $(\alpha h\nu)^2$ against photon energy. The linearity of the plot means that these films have a direct band gap material as seen from Fig. 7(a, b). The annealed samples revealed a relative decrement in band gap values, which may result from the reduction in strain within the films or from the increase in grain size. The influence of grain size on the optical band gap arises out of quantum confinement effect [25]. The extinction coefficient (k), which is a measure of the fraction of light lost by scattering and absorption per unit distance in the participating medium, is obtained from the relation $k = \alpha\lambda/4\pi$. The spectral dependence of k , n , ϵ_1 , ϵ_2 in Fig. 8(a, b) and Fig. 9(a, b) shows higher k values with increasing photon energy, but lower values with thermal annealing. Refractive index (n) is regarded as one of the

essential properties of optical materials due to its correlation with the electronic polarization of ions and local field inside the material. Evaluation of refractive indices of optical materials is substantial for application in some integrated optic devices, such as switches and filters and is a key parameter for the device design [26]. Fig. 9 shows the increase in refractive index value after annealing treatment, which is due to the increase in grain size. Calculation of real and imaginary parts of the dielectric constant was made by applying the relation [27]:

$$\epsilon_1 = n^2 - k^2 \quad \epsilon_2 = 2nk.$$

It is worth noticing that the behavior of ϵ_1 is similar to that of refractive index because of the smaller value of k^2 compared to n^2 , while ϵ_2 depends mainly on k values. Fig. 10(a, b) and Fig. 11(a, b) show the variation of ϵ_1 , ϵ_2 for as deposited and annealed films. The decrease in ϵ_2 is proposed to enhance the reduction in the concentration of lattice imperfections originating from lattice misfit in the film.

The photo-luminescence emission in semiconductors is affected by the stoichiometric defects in electronic levels. In the current study, since the effect of thermal annealing on photo-luminescence was small, we preferred to take

one temperature (573K). Fig. 12 shows the photo-luminescence of nanocrystalline $\text{Cd}_x\text{Pb}_{1-x}\text{S}$. When the films are excited at (520) nm, single red emission peaks were observed at wavelengths of (680) nm and (670) nm for PbS and $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$, respectively, which is attributed to both direct recombination and recombination through shallow surface states [28]. The intensity of peaks rises as x content increases. This is because PbS has a narrow band and exceptionally large exciting Bohr radius (-18 nm), which makes it susceptible to charge carrier quantum confinement effects. These features of PbS nano-crystals would prevent them from

producing high yield of PL, as most of the energy is lost through non-radiative processes. This enables us to produce high luminescence by either over-coating with a higher band gap material like CdS or by the attachment of ligands [29]. On the other hand, as the particle diameter (D) is reduced for CdPbS, the confinement energy increases and a blue-shift occurs due to the quantum confinement effect [30]. In this study, PL spectrum has a blue-shift with increasing x content by addition of Cd element to PbS, which also may enhance photo-luminescence properties [31], since PbS is weakly luminescent at room temperature [32].

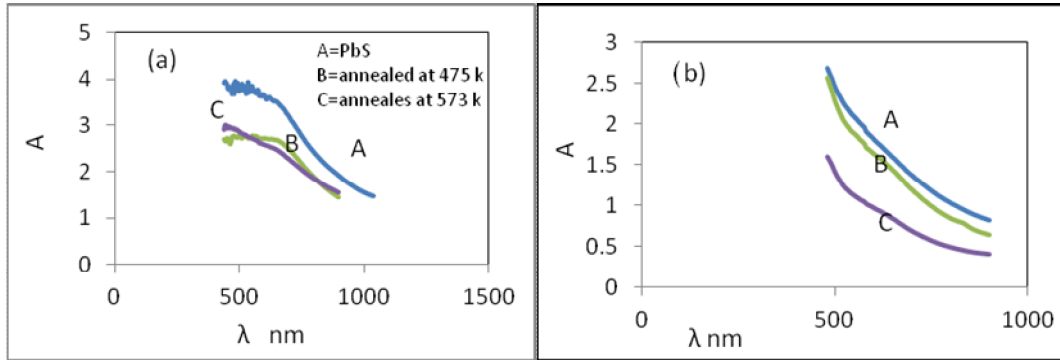


FIG. 5. Absorption spectra of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$.

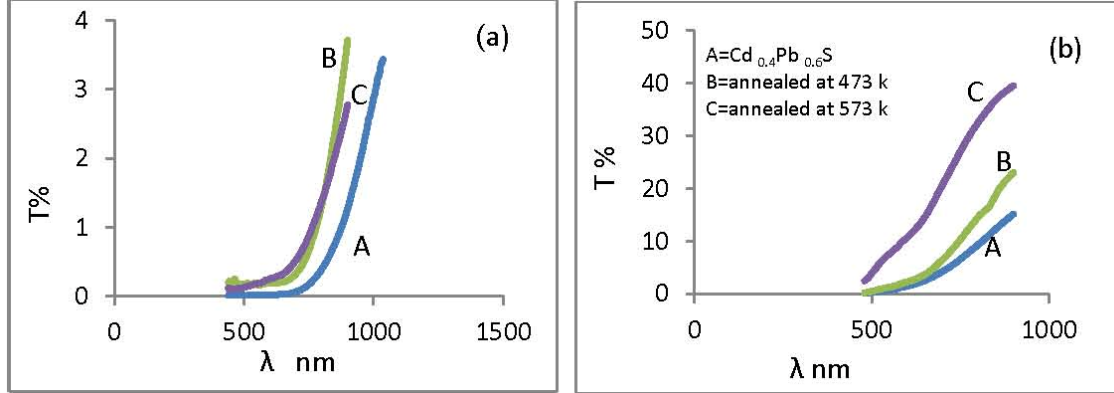


FIG. 6. Transmission spectra of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$.

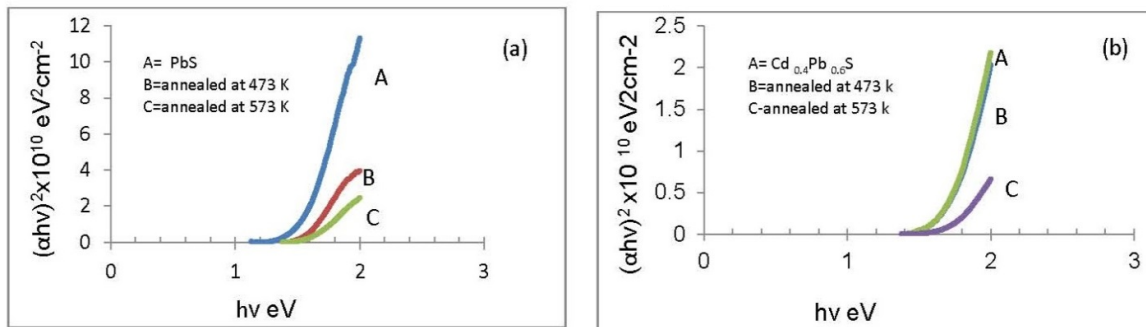


FIG. 7. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ annealed at different temperatures.

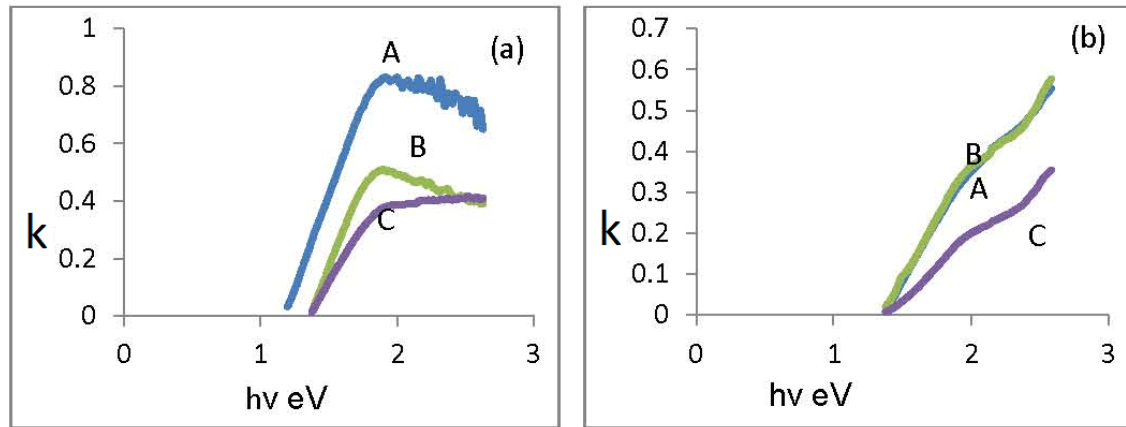


FIG. 8. Plot of k vs. photon energy of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ annealed at different temperatures.

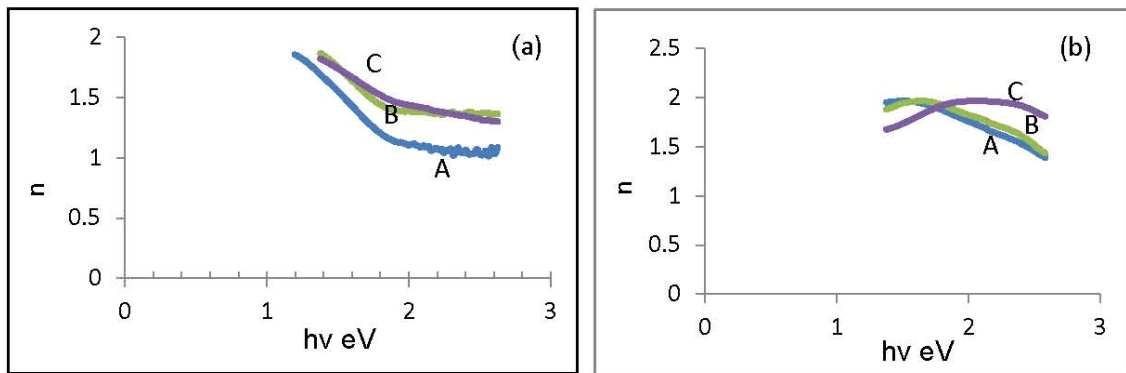


FIG. 9. Plot of n vs. photon energy of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ annealed at different temperatures.

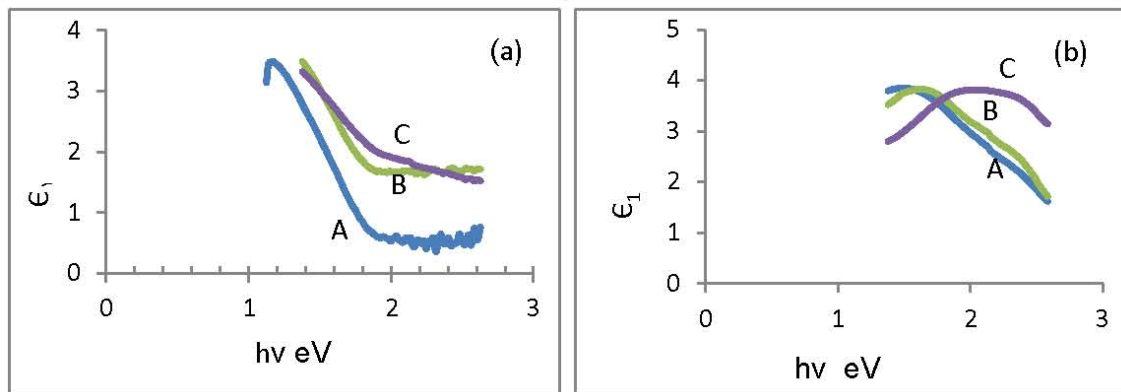


FIG. 10. Plot of ϵ_1 vs. photon energy of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ annealed at different temperatures.

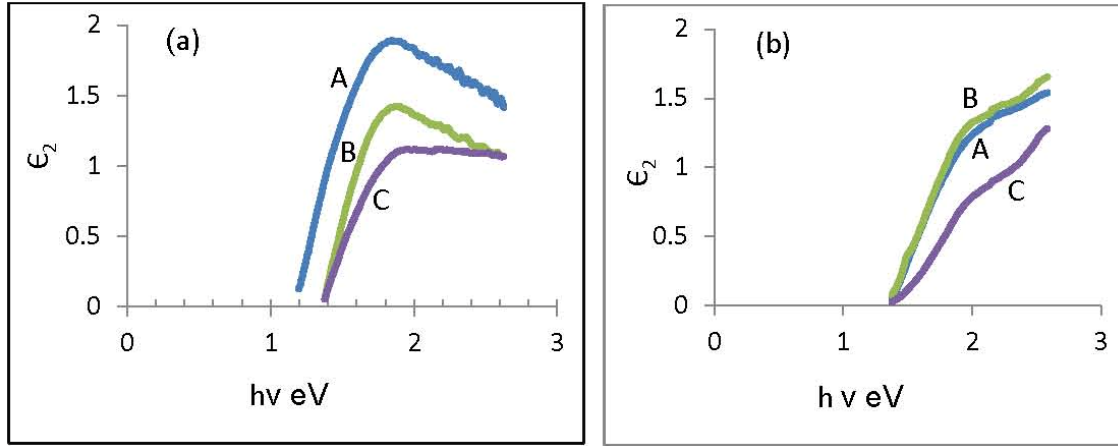


FIG. 11. Plot of ϵ_2 vs. photon energy of (a) PbS, (b) $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ annealed at different temperatures.

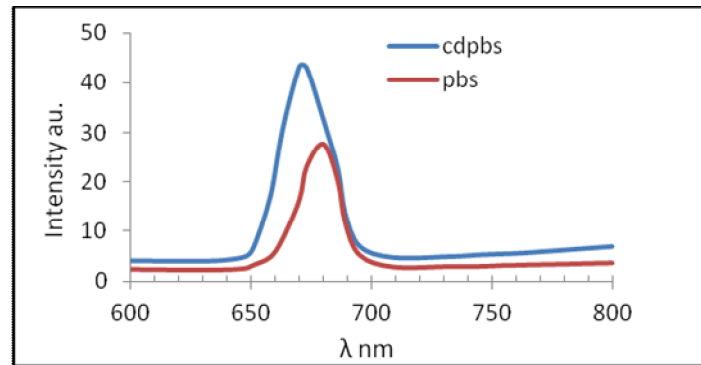


FIG. 12. PL luminescence spectra of PbS and $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$.

Conclusion

Nano-crystalline CdPbS thin films were prepared using chemical bath deposition (CBD) method. Thin films exhibited a good stoichiometry when analyzed by XRD. Also, XRD analysis showed that CdPbS thin films have a cubic structure with predominant (200) orientation. The influence of thermal annealing on structural and optical properties was investigated. It was revealed that the increase in grain size and the decrease in strain and dislocation lead to a decrease in the band gap with thermal annealing. This behavior makes the compound suitable to be used in IR optoelectronic devices. Optical constants, such as extinction coefficient (k), refractive index (n),

real and imaginary dielectric constants were calculated. From photo-luminescence spectra, two single peaks for PbS and $\text{Cd}_{0.4}\text{Pb}_{0.6}\text{S}$ were noticed. Moreover, we can improve the weak luminescence of PbS by adding Cd ion to form CdPbS.

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