



## Effect of Lead (Pb) Concentrations on Structural & Optical Properties of PbS Thin Films.

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Small lead sulphide films (PbS) are applied to the parts of the glass slide using a chemical bath processor (CBD) at room temperature for 60 minutes. The visual characteristics of the thin films were measured with a spectrophotometer and some solid state structures were determined by comparing the absorption data at a distance of 300-900 nm using software. The software used three types of simulation. SEM micrograph, Band gap ( $E_g$ ), Absorbance (A), and Raman shift were tested as a function of wavelength and photonenergy. Further analysis has shown that the band gap of PbS films increases as Lead concentration increases.

**Keywords:** Structural and Optical Processing of Chemical Bathing; Sulphide; wavelength, Band gap.

### 1 Introduction

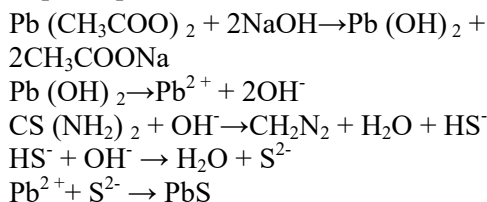
Over time, various types of semiconductor films have been studied from the IV-VI groups in the periodic table as it has a small electrical gap and a large concentration for use in solar and nerve cells. Lead sulphide (PbS) is a distinct straight band with a potential spacing of about 0.4 eV at 300K and Bohr exciton radius of 18nm<sup>1</sup>. Many studies have established relationships between its structures and growth conditions<sup>2</sup>. A variety of methods have been developed for the inclusion of Lead Sulphide (PbS) films<sup>3</sup> although the chemical process of Bath Deposition (CBD) has been found to be very economical. Recently, various sizes of PbS nanoparticles have been reported for film and the band gap has been found to increase with decreasing size; thus demonstrating the effect of quantum confinement on PbS nanoparticles<sup>3</sup>. The study also concluded that thin PbS films have a cubic structure that focuses on selective (200) preferential direction<sup>4</sup>. Nano-crystalline PbS-coated films with CBD had a band gap of 1.9 -2.6 eV<sup>5</sup> while those implanted with sono-chemical methods showed an increase in photosensitivity due to heat treatment<sup>6,7</sup>. The growth of PbS by CBD attracts a lot of attention as it does not require high-quality materials, is inexpensive, easy to handle, can be used for large area installation and produces small high-quality films<sup>8</sup>.

### 2 Experimental Procedure:

PbS film insertion is performed in an active chemical bath made of 100 ml beaker by incorporating 5 ml solutions of 0.5 M lead nitrate as a source of  $Pb^{2+}$ , 5 ml of 2 M sodium hydroxide as an alkaline medium, 6 ml of 1 M thiourea as a  $S^{2-}$  and 2 ml source of 1M tri-ethanolamine as a complex agent. Solutions of 1M thiourea, 1M tri-ethanolamine and 1M sodium hydroxide were prepared from chemical analysis grade. Lead nitrate solutions for varying concentrations from 0.5 to 0.8 at 0.1 M intervals were also adjusted. 5ml of lead nitrate was measured in a 100ml beaker followed by 5ml of 2M sodium hydroxide and the mixture was stirred thoroughly using an electric grinder to obtain a milk solution. In this milk solution, we added 6ml of 1M thiourea followed immediately by 2ml of 1M tri-ethanolamine. Finally, two minutes of stirring should be done to ensure consistency of the combination. The solution was mixed with non-ionized water to a volume of 100 ml while stirring. A glass slide substrate was placed sideways next to the beaker and the set was kept at room temperature for 120 minutes. Lead nitrate concentration varied by 0.1 times in subsequent films from 0.5 - 0.8M concentration of  $Pb^{2+}$  ion. The lower four sections were immersed in the bathtub and remained undisturbed for 2 hrs and then removed simultaneously. The films are then purified with distilled water obtained from a double-distilled water plant and dried at room temperature. Films are placed

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on both sides of the substrate; the set films were smooth, uniform, well aligned with the substrate. The response process can be considered as follows<sup>9</sup>



The structure of the crystallite and the shape of the different films were shown in an X-ray diffraction process using an X-ray diffractometer with a Cu-K $\alpha$  line. The morphology and microstructure of the different molarities of the films are tested by scanning an electron microscope (SEM). Optical measurements were tested at room temperature using UV-VIS- NIR in the range of 300 to 900 nm. The thickness of the films were 100, 140, 150 and 158 nm at 0.5, 0.6, 0.7 and 0.8 M respectively; measured with XP-200 Ambios Technology profilometer

### 3 Properties of structures:

Figure 1 shows X-ray distribution patterns of small PbS films embedded in the CBD process at room temperature on glass substrates. XRD patterns obviously

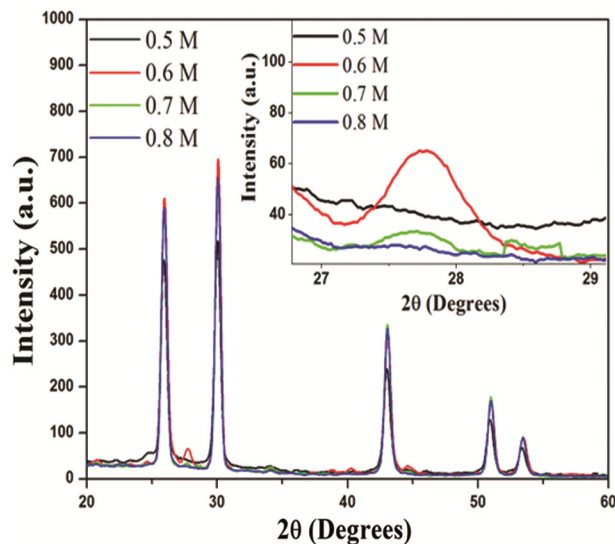


Fig.1 — XRD Spectrum of PbS Thin Films.

have peaks separated at 25.96 °, 30.10 °, 43.05 °, 50.99 ° and 53.49 ° corresponding (111), (200), (220), (311) and (222) cubic structure (Galena) PbS (PDF # 077-0244) respectively. These results indicate that crystalline films contain cubic rock salt (NaCl) of the genre structure. The narrow peaks indicate that the material has a good crystalline nature and is specially selected along the direction (200). The average crystallite size was measured using the Debye-Scherrer's formula<sup>10</sup>

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \dots (1)$$

When  $k$  is constant (0.94),  $\lambda$  is XRD length (0.15418nm) and  $\beta$  is fullwidth at half maximum (FWHM) of the defined deviation. Using the Debye formula, the size of the crystallite was found to be shown in Table 1. From the table it appears that the size of the Crystallite increases with increasing concentration of the Lead. The size of the crystals indicates the size of the films. However, at 0.6M of lead acetate, the size of the crystallite increases due to the internal pressure of the atoms.

It can be seen that as the size of the weight increases, the film size of the film becomes smaller and the film areas become smoother and smoother. As a result, the adhesion between the film and the substrate is strengthened. Various structural parameters *e.g.*, fixed lattice values ( $a$ ), Crystallite size, and Band gap for PbS small films are listed and are systematically represented in Table 1.

### 4 Estimation of Crystallite Size:

The size of Crystallite for all film pairs is estimated using Scherrer's formula and shown in Table 1.

In terms of the crystallite size of the films, we have adopted the Williamson-Hall (WH) method in which  $\beta \cos\theta$  is built against  $\sin\theta$  in all peak orientations and from direct equations to data, crystallite size values for films are estimated from in y-intercept of the fit as shown in Table 1. But from Table 1, it is evident that the size of the crystallite found in the WH plot is larger compared to Scherrer's Formula. It is because of the difficulty contained in the prepared PbS Films.

Table 1 — Structural Parameters of PbS Thin Films

Sample	Crystallite Size from		Bandgap (eV)	Urbach energy (meV)	Thickness(nm)
	Scherer (nm)	W-H plot (nm)			
0.5M	3.14	17.39	1.21	3.72	100
0.6M	2.47	20.31	1.17	3.99	140
0.7M	3.65	21.39	1.11	3.09	150
0.8M	3.69	21.58	1.10	3.51	158

In Fig. 1 high value is observed in 0.6M of Lead Acetate. This is due to a certain degree of impurity from oxidation of PbS. Due to the lack of complete stoichiometry or the oxygen content of the film 0.6M is much larger compared to the other three films.

The highest XRD value is found in  $2\theta \approx 27.74^\circ$  to 0.6M of Lead Acetate. This number may be due to non stoichiometry or oxidation of the films. Obviously from the EDX spectra of Fig. 2, the ratio of Pb and S is 1.23, 0.86, 0.87 and 0.84 for 0.5, 0.6, 0.7 and 0.8M respectively. It means that both the 0.7 and 0.8M films are almost almost stoichiometric.

**5 Raman Spectroscopy:**

Raman spectroscopy is a quick and non-destructive method for determining the properties of crystalline materials. The Raman spectrum of films with different concentrations is shown in Fig. 3. Two concentrations of 139.70 and 972.10  $\text{cm}^{-1}$  are shown in the film 0.5M as shown in Figs given the basic phonon mode (LO) mode and the first mode overtone

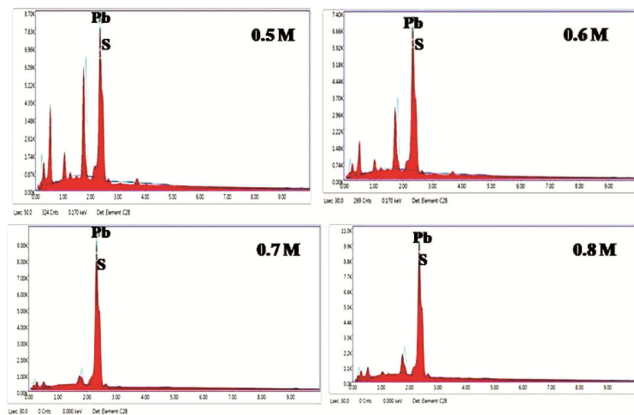


Fig. 2 — EDAX Pattern of Lead Acetate Concentration.

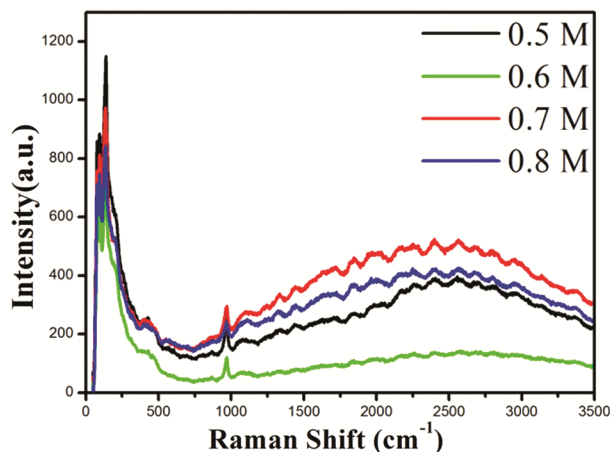


Fig. 3 — Raman Spectra of all the Samples.

(2LO) respectively. At 0.6M, two peaks are raised at 133.24 and 972.10  $\text{cm}^{-1}$  respectively. These peaks are divided as LO and 2LO respectively. Similarly 0.7 and 0.8M, two peaks 133.12, 965.15 and 133.70  $\text{cm}^{-1}$ , 965.51  $\text{cm}^{-1}$  respectively are given as LO and 2LO respectively. Gode *et al*<sup>11</sup> reported that effective Raman methods focused on approximately 94, 129, 187, 460, 826, 964, 970 and 1102  $\text{cm}^{-1}$ . But there are differences in our study that may be due to the polycrystalline nature of PbS thin films. From this Figure it appears that all LO peaks are moved to the side of the low-frequency wave indicating the closure of the phonon due to a decrease in particle size.

**6 Surface Morphology:**

Figure 4 (a) shows the morphology of PbS small films placed on a glass part of various composites tested by scanning electron microscopy (SEM) at a speed of 5 kV. Micrographs show granular formation with well-defined grain boundaries. In addition, films show homogeneous surface morphology with some microcracks and pinholes. Bullet sizes are found to be 200-300 nm. The percentage of Atomic weight of the Elements in EDAX measurement are shown in Table 2.

**7 Optical Properties:**

The optical Absorbance (A) variation of films with different concentrations relative to wavelengths is shown in Fig. 5. It is evident from the image that all films show high absorption in the visible region. This may be due to the brilliance of these films as seen in the XRD spectra. But in the IR region, 0.6M of films showed a significant decrease compared to the other

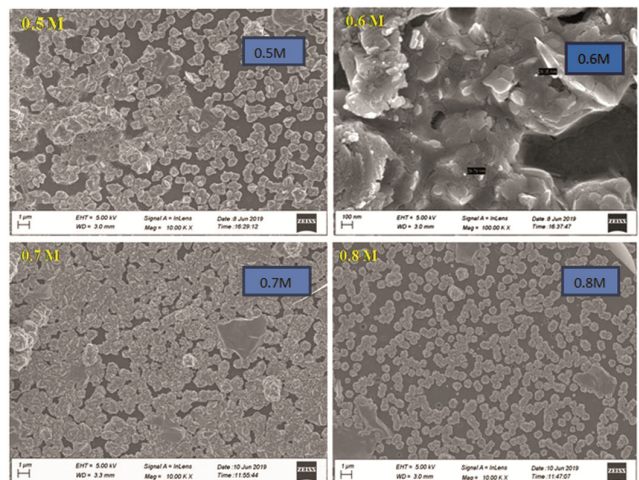


Fig. 4 — Scanning Electron Micrograph of PbS Thin Films.

Table 2 — Percentage of Atomic weight of the Elements in EDAX measurement.

Table 2(a) — Percentage of elements of 0.5M					Table 2(b) — Percentage of elements of 0.6M				
Element	Weight %	Atomic %	Net Int.	Error %	Element	Weight %	Atomic %	Net Int.	Error %
C K	4.86	15.02	90.09	12.19	C K	4.14	16.34	74.51	14.01
O K	17.80	41.31	571.10	9.49	O K	11.05	32.76	335.91	10.80
NaK	4.80	7.75	216.56	8.18	NaK	1.95	4.03	88.79	12.07
MgK	0.78	1.20	51.72	11.71	MgK	0.05	0.10	3.40	74.97
AlK	0.35	0.48	25.49	19.80	AlK	0.00	0.00	0.00	99.99
SiK	11.94	15.78	997.79	4.40	SiK	9.02	15.24	789.00	5.00
S K	6.41	7.42	420.25	4.49	S K	11.07	16.39	770.91	4.24
PbM	51.01	9.14	1273.00	2.85	PbM	61.90	14.18	1624.98	2.81
ClK	0.00	0.00	0.02	99.99	ClK	0.00	0.00	0.03	99.99
CaK	2.06	1.91	70.60	10.59	CaK	0.81	0.96	28.02	28.76

Table 2(c) — Percentage of elements of 0.7M					Table 2(d) — Percentage of elements of 0.8M				
Element	Weight %	Atomic %	Net Int.	Error %	Element	Weight %	Atomic %	Net Int.	Error %
C K	4.05	24.39	82.40	12.79	C K	4.78	23.75	112.18	12.45
O K	2.76	12.48	80.15	14.77	O K	5.26	19.59	187.77	11.77
NaK	0.30	0.94	13.69	50.93	NaK	1.19	3.08	66.44	15.70
SiK	1.61	4.15	147.50	8.27	SiK	3.87	8.21	425.25	6.15
S K	13.74	30.97	1057.05	3.89	S K	13.32	24.76	1210.35	3.84
PbM	77.54	27.06	2225.36	2.64	PbM	71.58	20.60	2434.45	2.65
ClK	0.00	0.00	0.03	99.99	ClK	0.00	0.00	0.03	99.99

three films. In this area high absorption is found, possibly due to the combined structure of PbO and PbS<sup>12</sup>. According to the composite structure the charge separation is always better than the clean system and that may be the reason for better absorption in the apparent 0.6 M range of Lead Acetate.

Depending on the optical absorption, the absorption square is efficient,  $(\alpha h\nu)^2$  vs photon energy is shown in Fig. 6. The strength of the vertical band gap is obtained by subtracting a straight line from the power axis at  $(\alpha h\nu)^2 = 0$  shown in Table 1 for the different concentration of Lead Acetate concentration.

According to Urbach's relationship, the absorption (A) depends on the wavelength ( $\lambda$ ) along the tail represented as<sup>13</sup>

$$A(\lambda) = A_0 \exp(hc / (E_u \lambda)) \quad \dots (2)$$

When  $E_u$  represents the power of Urbach,  $h$  is always plank constant and  $c$  is the speed of light in the free space.

The repetition of the slope to the equilibrium of the different molarities of 'ln A' vs '1/ $\lambda$ ' gives the value of Urbach energy ( $E_u$ ) in the following relationship:

$$E_u = 1240 / \text{slope} \quad \dots (3)$$

Also the Urbach energy ( $E_u$ ) values of the different molarities as given in Table 1.

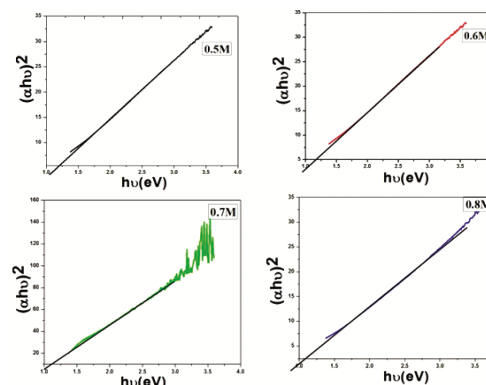


Fig. 6 — Band gap of PbS Thin Films.

The tail on the long side of the wavelength is visible due to the electronic changes between the local countries. Urbach strengths are calculated from the slopes of the exact proportions of the structure and the values shown in Table 1

## 8 Photoluminescence Properties:

The photoluminescence spectra of thin film of nanocrystalline PbS is shown in Fig. 7. This output of the wavelength range is blue compared to the larger PbS. This exit is due to the reunification of the electron with the hole pair. The intensity of photoluminescence has increased due to the Increase of concentration of PbS films. There are still two peaks focusing on 399 and 477 nm long wavelengths,



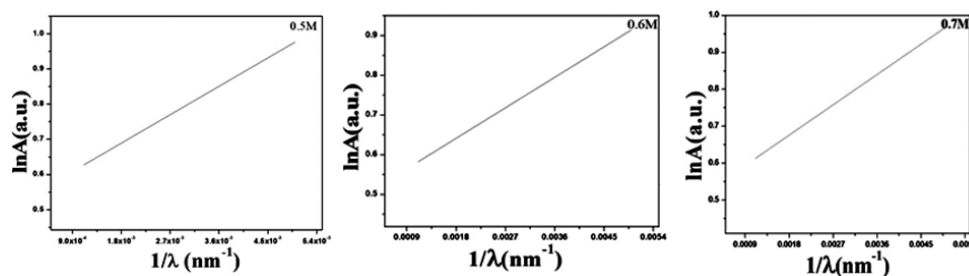


Fig. 7 — Urbach Energy of PbS Thin Films.

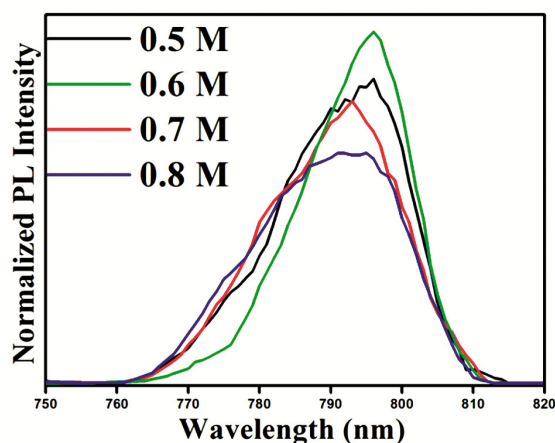


Fig.8 — PL Spectra of PbS Thin Films.

due to the change of nanocrystalline PbS films. On the fig tree. 8, it appears that the maximum strength is 0.7M of Lead acetate. This may be due to the presence of Lead Oxide (PbO) in the sample<sup>14</sup>

The photoluminescence (PL) film of nanostructured PbS films at room temperature is recorded using an F-2500 Fluorescence spectrophotometer at a distance of 700-900 nm. Figure 8 shows the spectra with concentrations of 0.5, 0.6, 0.7 and 0.8 M respectively. The PL emission spectra focuses on 795.84, 792.96, 796 and 791.47 nm respectively. High PL spectra shifting position towards long wavelength.<sup>15</sup>

## 9 Conclusion

PbS thin films have been successfully produced on glass sections by Chemical Bath deposition (CBD) in various concentration of Lead acetate. Films are characterized by XRD, SEM, EDAX and optical studies. The films showed preferential orientation along (200) direction with a cubic structure. The size of the Crystallite was calculated to be approximately 2.47 nm of 0.6 M Lead. The SEM study clearly showed the formation of round letters of random size of 0.6 M Lead. The EDAX exhibition has confirmed

the presence of the Lead in all the various film genres. From the absorption data, it has been shown that 0.6M Lead films with high absorption in the IR region suggest that films may be useful for IR detector. The film is very smooth and high with Urbach Energy. Considering the crystallinity and optical absorption properties, it can be concluded that the best film is obtained with 0.6 M of Lead Acetate.

## Acknowledgement

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