# Synthesis of PbS Nanostructures by Chemical Bath Deposition Method

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Lead sulfide (PbS) powders were prepared by chemical bath deposition (CBD) method by varying the synthesis temperatures. The influence of the synthesis temperature and the different molar concentration of lead acetates on the structure, morphology and optical properties of PbS nanostructures were investigated, respectively. The X-ray diffraction (XRD) patterns of the PbS nanostructures correspond to the various planes of a single phase cubic PbS. It was observed that a decrease in the synthesis temperature resulted into extra diffraction peaks due to the presence of impurity phases. It was observed that the estimated average grain sizes from XRD analysis increased slightly with an increase in the synthesis temperature and molar concentrations of lead acetate, respectively. The crystallinity of the cubic PbS improved significantly with an increase in synthesis temperature and the molar concentration of lead acetate. The surface morphology study revealed nanorod structures at low synthesis temperatures but a cubic structure at the high synthesis temperatures. It was also observed that by increasing the molar concentration of lead acetate does not influence the morphology of PbS nanorods but the grain sizes increases slightly with an increase in Pb acetate content. The reflectance spectra showed a partially increase in percentage reflectance and shift of the absorption edge to a higher wavelength with an increase in the synthesis temperature and molar concentration of Pb acetate. An additional absorption band in the visible region (647 nm) emerged with an increase in the synthesis temperature. The band gap energy of PbS was found to decrease with an increase in the synthesis temperature and molar concentration of P acetates, respectively. The luminescence intensity was found to decrease with an increase in the synthesis temperature and molar concentration of P acetates, respectively. The maximum luminescence intensity was found at a synthesis temperature of 55 °C and at 0.12M of Pb acetate, respectively.

Keywords: PbS; nanorods; Chemical bath deposition; defects; photoluminescence

## **1. INTRODUCTION**

In recent years, interest in the development of the semiconductor nanostructured materials has grown rapidly owing to their unique physical and chemical properties [1]. This is due to their potential application in the area of solar cells, optoelectronic devices, photoconductors, sensor and infrared detector devices [2]. Their attractiveness arises from their low synthetic cost, their solution processing ability and the dependence of their optoelectronic properties as a function of size, shape, doping and surface chemistry [3-4]. Therefore, many studies on shape controlled synthesis of semiconductor nanocrystals with different nanostructures have been reported [5-6]. Consequently, the synthesis of PbS nanocrystals with different morphologies and the corresponding effects on material properties is of great importance in the search for novel applications in electroluminescent devices such as light emitting diodes. PbS nanocrystals are attractive for infrared-related applications because the energy of their first excitonic transition can be easily tuned from the visible to the infrared [8]. As its large exciton Bohr radius (18 nm) [9-10], the effects of strong quantum confinement can be achieved even for relatively large structures [11]. The band gap energy of PbS can changed from 0.39 eV to the values up to 5.2 eV by varying the shape and size from the bulk materials to nanocrystal structures [12]. The preparation of PbS has been explored by a number of methods including sonochemical synthesis [9], liquid phase synthesis [13], chemical bath deposition (CBD) [14] and gas phase synthesis [15]. We have selected the CBD method owing to its many advantages such as low cost, large area production and simplicity in instrumental operation. In this present study, we demonstrated simple CBD for making different PbS nanostructures. Of particular interest of the study is the dependence of the optical properties of PbS on morphology and shape, with the hope that such knowledge will enable us to construct efficient nanomaterials for electroluminescent devices. The aim of this paper is to investigate the effect of synthesis temperature and molar concentration of lead acetate on the structure, morphology and optical properties of PbS nanoparticles prepared by the CBD method.

# 2. EXPERIMENTAL PART

## 2.1 Characterization

The preparation of PbS powders were carried out using the following procedure: The PbS precursors were prepared by dissolving 0.13 M of lead acetate, 0.18 M of thiourea and 98.8 mL of ammonia in 400 mL of deionised water, separately. During the preparation of the nano-powders, ammonia was used as a complexing agent. The chemical bath solution was prepared as follows: 60 mL of a lead acetate, thiourea and ammonia solutions were mixed. The amount of solutions of lead acetate, thiourea and ammonia was held constant at ratio of 1:1:1. Each mixture was continuous stirred for 10 minutes by varying the synthesizing temperature at 55, 65, 70 and 80°C, respectively. The PbS particles were washed with 60 mL of acetone and ethanol in that order. The precipitates formed were

left overnight and then filtered. The obtained particles were dried at ambient conditions for 5 days and ready to be characterized using various characterization technique.

The synthesis of PbS nanostructures by changing different molar concentrations of lead acetate and holding thiourea and ammonia constant at bath temperature of  $65^{\circ}$ C for 10 minutes was performed similarly. The different molar concentrations of lead acetates used are 0.12M, 0.13M and 0.15M.

#### 2.2 Characterization

The crystal structures of the samples were determined with a Bruker AXS Discover diffractometer with CuK $\alpha$  (1.5418 Å) radiation. The morphology of the prepared nanoparticles were determined with a scanning electron microscopy (SEM) using a Shimadzu model ZU SSX-550 Superscan. The optical measurements were carried out in the 200 to 800 nm wavelength range using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. Photoluminescent (PL) measurements were done on a Cary Eclipse Fluorescence Spectrophotometer system, equipped with a 150 W xenon lamp as the excitation source.

# **3. RESULTS AND DISCUSSIONS**

3.1 Structural and compositional analyses.



**Figure 1.** XRD patterns of PbS (a) prepared at different synthesis temperatures but at constant molar concentration of lead acetate and (b) XRD patterns of the (111) planes of the PbS powders prepared by the CBD method.

Figure 1(a) shows X-ray diffraction (XRD) patterns of the PbS powders synthesized at various bath temperatures as indicated (55, 65, 70 and 80 °C). All XRD patterns show four intense peaks at around  $2\theta = 25.99$ , 30.11, 43.09 and 51.03°. All these peaks corresponding to the cubic phase of PbS which matched well with the standard JCPDS card no. (05-0592, a = 5.936 Å). The estimated average

value of the cell constant *a* was 5.934 Å which match perfectly with the standard data. No significant changes were observed for the lattice parameter with the variations of the synthesis temperature.

The PbS powder prepared at 55 °C shows extra peaks which are marked with a star (\*) which are unreacted lead acetate oxide hydrate due to the low synthesizing temperature. This is confirmed by the JCPDS card no: 18-1740. However, as the bath temperature was increased from 65 to 80 °C the extra peaks disappeared and the intensity of the peaks attributed to PbS improved as shown in Figure 1(b). This improved intensity with well-defined sharper peaks indicates a higher crystallinity of the prepared material. The average crystallite size of the as-prepared nanocrystals was calculated from the Full Width Half Maximum (FWHM) of the diffraction peaks using the Debye formula [16]. All major diffraction peaks for all samples were chosen to estimate the average size of the nano crystallites by the least square method.



Figure 2. The dependence of average crystallite sizes of the PbS on the synthesis temperature of the CBD.

It is clear from Figure 2 that the estimated average size increased slightly with an increase in the synthesis temperature. Figure 3 shows the XRD patterns of the PbS nanostructures synthesized by varying the concentration of the precursors (Pb acetate). All the peaks match well with the standard cubic structure of PbS. It is clear that at the low molar concentration (0.12 M) and the highest molar concentration (0.14) there are extra peaks marked with star (\*) which were due to unreacted lead acetate oxide hydrate. It is observed that the best crystallite structure was obtained for PbS samples synthesized at 0.13 M of lead acetate. The estimated crystallite sizes from the Debye formula were 30

 $\pm$  1, 35  $\pm$  1 and 31  $\pm$  1 nm for 0.12, 0.13 and 0.14 mol% of lead acetate, respectively. No clear trend in the estimated crystallite sizes with an increase in lead was observed.



**Figure 3.** XRD patterns of PbS samples prepared with different molar concentration of lead acetates and constant synthesis temperature using the CBD method.

Figure 4 (a), (b), (c) and (d) show surface morphologies of the PbS powders synthesized at various temperatures ranging from 55 to 80 °C. All the samples were taken at 10 keV with a 0.05 nm field of view. Karami et al [2] have reported that by increasing the synthesis temperature there was no influence on particle sizes and morphology. On the contrary we observed that the surface aspects of the SEM images of the PbS powders were composed of uniform nanorods structures for the synthesis temperature of 55 to 70 °C, however, the nanorods size increased slightly with an increase in the synthesis temperature. With a further increase in the synthesis temperature to 80 °C, the nanorods structure broke up in mixed structures with the emergence of spherical nanoparticle and plate-like shapes. Figure 5 (a), (b) and (c) show surface morphologies of the PbS powders synthesized at various molar concentrations of lead acetates. The surface morphologies consisted of agglomerated nanorods structures. The nanorods also increased slightly in size with an increase in the molar concentration of lead acetate.

![](_page_5_Figure_2.jpeg)

**Figure 4.** The SEM micrograph of PbS powders synthesized at the various temperatures but at constant molar concentration of lead acetate: (a) 55 °C, (b) 65 °C, (c) 70 °C and (d) 80 °C.

![](_page_5_Figure_4.jpeg)

**Figure 5.** The SEM micrograph of PbS powders synthesized at the various molar concentrations of Pb acetate: (a) 0.12 M, (b) 0.13 M and (d) 0.14 M and constant synthesis temperature.

#### 3.2. Optical properties

![](_page_6_Figure_2.jpeg)

Figure 6. The absorbance spectra of PbS powders prepared at various temperature and at constant molar concentration of lead acetate.

![](_page_6_Figure_4.jpeg)

**Figure 7.** The absorbance spectra of PbS powders prepared at various molar concentration of lead acetates at constant synthesis temperature.

The UV-visible reflectance spectra of the as prepared samples are illustrated in Figure 6. The optical spectra of the samples prepared at 55, 65, 70 and 80 °C have reflection onset at about 550 nm. The reflection edge is strongly shifted to higher wavelengths. In addition, the three optical spectra at temperatures between 55 and 70 °C display one well-defined absorption band with a maximum at about 325 nm.

Figure 7 shows the diffuse reflectance spectra of the PbS nanostructure synthesised at different molar concentration of lead acetate. On increasing the molar concentration of lead acetate, the absorption edges shifted slightly to higher wavelength. We can ascribe the origin of the absorption bands at 335 and 647 nm to  $1s_e-1s_h$  and  $1p_e-1p_h$  transitions in PbS nanoparticles, respectively [17-18]. The shift of absorption edges to higher wavelengths can be attributed to the increase in grain size with an increase in synthesis temperature. While the small variation in crystallite size for the molar concentration of precursor (lead acetate) is reflected in the small variation in absorption edges. This result correlates well with the data obtained from the XRD and SEM analysis.

#### 3.3 Photoluminescence

![](_page_7_Figure_4.jpeg)

**Figure 8.** PL emission spectra of PbS nanostructures in the visible region and for infrared region (as an inset) synthesized at various synthesis temperatures but at constant molar concentration of lead acetate and with the deconvolution of the luminescence spectra taken from the 65 °C of synthesis temperature.

The PL emission spectra of the samples when excited at 277 nm are shown in Figure 8. The excitation wavelength which correspond to the  $1d_h \rightarrow 1d_e$  transition of PbS was confirmed by the UV

analysis. Deconvolution of the PbS (0.13 M lead acetate) emission spectra revealed two bands in the visible region. The bands are associated with the electronic transitions from the  $1p_e \rightarrow 1p_h$  (336 nm) and  $1s_e \rightarrow 1p_h$  (379 nm) energy levels [17]. The emissions in the UV region (336 and 379 nm) arose from the recombination of excitons and/or shallowly trapped electron-hole pairs [19-20]. An extra PL emission was observed in the infrared region, with a maximum of the broad emission at 725 nm and a shoulder at 825 nm. These emissions were due to deep level defects.

![](_page_8_Figure_2.jpeg)

**Figure 9.** PL emission spectra of PbS nanostructures in the visible region and for the near infrared region (as an inset) synthesized at various lead acetate molar concentrations at constant synthesis temperature.

Figure 9 shows the PL emission spectra of the PbS nanostructures excited at 277 nm. It is clear that the emission bands of the PbS nanostructures did not change, only the emission intensity changed as the synthesis temperature increased. The relative decrease of the PL intensity with the increase in the synthesis temperature suggested that the increase of the crystallite size played a major role in decreasing the defect densities [19]. In other words, the gradual decrease of PL emission intensities reveals a significant decrease in the surface/volume ratio for high temperature grown samples [21]. This decrease in luminescence intensity can be due to slightly increasing crystallite size as the synthesis temperature increased as confirmed by the SEM and XRD analysis. Therefore, it is well understood that the non-radiative recombination's increased with increasing particle size and as a result the luminescence intensity decreased [22]. In this work it was very interesting to find that the crystallite sizes, morphology, optical and luminescence properties of PbS nanostructures depend on the synthesis temperatures and the molar concentration of lead acetate.

# **5. CONCLUSION**

The PbS nanostructures have been successfully synthesized by the CBD technique at 55, 65, 70 and 80°C using different molar concentration of lead acetate. XRD showed that the structure of the material obtained was cubic PbS for both variation in synthesis temperature and molar concentration of (lead acetate). UV spectroscopy showed that the absorption edges of the PbS nanostructures shifted to a higher wavelength with an increase in the synthesizing temperature but stayed more or less the same for the different molar concentration of lead acetate. PL showed that the emission intensity of the nanostructures depended on the synthesizing temperatures and molar concentration of the lead acetate.

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