

## Synthesis and Electrical Properties of Low Dimensional Lead Sulfide (PbS) Aiming for Efficient Near Infra Red (NIR) Detector

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*The work shown in the thesis- Synthesis And Electrical Properties Of Low Dimensional Lead Sulfide (PbS) Aiming for Efficient NIR detector stresses on the fabrication of cost effective NIR detector. Thin films of lead sulfide (PbS) were deposited on an Indium Tin Oxide (ITO) coated glass substrate by simple and cost effective Chemical Bath Deposition (CBD) method. According to the few previous reports, lead sulfide structure should have a tunable band gap ranging from 0.39 to 5 eV. This property of lead sulfide enables it to be used as an effective NIR detector. Plenty of work has been carried out in this field with lead sulfide as detector material. Studies regarding this material have already suggested its high photoresponsivity, dielectric constant and high electrical resistivity, claiming the same as a promising material for photo detectors. This is why this material is selected for the NIR detector in this work. The synthesis was optimized by varying the molarity of the precursor and various synthesis parameters (annealing temperature and dip time). The prepared sample was characterized by XRD which shows the pure phase of lead sulfide confirming the successful synthesis. UV-VIS spectroscopy confirms the optical band gap of the material. I-V measurement was also carried out on the sample under dark and IR (Infra Red) irradiation. The current through the sample increases rapidly under IR irradiation which shows that lead sulfide can be used as a good detector material for infrared radiation.*

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### I. INTRODUCTION

Infrared sensing technology has huge application, in day to day life as well as in the industries, starting from remote controlled devices (in TV or any other electronic gadgets) to NASA's James Webb Space Telescope which is being used to sense Infrared (IR) and Mid Infrared (MIR) light from the early galaxies so that we can get to know about the formation of the universe. The light early galaxies emitted (was in the visible range) traveled through space, that space too was expanding, stretching the light to longer infrared wavelengths. Infrared detectors play an important role in various applications including image sensing, communication, night vision camera, proximity sensors, obstacle detection, day/night surveillance etc. The word Infrared and Near-infrared can be used alternatively, it is just about the range of electromagnetic radiation they can detect. IR radiation ranges from 700 nm to 1 mm (wavelength) which is greater than visible wavelength. This is divided into three regions: near-IR (NIR, 750 nm to 3  $\mu$ m), mid-IR (MIR, 3–15  $\mu$ m), and far-IR (FIR, 15  $\mu$ m to 1 mm).

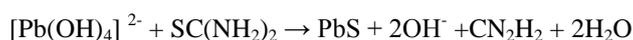
Metal sulfides have attracted a lot of attention due to their dimensionality, outstanding characteristics, and several uses in today's research. Lead Sulfide (PbS) is an important IV–VI group semiconductor with a small direct bandgap of 0.4 eV (bulk) at 300K among inorganic compounds. It features a cubic crystal structure with a high dielectric constant and carrier mobility. PbS is a semiconducting chalcogenide. Chalcogenides are a kind of semiconducting substance that contains one or more chalcogens, such as S, Se, Ge, As, or Te. One of the most popular and earliest photodetector materials used in infrared detectors is lead sulfide. The adjustable band gap (0.4 to 5eV) of lead sulfide, which results from remarkable size dependant characteristics at the nanoscale, has attracted researchers' curiosity. Depending upon the bandgap, it detects visible, IR, NIR, MIR regime of electromagnetic radiation. Furthermore, PbS in nanostructure form has been investigated in a variety of devices, including humidity and temperature sensors, solar cells, and so on. Chemical bath deposition, Spray pyrolysis, Spin coating, Deep coating, and other fabrication processes have been used in recent years to deposit/grow PbS for photo-detector applications on both hard (glass, quartz, alumina, etc.) and soft (paper, fabric, polymer, etc.) substrates. Among these, Chemical bath technique is easy, reasonably cost efficient, and convenient for wide area scaling. Lead Sulfide (PbS) can be characterized by several techniques to investigate the structural, optical and electrical properties. The X-Ray diffraction (XRD) pattern for PbS thin film according to the standard X-ray diffraction data files with reference No.03-065-0692, shows peaks (111), (200), (220), (311), (222) corresponding to  $2\theta$  angles ranging from 25.98<sup>o</sup> to 70.95<sup>o</sup>. PbS can be characterized using Scanning Electron Microscope (SEM) as well. It indicates that the PbS thin films formed by CBD were homogeneous in nature, with sparsely packed crystallites that appear to be randomly orientated with irregular and spherical shape of

comparable size distribution. This is consistent with Castillo et al. (2014) and Jana et al (2008). The UV-Vis analysis shows the variation of absorbance with wavelength. PbS samples have a strong reflectivity in the visible range that gradually decreases in the near infrared range. The thin film's high reflectivity and absorbance in the visible region make it an excellent material for anti-reflection coating as well as solar thermal applications; the films may be used as a solar control coating and are also used in near infrared (NIR) detectors.

## II. EXPERIMENTAL PROCEDURE

### *Materials and Chemicals*

Thin films of PbS were deposited from the solution containing [Pb(NO<sub>3</sub>)<sub>2</sub>], [SC(NH<sub>2</sub>)<sub>2</sub>] and [NaOH] under various experimental conditions. Lead nitrate (Aldrich, analytical 99.99%), thiourea (TU) (Aldrich, ACS 99.0%) and sodium hydroxide (Gadot, AR) were used without further purification. ITO coated glass plates (1.5x1.7 cm<sup>2</sup> rectangles), cleaned by wiping with ethanol, were used for substrates, were vertically immersed into the solution. The substrates were subsequently taken out of the chemical bath after 40, 60 and 80 min dip time, rinsed with distilled water and dried. The resulting films were uniform, homogeneous and well adhered to the substrate with dark surface. The suggested reactions are as follows (Tohidi et al., 2014; Osherov et al., 2007).



### *Synthesis*

The synthesis of Lead Sulphide (PbS) nanoparticles was carried out by Chemical Bath Deposition method. Lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>], Thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] and Sodium Hydroxide [NaOH] were the precursor compounds. The sulfide ion (S<sup>2-</sup>) source is thiourea, while the lead ion (Pb<sup>2+</sup>) source is lead nitrate. Lead Sulfide was constituted from the solution of 0.16g (4.8 mmol) of Lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] dissolved in 100 ml de-ionised (DI) water, 0.075g (50 mmol) of Thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] dissolved in 20 ml de-ionised water and 0.15g (125 mmol) of Sodium Hydroxide [NaOH] dissolved in 30 ml deionized water. First of all, in 1st beaker, 0.16g (4.8 mmol) of Lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] and 100 ml de-ionised water are taken and then the beaker, with a magnetic bead, is placed onto a magnetic stirrer so that the chemical get mixed thoroughly. Simultaneously, 0.075g (50 mmol) of Thiourea [SC(NH<sub>2</sub>)<sub>2</sub>] and 20 ml de-ionised water and 0.15g (125 mmol) of Sodium Hydroxide [NaOH] and 30 ml deionized water were kept in 2nd and 3rd beakers respectively and were placed in different magnetic stirrers. The solution of the 1st beaker was allowed to stir thoroughly for 15 minutes and then the solution of the 3rd beaker (NaOH solution) was added to the solution of the 1st beaker dropwise making it a total of 130 ml of solution. The addition of NaOH makes the solution more basic and raises the pH of the solution of the 1st beaker to around 12. Then finally, the solution of the 2nd beaker (Thiourea solution) was added to the solution of the 1st beaker dropwise and made it a total of 150ml of mixed solution in the 1st beaker. After few minutes the solution, in the 1st beaker, turns turbid and after that the color of the solution becomes shining black. The shining black color of the solution confirms the successful synthesis of lead sulfide (Fig 1). After that the solution was poured into the centrifugal tubes and placed in a centrifugal machine so that we can collect the PbS nanoparticles. In the centrifugal machine the tubes are placed and rotated at a speed of 10,000 RPM (Revolution Per Minutes) for 10 minutes. This results in the deposition of PbS nanoparticles at the walls and lower ends of the tube. Then the remaining de-ionised water in the tube was removed.



Fig1: Synthesis of PbS

Again some de-ionised water is taken into the tube and the tube is shaken well so that the PbS samples on the walls of the tube get dissolved in it and then it was poured on a petridish and kept for drying at normal room temperature. After drying, using a spatula, the samples are collected from petridish and kept it in a airtight container. The samples are now in a powder form. This complete process is repeated three different times for three different temperatures during synthesis (i.e 40<sup>0</sup> C, 60<sup>0</sup> C, 80<sup>0</sup>C). Now, we have three different samples of low dimensional PbS synthesized at 40<sup>0</sup> C, 60<sup>0</sup> C and 80<sup>0</sup> C.

#### **Characterization**

All three samples (i.e PbS at 40<sup>0</sup>C, PbS at 60<sup>0</sup>C and PbS at 80<sup>0</sup>C) were characterized by X- Ray diffractometer (XRD). The phase composition and the structure of all three prepared samples were characterized by X-ray diffraction pattern recorded with an powder X-ray diffractometer (Bruker D8 Advance) in the 2 $\theta$  range 20–70<sup>0</sup> using CuK $\alpha$  radiation of wavelength  $\lambda = 1.54 \text{ \AA}$  operated at 40 kV and 40 mA.

All samples were characterized by Source Measure Unit (SMU, KEYSIGHT B2902) for I-V (Current-Voltage) measurements. One of the most common types of precision power sources is the SMU, which gives voltage and current measurement resolution at or below 1mV or 1 $\mu$ A, respectively. They also include a four-quadrant output with bipolar voltages and the capacity to drain power.

UV-visible measurement was carried out at room temperature with a UV visible spectrophotometer (Shimadzu UV-3101PC) with the samples dispersed in alcohol.

### **III. RESULTS AND DISCUSSION**

#### **Phase and Composition Study**

The Fig 2 (a to c) depicts the X-ray diffraction patterns for PbS thin films obtained from standard X-ray diffraction data files with reference No.03-065-0692. All the samples have a similar XRD pattern. The diffraction peaks for face centered cubic lattice low dimensional PbS were found at peaks (111), (200), (220), (311), (222), (400), (331), (420) and (422) which correspond to 2 $\theta$  angles ranging from 20<sup>0</sup> to 80<sup>0</sup> for all samples. The peaks that appear are very strong and sharp, indicating that the samples are highly crystallized. The absence of diffraction peaks from the starting material or any residual species in the spectra confirms the samples' proper phase formation.

According to Full Width Half Maximum (FWHM) measurements and Debye-Scherrer formula, the crystalline size of the deposited nanoparticle ranges from 34 to 42 nanometers (Chaudhuri et al., 2005; Abbas et al., 2011).

$$D = 0.9 \lambda / (\beta \cos \theta)$$

Where **D**= Grain Size,  $\lambda$  s the wavelength of CuK $\alpha$  used,  $\theta$  is Bragg's diffraction angle in radians and  $\beta$  is Full width at half maximum of the peak in radians.

Lattice strain ( $\epsilon$ ) is also calculated from XRD data.

$$\epsilon = \beta / (4 \tan \theta)$$

Where  $\theta$  is Bragg's diffraction angle in radians and  $\beta$  is Full width at half maximum of the peak in radians.

Lattice Strain is increasing with increase in temperature during synthesis.

| Sample                   | D (Nanometer) | Lattice strain ( $\epsilon$ ) |
|--------------------------|---------------|-------------------------------|
| PbS at 40 <sup>o</sup> C | 40.17         | 0.003149                      |
| PbS at 60 <sup>o</sup> C | 42.45         | 0.003317                      |
| PbS at 80 <sup>o</sup> C | 34.17         | 0.003918                      |

**Optical Study**

Fig 3 depicts optical study plots for absorption measurements performed in the wavelength range of 200 to 800 nm. Fig 3(a) shows the variation of absorbance with wavelength for the deposited PbS thin films at different dip times. Absorption coefficients for the as prepared PbS products are calculated using the experimentally observed transmittance of the PbS products. The optical band gap energy of the products can be determined from the following equation

$$\alpha h\nu = K(h\nu - E_g)^n$$

where **K** is a Richardson’s constant, **hν** is the incident photon energy, **E<sub>g</sub>** is the band gap of the material, and **n** is a constant taken to be 1 for PbS as a direct band gap semiconductors.

The direct optical band gap energy can be determined by extrapolating the straight line portion of the  $(\alpha h\nu)^2$  versus  $h\nu$  plot to the energy axis for zero absorption coefficients (Fig 3b). The optical band gap energies of PbS crystals has been estimated to be in the range of 1.93 - 2.09 eV whereas the bulk PbS has a band gap energy value of about 0.41 eV. This is attributed to the quantum confinement of charge carriers in the nanoparticles.

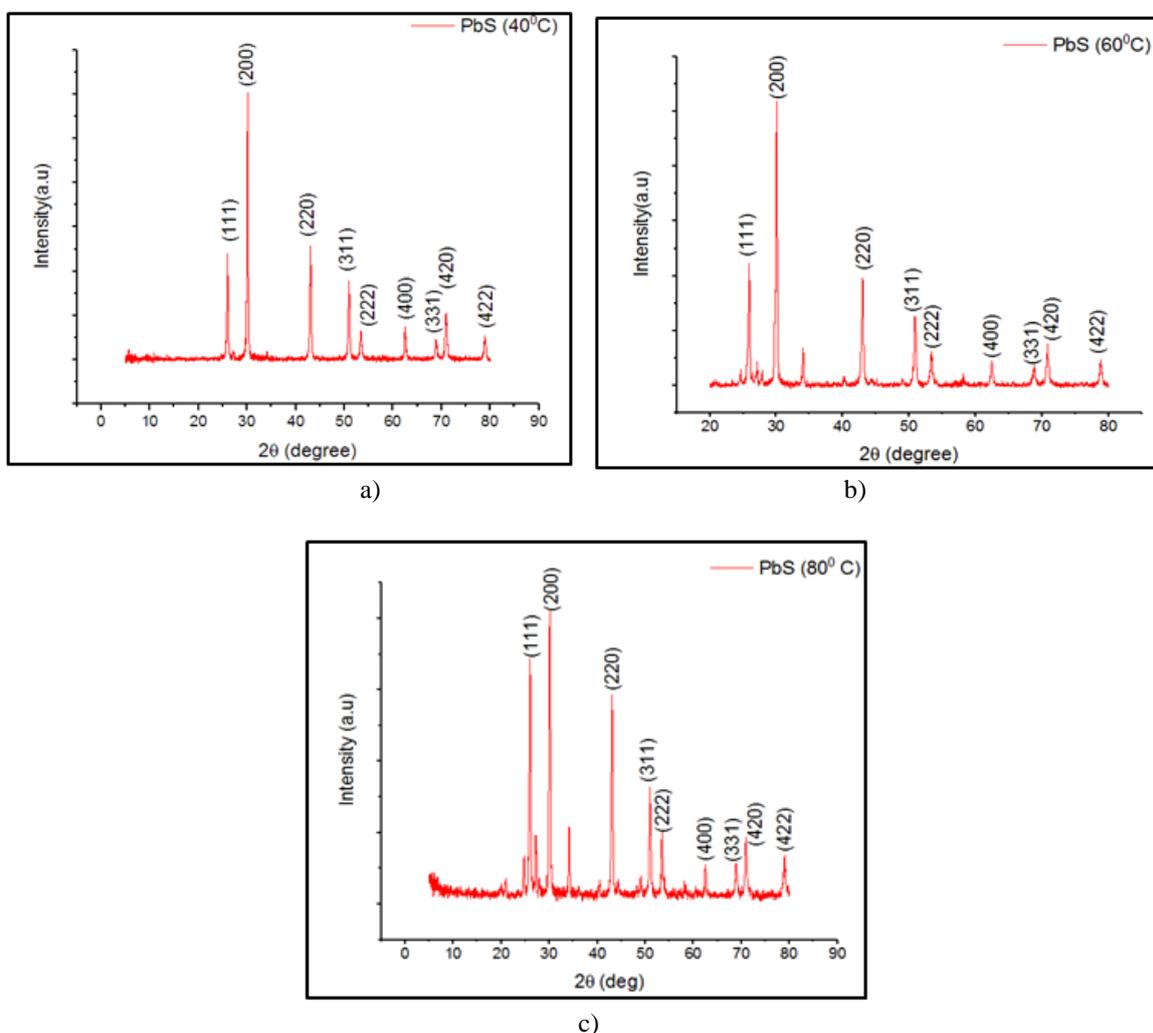


Fig 2: XRD pattern of PbS at annealing temp (a) 40<sup>o</sup>C (b) 60<sup>o</sup>C (c) 80<sup>o</sup>C

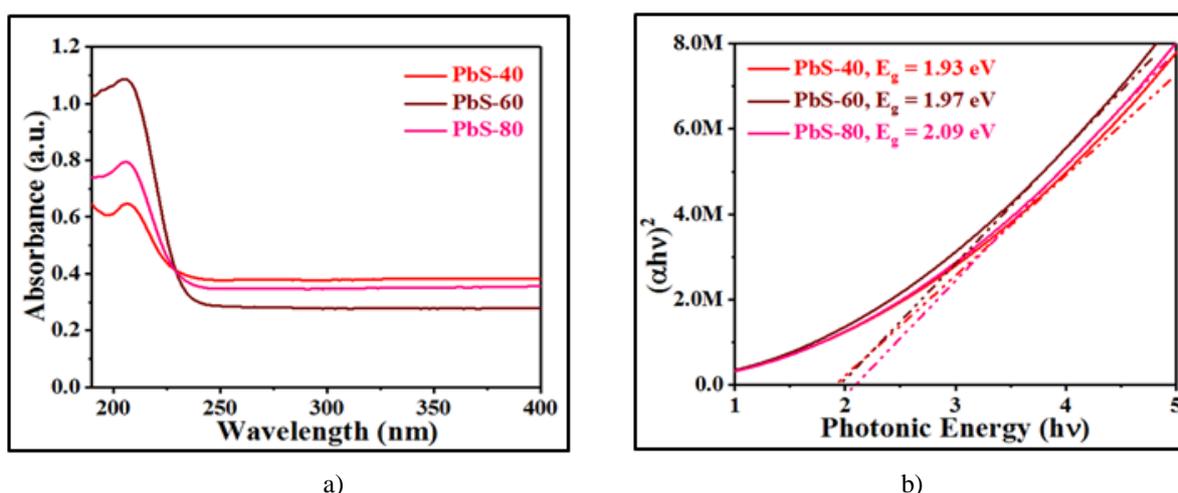


Fig 3: (a) Absorbance v/s Wavelength plot (b)  $(\alpha hv)^2$  as a function of energy  $hv$

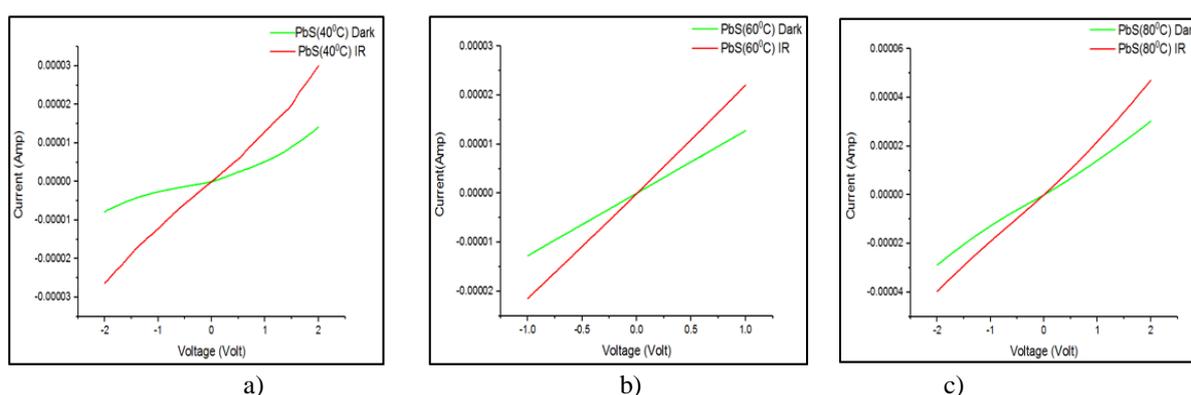


Fig 4: I-V plot under dark and IR irradiation of PbS at (a) 40°C (b) 60°C (c) 80°C

### Photoresponse Study

The samples were subjected to moderate intensity of infrared radiation to study their photoresponse properties. The samples showed a moderate current under dark condition. The sample current almost doubled after they were exposed under IR radiation [Fig 4(a to c)]. The PbS is a well known low band gap material. Due to exposure of infrared radiation, the sample therefore showed enhanced current through them. All samples synthesized in different temperatures showed appreciable enhancement of sample current compared to dark state. However, the enhancement of the sample current with synthesis temperature could be further analyzed considering the grain size and morphological alterations occurring within the samples.

## IV. CONCLUSION

In summary, we have demonstrated a simple and cost efficient method to fabricate a infrared light photodetector based on low dimensional lead sulfide (with grain size around 40 nm) via chemical bath deposition method. X-ray diffraction analysis reveals the composition and structure of low dimensional lead sulfide as a pure phase with a face centered cubic lattice. Grain size and lattice strain were also calculated from the xrd data. The lattice strain was found to be increasing with increase in temperature during synthesis. This is why the value of lattice strain for the sample synthesized at 80 degree celsius is highest.

Photo detection measurements reveal excellent photo response with high sensitivity. The present study introduces a simple and low cost method to fabricate high quality lead sulfide nanoparticles based photodetectors with excellent photocurrent reproducibility and stability.

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