

Investigation of Lead Sulphide nanoparticles synthesized by hydrothermal method

P.Sakthivel,S.Sharon Tamilselvi, T.Arokiya Mary, Joe Jesudurai

Abstract— Single-crystalline lead sulfide nanostructures were synthesized by a simple hydrothermal solution route. Cubic shaped PbS nanocrystals were synthesized using Lead(II) acetate trihydrate, Thioglycolic acid and Thiourea and treated at 180 °C for 20 hours. The reaction products were characterized by means of X-ray diffraction [XRD] studies confirming the highly crystalline cubic PbS phase formation. Scanning Electron Microscopy [SEM] study revealed cube like structures. From the UV-visible (UV-Vis) spectroscopy, the absorption spectrum indicates a blue shift in the band gap compared to the bulk PbS. The Photoconductivity studies and dielectric analysis were also carried out.

Index Terms— Blue shift, cubic phase, dielectric, hydrothermal, lead sulphide, nanoparticles, photoconductivity.

1 INTRODUCTION

The influence of the shape and size of inorganic nanocrystals in shaping their varying physical and chemical properties has led to increased interest in the morphological control of semiconductor nanoparticles [1–4]. Lead sulphide nanoparticles are important direct band gap semiconductor materials [5]. The properties of the nanocrystals are dependant not only on their chemical composition but also on their structural arrangement, phase, shape, size and size distribution. Moreover, the architectural control of nanosized materials with well-defined shapes is important for the success of future and potential nanodevices [6]. PbS has wide applications in many fields such as in Pb²⁺ ion selective sensors [7], IR detectors [8], display devices [9], and solar cells [10]. Moreover, as a consequence of its carrier confinement, an exceptional third order nonlinear optical properties of lead sulphide nanoparticles has been found, which may be applicable in many optical contraptions such as optical switches [11]. The size and shape dependant optical properties of nanocrystalline semiconductors can be exploited in optoelectronic nanodevices and for bioengineering applications. Various methods have been developed for the synthesis of lead sulfides including solid-state reactions [11, 12], self propagating high temperature synthesis [13], sonochemical routes [14], microwave irradiation techniques [15, 16], pyrolysis of single source precursors [17], hydrothermal synthesis [18–24] and so on. Among the above methods, the hydrothermal synthesis has opened up a prolific route for the synthesis of advanced nanomaterials including lead sulfides.

In the present work, lead sulphide nanocrystalline particles were synthesized by this simple hydrothermal process. The as-synthesized samples were analyzed by various characterizations such as Powder X-ray diffraction analysis, SEM, EDX, UV analysis, photo conductivity and Dielectric studies.

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2 EXPERIMENTAL PROCEDURE

All reagents used in the synthesis were of analytical grade and used without further purification. In a typical preparation process, 5.69 gm of lead (II) acetate trihydrate [(CH₃COO)₂Pb. 3H₂O] was taken together with 75 ml of double distilled water, and 5.7 gm of Thiourea [SC(NH₂)₂] was also taken and mixed with another 75 ml of double distilled water separately. The above two solutions were then mixed and 5.2 ml of Thioglycolic acid [HSCH₂CO₂H] was added. The final solution was later transferred to the Teflon-lined autoclave, placed inside a furnace at a temperature of 180 °C for 20 h and then gradually cooled to room temperature. The precipitate was then filtered and washed repeatedly with water and ethanol to remove any non reacted chemicals or impurities. The final products were then dried in air at 65 °C for 30 minutes and collected for characterization.

3 RESULT AND DISCUSSION

3.1 XRD Analysis

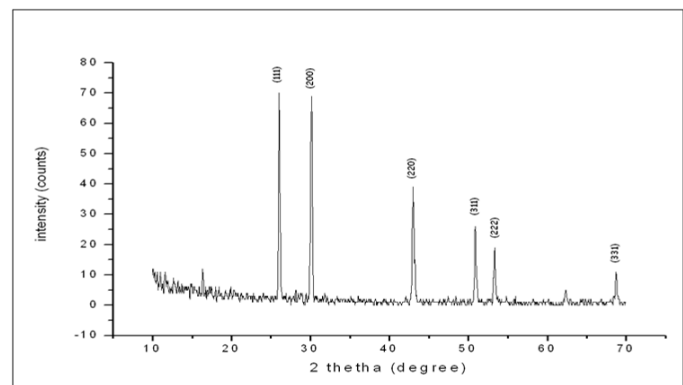


Figure 1: XRD pattern of lead sulphide nanoparticles

Figure 1 shows the XRD patterns of Lead Sulphide nanoparticles. All the diffraction peaks shown in the figure match well

with the standard XRD lines of the cubic Lead sulphide (JCPDS #: 05-0592) and are due to reflections from planes (111) (200) (220) (311) (222) and (331). The lattice cell constants ($a=b=c=5.925 \text{ \AA}$) calculated from the XRD pattern are consistent with the reported values and respond to the reflections of the cubic structure of PbS. The grain size estimated from the peak (200) of PbS was calculated using Debye Scherrer formula

$$D = k \lambda / \beta \cos \theta$$

The grain size obtained accordingly is 34.035nm.

3.1. UV ANALYSIS

The UV visible spectrum has been widely used to characterize the semiconductor nanoparticles. The UV-Vis absorption spectrum of the as-prepared Lead Sulphide sample is shown in the Figure 2. The band gap energy of the nanoparticles was calculated to be 3.63 eV which is 3.22 eV larger than that of the bulk PbS [$E_g \sim 0.41 \text{ eV}$]. This indicates that the nanoparticles exhibit a significant blue shift. The apparent blue shift from the bulk molecules can be attributed to exciton confinement.

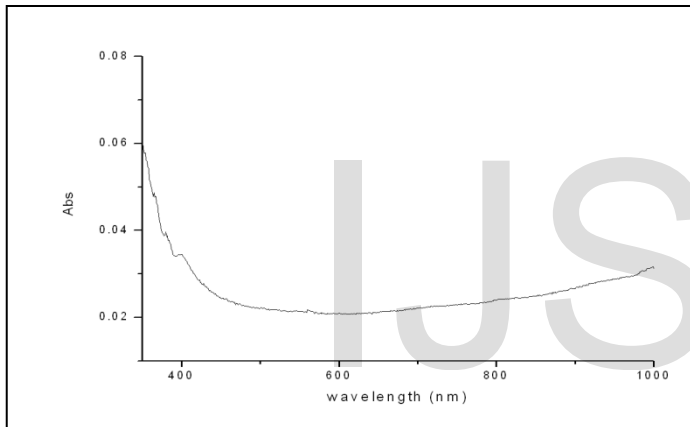


Figure 2: UV Studies of PbS nanoparticles

3.2. SCANNING ELECTRON MICROSCOPY & EDS ANALYSIS:

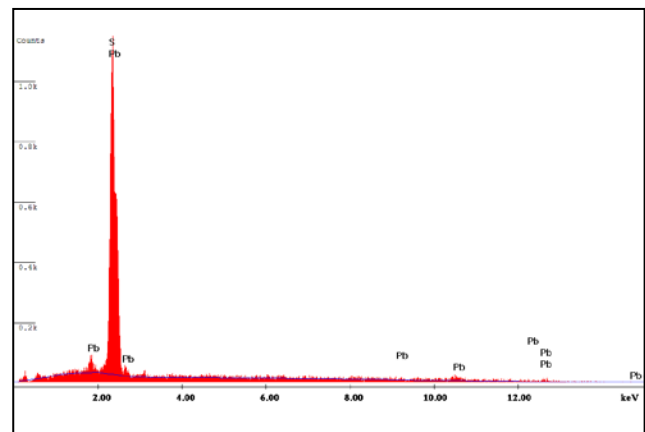
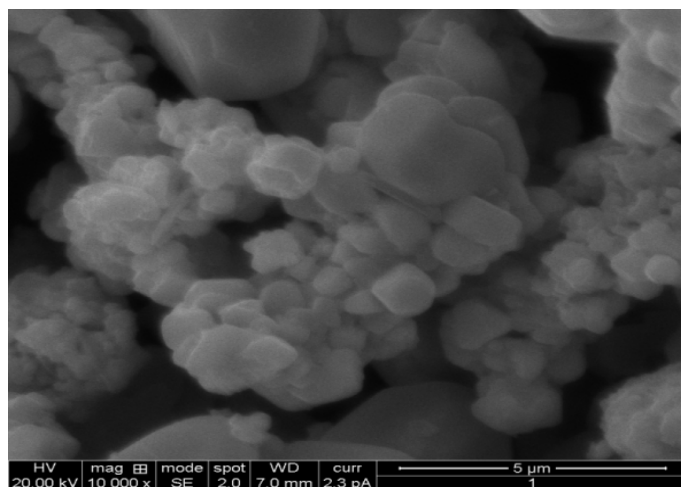


Figure 3: SEM and EDX spectrum of PbS nanoparticles

The surface morphology of lead sulphide particles has been studied using Scanning Electron Microscopy. Figure 3 represents the SEM and EDAX images of the PbS sample respectively. The EDAX analysis of the above sample confirms the presence of Lead and Sulphur with no other element present, implying its purity. The SEM image at a higher resolution reveals the morphology of the sample as a cluster of cubic particles with sizes ranging from 500 to 900 nm.

3.3. DIELECTRIC ANALYSIS

The dielectric constant (ϵ_r) of the material was calculated for different frequencies from the measured capacitance values. The plot of the dielectric constant versus $\log f$ is shown in Figure 4 (a). It is observed that the dielectric constant has high value in the low frequency region and thereafter decreases with increase in applied frequency. The high value of (ϵ_r) at low frequencies may be due to the presence of all the four polarizations namely space charge, orientation and, electronic and ionic polarization and the low values at higher frequencies may be due to the loss of significance of these polarizations gradually. The curve of dielectric loss with frequency is shown in Figure 4(b). The AC electrical conductivity was determined using the relation $\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan \delta$ ($\omega = 2\pi f$, f is the frequency). With the high AC resistance it can be mentioned that the space charge polarization plays an important role in the electrical property of the sample.

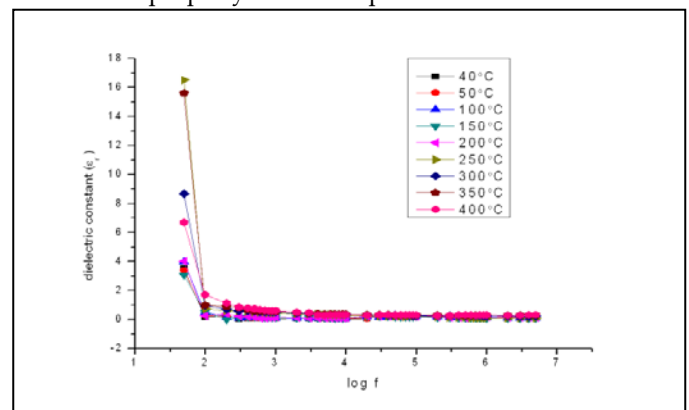


Figure 4 (a): log f versus Dielectric constant

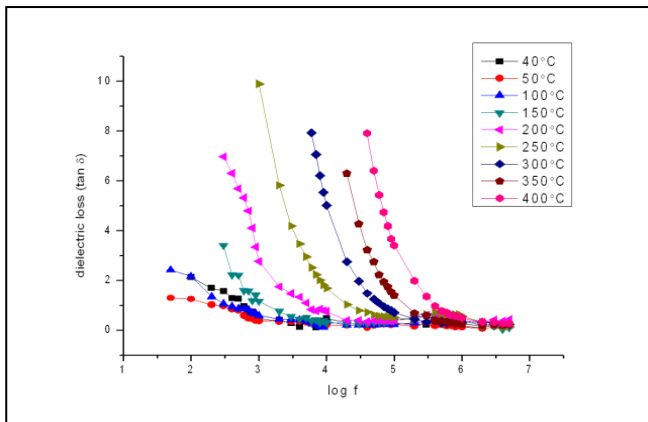


Figure 4(b): log f versus Dielectric loss

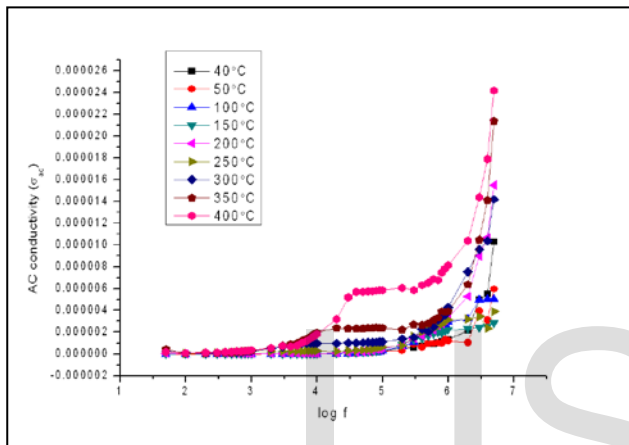


Figure 4 (c): log f versus AC conductivity

3.4. DC CONDUCTIVITY STUDIES

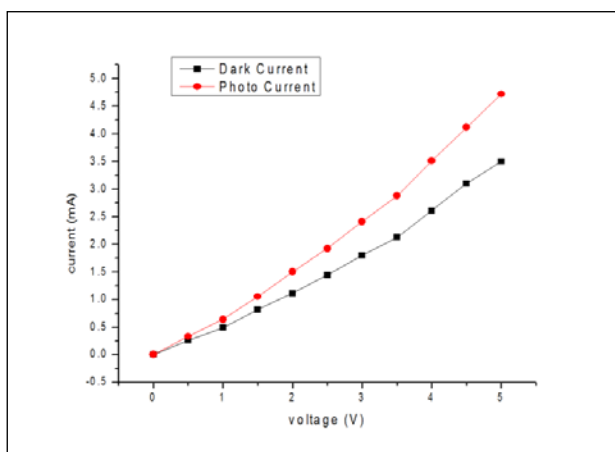


Figure 5: Conductivity Analysis

The DC input to the sample was increased from 0 to 5 volts in steps and the corresponding dark current was noted from the electrometer. For determining the photocurrent, the PbS-sample was illuminated with an incandescent light bulb (40 W) and the corresponding photocurrents were measured. The variation of photocurrent (I_p) and dark current (I_d) with applied field are shown in figure 5. Both photo and dark currents

of lead sulphide increases linearly with applied voltage. It is observed from the plot that the dark current is less than photocurrent, suggesting that PbS exhibits positive Photoconductivity, which can be attributed to the generation of mobile charge carriers caused by absorption of photons.

4. CONCLUSION

In conclusion, the lead sulphide nanoparticles have been successfully synthesized using hydrothermal method. The structural and microscopic investigations of the sample indicate formation of clustered cubic PbS nanoparticles with cubic crystal structure. The UV analysis demonstrates that the nanostructures are blue shifted compared with the bulk PbS's band gap which may be due to exciton confinement. The measurement of the dielectric properties of PbS NPs provides evidence of polarization effects and the Photoconductivity analysis for transport properties of the charge carriers.

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