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## THE OBTAINING OF PbS POWDERS FOR ORGANIC MATRIX COMPOSITES

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**Abstract:** PbS powders were obtained from solutions containing lead salts and thiourea, in alkaline environment. Lead sulphide is a photosensitive chalcogenide for IR wavelengths. Optical properties for the obtained powders were determined using UV-VIS spectroscopy. On the basis of optical properties the band gap of the obtained powders was determined. FT-IR spectroscopy was used in order to show that the obtained powder contains no unreacted reagents (lead salt, thiourea or sodium hydroxide). The obtained powders can be embedded in organic matrix for the obtaining of composites with special optical and electrical properties.

**Keyword:** PbS, organic matrix composites, band gap

### 1. INTRODUCTION

Organic matrix composites with special optical, electrical and photoelectrical properties have drawn attention of researchers due to their potential applications for photovoltaics.

PbS containing organic matrix composites presents photoconductivity for infrared wavelengths. Those materials contain conjugated polymers sensitized with PbS nanocrystals. The photocurrent is attributed to absorption in the nanocrystals with subsequent hole transfer to the polymer [1-3]. As a function of the obtaining conditions and matrix, composites with intense visible emission have been also prepared [4].

P.S. Nair [5] and coauthors suggest a procedure for the incorporation PbS nanoparticles in a polystyrene (PS) matrix. The method is based on the thermal decomposition of a lead xanthate complex within the solid polymer. The optical properties of the PS-PbS nanocomposites obtained by Nair [5], are similar to the one obtained by Zeng et al. [31] on a poly(methyl methacrylate-co-methacrylic acid)-PbS nanocomposite.

Spherical or cubic nano-sized particles of lead sulphide were grown under excess sulfur conditions and embedded in polyacrylamide (PAA) polymer films [6]. The obtaining of the films involved the mixing of a solution containing PAA with a solution containing lead nitrate. Then a solution containing thiourea (TU) was added and the resulted aqueous solution was spread on a glass substrate, and the excess water was evaporated, at a temperature of 375 K for 12 h [6]. The obtained nanoparticles show a substantial blue shift (up to 2 eV) with a decrease in the particle size, due to a strong quantum size effect.

Bulk lead sulphide is a narrow band semiconductor (0.41 eV, at 300K) [5] being sensitive for IR radiation. The valence and conduction band-edges are mainly composed of S (s, p-orbital) and Pb (p-orbital), respectively [6].

The high dielectric constant ( $\epsilon_{\infty} = 17.3$ ) and the small electron effective mass [7- 9] creates an exciton with a large effective Bohr radius (180 Å). The electron and hole Bohr radii are both about 100 Å. Thus, size quantization effects are strongly pronounced in PbS nanoparticles, showing a unique possibility to probe the strong confinement regime. Furthermore, the latter property offers potential photonic applications [10, 11].

Lead sulphide particles can be obtained by chemical bath deposition [12], sol gel [13-16], Langmuir-Blodgett technique [17], or applying a cyclic voltammetric method [18].

Ultrasounds influence the obtaining and the properties of materials due to acoustic cavitation. Acoustic cavitation effects in sol-gel liquid processing permits to obtain nanostructured materials, with size-dependent properties [19]. The so-called "hot spots" produce very high temperatures and pressures which act as nanoreactors. Ultrasounds enhance the dissolution and the reaction rate.

Ultrasonic irradiation was applied in order to obtain PbS particles, using an environmental friendly method [20]. from aqueous solution of lead acetate, thioacetamide and absolute ethanol in ionic liquid (1-ethyl-3-

methylimidazolium ethyl sulphate). The authors determined the band gap energy of about 4.27 eV which shows a high blue shift that can be attributed to very small size of PbS nanoparticles and quantum confinement effect. Rongguo Xie et al [21] obtained 30 nm nanoparticles of PbS, homogeneously coated on sub-micrometer silica spheres by a sonochemical method, using triethanolamine acted as complex agent. By dissolving the silica cores with a diluted hydrofluoric acid solution, stable PbS hollow structures were obtained. Hui Wang [22] and coauthors made a study related to sonochemical preparation of lead sulfide nanocrystals of 11 nm, in an oil-in-water microemulsion. The as-prepared PbS nanocrystals have a cubic structure. PbS nanocrystals have been prepared under microwave heating and ultrasonic irradiation [23] using lead acetate and thiourea as precursors. Different size and morphology of PbS nanocrystals can be obtained by using ethanol, distilled water, ethylene glycol and polyethylene glycol-200 as solvents. PbS hollow nanospheres with diameters of 80–250 nm have been synthesized by a surfactant-assisted sonochemical route by Wang [24]. Structural characterization indicates that shells of the hollow spheres are composed of PbS nanoparticles with diameters of about 12 nm. The formation of the hollow nanostructure was explained by a vesicle-template mechanism, in which sonication and surfactant play important roles [24]. Large-scale single-crystal cubic PbS nanorods were successfully achieved by using ultrasound irradiation in solutions containing ethylenediaminetetraacetic acid [25]. The results reveal that the PbS nanorods with straight and uniform structure have a diameter of about 70-80 nm and length of about 1000 nm. The successful synthesis of these cubic structure semiconductor PbS nanorods may open up new possibilities for using these materials as building blocks to create functional two-dimensional or three-dimensional nanostructured materials [25]. Other methods involved a sonochemical technique, for obtaining PbS nanobelts starting from solutions of  $\text{PbCl}_2$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . The as-synthesized PbS nanobelts have width of about 80 nm, length up to several millimeters, and width-to-thickness ratio of about 5 [26]. Different PbS structures including nanocubes, nanorods and nanotubes have been successfully prepared by a sonochemical route [27,28]. The concentration of surfactant, the reaction time and the anion of the lead source are important factors for the formation of PbS crystals [28]. Park et al [29] prepared both PbS nanoparticles (40–50 nm) and PbS-coated titanium dioxide under ultrasonic field in water solutions. Starting from lead acetate and TU, using ethanol at room temperature with the aid of ultrasound radiation, Wang et al obtained microtubes [30]. The PbS microtubes were grown from the initial PbS nuclei (formed by the decomposition of Pb–TU complex) to porous spheres, and then to the final tubes.

## 2. EXPERIMENTAL DETAILS

In a 150 ml beaker the deposition solution has been prepared adding in 75 ml water the appropriate amount of lead nitrate (Reactivul-Bucharest) or lead acetate (Reactivul-Bucharest) solution under vigorous stirring. In the next step a solution containing NaOH (S.C. Chemical Company S.A.) was added dropwise. A white precipitate appears and the precipitate dissolved when the total amount of NaOH solution was added. Then a solution containing thiourea (Fluka) was added to the clear solution containing lead nitrate/acetate and sodium hydroxide, followed by the addition of water until a total volume of 100 ml solution was obtained. The solution was homogenized and then was divided in two 50 ml Berzelius beakers. One of the beakers was placed in a thermostatic bath at 30 °C, and the other one in an ultrasonic bath (Elma Sonic S 30 H). In the first bath the deposition took place without mixing the solution while in the second one the deposition took places under sonochemical conditions. The deposition took places for 45 minutes both in the static and ultrasonic bath. After reaction, PbS precipitates were removed from the flasks, filtered and washed with distilled water.

UV-VIS spectra were measured using a double beam Perkin Elmer Lambda 35 spectrofotometer.

Spectrum BX FTIR spectrometer from Perkin Elmer was used for IR analysis. The measurements were made using an Attenuated Total Reflectance accessory, for lead salts and thiourea. PbS was embedded in KBr pellets.

## 3. RESULTS AND DISCUSSIONS

### 2.1. Optical properties

The recorded absorption (A) and transmission (T) spectra are presented in figure 1 and 2 respectively. The absorption spectra of all samples have a maximum in UV region. The increased absorption in UV region lead to the conclusion that we obtained nanopowders, and the blue shift of absorption took place due to quantum confinement effect. The spectra resemble very well the shape of the spectra obtained by [32] for PbS nanoparticles obtained by sonochemical method (small case (inset) in fig. 1. a).

The transmission of PbS decreased almost linearly for wavelengths higher than 260 nm. For better characterization UV-VIS-NIR spectra would be more useful.

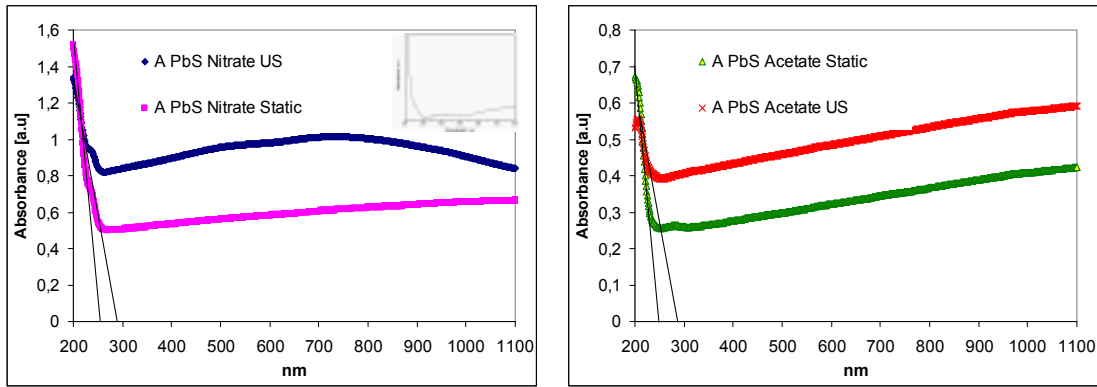


Figure 1. UV-VIS absorption spectra of PbS powders

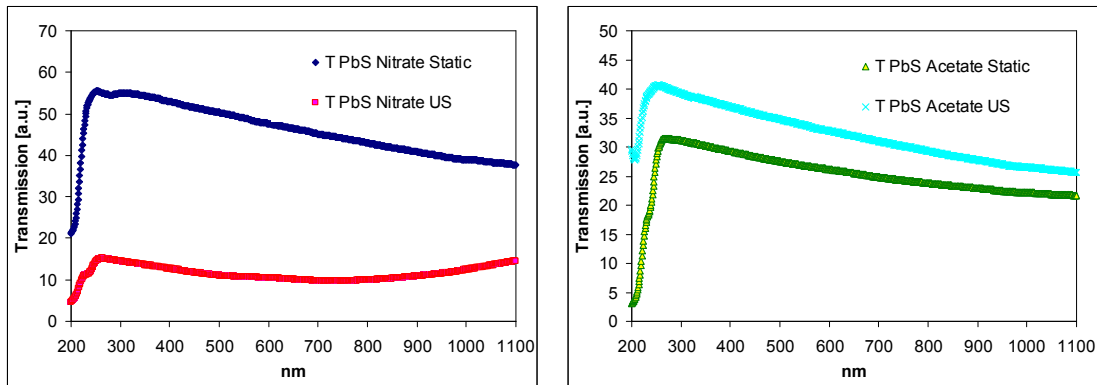


Figure 2. UV-VIS transmission spectra of PbS powders

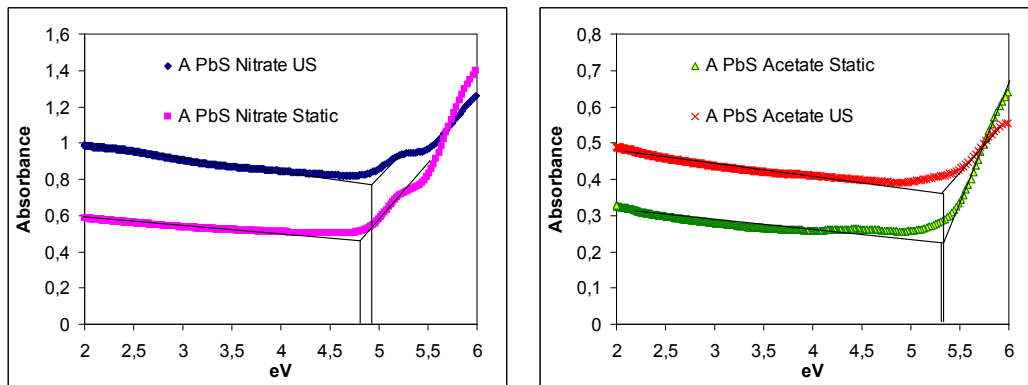


Figure 3. Band gap calculation based on the variation of absorbance as a function of photon energy

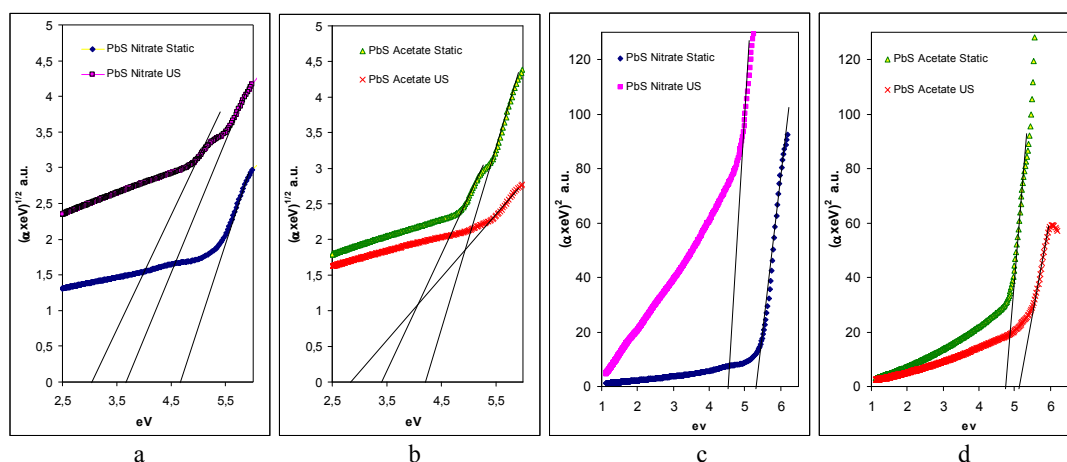
Based on absorption spectra the band gap can be calculated reading the value of wavelength obtained by extrapolation of linear portion of absorption spectrum to the absorption value equal to 0 (fig. 1 and table 1) [39]. Then, as a function of wavelength, the band gap can be calculated from the relation  $E=h \cdot c / \lambda$ , where  $h$  is the Planck's constant,  $c$  is the speed of light in vacuum, and  $\lambda$  is the wavelength (from the chart). Replacing the values for  $h$  and  $c$  the relation become:  $E=1240 / \lambda$ .

Another method that can be applied for the determination of band gap of semiconductors is presented in figures 3, using the variation of absorbance as a function of photon energy [40]. Even if the obtained value (table 1), using the presented methods differ, one can draw a clear conclusion on the magnitude of the obtained value. Another method generally accepted for band gap calculation is based on Tauc's formula [33,34]:

$$\alpha \cdot h\nu = A(h\nu - E_g)^n \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $A$  is a constant, and  $n$  is equal to  $1/2$  for allowed direct transitions and  $2$  for allowed indirect transitions [33,34].

In Figs. 4,  $(\alpha h\nu)^{1/2}$  and  $(\alpha h\nu)^2$  respectively is plotted against  $h\nu$ , for all samples. The linear region is extrapolated for  $(\alpha \cdot h\nu)^n = 0$  to obtain the values for the band gap.



**Figure 4.** Tauc plots ( $n=1/2$ ) for PbS (a,b) and ( $n=2$ ) for PbS (c,d)

**Table 1.** The values obtained for Band Gap applying different methods of calculation

Sample Info.	Band gap ( $n=1/2$ )	Band gap ( $n=2$ )	Band gap (from absorption extrapolation as a function of EV – fig. 3)	Band gap (from absorption extrapolation – fig. 1)
PbS Nitrate Static	4.70	4.50	4.77	4.77
PbS Nitrate US	3.00	5.30	4.80	4.27
PbS Acetate Static	3.40	4.70	5.30	4.96
PbS Acetate US	2.80	5.10	5.35	4.43

The indirect band gap decreased from 4.7 to 3 eV, in the case of PbS obtained from lead nitrate in ultrasonic baths, and 3.4 to 2.8 in the case of PbS obtained from lead acetate in the presence of ultrasounds.

In the case of direct transition, band gap was 4.5-4.7 eV, in the case of static baths. The direct band gap tends to increase when samples were obtained under ultrasonic agitation. One can see that the nature of the precursors also influenced the value of band gaps.

According to our calculations, the band gap of obtained PbS particles is extremely high, reaching values higher than 5 eV. Hoffmann and Entel show that by varying the size and shape from bulk material to nanoparticles it is possible to change the optical band gap up to 5.2 eV [34-36].

The band-gap of PbS nanoparticles are significantly blue-shifted from the near-infrared (IR) into the near ultraviolet (UV) region with decreasing particle size compared to bulk counterpart [37].

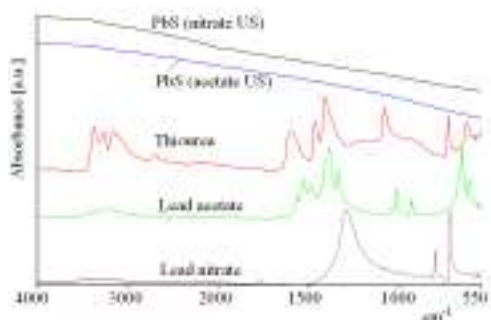
Indranil Chakraborty obtained PbS particle with diameters varied in the range of 1.9–4.1 nm with variation of band gap from 4.24 to 3.88 eV. Also band gap variation of 3.37 to 2.92 eV has been observed for a variation in particle size from 2.7 to 7.0 nm [33].

Y. Zhao et al showed that the liquid phase used for the reaction have an important role in the formation of PbS particles. Under ultrasounds, the use of ethylic alcohol and the use of solutions containing polyethylene glycol conducted to the formation of very small particles (10-30 nm), while in the presence of water and ethylene glycol the size of particles is between 80-150 nm [32].

## 2.2. FT-IR measurements

PbS have no adsorption peaks in IR region of spectrum, thus, the determination of FT-IR spectra was made in order to establish if the obtained PbS powders are pure. Fig. 5 presents FTIR spectra of PbS powders obtained using lead acetate and lead nitrate respectively as precursors as well as the spectra of reagents.

One can see that there are some very weak broad O-H adsorption bands near  $3400-3300 \text{ cm}^{-1}$  due to water vapours adsorbed in the powder. No other clear visible adsorption bands can be seen in the PbS spectra, leading to the conclusion that PbS was formed and all unreacted reagents were removed from the powder.



**Figure 5.** FTIR-ATR spectra of PbS powders, thiourea, lead acetate and lead nitrate

### 3. CONCLUSIONS

We obtained PbS powders using lead nitrate and lead acetate respectively and thiourea in alkaline environment using static and ultrasonic baths. For the obtained powder, the band gaps were calculated applying 3 methods. We concluded that the values for band gaps depend on the applied method for calculation. The most accepted methods involved the calculation using Tauc formula. Ultrasounds determined the increasing of band gap for direct transitions and the decreasing of band gap for indirect transitions. Because the band gap depends on the size of the particles, we concluded that in ultrasonic conditions, the size of the particles decreased. We also noticed an enormous blue shift of band gaps, for all obtained samples. FT-IR spectra revealed that the obtained PbS powders contain no unreacted or intermediate products of the reaction.

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