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Comparative analysis of Optical band gap and Urbach Energy of Lead Selenide (PbSe) Nano Crystalline structures

Dr. Jignesh B. Chauhan

Lecturer of Physics, Government Polytechnic, Kheda (Gujarat) Email ID: jbclph@gmail.com

Abstract
In this time of AI and Quantum Computing the semiconducting materials have become the backbone of these industries. It has been observed that Lead Selenide (PbSe) has some amazing properties such as direct band gap and it might be very much useful in semiconductor industries. Highly pure Nano crystalline structures of Lead Selenide such as thin film developed by CBD (Chemical Bath Deposition) technique and pallet are prepared. UV- Visible analysis of Nano crystalline PbSe structures have been carried out and nature of optical transition evaluated from the absorption data. The Urbach Energy and Optical band gap of both the Nano crystalline structures have been calculated and compared. The obtained results indicate that these semiconducting materials might be very useful in photovoltaic devices and Solar cells.

Keywords: Optical Band Gap; Lead Selenide (PbSe); Pallet; Thin film; UV-Vis; Semiconductor; Urbach Energy; Tauc's Plot; Absorbance;

1. Introduction

Recently AI and Nanotechnology has vastly revolutionized the human life. We have been able to achieve the things that previously thought of being unreachable. So as we deep dive into the root cause of this advancements then one and the most fundamental thing that appear into picture is Semiconducting material. So previously we know only basic semiconducting materials like Silicon and Germanium but with our technological advancements and rigorous research in this field have lead us to many more semiconducting materials far better than the basic one. So here we have been working on Lead Selenide semiconducting material which have shown very good potential in the field of semiconducting industries. [1] Lead selenide is an important semiconductor material with interesting properties such as direct band gap and abundance in nature. Thus, lead selenide have been widely used in a variety of fields such as solar cells, thermoelectric cooling, optical recording, light emitting diodes, sensors, laser and transistors.[2] The exceptional optical, electrical and semiconducting properties of CdSe and PbSe compounds form the backbone of the electronic industry and the foundation of contemporary technology.[3] Lead selenide (PbSe) thin films are important IV-VI
semiconductor materials with cubic structures and have proved to be promising because of their unusual characteristics such as high carrier mobilities, high dielectric constants and narrow band gaps which make them unique and have many important applications in the field of solid state basic research.[4] In past and recent years very few researchers have worked on the Nano crystalline powder form of Lead selenide. In this research work there is a vast study on Nano crystalline powder Lead Selenide.
The UV-VIS studies on optical absorption properties have been carried out of both highly pure Nano crystalline structures of Lead Selenide.

2. Synthesis of highly pure Nanocrystalline Lead Selenide (PbSe) structures :-

The highly pure (99.99%) nano crystalline powder form of Lead (Pb) and Selenium (Se) were weighted with extreme accuracy using Reptech RA-503 weighing scale and sampled as per specific experimentation. As the research demands semiconducting properties of any material can be carried out by analyzing highly pure nanocrystalline structures of that material. So here the research has been carried out by analyzing following two nanocrystalline highly pure structures of Lead Selenide (PbSe)

i. Highly pure pallet of PbSe
ii. Thin film grown by Chemical Bath Deposition method (CBD) of PbSe

2.1 Highly Pure Pallet of Lead Selenide (PbSe) :-

Highly pure Lead (Pb) and Selenium (Se) powder having purity 99.99% have been used to synthesize nanocystalline highly pure pallet of Lead Selenide. Synthesized pallet has been annealed at 200oC temperature in temperature controlled and precisely regulated hot air oven for required time period.

2.2 Thin film grown by Chemical Bath Deposition method (CBD) of Lead Selenide (PbSe):

Thin films are one of the most significant thing in order to characterize and study any semiconducting material. Wide range of methods available to develop thin films of any semiconducting material out of which here the research has been carried out on the thin films developed by Chemical Bath Deposition Method (CBD). Chemical Bath Deposition (CBD) is one of the highly appreciated method to develop thin films of semiconducting material. It is a very sophisticated and simple method that can be carried out by using not very advanced equipment's.

Here to develop Lead Selenide (PbSe) thin film Lead Nitrate Pb(NO3)2 is used as Lead source and Sodium Selenate (Na2SeO4) is used as selenium source. Tartaric Acid (C4H4O6) is used as a complexing agent and pH of the solution is adjusted using Ammonia (NH4OH). Prepared solution has been taken to instrument for specific temperature and time period. At 3rd attempt of the experimentation highly pure thin film of Lead Selenide (PbSe) has been developed.
UV-VIS (Ultraviolet- Visible) spectroscopy analysis has been carried out to study optical properties of these developed highly pure nanocrystalline structures of Lead Selenide (PbSe). UV-Vis NIR spectroscopy characterization has been carried out on the instrument Shimazdu UV-3600.

3. UV-VIS Analysis:-
The UV-VIS (Ultraviolet- Visible) spectroscopy is a technique of optical spectroscopy that uses visible, near infrared and ultraviolet light for evaluation of molecular and optical properties of the sample. [5,6]. The UV-Vis analysis is basically an optical process in which three types of light waves (i) Ultraviolet, (ii) Visible and (iii) Near Infrared which have wavelength from 150 nm to 3500 nm has been passed or transmitted through given sample material. Now when the light is transmitted through the sample some of the light is absorbed by the sample and some of the light is reflected by it. This phenomenon has been recorded by the detector in the instrument. Now the instrument will measure the intensity of the detected light and this intensity will give the most influential information regarding chemical composition of the material. [7]
As the synthesized highly pure nano crystalline structures of Lead Selenide (PbSe) gone under UV-Vis analysis the Fig-1 shows reflectance graph of highly pure nancrsyalline pallet and Fig-2 shows transmittance graph for Lead Selenide (PbSe) thin film. Fig-3 shows wavelength verses absorbance plot for highly pure Lead Selenide (PbSe) nanocrystalline pallet and Fig-4 shows absorbance verses wavelength plot for Lead Selenide (PbSe) thin film grown by Chemical Bath Deposition method.

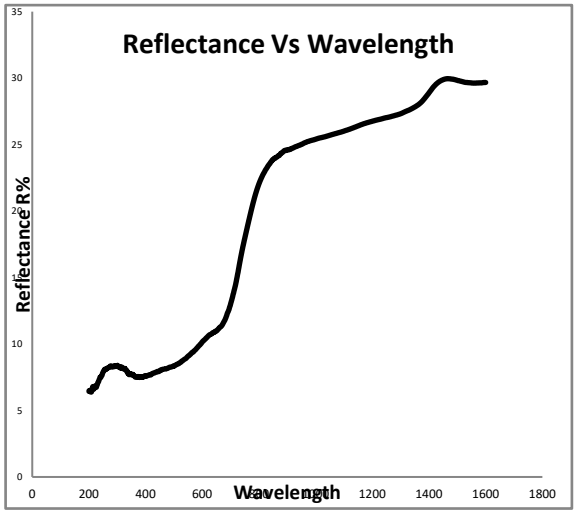


Fig-1 Reflectance Plot for Highly pure Pallet of PbSe.

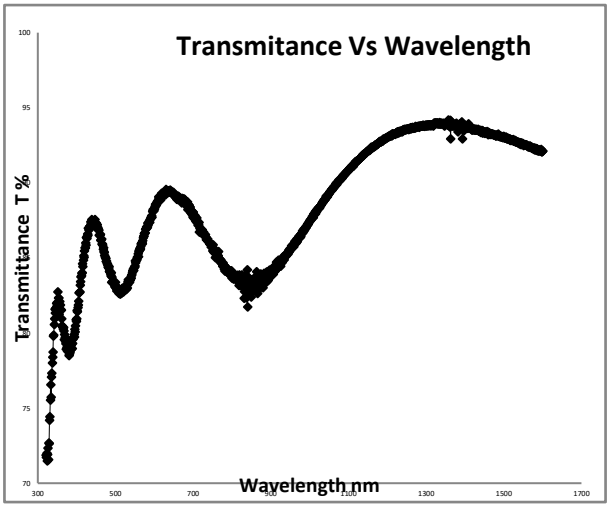


Fig-2 Transmittance Plot for Thin film of PbSe

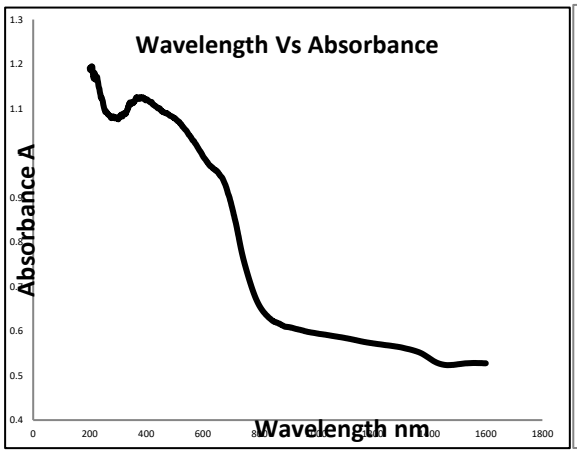


Fig-3 Absorbance Vs Wavelength Plot for PbSe Pallet.

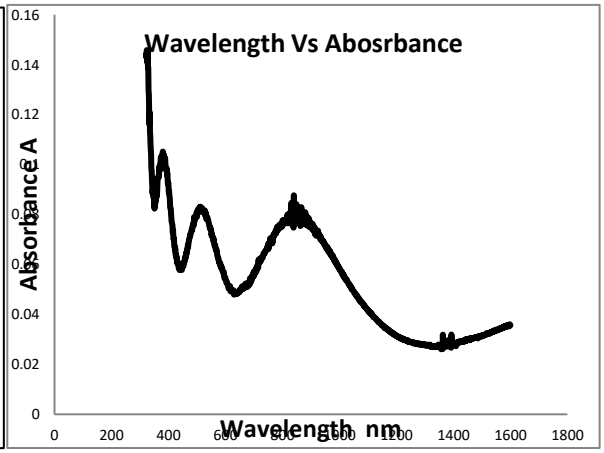
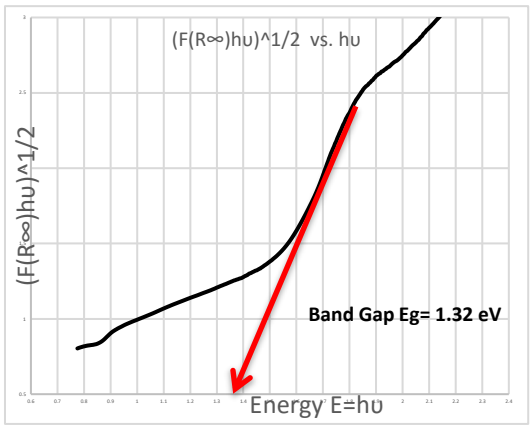


Fig-4 Absorbance Vs Wavelength Plot for PbSe Thin Film

3.1 Calculation of Optical Band Gap:-
The UV-Vis-NIR spectroscopy of highly pure pallet is done via reflectance of the incident light beam energy from the sample and for that the Shimazdu UV-3600 instrument is tuned Diffuse Reflectance Spectroscopy

(DRS) mode. While in order to do UV-Vis analysis of highly pure thin film done by transmittance of the incident light beam energy from the thin film and for that the Shimazdu UV-3600 instrument is tuned into transmittance mode.



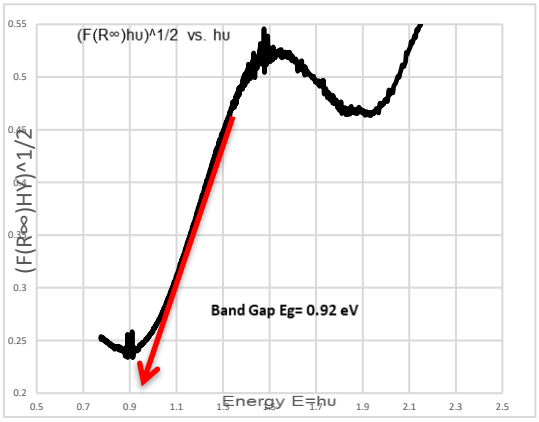


Fig-5 Tauc's Plot for for Pallet of PbSe.

Fig-6 Tauc's Plot for Thin Film of PbSe

The data of the reflectance and transmittance is received and further analyzed for the calculation of Band gap. In order to calculate optical band gap of synthesized nanocrystalline structures Tauc's plot and Tauc's equation has been used. By using Tauc's formula following plots has been developed for both structures. [8]

Above Fig-5 shows Tauc's plot for calculation of band gap of highly pure nanocrystalline pallet of Lead Selenide (PbSe) and Fig-6 shows Tauc's plot for Lead Selenide (PbSe) thin film. Now as per the calculation of Tauc's plot the measured band gap of highly pure PbSe pallet is 1.32 eV while the measured band gap of PbSe thin film is 0.92 eV.

4. Urbach Energy:-

Discovered by Franz Urbach the Urbach energy is very interesting and important phenomenon to understand the structural behavior of any semiconducting material. For any semiconducting material Urbach energy gives any type of imperfections or disorder present in its crystalline structure. [9] It has been observed that in crystalline material there has been a common sub band gap absorption existed which can be cultivated as Urbach tail. The existence of states that extend into the bandgap is what causes the Urbach tail. A statistic known as Urbach energy EU is used to quantify its width. Urbach energy is a temperature depended quantity. As it indicates disorder If the semiconducting material has low Urbach energy shows highly ordered crystalline structure while high Urbach energy indicates presence of high structural disorder. [10]

Further if we elaborate these facts then we can say that when any semiconducting material is incident with light the elctron present in them will go from valence band to the conduction band. Generally these bands (Valence and Conduction) have edges which is very sharp. Now these semiconducting materials have present in them structural imperfections, defects and impurities that make some kind of disturbance near the band edges. So Because of this, the absorption coefficient does not drastically drop below the fundamental band gap. Rather, it displays an exponential tail. And hence this exponential tail is called the Urbach tail the characteristic energy related with it is known as Urbach Energy. [11]

4.1 Characteristics of Urabch Energy:-

The energy breadth of the exponential absorption edge in any semiconducting material is called Urbach Energy of that semiconducting material. So in simple language Urabch energy indicates imperfections or disorder present in any semiconducting material. Following table shows the structural behavior of any semiconducting material with Urbach Energy value.

Urabch Energy value	What does it indicates
High	Greater structural disorder and flaws are indicated by higher Urbach energy
Low	Better structural order and fewer flaws are indicated by lower Urbach energy

4.2 Calculation of Urabch Energy:-

As we have studied earlier the UV-Vis analysis of any semiconducting material will give absorbance of that semiconducting material with wavelength. So the absorption coefficient has been illustrated as below.

$$\alpha = \alpha_0 \, e^{\frac{(E-E_0)}{E_U}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where α is an optical absorption coefficient, α_0 is constant related to absorption, E is Photon energy that is incident on that semiconducting material in eV, E_0 is reference energy in eV and E_U is known as Urabch Energy. Further analyzing above equation it will give us

$$E_U = \frac{1}{\text{Slope}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

So the slope of the plot ln α versus Photon energy will give the Urbach Energy. Applying the above formula and calculating the values of Urbach Energy for the highly pure nanocrstalline structures of Lead Selenide. The following table shows values of Urbach Energy for both nanocrystalline structures.

Nano crystalline Structure	**Urbach Energy**
Highly pure Lead Selenide (PbSe) Pallet	0.7970 eV
Thin film grown by CBD method of Lead Selenide (PbSe)	0.3610 eV

5. Conclusion:

Here in these research highly pure nano crystalline structures of Lead Selenide has been analyzed by UV-Vis analysis for calculating Optical Properties of them like Optical Band Gap and Urbach Energy. The Calculated values of Optical Band Gap for highly pure nanocrystalline Lead Selenide (PbSe) pallet is 1.32 eV while the Optical Band Gap for Lead Selenide (PbSe) thin film grown by Chemical Bath Deposition (CBD) method is 0.92 eV. So the value of Optical band gap of both the structures indicates that Lead Selenide (PbSe) Thin film has promising value of Optical Band Gap for its use in the photovoltaic devices and Solar Cells.

Now the calculated values of Urbach energy for both the nanocrystalline structures of Lead Selenide (PbSe) indicate following important facts. The evaluated value of Urbach Energy for highly pure nanocrystalline structure of Lead Selenide (PbSe) is 0.7970 eV while the Urbach Energy calculated for Lead Selenide thin film grown by CBD method is 0.3610 eV. So here the evaluated value of Urbach energy indicated that the highly pure nanocrystalline PbSe pallet has higher structural defects and imperfections. The structure of Lead Selinde Pallet is amorphous and has more thermal vibrations of atoms. Now the calculated value of Urbach Energy of Lead Selenide thin film grown by Chemical Bath Deposition (CBD) method is 0.3610 eV. So it is clear that the thin film of Lead Selenide (PbSe) has fewer defects and imperfections present in it and also it has fewer impurities.

So finally we can conclude that Lead Selenide (PbSe) thin film grown by Chemical Bath Deposition method has very great potential to be used in Photovoltaic devices and Solar Cells.

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