

Comparative investigation for the optical and molecular properties of various Lead Selenide nanocrystalline structures.

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Abstract— Nanocrystalline structures of Lead Selenide in the form of pallet grown by precisely adjusted temperature with pressure and thin film grown by chemical bath deposition method are compared on the scale of their optical and molecular properties. The optical properties of Lead Selenide pallet and thin film have been studied by UV-VIS-NIR spectrophotometer. The molecular properties of Lead Selenide pallet and thin film have been studied by Fourier Transformed Infrared Spectroscopy (FTIR). Band gap of both the nanocrystalline structures evaluated by UV-VIS-NIR spectrophotometer analysis using Tauc's equation and Tauc's plot. The calculated optical band gap for Lead Selenide pallet form is 1.33 eV and Lead Selenide thin film is 0.92 eV. The FTIR analysis gives the molecular functional groups present in both the nanocrystalline structures. The FTIR analysis suggest the presence of bonded structure like alcohol and alkene in both the nanocrystalline structures.

Keywords :- PbSe, Nanocrystalline, Pallet, Thin film, Chemical Bath Deposition method, UV-VIS-NIR Spectrophotometer, Fourier Transformed Infrared Spectroscopy (FTIR), Band gap, Functional group.

I. INTRODUCTION

We are leaving in the world having electronics and electrical items everywhere and almost in everything today. These electrical and electronics items are having no use without the fundamental elements of them that is semiconductor. Recently we have seen that the shortfall of semiconducting chips have affected many industries. Some of the companies have to shut their whole business and some have to reduce their production due to the shortfall of semiconducting chips. The world is not imaginable without the semiconductors and after their first discovery in 1947 this area has never looked back every day new advancement have kept it flourished.[1] The semiconducting materials or semiconductors are the building blocks for the production of optoelectronic devices, solar cells, Infrared arrays, gas sensors, high power microwave transistors, and solar thermal devices.

As we see the periodic table many elements possesses semiconducting nature and can be very useful in the development of the semiconductors. The Group XIV elements such as Silicon and Germanium are very pure and very well-

known in the field of Semiconductors. The other important semiconducting elements such as gallium arsenide lies between groups III and V also there are other elements that lies between group II and IV and IV and IV. Crystalline solids can play important role in the field of semiconducting materials.[3]

Lead Selenide is a Transition Metal Chalcogenide (TMC) of the group IV-VI element that is very important in the field of semiconducting material or semiconductors. Study of the characteristics of Lead Selenide (PbSe) nanocrystalline structures has attracted many researchers now days.

Here the optical properties of Lead Selenide nanocrystalline structures are studied by UV-VIS-NIR Spectrophotometer while the molecular properties has been analyzed by Fourier Transformed Infrared Spectroscopy (FTIR).

II. GROWTH OF NANOCRYSTALLINE LEAD SELENIDE STRUCTURES

The characterization of any semiconducting material can be studied in their nanocrystalline form. Here two types of Lead Selenide nanocrystalline materials are developed.

(A) Highly pure nanocrystalline pallet.

(B) Thin film by Chemical Bath Deposition (CBD) method.

A. Highly pure nanocrystalline pallet

In order to develop highly pure pallet of Lead Selenide Lead(Pb) powder and Selenium(Se) powder having purity 99.99% are mixed well by calculating and adjusting their precise molecular weight. The prepared sample is taken in highly accurate air pressure controlled pallet making machine. By applying 5 ton pressure for approx. 2 minute then a coherent and nice thin pallet is developed. The pallet is then annealed at 200 °C temperature for 30 minutes to 1 Hour. Now the pallet is taken in sample holder and ready for the characterization.

B. Thin film by Chemical Bath Deposition (CBD) method.

Chemical Bath Deposition (CBD) is the most

suitable and low cost method for the development of Lead Selenide (PbSe) thin film. The Lead Selenide thin film is deposited on the glass substrate. Before the deposition of thin film the cleaning of substrate is crucial. The substrate is first cleaned with normal tap water then scrubbed with detergent and again washed with water. Now it is scrubbed with ethyl alcohol and then washed with double distilled water. At last the substrate is dried in the air for 30 minutes. Lead Nitrate (PbNO_3) is used as Lead source while Sodium Selenate (Na_2SeO_4) taken as selenium source. Tartaric Acid ($\text{C}_4\text{H}_4\text{O}_6$) solution is used as complexing agent and the pH of the final solution is adjusted by adding Ammonia solution (NH_4OH). All the solution are prepared in double distilled water. 0.5 M 50 ml Lead Nitrate- $\text{Pb}(\text{NO}_3)_2$ is mixed well with 0.5 M 50 ml Sodium Selenate (Na_2SeO_4) solution. Now 0.5 M 25 ml Tartaric Acid ($\text{C}_4\text{H}_4\text{O}_6$) solution is added to the mixture with constant stirring with glass rod. The pH of the solution is adjusted to the desired level by adding 15 ml 30% Ammonia Solution (NH_4OH). A previously cleaned glass substrate is then inserted vertically into the solution beaker. The prepared solution beaker is then sealed with watch glass and inserted into self-developed instrument for the thin film growth. The temperature is kept constant 90°C for 120 minutes. After 120 minutes the beaker is removed from the instrument, glass substrate is taken out and cleaned with double distilled water. A nice, uniform and adherent thin film is seen developed on the glass substrate. Now it is then taken in the sample holder and ready for characterization.

III. UV-VIS-NIR SPECTROPHOTOMETER ANALYSIS

The UV-Vis-NIR is actually study of the absorption and reflectance of Ultraviolet, Visible and Near Infrared spectra from the sample. Here in the UV-Vis-NIR spectroscopy the electrons in the ground state are excited into higher energy states so it is also known as Electronic spectroscopy. The UV region is the light having wavelength 200 nm to 380 nm, Visible(Vis) is the light having wavelength 380 nm to 780 nm and Near Infrared(NIR) is the light having wavelength 800 nm to 2500 nm. The UV-Vis-NIR analysis is used from four decades and today it has become the most important analytical instrument.[5]

The principle of the UV-Vis-NIR spectroscopy is that a beam of light of Ultraviolet, Visible and Near Infrared of wavelength 160 nm to 3500 nm is transmitted through the sample. Depending on the sample the light beam can be either absorbed or transmitted or reflected and then detected and measured by the detector. Now the intensity of the measured light beam gives information regarding the chemical structure of the sample.[6]The UV-Vis-NIR spectroscopy technique will give the optical band gap for the taken sample of the nanocrystalline material. Band gap is the required energy for the electron or hole to move or jump from valence band to the conduction band. Band gap is the most important characteristic of semiconducting material as its value will leads towards the application of that material in various electronics and optoelectronic devices. The UV-Vis NIR spectroscopy analysis is done on the instrument Shimadzu UV-3600. Following Fig-1 shows the instrument used for UV-Vis-NIR spectroscopy.



Fig-1 Shimadzu UV-3600 Instrument

Here two types of nanocrystalline structures of Lead Selenide analyzed by UV-Vis-NIR spectroscopy using following methods.

- A. Highly pure pallet- Reflectance UV-Vis- NIR spectroscopy.
- B. Thin film- Transmittance UV-Vis-NIR spectroscopy.

A. Reflectance UV-Vis- NIR spectroscopy for highly pure pallet

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 Shimadzu UV-3600 instrument is tuned Diffuse Reflectance Spectroscopy (DRS) mode. The data of the reflectance is received and further analyzed for the calculation of Band gap.

Tauc's equation and Tauc's plot is used for the calculation of Band gap of the sample. The Tauc's equation is as following equation (1).

$$(\alpha h\nu)^\gamma = A(h\nu - E_g) \dots \dots \dots (1)$$

Here, α = Absorption Coefficient,

h = Planc's constant,

ν = Photon frequency,

A = Proportionality constant

(Which is 1 for amorphous material)

E_g = Band gap energy

γ = Nature of electronic transition.

In the Tauc's equation (1) γ is very important term as its value will define the electronic transition configuration. Following table-1 shows the nature of electronic transition from the value of γ .

TABLE I

Value of γ	Nature of Electronic Transition
2	Direct allowed transition
1/2	Indirect allowed transition



2/3	Direct forbidden transition
1/3	Indirect forbidden transition

Generally allowed transition are dominates over the forbidden transition so γ for 2/3 and 1/3 will not be taken into consideration.

Now for the Diffuse reflectance spectroscopy (DRS) in the equation (1) α has to be replaced by $F(R_{\infty})$.

So, $(F(R_{\infty})h\nu)^{\gamma} = A(h\nu - E_g) \dots \dots \dots (2)$

In the equation (2) $F(R_{\infty})$ is the Kubelka-Munk function, which is ratio of absorption coefficient (k) to scattering coefficient (s).

$$F(R_{\infty}) = \frac{k}{s} = \frac{(1 - R_{\infty})^2}{2 R_{\infty}} \dots \dots \dots (3)$$

Here R_{∞} is the percentage of reflectance obtained from the Diffuse reflectance spectroscopy data. As it is seen that the term R has subscript ∞ which denotes that the layer of the taken sample is thick enough to hide the support on which it is mounted.

Comparing above equation (2) with the linear equation $y = mx + c$ then it is seen that $(F(R_{\infty})h\nu)^{\gamma}$ is y axes, $h\nu$ is x axes, $A E_g$ is constant C. For the calculation of band gap of highly pure pallet two plots has to be drawn and analyzed for different values of γ .

1. For $\gamma = 2$, $(F(R_{\infty})h\nu)^2$ vs. Energy $h\nu$
2. For $\gamma = 1/2$, $(F(R_{\infty})h\nu)^{1/2}$ vs. Energy $h\nu$

Out of these two graphs the best suitable graph as per Tauc's theory is to be considered for the calculation of Band gap.

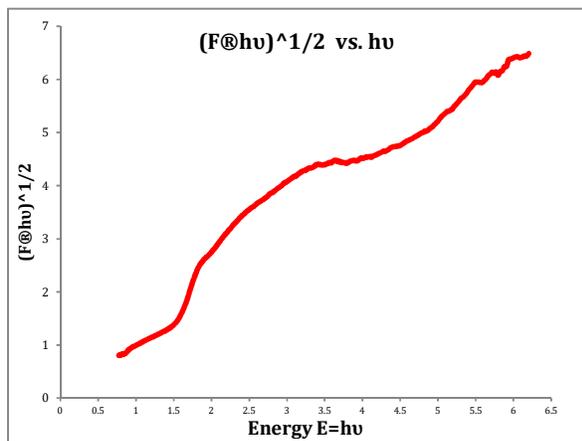


Fig-2 $(F(R_{\infty})h\nu)^{1/2}$ vs. Energy $h\nu$

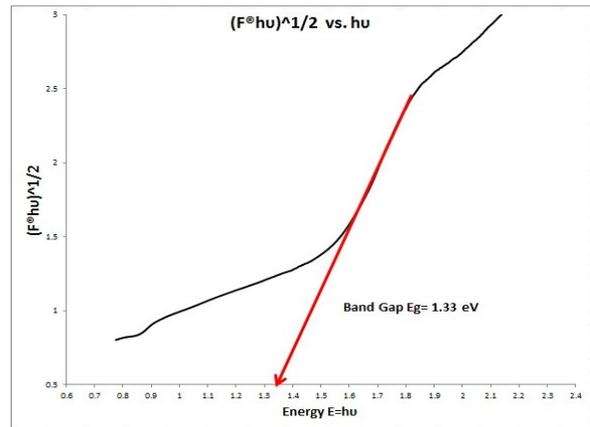


Fig-3 Band Gap Calculation

As per the Tauc's theory carefully analyzing both the plots the plot for the value of $\gamma = 1/2$ which is $(F(R_{\infty})h\nu)^{1/2}$ vs. Energy $h\nu$ for the indirect allowed transition is best suitable for the Band gap calculation. Fig-2 and Fig-3 are the plots for indirect allowed electronic transition for the calculation of optical Band gap of the Lead Selenide highly pure pallet. As shown in Fig-3 a linear line is drawn intercepting the x axis from the most linear part of the plot and this intercept gives the value of optical Band gap for Lead Selenide highly pure pallet which is for indirect allowed transition. The calculated value of Band gap is,

Band Gap $E_g = 1.33$ eV

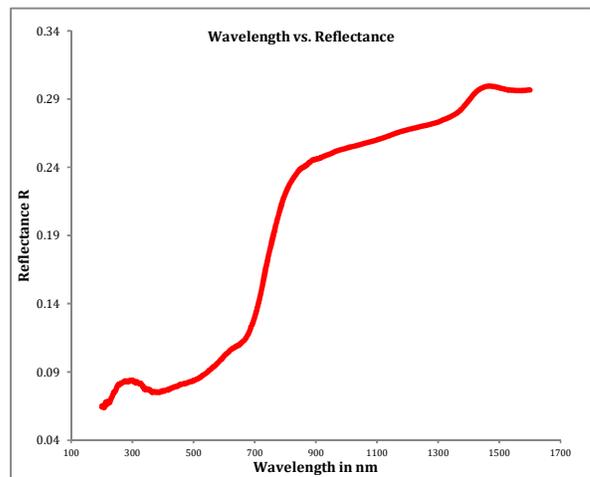


Fig-4 Reflectance vs. wavelength

Fig-4 shows the plot of Reflectance vs. Wavelength and it is observed that the reflectance of photons from the Lead Selenide sample is linearly increasing with the increase of the wavelength.



B. Transmittance UV-Vis- NIR spectroscopy for Thin film of Lead Selenide grown by CBD method.

The UV-Vis-NIR spectroscopy of highly pure pallet is done via transmittance of the incident light beam energy from the thin film and for that the Shimadzu UV-3600 instrument is tuned into transmittance mode. Here transmittance data is received from the instrument which is further characterized for the optical Band gap calculation.

Tauc's plot and Tauc's equation is used for the calculation of Optical Band gap for the Lead Selenide thin film. The Tauc's equation is shown in equation (1). For the calculation of absorption coefficient the Beer-Lambert law is used.

According to the Beer-Lambert law the transmittance energy is equal to the exponentially decaying incident energy. The below Figure-5 is the graphical representation for the theory given by Beer-Lambert.

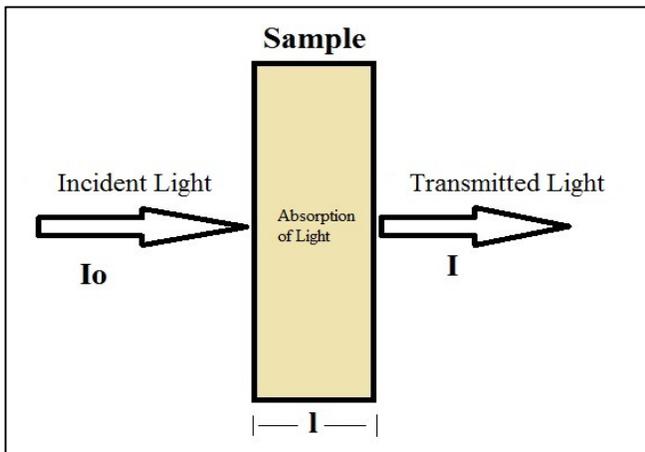


Fig-5 The Beer-Lambert law Image

From the Beer-Lambert law,

$$I = I_0 e^{-\alpha l} \dots\dots\dots (4)$$

Here, α = Absorption Co efficient of the sample

l = Thickness of the sample

Simplifying equation (4) we get,

$$\alpha = 2.302 \times A \text{ cm}^{-1} \dots\dots\dots (5)$$

Here A is absorbance and $A = \log (I/I_0)$

Above equation (5) is standard equation for the calculation of absorption coefficient from the transmittance data.

Now the incident energy $E = hv = \frac{hc}{\lambda} \dots\dots\dots (6)$

Simplifying above equation (6) and converting in the eV unit then we get,

$$\text{Energy } E = \frac{1240}{\lambda} \text{ eV} \dots\dots\dots (7)$$

Above equation (7) is the standard equation for the calculation of the incident energy. As discussed in section A now plotting the graphs for two different values of γ and selecting the best suitable plot as per Tauc's theory it is observed that the best suitable plot is for the indirect electronic transition (i.e $\gamma=1/2$).

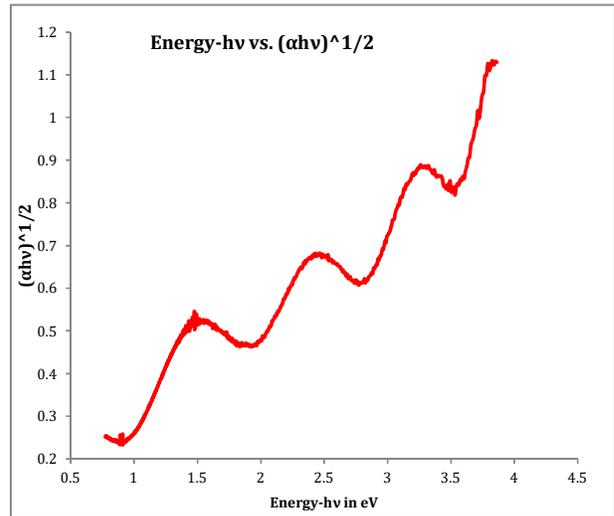


Fig-6 Plot of Energy-hv vs. $(ahv)^{1/2}$

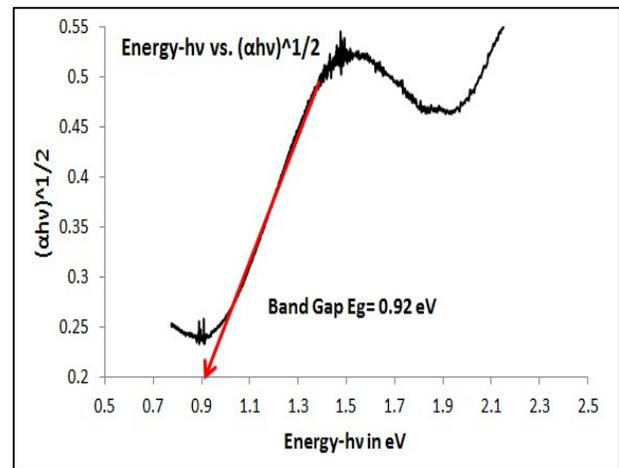


Fig-7 Band gap calculation

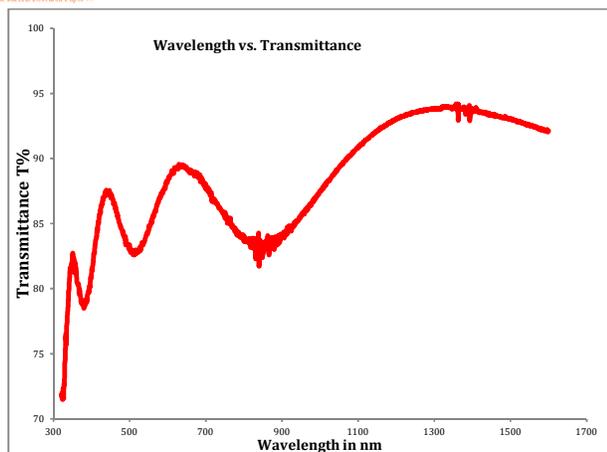


Fig-8 Transmittance vs. Wavelength

Now the above Fig (6) is the Plot of Energy- $h\nu$ vs. $(\alpha h\nu)^{1/2}$ for indirect electronic transition. Fig (7) is the plot for the Band gap calculation as per Tauc's theory. Analyzing the plot the intercept on x axis on the plot in the Fig (7) is the Optical Band gap for the thin film of Lead Selenide grown by Chemical Bath Deposition method. [2] proposed a system, this fully automatic vehicle is equipped with micro controller, motor driving mechanism and battery. The power stored in the battery is used to drive the DC motor that causes the movement to AGV. The speed of rotation of DC motor i.e., velocity of AGV is controlled by the microprocessor controller. This is an era of automation where it is broadly defined as replacement of manual effort by mechanical power in all degrees of automation. The operation remains an essential part of the system although with changing demands on physical input as the degree of mechanization is increased. [4] proposed a principle in which another NN yield input control law was created for an under incited quad rotor UAV which uses the regular limitations of the under incited framework to create virtual control contributions to ensure the UAV tracks a craved direction. Utilizing the versatile back venturing method, every one of the six DOF are effectively followed utilizing just four control inputs while within the sight of un demonstrated flow and limited unsettling influences.

Optical Band Gap $E_g = 0.92$ eV

IV. FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

FTIR gives the structural and molecular identification of any material sample analyzed under it. So it is a molecular property of the material.

The Fourier Transform Infrared Spectroscopy (FTIR) is the widely used techniques by researchers to determine the chemical functional groups present in any material sample. Each

element possesses various types of functional groups depending upon their atomic and molecular structures and each functional group absorbs specific range of Infrared Radiation (IR) frequency. The FTIR technique is capable of evaluating very broad range of functional groups presents in variety of material phases like solid, liquid and gas. So, it is regardless to say that the FTIR spectroscopy is phenomenal and widely acceptable technique for chemical compound and molecular structural identification in any material sample. [7]

Here in FTIR spectroscopy Infrared radiation is passed through the sample of any material. During which some radiation will be passed through (transmitted through) the sample while some of the IR radiation will be absorbed by the sample. This phenomenon of absorption and transmission will be recorded by the detector and as a result a spectrum will be created. This spectrum represents the molecular figure print of the sample as each molecular structure presents specific peak in the spectrum. Comparing the peak values observed in the spectrum with the standard data will give the molecular functional groups presents in the sample. [8] FTIR analysis is able to determine unknown materials, quality and consistency of the sample taken also the amount of components in the sample.

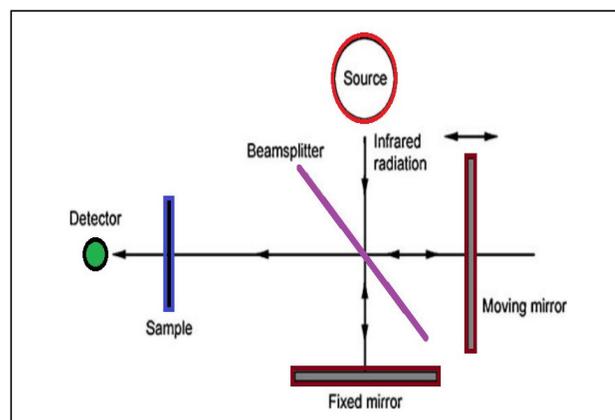


Fig-9 FTIR Analysis schematic diagram

The above Fig-9 is the schematic diagram for the FTIR analysis instrument. Here in the FTIR analysis the spectrum of the sample is generated by the interference of IR light incident on it. The instrument consist of (1) IR Source, (2) Moving Mirror, (3) Fixed Mirror, (4) Laser, (5) Detector and (6) Beam Splitter. In the instrument the combo of Beam splitter and the two mirrors are known as Interferometer. The light produced by IR source will strike the beam splitter as a result of this two light rays of almost same intensity will be produced. Out of the two beams one strikes the fixed mirror and returns back while the other goes towards the moving mirror. During this a beam of laser also goes parallel to the IR beam and passes through the interferometer. The moving mirror will oscillates at

a constant frequency which generates the interference pattern. This interference pattern is the record of the wavelengths transmitted through the sample and using the Fourier transform algorithm the interference pattern is converted into spectrum. The spectrum is digitized and processed using a computer. [9] The peaks observed in the spectrum represents the functional groups present in the sample. Following Table II show the functional groups representing the peaks in the IR spectrum.

TABLE II

Wavenumber of Peak	Intensity and Thickness of Peak	Functional Group
3700-3200	Medium and Sharp	Alcohol (O-H)
3550-3200	Medium	Amines (N-H)
3300	Strong	Alkyne (C≡C-H)
3300-2500	Strong and Broad	Carboxyl Acid (O-H)
3333-3267	Strong and Sharp	Alkyne (C-H)
3100-3000	Medium	Alkene (C-H)
3000-2840	Medium	Alkane (C-H)
2830-2695	Medium	Aldehyde (C-H)
2600-2550	Weak	Thiol (S-H)
2260-2100	Weak	Alkyne (C≡C)
2000-1650	Weak	Aromatic (C-H)
1875-1785	Strong	Acid Halide(C-O)
1678-1600	Weak and Sharp	Alkene (C=C)
1650-1550	Medium	Cyclic Alkene (C=C)
1550-1500	Strong	Nitro (N-O)

As shown in above Table II the peaks observed in the FTIR spectrum is classified in two ways.

- As per peak thickness- (i) Sharp, (ii) Broad
- As per peak intensity- (i) Strong, (ii) Medium (iii) Weak

Spectrum obtained from FTIR analysis is analyzed by the comparison of peaks thickness and intensity observed from the above Table II. Generally the FTIR spectrum is the plot of Transmittance in % versus Wave number in cm^{-1} . The FTIR analysis of Lead Selenide nano crystalline structures is done by Thermo Scientific nicolet 6700 which is shown in below Fig-10.



Fig-10 FTIR Analysis Instrument Nicolet 6700

A. FTIR analysis of Lead Selenide highly pure pallet

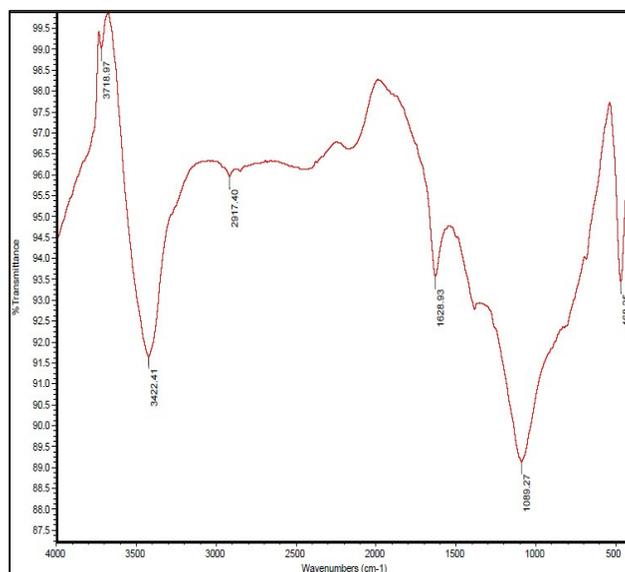


Fig-11 FTIR Spectrum of Lead Selenide Pallet

Fig-11 shows the FTIR spectrum of Lead Selenide highly pure pallet. Now the region above wavenumber 1500 is called functional group region while the region below 1500 wavenumber is known as fingerprint region. The analysis of the data for fingerprint region is seen conflicting in some

manner so it is advisable to avoid it for to the point analysis. Here analyzing the FTIR plot important results are obtained as shown in Table III.

TABLE III

Sr No	Wavenumber for the Peak	Peak Intensity and Thickness	Functional Group
1	3422.41 cm^{-1}	Medium and Sharp	Alcohol (O-H)
2	1628.93 cm^{-1}	Weak and Sharp	Alkene (C=C)

TABLE IV

Sr No	Wavenumber for the Peak	Peak Intensity and Thickness	Functional Group
1	3407.23 cm^{-1}	Medium and Sharp	Alcohol (O-H)
2	1555.49 cm^{-1}	Weak and Sharp	Alkene (C=C) or Cyclic Alkene (C=C)

Here as shown in above Table IV for the first peak is observed at 3407.23 cm^{-1} which represents the Alcohol (O-H) stretch present in the sample. The second peak observed at 1555.49 cm^{-1} which as discussed earlier almost in the figure print region so it can be said that the resultant functional group is either Alkene (C=C) or Cyclic Alkene (C=C).

V. CONCLUSIONS

Lead Selenide (PbSe) is very promising material in the field of semiconductors. Lead Selenide nanocrystalline structures in the form of highly pure pallet and Thin film grown by chemical bath deposition method are developed. Optical and molecular characterization comparative studies on both the nanocrystalline structures gives following important information.

B. FTIR analysis of Lead Selenide Thin film grown by CBD Method

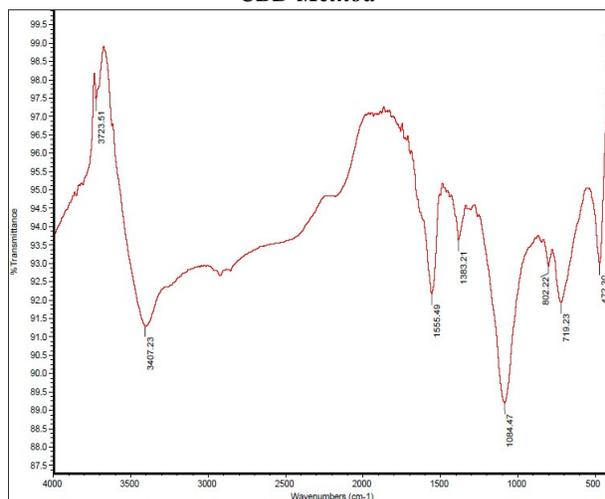


Fig-12 FTIR Spectrum of Lead Selenide Thin film

Fig-12 shows the FTIR spectrum of the Lead Selenide thin film grown by the Chemical Bath deposition method. Analyzing the FTIR spectrum shown in Fig-12 the obtained results are shown in following Table IV.

A. UV-Vis-NIR Spectrophotometer Analysis

UV-Vis-NIR Analysis Characteristics	PbSe Pallet	PbSe Thin film
Optical Band gap (Indirect electronic transition)	1.33 eV	0.92 eV

B. FTIR Analysis

FTIR Analysis Characteristics	PbSe Pallet	PbSe Thin film
Molecular functional Group	O-H (Alcohol) & Alkene (C=C)	O-H (Alcohol) & Alkene (C=C)

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