CHAPTER 4

OPTICAL BEHAVIOUR OF

MoS$_2$ AND MoSe$_2$ SINGLE CRYSTALS
4.1 INTRODUCTION

The optical band gap measurements on MoS$_2$ and MoSe$_2$ single crystals, grown by chemical vapor transport method are taken up a systematic study. It is desirable to give an adequate description of the experimental technique employed for this investigation.

The aim of this chapter is to provide an update information regarding the experimental and instrumental technique employed in the optical characterization of the grown crystals of MoS$_2$ and MoSe$_2$.

The optical band gap, $E_g$, is of fundamental importance in the fabrication of efficient solar cells. Therefore, it is highly desirable that a determination of the optical band gap of a semiconducting material is made before determining its use in the device fabrication.

Band gaps are usually classified [1] in direct allowed and forbidden transitions. Both direct as well as indirect optical band gaps can be determined using the following methods.

1. Optical absorption
2. Photoelectrochemical methods
   - Quantum yield $\eta$ vs $h\nu$ plot
   - Action spectrum
   - Capacitance measurements
3. Intrinsic conduction measurements at high temperature
4. Photoemission
5. Band structure calculations

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The binary VI compounds have attracted considerable attention because of their use in optoelectronic [3] and infrared production and detection system [4].

Both direct as well as indirect transitions have been observed to take place in the MoS$_2$ and MoSe$_2$. It was considered highly desirable that a thorough analysis of the absorption spectra obtained from the single crystals is carried out. Therefore, looking to the importance of the optical band gap in semiconducting materials and because of the fact that no detailed study of this kind exists for MoS$_2$ and MoSe$_2$, author has carried out an in-depth study of the determination of optical band gaps in these materials by optical absorption measurements. The results thus obtained have been described in this chapter and implications have been discussed.

### 4.2 UV-VIS-NIR SPECTROPHOTOMETER

The UV-VIS-NIR Spectrophotometer (Make: Perkin Elmer, Model: Lambda -19) as shown in figure 4.1 is the latest instrument, which is used for the analysis of various compounds to find out the absorbance value and wavelength maxima in UV-VIS-NIR region. This is used in the research and development of new compounds, chemicals, dyes, optical properties of thin films, thickness and various types of filters etc. The accessory “Integrating Sphere” with Lambda-19 spectrometer helps to analyze samples in reflectance mode. This accessory helps to analyze samples like cloth, lather, films, dye-products and color-products etc. The instrument is also useful to study kinetic behavior of chemical reaction with respect to time. It can also be used for various biological
samples and reaction studies. The instrument consists of double-beam double monochromator with ratio recording of UV/VIS spectrometer with microcomputer electronics, controlled by personal computer.

Figure. 4.1 UV-VIS-NIR Spectrophotometer

**Specifications**

Double Beam, Double Monochromator, Ratio Recording

Lamp: Deuterium (UV), Tungsten-Halogen (VIS/NIR)

Detectors: Photomultiplier tube for UV/V, Lead-Sulphide cell (PbS) for NIR

Wavelength Range : 185-3200 nm

Scan speed: 0.3 to 1200 nm/min

Wavelength Accuracy : ±0.15 nm for UV/VIS & ±0.6 nm for NIR

Base line flatness : ± 0.001 Å, 4 nm slit

Ordinate Mode: Scan, Time Drive, Wavelength Programming,

Concentration

Photometric Accuracy : ± 0.003 Å or ± 0.08 %T

PECOL Software for quantitative description of color
4.3 SAMPLE PREPARATION

For obtaining the absorption spectra using UV-VIS-NIR spectrophotometer from single crystal specimens, thin flakes of approximately 0.5 mm thickness are used. These flakes are pasted on a thick black paper with a cut exposing the crystal flake to the incident light. The reference used is a replica of the black paper, having the cut in exactly the same position as the crystal flake. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Blank glass slides are also used as replica. For reflectance measurement standard aluminum coated mirror is used as reference.

4.4 OPTICAL ABSORPTION

Optical absorption of grown crystals MoS$_2$ and MoSe$_2$ were taken with UV-VIS –NIR spectrophotometer in the wavelength range 700-1450 nm at room temperature. For measuring the band gap of a semiconducting material, an important technique is that of the absorption of an incident photon by that semiconducting material. In this technique, photons of selected wavelengths are bombarded at the sample and their relative transmission is observed. Since the photons with energies greater than the band gap energy are absorbed while photons with energies less than band gap are transmitted, the technique provides an accurate measurements of the energy band gap.

If a beam of photons with energy $h\nu > E_g$ falls on a semiconductor, there will be some predictable amount of absorption determined by the properties of that semiconducting material. The ratio of transmitted to
incident radiation intensities is expected to depend on photon wavelength and the thickness of the sample.

When a photon beam of intensity $I_0$ (photon/cm²·sec) transmits through a slab of a medium of thickness $x$, the beam of photons attenuates in accordance with the exponential law

$$ I = I_0 e^{-\alpha x} \quad (4.1) $$

where $\alpha$ is called as the absorption coefficient and has units of cm⁻¹. This coefficient $\alpha$ can be obtained simply by measuring $I_0/I$ of the intensities impinging and emerging from the samples respectively.

### 4.5 DIRECT AND INDIRECT TRANSITIONS

The absorption process-taking place in a semiconductor can be described as an example of electronic transition processes, which are fully quantum mechanical in nature. These electronic transition processes give rise to interband absorption in solids, which are of two types, known as direct and indirect (interband) transitions (figure. 4.2).

In a direct transition, an electron in a Bloch energy band state below Fermi level absorbs a photon and makes a vertical transition to an upper empty state in the conduction band. The characteristics of such transitions are defined by the following conditions:

$$ k_f = k_i \quad (4.2) $$
Figure 4.2  Schematic diagram showing (a) direct and (b) indirect transitions.

\[ E_c(k_f) - E_v(k_i) = \hbar \omega \]  

(4.3)
where $k_i$ and $k_f$ are, respectively, the initial and final electron wave vectors in the valence $E_v(k)$ and the conduction $E_c(k)$ bands and $\hbar \omega$ is the photon energy. Equation 4.2 expresses conservation of momentum essentially,

$$\hbar k_f = \hbar k_i + \hbar Q$$

(4.4)

where $Q$ is the photon wave vector, is usually so small compared with the dimensions of the Brillouin zone that one may take $\hbar Q \approx 0$. Equation 4.3 expresses energy conservation.

In general, however, at high temperatures phonons are present and can participate in the absorption process. Such phonon assisted transitions can not be vertical because the momentum $\hbar q$ must be added to the right hand side of the equation 4.2 and similarly the condition in equation 4.3 has to include the energy of the absorbed (or emitted) phonon. The optical transition is accordingly said to be non-vertical or indirect. Such indirect transitions are quite important in semiconductors and provide a means of determining the energy band gap separating the top of the valence band and the bottom of the conduction band when these band extrema occur at different values of the $k$ vector.

### 4.6 ENERGY GAP DETERMINATION

The relationship that exists for possible transitions across the energy gap of semiconductor, the absorption coefficient $\alpha$ is proportional as follow\[1\]

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

(4.5)

for direct transitions and
\[ \alpha \nu = \sum_j B_j (\nu - E'_g \mp E_{\nu j})^r \] 

for indirect transitions.

Here, \( \alpha \) is the absorption coefficient, \( \nu \) the energy of the incident photon, \( E_g \) the energy for the direct transition and \( E'_g \) the energy for indirect transition and \( E_{\nu j} \) the energies of the phonons assisting at indirect transition. \( A \) and \( B \) are parameters depending in a more complicated way on temperature, photon energy and phonon energies \( E_p \).

However, for the analysis of the experimental results obtained at constant temperature, equations 4.5 and 4.6 are sufficient and they are most often used while interpreting results on absorption spectra obtained from semiconducting materials. The exponent \( r \) in the above equations depends upon whether the transition is symmetry allowed or not and the constants \( A \) and \( B \) will assume different values for the allowed and forbidden transitions. For indirect transitions the detailed form of equation 4.6 \([5, 8, 9]\) is given as

\[
\alpha_i = \sum_{i=1}^2 \left\{ \frac{B_{ai}}{E} \left( \frac{1}{e^{E_{pi}/kT} - 1} \right) (E - E'_g + k\theta_i)^r + \frac{B_{ei}}{E} \left( \frac{1}{1 - e^{E_{pi}/kT}} \right) (E - E'_g - k\theta_i)^r \right\} \]  

(4.7)

where \( B_{ai} \) and \( B_{ei} \) are coefficients associated with absorption and emission of \( i^{th} \) phonon. \( E \) the photon energy, \( E'_g \) the indirect energy gap and \( \theta_i \) is a phonon equivalent temperature defined by the equation

\[
\theta_i = \frac{E_{pi}}{k} \quad \text{(A)}
\]

\( E_{pi} \) being the \( i^{th} \) phonon energy.)

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In these cases the density of states is a constant independent of the energy and the expressions showing the dependence of $\alpha$ in terms of direct and indirect transitions get modified [10] as

$$\alpha = A'(h\nu - E_g)^r$$

(4.8)

for direct transition and

$$\alpha_i = \sum_{l=1}^{2} \left\{ B_a' \left( \frac{1}{e^{\theta_i/T} - 1} \right) (E - E_g' + k\theta_i)^r + B_e' \left( \frac{1}{1 - e^{\theta_i/T}} \right) (E - E_g' - k\theta_i)^r \right\}$$

(4.9)


The symbols in above equations have the same meaning as explained [12-15]. Again, the exponent $r$ depends on the dimensionality of the bands and whether the transitions are symmetry allowed or forbidden. Once again the coefficients $A'$, $B_a'$, and $B_e'$ will be different for symmetry allowed and forbidden transitions. Possible values of $r$ are given in table 4.1 [10, 11, 16].

**Table 4.1 Values of exponent ‘r’ for different types of band gap Transitions**

<table>
<thead>
<tr>
<th>Types of transition</th>
<th>2-dimensional</th>
<th>Direct</th>
<th>3-dimensional</th>
<th>Indirect</th>
<th>3-dimensional</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allowed</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>(step function)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forbidden</td>
<td>1</td>
<td>$\frac{3}{2}$</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>
By plotting graphs of \((\triangleq hv)^{1/r}\) against \(hv\) for various values of \(r\) given in table 4.1, it is possible to determine which of the conditions given in table 4.1 dominate. Extrapolations of these plots to zero absorption will give the appropriate value of energy gap for MoS\(_2\) and MoSe\(_2\) single crystals.

### 4.7 EXPERIMENTAL

Single crystals of MoS\(_2\) and MoSe\(_2\) used in the present investigation were grown by CVT method. The crystals grew in the form of thin platelets, as grown crystals were used to obtain the absorption spectra. Thickness of the samples were measured with a micrometer or optical microscope. The 'a' and 'b' axis were contained in the plane of cleavage.

The optical absorption spectra were obtained by UV-VIS-NIR spectrophotometer in the range 700 nm to 1450 nm. The samples were pasted on a thick black paper with a cut exposing the crystals to the incident radiation. The reference used was a replica of the black paper having the cut in exactly the same position. All measurements were performed at room temperature with the incident beam normal to the basal plane i.e. along the c-axis of the grown crystal. Measurements parallel to basal plane could not be performed since the specimens were too thin to be mounted along this direction.

### 4.8 RESULTS

The absorption spectrum of MoS\(_2\) and MoSe\(_2\) single crystal is shown in figure 4.3 (a) and (b). A careful study of this spectrum reveals presence of absorption edges in the spectral range 700 nm to 850 nm.
Figure 4.3 (a) and (b) Absorption spectrum of MoS$_2$ & MoSe$_2$ single crystal
In order to analyze the results from this spectrum in the vicinity of the absorption edge on the basis of two as well as three-dimensional model, values of absorption coefficient $\alpha$ were determined at every interval of 5 nm. The interpretation of the experimental results viz. the dependence of absorption coefficient $'\alpha'$ in terms of direct and indirect transitions can be performed with the help of formulae 4.4 and 4.5 using the various values of $r$ from table 4.1.

Accordingly, figure 4.4 for MoS$_2$ and MoSe$_2$ single crystals shows the spectral variation of $(\alpha h\nu)^{1/2}$ vs $h\nu$. Since the curves indicate discontinuous straight lines, it is quite plausible that they represent indirect interband transitions involving the emission and absorption of phonons. In order to make an accurate determination of the points of discontinuities, we have followed the method earlier successfully used for layer compounds [17-20]. Accordingly, from the graphical differentiation of the data presented in figure 4.4 for MoS$_2$ and MoSe$_2$ single crystals, the dependence of the derivatives $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ on $h\nu$ has been shown in figure 4.5 (a) and (b) for MoS$_2$ and MoSe$_2$ single crystals. It can be clearly seen from these figure that the derivatives are step function of energy with four steps well defined in the range

\[ E_1 < E < E_2, \]
\[ E_2 < E < E_3, \]
\[ E_3 < E < E_4 \quad \text{and} \]
\[ E_4 < E. \]
Figure 4.4 The spectral variation of the quantity \((\alpha \nu^2)^{1/2}\) for MoS\(_2\) and MoSe\(_2\) single crystal

These values of \(E_1\), \(E_2\), \(E_3\) and \(E_4\) indicate the points of discontinuities in the plots of \(\delta(\alpha \nu^2)^{1/2}/\delta \nu\) vs \(\nu\).

The indirect energy gaps obtained from these values of \(E_1\), \(E_2\), \(E_3\) and \(E_4\) are given by

\[
E_G' = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2}
\]  

(4.10)
Figure 4.5 (a) & (b) The spectral variation of the derivative obtained by graphical differentiation of the data represented in fig.4.4 for MoS$_2$ & MoSe$_2$ single crystal.
and the phonon energies are given by

\[ E_{pl} = \frac{E_4 - E_1}{2} \quad \text{and} \quad E_{p2} = \frac{E_4 - E_2}{2} \]  

(4.11)

The values of indirect band gap \( E'_g \) and phonon energies thus obtained are presented in table 4.2. The values of the \( E'_g \) can also be obtained from the intersection of the linear portion of the curves in figure 4.4 for MoS\(_2\) and MoSe\(_2\) single crystals with energy axis for zero absorption. These values closely matches with the value obtained from equation 4.10.

**Table 4.2** Direct and Indirect (allowed) band gap, phonon energies, \( \theta_1 \) and \( \theta_2 \) for MoS\(_2\) and MoSe\(_2\) single crystals.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value of MoS(_2) 2-Dimension</th>
<th>Value of MoS(_2) 3-Dimension</th>
<th>Value of MoSe(_2) 2-Dimension</th>
<th>Value of MoSe(_2) 3-Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_1 ) (eV)</td>
<td>1.141</td>
<td>1.136</td>
<td>1.080</td>
<td>1.080</td>
</tr>
<tr>
<td>( E_2 ) (eV)</td>
<td>1.170</td>
<td>1.172</td>
<td>1.125</td>
<td>1.100</td>
</tr>
<tr>
<td>( E_3 ) (eV)</td>
<td>1.214</td>
<td>1.214</td>
<td>1.167</td>
<td>1.150</td>
</tr>
<tr>
<td>( E_4 ) (eV)</td>
<td>1.256</td>
<td>1.256</td>
<td>1.213</td>
<td>1.172</td>
</tr>
<tr>
<td>( E'_g ) (C) (eV)</td>
<td>1.19</td>
<td>1.19</td>
<td>1.14</td>
<td>1.12</td>
</tr>
<tr>
<td>( E'_g ) (E) (eV)</td>
<td>1.25</td>
<td>1.19</td>
<td>1.14</td>
<td>1.12</td>
</tr>
<tr>
<td>( E_{p1} ) (meV)</td>
<td>57.5</td>
<td>60</td>
<td>66.5</td>
<td>46</td>
</tr>
<tr>
<td>( E_{p2} ) (meV)</td>
<td>22</td>
<td>21</td>
<td>21</td>
<td>25</td>
</tr>
<tr>
<td>( \theta_1 ) (K)</td>
<td>667.5</td>
<td>696.8</td>
<td>771.9</td>
<td>534.2</td>
</tr>
<tr>
<td>( \theta_2 ) (K)</td>
<td>255.3</td>
<td>243.7</td>
<td>243.7</td>
<td>290.3</td>
</tr>
<tr>
<td>( E_g ) (eV)(Direct)</td>
<td>1.40</td>
<td>1.42</td>
<td>1.28</td>
<td>1.30</td>
</tr>
</tbody>
</table>

\( E'_g \) (C) = indirect band gap for calculation

\( E'_g \) (E) = indirect band gap for extrapolation

\( \theta_1 \) and \( \theta_2 \) can be find out by using equation (A)
The graph of \((\alpha h\nu)^{1/3}\) vs \(h\nu\) are shown in figure 4.6 for MoS\(_2\) and MoSe\(_2\) single crystals. It is seen that the nature of these graphs widely differs from that shown in figure 4.4 for MoS\(_2\) and MoSe\(_2\) single crystals. A graphical differentiation of the data presented in these figures and the intersection of the linear portion of these curves with energy axis for zero absorption will give widely different values. It is, therefore, conjectured that the indirect transition represented by the each absorption curve is an indirect allowed type.

In order to analyze the data from the absorption curve on the basis of two-dimensional model, variation of \(\alpha^{1/2}\) vs \(h\nu\) was studied. A graph showing the spectral variation of \(\alpha^{1/2}\) is shown in figure 4.7 for MoS\(_2\) and MoSe\(_2\) single crystals.

**Figure 4.6 The spectral variation of the quantity \((\alpha h\nu)^{1/3}\) for MoS\(_2\) and MoSe\(_2\) single crystal**

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Figure 4.7 The spectral variation of the quantity \((\alpha)^{1/2}\) for MoS\(_2\) and MoSe\(_2\) single crystal

A graphical differentiation of the data presented in figure 4.8 (a) and (b) for MoS\(_2\) and MoSe\(_2\) single crystals.
Figure 4.8 (a) & (b) The spectral variation of the derivative obtained by graphical differentiation of the data represented in fig. 4.7 for MoS$_2$ & MoSe$_2$ single crystal.
The values of indirect band gap $E'_g$ obtained from the intersection of the linear portion of the curves in figure 4.7 for MoS$_2$ and MoSe$_2$ single crystals with energy axis for zero absorption and that from the graphical differentiation of the data presented in figures 4.8 (a) and (b) for MoS$_2$ and MoSe$_2$ single crystals are shown in table 4.2. The values of the phonon energies obtained from figure 4.8 (a) and (b) for MoS$_2$ and MoSe$_2$ single crystals are also shown in table 4.2 respectively. The results obtained from three dimensional analysis are also confirmed by two-dimensional analysis of the data.

From Table 4.2 it is clearly evident that the optical energy gap in MoS$_2$ and MoSe$_2$ is indirect allowed. For the determination of the direct band gap $E_g$, the spectral variation of $(a\nu f)^2$ vs $\nu$ as shown in figures 4.9 were studied. The values of direct band gap $E_g$ obtained from the intersection of the linear portion of the curves in figure 4.9 for MoS$_2$ and MoSe$_2$ single crystals with energy axis for zero absorption are shown in table 4.2.

In order to obtain the value of $E_g$ on the basis of two-dimensional model the spectral variation of $\alpha^2$ vs $\nu$ as shown in figures 4.10 for MoS$_2$ and MoSe$_2$ single crystals were studied. Here also the values of direct band gap $E_g$ obtained from the intersection of the linear portion of the curves with energy axis for zero absorption were determined and are shown in table 4.2.
From table 4.2, it is clearly evident that the indirect optical energy gap is indirect allowed with absorption and emission of the phonons with energies $E_{p1}$ and $E_{p2}$ for MoS$_2$ and MoSe$_2$ single crystals are shown in table 4.2.

![Graph showing spectral variation of $(\alpha \nu)^2$ for MoS$_2$ and MoSe$_2$](image)

**Figure 4.9** The spectral variation of the quantity $(\alpha \nu)^2$ for MoS$_2$ and MoSe$_2$ single crystal

The values of direct band gap for MoS$_2$ and MoSe$_2$ represented in table 4.2 clearly confirms that the transition is direct allowed. From table 4.2, we come to the conclusion that the two-dimensional model gives nearly
the same values of the optical energy gap for MoS$_2$ and MoSe$_2$ as those obtained from three-dimensional model with a difference between the two models being $\approx 2\%$.

Thus, we observed that both direct as well as indirect symmetry allowed transitions give a good account of the optical absorption edge in MoS$_2$ and MoSe$_2$ crystals. The values of direct and indirect band gaps obtained in the present investigation are in agreement with the reported values as can be seen from table 4.2. A careful study of the data presented in table 4.2 indicates that both direct and indirect bandgaps are more in MoS$_2$ than MoSe$_2$ single crystals.

4.9 CONCLUSIONS

The works described in this chapter is an attempt to provide some explanation of the problem of dimensionality of the layered MoS$_2$ and MoSe$_2$ single crystals. The possibility of analyzing the absorption data from these crystals on the basis of two- and three-dimensional model clearly suggest us to conclude that, it should be considered as an intermediate case between layer like two-dimensional (2D) and three-dimensional (3D)[21].

In this context, author has come to the following conclusions:

- The analysis of the optical absorption in these crystals near the fundamental edge has been shown that both direct as well as indirect allowed transitions takes place in these compounds.
Figure 4.10 The spectral variation of the quantity \((\alpha)^2\) for MoS\(_2\) and MoSe\(_2\) single crystal

- The indirect allowed transitions are involving two different phonons.
- The fact that two-dimensional model can also be used satisfactorily to describe the main optical properties of these compounds reveals that these compounds are intermediate between two and three dimensional.
REFERENCES


