# CHAPTER 5

## OPTICAL BAND GAPS IN TUNGSTEN DISELENIDE SINGLE CRYSTALS INTERCALATED BY INDIUM

<table>
<thead>
<tr>
<th>Contents</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>171</td>
</tr>
<tr>
<td>5.1.1 Optical Absorption</td>
<td>172</td>
</tr>
<tr>
<td>5.1.2 Photoelectrochemical Methods</td>
<td>176</td>
</tr>
<tr>
<td>5.1.3 Intrinsic Conduction Measurements at High Temperature</td>
<td>178</td>
</tr>
<tr>
<td>5.1.4 Photoemission</td>
<td>178</td>
</tr>
<tr>
<td>5.1.5 Band Structure Calculations</td>
<td>179</td>
</tr>
<tr>
<td>5.2 Experimental</td>
<td>181</td>
</tr>
<tr>
<td>5.3 Results</td>
<td>181</td>
</tr>
<tr>
<td>5.4 Discussion</td>
<td>186</td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td>188</td>
</tr>
<tr>
<td>Tables</td>
<td>190</td>
</tr>
<tr>
<td>Captions to the figures</td>
<td>195</td>
</tr>
<tr>
<td>References</td>
<td>209</td>
</tr>
</tbody>
</table>
5.1 INTRODUCTION

The optical band gap of a semiconducting material plays an important role in deciding the photoconversion efficiency of a solar cell fabricated with the semiconductor, it is therefore highly desirable that a determination of its optical band gap is made.

Optical band gap (direct as well as indirect) can be determined from the following methods:

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

A detailed study on growth and characterisation of indium intercalated tungsten diselenide has already been presented in Chapter 4. However, looking to the importance of optical band gap in these materials and because of the fact that observation of this kind do not exist for indium intercalated compounds,
author has carried out a detailed study on the determination of optical band gap in these materials by optical absorption. The results thus obtained have been thoroughly described in this chapter and have been compared with those determined by other methods.

### 5.1.1 Optical Absorption

An important technique for measuring the band gap of a semiconductor is the absorption of incident photon by the material. In this technique, photons of selected wavelength are directed 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 measurement of the energy band gap.

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

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

$$I = I_0 \exp (-\alpha x) \quad (5.1)$$
where \( \alpha \) is called 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 sample.

**Direct and Indirect Transitions**

The absorption process taking place in a semi-conductor can be described as an example of electronic transition processes which are truly 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 Fig.5.1.

In a direct transition, an electron in a Bloch energy band state below the 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.

\[
\vec{K}_f = \vec{K}_i \tag{5.2}
\]

\[
E_c(\vec{K}_f) - E_v(\vec{K}_i) = \hbar\omega \tag{5.3}
\]

where \( \vec{K}_i \) and \( \vec{K}_f \) are respectively, the initial and the final
electron wave vectors in the valence \( E_v(\mathbf{k}) \) and the conduction \( E_c(\mathbf{k}) \) bands and \( \hbar w \) is the photon energy. Equation (5.2) expresses conservations of momentum essentially \( \hbar k_f = \hbar k_i + \hbar Q \), where \( \mathbf{Q} \), the photon wave vector, is usually so small compared with the dimensions of the Brillouin zone that one may take \( \hbar Q = 0 \). Equation (5.3) expresses energy conservation.

In general, however, at high enough temperatures, phonons are present and can participate in the absorption process. Such phonon assisted optical transitions cannot be vertical because the phonon momentum \( \hbar \mathbf{q} \), must be added to the right hand side of equation (5.2) and similarly the condition in equation (5.3) has to include the energy of the absorbed (or emitted) photon. 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 occurs at different values of the \( \mathbf{k} \) vector.

**Energy gap determination**

According to Bardeen et al. [1], the relationships that exist for possible transitions across the energy gap of a semiconductor show that the absorption coefficient \( \alpha \) is proportional to
where 'hv' is the photon energy and 'E_g' is the band gap energy.

The exponent 'r' depends on the dimensionality of the bands and on whether the transitions are allowed or forbidden. Indirect transitions require phonon for momentum conservation. The absorption coefficient is expected to vary as

$$\alpha_n = \sum_{i=1}^{2n} \left\{ B_{ar} \frac{1}{\Gamma} \exp \frac{1}{E_{pl}/kT} - \frac{1}{\Gamma} \right\} (E_v - E_g + E_{pr})^r$$

$$+ B_{er} \frac{1}{\Gamma - \exp -E_{pl}/kT} (E_v - E_g - E_{pl})^r \right\} (5.5)$$

where $B_{ar}$ and $B_{er}$ are temperature dependent coefficients representing the processes with phonon absorption and phonon emission, $E_{pl}$ is the energy of the phonon assisting at the transition. From the expression for $E_{pl}$, phonon equivalent temperatures $\theta_p$ are defined as

$$\theta_p = E_{pl}/kT \quad (5.6)$$
Again the exponent 'r' depends on the dimensionality of the bands and whether the transition is symmetry allowed or not. Possible values of 'r' are given in Table 5.1. [3].

By plotting graphs of \((\alpha h\nu)^r\) against \(h\nu\) for various values of 'r' given in Table 5.1, it is possible to determine which of the conditions given in the table dominate. Extrapolations of these plots to zero absorption will provide the appropriate values of the energy gaps of WSe₂ and its intercalated compounds.

5.1.2 Photoelectrochemical Methods

(i) Quantum yield \(\eta\) Vs \(h\nu\) plot

According to Bourezg [4], the quantum yield \(\eta\) is defined as

\[
\eta = \frac{I_{ph}}{(S\phi_o h\nu)}
\]

where \(I_{ph}\) is the photocurrent measured for the photoelectrodes dipped in the polyiodide aqueous electrolyte used in the photoelectrochemical (PEC) solar cell, 'S' is the sample area of the electrode surface, \(\phi_o\) is the incident power per unit of area, 'hv' is the photon energy.
Since \((\eta \nu)^{\frac{1}{r}} \propto (\alpha \nu)^{\frac{1}{r}}\) where \(\alpha\) is the absorption coefficient, plots of \((\eta \nu)^{\frac{1}{r}}\) versus the photon energy \(\nu\) for various values of \(r\) (Table 5.1) will give fairly good straight lines. The X-axis intercept of these lines will provide the value of the appropriate energy gap \(E_g\). The value of indirect band gap \(E_g\) obtained by [4] from the photo yield spectra is 1.27 eV.

(ii) Action Spectrum

A graph of short circuit photocurrent Vs wavelength for a PEC solar cell e.g. \([n-MoSe_2/1.0 \text{ M NaI}, 0.05 \text{ M I/Pt}]\) is called an action spectrum [5]. Since quantum efficiency \(\eta\) is proportional to short circuit current \(i_{sc}\), values of \(\eta\) at different wavelengths are obtained from the action spectrum. Plots of \((\eta \nu)^{\frac{1}{r}}\) against \(\nu\) will again give fairly good straight lines. The appropriate values of band gap \(E_g\) can than be determined from the intercept of these lines with the photon energy axis. Values of direct and indirect gaps [5] obtained from action spectrum for WSe₂ are 1.40 eV and 1.23 eV respectively.

(iii) Capacitance Measurements

As discussed in Chapter 7 capacitance measurements on electrodes prepared from TMDC crystals in aqueous solutions containing
various redox couples can be made to determine the conduction band edges and valence band edges of these compounds. The difference between $E_c$ and $E_v$ will then directly give the value of band gap energy $E_g$. Fan and Bard [5] obtained the value of direct band gap for WSe$_2$ using capacitance measurements as 1.4 eV.

5.1.3 Intrinsic Conduction Measurements at High Temperature

Electrical conductivity ($\sigma$) perpendicular to C-axis can be measured in single crystals of TMDC [6] over the temperature range extending from room temperature to higher temperature (1270 K in WSe$_2$ [6]). In $\sigma$ versus $10^9/T$ graphs shows linear behaviour in the high temperature region. Twice the slope of this linear portion directly gives the value of the indirect band gap in these semiconductors. The value of indirect band gap obtained from intrinsic conduction measurements above 890 K in WSe$_2$ [6] comes out to be 1.32 $\pm$ 0.1 eV.

5.1.4 Photoemission

From the photoelectron yield ($Y$) curves obtained from the photoemission studies of the layered crystals a plot of $Y^{1/3} (h\nu)^{2/3}$ against
photon energy, \( \text{hv} \) is drawn. The linear portion of this plot when extrapolated
to zero yield gives a value of the photo-threshold for the material. Subtracting
the value of electron affinity from this value provides the value of the energy
band gap \( E_g \). Williams et al. [7] using this method obtained the value of \( E_g \) for
\( \text{SnSe}_2 \) and \( \text{SnS}_2 \) as 1.00 eV and 2.1 eV respectively.

The photoemission data gathered over a wide energy
range, in addition to providing details relating to band widths also supplies
information relating to joint density of states and to the valence band density
of states and is most powerful when linked to a reliable theoretical model. It is
thus possible to develop a complete band model for TMDC crystals with the
help of ultraviolet photoemission spectroscopy (UPS) data. The band model
enables one to get a value of the semiconducting band gap for the material.
Mcmenamin and Spicer [8] gave a value in excess of 1.00 eV for the band
gap of \( \text{MoS}_2 \).

5.1.5 Band structure calculations

The band structure of the transition metal compounds
[9] is determined mainly by the following :

(a) The strong overlap and the covalent bonding between the metal and
chalcogen 's' and 'p' orbitals leads to bonding and antibonding
combinations of metal chalcogen wavefunctions. The resulting energy separation of the respective bonds is relatively large [10].

(b) The weaker interaction between the metal 'd' and the chalcogen 'sp' orbitals causes the 'd' bands to be located within the metal chalcogen 'sp' gap and to have relatively pure 'd' character.

(c) The strong hybridization between the $d_z^2$, the $d_{x^2-y^2}$ and the three $d_{xy}$ type subbands causes an energy gap within the metal 'd' bands. Both theoretical and experimental investigations [10-12] yield strong evidence that the highest occupied band has $d_z^2$ character, whereas the four other d-subbands are located energetically above the fermi level.

These properties are schematically illustrated in Fig. 5.2 for the case of n-WSe$_2$ assuming a band gap of 1.35 eV, Mattheiss [10] predicted an indirect band gap of 0.085 Ry i.e. 1.156 eV for MoS$_2$ based on his band structure calculations. Kautek et al. [13] have given a schematic representation Fig. 5.3 of the d-band structure close to the optical gap of 2H-MoS$_2$ [14] and density of states [10]. Hybrid band designations are from [15]. Possible direct and indirect transitions have been clearly indicated in the Figure. The position of $E_c$ conduction band minimum and the valence band maximum $E_v$ are also seen.
5.2 EXPERIMENTAL

As already stated in Chapter 3, all samples used in the present investigation were grown by the DVT technique. As grown samples of WSe$_2$ exhibit p-type conductivity whereas those of In$_x$WSe$_2$ show n-type conductivity with a carrier concentration of $6.01 \times 10^{15}$ cm$^{-3}$ to $6.36 \times 10^{15}$ cm$^{-3}$ respectively. The 'a' and 'b' axis were contained in the plane of cleavage. Since the crystals grow in the form of thin platelets, as grown samples were used to take the absorption spectrum. Thicknesses of the samples were measured with a micrometer or optical microscope. The spectrum were taken on a UV-VIS-NIR schimadzu spectrophotometer in the range 700 nm to 1450 nm. All measurements were performed at room temperature with the incident beam normal to the basal plane i.e. along the C-axis of the as grown crystal flakes. Measurements along the C-axis could not be performed since the specimens were too thin along this direction.

5.3 RESULTS

The absorption spectrum was taken for WSe$_2$ single crystal in the form of a thin flake over the spectral range 700 nm to 1400 nm. In order to analyse the results from this spectrum on the basis of two as well as three dimensional model, values of $\alpha$ were determined at every step of
5 nm. The interpretation of the results in terms of the direct and indirect transitions can be performed with the help of formula (5.4) and (5.5) using the various values of 'r' from Table 5.1. Figure 5.4 shows the spectral variation of $(\alpha \nu)^{1/2}$ vs $\nu$. Since the curve indicates discontinuous straight line it is quite plausible that it represents indirect interband transitions involving the emission or absorption of phonons. In order to make an accurate determination of the points of discontinuities author has followed the method adopted by Koshkin et al. [16] and Elkorashy [17]. Accordingly, from the graphical differentiation of the data presented in Figure 5.4 the dependence of the derivatives $\delta(\alpha \nu)^{1/2}/\delta E$ on $\nu$ has been shown in Fig. 5.5. It can be clearly seen from this figure that the derivatives are step functions of energy with four steps well defined in the range

$$E_1 < E < E_2$$

$$E_2 < E < E_3$$

$$E_3 < E < E_4$$

$$E_4 < E$$

The values of $E_1$, $E_2$, $E_3$ and $E_4$ indicate the points of discontinuities in the plot of $\delta(\alpha \nu)^{1/2}/\delta E$ vs $\nu$. The indirect energy gaps obtained from these values of $E_1$, $E_2$, $E_3$ and $E_4$ are given by
and the phonon energies are given by

$$E_p = \frac{E_4 - E_1}{2} \quad \text{and} \quad E_p = \frac{E_2 + E_3}{2} \quad (5.8)$$

The values of indirect band gap $E_g$ and phonon energies thus obtained are given in Table 5.2. The values of $E_g$ can also be obtained from the intersection of the linear portion of the graph in Fig. 5.4 with the energy axis. This value is close to the value obtained from equation (5.7).

Further a graph of $(\alpha \cdot h\nu)^{1/3}$ vs $h\nu$ is shown in Fig. 5.6. It is seen that it is not possible to fit all the experimental points on this curve. It is therefore conjectured that the indirect transition represented by the absorption curve is an indirect allowed type.

In order to analyse the data from the absorption curve on the basis of two dimensional model, variation of $\alpha^{1/2}$ vs $h\nu$ was studied. In this case, it was not at all possible to fit the experimental results on a straight
It was therefore inferred that the two dimensional model does not work in the present case.

Taking the values of $E_g$ and $E_p$ at room temperature from Table 5.2 the constants $B_{a_1}$, $B_{a_2}$, $B_{e_1}$, $B_{e_2}$, $\theta_1$, and $\theta_2$ have been determined with the help of formula (5.5) and (5.6) for $r = 2$. All these values are represented in Table 5.2.

For the determination of the direct band gap, the best fit for all the experimental points was observed in the case of $(\alpha h\nu)^2$ vs $h\nu$ plot (Fig. 5.7). The value of $E_g$ obtained from the intercept of the straight line portion of the curve on the $h\nu$ axis comes out to be 1.435 eV (Table 5.2).

In order to see that effect of intercalation by indium on the absorption spectrum of WSe$_2$, UV-VIS-NIR spectra were obtained for In$_x$WSe$_2$ for $x = 0.33$ and $x = 0.50$ in the spectral range 700 nm to 1450 nm. Similar to WSe$_2$, values of $\alpha$ were determined from the absorption spectrum and the graphs of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for single crystals of In$_{0.33}$WSe$_2$ and In$_{0.50}$WSe$_2$ are shown in Figs. 5.8 and 5.9 respectively. Graphical differentiation of the data presented in these figures was carried out and the graphs of $d(\alpha h\nu)^{1/2}/dE$ vs $h\nu$ are shown in Figs. 5.10 and 5.11.
The values of $E_1$, $E_2$, $E_3$ and $E_4$ indicating the points of
discontinuities in these figures, the value of the indirect band gap $E_g$ and the
phonon energies $E_{p1}$ and $E_{p2}$ obtained in the manner similar to WSe$_2$ are
represented in Table 5.2. The values of indirect band gap $E_g$ obtained from the
extrapolation of the straight line portions of the graphs in Figs. 5.8 and 5.9 are
also given in Table 5.2. In the case of intercalated compounds also, it was
seen that the experimental points could not be fitted on the graph of
$(\alpha \nu)^{1/3}$ vs $\nu$, thereby indicating that the indirect transitions represented by
the absorption curves are indirect allowed type. Similarly the data obtained
from the absorption curves could not be analysed on the basis of two
dimensional model.

Taking the values of $E_g$ and $E_{p}$ for In$_x$WSe$_2$ from Table
5.2, the constants $B_{a1}$, $B_{a2}$, $B_{e1}$, $B_{e2}$, $\theta_1$ and $\theta_2$ for these compounds were
estimated as before and are given in Table 5.2.

For the determination of the direct band gap for
intercalated compounds, the best fit for all the experimental points was observed
in the case of $(\alpha \nu)^2$ vs $\nu$ plots. These curves for In$_{0.33}$WSe$_2$ and In$_{0.50}$WSe$_2$
are shown in Figs. 5.12 and 5.13 respectively. The values of direct band gap
obtained by the extrapolation of the straight line portions in these curves on
$\nu$-axis are 1.335 eV and 1.330 eV respectively.
5.4 DISCUSSION

It is quite clear from the analysis of the absorption data (based on three dimensional model) presented above that direct and indirect symmetry allowed transitions give a good account of the absorption edge in WSe$_2$ and its indium intercalated compounds. Analysis based on two dimensional model does not provide a good fit, thus inspite of the high anisotropy, true two dimensional behaviour seems unlikely for these compounds.

The value of the phonon energy (21 MeV) for $I = 2$ matches closely with the value of optical mode phonon energies (22 to 33 MeV) at the centre of the Brillouin zone as obtained by Lucovsky et al. [18] and Mead and Irwin [19] in WSe$_2$. This shows that this is the phonon in one of numerous optical branches and not the acoustic phonon. The increase in the value of phonon energy upon intercalation with indium can only be explained from a detailed study of Infrared and Raman scattering data from the samples.

Table 5.3 shows the values of direct and indirect band gaps obtained by earlier investigators using different techniques. The value of direct band gap varies between 1.35 eV to 1.775 eV. The value of 1.435 eV
determined in the present work is close to the value obtained by most of the workers. Similarly the value of the indirect band gap lies between 1.12 eV to 1.4 eV. The values 1.18 eV by extrapolation and 1.026 eV from the graphical analysis are close to the value obtained by most of the workers. There is no significant change in the values of the indirect band gap upon intercalation by Indium.

A careful look at the data presented in Table 5.2 indicates that the direct band gap of WSe$_2$ decreases with an increase in the amount of indium in In$_x$WSe$_2$ single crystals. The decrease can be expressed by the relation

$$E(x) = E(0) + bx + cx^2$$

where 'c' is the bowing parameter. For our direct gap if we fit $E(x)$ to this expression, we get the results shown in Table 5.4.

The introduction of indium in the host lattice of WSe$_2$ introduces certain impurity levels close to the bottom of the conduction band. The direct band gap which is a measure of the separation between the bottom
of the conduction band and top of the valence band therefore decreases by
the intercalation of WSe$_2$ by indium. Since the indirect transition involve
phonons, they do not appear to be affected by the addition of these impurities
levels near the conduction band and so the indirect band gaps are not affected
by the intercalation.

Failure to account for the data on two dimensional
model suggests that although the material WSe$_2$ has been pointed out as
highly anisotropic, it does possess some conductivity along the c-axis because
of the presence of stacking faults [38] in them.

5.5 CONCLUSIONS

1. Both WSe$_2$ and its indium intercalated compounds have direct as well as
indirect band gaps.

2. The energies of the direct band gaps for all the materials have been
determined. The variation of direct energy gaps with amount of indium in
In$_x$WSe$_2$ indicates that the nature i.e. symmetries of the band edges in
WSe$_2$ and its indium intercalated compounds is the same.

3. The accurate analysis of the data has shown that the indirect transitions
represented by the absorption curves are indirect allowed involving two different phonons. The energies of these phonons have been determined.

4. It is concluded that the two dimensional model cannot be used satisfactorily to describe the main optical properties of $\text{In}_x\text{WSe}_2$ ($x = 0$, 0.33 and 0.50) single crystals.
TABLE 5.1
VALUES OF THE EXPONENT 'r' FOR DIFFERENT TYPES OF
BAND GAP TRANSITIONS

<table>
<thead>
<tr>
<th>Type of transition</th>
<th>Direct</th>
<th>Indirect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Two dimensional</td>
<td>Three dimensional</td>
</tr>
<tr>
<td>Allowed (step function)</td>
<td>0 1/2</td>
<td>1 2</td>
</tr>
<tr>
<td>Forbidden</td>
<td>1 3/2</td>
<td>2 3</td>
</tr>
</tbody>
</table>
### Table 5.2

**VARIOUS PARAMETERS AND CONSTANTS OBTAINED FROM THE INDIRECT BAND GAP MEASUREMENTS FOR In\textsubscript{x}WSe\textsubscript{2} SINGLE CRYSTALS**

<table>
<thead>
<tr>
<th></th>
<th>WSe\textsubscript{2}</th>
<th>In\textsubscript{0.33}WSe\textsubscript{2}</th>
<th>In\textsubscript{0.50}WSe\textsubscript{2}</th>
<th>WSe\textsubscript{2}</th>
<th>In\textsubscript{0.33}WSe\textsubscript{2}</th>
<th>In\textsubscript{0.50}WSe\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_1) (eV)</td>
<td>0.968</td>
<td>0.852</td>
<td>0.852</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_2) (eV)</td>
<td>0.996</td>
<td>0.955</td>
<td>0.965</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_3) (eV)</td>
<td>1.038</td>
<td>1.093</td>
<td>1.094</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_4) (eV)</td>
<td>1.084</td>
<td>1.199</td>
<td>1.178</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_g) (eV) (C^*)</td>
<td>1.01</td>
<td>1.02</td>
<td>1.01</td>
<td>1.435</td>
<td>1.335</td>
<td>1.330</td>
</tr>
<tr>
<td>(E_g) (eV) (E^*)</td>
<td>1.18</td>
<td>1.175</td>
<td>1.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_{p1}) (meV)</td>
<td>58</td>
<td>173.5</td>
<td>163</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(E_{p2}) (meV)</td>
<td>21</td>
<td>69</td>
<td>54</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\theta_1) (°K)</td>
<td>672</td>
<td>2011.59</td>
<td>1889</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(\theta_2) (°K)</td>
<td>243</td>
<td>800</td>
<td>626</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(B_{\alpha1}) (cm\textsuperscript{-1}eV\textsuperscript{-1})</td>
<td>375.12</td>
<td>3159.35</td>
<td>774.42</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(B_{\alpha1}) (cm\textsuperscript{-1}eV\textsuperscript{-1})</td>
<td>233.59</td>
<td>275.58</td>
<td>233.39</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(B_{\alpha2}) (cm\textsuperscript{-1}eV\textsuperscript{-1})</td>
<td>87.13</td>
<td>62.79</td>
<td>55.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(B_{\alpha2}) (cm\textsuperscript{-1}eV\textsuperscript{-1})</td>
<td>35.16</td>
<td>138.63</td>
<td>132.31</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

where \(E_g\) (eV) \(C^*\) \(\rightarrow\) indirect band gap from calculation

\(E_g\) (eV) \(E^*\) \(\rightarrow\) indirect band gap from extrapolation
# TABLE 5.3

DIRECT BAND GAPS (eV) AT 295° K

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Authors and Methods</th>
<th>$WSe_2$</th>
<th>$In_{0.33}WSe_2$</th>
<th>$In_{0.50}WSe_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>This work</td>
<td>1.435</td>
<td>1.335</td>
<td>1.330</td>
</tr>
<tr>
<td>2.</td>
<td>Kam and Parkinson (photoyield)</td>
<td>1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Gobrecht et al. (photoyield)</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Tributsch (photoyield)</td>
<td>1.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Fan and Bard (Action spectrum)</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Fan and Bard (Capacitance measurements)</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Cabrera and Abruna (PTF photoyield)</td>
<td>1.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Frindt (optical absorption)</td>
<td>1.60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.</td>
<td>Upadhyayula et al. (optical absorption)</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>Ortiz et al. (photocurrent action)</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Hofmann et al. (photoyield)</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Cabrera et al. (photoyield)</td>
<td>1.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Jakubowicz et al. (optical absorption)</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>Agarwal et al. (Optical absorption)</td>
<td>1.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Anneda et al.</td>
<td>1.775</td>
<td>[31]</td>
<td></td>
</tr>
<tr>
<td>16.</td>
<td>Baldassare and Cingolani</td>
<td>1.775</td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>Sr. No.</td>
<td>Authors/References</td>
<td>$W_{Se_2}$</td>
<td>$In_{0.33}W_{Se_2}$</td>
<td>$In_{0.50}W_{Se_2}$</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------</td>
<td>------------</td>
<td>--------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>1.</td>
<td>This work</td>
<td>1.18</td>
<td>1.175</td>
<td>1.18</td>
</tr>
<tr>
<td>2.</td>
<td>Kam and Parkinson (photoyield) [20]</td>
<td>1.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Lewerenz et al. (photoyield) [33]</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Kautek et al. (photoyield) [13]</td>
<td>1.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Bourezg et al. (photoyield) [4]</td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Tributsch (photoyield) [22]</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Pouzet et al. 1.12- [optical absorption in polycrystalline thin films (PTF)] [34]</td>
<td>1.125</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.</td>
<td>Jager Waldau and Bucher (PTF) 1.20- [35]</td>
<td>1.30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.</td>
<td>Cabrera and Abruna (PTF photoyield) [23]</td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.</td>
<td>Mahalawy and Evans (Intrinsic conduction measurements) [6]</td>
<td>1.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.</td>
<td>Ortiz et al. (photocurrent action spectra of polycrystals) [26]</td>
<td>1.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>Tenne and Wold (photoyield) [36]</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>After photoetching</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.</td>
<td>Cabrera et al. (photoyield) [28]</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.</td>
<td>Kam et al. (optical absorption) [37]</td>
<td>1.219</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**TABLE 5.4**

**BAND GAP OF In_xWSe_2 FOR VARIOUS VALUES OF x**

LEAST SQUARES FIT TO E(x) = E(O) + bx + cx^2

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>E_0 (ev)</th>
<th>b (ev)</th>
<th>c (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295 K</td>
<td>1.435</td>
<td>-0.177</td>
<td>0.088 ev</td>
</tr>
</tbody>
</table>
CAPTIONS TO THE FIGURES

Fig. 5.1  Schematic diagram showing direct and (a) and (b) indirect transitions.

Fig. 5.2  Schematic representation of the band structure of n-WSe₂ as extrapolated from a first principle calculation performed on transition metal chalcogenides.

Fig. 5.3  Schematic representation of the d-band structure close to the optical gap of 2H-MoS₂ and density of states.

Fig. 5.4  Plot of $(\alpha \nu)^{1/2}$ vs $\nu$ for WSe₂ crystal.

Fig. 5.5  Plot of $\delta(\alpha \nu)^{1/2}/\delta \nu$ vs $\nu$ for WSe₂ crystal.

Fig. 5.6  Plot of $(\alpha \nu)^n$ vs $\nu$ for WSe₂ crystal.

Fig. 5.7  Plot of $(\alpha \nu)^2$ vs $\nu$ for WSe₂ crystal.

Fig. 5.8  Plot of $(\alpha \nu)^{1/2}$ vs $\nu$ for Ln₀.₃₃WSe₂ crystal.

Fig. 5.9  Plot of $(\alpha \nu)^{1/2}$ vs $\nu$ for Ln₀.₅₀WSe₂ crystal.

Fig. 5.10 Plot of $\delta(\alpha \nu)^{1/2}/\delta \nu$ vs $\nu$ for Ln₀.₃₃WSe₂ crystal.

Fig. 5.11 Plot of $\delta(\alpha \nu)^{1/2}/\delta \nu$ vs $\nu$ for Ln₀.₅₀WSe₂ crystal.

Fig. 5.12 Plot of $(\alpha \nu)^2$ vs $\nu$ for Ln₀.₃₃WSe₂ crystal.

Fig. 5.13 Plot of $(\alpha \nu)^2$ vs $\nu$ for Ln₀.₅₀WSe₂ crystal.
FIG. 5.2

ANTIBONDING
\[ \text{sp}_{\text{W-Ge}} \]

\[ W \ 5d_{xy} \ 5d_{x^2-y^2} \]

\[ E_F \]

\[ E_{\text{gap}} = 1.35 \text{eV} \]

\[ W \ 5d_{z^2} \]

BONDING
\[ \text{sp}_{\text{W-Ge}} \]

FIG. 5.2
\[ \frac{\delta (\epsilon_{\text{cm}})}{\delta E} \]

FIG. 5.5
FIG. 5.7
FIG. 5.8
FIG. 5.9
REFERENCES

1. J. Bardeen, F. J. Blatt and L. H. Hall


4. R. Bourezg, G. Couturier and J. Salardenne

5. Fu-Ren F. Fan and A.J. Bard

6. S. H. El Mahalawy and B. L. Evans


8. J. C. McMenamin and W. E. Spicer
10. L. F. Mattheiss  

11. J. A. Wilson and A. D. Yoffe  

12. R. S. Title and M. W. Shafer  

13. W. Kautek, H. Gerischer and H. Tributsch  

14. N. J. Doran  

15. W. Kautek, H. Gerischer and H. Tributsch  

16. V. M. Koshkin, V. R. Karais and L. P. Galchinetskii  

17. A. M. Elkorashy  

18. G. Lucovsky, R. M. White, J. A. Benda, and J. F. Revelli  

19. D. G. Mead and J. C. Irwin  

20. K. K. Kam and B. A. Parkinson  
21. J. Gobrecht, H. Gerischer and H. Tributsch

22. H. Tributsch

23. C. R. Cabrera and H. D. Abruna

24. R. F. Frindt

25. L. C. Upadhyayula, J. J. Loferski, A. Wold, W. Giriat
    and R. Kershaw

26. Y. S. Ortiz, G. I. Torres, A. Diaz and C. R. Cabrera

27. W. K. Hofmann, H. J. Lewerenz and C. Pettenkofer


30. M. K. Agarwal, V. V. Rao and V. M. Pathak

31. A. Anedda, E. Fortien and F. Raga
32. L. Baldassare and A. Cingolani

33. C. J. Lewerenz, S. D. Ferris, C. J. Doharty and H. J. Leamy

34. J. Pouzet, J. C. Bernede, A. Khellil, H. Essaidi and S. Benhida

35. A. Jager-Waldau and E. Bucher

36. R. Tenne and A. Wold

37. K. K. Kam, C. L. Chang and D. W. Lynch

38. K. J. Singh