CHAPTER – 6

OPTICAL BAND GAP DETERMINATION OF COPPER DOPED TUNGSTEN DISELENIDE SINGLE CRYSTALS BY UV-VIS-NIR SPECTROPHOTOMETER

6.1 Introduction:

Transition metal dichalcogenides TMDCs (viz. WSe₂, MoSe₂) finds their important application in the field of photoelectrochemical solar cell. Since band gap of these materials plays an important role for this application hence, it becomes necessary to determine it accurately. Since the pioneering work of Tributsch [1], the behavior of covalent semiconducting layer-type group VI transition metal dichalcogenides, and in particular WSe₂ [2,3] and MoSe₂ [3,4] as electrodes in photoelectrochemical (PEC) solar cell for conversion of solar into electrical energy has been extensively studied. Such detailed studies [5] have however not been made on doped crystals of tungsten and molybdenum diselenides.

A survey of the literature on band gap measurements in TMDCs clearly indicates that band gaps in this material can be determined from the methods outlined below.

1. An analysis of the following optical spectra
   (i) absorption spectra
   (ii) reflectance spectra
   (iii) electroreflectance spectra
   (iv) thermoreflectance spectra

2. Photoelectrochemical methods
   (i) Quantum yield η vs hν plot
   (ii) Action spectrum
   (iii) Capacitance measurements
5. Band structure calculations

Out of different methods listed above for determing band gap we preferred optical absorption technique, which appeared to be more authentic than the rest of the methods.

The main types of light absorption [6] in semiconductors occurs because of

1. **Intrinsic, or fundamental light absorption** results in the transition of electrons from the bound to the free state, i.e. from the valence to the conduction band. Intrinsic absorption is possible if \( \hbar \omega \geq \Delta E_\text{g} \). Depending on the forbidden band width it takes place in the visible or in the near infrared part of the spectrum.

2. **Impurity absorption** is due to the ionization of the impurity atoms, i.e. the transition of electrons from impurity atoms to the conduction band or from the valence band to the impurity level.

3. **The absorption by free charge carriers** takes place as a result of their motion induced by the electric field of the light wave. The wave spends some of its energy to accelerate the carriers and is thereby attenuated.

4. The light wave interacts with the lattice vibrations with the resultant change in the number of optical photons. This absorption is termed **lattice absorption**.

5. Light absorption accompanied by the formation of bound electron-hole pairs is termed **exciton absorption**.

6. **Internal-band absorption** is observed in solids with a complicated band pattern, such as the valence band of germanium and silicon.

7. Light absorption by an ensemble of free electrons and holes is termed **plasma absorption**.

From the optical absorption spectra of Cu,WSe\(_2\) (x = 0, 0.5, 1.0) single crystals, the information on band gap, phonon energies assisting the indirect transitions are availed. The implications of this study are thoroughly discussed in this chapter.
6.2.1 UV-VIS-NIR spectrophotometer:

Beckman Model DK-A spectrophotometer provides a means for analyzing liquids, gases and solids through the use of radiant energy in the far and near ultraviolet, visible and near infrared regions of the electromagnetic spectrum. Analytical information can be revealed in terms of transmittance, absorbance or reflectance of energy in the wavelength range between 160 and 3500 nm.

![UV-VIS-NIR Spectrophotometer](image)

**Fig. 6.1 UV-VIS-NIR Spectrophotometer**

Fig. 6.1 shows Model DK-A Spectrophotometer instrument which utilizes a single beam of energy, which is chopped into alternate reference and sample beams to provide a double beam system within the sample compartment. Both sample and reference beams have common detection and amplification components. Qualitative and quantitative absorption data are obtained with the Model DK-A spectrophotometer by directing radiation into a sample and determining what portion of the radiant energy is absorbed. Two radiation sources are necessary,
since there is no single source that will provide energy over the entire wavelength range of the Model DK-A instrument. Radiation is provided in the wavelength range below 375 nm by a hydrogen lamp, the tungsten lamp is used in the 320-3500 nm wavelength range. From the source, radiation enters the optical system.

Fig. 6.2 Optical diagram of Spectrophotometer

Fig. 6.2 shows the path followed by a single ray within the radiation beam. The beam is reflected from the condensing mirror (A) to the slit entrance mirror (B), which directs the beam to the chopper (C). The chopped beam passes through the adjustable entrance slit (D) and into the monochromator. The beam is reflected from the collimating mirror (E) in parallel rays through a reflecting quartz prism (F), which disperses the beam into its spectrum of successive wavelengths.

The back surface of the prism is aluminized so that the beam is reflected back through the prism and further dispersed as it emerges. Rotation of the prism relative to collimating mirror changes the angle of incidence and enables selection of a particular group of wavelengths that comprise a spectral band. This band of radiation is directed back to the collimating mirror, which focuses the entrance slit image on the exit slit (G). Upon passing from the monochromator, the radiant
Energy is directed by lens (H) into the double beam optical system in the sample compartment.

The model DK-A instrument is double beam ratio recording spectrophotometer, i.e. radiant energies transmitted by the reference and sample beams (J and M) are compared, and the ratio of the sample energy to the reference energy is recorded as a percent transmission. The double beam optical system consists of two synchronized semi-circular rotating mirrors (I and N), and two stationary mirrors (L and K) in the sample compartment. The rotating mirrors consequently deflect and pass the radiant energy so that it is directed alternatively into sample and reference cells fifteen (or 12.5) times per second. Energy transmitted by the sample and reference cells is focused by the detector selector mirror (O) onto the detector.

Detection of transmitted radiant energy requires two detectors to cover the entire wavelength range of the instrument. One - the lead sulphide cell (P) - responds in the region between 400 to 3500 nm. For measurements in the wavelength range extending below 700 nm, a photomultiplier tube (Q) is used. Radiant energy that strikes the detector is converted to a proportional alternating current signal.

For obtaining the absorption spectra using this UV-VIS-NIR spectrophotometer from grown single crystals of Cu_xWSe_2 (x = 0, 0.5, 1.0), thin flakes of approximately 0.35 µm thickness are used. This 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.
Results and discussion:
The absorption spectra of Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals obtained from the above described spectrophotometer in the spectral range 700nm to 1450nm are shown in Fig.6.3 (a,b,c) respectively. In order to analyze the results from these spectras in the vicinity of the absorption edge, values of absorption coefficient $\alpha$ were determined at every step of 2.5 nm.

Fig.6.3 (a) The absorption spectra of WSe$_2$ single crystal
Fig. 6.3 (b) The absorption spectra of Cu$_{0.5}$WSe$_2$ single crystal

![Absorption Spectra](image1)

Fig. 6.3 (c) The absorption spectra of Cu$_{1.0}$WSe$_2$ single crystal

These absorption spectra can be analyzed on basis of three as well as two dimensional models as used by Takahashi et al. [7] and by Koshkin et al. [8] and Elkorashy [9]. Fig. 6.4 (a, b, c) and Fig. 6.5 (a, b, c) shows the spectral variation...
(αhν)\(^{1/3}\) vs hν for Cu\(_x\)WSe\(_2\) (x = 0, 0.5, 1.0) single crystals respectively.

Fig. 6.4 (a) Plot of (αhν)\(^{1/3}\) vs E (eV) for WSe\(_2\) single crystal.

Fig. 6.4 (b) Plot of (αhν)\(^{1/3}\) vs E (eV) for Cu\(_{0.5}\)WSe\(_2\) single crystal.
Fig. 6.4 (c) Plot of $(\alpha \nu)^{1/3}$ vs $E$ (eV) for Cu$_{1.0}$WSe$_2$ single crystal.

Fig. 6.5 (a) Plot of $(\alpha \nu)^{1/2}$ vs $E$ (eV) for WSe$_2$ single crystal.
Fig. 6.5 (b) Plot of \((\alpha \nu)^{1/2}\) vs E (eV) for Cu\(_{0.5}\)WSe\(_2\) single crystal

Fig. 6.5 (c) Plot of \((\alpha \nu)^{1/2}\) vs E (eV) for Cu\(_{1.0}\)WSe\(_2\) single crystal

All these plots show broken straight lines which indicates that the interband transition is associated with absorption and emission of two phonons. The knees indicated by \(E_1\), \(E_2\), \(E_3\) and \(E_4\) indicate the beginning of the following processes respectively: absorption 1\(^{st}\) phonon, absorption of 2\(^{nd}\) phonon, emission of 2\(^{nd}\) phonon and emission of the 1\(^{st}\) phonon. From above results, it is clear that Cu\(_x\)WSe\(_2\) (\(x = 0, 0.5, 1.0\)) exhibits an indirect interband transition near the
with two independent phonons. On the basis of three dimension model, it is not possible to decide if the indirect interband transition is of the forbidden or allowed type. As observed from Fig. 6.4 (a, b, c) and Fig. 6.5 (a, b, c) both types seem to be probable. This discrepancy can be resolved if measurements are carried out at low temperature [10]. It is being already shown by [11] that even if the measurements are not done at low temperature then analysis of the absorption spectra at room temperature on the basis of two dimensional model can provide this information. Fig. 6.6 (a, b, c) and Fig. 6.7 (a, b, c) shows the spectral variation of $\alpha^{1/2}$ vs $h\nu$ and $\alpha$ vs $h\nu$ for Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals i.e. indirect forbidden and indirect allowed respectively.

**Fig. 6.6 (a) Plot of $(\alpha)^{1/2}$ vs E (eV) for WSe$_2$ single crystal**
Fig. 6.6 (b) Plot of $(\alpha)^{1/2}$ vs E (eV) for Cu$_{0.5}$WSe$_2$ single crystal

Fig. 6.6 (c) Plot of $(\alpha)^{1/2}$ vs E (eV) for Cu$_{1.0}$WSe$_2$ single crystal
Fig. 6.7 (a) Plot of $\alpha$ vs $E$ (eV) for WSe$_2$ single crystal

Fig. 6.7 (b) Plot of $\alpha$ vs $E$ (eV) for Cu$_{0.5}$WSe$_2$ single crystal
Fig. 6.7 (c) Plot of $\alpha$ vs $E$ (eV) for Cu$_{1.0}$WSe$_2$ single crystal

Since discontinuity in steps is not being observed as seen in Fig. 6.7 (a, b, c) therefore the two dimensional indirect allowed transition is excluded. In order to make an accurate determination of the points of discontinuities in Fig. 6.4 (a, b, c), Fig.6.5 (a, b, c) and Fig.6.6 (a, b, c), author has followed the method adopted by Koshkin et al [8] and Elkorashy [9].

It can be clearly seen from these figures 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 Fig. 6.4 (a, b, c), Fig.6.5 (a, b, c) and Fig.6.6 (a, b, c). 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

\[ E_{\rho 1} = \frac{E_4 - E_1}{2} \quad \text{and} \quad E_{\rho 2} = \frac{E_3 - E_2}{2} \]  

(6.2)

The values of indirect band gap \( E_g' \) and phonon energies thus obtained are given in Table 6.1, Table 6.2 and Table 6.3 for all the samples. The values of \( E_g' \) obtained from the intersection of the linear portion of the graphs in Fig.6.4(a,b,c), Fig.6.5 (a,b,c) and Fig.6.6 (a,b,c) with the energy axis for zero absorption, for all the samples are also displayed in Table 6.1 and Table 6.2, which has close resemblance with the value obtained from equ\(^n\) (6.1).

**Table 6.1 Values of indirect band gap obtained using two dimensional model for Cu\(_x\)WSe\(_2\) ( \( x = 0, 0.5, 1.0 \) ) single crystal.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of transition</th>
<th>( E_g' ) (eV)</th>
<th>( E_g^* ) (eV)</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E4</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe(_2)</td>
<td>Allowed (Step Function)</td>
<td>1.37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(_{0.5})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(_{1.0})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WSe(_2)</td>
<td>Forbidden</td>
<td>1.36</td>
<td>1.29</td>
<td>1.24</td>
<td>1.28</td>
<td>1.33</td>
<td>1.34</td>
</tr>
<tr>
<td>Cu(_{0.5})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.39</td>
<td>1.36</td>
<td>1.39</td>
<td>1.41</td>
<td>1.43</td>
</tr>
<tr>
<td>Cu(_{1.0})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.39</td>
<td>1.36</td>
<td>1.39</td>
<td>1.41</td>
<td>1.43</td>
</tr>
</tbody>
</table>

**Table 6.2 Values of indirect band gap obtained using three dimensional model for Cu\(_x\)WSe\(_2\) ( \( x = 0, 0.5, 1.0 \) ) single crystal.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Type of transition</th>
<th>( E_g' ) (eV)</th>
<th>( E_g^* ) (eV)</th>
<th>E1</th>
<th>E2</th>
<th>E3</th>
<th>E4</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe(_2)</td>
<td>Allowed (Step Function)</td>
<td>1.35</td>
<td>1.30</td>
<td>1.24</td>
<td>1.28</td>
<td>1.32</td>
<td>1.35</td>
</tr>
<tr>
<td>Cu(_{0.5})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.40</td>
<td>1.36</td>
<td>1.39</td>
<td>1.41</td>
<td>1.43</td>
</tr>
<tr>
<td>Cu(_{1.0})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.40</td>
<td>1.36</td>
<td>1.38</td>
<td>1.41</td>
<td>1.43</td>
</tr>
<tr>
<td>WSe(_2)</td>
<td>Forbidden</td>
<td>1.33</td>
<td>1.29</td>
<td>1.24</td>
<td>1.27</td>
<td>1.32</td>
<td>1.35</td>
</tr>
<tr>
<td>Cu(_{0.5})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.39</td>
<td>1.37</td>
<td>1.39</td>
<td>1.41</td>
<td>1.43</td>
</tr>
<tr>
<td>Cu(_{1.0})WSe(_2)</td>
<td></td>
<td>1.44</td>
<td>1.38</td>
<td>1.32</td>
<td>1.39</td>
<td>1.41</td>
<td>1.43</td>
</tr>
</tbody>
</table>

\( E_g' \)  \( \tilde{\gamma} \) \hskip2em \text{Values of indirect band gap obtained from extrapolation.}

\( E_g^* \)  \( \tilde{\gamma} \) \hskip2em \text{Values of indirect band gap obtained from energy step functions.}
Table 6.3 Values of phonon energy of Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{p1}$ (meV)</th>
<th>$E_{p2}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WSe$_2$</td>
<td>53.5</td>
<td>23.5</td>
</tr>
<tr>
<td>Cu$_{0.5}$WSe$_2$</td>
<td>33.5</td>
<td>8.5</td>
</tr>
<tr>
<td>Cu$_{1.0}$WSe$_2$</td>
<td>36.0</td>
<td>8.5</td>
</tr>
</tbody>
</table>

For the determination of the direct band gap ($E_g$), using three dimensional model, we plotted variation of $(\alpha \nu)^2$ vs $\nu$ and $(\alpha \nu)^{2/3}$ vs $\nu$ for Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals for allowed and forbidden transitions. This did not give a good account of absorption edge in our case and hence are excluded. Thus according to the two and three dimensional model the indirect transition is confirmed for Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals and can be of forbidden or allowed type.

The values of phonon energies calculated are shown in Table 6.3 and indicates variation from 8.5 meV to 53.5 meV for Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) samples and matches closely with the value of optical mode phonon energies at the centre of Brillouin Zone as obtained by Lucovsky et al.[12] and [13].

The value of indirect band gap lies between 1.33 eV to 1.44 eV for Cu$_x$WSe$_2$ (x = 0, 0.5, 1.0) single crystals by extrapolation. Similarly the values of indirect band gaps lies between 1.29 eV to 1.39 eV by energy step functions as shown in Table 6.1 and Table 6.2 respectively and are having very close resemblance with each other. These results are matching with those reported by various workers [14-19]. This variation in indirect band gap might be occurring because of doping copper in host WSe$_2$ material.
References:


[19] R. Tenne and A. Wold