Optical Analysis of WSe₂ Single Crystals

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Abstract:

The WSe₂ single crystals having a layered structure were grown by chemical vapour transport technique. The crystals belong to transition metal dichalcogenides group, exhibiting very interesting physical and optical properties. Optical absorption of WSe₂ single crystals was measured at room temperature near the fundamental absorption edge. These spectra were obtained by means of UV-VIS-NIR spectrophotometer in the range of 200 nm–1500 nm. Both direct and indirect transitions are involved in the absorption process. The indirect transition found to be allowed with two phonons involved in the process. The direct as well as indirect energy gaps and phonon energies for all these crystals were estimated. Using absorption spectra transmission and reflection coefficient has been computed. The reflectivity, optical constants (like extrinsic coefficient and refractive index), dielectric constant Cauchy-Sellmaier function has been calculated. The results obtained are discussed in detail.

INTRODUCTION

Diselenide of molybdenum and tungsten and mixed compound of these two possess interesting optical and photo-absorption properties [1-3]. These semiconducting materials belong to TMDCs group and are found to possess layered structure. Several studies, mainly on the optical properties, have been carried out in the past few years, [4-10]. Bassani and Parravicini[11] treated some of the layered compounds as two-dimensional latticeFivaz and Mooser [12-14] discussed how pronounced anisotropic properties might affect the motion of free carriers in layered semiconductors. It was shown that in these structures, the free carriers might be localized within individual layers, behaving as if moving through a stack of individual layers, "independent layer approximations".

Since the interatomic distance in a crystal is not isotropic but rather varies with the crystallographic direction, one would expect this directional variation to affect the banding of states. Thus, although the energy gap, which characterizes a semiconductor, has the same minimum value in each unit cell, its topography within each unit cell can be extremely complex. In compound semiconductors a deviation from stoichiometry generates donors or acceptors depending on whether it is the cation or anion, which is excess. However, it has been shown that it is not the excess ion but rather the vacancy, which determines whether the material is n-type or p-type in nature [15].

The structures of several real and dummy layered transition metal dichalcogenides (i.e.NbSe₂, TaS₂, TaSe₂, WSe₂ and MoSe₂) were calculated by using the tight-binding method within the extended Huckel approximation (EHA) [16]. transition metal dichalcogenides (TMDC) of the type MX_2 (M=Chalcogen atoms) exhibit interesting Physical and Structural properties as have been reviewed by many researchers [17-20].

Band structure calculations were performed [21] with LACO method and [22] APW method. There after many band calculations have been reported up to now [23-27]. However, more experimental studies are required to understand the detailed band structure of the empty states of MX_{2} .

EXPERIMENTAL METHOD

The main aim of the work presented in this paper is to make analysis of the absorption spectra obtained from the crystals of WSe₂. This crystals grown in our laboratory by using the direct vapour transport technique. Its looks found shining surfaces. Since the crystals grew in the form of thin platelets, as grown samples were used to take the absorption spectrum. The optical absorption data were obtained by the above described Spectrophotometer in the range 200 nm to 3000 nm. For this measurement, thin as grown crystals of thickness about 25 μ m were chosen. The crystal was pasted on a thick black paper with a cut exposing the (001) plane of the crystals to the incident radiation. The reference used was a replica of the black paper having the cut in exactly the same position. This arrangement is necessary because the crystal size is smaller than that of the sample compartment. Both sample and reference were exposed to UV radiations through a chopped beam and by measuring the transmitted intensity through the sample, absorption spectrum was recorded.

All measurements were carried out at room temperature with the incident beam normal to the basal plane of as-grown crystals i.e. along c-axis of the grown crystals. Measurements along the other axis could not be performed since the specimens (too thin) were unable to be mounted along those directions.

OPTICAL BAND GAP DETERMINATION

The relationship that exists for possible transitions across the energy gap of semiconductor, the absorption coefficient α is proportional as follow [28],

$$\alpha h v = A(h v - E_{a})^{r} \qquad (1)$$

for direct transitions and

$$\alpha hv = \sum_{j} B_{j} (hv - E'_{g} \pm E_{pj})^{r}$$
(2)

or indirect transitions.

Here, α is the absorption coefficient, hv the energy of the incident photon, E_g the energy for the direct transition and E'_g the energy for indirect transition and E_{pj} 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 (1) and (2) 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 (Table 1).

Table 1: Values of the exponent 'r' for different types of transitions

Type of	Direct	Indirect		
transition	2D	3D	2D	3D
Allowed	0 (Step function)	1/2	1	2
Forbidden	1	3/2	2	3

For indirect transitions the detailed form of equation (2) [29,30] given as,

$$\alpha_{i} = \sum_{i=1}^{2} \left\{ \frac{B_{ai}}{E} \left(\frac{1}{e^{\theta_{i}/T} - 1} \right) (E - E'_{g} + k\theta_{i})^{r} + \frac{B_{ei}}{E} \left(\frac{1}{1 - e^{\theta_{i}/T}} \right) (E - E'_{g} - k\theta_{i})^{r} \right\}$$
(3)

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 θ_i is a phonon equivalent temperature defined by the equation,

$$\theta_i = \frac{E_{_{P}i}}{k} \tag{4}$$

where E_{pi} being the i^{th} phonon energy.

In these cases the density of states is a constant independent of the energy and the expressions showing the dependence of α in terms of direct and indirect transitions get modified [31] as

$$\alpha = A'(hv - E_g)^r \tag{5}$$

For direct transition and

$$\alpha_{i} = \sum_{i=1}^{2} \left\{ B_{ai}' \left(\frac{1}{e^{\theta_{i}/T} - 1} \right) (E - E_{g}' + k\theta_{i})^{r} + B_{ei}' \left(\frac{1}{1 - e^{\theta_{i}/T}} \right) (E - E_{g}' - k\theta_{i})^{r} \right\}$$
(6)

for indirect transition [32].

RESULTS AND DISCUSSION

The absorption spectra of WSe₂ single crystal is shown in Figure 1. A careful study of these spectra reveals the presence of absorption edges in the spectral range 200 nm to 2000 nm.



Figure 1: Optical absorption spectra of WSe₂ single crystal.

In order to analyze the results from this spectra in the vicinity of the absorption edge on the basis of two as well as three-dimensional model, values of absorption coefficient α were determined at every interval of 1 *nm*. The interpretation of the experimental results viz. the dependence of absorption coefficient α in terms of direct and indirect transitions can be performed with the help of formulae (5) and (6) using the values of *r* equal to $\frac{1}{2}$ and 2 respectively.

Accordingly, Figure 2 for WSe₂ single crystal shows the spectral variation of $(\alpha hv)^{1/2}$ vs *hv*. Since the curves indicate discontinuous straight lines, it is quite possible 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 [33-35].

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Figure 2: The spectral variation of $(\alpha hv)^{1/2}$ vs hv for WSe₂ single crystals.

Accordingly, from the graphical differentiation of the data presented in Figure 2 for WSe₂ single crystal, the dependence of the derivatives $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ on hv has been shown in Figure 3. It can be clearly seen from these figure that the derivatives are step function of energy with four steps well defined in the range E1 < *E* < *E*₂, *E*₂ < *E* < *E*₃, *E*₃ < *E* < *E*₄ and *E*₄ < *E*.



Figure 3: The spectral variation of $\delta(\alpha hv)^{1/2}/\delta hv$ on hv for WSe₂ single crystals.

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

$$E'_{g} = \frac{E_{1} + E_{4}}{2} = \frac{E_{2} + E_{3}}{2}$$
(7)
$$E_{p1} = \frac{E_{4} - E_{1}}{2} \text{ and } E_{p2} = \frac{E_{3} - E_{2}}{2}$$
(8)

The values of indirect band gap E'_{g} and phonon energies thus obtained are presented in Table 2. The values of the E'_{g} can also be obtained from the intersection of the linear portion of the curves with energy axis for zero absorption as shown in Figure 2. These values closely matches with the value obtained from equation (7).

For the determination of the direct band gap E_g , the spectral variation of $(\alpha hv)^2$ vs hv as shown in Figures 4 were studied. The values of direct band gap E_g obtained from the intersection of the linear portion of the curves in Figure 4 is shown in Table 2. The values of direct and indirect band gap obtained in the present investigation are in good agreement with the reported values as can be seen from Table 3.



Figure 4: The spectral variation of $(\alpha hv)^2$ vs hv for WSe₂ single crystal.

Parameter	WSe ₂
$E_1 (eV)$	1.430
$E_2 (eV)$	1.414
$E_3 (eV)$	1.397
$E_4 (eV)$	1.380
$E'_{g}(\mathbf{C}) (\mathbf{eV})$	1.405
$E'_{g}(\mathrm{E}) (\mathrm{eV})$	1.408
E_{p1} (eV)	0.025
$E_{p2} (eV)$	0.008
$\theta_1(\mathbf{K})$	289.85
$\theta_{2}(\mathbf{K})$	92.75
E _g (e V) (Direct)	1.44

Table 2: The values of o	ptical parameters	of WSe ₂ single crystals.
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 $E'_{g}(C) =$ indirect band gap from calculation

 $E'_{g}(E) =$ indirect band gap from extrapolation

 θ_1 and θ_2 can be find out by using equation (5.23)

Table 3: Comparative study of direct and indirect band gap of WSe₂ single crystal

Material		Direct Band gap	Indirect band gap	
		(eV)	(eV)	
WSe ₂	Obtained	1.44	1.405	
	Reported	1.39,1.435 [62],	1 16 1 18 [62] [63]	
		[63]	1.10,1.10 [02], [03]	
		1.40 [64]	_	

Using absorption spectra, transmission and reflection coefficients have been computed by equations (9) and (10).

 $%T = (1/A) \times 100$ (9) R = 1- (T+A) (10)

where symbols have their usual meaning. The relation between T, R and A in graphical form is shown in Figure 5.



Figure 5: The transmittance, reflectance and absorbance spectra of WSe₂ single crystals.

From Figure 5 it implies that transmittance and reflection possess almost the same trend. But the value of reflectance in percentile is more than that of the absorption. The reflectance data confirms the shining surface of the crystal under investigation. The inset of Figure 5 indicates that crystals are transparent in the range 1.0-1.4 eV less than the energy gap ($E < E_g$) representing the urbach tail [39].

Furthermore, the reflectivity (R),the optical constants like the extinction coefficient (K) and the refractive index (n) of crystals at certain constant wavelength (λ) are related through the following equations (11) and (12) [40].

$$K = \frac{\alpha \lambda}{4\pi}$$

(11)

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2}$$
(12)

Using these relations values of K and n have been calculated at different input wavelengths/ frequencies from measurements of T and R.

On the other hand, the frequency dependence of the real ϵ_r and imaginary ϵ_i parts of the complex dielectric constants are related to K and n have been determined through the following equations,

$$\varepsilon_r = n^2 - K^2;$$
 (13)
 $\varepsilon_i = 2nK$ (14)

where ε_r (real part) is the dielectric constant and ε_i (imaginary part) is the dielectric loss factor.

The relation of the extinction coefficient (K) and the refractive index (n) with λ for WSe₂ crystal are shown in Figure 6 and Figure 7 shows the energy dependence of the dielectric parameters of the direct vapour transport as grown single crystals. The general trend of variation in these parameters is fairly the same. For example, K and n values decreased sharply 950nm in WSe₂ and then further increased upto 1100 then increaseed/ decreased until 1400 nm. Same behaviour is observed with dielectric parameters too. The sharp increase and decrease in k reveals the waves at lower wavelength are extinguished.

Cauchy-Sellmaier function

Interestingly, for photon energies less than the energy gap ($E < E_g$), that is typically in the range of 1.0 to 1.4 eV, representing the Urbach tail [39], the spectral variation of the refractive index can be expressed by the Cauchy-Sellmaier function [41] expanded in even powers of E. The first approximation of this function gives the expression,

$$n(E) = n_0 + a_1 E^2 \tag{15}$$

where n_0 and a_1 are nonzero constants. The best fit of n against E^2 in the transparent range of E gives the values of these constants. The plots of n(E) versus E^2 are shown in Figure 8 for WSe₂ single crystals respectively. The linearity of these curves supports the evolution of the desired parameters. Table 4 contains the constants of equation (15) as determined for WSe₂. Further more, the results of refractive index dispersion (see Figure 6) below the interband absorption edge correspond to the fundamental electronic excitation spectrum that may assist evaluation of the opto-electronic constants of the material.

Single-effective oscillator model

Based upon the validity of Krammers-Kroning relationship, the real part of dielectric constant takes the form [66-68],

$$\varepsilon_r = 1 + \frac{F}{\left(E_0^2 - E^2\right)} \qquad (16)$$

where the two parameters E_0 and F have straight forward relation with the electric dipole strength and the corresponding transition frequencies of all oscillators.



Figure 6: Spectral variation of the extinction coefficient (K) and the refractive index (n) as a function of wavelength (λ) for WSe₂ single crystals



Figure 7: Variation of real and imaginary part of dielectric constant as a function of wavelength for WSe₂ single crystals



Figure 8: Plot of refractive index (n) as a function of E^2 in the region of Urbach tail for WSe₂ single crystals

By a special combination of these parameters, as defined by Wemple and Di Domenico $\left[68\right],$

$$E_d = \frac{F}{E_0} \qquad (17)$$

the equations (13), (14), (16) and (17), can be coupled together, neglecting the values of K in the transparent region, gives:

$$\varepsilon_r(E) = n^2(E) = 1 + \frac{E_d E_0}{E_0^2 - E^2}$$
 (18)

Thus, the values of E_0 and E_d have been estimated by plotting $(n^2-1)^{-1}$ versus E^2 and fitting the relation to a straight line as shown in the Figure 9 for WSe₂ crystals. The slope 0.2166 for WSe₂ (Figure 9) as obtained are, obviously the consequence of the corresponding n value. On the basis of the single-effective oscillator model [43], E_0 and E_d are connected to ε_r and the moments M₋₁ and M₋₃ of the $\varepsilon(E)$ optical spectrum through the relations,

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \qquad (19)$$

and

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (20)$$

where rth moment of the optical spectrum is given by

$$M_r = \frac{2}{\pi} \int_{E_i}^{\infty} \varepsilon^r \varepsilon_i(E) dE \quad (21)$$

Here E_t is the absorption threshold energy. Table 4 also gives the values of the computed single – effective oscillator parameters E_0 , E_d , M_{-1} and M_{-3} as worked out for the as-grown WSe₂ single crystals.



Figure 9: Plot of $(n^2-1)^{-1}$ versus E^2 for WSe₂ single crystals

Table 4: Optical parameters of the grown WSe₂ single crystals

n_0^{2}	a ₁ (eV) ⁻²	E ₀ eV	E _d eV	M-1 x 10 ⁻²	M-3 x 10 ⁻²	Ļ	E ₀ (meV)
0.902	0.12	2.331	6.935	281.11	47.12	12.22	81.83

Urbach Rule

Moreover, the absorption coefficient α is exponentially related to the sample temperature T', given as [40-42,44]

$$\alpha = \alpha_0 \exp\left[\frac{\sigma}{kT}(hv - hv_0)\right] \quad (22)$$

where α_0 and hv_0 are the material dependent constants and σ , known as the steepness parameter, is a temperature (T') dependent parameter which characterizes broadening of the absorption edge due to electron-phonon and/or exciton-phonon interactions. At constant (room) temperature, the graph representing $\ln\alpha$ on y-axis and hu on x-axis in the range of the Urbach tail yields a straight line. Figure 10, showing this typical variation, give fairly accurately the value of σ for WSe₂ single crystals. The obtained values are given in Table 4. The low value of the steepness parameter (see Table 4) as obtained in our crystals may be ascribed to a large concentration of excitons, resulting into much intense exciton phonon coupling strength, in our compounds. Interestingly, in the experimental curves (Figure 1) showing spectral variation of absorption, we can notice small yet distinct steps (in the region 950-1200nm) which overlap with the tail portion of the fundamental absorption edge. These may be because more than one phonon is participating in the transition, and that the phonons in the Urbach region allow connecting states with the same velocity dE/dk at phonon energies greater than those connecting the band edge excitons (where dE/dk = 0). As a consequence, one expects a strong exciton – phonon interaction.



Figure 10: Graphical plot of ln α against E for WSe₂ single crystals

Besides, inverse of slope gives the characteristic energy E_0 . E_0 is interpreted as the energy gap between the top of the upper valance band and the lowest minimum of the conduction band. The value of E_0 has been obtained above 80 meV. Since the inverse of slope is greater than kT (0.0259eV) (for example 0.081eV in WSe₂ compound), it appears that the absorption is broadened by some feeble disorder in the single crystals.

FREE CARRIER ABSORPTION

Free carrier absorption is characterized by a monotonic, often structureless, spectrum which grows as λ^p , where *p* can range from 1.5 to 3.5 and $\lambda = c /v$ is the photon wavelength. To absorb a photon, the electron must make a transition to a higher energy state within the same valley. Such a transition requires an additional interaction to conserve momentum. The change in momentum can be provided by the interaction with the lattice by way of phonons or by scattering from ionized impurities.

The Drude theory for the oscillation of an electron driven by a periodic electric field in a metal leads to a damping (attenuation) which increases as λ^2 . The collision with the lattice resulting in scattering by acoustic phonons leads [45] to an absorption increasing as $\lambda^{1.5}$. But scattering by optical phonons gives [46] a dependence in $\lambda^{2.5}$, while scattering by ionized impurities gives a dependence in $\lambda^{3.5}$ or λ^3 , depending on the approximations used in the theory [46]. In general, all three modes of scattering will occur and the resultant free carrier absorption α_f will be a weighted sum of the three processes.

Free-carrier absorption in given by [47], $\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5}$ (23)

where A, B and C are constants. The dominant mode of scattering will depend on the impurity concentration. The exponent 'p' in the dependence on λ^p should increase with doping or with compensation.

A plot (Figure. 11) of log α versus log λ gives the slope of magnitude 1.12 in WSe₂ crystals. This reveals that the transition is taking place due to scattering of acoustical phonons for WSe₂.



Figure 11: Plot of log α versus log λ for free carrier Absorption

CONCLUSION

In this work authors observed that both direct as well as indirect symmetry allowed transitions gives a good account of the optical absorption edge in WSe_2 single crystals. In this context, author has come to the following conclusions:

The energies of the direct band gaps have been determined. This is good agreement with reported values of direct band gapes.

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.

The general trend of variation of extinction coefficient (K), refractive index (n), dielectric constant ε_r and ε_i are fairly the same. The sharp increase and decrease in k reveals the waves at lower wavelength are extinguished.

Using the Cauchy-Sellmaier function, the results of refractive index dispersion below the interband absorption edge correspond to the fundamental electronic excitation spectrum that may assist evaluation of the opto-electronic constants of the material.

The computed single–effective oscillator parameters E_0 , E_d , M_{-1} and M_{-3} as worked out for the as-grown WSe₂ single crystals.

Urbach Rule predicts the steepness parameter (σ) reveals that the absorption is broadened by some feeble disorder in the single crystals.

Free-carrier absorption reveals that the transition is taking place due to scattering of acoustical phonons for WSe₂.

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