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Research Article

SPECTRAL ANALYSIS OF ZRSE$_3$ SINGLE CRYSTALS

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ABSTRACT

The spectral analysis of the ZrSe$_3$ single crystals has been carried out in UV-visible-near IR range. The presence of direct and indirect transition of photo-generated carriers has been investigated using this spectral analysis. The absorption, transmission and reflection coefficients have been computed. The reflectivity, extrinsic coefficient, refractive index, dielectric constant and Cauchy-Sellmaier function has been calculated. The obtained results are discussed in detail.

INTRODUCTION

The study of optical properties of this semiconductor gives a good understanding of its electronic properties and band structures. The optical band gaps of semiconducting materials play an important role in deciding the photoelectric properties of the optoelectronic devices. Thus, it is always interesting to investigate the nature of transport of carriers in a semiconducting material.

The transition metal trichaclogenide ZrS$_{3-x}$Se$_x$ compounds crystallize mono clinically and they grow as fibrous ribbons having linear chain of metal atoms located at the center of distorted prisms showing trigonal faces and forming isolated columns, that belongs to the $P2_1/m$ space group (Furuseth *et al.*, 1975). The linear chain of metal atoms is parallel to the crystallographic b-axis, which is the growth axis. Six chalcogen atoms surround each metal atom forming distorted trigonal prisms. The crystal s were grown in the form of layers, which run parallel to the b-axis, and each chain in the layer are displaced from the neighboring chain by half of the unit cell along the b-axis (Ikari *et al.*, 1983).

The trichalcogenides MX$_3$ of group IVA transition metal have recently aroused considerable experimental interest because of their significant "quasi"-one dimensional character. Despite numerous crystallographic, electrical and magnetic studies Grisel *et al.*, (1980), Deville and Jandl (1980), Jandl *et al.*, (1979), Zwick and Renucei (1979), only limited knowledge is at hand concerning the optical properties of these ZrSe$_3$ type layered structured materials and therefore considerable amount of their fundamental data are still lacking.

The direct and indirect band gap of ZrSe$_3$ and ZrS$_3$ single crystals have been obtained by Patel (Schairer and Schafer, 1973; Patel *et al.*, 2005). The comparative studies of the series of ZrS$_x$Se$_{3-x}$ single crystals were studied. The direct as well as indirect optical band gaps were increases with increasing sulphur proportion in this series (Patel, 2014). There have no more information available regarding absorption, transmission and reflection coefficients, reflectivity, extrinsic coefficient, refractive index, dielectric constant and Cauchy-Sellmaier function. In this paper authors are discussed about these parameters.

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 ZrSe$_3$. These crystals were grown by chemical vapour transport technique using iodine as transporting agent. 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 spectrophotometer in the range 200 nm to 3000 nm. For this measurement, thin as grown crystals were chosen. The crystal was pasted on a thick black paper with a cut exposing the 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 (Pankow, 1975),

$$\alpha hv = A(hv - E_g)^r \qquad (1)$$

for direct transitions and

$$\alpha hv = \sum_j B_j (hv - E'_g \pm E_{pj})^r \qquad (2)$$

for 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 Transition	**Direct**		**Indirect**	
	2D	**3D**	**2D**	**3D**
Allowed	0 (Step Function)	1/2		
Forbidden	1	3/2	2	3

For indirect transitions the detailed form of equation (2) (Elkorashy, 1986 and Vlachs *et al.*, 1976) given as,

$$\alpha_i = \sum_{i=1}^{2}\left\{\frac{B_{ai}}{E}\left(\frac{1}{e^{\theta_i/T}-1}\right)(E-E'_g+k\theta_i)^r + \frac{B_{ei}}{E}\left(\frac{1}{1-e^{\theta_i/T}}\right)\left(E-E'_g-k\theta_i\right)^r\right\}$$

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,

$$\theta_i = \frac{E_{Pi}}{k} \qquad (3)$$

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 (Elkorashy, 1988) as

$$\alpha = A'(hv - E_g)^r \qquad (4)$$

For direct transition and

$$\alpha_i = \sum_{i=1}^{2}\left\{B'_{ai}\left(\frac{1}{e^{\theta_i/T}-1}\right)(E-E'_g+k\theta_i)^r + B'_{ei}\left(\frac{1}{1-e^{\theta_i/T}}\right)\left(E-E'_g-k\theta_i\right)^r\right\} \qquad (5)$$

for indirect transition (Goldberg *et al.*, 1975).

RESULTS AND DISCUSSION

The absorption spectra of $ZrSe_3$ single crystal is shown in figure 1. A careful study of this spectra reveals the presence of absorption edges in the spectral range 200 *nm* to 3200 *nm*.

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 equation (4) and (5) using the values of *r* equal to ½ and 2 respectively.

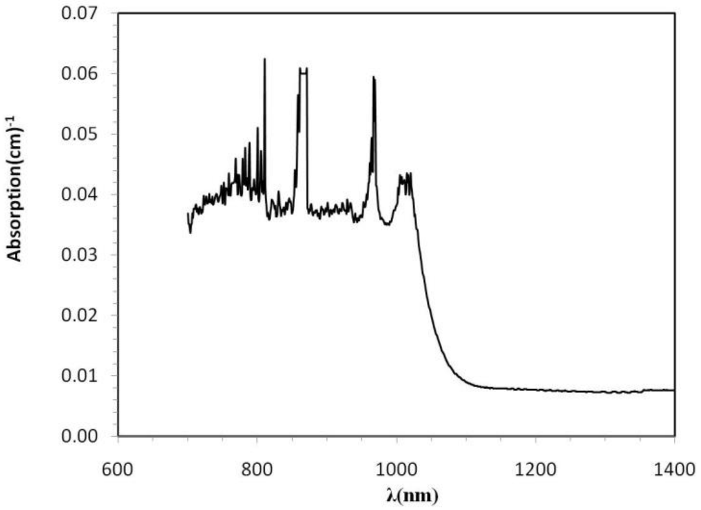

Figure 1: Optical Absorption Spectra of $ZrSe_3$

Using absorption spectra, transmission and reflection coefficients have been computed by equations (6) and (7).

$$\%T = (1/A) \times 100 \quad (6)$$

$$R = 1 - (T + A) \quad (7)$$

The relation between T, R and A in graphical form is shown in figure 2.

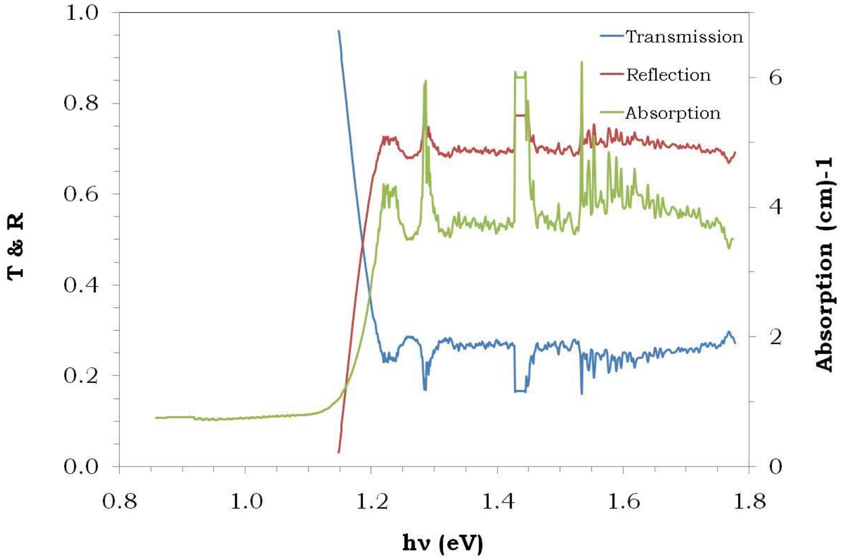

Figure 2: The Transmittance, Reflectance and Absorbance Spectra of $ZrSe_3$ Single Crystals

From figure 2 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 2 indicates that crystals are transparent in the range 1.0-1.2 eV less than the energy gap ($E<E_g$) representing the urbach tail (Itoh *et al.*, 2002).

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 (8) and (9) (Gaffar *et al.*, 2003)

$$K = \frac{\alpha\lambda}{4\pi} \tag{8}$$

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \tag{9}$$

Using these relations values of K and n have been calculated at different input avelengths/ 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,

$$\varepsilon_r = n^2 - K^2; \tag{10}$$

$$\varepsilon_i = 2nK \tag{11}$$

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 $ZrSe_3$ crystal are shown in figure 3 and figure 4 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 950 nm in $ZrSe_3$ 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.

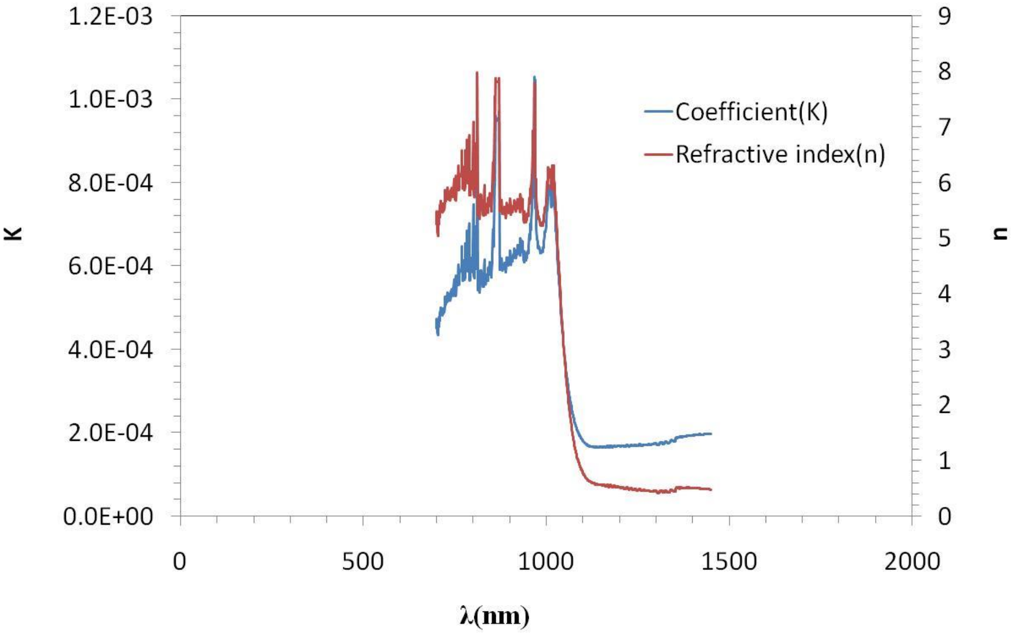

Figure 3: Spectral Variation of the Extinction Coefficient (K) and the Refractive Index (n) as a Function of Wavelength (λ) for $ZrSe_3$ Single Crystals

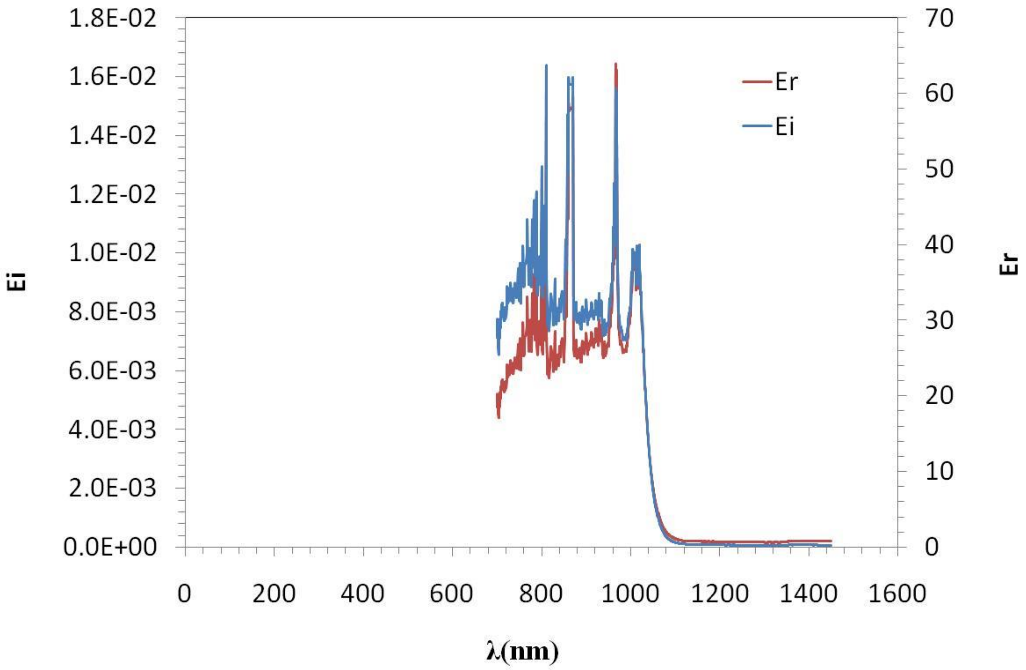

Figure 4: Variation of Real and Imaginary Part of Dielectric Constant as a Function of Wavelength for $ZrSe_3$ Single Crystals

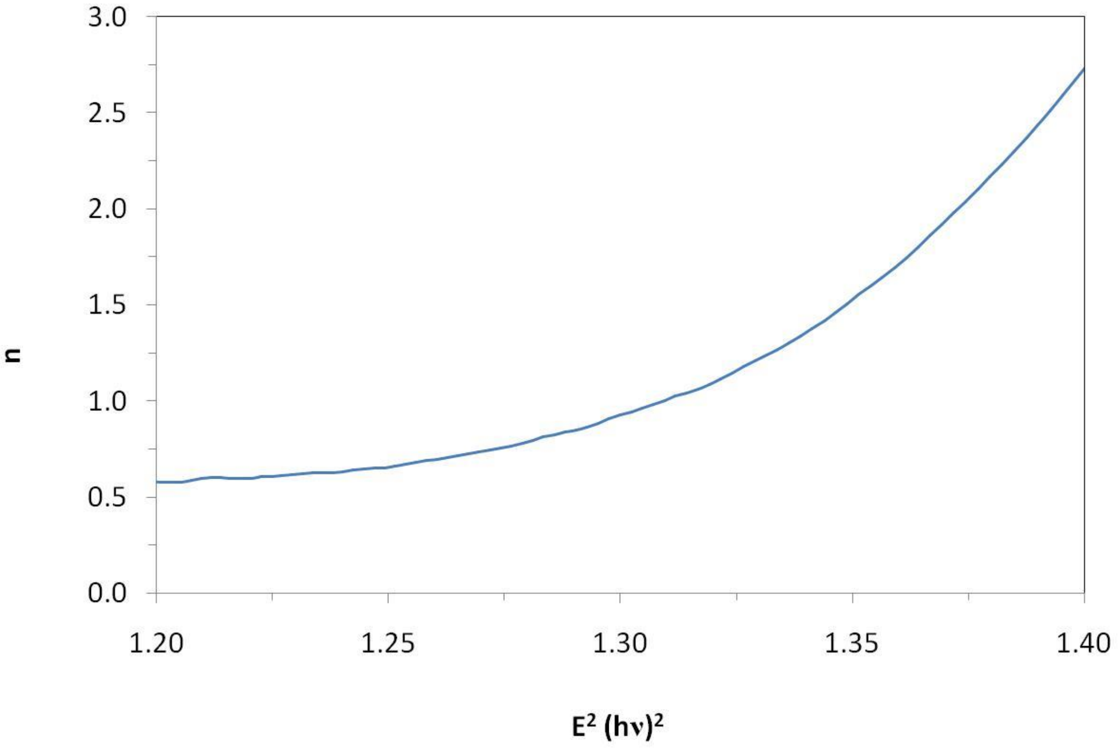

Figure 5: Plot of Refractive Index (n) as a Function of E^2 in the Region of Urbach Tail for $ZrSe_3$ Single Crystals

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 (Ithoh *et al.*, 2002), the spectral variation of the refractive index can be expressed by the Cauchy-Sellmaier function (Elkorashy, 1990) expanded in even powers of E. The first approximation of this function gives the expression,

$$n(E) = n_0 + a_1 E^2 \tag{12}$$

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 5 for $ZrSe_3$ single crystals respectively. The linearity of these curves supports the evolution of the desired parameters. Further more, 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.

Single-Effective Oscillator Model

Based upon the validity of Krammers-Kroning relationship, the real part of dielectric constant takes the form (Gaffar *et al.*, 20013, Elkorashy, 1990 and Wemple and Domenico, 1971),

$$\varepsilon_r = 1 + \frac{F}{\left(E_0^2 - E^2\right)} \tag{13}$$

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.

By a special combination of these parameters, as defined by Wemple and Di Domenico (1971)

$$E_d = {}^{F}\!/_{E_0} \tag{14}$$

the equations (10), (11), (13) and (14), can be coupled together, neglecting the values of K in the transparent region, gives:

$$\varepsilon_r(E) = n^2(E) = 1 + \frac{E_d E_0}{E_0^2 - E^2} \tag{15}$$

Thus, the values of E_0 and E_d have been estimated by plotting $(n^2\text{-}1)^{-1}$ versus E^2 and fitting the relation to a straight line as shown in the figure 6 for WSe_2 crystals. The slope 0.2166 for $ZrSe_3$ (figure 6) as obtained are, obviously the consequence of the corresponding n value. On the basis of the single-effective oscillator model Tributsh and Naturforsch (1977), 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,

$$E_0^2 = \frac{M_{-1}}{M_{-3}} \tag{16}$$

and

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{17}$$

where, rth moment of the optical spectrum is given by

$$M_r = \frac{2}{\pi} \int_{E_t}^{\infty} \varepsilon^r \varepsilon_i(E)\, dE \tag{18}$$

Here E_t is the absorption threshold energy.

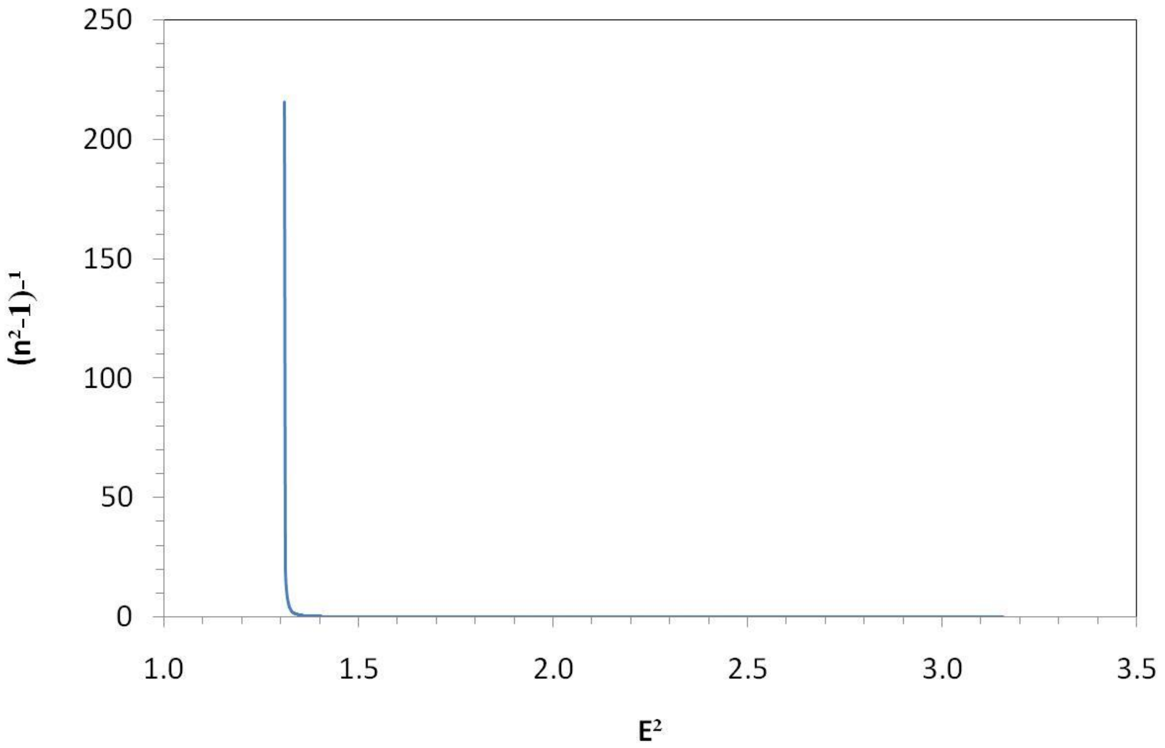

Figure 6: Plot of $(n^2-1)^{-1}$ Versus E^2 for $ZrSe_3$ Single Crystals

Urbach Rule

Moreover, the absorption coefficient α is exponentially related to the sample temperature T′, given as (Pacesova and Jastrabik, 1983)

$$\alpha = \alpha_0 \exp\left[\frac{\sigma}{kT'}(h\nu - h\nu_0)\right] \qquad (19)$$

Where α and hν□ 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 α on y-axis and hυ on x-axis in the range of the Urbach tail yields a straight line. Figure 5.14, showing this typical variation, give fairly accurately the value of σ for $ZrSe_3$ single crystals. The low value of the steepness parameter 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 5.5) 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.

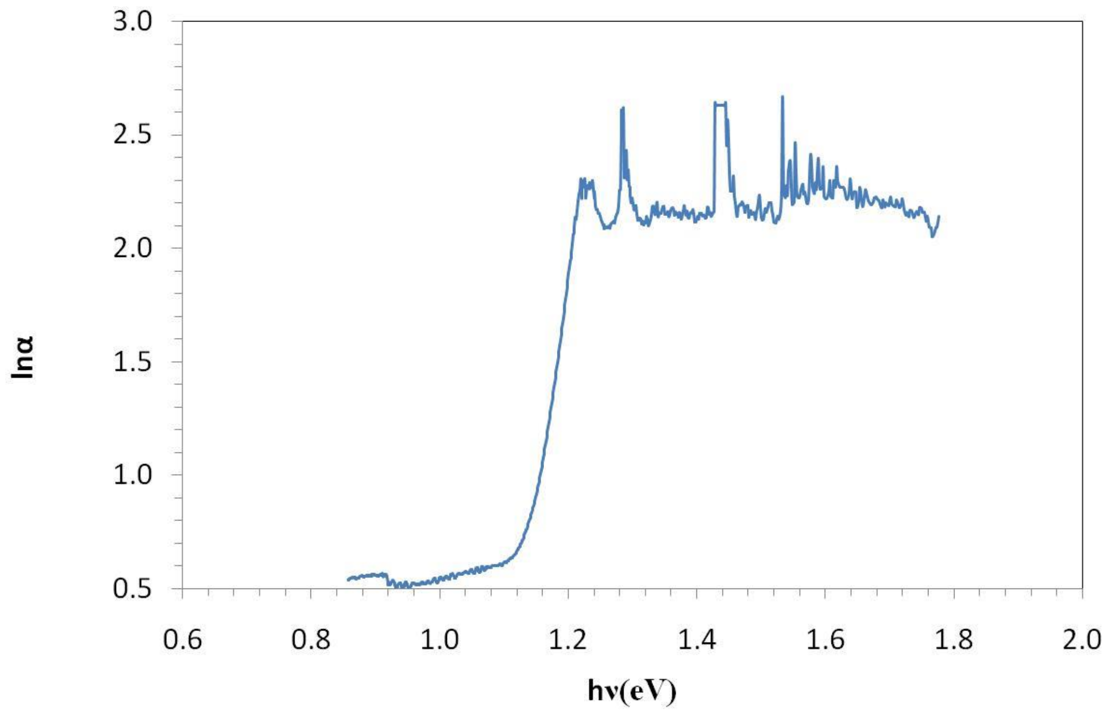

Figure 7: Graphical Plot of ln α Against E for WSe$_2$ Single Crystals

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), 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 $\lambda = c/\nu$ 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 (Han and Becker, 1951) to an absorption increasing as $\lambda^{1.5}$. But scattering by optical phonons gives (Visvanathan, 1960) 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 (Visvanathan, 1960).

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 Fan *et al*., (1956),

$$\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5} \qquad (20)$$

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.

Conclusion

In this paper 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:

1. 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.
2. 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.
3. The computed single–effective oscillator parameters E_0, E_d, M_{-1} and M_{-3} as worked out for the as-grown WSe_2 single crystals.
4. Urbach Rule predicts the steepness parameter (σ) reveals that the absorption is broadened by some feeble disorder in the single crystals.
5. Free-carrier absorption reveals that the transition is taking place due to scattering of acoustical phonons for WSe_2.

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