International Journal of Physics and Mathematical Sciences ISSN: 2277-2111 (Online)
An Open Access, Online International Journal Available at http://www.cibtech.org/jpms.htm
2014 Vol. 4 (4) October-December, pp. 100-110/Patel

Research Article

OPTICAL ANALYSIS OF ZIRCONIUM SULPHOSELENIDE SINGLE CRYSTALS

***Kaushik R. Patel**
Biogas Research Center, Mahadevbhai Desai Gramseva Mahavidhyalaya,
Gujarat Vidyapith, Sadra 382 320
**Author for Correspondence*

ABSTRACT

The optical absorption in the series of zirconium sulphoselenide 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. The results obtained are discussed in detail.

Keywords: *Optical Properties, Absorption Spectra, Direct and Indirect Band Gap*

INTRODUCTION

To understand the nature of semiconductors one must consider what happens when similar atoms are brought closer to form a solid such as a crystal. As two similar atoms approach each other the wave function of their electrons begins to overlap. The energy distribution of the states depends strongly on the interatomic distance. It is the extent of the energy gap and the relative availability of electrons that determine whether a solid is a metal, a semiconductor, or an insulator. In a semiconductor the energy gap usually extends upto 3 *eV* and the density of electrons in the upper band is usually less than 10^{20} cm^{-3}.

The transition metal trichalcogenides MX_3 (M = transition metal, X = S, Se & Te) are layer compounds of special interest, exhibiting both chain structure and cleavage properties. Their structural anisotropy results in highly anisotropic physical properties and induced a quasi-one-dimensional behaviour. The lattice properties of the IV_b trichalcogenides (Grisel *et al.*, 1980; Jandl *et al.*, 1979; Deville *et al.*, 1980; Zwick and Renucei, 1979) in contrast to the V_b compounds.

Preliminary optical absorption measurements on ZrS_3 were taken by Schairer and Schafer (1973). They observed two absorption peaks in the regions of the fundamental gap for light polarized parallel and perpendicular to *b*-axis. They estimated energy band gap of 2.8 *eV* by attributing the dip after the second peak of the absorption spectrum to the beginning of band-band transition. Jellinek *et al.*, (1974) assigned these absorption peaks to electronic transition between the Σ_g^+ states and Π_u of the 3p(4p) levels of $S_2(Se_2)$ in terms of a molecular orbital scheme. The direct band to band transition is allowed for both polarization ($E \parallel b$ and $E \perp b$) on ZrS_3, but for $E \parallel b$ on $ZrSe_3$. The indirect band gap of 2.055 *eV* ($E \parallel b$) and 2.085 ($E \perp b$) for ZrS_3 and of 1.535 *eV* ($E \parallel b$ and $E \perp b$) for $ZrSe_3$ are obtained at liquid helium temperature. A broad luminescence with peak energy of 1.76 *eV*, which shows strong polarization dependence, is attributed to an impurity in ZrS_3.

However, only limited results are available on the optical properties even for the $ZrSe_3$-type materials, which have the simplest crystals structure in the group of the MX_3 compounds. A single band at 2.55 *eV* and 2.43 *eV* was observed for light polarized parallel and perpendicular to the crystal b-axis, respectively. Jellinek *et al.*, (1974) have interpreted these absorption bands as originating from the excitation of the paired anion (S_2^{-2}) orbital. Kurita *et al.*, (1981) have measured detailed transmission spectra of ZrS_3 and $ZrSe_3$ thin samples at liquid helium temperature. It was proved that both materials have an indirect band gap allowed optically for both the $E \parallel b$ and the $E \perp b$ polarizations. The reflection spectra of ZrS_3 and $ZrSe_3$ were measured at room temperature and at 2 *K* (Kurita and Tanaka, 1993). A two dimensional behavior in the electronic band structure and its related properties is reported by Ait-Ouali and Jandl

(1994). The direct as well as indirect band gap of ZrS_3 single crystals were measured by optical absorption at room temperature (Patel *et al.*, 2005).

However, looking at the importance of optical band gap in these materials, the authors have carried out a detailed study on the determination of optical band gap in these materials by optical absorption. The results thus obtained have been described and discussed in this paper.

Experimental

The optical absorption data were obtained by means of UV-VIS-NIR Spectrophotometer (Make: Perkin Elmer, Model: Lambda –19). Prior to measurement samples were oriented both optically and by back reflection Laue techniques. Measurement were performed at room temperature with the electric field of the incident light parallel to the *a* and *b* crystallographic axes, respectively. Measurement along the c-axis were not performed because the crystal structure did not permit cutting and polishing. The energy range of incident photons was extended from 1.0 *eV* to 1.5 *eV*.

For obtaining the absorption spectra using UV-VIS-NIR spectrophotometer from single crystal specimens, thin flakes of as grown crystals 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 at 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 can also be used as replica. For reflectance measurement standard aluminum coated mirror can be used as reference.

Optical Analysis

The most direct and the simplest method for probing the band structure of semiconductors are to measure the absorption spectrum. In the absorption process, a photon of a known energy excites an electron from a lower-energy to a higher-energy state. Thus by inserting a slab of semiconductor at the output of a monochromator and studying the changes in the transmitted radiation, one can discover all the possible transitions an electron can make and learn much about the distribution of states. Absorption is expressed in terms of coefficient $\alpha(h\nu)$, which is defined as the relative rate of decrease in light intensity $L(h\nu)$ along its propagation path:

$$\alpha = \frac{1}{L(h\upsilon)}\frac{d[L(h\upsilon)]}{dx} \qquad (1)$$

Fundamental Absorption

The fundamental absorption refers to band-to-band or to excitons transition, *i.e.*, to the excitation of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transition are subject to certain selection rules, the estimation of the energy gap from the “absorption edge” is not a straightforward process-even if competing absorption process can be accounted for.

Because the momentum of a photon, h/λ, (λ is the wavelength of light), is very small compared to the crystal momentum h/a (a is the lattice constant), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient $\alpha(h\upsilon)$ for a given photon energy $h\upsilon$ is proportional to the probability P_{if} for the transition from the initial state, n_i, and also to the density of available (empty) final state, n_f, and this process must be assumed for all possible transitions between states separated by an energy difference equal to $h\upsilon$:

$$\alpha(h\upsilon) = A\sum p_{if} n_i n_f \qquad (2)$$

Here, for simplicity we shall assume that all the lower states are filled and that all the upper states are empty, a condition which is true for undoped semiconductor at 0 *K*.

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.

Direct Transition

Let us consider absorption transition between two direct valleys where all the momentum-conserving transition are allowed as shown in Figure 1. Every initial state at E_i is associated with a final state at E_f such that $E_f = h\upsilon - |E_i|$ (3)

But in parabolic bands, $$E_f - E_g = \frac{h^2k^2}{2m_e^*} \tag{4}$$

and $$E_i = \frac{h^2k^2}{2m_e^*} \tag{5}$$

Therefore, $$h\upsilon - E_g = \frac{h^2k^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \tag{6}$$

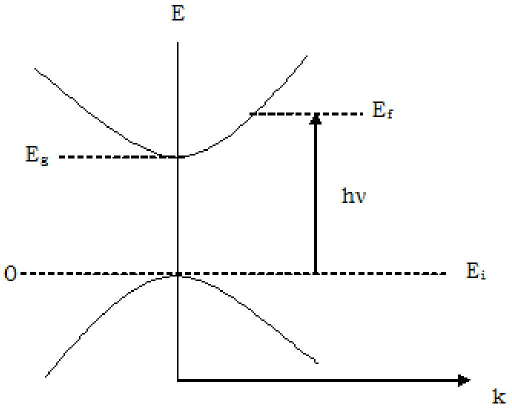

Figure 1: Schematic diagram showing direct transitions

The density of directly associated states is

$$N(h\upsilon)d(h\upsilon) = \frac{8\pi k^2 dk}{(2\pi)^3} \tag{7}$$

$$N(h\upsilon)d(h\upsilon) = \frac{(2m_r)^{3/2}}{2\pi^2\hbar^3}(h\upsilon - E_g)^{1/2} d(h\upsilon) \tag{8}$$

Where m_r is the reduced mass given by $\frac{1}{\mathrm{m_r}} = \frac{1}{\mathrm{m_e^*}} + \frac{1}{m_h^*}$. Hence the absorption coefficient is

$$\alpha(h\upsilon) = A^*(h\upsilon - E_g)^{1/2} \tag{9}$$

Where $$A^* \approx \frac{q^2\left(2\frac{m_h^* m_e^*}{m_h^* + m_e^*}\right)^{3/2}}{nch^2 m_e^*} \tag{10}$$

For an index of refraction n=4 and assuming the hole and electron effective masses equal the free electron mass, one gets,

$$\alpha(h\upsilon) \approx 2\times10^4 (h\upsilon - E_g)^{1/2}\ \text{cm}^{-1} \tag{11}$$

Indirect Transition between Indirect Valleys

$$\left.\begin{aligned} h\upsilon_e &= E_f - E_i + E_p \\ h\upsilon_a &= E_f - E_i - E_p \end{aligned}\right\} \qquad (12)$$

When a transition requires a change in energy and momentum, a double or two-step process is required because the photon cannot provide a change in momentum. Momentum is conserved via a phonon interaction, which is illustrated in Figure 2. Although a broad spectrum of phonon is available, only those with the required momentum changes are usable. These are usually the longitudinal and the transverse-acoustic phonon. Each of this phonon has a characteristic energy E_p. Hence to complete the transition E_i to E_f a phonon is either emitted or absorbed. These two processes are given respectively by

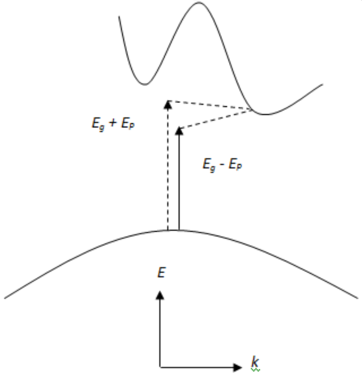

Figure 2: Schematic diagram showing indirect transitions

In general, however, at high temperature phonons are present and can participate in the absorption process. The optical transition is accordingly said to be non-vertical or indirect. Such indirect transitions are is great importance 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 extreme occur at different values of the *k* vector. Optical absorption spectra of zirconium sulphoselenide single crystals were taken with the help of UV-VIS –NIR spectrophotometer in the wavelength range of 200 *nm* - 1500 *nm* at room temperature. For determination of band gap for semiconducting materials, absorption of incident photon by semiconducting material is an important technique. In this technique, photons of selected wavelengths are bombarded on the sample and their relative transmission is observed. Since the photons with energies greater than the band gap are absorbed while photons with energies less than band gap are transmitted, the technique provides accurate measurements of the energy band gap. 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_o (photon/cm^{2}sec) transmits through a slab of a medium of thickness *x*, the beam of photons attenuates in accordance with the exponential law

$$I = I_0 e^{(-\alpha x)} \qquad (13)$$

where 'α' is called as the absorption coefficient and has units of cm^{-1}. This coefficient α can be obtained simply by measuring I_0/I of the intensities impinging and emerging from the samples respectively.

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 (Pankove, 1975),

$$\alpha hv = A(hv - E_g)^r \qquad (14)$$

for direct transitions and

$$\alpha hv = \sum_j B_j (hv - E'_g \pm E_{pj})^r \qquad (15)$$

for indirect transitions.

Here, α is the absorption coefficient, $h\nu$ the energy of the incident photon, E_g the energy for the direct transition and E'_g the energy for indirect transition and E_{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 (14) and (15) 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 (15) (Elkorashy, 1986; Vlachs, 1976) is given as,

$$\alpha_i = \sum_{i=1}^{2}\left\{\frac{B_{ai}}{E}\left(\frac{1}{e^{\theta_i/T}-1}\right)(E-E'_g+k\theta_i)^r + \frac{B_{ei}}{E}\left(\frac{1}{1-e^{\theta_i/T}}\right)\left(E-E'_g-k\theta_i\right)^r\right\} \tag{16}$$

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,

$$\theta_i = \frac{E_{pi}}{k} \tag{17}$$

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

$$\alpha = A'(h\nu - E_g)^r \tag{18}$$

for direct transition and

$$\alpha_i = \sum_{i=1}^{2}\left\{B'_{ai}\left(\frac{1}{e^{\theta_i/T}-1}\right)(E-E'_g+k\theta_i)^r + B'_{ei}\left(\frac{1}{1-e^{\theta_i/T}}\right)\left(E-E'_g-k\theta_i\right)^r\right\} \tag{19}$$

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

RESULTS AND DISCUSSION

The absorption spectra of ZrS_xSe_{3-x} (where $0 \le x \le 3$) single crystal are shown in Figure 3 (a-g). A careful study of these spectra reveals the presence of absorption edges in the spectral range 200 *nm* to 1500 *nm*.

Table 1: The values of optical parameters of zirconium sulphoselenide single crystals

Parameter	**Compounds**						
	$ZrSe_3$	**$ZrS_{0.5}Se_{2.5}$**	**$ZrSSe_2$**	**$ZrS_{1.5}Se_{1.5}$**	**ZrS_2Se**	**$ZrS_{2.5}Se_{0.5}$**	**ZrS_3**
E_1 (eV)	1.03	1.24	1.26	1.06	1.27	1.04	1.64
E_2 (eV)	1.06	1.28	1.31	1.35	1.46	1.51	1.75
E_3 (eV)	1.09	1.31	1.37	1.64	1.64	1.99	1.85
E_4 (eV)	1.12	1.35	1.42	1.94	1.83	2.46	1.96
E'_g (C) (eV)	1.07	1.30	1.34	1.50	1.55	1.75	1.80
E'_g (E) (eV)	1.12	1.30	1.33	1.50	1.54	1.75	1.80
E_{p1} (meV)	45	52	80	438	279	710	162
E_{p2} (meV)	15	19	27	146	93	236	54
θ_1 (K)	522.39	603.65	928.69	5084.60	3238.60	8242.17	1880.6
θ_2 (K)	174.13	220.56	313.43	1694.86	1081.93	2739.65	626.87
E_g (eV) (Direct)	1.18	1.36	1.48	1.73	1.82	2.1	2.24

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 (6.17)

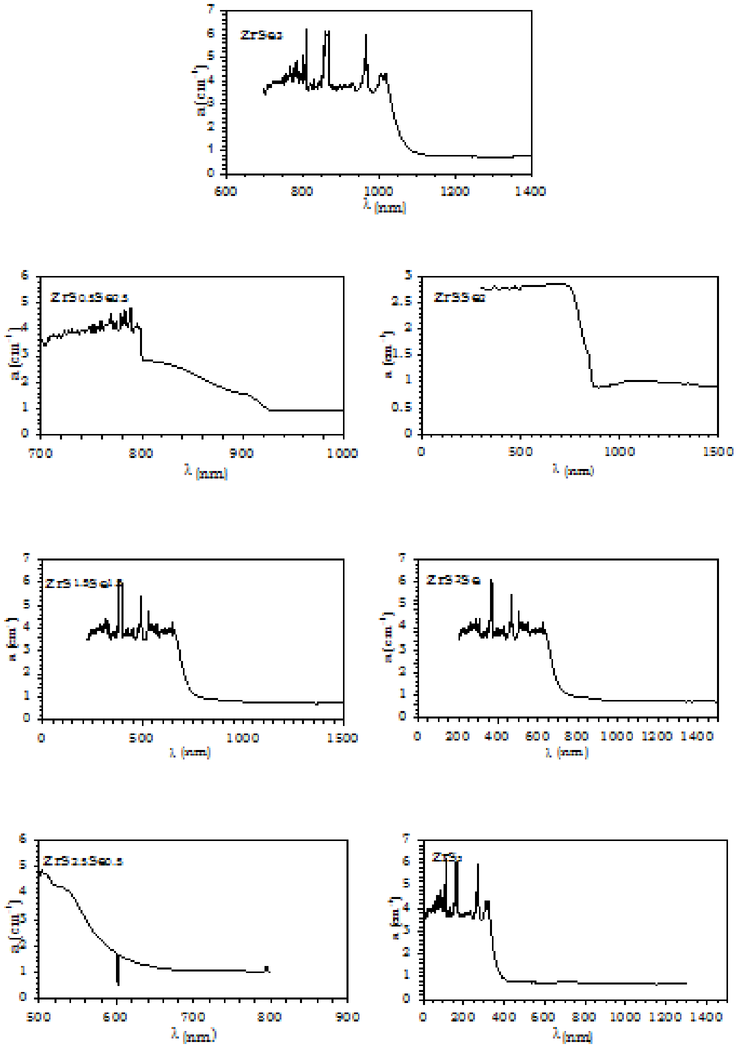

Figure 3: The optical absorption spectrum for as grown crystals of zirconium

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 (14) and (15) using the values of *r* equal to ½ and 2 respectively.

Accordingly, Figure 4 (a-g) for ZrS_xSe_{3-x} (where $0 \leq x \leq 3$) single crystal shows the spectral variation of $(\alpha h\nu)^{1/2}$ vs. $h\nu$. Since the curves indicate discontinuous straight lines, it is quite possible that they represent indirect interaband 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 (Kam *et al.*, 1984; Koshkin *et al.*, 1970; Dholakiya *et al.*, 2001; Dholakiya *et al.*, 2003).

Accordingly, from the graphical differentiation of the data presented in Figure 4 (a-g) for ZrS_xSe_{3-x} (where $0 \leq x \leq 3$) single crystal, the dependence of the derivatives $\delta(\alpha h\nu)^{1/2}/\ \delta h\nu$ on $h\nu$ has been shown in Figure 5 (a-g). It can be clearly seen from these figure that the derivatives are step function of energy with four steps well defined in the range $E_1 < E < E_2$, $E_2 < E < E_3$, $E_3 < E < E_4$ and $E_4 < E$.

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

$$E'_g = \frac{E_1 + E_4}{2} = \frac{E_2 + E_3}{2} \qquad (20)$$

$$E_{p1} = \frac{E_4 - E_1}{2} \quad \text{and} \quad E_{p2} = \frac{E_3 - E_2}{2} \qquad (21)$$

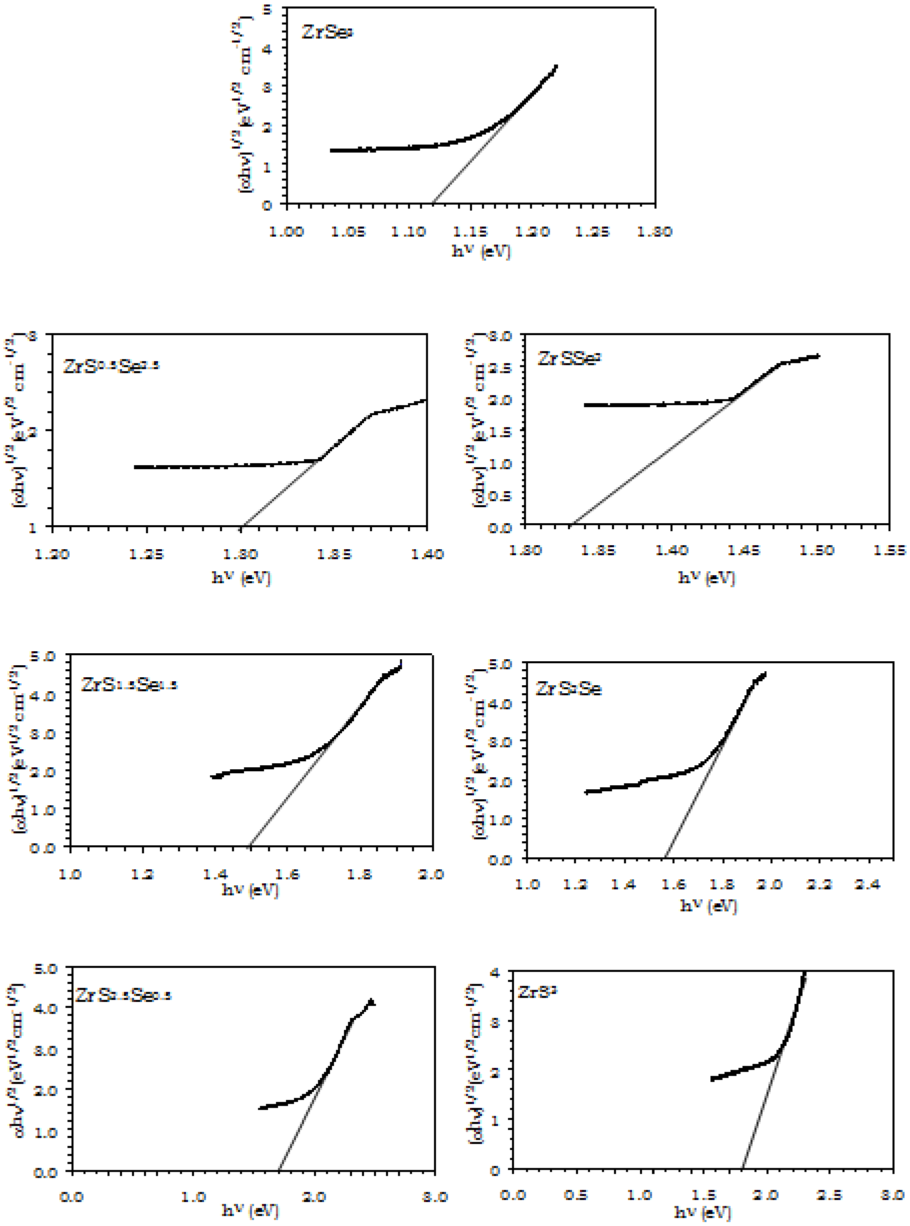

Figure 4: The graph of $(\alpha h\nu)^{1/2}$ versus hν for as grown crystals of zirconium trisulphoselenide

The values of indirect band gap E'_g and phonon energies thus obtained are presented in Table 1. 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 4 (a-g). These values closely matches with the value obtained from equation (20).

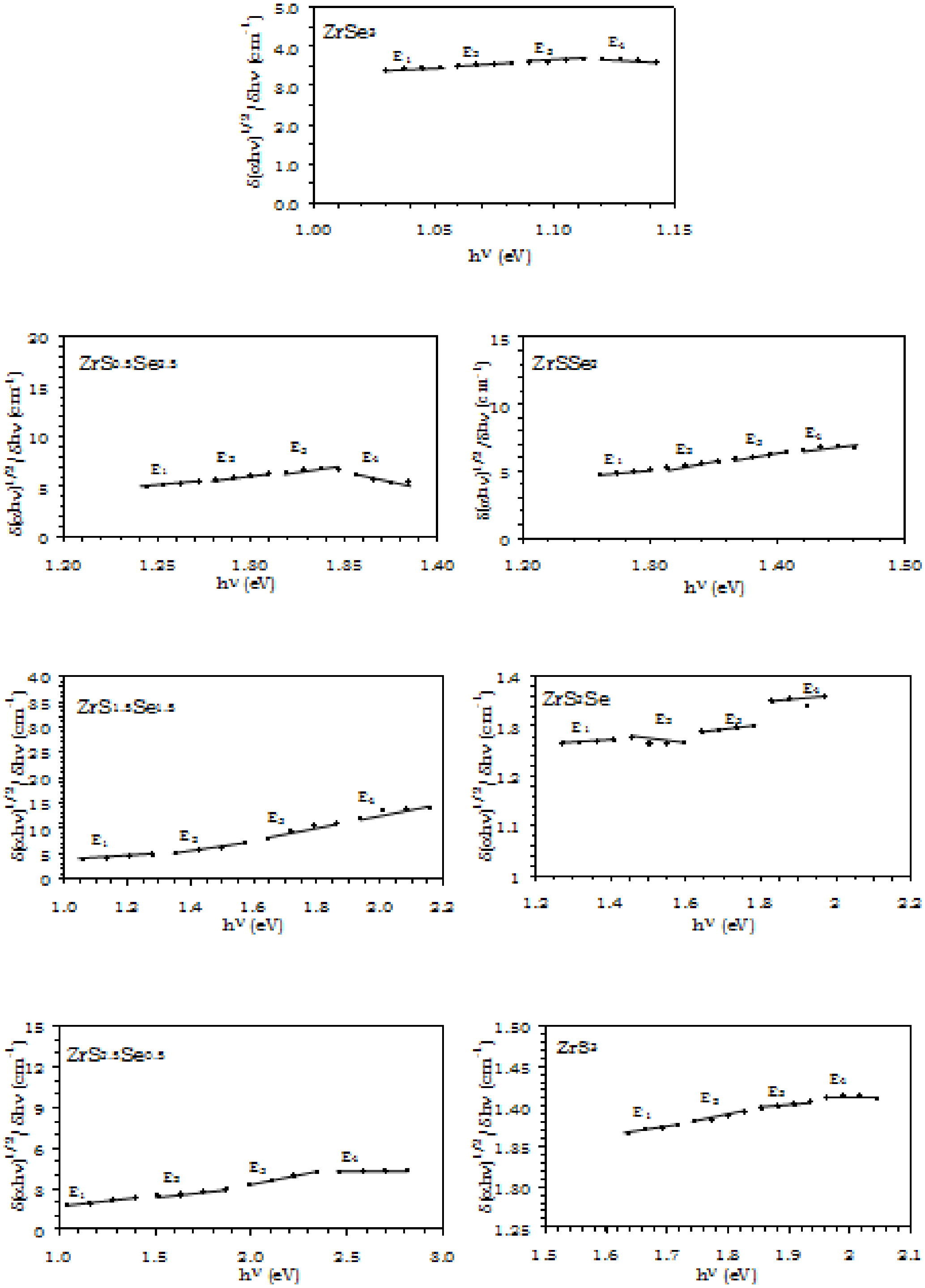

Figure 5: The spectral variation of $\delta(\alpha h\nu)^{1/2}/\delta h\nu$ versus hν for as grown crystals of zirconium trisulphoselenide

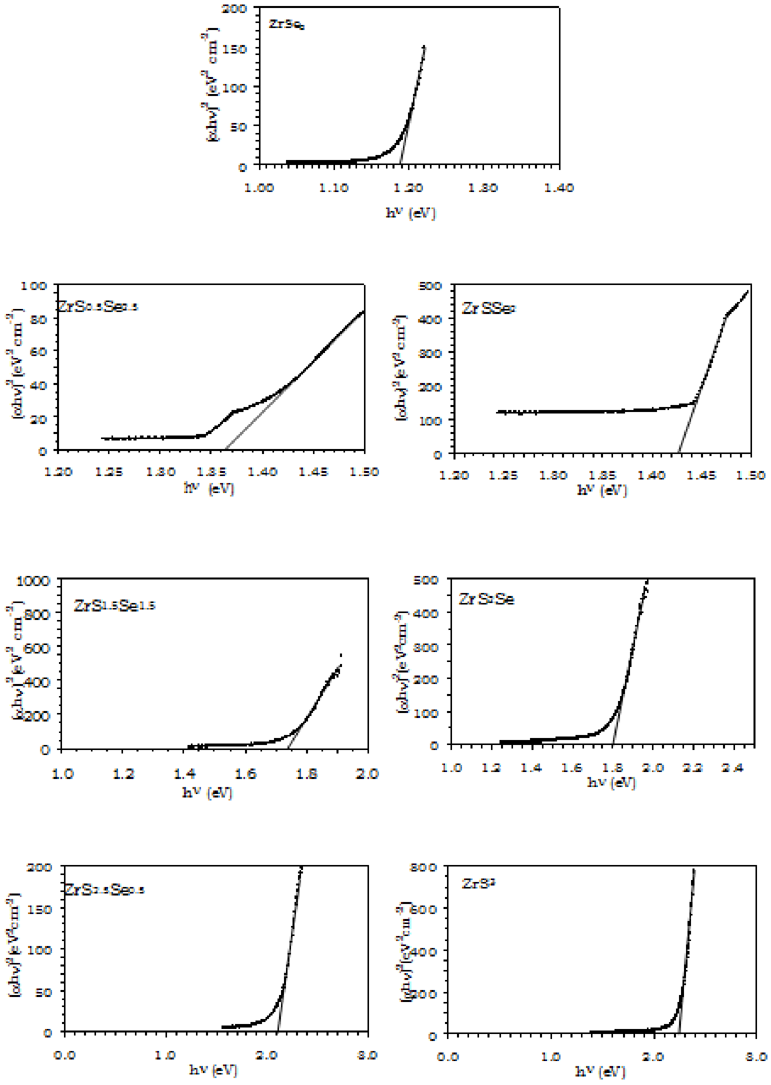

Figure 6: The graph of $(\alpha h\nu)^2$ versus hν for as grown crystals of zirconium trisulphoselenide

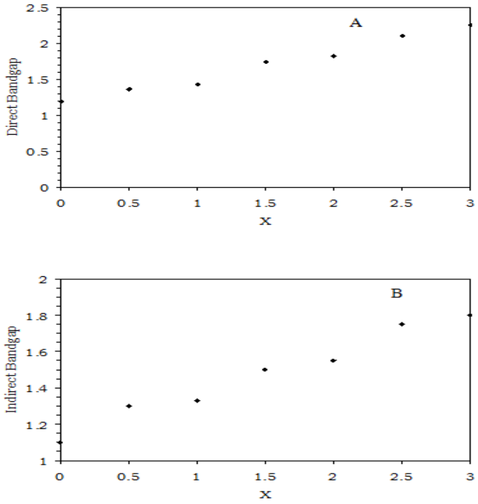

Figure 7 (A & B): The graph of direct band gap and indirect band gap vs. composition X

For the determination of the direct band gap E_g, the spectral variation of $(\alpha h\nu)^2$ vs $h\nu$ as shown in Figures 6 (a-g) were studied. The values of direct band gap E_g obtained from the intersection of the linear portion of the curves in Figure 6 (a-g) are shown in Table 1. 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 1. A detailed study of the data presented in Table 1 and Figure 7 (A & B), indicates that both indirect as well as direct band gap increase with increase of sulphur proportion in single crystals of the series ZrS_xSe_{3-x}.

Conclusion

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

1. The direct and indirect band gap for all the samples has been determined. The variation of band gap with sulphur proportion in ZrS_xSe_{3-x} (where $0 \leq x \leq 3$) indicates the symmetries of the band edges in grown crystals is the same.
2. The accurate analysis of the data has shown that the indirect transition represented by the absorption curves is indirect allowed involving two different phonons. The energies of these phonons have been determined.
3. The indirect as well as direct band gap of grown crystals is increases with increase the sulphur content in the ZrS_xSe_{3-x} single crystals.

REFERENCES

Ait-Ouali and Jandl S (1994). Two-dimensional indirect excitons in the layer-type trichalcogenide ZrS3, *Physical Review B* **49** 1813.

Deville Cavellin C and Jandl S (1980). Raman spectra of HfS3. *Solid State Communication* **53** 813.

Dholakiya DA, Solanki GK, Patel SG and Agarwal MK (2001). Two- and three-dimensional models for analysis of optical absorption in tungsten disulphide single crystals. *Bulletin of Material Science* **24**(3) 291.

Dholakiya DA, Solanki GK, Patel SG and Agarwal MK (2003). Optical band gap studies of Tungsten sulphoseleide single crystals Grown by a DVT technigue. *Scientia Iranica* **10** 373.

Elkorashy AM (1986). Optical absorption in tin monoselenide single crystal, *Journal of Physics and Chemistry of Solids* **47** 497.

Elkorashy AM (1988). Temperature Dependence of Two-Dimensional Optical Energy Gap for Germanium Selenide Single Crystals, *Physica Status Solidi (b)* **146** 279.

Goldberg AM, Beal AR, Levy FA and Davis EA (1975). The low-energy absorption edge in 2H-MoS2 and 2H-MoSe2. *Philosophical Magazine* **32** 367.

Grisel A, Levy F and Wieting TJ (1980). Optical-phonon anisotropies in crystalline IVB trichalcogenides, *Physics B+C* **99** 365.

Jandl S, Deville Cavellin C and Harbec JY (1979). Raman spectra of ZrS_3, *Solid State Communicaton* **31** 351.

Jellinek F, Pollak RA and Shafer MW (1974). X-ray photoelectron spectra and electronic structure of zirconium trisulfide and triselenide, *Materials Research Bulletin* **9** 845.

Kam KK, Chang CL and Lynch DW (1984). Fundamental absorption edges and indirect band gaps in $W_{1-x}Mo_xSe_2$(O≤x≤1). *Journal of Physics C: Solid State Physics* **17** 4031.

Koshkin VM, Karas VR and Gal'chinestski P (1970). Two- and three-dimensional models for analysis of optical absorption in tungsten disulphide single crystals. *Soviet Physics: Semiconductors* **3** 1186.

Kurita S and Tanaka M (1993). Optical spectra near the band edge of **ZrS3** and **ZrSe3,** *Physical Review B* **48** 1356.

Kurita S, Staehli JL, Guzzi M and Levy F (1981). *Physica B* **105** 169.

Pankove JI (1975). In: *Optical Processes in Semicondcuctors* (New York: Dover Publ. Inc.) 1.

Patel KR, Prajapati JH, Vaidya RD and Patel SG (2005). Study of optical and electrical properties for ZrS_3 single crystals, *Indian Journal of Physics* **79**(4) 373.

Schairer W and Schafer MW (1973). Growth and optical absorption spectra of the layer-type trichalcogenides ZrS3 and HfS_3, *Physica Status Solidi A* **17** 181.
Vlachs SV, Lambros AP, Thanailakis A and Economou NA (1976). Anisotropic Indirect Absorption Edge in GeSe, *Physica Status Solidi (B)* **76** 727.
Zwick A and Renucei MA (1979). Long-wavelength optical phonons in $ZrSe_3$, *Physica Status Solidi (B)* **96** 757.