

Optical and electrical properties of $ZrSe_3$ single crystals grown by chemical vapour transport technique

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Abstract. Single crystals of the lamellar compound, $ZrSe_3$, were grown by chemical vapour transport technique using iodine as a transporting agent. The grown crystals were characterized with the help of energy dispersive analysis by X-ray (EDAX), which gave confirmation about the stoichiometry. The optical band gap measurement of as grown crystals was carried out with the help of optical absorption spectra in the range 700–1450 nm. The indirect as well as direct band gap of $ZrSe_3$ were found to be 1.1 eV and 1.47 eV, respectively. The resistivity of the as grown crystals was measured using van der Pauw method. The Hall parameters of the grown crystals were determined at room temperature from Hall effect measurements. Electrical resistivity measurements were performed on this crystal in the temperature range 303–423 K. The crystals were found to exhibit semiconducting nature in this range. The activation energy and anisotropy measurements were carried out for this crystal. Pressure dependence of electrical resistance was studied using Bridgman opposed anvils set up up to 8 GPa. The semiconducting nature of $ZrSe_3$ single crystal was inferred from the graph of resistance vs pressure. The results obtained are discussed in detail.

Keywords. $ZrSe_3$ single crystal; optical band gap; resistivity; Hall parameters; Bridgman anvil cell.

1. Introduction

The zirconium triselenide, $ZrSe_3$, has a chain-like structure belonging to the space group $P2_1/m$ (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 growth in the form of layers run parallel to the b -axis and each chain in the layer is displaced from the neighbouring chain by half of the unit cell along the b -axis. Resistivity, Hall coefficient and thermoelectric power measurement of $ZrSe_3$ single crystal along the chain axis have been carried out in the temperature range from 200–400 K (Ikari *et al* 1983).

The $ZrSe_3$ exhibits a rather layer-like semiconducting behaviour (Wilson 1979; Sourisseau and Mathey 1981; Khumalo *et al* 1981; Zwick *et al* 1982; Ikari *et al* 1983; Deslandes and Jandl 1984). An indirect band gap of 1.1 eV was measured for $ZrSe_3$ (Brattas and Kjekshus 1972). Transition metal dichalcogenides (TMDCs) of group IVB, VB, VIB including intercalated materials exhibit charge density wave and/or superconducting transitions. Investigations have established interrelationships among these transition and inter and intra layer distances. These compounds have special interest on account of their structural anisotropy. The need for developing a cheap yet effective

method of converting solar energy into electrical or chemical energy stimulated rapid advancement of semiconductor electrochemistry in the past decades. As a result certain useful materials, e.g. metallic chalcogenides, which have potential in photovoltaic and photoelectrochemical solar cell studies have attracted attention of crystal growers. Among them, disulphide and diselenide of zirconium present some interesting switching and memory effects (Lee *et al* 1969) with some possible application in solid state solar cell (Tributsch 1981). A complete crystal structure determination was reported for the prototype, $ZrSe_3$ (Kronert and Plieth 1958, 1965).

ZrS_xSe_{3-x} exhibits continuous regions of solid solubility. Diffuse reflectance measurements show that $ZrS_{3-x}Se_x$ exhibit semiconduction (Brattas and Kjekshus 1972). Raman scattering for ZrS_3 was reported as a function of hydrostatic pressure (Deville Cavellin *et al* 1982). Thermoreflectance spectra of $ZrS_{3-x}Se_x$ single crystals have been measured at 50 K. The thermoreflectance spectra of ZrS_3 and $ZrSe_3$ are discussed through direct and indirect exciton transitions (Provencher *et al* 1988). The first-order Raman spectra of one-dimensional solid solution, $ZrS_{2.5}Se_{0.5}$, have been obtained and studied (Jandl and Provencher 1981). The semiconducting nature of ZrS_3 is inferred from the resistance vs temperature measurements (Patel *et al* 1993).

The electrical resistance measurement of $ZrSe_3$ single crystal for various pressure measurements up to 7.5 GPa is carried out using Bridgman anvil set up. Pressure, as a

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Table 1. Growth parameters of ZrSe₃ single crystal grown using chemical (iodine) vapour transport technique.

Ampoule dimension		Temperature distribution		Physical characteristics of crystals			
Length (mm)	ID (mm)	Hot zone (K)	Cold zone (K)	Growth time (h)	Plate area (mm ²)	Thickness (mm)	Colour
250	22	1173	1123	370	45	0.09	Red shining

relatively cleaner way of controlled change of inter-atomic distances, holds promise in the investigation of these materials to identify the novel properties and phase changes exhibited by them. A detailed study of the valence band by synchrotron radiation photoemission spectroscopy had demonstrated the existence of paired-anion ligands in zirconium trichalcogenides (Margaritondo *et al* 1980).

In this paper, we report the growth, measurements of d.c. resistivity and anisotropy in electrical resistivity in the temperature range 303–423 K carried out to identify any possible temperature induced transitions in them.

2. Experimental

The single crystals of ZrSe₃ were grown by the chemical vapour transport (CVT) method using iodine as a transporting agent. The charge of ZrSe₃ was prepared using high purity elements. The temperature for compound preparation was about 900°C for 3 days. The charge of compound was then put into another quartz ampoule and then sealed together with 5 mg/cc iodine. The ampoule was placed in the two-zone furnace with appropriate gradient. The details of growth parameters are given in table 1. The stoichiometry of the as grown crystals was confirmed by energy dispersive analysis by X-ray (EDAX). The stoichiometric proportion of ZrSe₃ single crystals is shown in table 2.

The absorption spectra were obtained by means of a UV–VIS–NIR DK 2A spectrophotometer in the range 700–1450 nm. All measurements were taken at room temperature with the incident beam normal to the basal plane i.e. along the *c*-axis of the as grown flakes.

The electrical resistance was measured by van der Pauw method at room temperature. The values of mobility, Hall coefficient and carrier concentration were determined from the Hall effect measurements and represented in table 2.

The high temperature resistivity measurement perpendicular to *c*-axis i.e. along the basal plane, was carried out on ZrSe₃ single crystal in the temperature range 303–423 K, using the four-probe set up manufactured by Scientific Equipments, Roorkee. Resistivity measurement parallel to *c*-axis i.e. normal to the basal plane, was carried out for the same temperature range using an experimental set up designed and prepared by the University Science

Table 2. The stoichiometric proportion and EDAX data of ZrSe₃ single crystals.

Element	Stoichiometric proportion (Wt%)	From EDAX (Wt%)
Zr	27.80	25.26
Se	72.20	74.74

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Using the resistivity values parallel and perpendicular to *c*-axis, the anisotropy ratio $g = r_{\parallel}/r_{\perp}$ for all the different samples has been determined in the temperature range 303–423 K.

The resistance was measured for this crystal as a function of pressure up to 8 GPa. Pressure was generated with a Bridgman type tungsten carbide opposed anvil apparatus. The sample was contained in a pyrophyllite gasket with talc as pressure transmitting medium. A four-probe method was used to evaluate the resistance of ZrSe₃ sample. A constant current was passed through the sample and the voltage across it was measured using d.c. nanovoltmeter.

3. Results and discussion

The interpretations of experimental results, viz. the dependence of absorption coefficient '*a*' in terms of the direct and indirect transitions is most often performed with the help of formula derived for three-dimensional (3D) crystal. Their simplest form is as follows (Pankov 1975).

For direct band gap,

$$ah\nu = A(h\nu - E_g)^r, \quad (1)$$

for indirect band gap,

$$ah\nu = \sum_j B_j (h\nu - E_g' \pm E_{pj})^r, \quad (2)$$

here *a* is absorption coefficient, calculated as a function of photon energy from absorption vs wavelength curve, *hν* the energy of the incident photon, *E_g* the energy for the direct transition, *E_g'* the energy for the indirect transition and *E_{pi}* the energy of the phonons assisting at indirect transition. *A* and *B* are parameters which depend in a

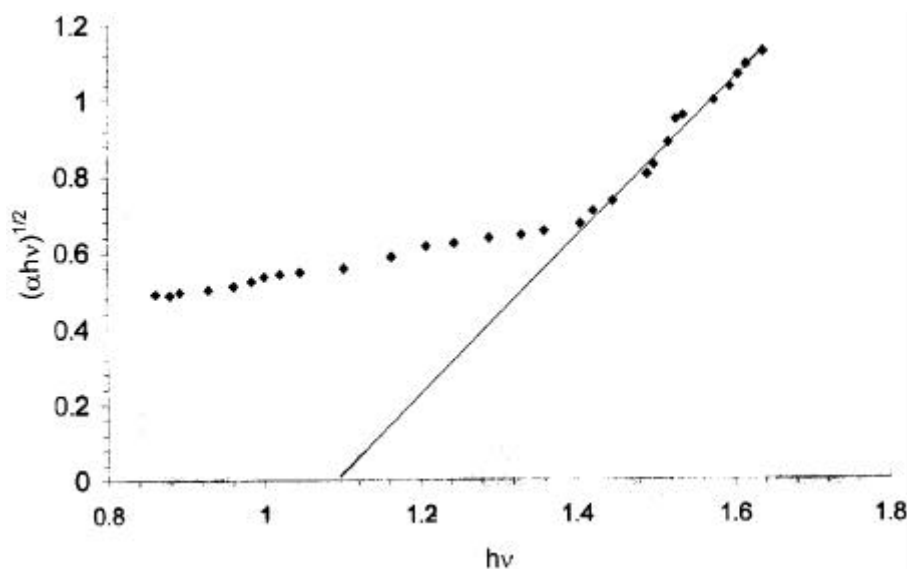


Figure 1. The plot of $(\alpha h\nu)^{1/2}$ vs photon energy ($h\nu$) for ZrSe₃ single crystal.

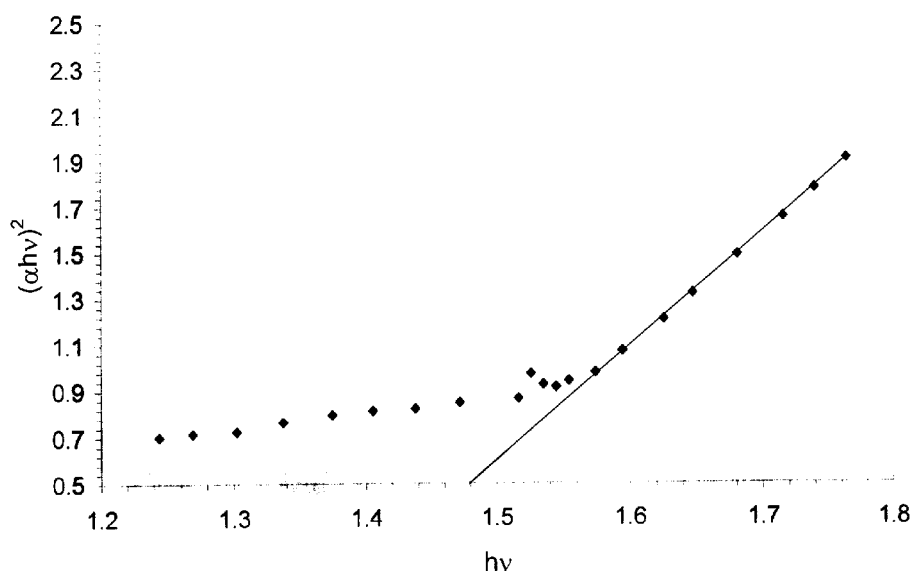


Figure 2. The plot of $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for ZrSe₃ single crystal.

more complicated way on temperature, photon energy and phonon energies, E_p .

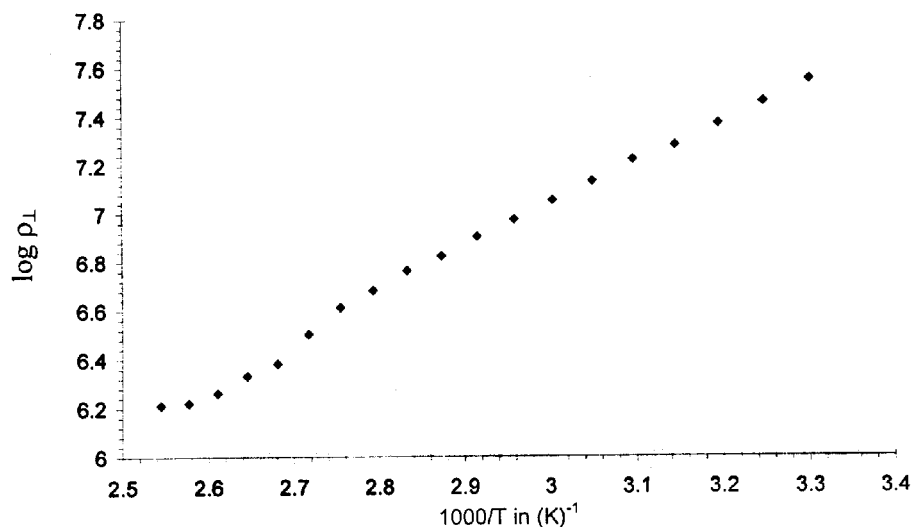
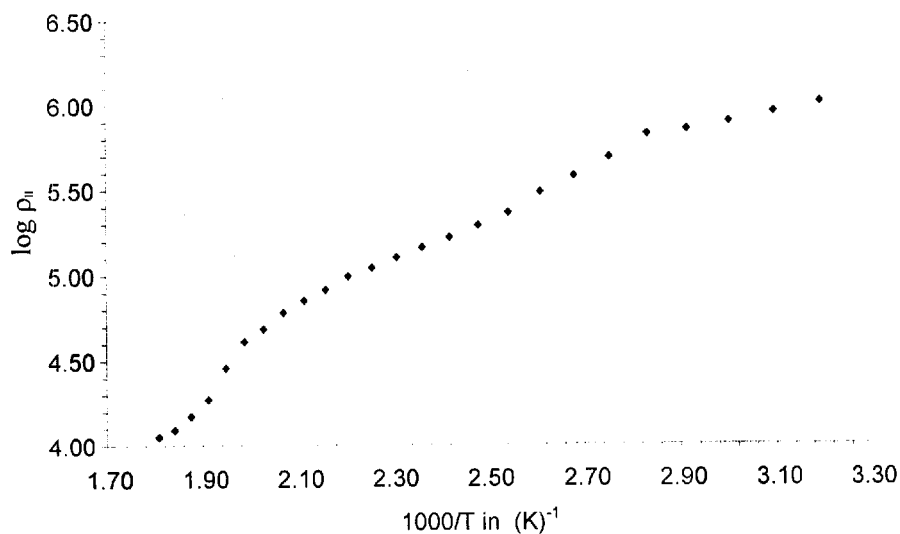
By plotting graph of $(\alpha h\nu)^{1/2}$ vs $h\nu$ and $(\alpha h\nu)^2$ vs $h\nu$ as shown in figures 1 and 2, it is possible to determine the indirect as well as direct band gap, respectively for ZrSe₃ single crystal. In figure 1, the curve indicates a discontinuous straight line and represents interband transition involving the emission or absorption of phonons. The band gap is obtained by extrapolating the linear part to zero of the ordinate. The indirect and direct band gaps are found to be 1.1 eV and 1.47 eV, respectively. The values of indirect band gap can also be obtained from the graphical calculation of the discrete energy levels. It is quite clear

from the analysis of the absorption data that direct and indirect symmetry allowed transitions to give a good account of the absorption edge in ZrSe₃ single crystals.

The graph of $\log r_{\perp}$ vs $1000/T$ for as grown crystal is shown in figure 3. The graph of $\log r_{\parallel}$ vs $1000/T$ is shown in figure 4. In figures 3 and 4 the resistivity decreases with increase in temperature. It suggests the semiconducting nature of ZrSe₃ crystal in the temperature range 303–423 K. The variation of resistivity along the basal plane is attributed to the change in nature of chemical bonding between the cation and anion. Layered crystals often show predominance of stacking faults. Perpendicular to the layers, however, there is a probability of transport

Table 3. Hall parameters, resistivity, conductivity, Hall coefficient, mobility and carrier concentration at room temperature for ZrSe₃.

Resistivity ($r\Omega$ cm)	Conductivity (s Mho cm^{-1})	Hall coefficient (R_H cm^3 cb^{-1})	Mobility (μ cm^2/Vs)	Carrier concentration (h cm^{-3})
143.9	6.947×10^{-3}	-5.76×10^5	3990	1.084×10^{13}

**Figure 3.** The plot of $\log r_{\perp}$ vs $1000/T$ for ZrSe₃ single crystal.**Figure 4.** The plot of resistivity r_{\parallel} vs $1000/T$ for ZrSe₃ single crystal.

due to the localization of the electron states because of the presence of stacking faults. This will therefore give rise to a fairly large amount of conduction parallel to c -axis. The graph of anisotropy ratio, g vs $1000/T$ for ZrSe₃ single crystal is shown in figure 5. This anisotropy ratio increases as the temperature decreases for as grown crystals. For the materials, which are intermediate between two and three dimensions, there is an anisotropy of strength

of the bond between atoms. Application of temperature or chemical alloying causes greater changes in the length of weaker bonds than those of stronger ones. This type of anisotropy behaviour is an interesting question for the strongly layered materials and it can also be explained as an effect of stacking disorder.

Under normal conditions solids exhibit a particular crystal structure for which the total energy is minimum.

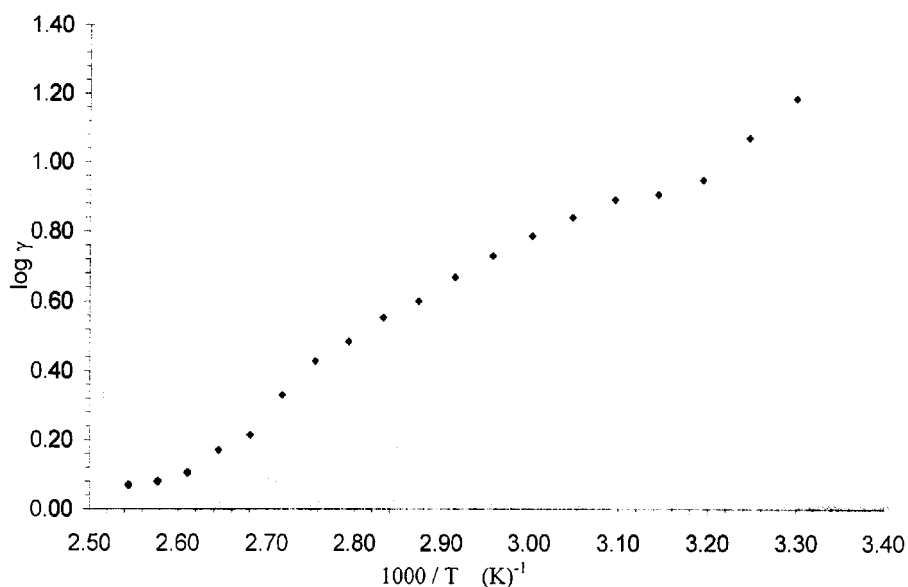


Figure 5. The plot of anisotropy ratio g vs $1000/T$ for ZrSe_3 single crystal.

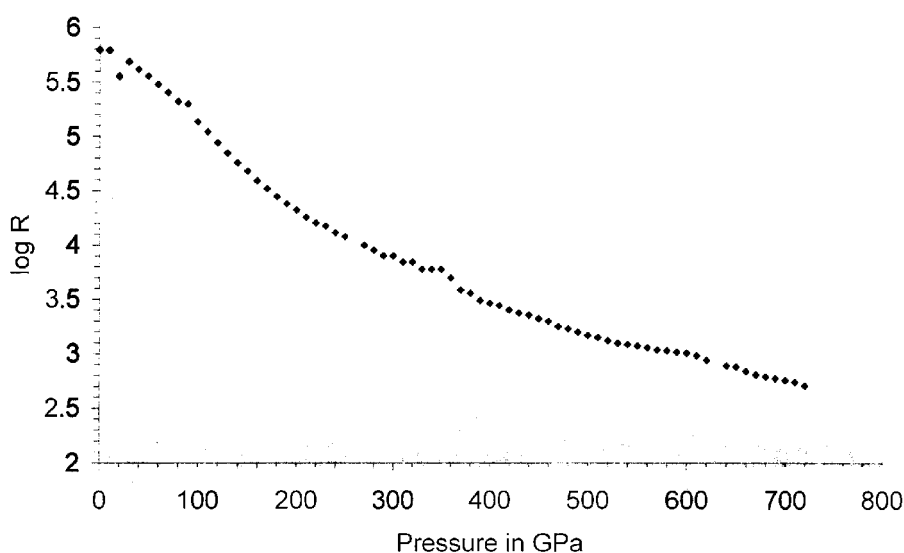


Figure 6. The plot of $\log R$ vs pressure for ZrSe_3 single crystal.

However, on application of high pressure, the atomic arrangements in solids change, resulting in changes in interatomic distances and crystal structure. The graph of $\log R$ vs pressure is shown in figure 6. The resistance decreases with increase in pressure as shown in figure 6. No phase transition is found in ZrSe_3 crystals up to 8 GPa. The sample becomes more conducting as pressure increases which show the linear dependence of resistance with pressure.

4. Conclusions

(I) The single crystal of ZrSe_3 has been grown by the chemical vapour transition (CVT) technique using iodine as a transporting agent.

(II) EDAX analysis of the grown sample shows that stoichiometry is nearly preserved in the as grown crystals of the said compounds.

(III) The indirect and direct band gaps are 1.10 eV and 1.47 eV, respectively for ZrSe_3 single crystals.

(IV) The negative value of Hall coefficient clearly indicates that ZrSe_3 is an n -type semiconductor.

(V) The electrical resistivity perpendicular to c -axis as well as parallel to c -axis decreases with increasing temperature for ZrSe_3 single crystal suggesting their semi-conducting nature in the temperature range 303–423 K.

(VI) The anisotropy ratio decreases with increase in temperature in the range 303–403 K for this crystal.

(VII) From figure 6, it is concluded that the sample becomes

more conducting as pressure increases, which shows linear relation of resistivity with pressure.

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