

# STRUCTURAL CHARACTERIZATION AND TRANSPORT PROPERTIES OF CVT GROWN ZrSe, AND ZrS, CRYSTALS

A.K. Dasadia\*, B.B. Nariya and A.R. Jani

Department of Physics, Sardar Patel University, Vidyanagar-388 120, Gujarat, India

## ABSTRACT

Single crystals of ZrSe<sub>3</sub> and ZrS<sub>3</sub> are family of materials with low symmetry structure were grown by chemical vapour transport technique using iodine as a transporting agent. The grown crystals were characterized by energy dispersive analysis of X-ray (EDAX) for confirmation of stochiometric proportion of constituent elements and structure of grown crystals was determined by X-ray diffraction (XRD) technique. The resistivity and thermoelectric power measurements were carried out in the temperature range 308 K to 573 K. The Hall coefficient, carrier concentration and Hall mobility were determined from Hall Effect measurements at room temperature.

Key words: Monoclinic structure, Hall coefficient, Carrier concentration, Hall mobility and Thermoelectric power

### **INTRODUCTION**

Layered transition metal dichalcogenides have been studied in past years [1-2] but few data are available for transition metal trichalcogenides. This is due to the difficulty of growing large size and good quality crystals of the MX<sub>3</sub> compounds. Transition metal trichalcogenides, MX,, (M is a transition metal of group IVB, VB and VIB where X is a chalcogen) constitute structurally well defined family of compounds. These trichalcogenides are thin fibrous ribbons and offer several interesting phenomena originating from their strong anisotropy. Zirconium triselenide and zirconium trisulphide have a chain-like structure belonging to space group P21/m [3]. Trisulphides and triselenides of Zirconium constitute a family of structurally related solids and form MX<sub>6</sub> trigonal prisms that share opposite faces resulting in MX<sub>3</sub> chains. The rich variety of physical properties of the various members of this family arises from variation of X-X and M-M bonds. Transition metal trichalcogenides of ZrSe3 and ZrS3 family belong to the first group possessing a single type of MX<sub>3</sub> chains [4] and have been, for over a decade, the subject of intense interest related to their anisotropic character. [5-10]. These crystals have a monoclinic-type structure with a symmetry described by the C point group. As shown in fig.1 metal ions are located in the center of distorted trigonal prisms which share trigonal faces forming, parallel to the b axis, chains that are linked together in two-dimensional slabs by the metal-chalcogene bonds. The layers are bound by sulphure-sulphure Van der-Waals interactions. Figure 1 shows the basic structure of unit cell for the ZrSe<sub>3</sub> in which MX<sub>6</sub> trigonal prisms are formed. Here columns run parallel to the crystallographic b-direction and displaced from the neighboring columns by one half of the unit cell and ZrS, have same monoclinic crystal structure like ZrSe<sub>3</sub>. Cleavage plane



**Fig. 1** Crystallographic structure of ZrSe<sub>3</sub>-type compound. \*Corresponding author: abhi4physix@yahoo.com

Resistivity measurements and Hall Effect measurements were performed in order to determine resistivity, conductivity, mobility and carrier concentration along the basal plane of as grown  $ZrSe_3$  and  $ZrS_3$  crystals. The thermo electric effect offers a distinctive advantage over other methods because the measured thermoelectric voltage is directly related to the carrier concentration, which makes the thermo electric measurements simpler even for high mobility materials. The study of thermo electric power provides an independent way to determine the carrier sign, density and position of Fermi level in semiconductors. In this paper we present results on thermoelectric power measured in temperature range 313K-573K.

#### **EXPERIMENTAL**

With a view to allowing effective and faster transport of constituent to produce the necessary super saturation for crystal growth in a vapour phase system, the chemical vapour transport method was employed. For preparation of starting material from available powders of zirconium (99.9% purity, Alfa Aesar), sulphur (99.9% purity, Alfa Aesar) and selenium (99.9% purity, Alfa Aesar) corresponding to a stochiometric charge of 10 g was introduced into a thoroughly cleaned quartz ampoule and sealed at a pressure of 10-5 mbar. In the sealed ampoule, the constituent element in the powder form was then distributed uniformly all over the length and kept in the horizontal furnace co-axially in the centre. The temperature was slowly increased at a rate of 2K/min. In the present case, the required temperature was 1073 K. The ampoule was kept at this constant temperature for 18 hrs. After this period, the furnace was slowly cooled down to room temperature at the same rate 2 K/min and then switched off. As a result fine free flowing; shiny homogenous polycrystalline material was obtained for both compounds. Now once we

Table-1: Growth parameters for ZrSe<sub>3</sub> and ZrS<sub>3</sub> single crystals.

Crystal	Temperature	Growth Period	
	Reaction Zone (K)	Growth Zone (K)	(hrs)
ZrSe <sub>3</sub>	1173	1073	76
ZrS <sub>3</sub>	1153	1003	87

83

successful to synthesize compounds in these manner then these compounds are used for the growth of  $ZrS_3$  and  $ZrSe_3$  single crystals.

The energy dispersive spectra are obtained for determining the stochiometric proportion of the as grown samples of  $ZrS_3$  and  $ZrS_3$  single crystals. The X-ray diffraction is generally important because the d-spacing can be calculated from the observed diffraction angles. X-ray diffractogram were taken with the help of a Philips X'PERT MPD X-ray diffractometer employing CuK radiation. For X-ray diffraction study, several small crystals were finely ground with the help of an agate mortar and filtered through 37-micron sieve to obtain grains of nearly equal size and used for XRD technique for determination of lattice parameter, volume of unit cell and crystallites density. Fig. 2 (a) shows the sample holder designed at our laboratory for the measurement of temperature dependent resistivity by four-probe technique. The four probes are placed on a flat surface of the material whose resistivity is to be measured.

At this time, constant current is allowed to pass through the two outer electrodes and the potential difference is measured across the inner probes.

The sample under investigation is kept in a known magnetic field produced by an electromagnet. The experimental set up for this technique is shown in Fig. 2(b)



Fig. 2 (a) Four probe holder and (b) Hall effect measurement set up



## **RESULTS AND DISCUSSION**

Different growth runs were carried out for the growth of  $ZrSe_3$ and  $ZrS_3$  single crystals by chemical vapor transport technique using iodine as a transporting agent and growth parameters are shown in Table 1. The energy dispersive spectra are obtained for determining the chemical composition of the as grown samples of  $ZrSe_3$  and  $ZrS_3$  single crystals. The X-ray diffraction pattern obtained for  $ZrSe_3$  and  $ZrS_3$  are as shown in Fig 3. The indexing and lattice parameters were determined using powder-X software.

Obtained value of lattice parameters of  $ZrSe_3$  having good resemblance with the reported values. This reflects that  $ZrSe_3$ exhibits monoclinic structure. Similarly,  $ZrS_3$  exhibits monoclinic structure having good agreement with the reported JCPDS data and volume of the unit cell as well as crystallite density also determined which are shown in Table 2.

As shown in the figure 4, the resistivity decreases with increase in the temperature for  $ZrX_3(X=S, Se)$  crystals.



Fig. 4 Variation of resistance with temperature of  $ZrSe_3$  and  $ZrS_3$ 



Fig. 3 Diffractogram of ZrSe<sub>3</sub> and ZrS<sub>3</sub> crystals

Table - 2 Structural parameters for ZrSe<sub>3</sub> and ZrS<sub>3</sub> single crystals

crystal	a (Å)	b (Å)	<b>c</b> (Å)	β	Volume (Å <sup>3</sup> )	X-ray density(kg/m <sup>3</sup> )
ZrSe <sub>3</sub>	5.3	3.8	9.49	97.47	189.50	57.5
ZrS <sub>3</sub>	5.12	3.62	8.98	97.28	165.09	29.6

The magnetic field modifies the path of the electrons producing Hall voltage. Knowing the value of difference in resistance (R), magnetic field (B) and thickness of the sample t, the mobility of charge carriers is evaluated using the relation

$$\mu_{\rm H} = \frac{t}{\Delta B} \times \frac{\Delta R}{\rho} \tag{1}$$

The Hall coefficient ( $R_{\mu}$ ) and carrier concentration (*n*) are evaluated using the following formula;

$$\mathbf{R}_{\mathrm{H}} = \boldsymbol{\mu}_{\mathrm{H}} \times \boldsymbol{\rho} \tag{2}$$

$$\eta = \frac{1}{R_{\rm H} \cdot e} \tag{3}$$



Fig. 5 The variation of thermoelectric power (S) with temperature (T) for  $ZrSe_3$  and  $ZrS_3$  single crystals.

Table - 3	Various electrical	properties of ZrX	, (X=S, Se)	single crystals.
-----------	--------------------	-------------------	-------------	------------------

Sample	Resistivity ρ(Ω?m)	$\begin{array}{c} Conductivity \\ \sigma(\Omega?m)^{\text{-1}} \end{array}$	Hall coefficient R <sub>H</sub>	Mobility µ (m²/V3s)	Carrier concentration N <sub>c</sub> ×10 <sup>5</sup> (m) <sup>-3</sup>
ZrSe <sub>3</sub>	2.62	0.38	-760	290	$8.22 \times 10^{15}$
ZrS <sub>3</sub>	18.74	0.05	-895	48	$0.66 \times 10^{15}$

The variation of thermoelectric power (S), with temperature (T) for single crystals of  $ZrX_3$  (X=S, Se) are shown in Figures 5. For the study of temperature dependent thermoelectric power S of a semiconductor the expression is given [11] as;

$$S = \pm \frac{k}{e} \left[ A + \frac{E_{Fv}}{kT} \right]$$
(4)

## CONCLUSION

The work described in this paper attempt to provide some explanation of unit cell structural information as well as some electrical properties of ZrSe3 and ZrS3 crystals. Unit cell of ZrX3 (X=S, Se) possess MX6 trigonal prisms in which centre of this prism metal ions are located and three chalcogen ions are attached at the upper and lower part of the metal ions. This kind of arrangement of metal chalcogen ions forms columns or chains of distorted prisms in the monoclinic b-direction. Here columns run parallel to the crystallographic b-direction and displaced from the neighboring columns by one half of the unit cell. Both of have same monoclinic crystal structure which is confirmed by X-ray diffraction analysis. The resistivity along the basal plane decreases with increase in the temperature which indicates the semiconducting nature of the grown crystals. The negative values of the Hall coefficient and the TEP measurement of the single crystals of ZrX<sub>3</sub> (X=S, Se) indicate that all crystals are ntype in nature and majority charge carriers in them are electrons. The variation of TEP with respect to temperature shows that the charge impurity scattering predominates in ZrX<sub>3</sub> (X=S, Se) single crystals.

## REFERENCES

- [1] Okazaki (1958), The crystal structure of germanium selenide, *J. Phys. Soc. Japan*, **13**: 1151-1155.
- [2 Logothetidis, S. and Polatoglou, H. M. (1987), Ellipsometric studies of the dielectric function of

SnSe and a simple model of the electronic structure and the bands of the orthorhombic IV-VI compounds, *Phys. Rev.*, **B36**: 7491-7499.

- [3] Valiukonis, G., Gussienova, D. A., Krivaite, G. and Sileika, A. (1986), Optical spectra and energy band structure of layer-type AIV-BVI compounds, *Phys. Stat. Solidi* (b), **135**: 299-307.
- [4] Parentau, M. and Carlone, M. (1990), Influence of temperature and pressure on the electronic transitions in SnS and SnSe semiconductors, *Phys. Rev.*, B41: 5227-5234.
- [5] Bletskan, D.I., Taran, V.I. and Sichka, M. YU. (1976), Switching effect in layered IV-VI crystals, *Ukr. Fiz. Zh.*, 21: 1436-1441.
- [6] Singh, J.P. and Bedi, R.K. (1990), Tin selenide films grown by hot wall epitaxy, *J. Appl. Phys.*, **68**: 2776-2779.
- [7] Lofersky, J.J (1956), Theoretical considerations governing the choice of optimum semiconductor for photovoltaic solar energy conversion, *J. Appl. Phys.*, 27: 777-784.
- [8] Lofersky, J.J (1963), Recent research on photovoltaic solar energy converters, *Proc. I.E.E.E.*, 51: 667-674.
- [9] Elkorashy, A. M. (1986), Optical absorption in Tin monoselenide single crystals, J. Phys Chem. Solids, 47: 497-500.
- [10] Dholakiya, A. D., Solanki, G. K., Patel, S. G. and Agarwal, M. K. (2001), Two and Three dimensional models for analysis of optical absorption in Tungsten disulfide single crystals, *Bull. Mater. Sci.*, 24 (3): 291-296.
- [11] Static, V., Pierre, A. C., Etsall, T. H. and Mikula, R. J. (1997), Preparation of Tungsten Sulfides by sol gel processing, *J Non-Cryst Solid*, **220**: 58-62.