



STRUCTURAL CHARACTERIZATION AND TRANSPORT PROPERTIES OF CVT GROWN ZrSe₃ AND ZrS₃ CRYSTALS

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ABSTRACT

Single crystals of ZrSe₃ and ZrS₃ 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 stoichiometric 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 MX₃ compounds. Transition metal trichalcogenides, MX₃, (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 MX₃ trigonal prisms that share opposite faces resulting in MX₃ 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 MX₃ 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_{2h}² 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 ZrSe₃, in which MX₃ 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 ZrS₃ have same monoclinic crystal structure like ZrSe₃.

Cleavage plane

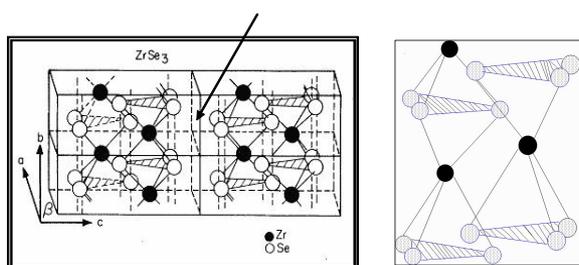


Fig. 1 Crystallographic structure of ZrSe₃-type compound.

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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 ZrSe₃ and ZrS₃ 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 stoichiometric 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 ZrSe₃ and ZrS₃ single crystals.

Crystal	Temperature distribution		Growth Period (hrs)
	Reaction Zone (K)	Growth Zone (K)	
ZrSe ₃	1173	1073	76
ZrS ₃	1153	1003	87

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

$$\mu_H = \frac{t}{\Delta B} \times \frac{\Delta R}{\rho} \quad (1)$$

The Hall coefficient (R_H) and carrier concentration (n) are evaluated using the following formula;

$$R_H = \mu_H \times \rho \quad (2)$$

$$\eta = \frac{1}{R_H \cdot e} \quad (3)$$

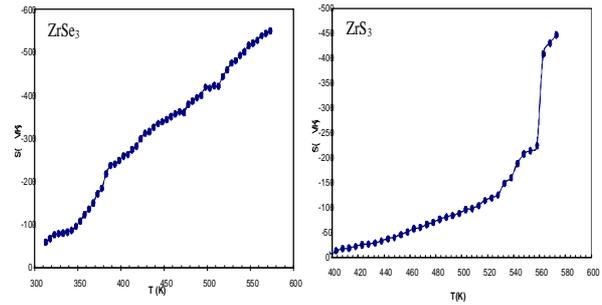


Fig. 5 The variation of thermoelectric power (S) with temperature (T) for ZrSe₃ and ZrS₃ single crystals.

Table - 3 Various electrical properties of ZrX₃ (X=S, Se) single crystals.

Sample	Resistivity $\rho(\Omega\text{m})$	Conductivity $\sigma(\Omega\text{m})^{-1}$	Hall coefficient R_H	Mobility μ (m^2/Vs)	Carrier concentration $N_c \times 10^5 (\text{m})^{-3}$
ZrSe ₃	2.62	0.38	-760	290	8.22×10^{15}
ZrS ₃	18.74	0.05	-895	48	0.66×10^{15}

The variation of thermoelectric power (S), with temperature (T) for single crystals of ZrX₃ (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;

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

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 ZrX₃ (X=S, Se) indicate that all crystals are n-type 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 ZrX₃ (X=S, Se) single crystals.

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