Microstructural analysis of zirconium triselenide single crystals

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The zirconium triselenide (ZrSe$_3$) single crystal has been grown by chemical vapour transport technique using iodine as a transporting agent. The optimum condition for the growth of this crystal is given. The stoichiometry of the grown crystals was confirmed on the basis of energy disperse analysis by X-ray (EDAX) and remaining structural characterization was accomplished by X-ray diffraction (XRD) studies. The lattice parameters obtained from the XRD analysis were $a=5.45$ Å, $b=3.74$ Å and $c=9.44$ Å. This crystal is found to possess monoclinic, layered structure. The X-ray density was found to be 5.63 g/cc and volume was calculated about 193.50 Å$^3$. The optical band gap of the as-grown crystal has been carried out with the help of optical absorption spectra in the range 700 - 1400 nm.

Keywords: ZrSe$_3$ single crystal, EDAX, Optical band gap, Microstructural analysis, Chemical vapour transport, X-ray diffraction, Optical absorption spectra

IPC Code: C30B

1 Introduction

The zirconium triselenide ZrSe$_3$ is a member of transition metal trichalcogenide, which possesses chain like structure belonging to the crystal space group $P2_1/m$. 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 crystals were grown in the form of layers, which 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. The measurement of resistivity, Hall coefficient and thermo electric power of ZrS$_3$ single crystal along the chain axis has been carried out in the temperature range 200–400 K.

The crystals ZrS$_3$ and ZrSe$_3$ exhibit a rather layer like semiconducting behaviour$^{2,7}$. At the lowest temperature, the ZrSe$_3$ measurements can be analyzed in terms of the familiar Debye $T^3$ law yielding characteristic Debye temperature at absolute zero $\theta_D = 110 \pm 2$ K in satisfactory arrangement with the value extracted from the available experimentally sound velocities. In contrast, the ZrS$_3$ measurement does not behave according to the Debye law$^8$ ZrS$_3$Se$_{3-x}$ exhibits continuous regions of solid solubility. Diffuse reflectance measurements show that ZrS$_3$Se$_x$ exhibits semiconductor$^9$ property. The (0 0 1) Van der Waals surfaces of ZrSe$_3$ and ZrTe$_3$ single crystals were studied by scanning tunneling microscopy at room temperature. It is shown that both the semiconducting ZrSe$_3$ and the semi-metallic ZrTe$_3$ crystals show charge instability between various selenium/tellurium chains forming the surface$^{10}$. The X-ray diffraction pattern of ZrS$_3$ shows the monoclinic cell with the lattice constants$^{11} a=5.128$ Å, $b=3.611$ Å, $c=9.012$ Å, $\beta=97.13^\circ$. The development of stresses by variation in high temperatures of the two zones involved, resulting into slip lines and vapour inclusions, might possibly lead to generation of favourable screw dislocation sites for ZrS$_3$ single crystals$^{12}$.

In this paper, we report the growth of ZrSe$_3$ single crystal using chemical vapour transport technique with iodine as a transporting agent in order to get single crystals with maximum dimensions. The structural characterization is carried out and results are discussed in detail.

2 Experimental Details

The single crystal of ZrSe$_3$ has been grown by chemical vapour transport technique using iodine as a transporting agent. A mixture of 5 g Zr (purity: 97%) and Se (99.99%) was filled in the dried quartz ampoule. The iodine of the quantity 2 mg/cc of the ampoule volume was sealed in the thin capillaries and placed in the ampoule as transporting agent. Then the ampoule was sealed at the pressure of $10^{-5}$ torr. The
sealed ampoule was introduced into two-zone furnace at a constant reaction temperature to obtain the charge of ZrSe$_3$. The charge so prepared was rigorously shaken to ensure proper mixing of the constituents and kept in quartz ampoule. Then the ampoule was sealed at the pressure of 10$^{-5}$ torr. The sealed ampoule was again placed in furnace under appropriate condition to obtain single crystals of ZrSe$_3$. The optimum conditions for growth of large size layered single crystals are presented in Table 1.

The compositions of the grown crystals were checked with the help of energy dispersive analysis by X-ray (EDAX). The energy dispersive spectra for determining the chemical composition of grown sample of ZrSe$_3$ single crystals is shown in Fig. 1 and their results are shown in Table 2. The X-ray diffraction (XRD) study has been performed for the structural characterization. The X-ray diffractograms were obtained with Philips X-ray diffractometer (model: PW1820) employing CuK$_\alpha$ radiation. The microstructure was accomplished with the help of computer aided optical zoom microscope (model: Axiotech 100 manufactured by Carl Zeiss, Germany).

The absorption spectra were obtained by means of UV-VIS-NIR DK 2A spectrophotometer in the range 700 – 1400 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 band gap i.e. direct as well as indirect band gap of the grown crystals was found to be 1.48eV and 1.1eV, respectively.

### 3 Results and Discussion

The single crystal of ZrSe$_3$ was grown by chemical vapour transport technique. The crystal structure of ZrSe$_3$ crystals is monoclinic with the space group $P2_1/m$. The X-ray diffractograms obtained for ZrSe$_3$ is shown in Fig. 2. The pattern consists of well-defined sharp diffraction lines, indicating good crystallinity of the specimen. The lattice parameters ($a$, $b$ and $c$), unit cell volume ($V$) and X-ray density ($\rho$) determined from the X-ray diffractograms are presented in Table 3, which are very well matched with the values obtained by Leif Bratts.$^{13}$
Table 4—XRD data for ZrSe$_3$ single crystals

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The XRD data obtained for ZrSe$_3$ were used for the estimation of particle size using Scherrer’s formula given by Srivastava$^{14}$

$$t = \frac{K \lambda}{\beta \cos \theta}$$

where $t$ is the crystallite size as measured perpendicular to the reflecting plane, $K$ the Scherrer constant whose value is taken to be unity assuming the particles to be spherical, $\lambda$ the wavelength of X-ray radiation, $\beta$ the half intensity which is measured in radians and $\theta$ is the Bragg angle. The values $(h \ k \ l)$ corresponding to prominent reflection $d$-values, peak width, peak intensities and particle size for ZrSe$_3$ single crystals are shown in Table 4. The micrographs taken from the surfaces of the as-grown single crystals of the ZrSe$_3$ is shown in Fig. 3 which shows layer like layered screw dislocation.

4 Conclusion

The chemical (iodine) vapour transport (CVT) technique is most suitable for the growth of large size; needle shaped layered single crystals of ZrSe$_3$. EDAX analysis of the grown samples has shown that stoichiometry is nearly preserved in the as-grown crystals of the said compounds. X-ray diffraction analysis of the crystals has shown that the structure of ZrSe$_3$ is monoclinic layered.

ZrSe$_3$ possesses layer type crystals structure, which can exhibit screw dislocation.

References