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Growth and Structural Analysis of Zirconium Trisulphide Single Crystals

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Abstract

Single crystal of zirconium trisulphide (ZrS_3) having a layered structure were grown by chemical vapour transport technique using iodine as a transporting agent. The stoichiometry of the crystals was confirmed on the basis of energy disperse analysis by X-ray (EDAX) and structural characterization was accomplished by X-ray diffraction (XRD) studies. The grown crystals have been examined using optical microscope to study the growth patterns on their shining surfaces. This study reveals the screw dislocation mechanism by which the crystals have grown. The Hall effect measurements, Hall mobility, Hall coefficient, resistivity and carrier concentration were carried out on grown crystals at room temperature. The electrical resistivity perpendicular as well as parallel to c-axis (i.e. along to the basal plane and perpendicular to the basal plane) have been carried out in the temperature range of 303 - 423 K. The as grown crystals are found to possess semiconducting nature within this temperature range. Anisotropy ratio has also been determined for the as grown crystals in this range.

Keywords: ZrS_3 single crystal, XRD, resistivity, anisotropy, stacking fault

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Introduction

The zirconium trisulphide (ZrS_3) is a member of transition metal trichalcogenide, which possesses chain like structure belonging to the crystal space group $P2_1/m$. It is a two dimensional compound with great anisotropy within layers. Each layer is build of interacting parallel one dimensional fiber¹. 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 are displaced from the neighboring chain by half of the unit cell along the b-axis².

The ZrS_3 exhibits a layer like semi conducting behavior²⁻⁷. Moreover, it is suitable electrode for solar energy conversion due to its ability to obtain large photocurrents in aqueous electrode⁸. 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 favorable screw dislocation sites for ZrS_3 single crystals⁹.

In this paper, we report the growth of ZrS_3 single crystal. Electrical properties are studied for the confirmation of semiconducting behaviour. Surface morphology also studied to understand the

growth mechanism. The structural characterization is carried out and results are discussed in detail.

Experimental

The single crystal of zirconium trisulphide (ZrS_3) has been grown by chemical vapour transport technique using iodine as a transporting agent. For the growth of ZrS_3 single crystals, stoichiometric proportion of zirconium powder (97% pure) and sulphur powder (99.95% pure) were taken in quartz ampoule. The ampoule containing the source material was evacuated to 10^{-5} torr pressure. The homogeneous mixture was properly distributed along the length of the ampoule and it was placed into the dual zone furnace. The temperature of furnace was increased slowly to avoid any explosion, which might occur due to the strongly exothermic reaction between the elements. The temperature for then maintained at $800^\circ C$ for three days to allow the complete reaction. After three days the furnace was cooled down slowly up to room temperature. The charge so prepared inside ampoule was rigorously shaken to ensure the proper mixing of the constituents. For crystal growth the synthesized charge was transferred into another evacuated (10^{-5} torr) quartz ampoule with iodine (2 mg/cc) and evacuated at 10^{-5} torr pressure. The sealed ampoule was introduced into the two zone horizontal furnace with reaction zone at higher temperature and the growth zone at a lower temperature for a definite time period. The detail of growth conditions for large size, needle shaped, reddish layered single crystals are as shown in **Table 1**.

The stoichiometry of the ZrS_3 single crystals was confirmed on the basis of energy dispersive analysis by X-ray (EDAX). The stoichiometric proportion and EDAX data are given in **Table 2**. X-ray diffraction (XRD) analysis 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 manufactural by Carl Zeiss, Germany).

The morphology of as grown crystals is observed with the help of transmission electron microscope (TEM). TEM images were taken with a Philips-Technai 20 transmission electron microscope; using an accelerating voltage of 200 kV.

The electric resistivity perpendicular to c-axis in the temperature range 303-423 K was measured using four probe set-up developed by Scientific Equipment, Roorkee, India. The set-up consist of four collinear and equally spaced spring loaded four probes coated with zinc at the tips to ensure good electrical contact with the crystal. For voltage and current measurements suitable leads are provided. A small oven has been provided to facilitate measurements at various temperatures. The electrical resistivity measurements parallel to c-axis were carried out using the experimental set-up designed by University Scientific Instrumentation Centre, Sardar Patel University, Vallabh Vidyanagar, Gujarat. The temperature of the crystals was increased by introducing the sample chamber into a vertical single zone furnace.

Table 2. The EDAX data of ZrS_3 single crystals

Elements	Stoichiometric proportion (weight %)	From EDAX (weight %)
Zr	27.80	25.26
S	72.20	74.74

Results and Discussion

The large size reddish needle shaped single crystal of ZrS_3 was grown by chemical vapour transport technique. The X-ray diffraction pattern obtained for ZrS_3 is shown in **Figure 1**. 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 (ρ) were determined from the analysis of X-ray diffractograms, and presented in **Table 3**, which are very well matched with the values obtained by Leif Bratts¹⁰.

Table 1. Growth parameters of ZrS_3 single crystals grown using chemical vapour transport technique

Sample	Ampoule dimension		Temperature distribution ($^\circ K$)		Physical characteristic of crystals			
	Length (mm)	ID (mm)	Reaction Temp.	Growth Temp.	Growth time (hr)	Plate area (mm^2)	Thickness (mm)	Color and appearance
ZrS_3	250	22	1173	1023	370	07	0.05	Red shining

Table 3. The crystallographic data of ZrS₃ single crystals.

Parameters	Obtained values	Reported values ¹²
a (Å)	5.08	5.13
b (Å)	3.58	3.61
c (Å)	8.97	9.01
β	97.28	-
X-ray Density (gm/cc)	3.84	-
Volume V(Å) ³	162.06	-

The XRD data obtained for ZrS₃ were used for the estimation of particle size using Scherrer's formula given by Srivastava¹¹,

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

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, λ the wave length of X-ray radiation, β is the half intensity which is measured in radians and θ is the Bragg angle. (h k l) values corresponding to prominent reflection d-values, peak width, peak intensities and particle size for ZrS₃ single crystals are shown in **Table 4**.

The microstructure of as grown crystals is shown in **Figure 2**, which possesses layered **Table 4**. The XRD data for ZrS₃ single crystals

h k l	D spacing	Peak width 2θ counts/sec	Peak intensity	Particle size (Å)
0 0 1	8.9582	9.86	2335.05	859.04
0 0 2	5.0978	17.38	40.56	649.35
0 1 0	4.4676	19.85	1013.80	868.85
0 0 3	3.5862	24.80	75.74	657.23
2 0 0	2.8171	31.73	505.82	889.73
1 1 3	2.2299	40.41	982.03	911.95
2 1 1	2.0794	43.48	157.81	691.04
1 2 0	1.7538	52.10	162.31	714.48
0 0 6	1.4865	62.41	694.95	205.73
1 3 4	1.0386	95.75	39.50	478.44

Table 5. Hall mobility, Hall coefficient, resistivity and carrier concentration of the single crystal of zirconium trisulphide.

Resistivity ρ (Ω cm)	Conductivity σ (Ω cm ⁻¹)	Hall coefficient RH (cm ³ /coul)	Mobility (cm ² /V. sec)	Carrier concentration η (cm ⁻³)
133.32	7.5 x10 ⁻³	-1.52x10 ⁵	1.14 x10 ³	4.10 x10 ¹³

structure. The TEM image of ZrS₃ nanoclusters is shown in **Figure 3**. The nano crystallites of average 80 nm in size are found to present. The selected area diffraction pattern of crystallites is shown in **Figure 4**.

The electrical resistance of crystals along the basal plane was determined by van der Pauw method. Hall effect measurements were carried out to determine Hall mobility, Hall coefficient, resistivity and carrier concentration. The results are listed in **Table 5**.

The variation of log of electrical resistivity parallel to c-axis (ρ_{||}) and perpendicular to c-axis (ρ_⊥) in the temperature range of 303-453K are shown in **Figures 5 and 6**, respectively. The decrease in resistivity with increase in temperature suggests the semiconducting nature of the as grown crystals. Using the resistivity values, anisotropy

ratio was calculated using the relation $\gamma = \rho_{||} / \rho_{\perp}$

activation energy of as grown crystals for parallel and perpendicular c-axis is 401.2 meV and 166.6 meV respectively. **Figure 7** shows the variation of anisotropy ratio with reciprocal of temperature for ZrS₃ single crystal. The anisotropy ratio also decreases as the temperature increase for as grown crystals.

Conclusion

The large size, needle shaped shining & layered single crystals of ZrS₃ have been grown by chemical (iodine) vapour transport (CVT) method. The microstructure of ZrS₃ possesses layered

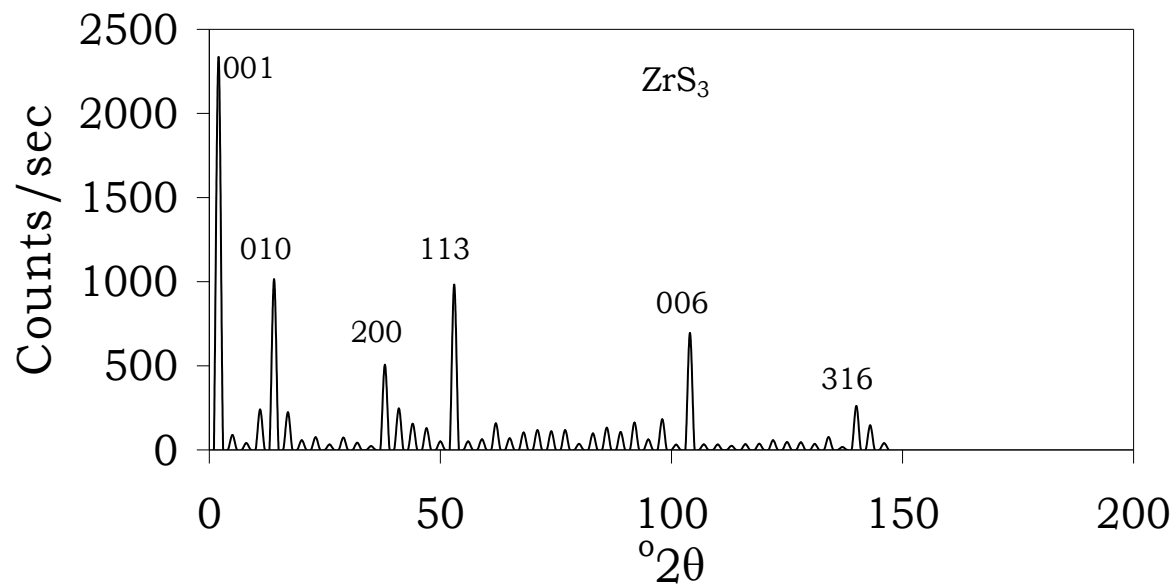


Figure 1 The X-ray diffractograms obtained for ZrS_3 single crystals



Figure 2 The microstructure on the surface of ZrS_3 single crystal

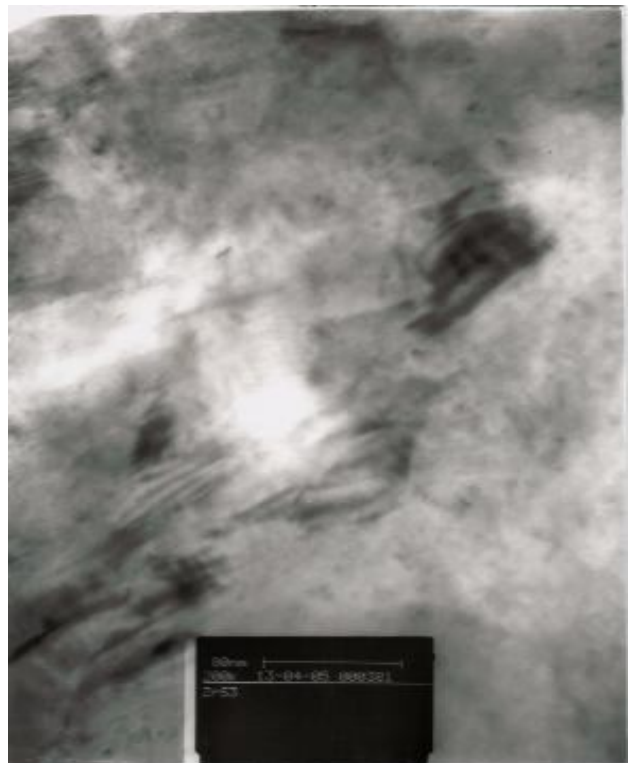


Figure 3 The TEM photograph of nano cluster present in as grown crystals of ZrS_3 .



Figure 4 The SAD pattern of as grown ZrS₃ single crystals

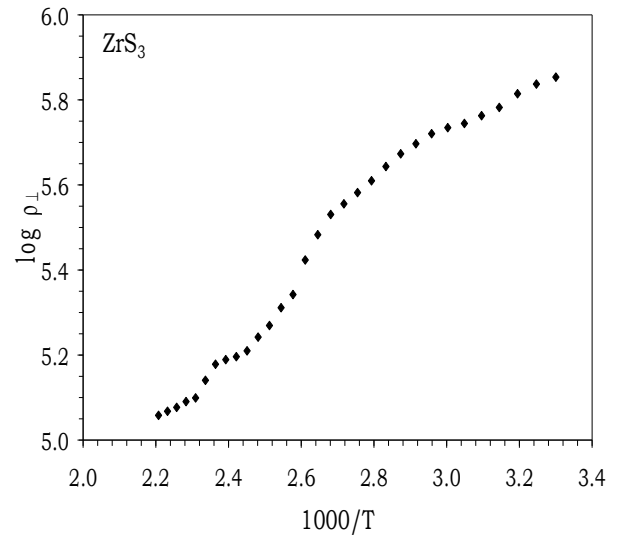


Figure 5 $\log \rho_{\perp}$ versus $1000/T$ for ZrS₃ single crystal in the temperature range 303-453K

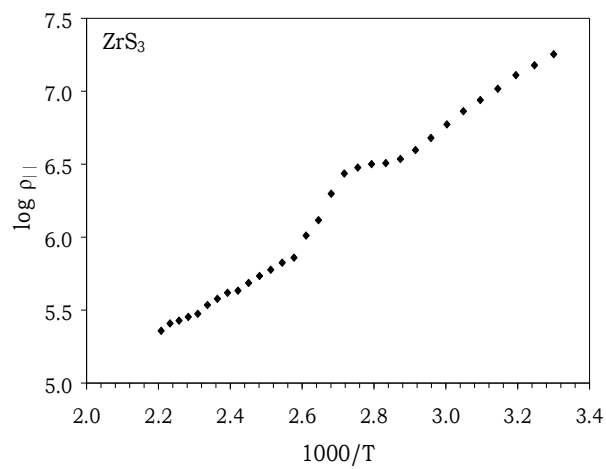


Figure 6 $\log \rho_{\parallel}$ versus $1000/T$ for ZrS₃ single crystal in the temperature range 303-453K

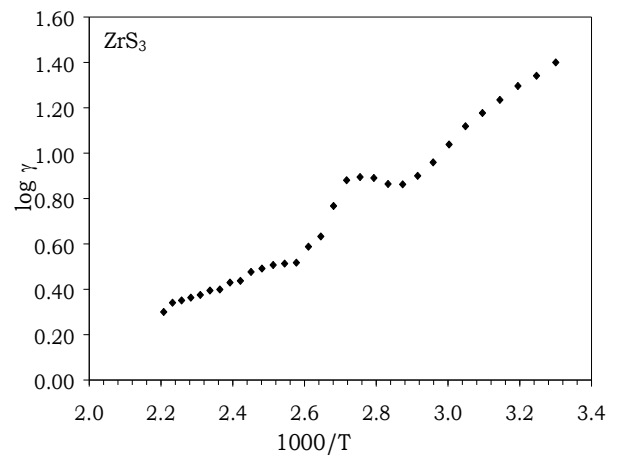


Figure 7 $\log \gamma$ versus $1000/T$ for ZrS₃ single crystal in the temperature range 303-453K

structure, which can exhibit screw dislocation. From the analysis of the morphology of these structures, it may be concluded that nanoparticles of compounds crystallizing in layered structures tend to form closed shapes. From the sign of the Hall coefficients it is clear that these crystals is n-type in nature. The electrical resistivity, perpendicular to c-axis as well as parallel to c-axis, decreases with increase in temperature for as grown crystals. Crystals possesses the semiconducting nature in the temperature range of 303-453 K.

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