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Research Article

STRUCTURAL ANALYSIS OF ZrS_3 CRYSTALS

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ABSTRACT

The needle shaped large size single crystals of zirconium trisulphide (ZrS3) were grown by chemical vapour transport (CVT) technique. 2mg/cc Iodine was used as a transporting agent. Through EDAX, the stoichiometric of the as grown crystals were confirmed. The structural parameters were obtained from X-ray diffraction (XRD) studies. The as grown single crystals have been examined by optical microscope. The growth pattern on their shining surfaces has been studied. The morphology of as grown crystals has been studied using TEM.

Keywords: *ZrS_3 Single Crystal, XRD, TEM*

INTRODUCTION

The zirconium trisulphide (ZrS_3) is 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 layers is build of interacting parallel one dimensional fibers (S 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 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-axis (Ikari T *et al.,* 1983).

The ZrS_3 exhibits layer like semi conducting behavior (Sourisseau C and Mathey Y, 1981, Zwick A, *et al.,*1982, Khumalo F, *et al.,* 1981, Deslandes J and Jandl S, 1984, Patel K R, *et al.,* 2008). Moreover, it is suitable electrode for solar energy conversion due to its ability to obtain large photocurrents in aqueous electrode (Redon A M *et al.,* 1985). 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 crystals (Patel S G, *et al.,* 1996).

The optical properties like absorption, direct band gap, indirect band gap etc. have been studied. The results indicate zirconium trisulphoselenide single crystals possess semiconducting behavior (Patel Kaushik, 2014).

In this paper, authors report the growth mechanism of ZrS_3 single crystal, structural parameters and surface morphology for understanding the growth mechanism etc. The results are discussed in detail.

MATERIALS AND METHODS

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^{o} C temperature was three days to allow the complete reaction. After 3 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 photograph of as grown crystals is shown in Figure 1.

Several small crystals were finely ground with the help of an agate mortar and filtered through 106-micron sieve to obtain grains of nearly equal size for X-ray diffraction (XRD) studies. The X-ray diffractograms was obtained from X-ray diffrractometer (Make: Philips Model: PW1820) employing CuK$_\alpha$ radiation. The surface microstructure of as grown crystal was examined by computer added optical zoom microscope (Make: Carl Zeiss, Model Axiotech 100HD).

The surface morphology of as grown crystals was observed with the help of transmission electron microscope. TEM images were taken with a Philips- Technai 20 transmission electron microscope; using an accelerating voltage of 200 kV. The electron microscope specimen was prepared by crushing and collecting the crystals on a carbon film or by gluing thin crystal plates or needle to a grid.

RESULTS AND DISCUSSION

The grown crystals were dark reddish colored and needle shaped. The combination of chemical vapour transport technique and iodine as transporting agent were most suitable for these crystals. The obtained X-ray diffraction pattern of ZrS_3 is shown in Figure 2. The pattern consists of well-defined sharp diffraction lines, indicating good crystallinity of the sample. The lattice parameters, unit cell volume (V) and X-ray density (□) were calculated from X-ray diffractogram, and is presented in Table 3. These obtained data are very well matched with earlier researcher (Brattas L and Kjekshus A 1972).

Using the data of XRD, the particle size (grain size) of ZrS_3 crystals was using Scherrer's formula and it given by Srivastava (Srivastava S K and Avasthi B N, 1986),

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

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 ZrS_3 single crystals are shown in Table 4.

The microstructure of as grown crystals is shown in Figure 3. The growth of these needles has taken mainly by screw dislocation mechanism since no evidence for layered growth is visible from the studies of microstructure. The development of stresses due to high temperature growth introduces imperfection on the surface. There is a profound evidence for the presence of slip lines and screw dislocation on the surface of the needle. It appears from the studies of above microstructures that the supersaturation rate prevailing during the growth of the crystals is not suitable for layered growth, while it is quite suitable for spiral growth. Thin growth layers can therefore start freely form screw dislocations present on the crystal surface. The estimation of super saturation rate from the width of the spiral turns can be made.

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

Sample	Ampoule dimension		Temperature		Physical characteristic of crystals			
	Length mm	ID mm	Reaction temperature	Growth temperature	Growth time hr	Plate area mm^2	Thickness mm	Colour & appearance
ZrS_3	250	22	1173	1023	370	07	0.05	Red shining

Table 2: The EDAX data of ZrS_3 single crystals

Elements	Stoichiometric proportion Wt %	From EDAX Wt %
Zr	27.80	25.26
S	72.20	74.74

Table 3: The crystallographic data of ZrS_3 single crystals.

Parameter	Obtained values	Reported (13)
a (Å)	5.08	5.13
b (Å)	3.58	3.61
c (Å)	8.97	9.01
□	97.28	-
X-ray Density (gm/cc)	3.84	-
Volume V(Å)^3	162.06	-

Table 4: The XRD data for ZrS_3 single crystals

h k l	d spacing	Peak width 2θ	Peak intensity counts/sec	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

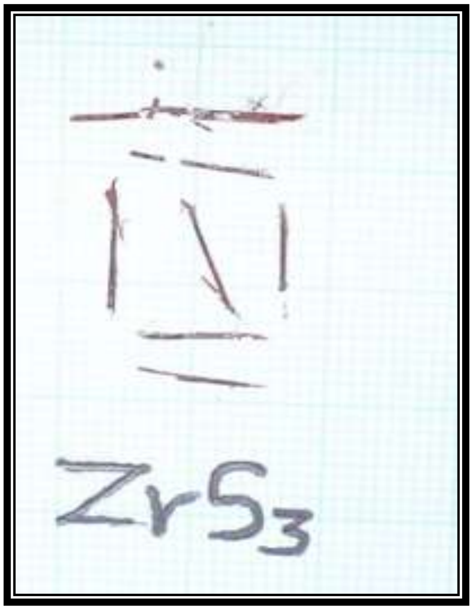

Figure 1: The photograph of ZrS_3 crystals

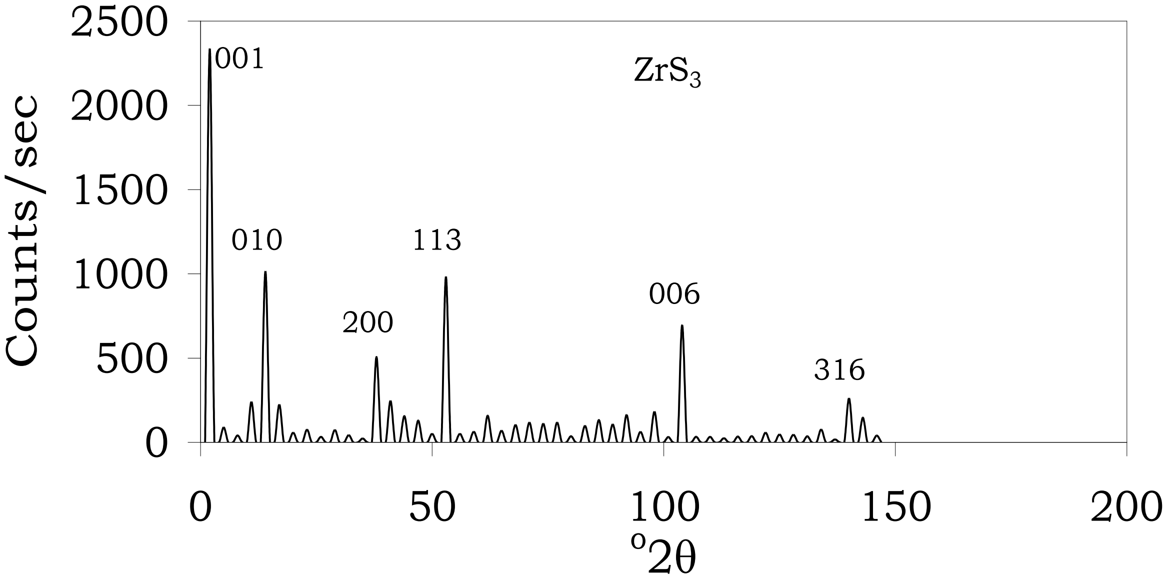

Figure 2: The X-ray diffractograms obtained for ZrS_3 single crystals

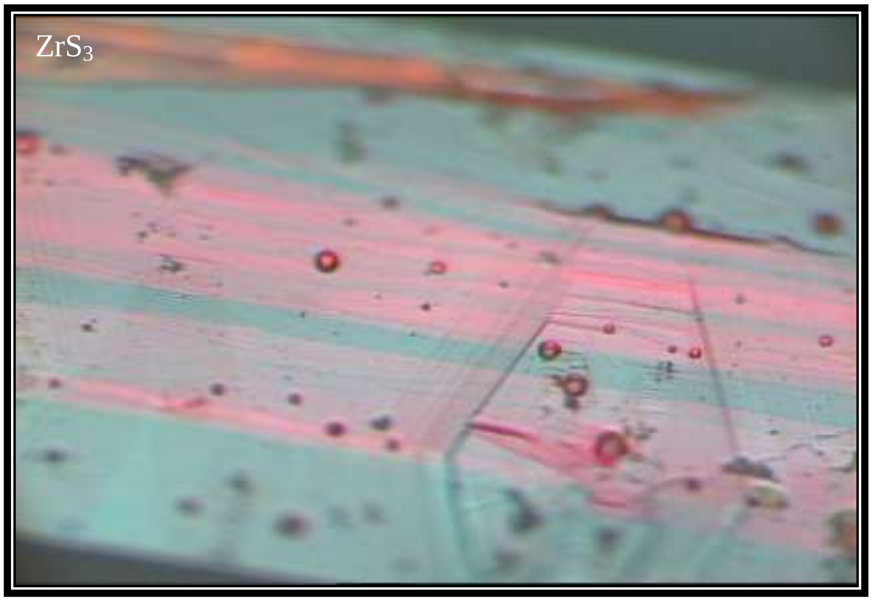

Figure 3: The microstructure on the surface of ZrS_3 single crystal

Figure 4: The TEM photograph of nano cluster present in as grown crystals of ZrS_3

Figure 5: The SAD pattern of as grown ZrS_3 single crystals

The TEM image of ZrS_3 nano clusters are shown in Figure 4. The nano crystallites of average 80 nm insize are found to present. The selected area diffraction pattern (SADP) of crystallites is shown in Figure 5. For nano particles of compounds crystallizing in layered structures intuitively one expects either normal layered crystals or closed structures minimizing the number of dangling bonds at the periphery of the lattice planes. The latter assumption leads to fullerene-like onion crystals, tubes or polyhedron shaped closed aggregates. Assuming defects stemming from metal ions with varying valency, one may obtain particles with three-dimensionally bent planes or in special cases step dislocations, Reality is more complex.

CONCLUSION

The chemical (iodine) vapour transport (CVT) technique is most suitable technique for growth of large size, needle shaped shining single crystals of ZrS_3. The X-ray diffraction data of as grown crystals possesses the monoclinic structure. The microstructure of ZrS_3 possesses layered structure, which can exhibit screw dislocation. From the study of morphology, author may conclude the general rule that nanoparticles of compounds crystallizing in layered structures tend to form closed shapes.

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