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Physics

CRYSTAL GROWTH AND STRUCTURAL ANALYSIS OF ZRS_XSE_{2-X} SINGLE CRYSTALS

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ABSTRACT The series of zirconium sulphoselenide (ZrS_xSe_{2-x} where x= 0, 1 and 2) single crystals were grown by chemical vapour transport technique using iodine as a transporting agent. The stoichiometry of the as grown crystals was confirmed with the help of Energy Dispersive Analysis by X-ray (EDAX). The structural characterization was accomplished by X- ray diffraction (XRD) analysis. The crystals are found to possess hexagonal crystal structure. The lattice parameters, volume, particle size and X-ray density have been carried out for these crystals. The effect of sulphur proportion on the lattice parameter, unit cell volume and X-ray density in the series of ZrS_xSe_{2-x} single crystals was studied and found decrease in all these parameters with rise in sulphur proportion. The grown crystals were examined under optical zoom microscope for their surface topography study. The results obtained are discussed in detail.

KEYWORDS : TMDC material, Single crystal, EDAX, XRD, Microstructure

Introduction

Several layered materials possess favourable semiconducting properties and have attacted attention as a new class of solar cell materials. Significant solar to electrical/chemical energy conversion efficiencies have been obtained in solid-state "photovoltaic" and "photoelectrochemical" cells. Research into electronic device characteristics of this class of materials is rather recent and of growing interest. Their potential has not been fully explored mainly because of the unavailability of suitable materials. Attempts have therefore been made in the present work to concentrate upon the IV-VI family of the layered materials having a CdI_2 type structure.

The more dense materials prepared by Hahn et al. [1] and McTaggart et al. [2] were prepared by direct synthesis from elements at 1073 K. and by degradation of diselenide at 1173 K respectively. McTaggart determined the resistivity, type of condution, thermo e.m.f. and rectifying ability of $ZrSe_{1.95}$. It was also noted that specific resistivity as well as thermo e.m.f. increases with the increase of selenium atoms [3]. The transition metal diselenide single crystals were grown by direct vapour and chemical vapour transport techniques. The structural, optical, electrical, magnetic and thermal properties were carried out for transition metal diselenide single crystals by various researchers [4-10].

Onuki et al. [11] found $ZrSe_2$ to react reversibly with lithium in electrochemical cells. The energy density of $ZrSe_2$ as cathode material was determined to the 240Wh/kg for one lithium intercalation per unit cell. It was also found for $ZrSe_2$ that more than two lithium ions per unit cell could be intercalated in the first discharge when the cell temperature was increased to 333 K, while one lithium ion could be intercalated at 293 K. Voltage-controlled negative resistance (VCNR) has been observed in the semiconducting layered compound $ZrSe_2$ at a field of ~ 50–100 V cm−1, at room temperature [12].

Experimental

The single crystals of zirconium sulphoselenide (ZrS_xSe_{2-x}) were grown by chemical vapour transport technique with iodine as a transporting agent. A highly pure compound of zirconium powder (97% make: Riedel-de Haen), sulpher (99.97% make: Chiti-Chem Corporation, India) and selenide (99.98% Make: Aldrich, USA) were taken in a stoichiometric proportion in the quartz ampoule for charge preparation. It was evacuated to a pressure of 10^{-5} torr and then sealed. This sealed ampoule was introduced into a dual-zone horizontal furnace at a constant reaction temperature to obtain the charge. During the synthesis the temperature was slowly increased upto 1073 K with 20 K/h. The ampoule was kept at this temperature for 3 days. Then the furnace was slowly cooled (20 K/h) and brought to room temperature. The resulting brown and/or reddish charge was obtained in the ampoule. This charge was crushed and transferred to other quartz ampoule. The iodine (2mg/cc) as a transporting agent was taken in glass capillaries. The capillaries were sealed and placed in the quartz ampoule before evacuation. It was also evacuated upto pressure of 10^{-5} torr. This ampoule was placed in a dual zone horizontal furnace for 10 days with a temperature gradient shown in Table 1. After then furnace was cooled up to room temperature with a rate of 20 K/hr. The entire material got converted into the form of crystals at the cooler end of the ampoule. The grown crystals were collected after break the ampoule. The optimum conditions and growth parameters for as grown crystals are shown in Table 1.

The stoichiometry of the as grown crystals was confirmed with the help of energy dispersive analysis by X-ray (EDAX). The stoichiometric proportion of as grown crystals and EDAX results are shown in Table 2.

For X-ray diffraction (XRD) analysis, 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. The X-ray diffractograms were taken with Philips X-ray diffrractometer (model: PW1820) employing CuKradiation.

Close examination of the surface composed of layers helps a great deal in understanding the mechanism by which a crystal grow. Therefore, it was thought worthwhile to make surface characterization of these grown crystals by optical microscopy. The surface microstructure of as grown crystals was examined by computer added optical zoom microscope (Make: Carl Zeiss, Model Axiotech 100HD).

Discussion

The needle shaped, black or radish shining layered single crystals of zirconium sulphoselenide were successfully grown by chemical vapour transport technique. From **Table 2**, the stoichiometry of as grown crystals is nearly preserved. The X-ray diffractogram obtained for ZrS_xSe_{2-x} (x = 0, 1 & 2) are shown in **Figure 1**. The pattern consists of well-defined sharp diffraction peaks, indicating good crystallinity of the specimen.

The lattice parameters, unit cell volume (V) and X-ray density (r) were obtained from the X-ray diffractogram data for as grown crystals are shown in **Table 3**. The obtained values of as grown samples possess monoclinic layered structure with space group12/*Pm*. In order to obtain an idea about the grain size distribution and particle size for each sample was calculated using Scherrer's formula given by Srivastava [13];

$$t = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

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, the wave length of X-ray radiation, the half intensity which measured in radians and is the Bragg angle. The (h k l) values corresponding to prominent reflection d-values, half width, peak intensities and particle size for ZrS_xSe_{2-x} crystals are shown in **Table 4**.

Systematic of the changes in the structural parameters could be of importance in obtaining an insight. Extraction of such chemical insights depends strongly on structure-property correlations, and the most basic of these is the changes in lattice parameters. The quality of a solid solution is usually examined from the composition-dependent lattice parameter changes in terms of the empirical Vegard law [14]. This law states that in the absence of strong electronic effects the variation of lattice parameters is linear with composition in a true three-dimensional solid solution. The Vegard law is a consequence of the way a solid solution reduces strain by an expansion (or compression) when species of different sizes are involved. In two-dimensional system, the non Vegard law behavior (nonlinear changes in lattice parameter with composition has been well documented [15,16]. The variation of lattice parameter with the composition x is shown in **Figure 2**. In this graph the values of lattice parameter is decreases with increase the sulphur proportion (composition).

A typical micrograph showing the initiation of growth layers from the corner of a crystals periphery is presented in **Figure 3**. Looking at this micrograph one is inclined to conclude that layer mechanism is operative during crystal growth. In support to this we have micrograph shown in **Figure 4** in which the growth layers are seen to initiate from crystal edge or boundary. Obviously, because corners and edges provide to become good sources of kinks and steps, the layers find it easy to originate from such starting and favourable points on crystal surfaces. An obvious and prominent support to the theory of layer growth of $ZrSe_2$ crystals is further provided by the micrograph of **Figure 5**. A flat face is a sure test of the two dimensional layer mechanisms. In these micrograph one can clearly see the flat surface as well as the presence of growth layers. There is not a single evidence of spiral growth on $ZrSe_2$. The microstructure on the as grown surfaces of ZrS_2 and ZrSSe were similar to those observed on $ZrSe_2$.

Conclusions

1. The large size layered single crystals of zirconium disulphoselenide were successfully grown by chemical vapour transport technique.
2. The EDAX analysis shows that the grown crystals are stoichiometrycally perfect without any impurities.
3. X-ray diffraction studies of the series of ZrS_xSe_{2-x} (x = 0, 1 &2) indicate that all solutions formed are single phase compounds, isomorphous with CdI_2 type structure.
4. The lattice parameters, unit cell volume and X-ray density varies with composition.
5. Growth of ZrS_xSe_{2-x} is free from spirals but layer growth is clearly visible.

Table 1 Growth parameters of zirconium sulphoselenide single crystal grown using chemical vapour transport technique.

Sample	Reaction Temperature (K)	Growth Temperature (K)	Physical characteristics of the crystals			
			Growth time hr	Plate area mm^2	Thickness mm	Color & Appearance
$ZrSe_2$	1123	1073	240	16	0.20	Dark bronze green
ZrSSe	1153	1103	240	12	0.09	Violet metallic
ZrS_2	1183	1133	240	10	0.32	Violet brown

Table 2 The EDAX data for zirconium sulphoselenide single crystals.

Sample	Stoichiometric Proportion (Wt%)			EDAX results (Wt%)		
	Zr	S	Se	Zr	S	Se
ZrSe2	36.61	-	63.39	36.56	-	63.44
ZrSSe	45.11	15.85	39.04	45.21	15.80	38.99
ZrS_2	58.72	41.28	-	58.65	41.35	-

Table 3 The crystallographic data of zirconium sulphoselenide single crystals.

Sample	a (Å)	c (Å)	V $(Å)^3$	X-ray density gm/cc
$ZrSe_2$	3.760	6.114	74.9	3.326
ZrSSe	3.711	5.994	71.5	2.829
ZrS_2	3.658	5.807	67.3	2.308

Table 4 The (h k l) values corresponding to prominent reflection d-values, Peak width, Peak intensity and Particle size for zirconium sulphoselenide single crystals.

Sample	h k l	d- spacing	Peak width 2θ	Peak intensity counts/ sec	Particle size (nm)
$ZrSe_2$	1 0 0	3.775	24.55	383	201.44
	0 0 2	3.001	30.25	779	164.13
	0 0 3	2.067	44.28	220	136.36
	1 1 1	1.767	51.58	118	118.12
ZrSSe	0 0 2	2.829	31.25	475	238.51
	1 0 2	2.189	40.55	534	148.31
	0 0 3	1.996	39.32	309	127.29
	0 0 4	1.499	62.36	351	82.72
ZrS2	1 0 1	2.782	31.52	756	344.09
	1 1 0	2.142	41.46	569	145.19
	1 0 3	1.940	45.90	376	109.83
	2 0 2	1.455	63.36	389	81.54

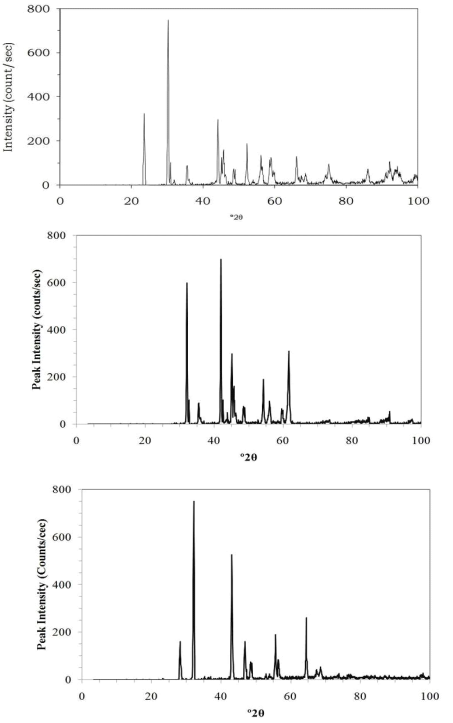

Figure 1: The X-ray diffractogram of ZrS_xSe_{2-x} single crystals

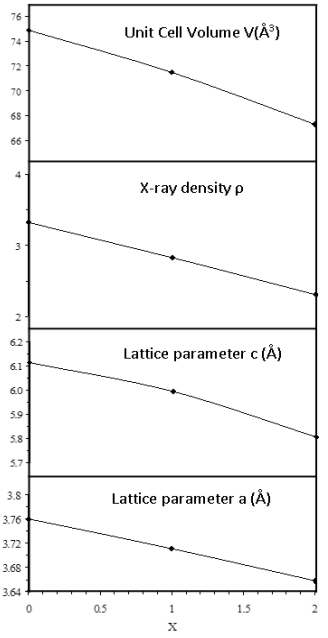

Figure 2: The graph of lattice parameter versus composition X

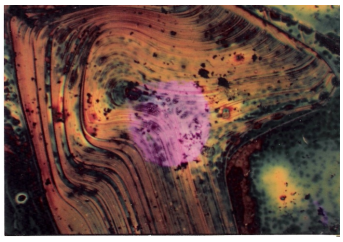

Figure 3: A typical micrograph showing the initiation of growth layers from the corner of a crystal periphery.

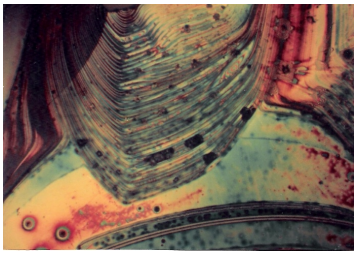

Figure 4: A typical micrograph showing the initiation of growth layers from the crystal edges or boundary.

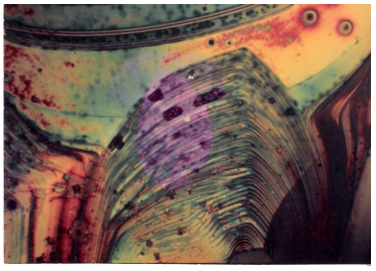

Figure 5: A typical micrograph showing flat surface as well as the presence of growth layers.

References

1. Hann H and Ness P, 1957 Naturewiss 44, 534.
2. McTaggart F K and Wadsley A D, 1958 Austr. Journal of Chemistry 11, 445.
3. McTaggart F K, 1958, Austr. Journal of Chemistry 11, 471.
4. Patel K R, Vaidya R V, Dave M S and Patel S G, 2010, Sciencia Acta Xaveriana, 1(1), 5-15
5. Patel P R, Patel K R and Pathak V M, 2012 Journal of Advances in Developmental Research 3 (1) 127-132.
6. Patel C A, Patel K R and Patel K D, 2012 International Journal of Physics and Mathematical Sciences, 2(4), 17-26.
7. Dave Mehul, Vaidya Rajiv and Patel S. G., 2005, Indian J. Phys., 79 (1) 85.
8. Dave M S, Patel K R, Vaidya Rajiv and Patel S G, 2006 Indian Journal of Physics, 80 (8) 797-800.
9. Patel C A, Patel K R and Patel K D, 2014 International Journal of Physics and Applications, 6(2) 115-130.
10. M.P. Deshpande, P.D. Patel, M.N. Vashi, M.K. Agarwal, 1999,Journal of Crystal Growth 197 833-840
11. Onuki Y, Inada R, Tanuma S, Yamanaka S and Komimura H, 1981 Jap. J. Applied Physics, 20(8) 1583
12. K. S. BartwalC:\Users\Admin\Research Related\Reprints\ZrSe2\1.htm - aff1 and O. N. Srivastava, 1993, Materials Science and Engineering B, 18(1) 88-90
13. Srivastava S K, and Avasthi B N, 1986 J. Less common, 124 85
14. Vegard L 1921 Z,Phys. 5 17
15. Vegard L Z and Dale H Z, 1928 Krist. 67 148
16. Whittingham M S and Gamble F R, 1975 Mater. Res. Bull. 10 363