

CHAPTER 1
LITERATURE SURVEY OF WS_2 AND WS_2
SINGLE CRYSTALS

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1.1 Introduction

Most of the transition metals of groups IV to VIII form compounds with sulphur, selenium and tellurium having the composition MX_2 , where M is one of the metals and X is a chalcogen. These layered transition metal dichalcogenides have aroused a remarkable degree of interest in recent years which has been reviewed by various authors /1-3/. This interest stems essentially from the quasi-two dimensional nature of the compounds. During the last decade, some of the transition metal dichalcogenides out of existing sixty, have been found to be very much useful in the fabrication of photoelectrochemical (PEC) solar cells /4/. Some of these crystals are available in the natural form also. But for the advanced technological applications, the requirement of high quality crystals demands the extreme purity standard and so the art and science of crystal growth has gained tremendous momentum in the recent developments. This has boosted the author to go for studies of different properties of WS_xSe_{2-x} (where $x = 0$ to 2) system which have been described in the present work. To arrive at a particular task of the work, the historical survey of the previous work on WSe_2 and WS_2 is presented briefly in the following sections.

1.2 Synthesis

(A) WSe₂

Usually, the material tungsten diselenide (WSe₂) is not known to occur naturally and so has to be synthesized in the laboratory. It is a gray black substance, having covalent character and is one of the best known layered transition metal dichalcogenide.

Several reports /5-8/ exist on the preparative conditions of such compounds. Silverman /5/ used high pressure upto 70 Kbar and temperature upto 2400°C and got the hexagonal form of WSe₂. Wildervanck /6/, Al Hilli and Evans /7/ and Hicks /8/ reported the preparation of the polycrystalline powder of WSe₂ by the direct reaction of the elements in the stoichiometric ratio.

In Wildervanck's /6/ experiment only bromine and iodine were used as transporting agents. With bromine, transport took place from T_H (High zone) = 800°-850°C, T_L (Low zone) = 750°C and with iodine the gradient was T_H = 1055° → T_L = 890°C. The produced samples have been described as thin small crystals having the hexagonal 2H-NbS₂ type lattice. Al Hilli and Evans /7/ have grown WSe₂ with and without bromine as transporting

agent. Transport was from $T_H = 850^\circ\text{C} \rightarrow T_L = 700^\circ\text{C}$ with $2.7 \text{ mg Br}_2 \text{ cm}^{-3}$ in four days. The produced material consisted of thin buckled crystals with no obvious surface features and crystals grown without Br_2 were platelets with hexagonal growth features. In both cases the lattice parameters were similar to those published by Gleason et al. /9/.

Brixner /10-b/ used iodine transport to grow the crystals of WSe_2 . Karshov et al /11/ used a modification of Brixner's procedure to produce large homogeneous melt formed crystals. They employed a three zone furnace.

The information on preparation and growth conditions are given in Table 1.1.

(B) WS_2

Tungstenite is an isomorph of molybdenite. It belongs to a class of group VI dichalcogenides having C_7 type crystal structure. It is a grey black semi-conducting compound. WS_2 is found in nature as mineral tungstenite. On the basis of whatever information is available in the literature, it can be said that it is earthy or foliated. It is found at Emma mine, Salt Lake

Company, Osh.

Procedures for the preparation of WS_2 can be grouped into two categories. Some procedures yield hexagonal modification, while others rhombohedral form /6/. Wildervanck /6/ reported the synthesis of WS_2 from the elements at $900^\circ - 1000^\circ C$, which gave 2H-product without too much stacking disorder. According to D.F.A. experiments /12/ the temperature of formation for WS_2 lies at $\leq 400^\circ C$.

Glesner et al /9/ have reported that WS_2 synthesizes at $800^\circ C$ in 24 hours. As in the case of MoS_2 , the thermal decomposition of WS_3 yields hexagonal WS_2 at $1100^\circ C$. It gives a well crystallized disulphide and is isostructural with 2H- MoS_2 . Wildervanck and Jellinek /13/ have prepared 3R- WS_2 by a carbonate flux method. They pointed out that the yield of crystals, however, was much lower than that of MoS_2 and the attempts made to improve the yield resulted in products with larger degree of stacking disorder. Tiede and Lemke /14/ prepared WS_2 by the reaction of tungsten trioxide and sulphur. The high pressure and temperature technique of Silverman /5/ has also been successfully applied to obtain 3R- WS_2 . Heating of W-S (1:2) mixture, compressed at 45 Kbar and $1800^\circ C$ for 2-3 minutes, formed

a rhombohedral silver-grey soft powder.

Well defined experiments to grow WS_2 have also been proposed by Nitsche /5/, Wildervanck /6/ and Schafer and coworkers /16, 17/. Nitsche /5/ used bromine transport for the growth of these crystals. Wildervanck attempted to grow them with Cl_2 , Br_2 , I_2 and NH_4Cl as transporting agents. He obtained pure 2H and 3R products in bromine assisted transport but the size of most of the crystals was small.

Schafer and co-worker /16/ indicated in 1968 the possibility of sulphur assisted transport of WS_2 . They reported the influence of water on the iodine assisted transport of WS_2 /17/. Preparation and crystal growth data of various workers are given in Table 1.2.

1.3 Structure

(A) WS_2

Tungsten diselenide belongs to the general family of group VI, MX_2 layered materials and in general, it arises from the stacking of hexagonally packed planes in the sequence as shown in Fig. 1.1, 6:3 coordination results, that around the metal atoms being either trigonal prismatic or octahedral (Fig. 1.2).

The arrangement of such units in a single layer brings about hexagonal symmetry (Fig. 1.3). The stacking sequences of these basic units determine the polytypism and is either (AbA BaB)/(2H-polytype) or (AbA BaB CaC)/(3R-polytype) (Figs. 1.3 and 1.4). There are two molecules per unit cell in the 2H form (Fig. 1.5(a)) and 3 molecules per unit cell in the 3R form (Fig. 1.5(b)). In the 2H form the space group is D_{6h}^A (or P6/mmc) with the anions centered at $\pm (1/3, 2/3, 4)$, $\pm (2/3, 1/3, 1/2)$ and the cations at $\pm (1/3, 2/3, 1/4)$ positions. For the 3R form the space group is C_{3v}^5 (R_{3m}) with anions centered at $(0, 0, 0)$, $(0, 0, 1/12)$ and cations at $(0, 0, 5/12)$. Figure 1.6 shows these structures. The lattice parameter and relevant structure data are given in Table 1.3.

(B) WS₂

WS₂ belongs to the general family of group VI, MX₂ layer chalcogenides. A 6:3 coordination exists in which the metal atom is surrounded octahedrally or trigonal prismaticly by the chalcogens. The layered structure of WS₂ is the same as that of WSe₂.

The normal structure of tungsten disulphide is hexagonal with two atoms per unit cell. Atoms are in

special positions of space group $P6_3/mmc$ with cations at $\pm (1/3, 2/3, 1/4)$ and anions at $\pm (1/3, 2/3, u)$; $\pm (2/3, 1/3, 1/2 + u)$, where 'u' for WS_2 is 0.629.

A second form of tungstenite is known as rhombohedral in space group $R\bar{3}m$ with atoms at sites $(0, 0, 0)_6$, $(0, 0, 1/2)_6$ and $(0, 0, 5/12)_6$. The lattice parameters and the relevant structure data of WS_2 are listed in Table 1.3.

1.4 Electrical Properties

(A) WSe_2

The important data for electrical and thermoelectric properties obtained by different workers of WSe_2 crystals are summarized in Table 1.4.

(B) WS_2

Tungstenite is an extrinsic semiconductor and possesses paramagnetic properties. Details about the electrical properties of tungstenite crystals have also been included in Table 1.4.

1.5 Optical Properties

(A) WSe_2

Reflectivity spectra (78 K) were obtained

by Liang /18/ for single crystals of $2H-WSe_2$ grown by bromine vapour transport. It is seen that E (polarization) $\perp c$ spectra show sharp exciton peaks above threshold with further peaks at higher energies which are attributed to inter-band transitions.

Optical properties of group VI \bar{A} transition metal dichalcogenides have been studied by transmission measurements in the visible and infrared parts of the spectrum at room temperature, liquid nitrogen temperature and near liquid helium temperature by several workers /19-23/. The reflectivities of the compounds have also been measured at various temperatures in the visible and ultraviolet parts of the spectrum /24-27/.

(B) WS_2

The reflectivity spectra of $3R-WS_2$ single crystals grown by Br_2 vapour transport has been studied by Liang /18/ at 78 K. The transmission spectra of the iodine transport grown compounds have also been measured /20/. In both compounds the $E \perp c$ spectra show sharp exciton peaks above threshold with further peaks at higher energies attributed to inter-band transitions. In terms of the two dimensional WS_2 band structure obtained by Brenley et al /28/, the labelled $E \perp c$

reflectivity structure is identified as follows /18/

A, B excitons with $\bar{3} \rightarrow \bar{3}$.

d = $\bar{3}^+ \rightarrow \bar{3}^+$. c = $\bar{3}_2 \rightarrow \bar{3}_2$.

D = $\bar{3} \rightarrow \bar{3}$

For E||C transition

between the highest valence band and lowest conduction band are only weakly allowed due to the d \rightarrow type character of these bands. The lowest energy allowed transitions, E||C are $\bar{3}_2^+ \rightarrow \bar{3}_2^-$

giving the transitions at 3.02 eV in WS_2 . Transitions $\bar{3}^+ \rightarrow \bar{3}^-$ and $\bar{3}^- \rightarrow \bar{3}^+$ also allowed for E||C, are thought to be responsible for the feature at 3.42 eV in the WS_2 (E||C) spectrum.

1.6 Solid Solution of WS_2 and WSe_2 Systems

Since importance of WSe_2 and WS_2 crystals have considerably increased because of their potential applications in the various fields, many

workers [29-31] have grown such crystals either by chemical vapour transport technique or direct vapour transport technique.

While going through such work in the literature, it is felt that attempts have not been made till today to grow the single crystals of $W_5S_xSe_{2-x}$ ($0 \leq x \leq 2$) by direct vapour transport technique.

In the present work, author could grow successfully such crystals in the series of $W_5S_xSe_{2-x}$ ($0 \leq x \leq 2$) single crystals. This thesis deals with the studies of growth and characterization, electron microscopy and application of these crystals in the fabrication of PHE solar cells.

Table 1.1

Compound preparation and crystal growth techniques for WSe_2 crystals

Compound	Crystal growth techniques
(a)	<p>Reaction of elements at $900 - 1000^\circ\text{C}$ for one week /6/ at $600 - 700^\circ\text{C}$, 24 hours then at $1000 - 1050^\circ\text{C}$ for one week in $190 \text{ mm} \times 22.5 \text{ mm}$ tubes /7/ at $600 - 700^\circ\text{C}$ for 10-15 hours } /10b,32/ then second firing</p> <p>at $1000 - 1200^\circ\text{C}$ for 72 hours /32/ at 950°C, 30 minute mixing and second heating at 1000°C /8/ at 600°C for 4 days, then refiring at 800°C for 4 days /10a/.</p> <p>In all the cases the yield is Zn-WSe_2.</p>
(b)	<p>Ultrahigh pressure - high temperature technique gives Zn-WSe_2 with 70 Kbar, and 2400°C /9/.</p> <p>Also transport without halogen /7/ conditions reported in references /10b,11/ are also valid for crystal growth of WSe_2.</p>

Table 1.2
 Details of the growth of WS₂ by vapour transport method

W _S transport	Cl ₂ transport	I ₂ transport	NH ₄ Cl transport
(a) T _H = 900°C → T _L = 800°C yields 2H+WS ₂ / 6, 15, 17/	T _H = 960°C - 1030°C → T _L = 875°C - 945°C	T _H = 850°C - 950°C → T _L = 800°C - 870°C	T _H = 900°C → T _L = 800°C
(b) T _H = 885°C - 1090°C → T _L = 787°C - 1009°C Growth period 1-2 weeks.	Growth period 10 days to 2.5 weeks	Period 2-4 weeks 2H as a source material	Transport is incomplete, yields 2H WS ₂ .
2H as a source material and obtained 2H and 3R type WS ₂ .	2H+WS ₂ as a source material and resulting yield is 2H and 3R WS ₂	2H+WS ₂ as a source material and resulting yield is 2H+3R WS ₂	Resulting material was 2H+3R WS ₂

Table 1.3

The lattice parameters and the relevant structure data of WS_2 and MoS_2

	WS_2	WS_2	
	2	3	
1. Luster	Highly shining metallic	Highly shining metallic	
2. Colour	Grey black	Grey black	
3. No. per unit cell, Z	2 /10b/	2 /10b/	
4. Type	MoS_2	MoS_2	
5. Character	Covalent	Covalent	
6. Group	VI, $d_{2h}^4 - r_6 / \text{ms}$	VI, $d_{2h}^4 - r_6 / \text{ms}$	
7. Structure	Trigonal prismatic Layer structure	Trigonal prismatic Layer structure	
8. ρ , X-ray density g.cm^{-3}	9.40 /10b/ 9.35 /10a/	Specific density } 7.5	
9. ρ , Pyrometric density g. ml^{-1}	9.0 /10b/	-	
10. Unit cell volume \AA^3	120.7 /10b/	-	
11. Molecular weight	-	248.05	
12. Hardness in Mohs.	-	2.5	
13. Lattice Parameters (\AA)	a' 2H:3.286 b' 2H:3.280 c' 2H:3.282 3.286	a' 12.976/10a/ b' 12.950/10b/ c' 12.937/7/ 12.979/8/	a' 2H:3.180 b' 2H:3.155 c' 3H:3.162 12.35/64 12.36 /34/

Table 1.4
Electrical properties of WSe_2 and WS_2 crystals

	WSe_2	WS_2
1	2	3
1. Electrical resistivity ($\mu\Omega\text{cm}$)		
(I) at 25°C	5.0×10^2	-
(II) at -196°C	1.5×10^4	-
2. Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)	2.5×10^{-3} 0.78 0.72	(I) 10^{-8} /33/ (II) 3.9×10^{-6} /33/
3. Type	P-type	P-type
4. Activation energy in (eV)	0.09	0.11 and 0.18 /33/
5. Seebeck coefficient ($\mu\text{V}/^\circ\text{C}$)	990	-
6. Thermoelectric power at an ambient temperature 312 K ($\mu\text{V}/^\circ\text{C}$)	-	4.7 /33/
7. Paramagnetic susceptibility along basal planes c.g.s. (e.s.u.)	-	6514 2×10^6

Table 1.4 (contd.)

1	2	3
8. Thermal conductivity ($\text{W}^\circ\text{C}^{-1}\text{cm}^{-1}$)	0.017	-
9. Figure of merit, Z (0°C^{-1} at 25°C)	1.15×10^{-6}	-
10. Thermodynamic data	$\Delta\bar{H}_{298}^\circ = -45$ $S_{298}^\circ = 21.5$	- -
11. Hall mobility	$\mu_p = 80 \text{ cm}^2/\text{V}\cdot\text{Sec.}$ $\mu_n = 100 \text{ cm}^2/\text{V}\cdot\text{Sec.}$	- -
12. Charge carrier density	$n_p = 10^{16}/\text{cm}^3$ $n_n = 10^{17}/\text{cm}^3$ at 295 K	- -

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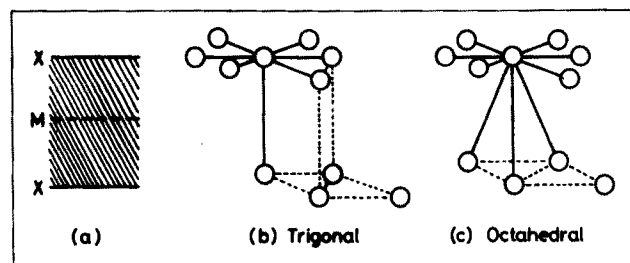


Fig. 1.1

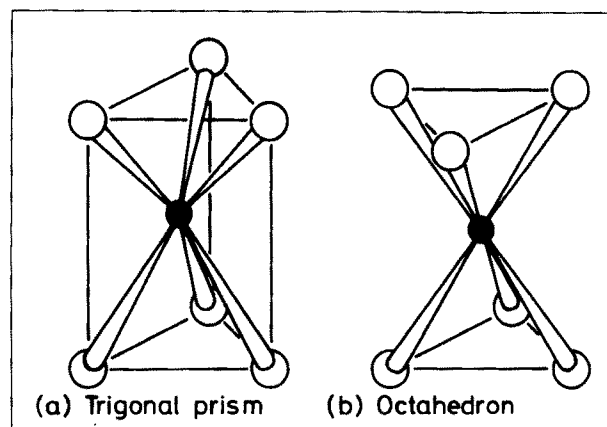


Fig. 1.2 (a, b)

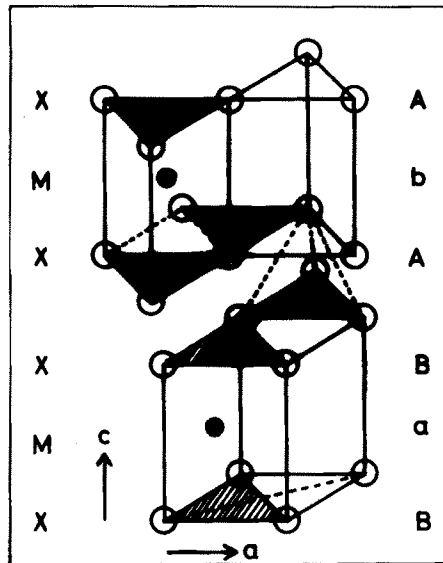


Fig. 1.3(a)

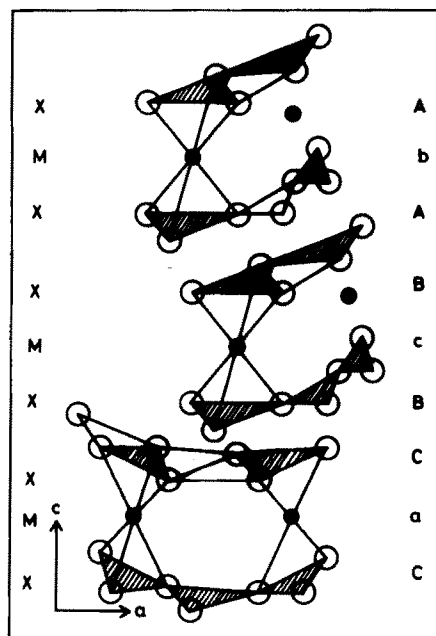


Fig. 1.3(b)

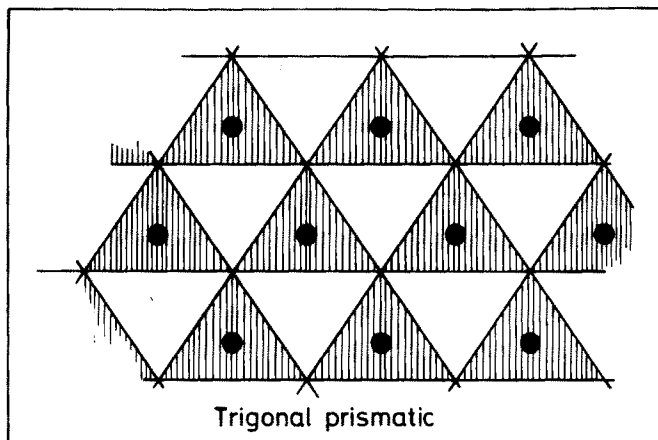


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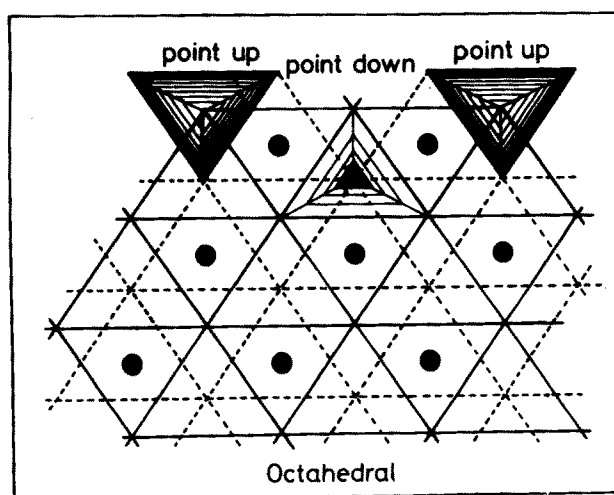


Fig. 1.4(b)

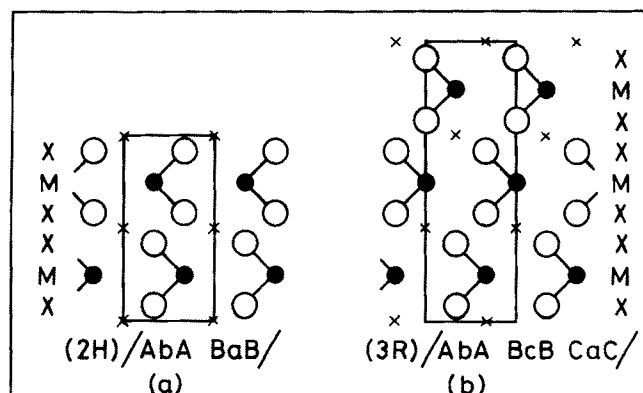


Fig. 1.5(a,b)

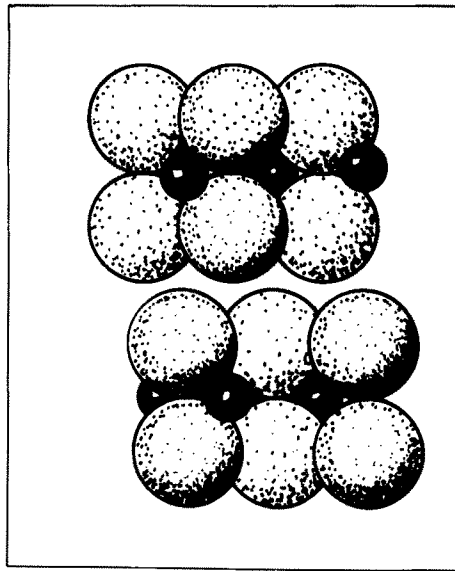


Fig. 1.6(a)

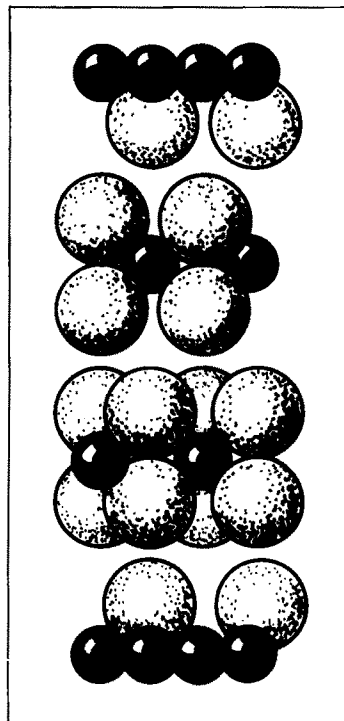


Fig. 1.6(b)