CHAPTER 2.1

Existing Information on WSSe single crystals

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I INTRODUCTION

Most of the transition metals of group IV to VIII form compounds with sulphur, selenium and tellurium having the composition $MX_2$, where $M$ is one of the transition metals and $X$ is the 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. Recently, these TMDC compounds have
been used for constructing photoelectrochemical (PEC) solar cells [4], as solid lubricants [5-12], as optical windows and semiconducting materials for fabricating conducting devices.

Among the layered compounds of transition metal dichalcogenides, all research activities of solid state photovoltaic cells have been limited to WSe$_2$. WS$_2$ which is used as lubricating agent at high temperature and in UHV studies, is also suitable in photoconversion studies. Both these compounds (WSe$_2$ and WS$_2$) have been used thoroughly in the fabrication of photoelectrochemical cells.

It is seen that the band gap of WSe$_2$ is 1.35 eV whereas that of WS$_2$ is 2.1 eV. By suitable adjustment of the sulphur and selenium content in WS$_x$Se$_{2-x}$ the band gap can be altered and a material suitable for solar energy conversion can be prepared. This has prompted the author to take equal portion of sulphur and selenium in WS$_x$Se$_{2-x}$ and undertake the growth of single crystals of tungsten sulphoselenide (WSSe) and study their suitability in photoelectrochemical studies. To begin with a brief survey of the existing information on WSSe find its place in the following sections.
II SYNTHESIS

Usually, the material tungsten suphposelenide [WSSe] is not known to occur naturally and so has to be synthesised in the laboratory. The normal procedure of growing such materials is vapour transport method. Here either the crystals can be grown by direct vapour transport method or by a chemical vapour transport method. Since WSSe is grown by the methods exactly similar to WSe$_2$ and WS$_2$ and they are also the end compounds of the series WS$_x$Se$_{2-x}$, it is considered worthwhile to describe the work already done on the synthesis of these materials. Tables 1, 2 and 3 describe the existing information on synthesis of WSe$_2$, WS$_2$ and WSSe.

III STRUCTURE

Tungsten sulphoselenide 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, 6:3 coordination results, that around the metal atoms being either trigonal prismatic or octahedral (Fig. 2).

The arrangement of such units in a single
layer brings about hexagonal symmetry (Fig. 3). The stacking sequences of these basic units determine the polytypism and is either (AbA BaB) (2H-polytype) or (AbA BCB CaC) (3R-polytype) (Figs. 3 and 4). There are two molecules per unit cell in the 2H form [Fig. 5(a)] and 3 molecules per unit cell in the 3R form [Fig. 5(b)]. In the 2H form the space group is D_{6h}^4 (or P6/mmc) with the anions centered at \((1/3, 2/3, 4) + (2/3, 1/3, 1/2)\) and the cations at \((1/3, 2/3, 1/4)\) 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 \((0, 0, 5/12)\). Fig. 6 shows these structures. The lattice parameter and relevant structure data are given in table 4.

**IV CONCLUSION**

Synthesis, crystal structure of WSSe have been described. Some important uses of this compound have also been mentioned in the introduction.
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Vallabhbh Vidyanagar.
TABLE 1

Compound preparation and crystal growth techniques for WSe₂ crystals

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal growth techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Reaction of elements at 900-1000°C for one week [14] at 600-700°C, 24 hours then at 1000-1050°C for one week in 190 mm x 22.5 mm tubes [15] at 600-700°C for 10-15 hours then second firing at 1000-1200°C for 72 hours at 550°C, 30 minutes mixing and second heating at 1000°C [16] at 600°C for 4 days then refiring at 800°C for 4 days [18]. In all the cases the yield is 2H-WSe₂</td>
<td>Br₂ transport [14] TH = 800-850°C, TL = 750°C in 2.5 to 3.0 weeks</td>
</tr>
<tr>
<td>(b) Ultra high pressure - high temperature technique gives 2H-WSe₂ with 70 Kbar and 2400°C [13]</td>
<td>Also transport without halogen [15] conditions reported in references [18, 19] are also valid for crystal growth of WSe₂</td>
</tr>
</tbody>
</table>
TABLE 2

Details of the growth of WS₂ by vapour transport method

<table>
<thead>
<tr>
<th></th>
<th>Br₂ transport</th>
<th>Cl₂ transport</th>
<th>I₂ transport</th>
<th>NH₄Cl transport</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_H = 900°C</td>
<td>T_H = 960°C - 1030°C</td>
<td>T_H = 830°C - 930°C</td>
<td>T_H = 900°C</td>
</tr>
<tr>
<td></td>
<td>T_L = 800°C</td>
<td>T_L = 875°C - 945°C</td>
<td>T_L = 800°C - 870°C</td>
<td>T_L = 800°C</td>
</tr>
<tr>
<td>Yield</td>
<td>2H-WS₂ [14]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b)</td>
<td>T_H = 865°C -1090°C</td>
<td>Growth period</td>
<td>Period 2-4 weeks</td>
<td>Transport is</td>
</tr>
<tr>
<td></td>
<td>T_L = 787°C -1009°C</td>
<td>10 days to</td>
<td>2H as a source material</td>
<td>incomplete, yields</td>
</tr>
<tr>
<td></td>
<td>Growth period</td>
<td>2.5 weeks</td>
<td></td>
<td>2H-WS₂</td>
</tr>
<tr>
<td></td>
<td>1-2 weeks.</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>2H as a source material and obtained 2H and 3R type WS₂</td>
<td>2H-WS₂ as a source material and resulting yield is 2H and 3R WS₂</td>
<td>Resulting material was 2H+3R WS₂</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>Crystal growth technique</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>----------</td>
<td>-------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reaction of elements at 800°C for 72 hours and then placed for crystal growth [20]</td>
<td>Direct vapour transport growth temperature = 1010°C in 240 hours [20]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 4

The lattice parameters and relevant structure data of WSSe

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Luster</td>
<td>Highly shining material</td>
</tr>
<tr>
<td>2.</td>
<td>Colour</td>
<td>Black opaque</td>
</tr>
<tr>
<td>3.</td>
<td>Moles per unit cell, Z</td>
<td>2</td>
</tr>
<tr>
<td>4.</td>
<td>Type</td>
<td>MoS₂</td>
</tr>
<tr>
<td>5.</td>
<td>Character</td>
<td>Covalent</td>
</tr>
<tr>
<td>6.</td>
<td>Structure</td>
<td>Trigonal prismatic layer structure</td>
</tr>
<tr>
<td>7.</td>
<td>( \rho ), X-ray density ((\text{gm cm}^{-3}))</td>
<td>8.54 [21]</td>
</tr>
<tr>
<td>8.</td>
<td>Unit cell volume ( \text{A}^3 )</td>
<td>114.672 [20]</td>
</tr>
<tr>
<td>9.</td>
<td>Lattice parameters ((\text{A}^\circ))</td>
<td>'a' 2H : 3.229 [21] 'c' 2H : 12.707 [21]</td>
</tr>
</tbody>
</table>
CAPTIONS TO THE FIGURES

Fig. 1 Sandwich of X-M-X sheets
Fig. 2(a) Trigonal prismatic unit
Fig. 2(b) Octahedral unit
Fig. 3(a) Stacking of trigonal prismatic units
Fig. 3(b) Stacking of octahedral units
Fig. 4(a) Plane view of stacking in 2H-polytype
Fig. 4(b) Plane view of stacking in 3R-polytype
Fig. 5(a) 2H-unit cell
Fig. 5(b) 3R-unit cell
Fig. 6(a) Layer structure in 2H-polytype
Fig. 6(b) Layer structure in 3R-polytype.
Fig. 1

Fig. 2
Fig. 3(a)

Fig. 3(b)
Fig. 4(a)

Fig. 4(b)
Fig. 5

Fig. 6(a, b)
CHAPTER 2.2

Growth of single crystals by vapour phase method

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I INTRODUCTION

There are several methods for growing single crystals, the technique being fully described in textbooks and reviews [1-11]. It is well established that compounds of "transition metal chalcogenide" family are insoluble in water, which naturally prevents their growth from aqueous solutions. Following two methods of crystal growth were therefore considered.

1. Growth from melt
2. Growth from vapour phase.
The former was rejected because of the high melting point of the compounds, including WSSe, WSe$_2$, MoSe$_2$. They decompose before reaching their melting points, sometimes melt incongruently or the vapour pressure is too high at melting point. Hence growth from vapour phase was found more suitable. The method of growth from vapour phase can be divided into following two categories.

1. Chemical vapour transport method
2. Direct vapour transport method

II VAPOUR GROWTH TECHNIQUE

(a) Chemical vapour transport method

This method, for the preparation of single crystals has been reported and found as a reliable method for crystal growth of metal dichalcogenides [12-17]. New theoretical attempts of vapour transport of solids are given by Lever [18,19], Mandel [20,21] and Arizumi and Nishipanaga [22]. Kaldis and coworkers [23,24] have shown that it is possible to grow crystals upto several cm in size by chemical transport under well controlled nucleation conditions at smaller supersaturations.
Transport reactions have been studied systematically by Schafer [25] for the preparation of high purity refractory metals.

Chemical vapour transport technique mainly depends on a chemical reaction between the source material to be crystallized and a transporting agent. The reaction product is volatile and can be transported in the vapour phase at temperature well below the melting point of the compounds. Transport occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at the lower temperature to deposit molecules of compound at the most favourable crystalline sites. Initially, random deposition occurs and seed crystals are formed. The transport of the reaction product in the vapour phase can be obtained by continuous gas flow from external supplies or by its recirculation within a tubular ampoule. This is illustrated in fig. 1. As a result, in principle, one can transport unlimited amount of the starting material with only a small amount of transporting agent.

The rate of transport of the compound in gm/sec is given by Nitsche et al. [13] as
\[ m = L \cdot dp(T', T'', dG, C_t) \]  

where,

\( T', T'' \) are the temperatures at hot and cold ends respectively,

\( dp \) difference between the partial pressures of the reaction product at temperature \( T' \) and \( T'' \).

\( dG \) Change in Gibb's free energy in the reaction,

\( C_t \) Concentration of transporting agent,

\( L \) Conductance of the system, a function of the ampoule geometry and the physical processes involved in the vapour transport.

Different parameters mentioned in the transport equation (1) have the following significance.

\( dG \) It has been found by Schafer [15] that optimum transport occurs when the reaction is not far from the equilibrium, that is, \( dp \) is a maximum for values of \( dG \) near zero. For chalcogenides, the halogens are most commonly used as transporting agents, since their \( dG \) values are quite low.
Nitsche [16] found a value of 5 mg/cc for \( C_L \) to be a good starting point for experiment.

The "conductance" of the system depends on the mode of transport of the reaction product. This is controlled principally by the total vapour pressure inside the ampoule, most of which is due to the volatile transporting agent. Three different mechanisms are possible.

(a) At low pressure and with small ampoule diameter, diffusion is the only important transport mechanism.

(b) As the pressure or the diameter is increased, convection currents set up by the thermal gradient rapidly become more important.

(c) In the initial reaction equation compound + transporting agent = Reaction product. There are equal number of molecules in the vapour phase on each side. If this is not so, there will be a change in pressure gradient along the ampoule, and a laminar flow of the reaction product will take place.
T', T'' depends strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature [16]. Many compounds including MoS$_2$ have more than one possible crystal structure, and their stability is often temperature dependent. T'', the crystallization temperature should be within the stability range of the required crystal type.

(T',T'') the temperature difference is altered to control dp, and so to vary the vapour transport rate. However, this cannot be increased indefinitely without causing polycrystallization, as explained below.

Molecules condensing on to a flat surface from the vapour lose potential energy, that is they acquire a binding energy, E'. However, their thermal energy gives them a probability, P' of evaporation.

\[ P' \ll \exp \left( \frac{E'v}{kT} \right) \]  \hspace{1cm} (2)

The rate of condensation, n (mole/sec/cm$^2$) is controlled by the partial pressure of the vapour P (atmosphere) and the average molecular velocity, V (cm/sec).
\[ n = L_0 \cdot p \cdot v \]  

where, \( L_0 \) is the Loschmidt's constant  
\[ = 2.687 \times 10^4 \text{ per (cm}^3 \text{ atom)} \]

There will be a pressure \( P' \), when the rates of condensation and evaporation are equal.

In reality, when a molecule condenses on to a crystal, it will tend to migrate over the surface before evaporation. If whilst migrating, it finds a site of greater binding energy, \( E'' \), such as a step on the crystal surface, the probability of evaporation drops. Equilibrium will occur at low pressure, \( P'' \).

If the partial pressure has a value between \( P' \) and \( P'' \), molecules will only condense on the sites of greater binding energy \( E'' \). Under these conditions crystals that have already formed will grow but no new crystals will form unless impurities bind some molecules more firmly to the ampoule wall to form seed crystal. Since the net number of condensing molecules is limited by the number of grown sites, the rate of transport must not be too great. Otherwise the partial pressure of the
reaction product will exceed $P'$ and polycrystallization will occur.

Finally, Nitsche [13] gave the following rules for the successful growth by vapour transport technique.

1. The rate of transport must not exceed the rate of growth by the seeds.

2. The optimum crystallization temperature must be evaluated empirically for each system taking into account the possibility of polymorphism.

3. The crystallization chamber should be larger in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.

4. The temperature distribution in the crystallization chamber should be as uniform as possible to avoid partial re-evaporation of already grown crystals.

5. Well developed crystals form more easily in large diameter tubes, where transporter convection determines the rate of transport.
6. The temperature difference between the reaction and the growth chambers can be made smaller when wider tubes are used. (Thus facilitating an even distribution of growth products along the crystallization chamber) since the gas flow here is the rate determining parameter.

(b) Growth without using transporting agent

Crystal growth by chemical vapour transport technique using either iodine or bromine as an agent will give very large crystals, sometimes more than one centimeter in basal extent. But these transporting agents always contaminate the grown materials. Therefore to grow crystals without such contamination, a method of growth which avoids the use of transporting agent is found to be more satisfactory.

Such a method was used by Al-Hilli and Evans [26] to grow single crystals of certain transition metal dichalcogenides. This method of growth of crystals without a chemical transporting agent (called as direct vapour transport method) has been used in the present work to grow single crystals of WSSe.
III EXPERIMENTAL DETAILS OF VAPOUR TRANSPORT TECHNIQUE

(a) Dual zone horizontal furnace

The first and the foremost basic essential piece of the apparatus required for vapour transport method is a furnace capable of providing an appropriate temperature gradient all over the ampoule. The furnace must be capable of reaching higher temperatures of the order of 1200°C and it should be able to produce temperature gradients of different magnitudes over a length of about 25 cm. To obtain the temperature stability during growth, electronic temperature controllers were used in the furnace heating circuits. Furnace was constructed in our workshop by using a special sillimanite threaded tube (grade KR 80 GAHG), closed at one end, 45 cm in length, 7 cm outer diameter, 5.6 cm inner diameter with thread pitch 0.3 cm, imported from Koppers Fabriken Feuerfester, Germany. Super Kanthal A-1 wire 17 SWG was wound directly on to the furnace tube in different regions.

The tube was then enclosed in the hot face insulating brick slabs. The complete brick shell was fully encased in thick asbestos sheets and the entire assembly was supported in a steel frame work (fig. 2).
As the growth of sizeable crystals require larger time the temperature in the furnace must be accurately controlled. The power supplied to the furnace windings was regulated by the controlled circuit (fig. 3). The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70, 80 and 100 v taps with 20 A current capacity in secondary were used to supply sufficient power in order to achieve the required high temperature. Controllers used were "Eurotherm controllers" which were of "fast cycling" type switching the power on and off regularly at every 10 cycles of mains frequency. The ON time was continuously variable, controlling the power fed to the Kanthal A-1 windings. The control units have 'integral' and 'derivative' controls to correct the change in furnace temperature with no overshoot. Combined with cold junction compensation, this gives a stability of + 1°C.

The fluctuations in the local electrical supply were controlled by using an A.C. voltage stabilizer with 180 to 260 V input and 230 + 1% output volts, of capacity 3 KVA. The output which was fed to the primary of the transformer heats the furnace windings and
helps to maintain the stability of growth conditions. By controlling the input power to the two steps of windings a required temperature gradient could be established across the length of the work tube in the proper temperature range. Thermocouples used were Pt (13%)-Rh-Pt, and the Eurotherm temperature controllers were calibrated for the above thermocouples. It was seen that thermocouples were stable over the prolonged use in the furnace and they were supported within the furnace tube itself, showing the furnace tube temperatures correctly.

(b) Ampoule

High quality fused quartz tubes used in growth experiments have a melting point of about 1500°C. Tubes of various diameters were used. Tubes with internal diameter of 2.4 cm and length 25 cm were found to be more suitable for the present growth experiments. One end of the tube was sealed and other was drawn into a neck joined to a silicon tube of 1 cm inner diameter to connect it to the vacuum system for evacuation after introducing the source material.
IV. CRYSTAL GROWTH

(a) Cleaning of the ampoule

First of all the ampoule was washed with boiling water and then with boiling concentrated HNO₃ and HF (49%) taken in equal proportion (i.e. 1:1). Afterwards it was washed with distilled water. A further washing was carried out with concentrated H₂SO₄ and HNO₃ in equal proportions followed by a final washing for about ten to twelve times with doubly distilled water. The ampoule was then kept in a SICO constant temperature furnace at 100°C and left for overnight heating to make it moisture free.

(b) Charge preparation

For the charge preparation the required materials (Table 1) for growth are taken in a stoichiometric ratio and filled up in a transparent ampoule duly cleaned and dried by the process explained above. The ampoule containing source material is then connected to a vacuum system and precaution is taken to see that the vacuum is brought so slowly that none of the materials from the ampoule enter the vacuum system. A total charge of about 10 gm was used in each experiment.
When the vacuum is being reached, the ampoule is tapped slowly so that any air between the particles of the materials is removed, when a vacuum of the order $10^{-5}$ torr is reached, the ampoule is sealed off at the neck.

The sealed ampoule with the elemental powder is shaken thoroughly to ensure proper mixing of the contents. The mixture is then distributed uniformly all over the length of the ampoule. The ampoule is thus ready for keeping it in the furnace.

After keeping the ampoule at an appropriate place in the horizontal furnace, the temperature is slowly increased. The temperature and the period for which the ampoule is kept in the furnace depends upon the material which is being grown. The slow heating is necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. Comparatively large size of the ampoule and well uniform distribution of the powder will minimise the temperature rise to prevent an explosion. After specific time of heating at the required temperature the furnace is switched off and after bringing it to room temperature it will be seen that the ampoule has a fine free flowing shiny homogeneous polycrystalline material.
The growth procedure and conditions for the growth of WSSe single crystals are well described and discussed in next chapter.

V CONCLUSIONS

Salient features of growth procedure by chemical and direct vapour transport methods have been thoroughly explained. Rules for successful growth by vapour transport technique as pointed out by Nitsche have also been outlined.
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### Table 1

Materials for which the crystals were grown with source of supply

<table>
<thead>
<tr>
<th>Materials</th>
<th>Purity</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten (W)</td>
<td>99.999</td>
<td>Koch-light Laboratory Ltd., England</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>99.999</td>
<td>Johnson Matthey Chemicals Ltd., England</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>99.9999</td>
<td>Koch-Light Laboratory Ltd., England</td>
</tr>
</tbody>
</table>
CAPTIONS TO THE FIGURES

Fig. 1 Illustration of the cyclic process of chemical vapour transport in a closed system.

Fig. 2 Schematic representation of the furnace.

Fig. 3 Control circuit for regulating the power.
Growth by iodine vapour transport

Fig. 1

Fig. 2
CHAPTER 2.3

Growth and characterization of WSe crystalline single crystals

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I INTRODUCTION

A complete information about WSe$_2$, WS$_2$ and WSSe crystals has been given in the earlier chapter. As pointed out there, several authors [1-3] have successfully applied the technique of direct vapour transport to grow the single crystals of tungsten dichalcogenides. As these crystals are semiconductors, they can serve as promising materials for photoelectro-chemical (PEC) solar cells [4-7]. It appears from a review of the literature that so far no attempt has been made to grow the tungsten sulphoselenide (WSSe) single
crystals by chemical vapour transport technique.

In this chapter, preliminary results concerning the growth of single crystals of WSSe and their X-ray characterizations are described and discussed.

II EXPERIMENTAL

(a) Charge preparation

Stoichiometric amounts of 99.999% pure tungsten, spectroscopically standard (99.9999% pure) sulphur and 99.999% pure selenium powder were sealed under pressure of less than $10^{-5}$ torr in 24 mm bore x 250 mm long fused quartz ampoules. The total charge used was about 8 to 12 gm. Prior to introduction of the elements, the quartz ampoules were thoroughly cleaned, etched and vacuum baked.

The powders were thoroughly mixed by vigorous shaking and the mixture was distributed all along the length of the ampoule. The ampoule was introduced horizontally into the furnace and the temperature was slowly increased to 800°C in the manner described in the earlier chapter. The ampoule was left at this temperature
for 72 hours. Then the furnace was shut down and allowed to cool down to the room temperature. A free flowing shining dark mixture resulted from reaction.

(b) Growth of single crystals of WSSe by direct vapour transport

The charge thus prepared was well mixed by vigorous shaking of ampoule. The powder was then distributed along the length of the ampoule and ampoule was kept in the furnace for the growth of crystals as shown in fig. 1. The furnace temperature was increased slowly, as was done for the charge preparation to the required final temperature for growth.

The exact growth conditions are described in table 1. After the required period of growth the furnace was shut off and allowed to cool down to room temperature. The ampoule was broken and crystals were found to grow along the entire length of tube.

The crystals obtained were black, opaque in colour and were plate like with the C-axis normal to plane of the plates. All of them grew vertical to each other inside the ampoule. The description of growth
product is presented in table 1. Fig. 2 shows the temperature gradient maintained along the ampoule.

(c) Growth of single crystals of WSSe by chemical vapour transport.

The charge prepared in the manner described in the earlier part of this chapter was used for single crystal growth of WSSe using the chemical vapour transport method. The charge was taken in an ampoule of similar dimensions as used for the charge preparation and transporting agent iodine was introduced in it. The quantity of iodine introduced was 5 mg per unit volume of the ampoule. Finally, after sealing the ampoule containing the charge and the transporter to a pressure of $10^{-5}$ torr it was kept in the appropriate temperature gradient. After the completion of the growth period, the ampoule was cooled slowly. A large number of crystals were found to grow at the colder end of the ampoule.

Here also the crystals obtained were black, opaque in colour and plate like with their c-axis normal to the plane of the plate. Some of the growth parameters like growth time, concentration of transporting agent, size of crystal etc. are given in table 1. The details of
the position of the source material and temperature distribution along the ampoule are shown in fig. 2.

III STRUCTURE

The WSSe system possesses a hexagonal $2H$-$MoS_2$ structure ($C_7$ type). The metal atoms are in trigonal prismatic coordination between two superimposable sheets of hexagonally packed chalcogen atoms. The $M$-atoms of a sandwich $X-M-X$ lie over the $X$ atoms of the adjacent sandwich. No strong bond exists between the layers, only long range Van der Wall's forces hold atomic sandwiches together. This gives the crystals their characteristic platy habit, with extended growth and pronounced cleavage perpendicular to $c$-axis. The stacking sequence is $ABAB$, with the space group $D^{4}_{6h}$ ($P6_3/mmc$).

IV LATTICE PARAMETER

In order to determine the unit cell parameters of the grown crystals, $d$ values were obtained using X-ray diffractograms (shown in fig. 3(a, b)). These were obtained with the help of X-ray diffractometer employing CuK$\alpha$ radiation.

The unit cell parameters of all the crystals
grown by the two different methods have been determined from the above data in the present work. The values of 'a' and 'c' parameters estimated from the analysis are given in table 2. All the parameters match well with the reported values [8.9].

V COMPOSITION DETERMINATION USING ENERGY DISPERSIVE ANALYSIS OF X-RAYS (EDAX)

A semi quantitative analysis of the crystals has been done by using the EDAX facilities available in the department (chapter 1.1) in the present study. As the samples were neither bulky nor thin i.e. partially transmitting the electron beam, ZAF correction was not applied to the results.

The weight percentage of tungsten, sulphur and selenium in different crystals determined from the EDAX data are shown in table 3. It is remarkable to note that the samples do not show the presence of any impurity.

VI CONCLUSIONS

1. Single crystals of WSSe have been grown by direct vapour transport technique in which crystals were
observed free from contamination of any transporting agent.

2. The crystals grown by chemical vapour transport technique using \( \text{I}_2 \) as transporting agent have proportionate elemental composition, and are stoichiometrically pure and perfect. The fact that these crystals have smooth surfaces also speaks about their perfect growth.

3. Single crystals of WSSe have been grown for the first time by using chemical vapour transport technique.

4. A selection of the appropriate ampoule and a proper temperature gradient is necessary to increase the size of the crystals.
REFERENCES

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2. Al. Hilli, A. A. and Evans, B. L. 1972
   J. Crystal Growth 15, 93.


TABLE 1
Growth parameter of WS\textsubscript{2}Se single crystals

<table>
<thead>
<tr>
<th>Method of growth</th>
<th>Reaction temperature (°C)</th>
<th>Growth temperature</th>
<th>Growth time (hours)</th>
<th>Size of crystals mm</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct vapour transport</td>
<td>800</td>
<td>1040</td>
<td>1000</td>
<td>240</td>
<td>12x8x0.12</td>
</tr>
<tr>
<td>Chemical vapour transport using Iodine as transporting agent (5 mg per unit volume)</td>
<td>800</td>
<td>1000</td>
<td>960</td>
<td>192</td>
<td>20x10x0.12</td>
</tr>
</tbody>
</table>
**TABLE 2**

Obtained lattice parameters of WSSe single crystals grown by different method

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>C (Å)</th>
<th>Unit cell volume (Å³)</th>
<th>X-ray densities (gm.cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct vapour transport</td>
<td>3.304 ± 0.043</td>
<td>12.700 ± 0.056</td>
<td>120.13</td>
<td>8.149</td>
</tr>
<tr>
<td>Chemical vapour transport</td>
<td>3.291 ± 0.028</td>
<td>12.903 ± 0.012</td>
<td>121.03</td>
<td>8.094</td>
</tr>
</tbody>
</table>

(using I₂ as transporting agent)
<table>
<thead>
<tr>
<th>Element</th>
<th>Calculated weight percentage of individual elements</th>
<th>Observed weight percentage of individual elements in different methods</th>
<th>Calculated weight percentage of individual elements</th>
<th>Chemical vapour transport</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>62.348</td>
<td>65.177</td>
<td>62.148</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>10.875</td>
<td>8.851</td>
<td>10.103</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>26.777</td>
<td>25.972</td>
<td>27.749</td>
<td></td>
</tr>
</tbody>
</table>
CAPTIONS TO THE FIGURES

Fig. 1 Schematic view of the furnace showing the position of the ampoule inside the two zone furnace during crystal growth.

Fig. 2 Details of the positions of the ampoule source material and temperature distribution along the ampoule for WSSe growth.

Fig. 3(a) X-ray diffraction peaks for WSSe single crystal grown by direct vapour transport.

Fig. 3(b) X-ray diffraction peaks for WSSe single crystals grown by chemical vapour transport.
Fig. 1

- Furnace windings
- Cold zone
- Quartz ampoule
- Hot zone
- Furnace tube
- Powder
- Crystals
- Variable transformers
Fig. 2

Source Zone

Growth Zone

Distance (Cm.)

Temperature (°C)

200

25 Cm

900

940

980

1020

1040

- CVT

- DVT
Fig. 3(a)
Fig. 3(b)
CHAPTER 2.4

Transport properties of tungsten sulphoselenide crystals

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II Electrical contacts 076
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I INTRODUCTION

About two-third compounds of transition metal dichalcogenides assume layered structures. Within a layer the bonds are strong, while between adjacent layers they are remarkably weak. As a consequence the crystals possess facile basal cleavage [1], lubricity [2,3] and marked anisotropy in their physical and chemical properties [4]. Electrically [5] they cover a wide spectrum of properties. They are insulators like HfS$_2$, semiconductor like MoS$_2$, MoSe$_2$ and WSe$_2$, semimetals like WTe$_2$ and true metals like NbS$_2$. 
Since the crystals of Tungsten sulphoselenide (WS\textsubscript{2}Se) grown by the author (Chapter 2.3) possess a considerable potential [6] for the fabrication of PEC solar cells, it was decided to study their electrical properties. Since this study will help in understanding the photoelectrochemical behaviour of the materials better attention has therefore been paid to the resistivity and Hall coefficient measurements of single crystals of tungsten sulphoselenide.

II ELECTRICAL CONTACTS

In order to study the electrical properties, the most important problem is to make ideal contacts. The ideal contact to a crystal is one which satisfies the following properties:

a. No resistance on the flow of the current is induced.

b. It does not react chemically with the semiconducting material.

c. It should not be affected by variation of illumination, temperature, electrical field or any other ambient conditions, and it should be perfectly ohmic in nature.
III RESISTIVITY MEASUREMENT

The measurement of resistivity were performed with separate current and voltage probes in order to eliminate contributions due to the contact resistances. The most appropriate method for measurements on plane parallel crystals of arbitrary shape is that described by L. J. Vander Pauw. For the evaluation of the resistivity of such flat samples, contacts are taken in an arbitrary way along the periphery of the sample (Fig. 1) and two resistance measurements are then carried out. When a current $I_1$ is passed through the contacts A and B, a voltage $V_1$ appears across the contacts C and D. The ratio $V_1/I_1$ is represented by a resistance $R_1$. In an analogous way the resistance $R_2$ is determined by passing a current $I_2$ through the electrodes B and C while the voltage $V_2$ is measured across A and D. The specific resistivity $\rho$ can then be evaluated by using the relation

$$\rho = \frac{\pi d}{2 \ln 2} \frac{R_1 + R_2}{f(R_1/R_2)}$$

where $d$ is the thickness of the sample. The function $(R_1/R_2)$ is presented in graphical form as shown in Fig. 2. According to the theory, the following conditions
have to be fulfilled for the applicability of this method.

(a) The contact must be at the circumference of the sample.
(b) The contacts must be sufficiently small compared to sample dimension.
(c) Sample must be homogeneous in thickness.
(d) There must be no isolated holes in the samples.

Experimental set up

Electrical connections for resistivity measurements were made by four copper wires at periphery of thin crystals and attached to the crystal surface by means of conducting silver paste. A ceramic switch, which enables rapid changing from one current voltage combination to other was used. The circuit diagram for resistivity measurement is shown in fig. 3. The important features of the measurements are as follows.

(a) Independent measurement of V and I.
(b) The use of voltmeters with a high input impedance.
(c) The use of low capacity leads from sample to ammeter and voltmeter.
IV HALL MEASUREMENTS

Hall mobility was determined by measuring the change of the resistance $R_{BD,AC}$ when a magnetic field was applied perpendicular to the basal plane of the sample. Hall mobility $\mu_H$ is given by the relation

$$\mu_H = \frac{d}{B} \left( \frac{\Delta R_{BD,AC}}{I} \right)$$

where $B$ is the applied magnetic field, $\Delta R_{BD,AC}$ is the change of the resistance and $R_{BD,AC}$ due to the magnetic field.

Experimental set up

The specimen having an arbitrary shape was placed on the specimen holder. The electrical contacts were made in the manner described for resistivity measurements. The specimen was then placed in a magnetic field in such a way that its surface was perpendicular to the direction of magnetic field. A current was passed through the specimen with the help of batteries. The applied magnetic field was in the range of 3 to 5 K gauss.
V FOUR PROBE METHOD

Many conventional methods for measuring resistivity are unsatisfactory for semiconductors because metal semiconductor contacts are usually rectifying in nature. Also there is generally minority carrier injection by one of the current carrying contacts. An excess concentration of minority carriers affects the potential of other contacts and thereby modulates the resistance of the material.

The method described here overcomes the difficulties mentioned above and also offers several other advantages. It permits measurements of resistivity in sample having a wide variety of shapes, including the resistivity of small volumes within layer pieces of semiconductor.

The basic model for all these measurements is indicated in fig. 4. Four probes are placed on a flat surface of the material resistance of which is to be measured. Current is passed through the two outer electrodes, and the floating potential is measured across the inner pair. If the flat surface on which the probes rest is adequately large and the crystal is big the
semiconductor may be considered to be a semi-infinite volume.

Experimental set up

Four Probe Resistivity Set up comprises of following equipment:

1. Cryostat LN-DP
2. Sample changer SMC-4
3. Constant current source CCS-10
4. Heater Power Source CCH-1000
5. Resistance Indicator PTR-200

The experimental set up for low temperature resistivity measurement is shown in fig. 5.

The cryostat LN-DP is designed specially for the experiments in temperature range 77 K to 300 K. This consists of a sample chamber and a sample holder. The system is portable and very easy to use. It is designed to fit directly into any of the standards LN$_2$ storage containers. The system is supplied with a standard 1/2" valve for evacuating and a 1/4" valve for introducing the exchange gas, monitoring vacuum etc.
The sample holder consists of a gold plated copper assembly, mounted with a standard platinum thermometer (Pt-100), and a heater which can be used for temperature control. Electrical leads for thermometer and the heater are brought at the top of the cryostat at a D type 9 pin connector. The samples can be mounted on the rectangular projection.

The constant current source CCS-10 (developed by simple solutions) is ideal for four probe resistivity measurements where a stable but variable constant current is the basic requirement.

The constant current source CCH-1000 (developed by simple solution) has been specially designed for use as a heater supply for a 30-40 ohm heater. The CCH-1000 is capable of supplying a maximum of 25 watts of power to the heater, which is adequate for cryogenic purposes.

VI RESULTS AND DISCUSSION

As described earlier (Chapter 2.3) single crystals of tungsten sulphoselenide (WSSe) have been grown in the present work by direct vapour transport
(DVT) and by chemical vapour transport (CVT) using iodine as the transporting agent. Usually there are large discrepancies in the electrical properties of crystals grown by CVT and DVT methods. Two important factors which may cause these discrepancies are:

(i) the inclusions of halogen impurity during the growth of the crystal, and
(ii) Slight departures from stoichiometry.

The Hall effect measurements on crystals grown by the two different techniques are reported in table 1. The Hall coefficient 'R_H' and carrier concentration 'n' have been calculated, assuming the single carrier conduction model and using the relation

$$\mu_H = \frac{R_H}{\rho} \quad \text{and} \quad n = -\frac{1}{e} R_H$$

where e is the electronic charge.

It is interesting to note that Hall coefficient has a positive value for the crystals grown by DVT and a negative value for the crystals grown by CVT. This clearly shows that the former crystals are p-type and the later are n-type.
WSSe grown by DVT is a low resistivity material exhibiting a resistivity $\rho = 0.91 \ \Omega \cdot \text{cm}$ at 25°C while for crystals grown by CVT the resistivity increases to $1.68 \times 10^2 \ \Omega \cdot \text{cm}$.

In order to account for this large variation in the room temperature resistivity of these crystals a stoichiometric analysis of the grown crystals was carried out using the EDAX facilities of the electron microscope EM 400. Table 3 (chapter 2.3) shows the analysis thus made. It is seen that crystals grown by CVT are stoichiometrically more perfect as compared to those grown by DVT. EDAX analysis of CVT grown crystals did not show any evidence of iodine. In fact iodine could also not be detected in the chemical analysis of our crystals.

It is therefore a fact that the difference in the room temperature resistivities is due to the departure of the samples from the stoichiometry. EDAX analysis clearly supports this conjecture.

Further differences between the electrical properties of crystals grown by CVT and DVT are shown by the temperature dependence of resistivity. Resistivity at each temperature was measured using four probe method.
The resistivity of the sample was calculated with the help of the formula,

\[ \rho = \rho_0 / G \]

where \( \rho_0 = V/I \times 2\pi S \)

'S' is the distance between any two consecutive probes.

Typical plots of \( \log \rho \) vs \( 1/T \) are shown in fig. 6. It is seen that both the type of crystals show the classical semiconductive behaviour i.e. the resistivity decreases with increasing temperature. However, the graph for CVT crystals shows only a slight deviation from the ideally linear case of a classical semiconductor while that for DVT crystals shows a marked deviation from linearity which can be attributed to donor states arising from the non-stoichiometry.

The activation energies obtained from the linear parts of plots of \( \log \rho \) vs \( 1/T \) are found to be 0.033 eV for DVT crystals and 0.043 for CVT crystals. Evans et al. [7] obtained widely differing values for low temperature activation energies of conduction in crystals of MoTe\(_2\) grown with bromine as transporting agent as
contrasted with the consistent values obtained for MoS\textsubscript{2}, MoSe\textsubscript{2} and WSe\textsubscript{2} grown by a DVT technique. This difference in activation energies was attributed to the incorporation of bromine in MoTe\textsubscript{2} crystals.

In the present case there is no wide variation in the activation energies since iodine does not get incorporated to an extent it will effect the electrical properties. Whatever difference in activation energies appear may be attributed to the non-stoichiometry of the samples.

VII CONCLUSIONS

Single crystals of tungsten sulphaselenide were grown by direct vapour transport as well as chemical vapour transport method with iodine as the transporting agent. Crystals grown by direct vapour transport were found to be low resistive and p-type semiconducting in nature where as those obtained by chemical vapour transport with iodine as the transporting agent were of high resistive and n-type. Crystals obtained from the chemical vapour transport were found to be more stoichiometric than those obtained from the direct vapour
transport and hence causing the observed differences in the electrical characteristics.
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   Wear, 10, 421.


5. Lieth, R. M. A. and Terhell, J. C. J. M.

6. Vashi, M. N. 1985

7. El-Mahalawy, S. H. and Evans, B. L. 1977
Data obtained for WSSe crystals grown by different technique

<table>
<thead>
<tr>
<th>Method of growth</th>
<th>Resistivity ($\rho$) (ohm cm)</th>
<th>Hall mobility ($\mu_H$) (cm$^2$ V$^{-1}$ sec$^{-1}$)</th>
<th>Hall coefficient ($R_H$) (cm$^3$ cb$^{-1}$)</th>
<th>Carrier concentration ($n$) (cm$^3$)</th>
<th>Activation energy (eV)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct vapour transport</td>
<td>0.9138</td>
<td>172.35</td>
<td>157.5</td>
<td>$3.96 \times 10^{16}$</td>
<td>0.033</td>
<td>p</td>
</tr>
<tr>
<td>Chemical vapour transport</td>
<td>168.136</td>
<td>74.34</td>
<td>-12500</td>
<td>$5 \times 10^{14}$</td>
<td>0.043</td>
<td>n</td>
</tr>
</tbody>
</table>
CAPTIONS TO THE FIGURES

Fig. 1 A sample of arbitrary shape with four small contacts at arbitrary places of the circumference to measure the specific resistivity and Hall effect.

Fig. 2 The function 'f' used for determining the specific resistivity of the sample, plotted as function of $R_1/R_2$.

Fig. 3 Schematic circuit diagram for measurements of resistivity
S - specimen
P - battery
V - V.T.V.M.
SW - Switch

Fig. 4 Model for the four probe resistivity measurements.

Fig. 5 Experimental set up for low temperature resistivity measurements.

Fig. 6 Variation of resistivity with reciprocal temperature for WSSe single crystal.
Fig. 6