CHAPTER 2

GROWTH OF TRANSITION METAL DISELENIDE (NbSe$_2$, MoSe$_2$, TaSe$_2$ and WSe$_2$) SINGLE CRYSTALS
2.1 INTRODUCTION

The transition metal dichalcogenide (TMDC) assume layered structure. Among the layered compounds, TMDCs have been recognized as an ideal model compounds for the studies involving surfaces, photoreactions, adsorption phenomena, catalysis, scanning tunneling microscopy, spectroscopy and epitaxial growth of thin films.

The extremely anisotropic character of the layer compounds built in at the atomic level dominates all the properties of such materials, both mechanical and electrical. It opens up new opportunities for the application of layered materials. The potential of this class of materials has not been fully explored yet but appears to be limited mainly by the availability of suitable materials. Attempts have been made to produce good quality crystals and thin films of the layered semiconductors for different uses.

In the present work author has concentrated his efforts on the growth of MSe₂ (M = Nb, Mo, Ta and W) single crystals of group V and VI for purpose of comparison and contrast.

2.2 DIFFERENT METHODS FOR CRYSTAL GROWTH

Different methods for crystal growth are:

1. Vapour Growth : Growth from vapor phase
2. Solution Growth : Growth from an aqueous solution
3. Melt Growth : Growth from a supercritical or fluid phase
4. Solid Growth : Growth from one or more solid phases

These techniques are adequately described in various textbooks and reviews (Buckley, 1951; Lawson et al., 1958,1963; White, 1970; Laudise, 1970; Henisch, 1970; Mullin, 1972; Honig, 1981). Figure 2.1 shows these main categories with their subfamilies.
Figure 2.1 The different crystal growth techniques.
Single crystals of MSe$_2$ (M = Nb, Mo, Ta and W) are not available in nature, so they have to be synthesized in the laboratory. These compounds having layered structure are insoluble in water and decompose before their melting point is reached. They are sublime at a higher temperature; hence, the growth of single crystals of such compounds from the melt and aqueous solution is not possible. The vapour transport method offers the advantage of growth at lower temperature below their melting point and found to be most suitable. Hence, vapour transport method is used for the growth of MSe$_2$ (M = Nb, Mo, Ta and W) single crystals.

The preparation of single crystals from the vapor phase has been described (Wildervanck, 1970; Schafer et al., 1973; Nitsche, 1967). A method of direct vapor transport without using halogen has been devised (Al-Hilli et al., 1972). Thick, 2H-NbSe$_2$ crystals with mosaic structures ≤0.2° have been grown by breaking with tradition and using small diameter ampoules for iodine vapour transport (IVT) (Oglesby et al., 1994). Large single crystals of NbSe$_2$-2H were grown at 1060 K using iodine vapour transport method (Ayache et al. 1992).

2.2.1 Growth from vapour transport methods

Vapour growth method is mostly preferred for the growth of layered single crystals as well as for the fabrication of thin layers of metals, insulators and semiconductor type materials. It is convenient for large scale operations i.e. from the coating of turbine blades to grow epitaxial layers of semiconductor materials. An excellent review of various methods for the growth of layered compounds has been given (Leith, 1977). The materials aspect of layered semiconductors in which information is available about the growth of layered materials has been discussed (Aruchamy et al., 1992). The present investigation is also a step forward in the field of material science. The present investigations aims to describe attempts made to grow single crystals of MSe$_2$ (M = Nb, Mo, Ta and W) using the vapour transport method.
Vapour transport methods are generally preferred due to their relative simplicity and wide applicability.

Vapour transport methods is classified into two classes:
1. Chemical Vapour Transport (CVT) method and
2. Sublimation or Direct Vapor Transport (DVT) method

2.2.1.1 Chemical vapour transport (CVT) method

Several compounds which are not accessible by usual crystal growing methods such as modified Czochralski or Bridgmann - Stockbarger techniques can be prepared by this method. It is particularly suited for high melting compounds or for those which decompose without melting. Application of this technique stems on the growth of metal single crystals in halogen atmosphere. It was also used for the growth of layered compounds (Nitsche et al., 1961). Also, ternary compounds containing phosphorus such as NiPS₃, FePS₃, FePSe₃ (Aruchamy et al., 1988, 1989), MnPSe₃, CdPSe₃ (Husser, 1985), Ga₂/₃PS₃, Al₂/₃PS₃ (Klingen et al., 1973) and PdPS, PdPSe (Marzik et al., 1982; Folmer et al., 1987) have been prepared by CVT technique.

CVT technique mainly relies 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 compound. Transportation occurs between two zones having different temperatures. Usually the starting reaction occurs at a higher temperature and is reversed at the low temperature to deposit molecules of the compound at the most favourable crystalline sites. Initially random deposition occurs until seed crystals are formed. Thereafter growth preferentially occurs on these seeds and large single crystals are formed. The transportation of the reaction products in the vapour phase can be obtained by a continuous gas flow from external
supplies or by its recirculation within a closed tubular ampoule. The process is depicted in Figure 2.2.

\[ \text{Equation} \]

**Figure 2.2** Illustration of the cyclic process of chemical vapour transport in a closed system

In principle, the resultant is, one can transport unlimited amount of starting material with a small amount of transporting agent. The rate of transport of the compound in \( \text{gm/cc} \) is given as (Nitsche et al., 1961),

\[ M = L \text{ dp} (T', T'', dG, C_d) \]  

(2.1)
where $T'$ and $T''$ are the temperature at hot end and cold end respectively which should be within the stability range of the required crystal type. $T'$ and $T''$ depend strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature.

$(T' - T'')$ is the temperature difference is altered to control $dp$, and so to vary the vapor transport rate. However, this cannot be increased indefinitely without causing polycrystallization (Wiedemeier, et. al., 1969) as explained below:

Molecules condensing on to a flat surface from the vapor loose potential energy, i.e. they acquire binding energy, $E'$. However, their thermal energy gives them a probability, $p'$ of evaporation as

$$p' \alpha \exp(Ev/kT) \quad (2.2)$$

dp is the difference between partial pressures of the reaction product at temperature $T'$ and $T''$.

$C_t$ is concentration of the transporting agent. A value of 5 mg/cc for $C_t$ has been found to be a good starting point for experiment (Nitsche, 1961).

$L$ is conductance of the system, which is a function of the ampoule geometry and the physical processes involved in the vapour transport, and 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.

dG is the change in Gibb's free energy in the reaction. It has been found that optimum transport occurs when the reaction is not far from equilibrium, i.e. $dp$ is maximum for values of $dG$ not far from zero (Schafer, 1964). For chalcogenides, the halogens are most

commonly used as transporting agents, since their dG values are quite low.

There are three possible mechanisms:

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

(2) As the pressure or the diameter is increased, convection current set up by the thermal gradient rapidly becomes more important.

(3) In the initial reaction equation,

\[
\text{compound} + \text{transporting agent} = \text{reaction product.}
\]

There are usually equal numbers of molecules in the vapour phase on each side. If this is not so, there will be a pressure gradient along the ampoule and a laminar flow of the reaction product will take place.

The rate of condensation, \(n\) (mole/sec/cm\(^2\)) is controlled by the partial pressure of the vapour \(P\) (atm) and average molecular velocity \(V\) (cm/sec).

\[
n = L_0 PV
\]

where \(L_0\) is the Loschmidt's constant = \(2.687 \times 10^{19}\) mole/cm\(^3\)atm

There will be a pressure, \(P'\), where the rate of condensation and evaporation are equal. In reality, when a molecule condenses on 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 kink or step on the crystal surface, the probability of evaporation drops. Equilibrium in such cases, will occur at pressure, \(P''\).

If the partial pressure has a value between \(P'\) and \(P''\), molecules will only condense on the site of greater binding energy, \(E''\). Under this condition, 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 a seed crystal.

Since the net number of molecules condensing is limited by the number of growth sites, the rate of transport must not be too high. Otherwise, the partial pressure of the reaction product will exceed $P'$ and polycrystallisation will occur.

Finally, Nitsche, 1961 arrived at the following rules for the successful growth of crystals by vapour transport technique:

1. The rate of transport must not exceed the rate of growth of 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 large 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 can be formed more easily in large diameter tubes, where transporters convection determines the rate of transport and
6. The temperature difference between the reaction and the growth chamber can be made smaller when wider tubes are used, since the gas flow is the rate determining parameter.

In the present investigation author has made a complete use of this technique to grow single crystals of $\text{MSe}_2$ ($\text{M} = \text{Nb}, \text{Mo}, \text{Ta}$ and $\text{W}$).
2.2.1.2 Direct vapour transport (DVT) method

The CVT method is very useful for the growth of large size layered single crystals. Although the crystal size can be grown large, the grown crystals are usually incorporated with an active impurity in the form of a small amount of the transporting agent during the growth process. This affects the thermal and electrical properties of the grown crystals at a considerable extent. In some cases, for example ZrSe$_2$ grown using I$_2$, the transport agent remains strongly adsorbed on the surface or incorporated between the layers and becomes difficult to remove it completely (Al Hilli et al., 1972).

The direct vapour transport or sublimation method (without transporting agent) were used in order to avoid the contamination due to transport agent (Al Hilli et al., 1972; Leith, 1977; Aruchamy et al., 1992; Agarwal et al., 1994,1998; Nitsche et al., 1960,1961,1968; Mercier, 1982). Their work shows that it is possible to grow fairly large crystals of TMDCs and their solid solutions.

2.3 EXPERIMENTAL SET UP

2.3.1 Dual zone horizontal furnace

The furnace is the most important part of present research work to grow the crystals of TMDCs. Two-zone furnace provides an appropriate temperature gradient over the entire ampoule. Normally the temperatures employed are fairly high. The temperature gradient within the furnace is required over a length of about 25 cm. Stability of the temperature plays an important role, therefore, for this purpose electronic temperature controllers were used.

The furnace was constructed in our University Science and Instrumentation Center (USIC) by using a special sillimanite threaded tube (grade KR 80 GA HG) closed at one end, 50 cm in length, 7 cm outer diameter, 5.6 cm inner diameter with threaded pitch of 3 mm.
Super Kanthal A1 wire of 17 SWG was wound directly on the furnace tube into two different zones or regions. The tube was enclosed in the hot face insulating brick slabs constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and the entire assembly was supported in a steel framework. This arrangement is shown in Figure 2.3. The power supplied to the furnace windings was regulated by the control circuit shown in Figure 2.4. The two regions of windings were provided with independent power supplies and temperature controllers. Transformers with 70, 80 and 100V taps with 20A current capacity in secondary windings were used to supply sufficient power in order to achieve the required higher temperature.

![Dual Zone Horizontal Furnace with Axially Loaded Ampoule](image)

**Figure 2.3** The dual zone horizontal furnace with axially loaded ampoule.
Figure 2.4 Control circuit for regulating the power

Microprocessor based temperature programmers purchased from M/s. Indotherm Instruments Pvt. Ltd., Mumbai, were used to control the temperatures in the two zones of the furnace. The fluctuations in the local electrical supply was controlled by AC voltage stabilizer with 180-260 V input and 230 ± 1% output volts of capacity 3 kVA. The output of stabilizer was fed to the primary windings of the transformer, which heated the furnace windings and helped to maintain the stability of growth conditions. With the help of temperature programmers, a required temperature gradient could be established across the length of the working tube in the required temperature range. Cr–Al thermocouples were used and temperature programmes were calibrated using thermocouples. It was found that the thermocouples were stable over the prolonged use in the furnace, and they were supported within the furnace tube itself showing the temperature of furnace tube.
2.3.2 Ampoule

High quality fused quartz tubes of various diameters, having a melting point of about 1500 °C were used for growth of crystals. Tubes having internal diameter 22 mm, outer diameter 25 mm and length 250 mm were found to be more suitable. One end of the ampoule was sealed and the other end was drawn into a neck and joined to another 8 mm inner and 10 mm outer diameter glass tube to connect it to the vacuum system for evacuation after introducing the source materials. Such a quartz tube and an ampoule generally used for the crystal growth are shown in Figure 2.5.

![Figure 2.5 A quartz tube and an ampoule used for crystal growth.](image)

2.3.3 Cleaning of Ampoule

Cleaning of ampoule is an important step in the crystal growth process. The ampoule was first washed with boiled water along with a suitable detergent, after that it was washed with a hot mixture of concentrated HNO₃ and HF (49%) taken in equal proportion. Then the washing was followed by double distilled water. Again it was washed with a mixture of concentrated HNO₃ and H₂SO₄ taken in equal volume. Ampoule was then filled with 20 ml HF and heated at 70 °C temperature for about half an hour in order to make the inner surface...
of ampoule slightly rough which is useful for the better growth of crystals. Finally washing was done by double distilled water for 8 to 10 times. Then the clean ampoule was transferred into the oven kept at 100 °C temperature and left overnight to make it moisture free.

### 2.3.4 Sealing of Ampoule

For the crystal growth of transition metal diselenide, the required materials in the elemental form were taken in a stoichiometric proportion using the “AFCOSET” electronic weighing machine and filled up in a transparent ampoule duly cleaned and dried by the process explained above. A total amount of constituent materials used was 10 gm in each experiment. The ampoule containing the source material was then connected to a vacuum system. In this process, proper precaution was taken for slow vacuum, so that materials from the ampoule could not enter into the vacuum system and the proportion of the constituent elements remains constant. The ampoule was sealed at a pressure of about $10^{-5}$ torr. The sealed ampoule was shaken thoroughly for proper mixing of the constituent materials. The sealed ampoule is as shown in Figure 2.6.

![Figure 2.6](image_url)

**Figure 2.6** The sealed ampoule - contains the constituent elements for the crystal growth of appropriate compound
2.4 GROWTH OF MSe₂ (M = Nb, Mo, Ta and W) SINGLE CRYSTALS

2.4.1 Charge preparation

In the present work author has prepared the charge of the compounds of MSe₂ (M = Nb, Mo, Ta and W (transition metal)). The Materials used for preparing the charge of single crystals of NbSe₂, TaSe₂, MoSe₂ and WSe₂ are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Purity (%)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium (Nb)</td>
<td>99.95</td>
<td>Aldrich Chem. Co., USA</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>99.99</td>
<td>Koch-Light Lab. Ltd., England</td>
</tr>
<tr>
<td>Tantalum (Ta)</td>
<td>99.90</td>
<td>Johnson Matthey P/C</td>
</tr>
<tr>
<td>Tungsten (W)</td>
<td>99.99</td>
<td>Aldrich Chem. Co., USA</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>99.99</td>
<td>Chiti Chem Corp., Vadodara</td>
</tr>
<tr>
<td>Iodine (I₂)</td>
<td>99.50</td>
<td>Chiti Chem Corp., Vadodara</td>
</tr>
</tbody>
</table>

In the sealed ampoule, the constituent element in the powder form was then distributed uniformly all over the length and kept in the horizontal furnace co-axially in the centre. The temperature was slowly increased at a rate of 50 °C/hr. The temperature and the period for which the ampoule was kept in the furnace depended upon the material, which was being grown. The slow heating was necessary to avoid any possibility of explosion due to the strong exothermic reaction between the elements. Comparatively larger size of the ampoule and the uniform distribution of the powder minimize the temperature rise to prevent any explosion. In the present case, the required temperature was 700°C. The ampoule was kept at this constant temperature for 3 days. After this period, the furnace was slowly cooled down to room temperature at the same rate 50 °C/hr.
and then switched off. As a result fine free flowing; shiny homogenous polycrystalline material was obtained for each compound.

2.4.2 Crystal Growth

The charge prepared in the above manner was well mixed by vigorous shaking of the ampoule. For actual growth process, the material was transferred into another thoroughly cleaned quartz ampoule. Iodine of the quantity 5 mg/cc of the ampoule volume was sealed in the thin glass capillaries were placed in a quartz ampoule as a transporting agent. This ampoule with charge of material and capillaries filled with iodine was evacuated at $10^{-5}$ torr pressure and then sealed. The ampoule was then inserted into a two-zone horizontal temperature gradient furnace. The front zone (reaction zone) of the furnace was maintained at 1123 K while the back zone (growth zone) was kept at 1023 K for the growth of NbSe$_2$ single crystals. The growth of single crystals of any compound depends upon different parameters such as length of the ampoule, purity of the source materials used, quality of the quartz tube, proper vacuum, amount and type of transporting agent, temperature distribution of the furnace, appropriate proportion of constituent element, time duration for crystal growth, availability of the continuous power i.e. electricity, the rate of increase and decrease of temperature etc. The growth parameters for MSe$_2$ ($M = Nb, Ta, Mo$ and $W$) single crystals are shown in Table 2.2. In all the cases iodine was used as a transporting agent. The temperature profile along the length of the furnace is shown in Figure 2.7. The temperature was increased at the rate of 20 °C/hr, till it attained the required temperature in both zones. For the growth of NbSe$_2$, the ampoule was left in the furnace for 7 days after that the temperature was decreased at the rate of 20 °C/hr till the room temperature. After this furnace was switched off and the ampoule was carefully taken out from the furnace. The ampoule was finally broken and resulting crystals were collected. The photographs of the
‘as grown’ crystals of NbSe$_2$, TaSe$_2$, MoSe$_2$ and WSe$_2$ are shown in Figure 2.8.

**Table 2.2** Growth parameters of MSe$_2$ (M = Nb, Mo, Ta and W) single crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temperature distribution</th>
<th>Growth Period (hr)</th>
<th>Dimension (mm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reaction Zone (K)</td>
<td>Growth Zone (K)</td>
<td></td>
</tr>
<tr>
<td>NbSe$_2$</td>
<td>1173</td>
<td>1123</td>
<td>192</td>
</tr>
<tr>
<td>TaSe$_2$</td>
<td>1148</td>
<td>1098</td>
<td>240</td>
</tr>
<tr>
<td>MoSe$_2$</td>
<td>1123</td>
<td>1073</td>
<td>168</td>
</tr>
<tr>
<td>WSe$_2$</td>
<td>1098</td>
<td>1048</td>
<td>168</td>
</tr>
</tbody>
</table>
Figure 2.7 The temperature profile used for the growth of MSe₂ (M = Nb, Ta, Mo and W) single crystals.
2.4 CONCLUSION

1. It is possible to grow large size single crystals of NbSe₂, MoSe₂, TaSe₂ and WSe₂ by chemical vapour transport technique using iodine as a transporting agent.

2. Single crystals of NbSe₂, TaSe₂, MoSe₂ and WSe₂ were found to grow in form of thin platelets showing a mirror like metallic luster.

3. Growth conditions and growth mechanism for the growth of large size NbSe₂, TaSe₂, MoSe₂ and WSe₂ single crystals have been determined by trial and error method.
References

Ayache C., Currat R., Molinie P.
Physica B, **180 & 181** 333-335 (1992)

Al Hilli A. A., Evans B. L.
J. Cryst. Growth, **15** 93 (1972)

Aruchamy A., Berger H., Levy F.

Aruchamy A., Berger H., Levy F.

Aruchamy A., Agarwal M. K.

Buckley H. E.
“Crystal growth”, John Wiley and Sons, New York, (1951)

Folmer J. C. W., Turner J. A., Parkinson B. A.

Gilman J. J.

Henisch H. K.
Honig J. M., Rao C. N. R.

Huesser O. E., Kaenel H. von, Levy F.

Klingen W., Eulenberger G., Hahn H.
anorg. allg. Chem., 401 97 (1973)

Klingen W., Ott R., Hahn H.
anorg. allg. Chem., 396 271 (1973)

Laudise R. A.

Lawson W. D., Nielson S.

Lawson W. D., Nielson S., Gilman J. J.

Leith R. M. A.

Marzik J. V., Kershaw R., Dwight K., Wold A.
Mercier J.

Mullin J. W.

Mulllin J. W.

Nitsche R.

Nitsche R., Boelsterli H. V., Lichtensteiger M.

Nitsche R.

Oglesby C. S., Bucher E., Kloc C., Hohl H.
Journal of Crystal Growth, 137 (1-2) 289 (1994)

Schafer H.
Schafer H., Grofe T., Trenkel M.

White E. A. D.

Wiedemeier H., Segal A. G.

Wildervanck J. C.