

CHAPTER 2

GROWTH OF SINGLE CRYSTALS BY A VAPOUR PHASE METHOD

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2.1 Introduction

The growth of crystals depends on their various parameters like melting point, vapour pressure and solubility in water. Hence, in the light of these features only, different methods of crystal growth were considered which are :

- (i) growth from melt
- (ii) growth from vapour phase, and
- (iii) growth from aqueous solution

Now, so far as the growth of crystals of transition metal dichalcogenides group is concerned, the methods of growth from melt as well as from aqueous solution is highly impracticable, because these compounds are insoluble in water and they have high melting points and premature decompositions. Therefore the only alternative or possible method for their growth is from vapour phase. The method of growth from vapour phase can be divided into following two categories

- (i) Chemical vapour transport method
- (ii) Direct vapour transport method.

A description of both these processes has been given below.

2.2 Vapour Growth Techniques

2.2.1 Chemical vapour transport method

Now theoretical attempts of vapour transport of solids have been given by Lever /1,2/, Mandel /3,4/ and Arizumi and Nishinaga /5/. Kallides has shown that it is possible to grow crystals upto several cm³ in size by chemical transport under well controlled nucleation conditions at small supersaturation (Cd₃GeS₆) /6/ and iron oxide (ZnSe) /7/. The transport of solid matter through the various phases via gaseous intermediates, utilizing the temperature dependence of heterogeneous equilibria (chemical transport reactions), has gained considerable attention in recent years.

Originally used by van Arkel and De Boer /8/ for the preparation of high purity refractory metals (iodide metals), transport reactions have been studied systematically by Schaefer and coworkers /9/. It enabled investigators to grow single crystals of substances hitherto known as "difficult materials".

The chemical vapour transport technique /10-15/ relies on a chemical reaction between the compounds to be crystallized and transporting agent. The reaction

product is volatile and can be transported in the vapour phase at temperatures well below the melting point of the compound. Transport occurs between two zones of different temperatures. Usually the initial reaction occurs at the high temperature and is reversed at the low temperature to deposit molecules of the compounds at the most favourable crystalline sites. Initially, random deposition occurs until seed crystals are formed. Thereafter, growth should only occur on these seeds, and large single crystals should be formed.

The transport of the reaction product in the vapour phase can be achieved by a continuous gas flow from external supplies, or by its recirculation within a closed tubular ampoule.

The rate of transport of the compound in gms/sec. given by Mitsche et al /11/ is

$$m = L \cdot dp (T^1, T^2, dG, Ct) \quad (2.1)$$

where T^1, T^2 are the temperatures at the hot and cold ends respectively.

dp is the difference between the partial pressures of the reaction product at temperatures T^1

and T'' ,

dG is the Gibbs free energy change in the reaction,

C_t is the concentration of transporting agent,

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

These parameters of the transport equation (2.1) have the following significance.

2.1

It has been found by Schatzler /13/ that optimum transport occurs when the reaction is not far away from equilibrium, that is, d_p is maximum for values of dG not far away from zero. For chalcogenides the halogens are most commonly used as transporting agents, out of these, iodine gives the lowest dG value and is usually the best choice. However, for some compounds bromine gives better results /12/.

2.2

Nitsche /15/ found a value of 5 mg/cc for C_t to be a good starting point for experiment.

L

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

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 currents set up by the thermal gradient rapidly become more important.
3. In the initial reaction equation,

Compound + transporting agent = Reaction products.

There are usually 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.

L.I.R

dp depends strongly on the temperature gradient along the ampoule and to a lesser extent on

the absolute temperature /15/.

$T' - T''$ (the temperature difference) is altered to control dp , and so to vary the vapour transport rate. However, this can not 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.

$$p' \propto \exp (E'/RT)$$

The rate of condensation, n (molecules/sec/cm²) is controlled by the partial pressure of the vapour p (atmosphere), and the average molecular velocity, v (cm/sec)

$$n = L_0 p v$$

L_0 = Loschmidt's constant
= 2.687×10^{19} per (cm³ atm).

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 evaporating. 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 lower 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 any 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.

Finally, Hitashi et al. /11/ gave 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 larger in order to prevent intergrowth between adjacent

seeds. Sometime symmetric heating is 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 crystal gets formed 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.

2.2.2 Growth without using transport agent

Crystals grown by chemical vapour technique are sometimes several cm square in size, even though there is evidence that they suffer from the obvious disadvantage of contamination by the transporting agents.

The possibility of the entry of the transporting agent such as bromine or iodine to the crystal lattice can not be ignored. And as a consequence of this the electrical and chemical properties

of the crystal will be affected. Since the aim of growing the single crystals of WS_xSe_{2-x} was to obtain crystals which are as pure and defect free as possible, the method of growth without using any transporting agent was adopted. Al-Hilli and Evans /16/ used such a method for growing single crystals of certain transition metal dichalcogenides. This method of growth of crystals without a chemical transporting agent will be called as sublimation method or the direct vapour transport method.

2.3 Experimental Set Up of Direct Vapour Transport Method

2.3.1 Two zone horizontal furnace

The first and the foremost basic essential piece of the apparatus required for this technique is a furnace fulfilling the appropriate temperature gradient all over the ampoule. As compared to chemical vapour transport method, here in the sublimation technique, higher temperatures are required to raise the vapour pressure sufficiently large for obtaining, reasonable rate of growth. The furnace should, therefore be capable of reaching higher temperatures with required temperature gradients over a length of about 25 cms. To ensure temperature stability during growth, electronic temperature controllers were

used for the furnace.

Economically it was considered advisable to construct such experimental furnace locally in our University Service and Instrumentation Centre rather than purchasing one of similar specifications. In designing the furnace special sillimanite threaded tubes (Grade KR 80 GA(HG)) closed at one end and having 45 cms length, 70 mm outer diameter, 56 mm inner diameter and a thread pitch of 3.0 mm, (imported from Koppers Fabriken Feuerfester, Germany) were used. Super kenthal A-1 wire 17 SWG was wound directly to the furnace tube into different regions as shown in Fig. 2.1. The tube was enclosed in the hot face insulating brick slab constructed locally and the brick shell was fully enclosed in thick asbestos sheets, and the entire assembly was supported in steel frame work. This arrangement is shown in Fig. 2.2.

As sizeable crystals require longer time to grow, the temperature in the furnace must be accurately controlled. The power supplied to the furnace windings was regulated by the controlled circuit (Fig. 2.3). The two regions of windings were provided with independent power supplies and temperature controllers.

Transformers with 70, 80 and 100 V taps with 20 Amp 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 $\pm 1^{\circ}\text{C}$.

The fluctuations in the local electrical supply were controlled by using an A. C. voltage stabilizer with 180 to 260 V input and $230 \pm 1\%$ 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 sets 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 temperature.

2.3.2 Ampoule

High quality fused quartz tubes used in the growth experiments have a melting point of about 1500°C . Tubes of various diameters were used. Tubes with internal diameter of 25 mm and length 240 mm 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 and joined to a silicon tube of 10 mm inner diameter to connect it to the vacuum system for evacuation after introducing the source material.

2.4 Crystal Growth

2.4.1 Cleaning of the ampoule

First of all the ampoule was washed with boiled water and then with boiling concentrated HNO_3 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 H_2SO_4 and HNO_3 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.

2.4.2 Charge preparation

For the charge preparation the required materials (Table 2.1) 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 the source material is then connected to a vacuum system and precaution being taken that the vacuum be brought so slowly that none of the materials from the ampoule can enter the vacuum system. 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 of 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.

2.4.3 Growth procedure

Just as the specified conditions of temperature and reaction time was different for charge preparation, in the same way actual growth procedure varies from material to material. The methods of crystal preparation used by some of the workers /10-13, 17/ are found to yield crystals of very high crystallographic quality.

The growth procedure and conditions for the growth of WS_xSe_{2-x} single crystals are well described and discussed in the next chapter.

Table 2.1

Materials for which the crystals were grown with source of supply

Material	Purity (%)	Supplier
1. Tungsten (W)	99.999	Koch-light Laboratory Ltd., England
2. Sulphur (S)	99.9999	Koch-light Laboratory Ltd., England
3. Selenium (Se)	99.95	Nuclear Fuel Complex (NFC) Ltd., Hyderabad (India)

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Captions to the Figures

- Fig. 2.1** **Kanthal A-1 wire windings for
the two zone crystal growth
furnace.**
- Fig. 2.2** **Schematic representation of
the furnace.**
- Fig. 2.3** **Control circuits for regulating
the power.**

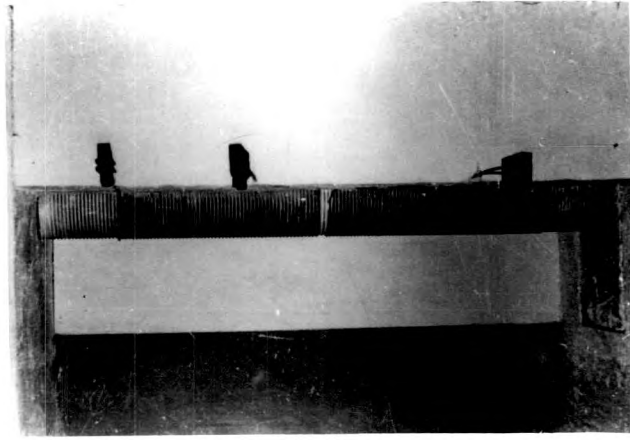


Fig. 2.1

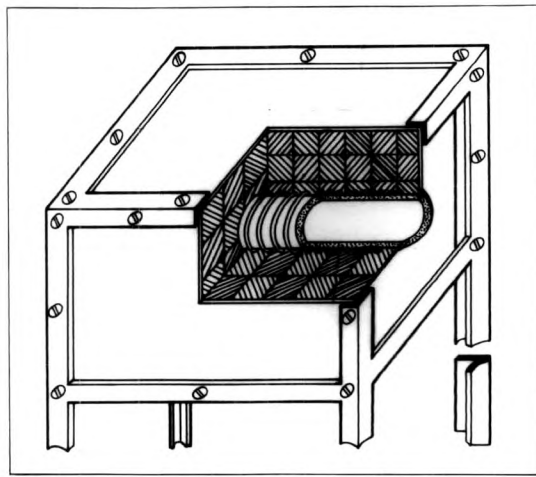


Fig. 2.2

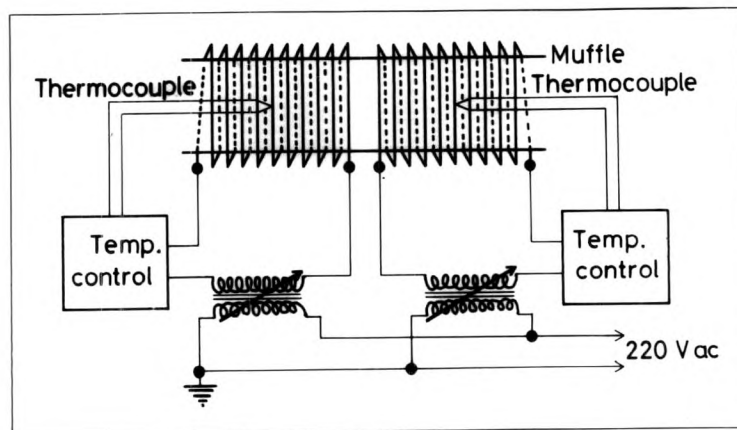


Fig. 2.3