

GROWTH OF SINGLE CRYSTALS BY A VAPOUR PHASE METHOD

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2.1 Introduction

The growth of crystals depends upon their melting point, vapour pressure and solubility in a medium. On this basis, there are several methods for growing single crystals. The techniques being fully described in the text books and reviews¹⁻¹¹). The majority compounds of transition metal dichalcogenides TC group are insoluble in water and they decompose before their melting points are reached. This naturally prevents their growth from aqueous solutions and from melt. Therefore attempts have been made to grow these crystals from vapour phase.

This method can be classified in the following two categories :

- (1) Chemical Vapour Transport Method
- (2) Direct Vapour Transport Method

2.2 Vapour Growth Technique

2.2.1 Chemical Vapour Transport Method

This method, for the preparation of

single crystals has been reported and found to be a reliable method for crystal growth of metal dichalcogenides¹²⁻¹⁷⁾. New theoretical attempts of vapour transport of solids are given by Lever^{18,19)}, Mandel^{20,21)} and Arizumi and Nishipanaga²²⁾. Kaldis and coworkers^{23,24)} have shown that it is possible to grow crystals upto several cm in size by chemical vapour transport method under well controlled nucleation conditions at smaller supersaturations. Transport reactions have been studied systematically by Schafer²⁵⁾ for the preparation of high purity refractory metals.

Chemical vapour transport technique mainly depends on a chemical reaction between the source material to be crystallised and a 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 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 products 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. 2.1. 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 al¹³⁾ as,

$$m = L \cdot dp(T', T'', dG, C_t) \quad (2.1)$$

where T', T'' are the temperatures at hot and cold ends respectively.

dp is difference between 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 conduction of the system, a function

of the ampoule geometry and the physical processes involved in the vapour transport.

The above parameters in the transport equation (2.1) 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.
- (C_t) Nitsche ¹⁶⁾ 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. Three different mechanisms are possible.

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- (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 pressure gradient along the ampoule and a laminar flow of the reaction product will take place.

(T', T'') dp depends strongly on the temperature gradient along the ampoule and to a lesser extent on the absolute temperature¹⁶⁾. Many compounds 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 a flat surface from the vapour loose potential energy, that is they acquire a binding energy, E' . However, their thermal energy gives them a probability P' of evaporation.

$$P' \propto \exp (E_v / kT)$$

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

where $n = L_0 PV$

$L_0 =$ Loschmidts constant

$= 2.687 \times 10^{19}$ per (cm^3 atm).

There will be 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 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 seed crystals.

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

Finally, Nitsche¹³⁾ gave the following rules for the successful growth 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 polycrystallisation.
3. The crystallisation chamber should be larger in order to prevent intergrowth between adjacent seeds. Asymmetric heating is sometimes useful.
4. The temperature distribution in the crystallisation chamber should be as uniform as possible to avoid 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 crystallisation chamber, since the gas flow here is the rate determining factor.

2.2.2 Growth without using a transporting agent

This method of crystal growth avoids the use of transporting agent, hence it is called direct vapour transport technique. This method has been used by Al-Hilli and Evan²⁶⁾ to grow single crystals of certain transition metal dichalcogenides.

2.3 Experimental Details

2.3.1 Dual Zone Horizontal Furnace

Furnace is the most essential and almost basic piece of apparatus needed for this technique. Therefore it was designed to be adopted to allow the necessary changes of temperature gradient with different growth conditions. As higher temperatures 900-1140°C are required to make the vapour pressure sufficiently large to obtain a reasonable growth, 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

of different magnitudes over a length of 25 cm. To obtain the temperature stability during growth, electronic temperature controllers were used in the furnace heating circuit.

Furnace was constructed locally in our University Science and Instrumentation Centre (U.S.I.C.) by using a special sillimanite threaded tube (grade KR 80 GA HG), closed at one end, 450 mm in length 70 mm outer diameter, 56 mm inner diameter with threaded pitch 3 mm, imported from Koppers Fabriken Feuerfester, Germany. Super kanthal A-1 wire 17 SWG was wound directly on to the furnace tube in two different regions as shown in Fig. 2.2. Then the tube was 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. 2.3).

As the growth of 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 control circuit shown in Fig. 2.4. The two regions of windings are provided with independent power supplies and

temperature controllers. Transformer with 70, 80 and 100 V taps with 20 A current capacity in secondary were used to supply sufficient power in order to reach the required high temperature. Controller used are "Eurotherm controllers" which are of "fast cycling" type switching the power and off regularly at every 10 cycles of main frequency. The on time is continuously variable, controlling the power fed to the elements. The units have "integral" and "derivative" controls to correct the changes 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 was controlled by AC voltage stabilizer with 180 to 260 V input and $230 \pm 1\%$ output volts, of capacity 3 KVA. The output of stabilizer was fed to the primary of the transformer which 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 working tube in the required temperature range. Thermocouples used were Pt (13 %)

Rh-Pt, and the Eurotherm temperature controllers were calibrated for the above 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.

2.3.2 Ampoule

The high quality fused quartz tubes of various diameter having a melting point of about 1500°C were used for growth experiments. Tubes having internal diameter 20 mm and length 210 mm were found more suitable for growth experiments. One end of the ampoule was sealed and other was drawn into the neck and joined to the other 10 mm inner diameter quartz tube to connect it to the vacuum system for evacuation after introducing the source material.

2.4 Crystal Growth

2.4.1 Cleaning of Ampoule

First the ampoule was washed with boiled water and detergent powder, after that it was washed with a hot mixture of concentrated HNO_3 and HF (49 %) taken in

equal proportions. Then the washing was followed by double distilled water. Again washed with a mixture of HNO_3 and H_2SO_4 taken in equal quantities. Final washing was done by double distilled water for not less than a dozen times. After which, the cleaned quartz ampoules were transferred into a SICO constant temperature furnace at 100°C and left overnight to make them moisture free.

2.4.2 Preparation of Charge

For the preparation of starting material, elemental powders were introduced into thoroughly cleaned quartz ampoule 25 mm inner diameter and 200 mm long, in stoichiometric proportions. The materials used and their sources of supply are listed in Table 2.1. A total charge of 9-12 gm was used in each experiment. The ampoule containing the source material was evacuated to a pressure of 10^{-5} Torr. Proper care was taken while evacuating so that the material from the ampoule did not enter into the vacuum system. The ampoule was sealed off at the constriction 3 mm in diameter. Then the charged ampoule was thoroughly shaken to ensure a proper mixing of the elemental powders, and the mixture was distributed along the length of the ampoule and was

Table 2.1

Materials from which crystals were grown, with their
sources of supply

Material	Purity %	Supplies
1. Tungsten (w)	99.95	Koch-Light Laboratories Ltd., England.
2. Molybdenum (Mo)	99.999	Koch-Light Laboratories Ltd., England
3. Selenium (Se)	99.999	Johnson Matthey Chemicals Ltd., England.
4. Tellurium (Te)	99.999	Koch-Light Laboratories Ltd., England

introduced into the furnace. The temperature of the furnace was increased in steps of 40°C per half an hour until the desired values were reached. This slow heating was necessary to avoid any possibility of explosion due to strong exothermic reaction between the elements. The temperature of the furnace was controlled to within $\pm 1^{\circ}\text{C}$ with the help of Eurotherm controllers. After 72 hours, the furnace was switched off and the ampoule was allowed to cool to room temperature. At this stage, the compound was in the form of a free flowing, shining, homogeneous polycrystalline material.

The growth procedure and conditions for the growth of single crystals utilized for the present work are well discussed in the subsequent chapters.

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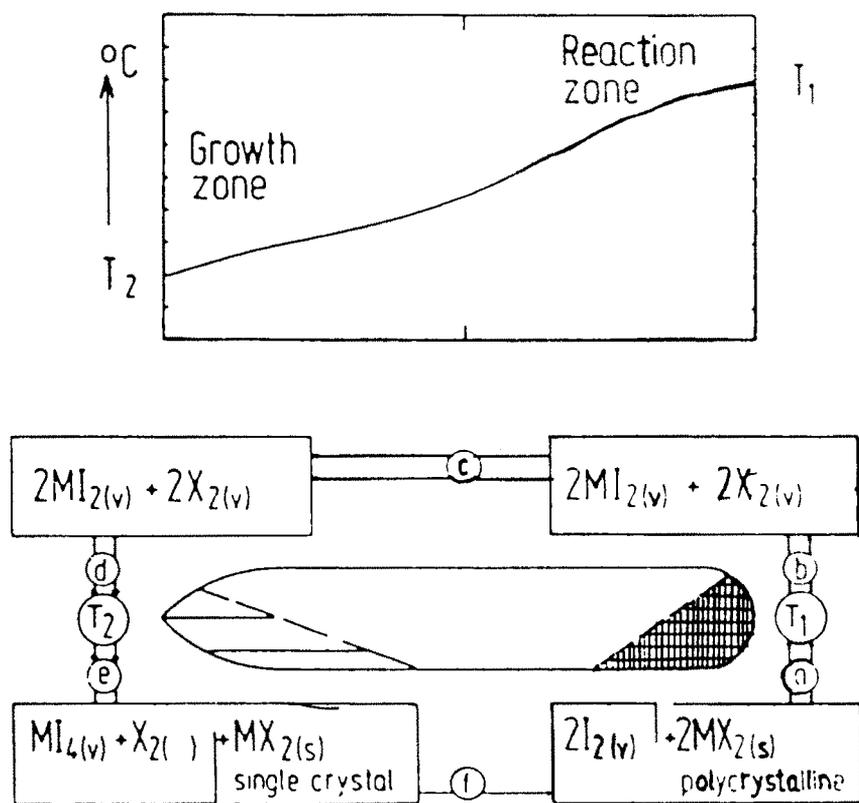


Fig. 2.1 Illustration of the cyclic process of chemical transport in a closed system.

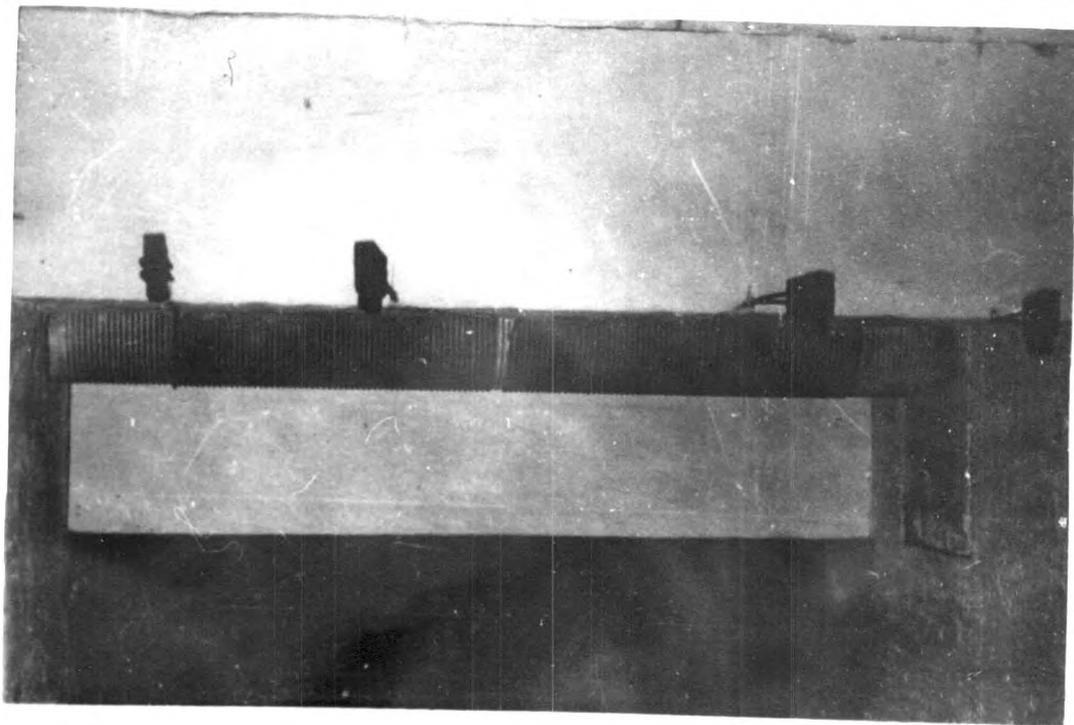


Fig. 2.2 Kanthal A-1 wire windings for the two zone crystal growth furnace.

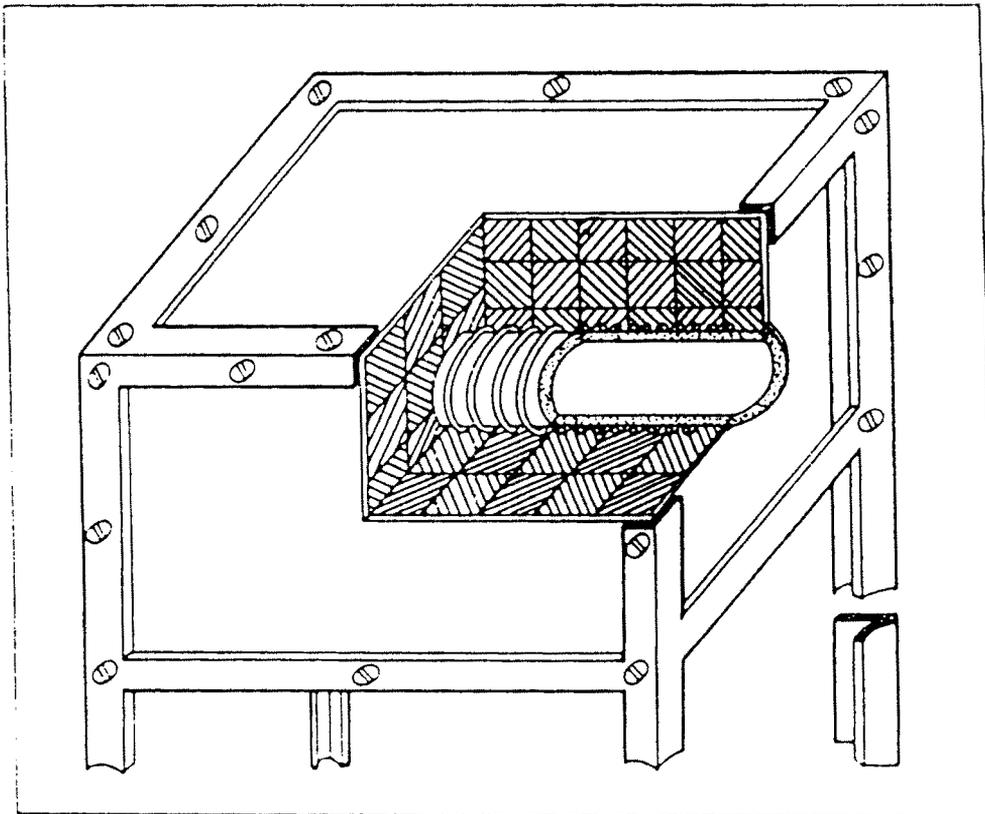


Fig. 2.3 Schematic representation of the furnace

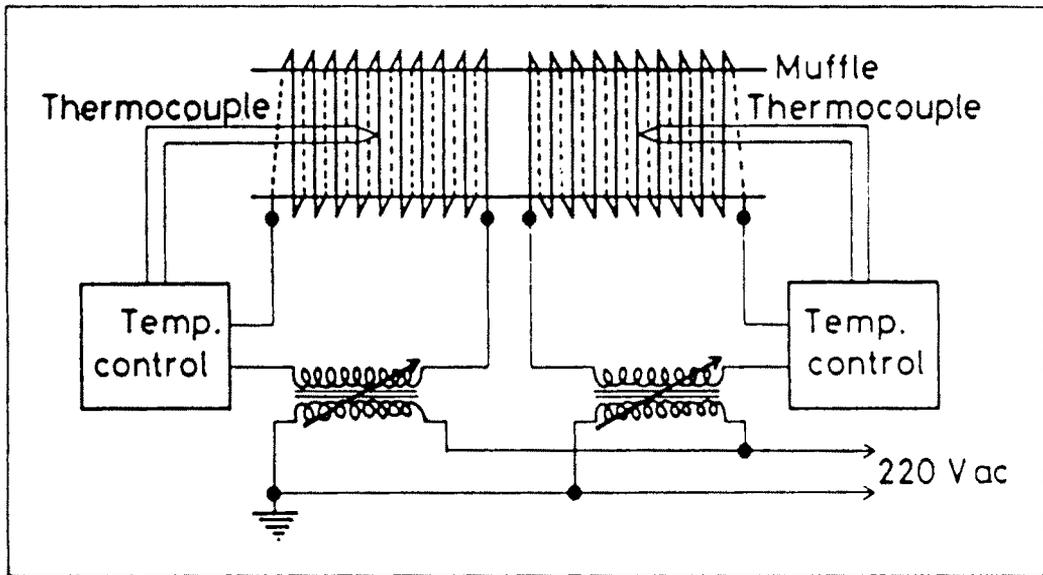


Fig. 2.4 Control circuit for regulating the power.