

**CHAPTER 2**  
**BRIEF SURVEY OF CRYSTAL GROWTH METHODS**

**2.1 INTRODUCTION**

At the present time crystals of more than two hundred materials are commercially available. A survey of the methods of growth suggests that almost 80% are grown from the melt compared with roughly 5% from the vapour, 5% from low temperature solution, 5% from high temperature solution, 3% from the solid and only 2% by hydrothermal methods. This chapter gives a brief introductory review of the methods by which crystals may be grown with emphasis on vapour growth.

**2.1.1 Crystal growth from the melt**

All the methods of crystal growth from a melt rely on cooling the liquid below its freezing point. If care is exercised, single crystal can be made to propagate which will otherwise end up with a polycrystalline mass.

In the Bridgman technique the melt is contained in a crucible and is progressively frozen from one end which can be achieved by

1. moving the crucible down the temperature gradient
2. moving the furnace over the crucible or

3. by keeping both the furnace and the crucible stationary and cooling the furnace so that the freezing isotherm moves steadily through the originally molten charge (figure 2.1). The latent heat of solidification, which is evolved as the crystal grows, is removed by conduction through the crystal and the crucible. In this method at least some part of the solid-liquid interface is in contact with the crucible. The advantageous aspect of this is that the shape of the crystal can be controlled by the crucible while the disadvantage lies in the fact that the crystal gets strained and the melt-crystal-crucible contact can result in the nucleation of new differently aligned crystals.

In the Czochralski method the melt is contained in a crucible but the crystal is grown at the free top surface of the melt so that there is no contact between the crystal and the crucible (figure 2.2). In this method, the crystal is slowly pulled upwards as it grows, so that solid-liquid interface is just above the level of the liquid surface. The melt temperature and pulling rate depend upon the rate at which the heat is removed and they can be changed independently. By the rotation of the crucible and the crystal, dissymmetries in the temperature gradient of the melt is reduced and a better mixing of melt is achieved.

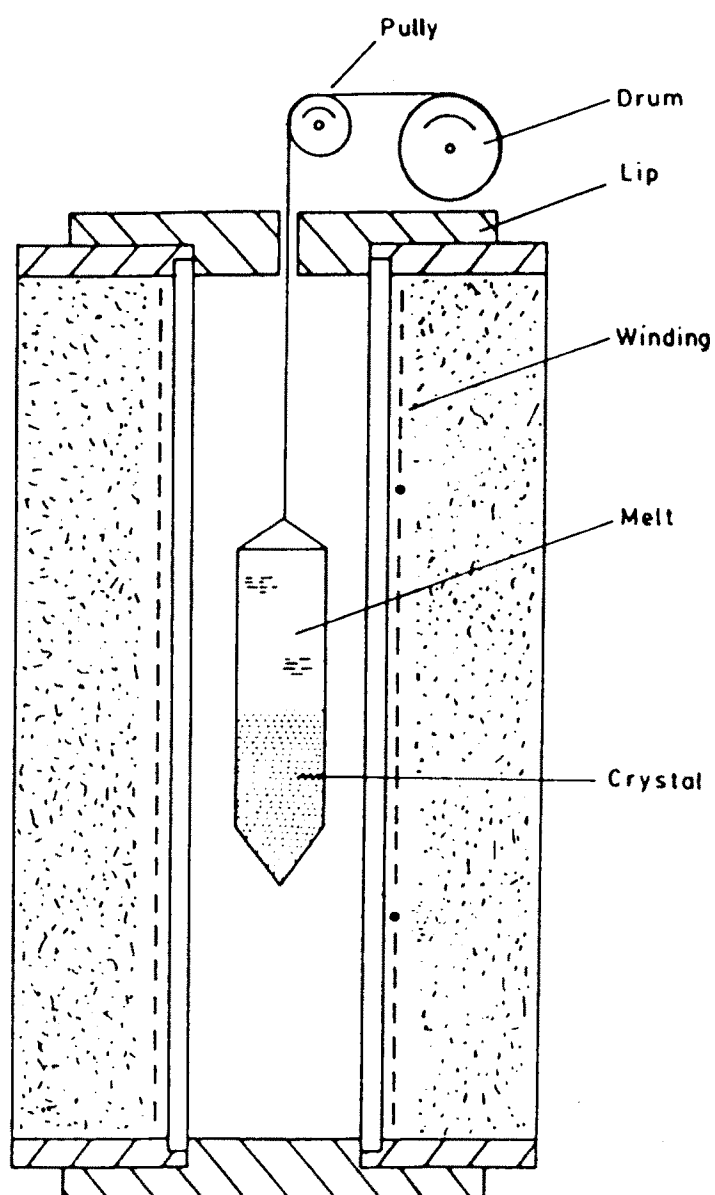


Figure 2.1 Bridgman apparatus

In the Kyropoulos version of the method, the melt temperature is lowered slowly causing the crystal to grow out from the seed into the melt. These methods have the advantage that there can be no strains due to crystal-crucible contact, but the melt is still contained within crucible and for very reactive materials it may be difficult to find a container which is not attacked by the melt.

In the Verneuil method, also called flame fusion method, a fine dry powder of the material (particle size 2-100  $\mu\text{m}$ ) to be grown is fed through the wire mesh. The powder melts while it falls through the oxygen-hydrogen flame (figure 2.3). A film of liquid is formed on top of seed crystal. This freezes progressively as the crystal is slowly lowered. To maintain symmetry the seed is rotated. The art of the method is to balance the rate of powder feed and the rate of lowering to maintain a constant growth rate and diameter. The method is used extensively for the production of ruby, sapphire, aluminium-magnesium spinel and rutile ( $\text{TiO}_2$ ) crystals.

Zone melting was originally developed for the removal of contaminants from a substance (Pfan, 1966). Floating zone technique is a modification of the zone melting method. In this method, a molten zone is maintained by the surface tension in the rod of solid and is moved slowly, usually upwards. Symmetry is maintained by rotation

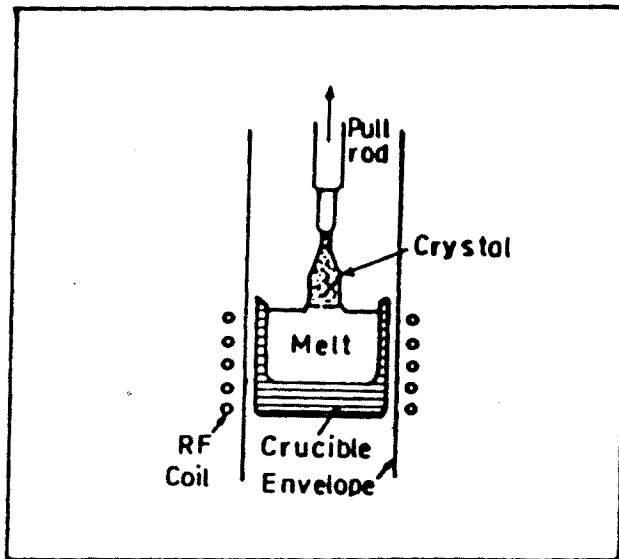


Figure 2.2 Czochralski apparatus

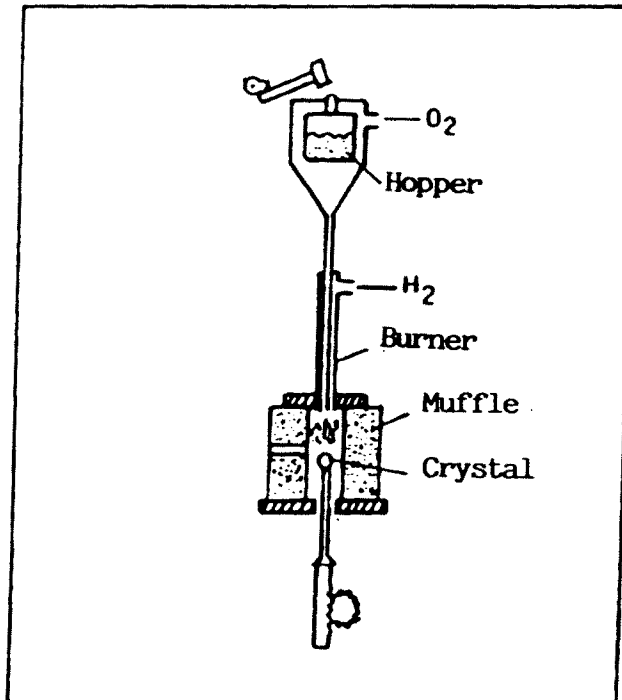


Figure 2.3 Verneuil apparatus

of either or both the solid parts of the rod. The method is most easily applied to materials with large surface tensions - silicon and variety of metals. In these methods, crucibles are completely eliminated and the melt is supported by its own solid.

### 2.1.2 Crystal growth from solution

Crystal growth from solutions is the most widespread technique of growing crystals. The commonly used solvents are water, aqueous and non-aqueous solutions and melts of some chemical compounds. Crystals will grow from solution if the solution is supersaturated, i.e it contains more of the solute than it can hold in equilibrium with the solid. Three principal methods are used to produce the required supersaturation.

1. the slow cooling of the solution.
2. the slow evaporation of the solvent,
3. the establishment of a temperature gradient between hot zone containing undissolved solid, and a cooler zone in which the crystal grows (figure 2.4).

It is worth noting that in both the evaporation and temperature gradient methods, the growing crystal is at a fixed temperature. Growth at a high temperature is often more stable than at a lower one and the habit of a crystal may be a function of the growth temperature so that the most useful habit can be obtained by a correct solution. The

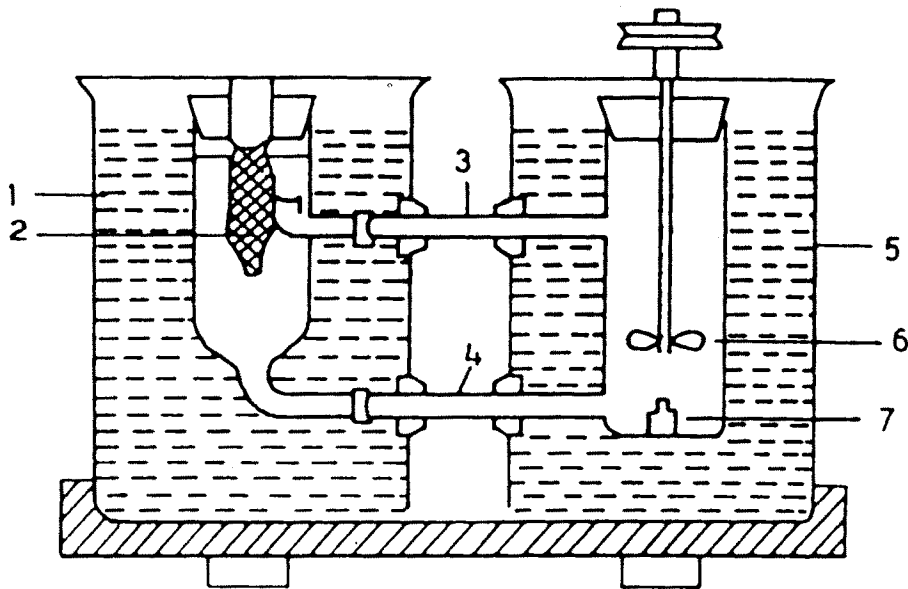


Figure 2.4 Solution Growth apparatus

1. Thermostat for dissolution at a temperature  $T_1$ ,
2. Nutrient,      3,4. Connecting tubes
5. Thermostat for growth at a temperature  $T_2$ ,  $T_2 < T_1$ ,
6. Vane type agitator      7. Growing crystal

choice of the solvent is probably the most critical step in low temperature solution growth.

Flux growth or the high temperature solution growth is frequently used in growing crystals as they permit the crystallisation of complex multicomponent systems by simple techniques taking into account the specifics of the phase diagrams of the system. In the high temperature solution growth (flux growth), the crucible with the charge is heated to a high temperature at which all the solid dissolves in the solvent. The necessary supersaturation can be obtained by reducing the temperature or evaporating the solvent. The flux method can be divided into two types: spontaneous crystallisation and crystallisation on a seed. The latter method has undergone considerable development to the extent of pulling crystal from solution called top seeded solution growth.

### **2.1.3 Crystal growth in the solid state**

There are several methods for the growth of crystals in solid state. In the strain-anneal technique (Aust 1968, 1972) useful for metals, a fine grained structure is produced by working and annealing at low temperatures. The sample is then deformed by a small but a critical amount and then annealed for a long time at high temperature. In materials with solid state transitions, the specimen is



annealed alternatively above and below the transition temperature. Another technique is the Pintsch method (Brice 1973) in which a hot zone is moved along a wire producing a thin single crystal. Travelling heater can also be used to produce thicker single crystals. It is also possible to use other annealing processes starting from sintered bodies. With all the solid state processes, effective growth rates are small and usually inversely proportional to the size of the growing grain, the outcome of the operation is uncertain and the crystals produced are inevitably strained and imperfect. However, growth in the solid has the considerable advantage that the equipment needed is simple (a furnace and temperature control) so that the method will continue to be used particularly for the small scale production of research specimens.

#### 2.1.4 Gel growth

Gel growth which can be regarded as an intermediate case between growth in the solid and in solution, relies on reaction and precipitation of species diffusing in gels (Dennis et al 1967, Henisch 1970). Typical gels are 10-20% gelatin, 1-5% agar-agar and water glass plus acid. Growth is usually limited by diffusion. The apparatus (figure 2.5) used by Henisch (1970) is very simple; the water glass of specific gravity (1.03-1.06 g/cm<sup>3</sup>) is mixed with acid solution and allowed to gel. The setting time of the gel is

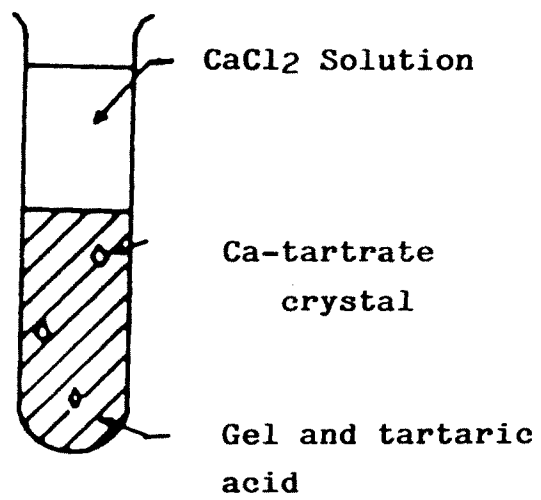


Figure 2.5 Gel growth apparatus

dependent on the acidity of the solution and silicate concentration. Once the gel is set, the outer reactant is poured on the top of the gel without damaging the gel surface. This solution supplies one of the components of reaction and also prevents the gel from drying out. The particular advantage of this method is that the growing crystal is held in the gel in a strain free condition.

#### 2.1.5 Crystal growth from vapour

Crystal Growth from the vapour phase has remained for a long time as under developed research area compared to crystal growth from the melt which has already reached a high degree of perfection. The main reason for this difference has been the much greater difficulty of controlling nucleation in the vapour-solid transformation than in the liquid-solid transformation. From the point of view of crystal growth this difference is very instructive. Unlike the case of nucleation from the vapour, which begins explosively at a certain critical supercooling, nucleation from the melt increases rather slowly with decreasing temperature, after reaching the critical supercooling, until it reaches a maximum. At still higher supercooling the nucleation rate decreases again and eventually reaches zero. The physical explanation is that both nucleation and growth from the melt are strongly influenced by diffusion which

takes place through a medium much more viscous than in the case of vapours.

#### 2.1.5.1 Control of nucleation

Ideal conditions for the growth of large single crystals are encountered if, as a result of nucleation control, only one nucleus of the solid can be formed in the system. Without competition of other nuclei this crystal would then grow to as large dimension as growth rate and size of the apparatus would allow. Such condition can be realised at a value of supercooling (supersaturation) low enough to allow nucleation to take place only on active site and high enough to allow an appreciable growth rate (Ganesha et al 1991).

Data concerning the critical supersaturation or supercooling in the case of crystallisation from the vapour phase are very few. Earlier results (Honigman 1958) showed very narrow metastable regions giving the impression that control of nucleation in vapour growth would be very difficult. Impetus for further investigations of vapour growth was generated by the successful growth of II-VI compounds in the early 60s (Gilman 1963), which for the first time showed that the great possibilities for single crystal growth are existing in vapour methods. On the other hand the pioneering work of Shaefer (1964), Nitsche (1977)

and others showed the great preparative possibilities inherent in chemical transport.

For the growth of large single crystal in evacuated and sealed silica ampoules from the vapour phase three rules have been formulated by Kaldis (1969).

1. Use of undercritical supercooling allows only selective nucleation on a small number of active sites on the walls; tapered ampoule tip is used to localise nucleation and promote the formation of one large single crystal at the tip of the ampoule.
2. Pulling rate matching the linear growth velocity of the growing crystal in the direction of the ampoule axis. This ensures that the front of the supercooling coincides with the crystallisation front so that nucleation takes place on the growing surface of the crystal and not on the silica walls.
3. Use of cylindrical-conical ampoule geometry with large tube diameters to stimulate 'Convective transport'.

Possible source of nucleation sites is the charge material itself. During the charging of the ampoule the walls often come in contact with the powder of the starting material. Particles attached on the walls then function during growth as nucleation sites. For this reason a reverse-transport period is introduced after sealing and before starting growth. Better results can be achieved by

using recrystallised starting material and filling via a tube on the side of ampoule, the material being introduced with a funnel.

The geometry of the ampoule employed for crystal growth is one of the governing factors. Tapered cylindrical ampoules have been proved to be able to fetch massive single crystals. The ampoules with this geometry were used for the first time by Pizzarello (1954) and later modified by Piper and Polich (1961) who used the tapered ampoule geometry (figure 2.6). The support rod not only acts as thermal conductor for removing the heat generated by the process of crystallisation but also allows the movement of the tube. As was shown later, this approach, however, does not offer any advantages in comparison with the simple vertical ampoule of Pizzarello. Although this fact is well accepted now, the name of Piper and Polich is still often mentioned in conjunction with Pizzarello's ampoule geometry.

An alternative method for localising nucleation is to use a colder spot on the side-wall of the crystal vessel. This method was first used by Honigmann (1958) to successfully grow large single crystals of hexamine ever grown from the vapour phase.

Although seeds have long been used to control nucleation from solutions and melts, they have until

recently been neglected for the control of nucleation from the vapour phase. The reason for this has been probably the difficulty of observing any metastable region in vapour growth experiments, since without an appreciable metastable region, growth limited to a seed is not possible.

A different approach to nucleation control and growth of one single crystal in a closed system has been made by Scholtz (1967). He used a periodically reversing supercooling in order to let only one nucleus grow at over critical supersaturation. The principle of the method is to allow nucleation to take place on a spot on the wall of the silica tube at a moderately over-critical supercooling. After a short period of time, many crystallites with varying dimensions nucleate. By applying a reverse supercooling for a short period most crystallites and nuclei reevaporate. Periodic repetition of this process leads to the intermittent growth of one single crystal. This is possible because (a) not all nuclei are formed simultaneously (the ones on the most active wall centres appearing first) and (b) the dissolution velocity of each individual nucleus depends on its size, the smaller having higher vapour pressure and therefore evaporating with higher velocity (Ganesha et al 1992). According to Scholtz (1967) the observed differences of growth and dissolution rates between perfect and imperfect crystallites are even more important.

Imperfect seeds disappear due to their higher dissolution velocity.

#### 2.1.5.2 Physical Vapour Transport (Sublimation)

The vapours obtained from a solid phase at an appropriate temperature is made to condense at a lower temperature. Thus the shift of equilibrium between the solid and its vapour is introduced by the difference between temperatures of the sublimation zone (source) and condensation zone (growth zone). Condensation can be done either in a closed tube system or in an open tube system. In a closed tube system shown in figure 2.7, the material to be transported is placed inside an ampoule and the tube is evacuated and sealed. The ampoule is then placed in a furnace having desired temperature gradient. After some period crystal grows in the cold zone. The open tube system (Shaefer 1964) is shown in figure 2.8. Here the reactant gases are passed through a reactor tube having predetermined temperature gradient. The crystal seed or substrate is placed in the cold zone where crystals grow (Mee 1969). In open tube method only a few percent of the starting material is deposited in useful form as a single crystal or monocrystalline layer. This system is a dynamic system so that impurities do not accumulate in the vapour.



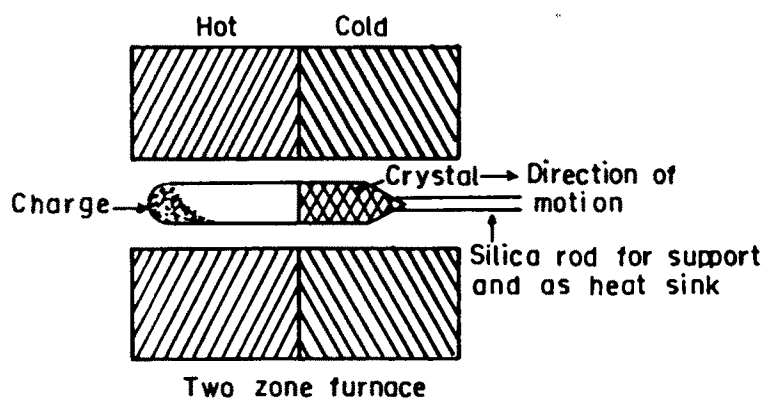


Figure 2.6 Piper and Polich apparatus

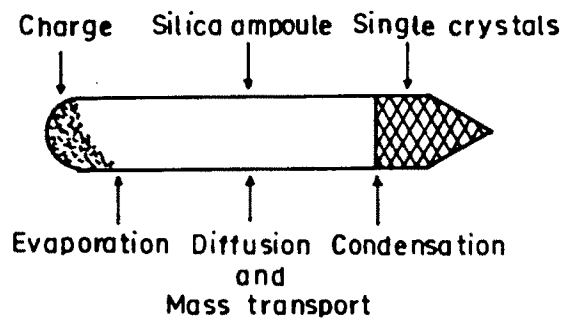


Figure 2.7 Closed tube system



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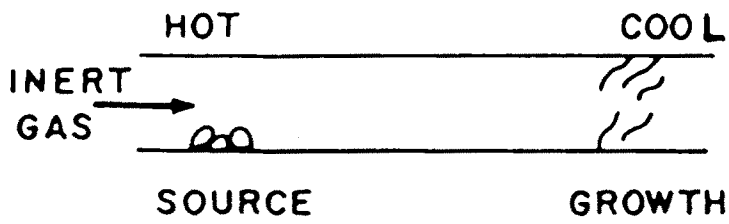
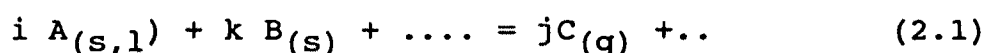


Figure 2.8 Open tube system

### 2.1.5.3 Chemical Vapour Transport

Chemical vapour transport reactions are those in which a solid or liquid substance A reacts with a gas to form exclusively vapour phase reaction products, which in turn, undergo the reverse reaction at a different place in the system, resulting in the reformation of A.



The process appears to be one of sublimation. Substance A, however, does not possess an appreciable vapour pressure at the applied temperatures. The substance is transported chemically. In addition to a reversible heterogeneous reaction, a concentration gradient must be established. The latter can be the result of temperature gradients, changes in the relative pressures or the differences in the free energy of formation of two substances. If the products are gaseous a cyclic process is possible in a closed system and thermodynamic cycle is also possible in an open system. The essential conditions to be satisfied for a successful transport are, (i) the desired phase in a chemical reaction should be the only stable solid product in the temperature range of interest at the partial pressures of gaseous species chosen. (ii) the free energy should be close to zero for reversibility of the reaction and to ensure that significant amount of reactants and products are present at equilibrium. The free energy of

formation should be non-zero, for the equilibrium to be shifted towards crystal formation in the growth zone and reverse in the volatilisation zone by means of temperature difference between zones (Jeffes 1968, Ballentyne et al 1970). If the transport reaction is endothermic the transport takes place from the hot zone to the cold zone, the transporting phase being unsaturated in the hot zone and supersaturated in the cold zone, with a supersaturated boundary lying in between. If the reaction is exothermic the transport is in the opposite direction.

According to Shaefer (1964) in the growth by a reversible reaction, the transport process can be divided into three separate steps : the heterogeneous reaction on the starting material, the transport of volatile species in the gas and the heterogeneous reverse reaction at the place where the crystals are formed. At pressures less than 0.001 atm. the mean free path of atoms in the gas phase is comparable with or greater than the dimensions of typical apparatus used and so atomic or molecular collisions are negligible. If one works at pressures between 0.001 and 3 atm, the gas motion is essentially determined by diffusion. At pressure greater than three atm, thermal convection will be of overriding importance in determining gas motion and the transition from diffusion to convection controlled transport is often determined by the geometry of the

apparatus. In most practical cases of vapour growth, the growth rate is diffusion limited (figure 2.7).

## 2.2. CONCLUSION

Although crystals can be grown in many ways, particular choice of the growth method is to be decided by the size of the crystal and material of the crystal to be grown. A brief survey of the various crystal growth methods with emphasis on the growth from vapour is presented.