

## 4.1 Czochralski technique

The material to be grown in to single crystal is melted in a suitable non-reacting container under a controlled atmosphere by induction or resistance heating. The temperature of melt is set slightly above the melting point and the seed crystal (single crystal of same material) is lowered close to the melt surface with continuous rotation. After thermodynamical equilibrium, the seed is contacted with melt and the melt temperature raised to establish the desired growth interface configuration. The pulling mechanism started to withdraw seed from melt at slow rate. During this process the crystal diameter is gradually increased to the desired value. Growth at constant diameter is achieved by maintaining the solidification isotherm in a vertical position intersecting the meniscus at the point where the isotherm becomes perpendicular to the melt surface. This condition is maintained by the adjustment of following parameters: rate of pulling, rate of liquid level drop, heat fluxes into and out of the system, and to a lesser extent by seed/crucible rotation.

## 4.2 Crystal pulling, Controlling parameters

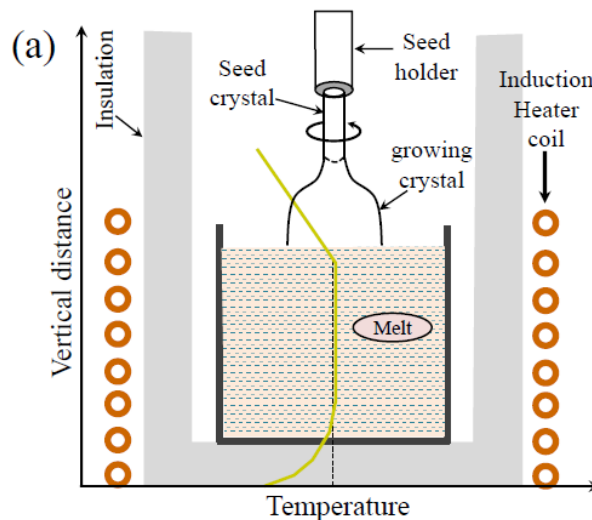


Figure 4.1: The relation between liquid solid interface shape and heat flow across interface. a. convex, b. flat and c. concave

A schematic of crystal pulling from melt is shown in figure 4.1. The seed crystal is clamped to a holder which is attached to the pull rod. It provides rotation and facility to lift and lower the crystal. The crystal dips into melt which is held in a crucible and is then heated by resistive furnace or induction heater. Good thermal

conditions are crucial in the growth of good quality crystal. The control of gaseous and liquid convection is very important in achieving good crystal growth. The rate of pulling is another important factor. If the rate of shaft withdrawal is  $f_p$  and the crystal of radius 'r' is growing from a crucible of radius  $r_c$ , then since the material is conserved, the average growth rate  $f$  can be obtained by equating the mass of solid that has formed and effective decrease in mass of liquid. If  $d_s$  and  $d_l$  are the densities of solid and liquid, respectively, then,

$$\pi r^2 d_s f = \pi r_c^2 d_l f - \pi r_c^2 d_l f_p \quad (4.1)$$

$$f(r_c^2 d_l - r^2 d_s) = r_c^2 f_p d_l \quad (4.2)$$

$$f = \frac{r_c^2 f_p d_l}{r_c^2 d_l - r^2 d_s} \quad (4.3)$$

If the densities of the liquid and solid are same then the average growth rate is given by,

$$f = \frac{r_c^2 f_p}{r_c^2 - r^2} \quad (4.4)$$

Thus the average growth rate of crystal is determined by the pulling rate and the radii of the crucible and the crystal. The radius of the crystal is however controlled by the melt temperature and the temperature gradient at the growing interface.

### 4.3 Convection in melts

When a melt is heated from below the buoyancy forces generated cause the hotter (less dense liquid) to rise and the cooler liquid (denser) to fall generating convective flow. The convective flow may also result from gradient of surface tension forces or gradient in solute or alloy concentration. The important parameters governing the onset and nature of convection patterns in melts are thermal characteristics of the material, aspect ratio of container and the imposed temperature gradients. The Prandtl number  $N_{Pr}$  is an important factor governing fluid flow patterns and is defined as the ratio  $\nu/K$ , where  $\nu$  is the kinematic viscosity of the liquid and  $K$  is the thermal diffusivity. It depends on the thermal characteristics of the liquid and is independent of container geometry or applied temperature gradient. In high Prandtl number systems ( $N_{Pr} \gg 1$ ) such as oxides, strong fluid flow is largely confined to boundary layer regions whereas in low high Prandtl number materials such as metals and semiconductors the streamlines are more generally distributed throughout the bulk but the stream velocities are much higher under high temperature gradients. As the Rayleigh number increases with increase in  $\Delta T$ , the fluid flow begins to move by convective flow and further increases lead to progressive breakdown into smaller convection cells as shown in figure. Further increase in Rayleigh and Prandtl numbers leads to development of instability in the flow patterns usually in form of oscillatory motion of convection cells within the melt.

### 4.4 Liquid solid interface shape

The shape of the crystal is controlled by angle of contact of meniscus with the crystal (cylinder) as shown in the inset of Fig. 4.2. When  $\theta < 0$  diameter will decrease, at  $\theta = 0$  diameter will remain constant and when  $\theta > 0$  the diameter will increase and this can be controlled by controlling the power to melt. The contact angle decreases with increase in the power to melt and vice versa. The three different possible interface shapes are illustrated in the figure 4.2, which in turn depends on the magnitude and sign of  $d$  (depth of centre of interface with respect to edge).

The shape of growth surface is dependent upon its crystallographic orientation and the local temperature gradient. The possible shapes of the liquid-solid interfaces are given in Fig. 4.2. For good quality, growth

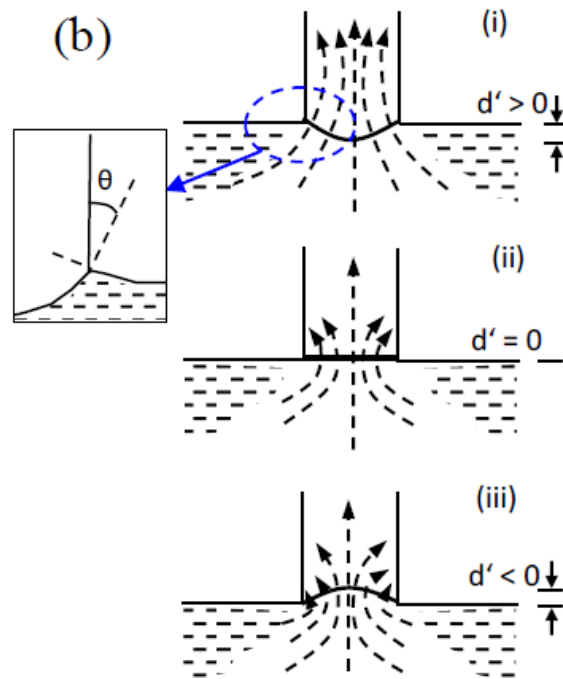


Figure 4.2: The relation between liquid solid interface shape and heat flow across interface. a. convex, b. flat and c. concave

interface must be with  $d = 0$ , however it is difficult to maintain this condition. The slight thermal fluctuations generate concave interface with  $d < 0$ , due to excess input power to melt. In oxide materials due to high surface tension, the excess input power raises liquid-solid interface by several millimeters above the plane of melt surface. Under such conditions the radial heat loss at the periphery of crystal become important and may lead to the formation of spines and ring facets, due to rapid solidification. This condition may also lead to the entrapment of air bubbles and propagation of elongated voids in grown crystals. The optimum interface shape for CZ growth is slightly convex. In Bridgman growth, the concave interface result in poor crystallinity since it promotes edge grain nucleation at the wall of growth ampoule where as slightly convex interface tends to conclude such growth. Hence Czochralski growth is more favourable situation.

## 4.5 Zone melting

Zone melting, any of a group of techniques used to purify an element or a compound or control its composition by melting a short region (i.e., zone) and causing this liquid zone to travel slowly through a relatively long ingot, or charge, of the solid. As the zone travels, it redistributes impurities along the charge. The final distribution of the impurity depends on its distribution in the starting charge of material; its distribution between the liquid and solid phase of the material (called its distribution coefficient,  $k$ , which is a characteristic of the particular impurity); and on the size, number, and travel direction of the zones.

Zone melting is a means of using the freezing process to manipulate impurities. It combines the fact that a freezing crystal differs in composition from the liquid from which it crystallizes with the idea of passing a short liquid zone along a lengthy solid.

**Zone refining** is the most important of the zone-melting techniques. In zone refining, a solid is refined by passing a number of molten zones through it in one direction. Each zone carries a fraction of the impurities to the end of the solid charge, thereby purifying the remainder. Zone refining was first described by the U.S. scientist W.G. Pfann and was first used in the early 1950s to purify germanium for transistors. The purity achieved was hitherto unheard of less than one part of detectable impurity in 10,000,000,000 parts of germanium. The method was adopted in transistor manufacture around the world.

The principles of zone refining are quite general, and so the method has been applied to many substances. More than one-third of the elements and hundreds of inorganic and organic compounds have been raised to their highest purity by zone refining. Many of these were, for the first time, made pure enough for their intrinsic properties to be determined.

### 4.5.1 PRINCIPLES OF ZONE REFINING

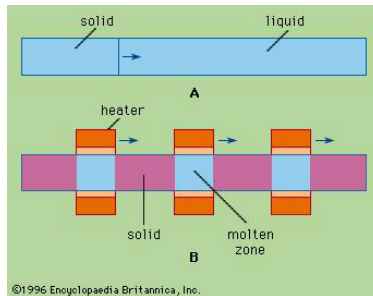


Figure 4.3: Schematic representation of (A) normal freezing, (B) zone refining

When a cylinder of a substance A containing an impurity B is melted and then slowly frozen from one end to the other, as in Figure 4.3A, the impurity is usually concentrated in the last-to-freeze region of the cylinder. This procedure is normal freezing. Component B is redistributed in this example because the atoms (or molecules) of B at the liquid-solid interface prefer the liquid phase to the solid phase. A measure of this preference is the distribution coefficient,  $k$ , defined as the ratio of the concentration of B in the just-forming solid A to that in liquid A. At very slow freezing rates an equilibrium exists; the distribution coefficient under these equilibrium conditions is termed  $k_0$ . At moderate freezing rates, about 1 to 30 centimetres per hour (0.4 to 12 inches per hour), the effective distribution coefficient,  $k$ , will lie somewhere between  $k_0$  and unity. This is because, for  $k$  less than unity, the rejected impurity B accumulates in the liquid just ahead of the advancing solid, so that the just-forming solid sees a liquid more impure than the bulk liquid. If freezing is rapid enough,  $k_0$  may approach unity; that is, the impurity concentration would be the same in the liquid

and solid phases. Under these conditions, there would be no zone refining, and the interface probably would become dendritic or branching in shape.

The normal freezing operation is the basis of the long-known technique of repeated fractional crystallizations. Although this technique was employed by the Curies to isolate radium it never became widely used because it entailed a lengthy and troublesome sequence of operations: partial freezing, separation of the crystals from the unfrozen liquid, remelting, and recombining with other fractions.

Zone refining achieves the same result very simply. A series of molten zones traverse the ingot in the same direction, usually through a series of heaters, as suggested in Figure 4.3B. Each zone takes in impurity at its melting interface and freezes out solid purer than the liquid at its freezing interface. There is no need to separate and recombine fractions, or even to touch or move the charge at all.

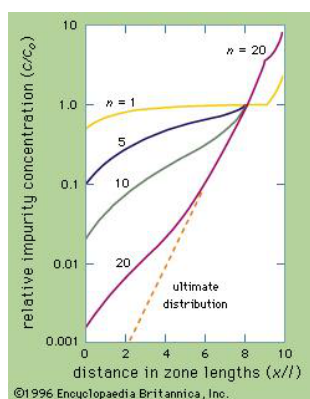


Figure 4.4: Semilogarithmic plots of relative impurity content along ingot for various numbers ( $n$ ) of zone passes for a distribution coefficient of 0.5 in an ingot 10 zone lengths long

The distribution of impurity B after successive zone passes for an ingot 10 zones long and for a distribution coefficient  $k$  equal to 0.5 (a value neither especially favourable nor especially unfavourable) is shown in Figure 4.4.

As more zone passes are made the impurity concentration at the beginning of the ingot drops lower and lower until it eventually reaches a limit called the ultimate distribution. The lowest concentration of impurity B is extremely small, less than 0.0001.

## 4.5.2 Techniques of zone refining

The liquid zones are formed by heating (and by cooling the adjacent solids). Many practical heating methods have been used: electrical resistance coils, induction heating, electric arc, and electron beam, radiant energy, plasmas (ionized gases), solar heating, lasers, and Peltier heating and cooling (produced by an electric current flowing across the junction between two different materials). For organic compounds resistance-heated coils of wire are most common, although radiant heating has been used. If a compound or element is liquid at room temperature, the operation is conventionally done in a refrigerator.

The usual container is one that will not contaminate the material. Glass, Vycor (heat- and chemical-resistant glass), fused silica, molybdenum, tantalum, and graphite have all been used. If zone refining is done vertically, a transparent container is helpful, but good work has been done using opaque containers such as stainless steel. If the container is a horizontal, semicircular cross-section boat, it can be opaque, because the liquid zone is readily distinguished from the solid. If a filled container, horizontal or vertical,

is used, care must be taken to prevent cracking either by change in volume during freezing (or melting) or by differential thermal contraction (if the charge sticks to the containing wall). Various solutions have been found for these problems.

## 4.6 Verneuil's technique

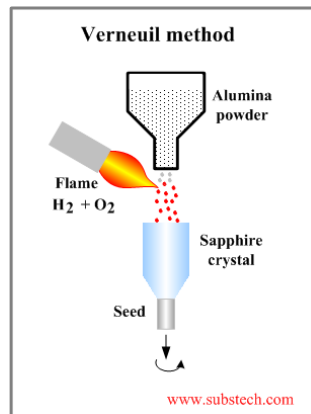


Figure 4.5: Schematic of Verneuil's method

The schematic of the scheme is shown in figure 4.5. This starting material is finely powdered, and placed in a container within a Verneuil furnace, with an opening at the bottom through which the powder can escape when the container is vibrated. While the powder is being released, oxygen is supplied into the furnace, and travels with the powder down a narrow tube. This tube is located within a larger tube, into which hydrogen is supplied. At the point where the narrow tube opens into the larger one, combustion occurs, with a flame of at least  $2000^{\circ}\text{C}$  at its core. As the powder passes through the flame, it melts into small droplets, which fall onto an earthen support rod placed below. The droplets gradually form a sinter cone on the rod, the tip of which is close enough to the core to remain liquid. It is at that tip that the seed crystal eventually forms. As more droplets fall onto the tip, a single crystal, called a boule, starts to form, and the support is slowly moved downward, allowing the base of the boule to crystallise, while its cap always remains liquid. The boule is formed in the shape of a tapered cylinder, with a diameter broadening away from the base and eventually remaining more or less constant. With a constant supply of powder and withdrawal of the support, very long cylindrical boules can be obtained. Once removed from the furnace and allowed to cool, the boule is split along its vertical axis to relieve internal pressure, otherwise the crystal will be prone to fracture when the stalk is broken due to a vertical parting plane.

When initially outlining the process, Verneuil specified a number of conditions crucial for good results. These include: a flame temperature that is not higher than necessary for fusion; always keeping the melted product in the same part of the oxyhydrogen flame; and reducing the point of contact between the melted product and support to as small an area as possible. The average commercially produced boule using the process is 13 mm (0.5 in) in diameter and 25 to 50 mm (1 to 2 in) long, weighing about 125 carats (25 g). The process can also be performed with a custom-oriented seed crystal to achieve a specific desired crystallographic orientation.

Crystals produced by the Verneuil process are chemically and physically equivalent to their naturally occurring counterparts, and strong magnification is usually required to distinguish between the two. One of the telltale characteristics of a Verneuil crystal is curved growth lines formed as the cylindrical boule grows upwards in an environment with a high thermal gradient; the equivalent lines in natural crystals are parallel.

Another distinguishing feature is the common presence of microscopic gas bubbles formed due to an excess of oxygen in the furnace; imperfections in natural crystals are usually solid impurities.

## 4.7 High temperature solution growth

Crystal growth from high temperature solutions or molten salt solutions or fluxed melts called “Flux Growth” technique is perhaps the most generally applicable crystal growth method for the growth of crystals if the starting materials (a) have different melting, (b) undergo a phase transition which results in severe strain, (c) have very high vapour pressure and (d) have a very volatile constituent. This method is used mostly for the growth of crystals for the scientific investigations but at the same time, it is independent method of growing thin films and bulk crystals for technological applications. Since the method does not require knowledge of the melting behaviour of the desired materials it is particularly appropriate for the growth of single crystals of new materials.

### 4.7.1 Practical aspects of flux growth

The general procedure for growth of crystals from high temperature solution consists of mixing the starting materials, compacting them into suitable crucibles, heating to maximum temperature for several hours and then cooling at a suitable rate depending upon the growth method. The size, habit, etc., of the crystals, grown by flux method, are noticeably influenced by the growth conditions such as the chemical composition of the solute and flux, the soaking temperature and time, the kind of dopant, cooling rate of growth solution and the size and type of the crucible. The success of crystal growth depends on the proper choice of these parameters.

### 4.7.2 Principle of growth

There exist three modes of producing supersaturation and hence the crystal growths, which are solvent evaporation, slow cooling and transport technique.

#### 4.7.2.1 Solvent evaporation

In this technique, the temperature of the solution during growth is maintained constant. It results in homogeneous concentration of dopants or impurities, homogenous density of equilibrium defects, no variation of the composition in the case of solid solutions and possibility to grow materials with a specified valence state. Evaporation rate can be controlled by the temperature, gas flow, removing the solvent vapours, free surface area of the melt, etc. The main disadvantage arises from the solvent vapours being very corrosive and attacking the insulation ceramic materials as well as heating elements.

#### 4.7.2.2 Slow cooling

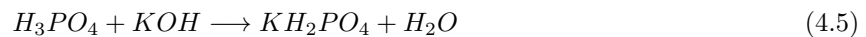
In this technique the nucleation and crystal growth process are induced by reducing the solubility of the solute with decreasing temperature. The different versions of slow-cooling technique are spontaneous uncontrolled nucleation, temperature oscillation technique, localized cooling, stirring by Accelerated Crucible Rotation and Top Seeded Solution Growth.

### 4.7.2.3 Transport technique

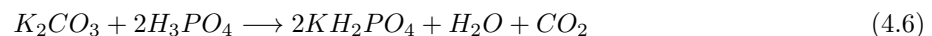
Transport technique is used for cases where supersaturation is achieved only by transport of solute or solute constituents which were initially not dissolved in the solution. The transport technique includes transport in a temperature gradient, travelling solvent zone technique, electrolytic growth in high temperature solution, etc. The advantage of these techniques is isothermal growth. In the case of transport in a temperature gradient, a nutrient is held at higher temperature near the bottom of the crucible and the seed below the liquid level at the lower temperature. Mass transport from the dissolved nutrient to the seed is assured either by the natural convection and diffusion through boundary layer or by stirring. A real application meets difficulties because of the necessity to dissolve the nutrient crystals just before the growing process starts.

## 4.8 Growth of KDP and ADP

Potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) found fairly wide practical applications and are used as piezoelectric transducers in microphones. They are widely used in nonlinear optical devices and electro-optic materials. Growth of ADP type crystals from solution is very much influenced by the growth parameters like supersaturation, temperature, pH, impurity and hydrodynamics of the solution. In the present investigation, ADP and KDP crystals are grown from aqueous solution under static and dynamic conditions by non-steady state and steady state processes; the non-steady state process includes the slow cooling and slow evaporation methods and the isothermal growth under supersaturation is the steady state process. It is necessary to change the pH of the mother liquor to adjust the growth rates of ADP and KDP crystals along the three directions. The pH adjustments have been carried out with KOH and NH<sub>4</sub>OH for KDP and ADP crystals respectively, along with concentrated phosphoric acid. The mother liquor has been kept in a sealed container at constant temperature. Due to a concentration gradient set in the solution with a higher concentration at the bottom, spontaneous nucleation occurs, resulting in the formation of small crystals of a few millimeter dimensions. These potassium salts were prepared from phosphoric acid and potassium hydroxide or potassium carbonate, respectively. The preparation of KDP ( $KH_2PO_4$ ) was initially performed by a neutralization reaction using stoichiometric quantities of  $H_3PO_4$  and KOH in aqueous solution. The reaction is:



As an alternative, an aqueous solution of  $K_2CO_3$  is reacted with  $H_3PO_4$  in the correct stoichiometry according to this equation,



The synthesis of ADP ( $NH_4H_2PO_4$ ) can be accomplished by the direct reaction of alkali carbonate [ $(NH_4)_2CO_3$ ] with the respective deuterated acids. The preferred synthesis method is described by the following reactions:

