Chapter 1

Introduction

1.1. History of Crystal Growth

Present day advanced technologies heavily rely on precisely characterized high quality crystals. Crystals have intrigued mankind since ancient times. The main applications of crystals till the 19th century were as precious stones in jewelry, in medical prescriptions, and in mysticism because of the belief in special virtues of gemstones and superstitions which still exist in modern times. Only in the 17th-18th centuries, when the laws governing crystal habits were discovered, crystallography became an independent branch of science. Earlier it was connected with mineralogy, the most perfect objects of investigation of which were crystals. Later, crystallography became associated more with chemistry, because it was apparent that the habit of crystals depends directly on their composition, and can only be explained on the basis of atomic or molecular concepts. In the 20th century, crystallography became more oriented towards physics, and an increasing number of new optical, electrical, mechanical and magnetic phenomena inherent to crystals were discovered. In the early 20th century, the discovery of X-ray diffraction by crystals led to a complete change in the content and substance of crystallography, as also in the whole science of the atomic structure of matter. The quest for knowledge has made mankind to grow synthetic crystals as an alternative to the limited availability of natural crystals of the requisite quality or size.

Rapid advances in solid-state physics have been responsible for the development of a wide range of materials/crystals. With the advent of electronic devices, use of crystals became inevitable for further developments in modern technology. Crystal growth, which was earlier a relatively narrow field of materials science, has now been identified as a thrust area of science and technology. This became true after the discovery of novel materials which bridge the gap between technology and human life. Crystal growth is a universal phenomenon in the field of materials. It has a long history of evolution from "a substance potting art" to a science in its own right which was accelerated by the invention of the transistor in 1948, and the
subsequent need for high purity semiconductor single crystals. As a result, crystal growth has developed into a core discipline in materials science and a comprehensive work on crystal growth mechanism has come up [1-8]. Crystals find applications in electronics, lasers, light valves, laser communication devices [9-10], light emitting diodes, thermal imaging, pyroelectric detectors [11], X-ray spectroscopy [12], inertial confinement fusion [13], etc. Large crystals are usually essential for device fabrication, and it must be possible to grow crystals of good optical quality for utilization [14]. Efforts are made to grow large crystals in short durations by fast-growth techniques.

1.2. Relevant Theory of Crystal Growth

An ideal crystal is an infinite lattice of atoms arranged in patterns which repeat in all three dimensions but real crystals are finite and contain defects. It is the periodic nature of the atoms and the properties arising due to the periodicity in crystals that is exploited to meet various technological feats. For at least 50 years crystals have fascinated engineers as the key materials of modern electronics, optoelectronics and other technical fields of application. The technological revolutions in the semiconductor, optics and communication industries are the examples [15]. The formation of crystal in nature, like snowflakes and minerals, as well as the preparation of the crystals in laboratories and factories for technical applications is called Crystal Growth. The growth of single crystals is both scientifically and technologically important, and the applications of such crystals today range from electronics to thermal management to synthetic gemstones. Single crystal growth helps to study many physical properties of solids and effects of grain boundaries. The full range of tensor relationship between applied physical cause and observed effect (property) can be obtained only if the full internal symmetry of the crystal structure is maintained throughout the specimen. The grain boundaries present in the crystal and the part played by imperfection are helpful in determining the physical and chemical properties of solids [16]. Single crystals reveal the fundamental properties of materials, especially properties with directional dependencies, which make crystals unique as compared to ceramics or glasses. These properties are often a key to technological applications, as illustrated in the case of the semiconductor silicon. A single crystal is defined by long-range atomic order extending over many atomic diameters, and having a repetitive structure. As a result, crystals have rigidity, fixed shape and mechanical strength. In crystals, strong connection between the optical, electrical and
mechanical responses with the crystal structure is often observed, and these features are used in many current technologies. Beyond utility, the beauty and mystery of crystals are continuing sources of fascination, and in many cases their growth remains a challenge. Single crystals have played a major role in most of these applications either in the form of bulk crystals (three dimensional), epitaxial thin films (two dimensional) or fiber crystals (nearly one dimensional). The anisotropy in the crystals gives them enhanced properties as required in the field of non-linear optics. The field of non-linear optics became practically a reality after the invention of lasers. The coherent and monochromatic optical beams in the visible and ultraviolet ranges are in high demand due to their application in the fields like material processing, semiconductor lithography, laser micromachining, laser spectroscopy, photochemical synthesis, inertial confinement fusion and other basic scientific studies. In this thesis, work on the growth and characterization of technologically important semi organic non-linear optical crystals have been carried out.

1.3. Nucleation

Nucleation is an important phenomenon in crystal growth and is the precursor of crystal growth and of the overall crystallization process. The condition of Supersaturation alone is not sufficient cause for a system to begin crystallization [17]. Before crystals can grow there must exist in the solution a number of minute solid bodies known as centers of crystallization, seeds, embryos or nuclei.

In a supersaturated or super cooled system when few atoms or molecules join together a change in free energy takes place in the process of formation of a cluster in a new phase. The cluster consisting of such atoms or molecules is called nuclei. The kinetics of phase change take place in four different stages:

(i) The development of the supersaturated state which may arise due to chemical or photo-chemical reaction or the consequence of a change in temperature, pressure, tension or other chemical or physical condition.

(ii) The generation of minute specks or nuclei.

(iii) The growth of nuclei to form particles of macroscopic dimensions or domains of the new phase.

(iv) The relaxation processes such as agglomeration by which the texture of the new phase changes.
Nucleation may occur spontaneously or it may be induced artificially; Based on this nucleation is classified as two kinds viz.

(i) Homogeneous nucleation
(ii) Heterogeneous nucleation

The spontaneous formation of crystalline nuclei in the interior of the parent phase is called homogeneous nucleation. Though the spontaneous formation of the nuclei in the bulk of supersaturated systems is comparatively rare occurrence, its basic principles form the necessary background for the understanding of numerous processes in science and technology as well as in nature when phase transitions are involved [18-20].

On the other hand if the nuclei form heterogeneously around ions, impurity molecules or on dust particles, on surfaces or at structural singularities such as dislocations or other imperfections, it is called heterogeneous nucleation [21].

The nucleation process can be understood by realizing the under cooled and supersaturated phases, which refer to unstable conditions. When the pressure of a vapor P is less than, equal to, or greater the vapor pressure of the liquid phase at the same temperature known as equilibrium pressure $P^*$, the vapor is described as under saturated, saturated or supersaturated with respect to the liquid phase. The unsaturated state and saturated state are thermodynamically stable. But the supersaturated state is unstable; i.e. a supersaturated vapor in contact with the bulk liquid phase will condense onto the liquid until saturation is obtained.

In a supersaturated vapor, not only single molecules $A_1$ are present but also embryos which are clusters of molecules bound together by their intermolecular interactions. The mechanism of formation of such embryos is the simple collision process consisting of a single molecule $A_1$ with a cluster $A_{i-1}$ consisting of (i-1) molecules and thus giving rise to a cluster $A_i$ i.e.,

$$A_1 + A_{i-1} \rightarrow A_i$$

The cluster $A_i$ may also be formed by the evaporation of a molecule from some cluster $A_{i+1}$: i.e.,

$$A_{i+1} \rightarrow A_i + A_1$$
The phase change takes place by single molecules becoming attached to embryos of various sizes; these processes predominate over the reverse processes in which various embryos lose single molecules. The size distribution of embryos changes with time. There is a critical size which is in unstable equilibrium with the supersaturated vapor; this is a critical nucleus the formation of which constitutes the bottleneck of the phase change. Once embryos achieve this critical size there is a high probability that they will grow, relatively unhindered, to macroscopic size.

Further, the creation of a new phase in the homogeneous solution requires a certain quantity of energy. The total Gibbs free energy change, $\Delta G$ of the embryo between the two phases associated with this process is then given as:

$$\Delta G = \Delta G_s + \Delta G_V$$

(1.1)

where $\Delta G_s$ is the surface free energy and $\Delta G_V$ is the volume free energy. For a spherical nucleus of radius $r$,

$$\Delta G_{\text{total}} = \frac{4}{3}\pi r^3 \Delta G_p + 4\pi r^2 \gamma$$

(1.2)

where $r$ is the radius of embryo or nucleus, $\Delta G_v$ is the specific volume free energy change, $\gamma$ is the specific surface free energy. The quantities $\Delta G$, $\Delta G_s$ (+ve) and $\Delta G_V$ (-ve) are represented in Figure 1.1:

![Fig. 1.1: Change in free energy during the formation of nucleus](image)

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Since surface free energy increases with $r^2$ and the volume free energy decreases with $r^3$, the total net free energy change increases with increase in size, attains a maximum and decreases for further increase in the size of the nucleus. The size corresponding to the maximum free energy change is called critical nucleus. The radius of the critical nucleus is obtained by setting the condition

$$\frac{d\Delta G}{dr^*} = 0$$  \hspace{1cm} (1.3)$$

and the expression for critical radius then is given by

$$r^* = -\frac{2\gamma^* \nu}{\Delta\mu}$$ \hspace{1cm} (1.4)$$

If $r < r^*$, droplet will shrink or dissolve.

& if $r > r^*$, droplet grows.

Growth cannot proceed until a droplet with radius at least as large as $r^*$ forms.

Substituting the values of $r^*$ in the above equation the free energy change associated with the critical nucleus is given by,

$$\Delta G^* = \frac{16\pi \gamma^* \nu^2}{3\Delta\mu^2}$$ \hspace{1cm} (1.5)$$

Expressions for heterogeneous nucleation can be obtained in a similar manner.

The probability of this happening by chance is:

$$P_{\text{nucleation}} \propto e^{\Delta G^*/kT} = e^{\frac{-2\pi R \gamma^* \nu}{kT}}$$ \hspace{1cm} (1.6)$$

The number of molecules in the critical nucleus is expressed as:

$$N^* = \left(\frac{4}{3}\pi R^3 \gamma^* \nu^2 \right)^{1/3}$$ \hspace{1cm} (1.7)$$

The interfacial tension $\gamma$ has been determined experimentally [3,20].
1.4. Metastable Zone Width

Crystal growth from solution is based on the existence of a metastable region where formation of crystalline nuclei in the solution volume is impossible, but it is possible to grow crystals on a seed. Figure 1.2 presents a part of a classical phase diagram of a two component system for a solute with a positive temperature coefficient of solubility $dC_o/dT > 0$ [22].

![Phase diagram for a binary system of solid-liquid](image)

**Fig. 1.2: Phase diagram for a binary system of solid-liquid**

The diagram can be described in terms of three zones:

(i) The stable zone of unsaturated solution where crystal growth is impossible.

(ii) The metastable zone where spontaneous crystallization is improbable but crystal growth on a seed occurs and

(iii) The labile zone of spontaneous nucleation.

Cooling a solution with concentration ‘C’ from the initial point A’ leads to the point A on the solubility curve. At this point, the solution becomes saturated and can exists in equilibrium with the solid if $C = C_o \left(T_o\right)$. Further cooling leads to a state where the concentration $C_o \left(T\right)$ at a given temperature and the solution becomes supersaturated. However, spontaneous formation of the solid phase does not occur in this region until a point B on the metastable boundary is reached. If crystallization in a
solution saturated at the temperature $T_o$ starts at the temperature $T$, the position of the Metastable boundary can be expressed in the units of maximum overcooling $\Delta T_{\text{max}} = T_o - T$, the absolute supersaturation

$$\Delta C_{\text{max}} = C_o (T_o) - C_o (T)$$

(1.8)

or in the units of relative supersaturation

$$S = \frac{\Delta C_{\text{max}}}{C_o (T_o)}$$

(1.9)

One more important parameter that characterizes the metastable zone width is the induction period $\tau_i$. It corresponds to the time during which the system can remain without spontaneous nucleation at constant supersaturation within the metastable zone. Growing a crystal without spontaneous nucleation is possible only within the metastable zone. The quantitative estimation of parameters like width of the metastable zone, degree of Supersaturation, induction time, critical radius and critical free energy decide the stability of the solution for the successful growth of crystals.

1.5. Thermodynamics of Crystal Growth

The process of crystal growth involves a phase transformation. A transformation occurs when it leads to the lowering of free energy of the system. This situation in a solid is described by the formalism of thermodynamics [5].

The thermodynamic equilibrium between solid and liquid phase occurs when the free energy of the two phases are equal

$$G_L = G_s$$

(1.10)

The free energy of a system is related to the internal energy and the entropy of the system by the Gibb’s equation:

$$G = H - TS$$

(1.11)

where $H$ is the enthalpy, $S$ is the entropy and $T$ is the temperature.

If a system has certain excess energy, it tries to expel this and try to attain stability. The free energy release during such a transition is
\[ \Delta G = \Delta H - T \Delta S \]  \hspace{1cm} (1.12)

where \( \Delta H = H_L - H_S \)

\[ \Delta S = S_L - S_S \]

\[ \Delta G = G_L - G_S \]

At equilibrium \( \Delta G = 0 \)

Therefore,

\[ \Delta H = T_c \Delta S \]  \hspace{1cm} (1.13)

where \( T_c \) is the equilibrium temperature.

\[ \Delta G = \Delta H \Delta T / T_c \]  \hspace{1cm} (1.14)

where \( \Delta T = T_c - T \)

\( \Delta G \) is positive when \( T_c > T \) and it depends on the latent heat of transition. In general \( \Delta G \) is the product of the entropy change and supercooling, \( \Delta T \). This is the very powerful relation when the growth happens from the melt. In the case of solution growth or vapor growth one may use the concentration profiles rather than the supercooling, \( \Delta T \) and thus the equation modifies to

\[ \Delta G = RT \ln \rho \]  \hspace{1cm} (1.15)

where \( \rho \) is the supersaturation ratio. The rate of growth of a crystal can be regarded as a monotonically increasing function of \( \Delta G \), if the other parameters remain undisturbed.

### 1.6. Crystal Growth Techniques

The process of crystal growth is controlled by change of state, or phase change, to the solid state. This transition may occur from the solid, liquid or vapor state. Depending on the phase transitions involved in the process, the crystal growth methods can generally be classified into four main categories [5-8].

(i) Solid growth (solid \( \rightarrow \) solid)

(ii) Vapor growth (vapor \( \rightarrow \) solid)

(iii) Melt growth (liquid \( \rightarrow \) solid)

(iv) Solution growth (liquid \( \rightarrow \) solid)
The conversion of a polycrystalline piece of material into single crystal by causing the grain boundaries to be swept through and pushed out of the crystal takes place in the solid-growth of crystals [21]. Solid growth processes are rarely used except for certain metals where strain annealing is effective and certain cases where a crystal structure change occurs between the melting point and room temperature. An efficient process is the one, which produces crystals adequate for their use at minimum cost. Better choice of the growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics. It seems that the essential task for the crystal growers at present is to gain basic knowledge about the correlation of given material with crystal growing method and the growth conditions defined to be special parameters. On analyzing these points one can find which technique is appropriate for a given material. Various growth techniques are discussed in further sections with more emphasis on solution growth technique.

1.6.1. Growth from Solution

The growth of crystals by precipitation from aqueous solution is the most simple and oldest technique. Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. In this process, a saturated solution of the material in an appropriate solvent is used from which crystallization takes place as the solution becomes critically supersaturated. The Supersaturation can be achieved either by lowering the temperature of the solution or by slow evaporation [23]. The advantage of the method is that crystals can be prepared from a solution at temperatures well below its melting point, perhaps even at room temperature and therefore it turns out to be more applicable in many cases [5,24].

Depending on the solvent and solubility of the solute, solution growth can be broadly classified as:

(i) High temperature solution growth
(ii) Hydrothermal method
(iii) Gel growth
(iv) Low temperature solution growth
1.6.1.1. High Temperature Solution Growth (Flux Growth)

In high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent (molten salts are used as solvents) and crystallization occurs as the solution becomes critically supersaturated. Molten salts of such composition should be contained in platinum or iridium crucibles [25]. Flux growth is carried out at much lower temperatures than corresponding growth from melt. A distinct advantage of the method is that this is the only method for obtaining certain oxide solid solutions. However, flux growth is very slow and requires precise temperature control. The purity of the crystals grown by this method is often marginal. Flux growth is an expensive technique, since it requires the use of noble-metal crucible and seed holders [26]. Stoichiometry is also difficult to control in this method. This growth method can be divided into two major categories:

(i) Growth from single component system
(ii) Growth from multi component system

This method is widely used for the growth of oxide crystals. The procedure is to heat the container having flux and the solute to a temperature so that all the solute material dissolves. This temperature is maintained for a ‘soak’ period of several hours and then the temperature is lowered very slowly.

1.6.1.2. Hydrothermal Method

Hydrothermal method is an aqueous solution method at elevated temperatures and pressures [27]. The main reason for resorting to elevated temperatures is the limited solubility of the material under ordinary conditions. Although a large number of materials can be grown by this method, it is primarily used for the growth of large high quality α-quartz crystals which are widely used in piezoelectric applications [26]. With this method, high quality large single crystals can be obtained. This method requires autoclave as the growth takes place at elevated temperatures and pressures. The disadvantages of this technique are mainly associated with high pressure and inability to observe growth during the process. Temperatures are typically in the range of 400° C to 600° C and the pressure involved is large (hundreds or thousands of atmospheres).
Growth is usually carried out in steel autoclaves with gold or silver linings. Depending on the pressure the autoclaves are grouped into low, medium and high-pressure autoclaves. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement of high pressure presents practical difficulties and there are only a few crystals of good quality and large dimensions grown by this technique. Quartz is the outstanding example of industrial hydrothermal crystallization. One serious disadvantage of this technique is the frequent incorporation of OH⁻ ions into the crystal, which makes them unsuitable for many applications [7].

1.6.1.3. Gel Growth

Gel technique is a simple and elegant method of growing single crystals under controlled growth and at room temperatures. The principles used in this crystal growth technique are very simple. Solutions of two suitable compounds which give rise to the required insoluble crystalline substance by mere chemical reaction between them are allowed to diffuse into the gel medium and chemically react as follows:

$$AX + BY \rightarrow AB + XY$$

where AX and BY are the solutions of two compounds which on reactions give rise to the insoluble or sparingly soluble substance AB and also the waste product XY being highly soluble in water. This method is also useful for substances having very high solubility. This method has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds. This is an alternative technique to solution growth with controlled diffusion and growth process is free from convection. A large number of substances having problems in conventional methods can be grown by this technique [20].

1.6.1.4. Low Temperature Solution Growth

The method of crystal growth from low temperature aqueous solution is extremely popular in the production of many technologically important crystals. Material having moderate to high solubility in temperature range, ambient to 100°C at atmosphere
pressure can be grown by low temperature solution growth method [28]. The mechanism of crystallization from solutions is governed by the interaction of ions or molecules of the solute and the solvent that is based on the solubility of substance on the thermo dynamical parameters of the process, temperature, pressure and solvent concentration [7]. The low temperature solution growth technique is well suited to those materials, which suffer from decomposition in the melt or in the solid at high temperature and which undergo structural transformations while cooling from the melting point. At least 90% of the crystals produced by low temperature solution methods are soluble in water. Rates of growth from solution fall in the range of 0.1 to 1 mm/day [7]. Solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity. For a given solute, there may be different solvents. The solvent must be chosen taking into the account the following factors to grow crystals from solution.

A solvent of choice is the one with

(i) a good solubility for the given solute
(ii) a good solubility gradient
(iii) less viscosity
(iv) less volatility
(v) less corrosion and
(vi) non-toxic

The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of raw material can destroy months of work. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent [7]. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low [8].
In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated i.e., it contains more solute than it can be in equilibrium with the solid. Three principal methods are used to produce the required Supersaturation:

(i) Slow cooling of the solution
(ii) Slow evaporation of the solvent
(iii) The temperature gradient method

Low temperature solution growth is a well-established technique due to its versatility and simplicity. It is possible to grow large crystals of high perfections as the growth occurs close to equilibrium conditions [29]. It also permits the preparation of different morphologies of the same material by varying the growth conditions.

1.6.1.4.1. Slow Cooling Technique

It is the best way to grow single crystals by solution technique. The main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.

1.6.1.4.2. Slow Evaporation Method

This method is similar to the slow cooling method in view of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005°C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of solubility.
1.6.1.4.3. Temperature Gradient Method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are that

(i) Crystal grows at a fixed temperature
(ii) This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change
(iii) Economy of solvent and solute

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate.

Excellent quality crystals of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.

Bulk single crystal growth by Low temperature solution growth can be employed by two well known methods:

(i) S-R method
(ii) Seed rotation method

These methods are used to grow bulk large size single crystals without any inclusion for use in devices. The only disadvantages of these methods are that they requires a lot solution to start the experiment and also a lot of time and patience are required for these methods. From a lot of attempts only few give fruitful results.

1.6.1.4.4. S-R Method

SR method is one of the solution growth methods. In the case of melt, extremely low growth rate and thermal gradients are usually required to grow single crystals having reasonable size and quality. In addition, crystal growth at elevated temperature leads to thermal induced grown-in-defects. The growth of organic crystals with specific orientation has tremendous value in terms of its significance towards device application.
The recently invented Sankaranarayanan-Ramasamy (SR) method [30-31] has made it possible to grow bulk-size single crystals along a desired orientation needed for device fabrication.

Figure 1.3 shows the SR set-up for crystal growth consisting two ring heaters positioned at the top and bottom of the growth ampoule each connected to a temperature controller maintaining constant temperature. The daily variation in temperature is avoided by placing the entire SR set-up in a water bath. The top heater provides the necessary temperature for solvent evaporation, while the bottom one is used to maintain the solid-liquid interface at the saturation temperature. The ampoule or container used in this method is made up of an ordinary hollow glass tube with a tapered V-shaped bottom to mount the seed crystal and a big diameter top portion to fill a good amount of supersaturated solution to grow a relatively good size crystal. For controlled evaporation, the top portion is closed with some opening at the center. The whole tube is housed in a constant temperature bath with a setting temperature of 25 °C, which is the optimized growth temperature. The experimental conditions are closely monitored, and we find that the seed crystal start to grow after 10 days. In a time span of 40-45 days, a good quality single crystal of a given material can be harvested.

Fig. 1.3: Schematic diagram of experimental setup of SR method
1.6.1.4.5. Seed Rotation Method (Self Designed)

Seed crystals grown from solvent evaporation technique can be made into large size by using them in seed rotation set-up. The quality of crystal growth depends on the precise control of uniformity of solute concentration and temperature gradient in the growth chamber. A solution growth system with the provision of controllable bidirectional rotation of top seeded growth has been designed and fabricated. A controlling circuit was fabricated for bidirectional rotation of seed holder by using various IC’s like 555 (timer), 7809 (voltage regulator), 4017 (rotation controller) and dc motor. Bottom part of the growth chamber was made tapered in the tube shape so that it can be fitted in the tubular furnace to avoid any spurious nucleation at the bottom of beaker. The temperature at the bottom of the chamber and around the seed can be precisely controlled. The rpm of seed holder and the time period of the bidirectional rotation can be changed as per the requirement of the growth condition.

The system has been used to grow a number of crystals in three conditions: static seed, one directional rotation of seed and bidirectional rotation of seed after optimizing the rpm and frequency of seed rotation. A schematic diagram of seed rotation set-up is shown in Figure 1.4.

![Seed rotation set-up](image)

**Fig. 1.4: Seed rotation set-up**

1.6.2. Growth from Melt

This is the fastest of all crystal growth methods and is widely used for the preparation of bigger and larger quantity of crystals. It is the process of crystallization by fusion and
resolidification of the pure material. All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. [32]. One of the foremost advantages of this technique is the requirement of simple systems. Primarily the material to be grown is melted and afterwards progressively cooled to yield crystalline form. This method has been utilized to produce commercially important semiconductors, metals and laser host crystals. The availability of pure and perfect crystals is the main advantage of this technique. Depending on the thermal characteristics melt growth techniques can be grouped into following categories:

(i) Bridgman technique
(ii) Czochralski technique
(iii) Kyropoulos technique
(iv) Zone melting technique
(v) Verneuil technique

The major factors to be considered during growth of crystals from melt are

(i) Volatility
(ii) The chemical reactivity
(iii) Melting point

1.6.2.1. Bridgman Technique

This technique was named after its inventor (Bridgman 1925; Stockbarger 1938). In this process the material to be grown is taken in a vertical cylindrical container, tapered conically with a point bottom and made to melt using a suitable furnace. The container is lowered slowly from the hot zone of the furnace into the cold zone. The rates of movement mostly taken in the range 1-30 mm/hr. Crystallization begins in the tip and continues usually by growth from the first formed nucleus [5, 26, 32, and 33]. The relative advantages of this technique are low cost, with added advantage that the melt temperature increases with distance from the solid-liquid interface and the system is therefore density stable.
The Bridgman technique cannot be used for materials which decompose before melting or which undergo solid state phase transformation between their melting points and the temperature to which they will be cooled. A complete Bridgman set-up is shown in Figure 1.5.

![Bridgman set-up](image)

Fig. 1.5: Bridgman set-up

A disadvantage is that the melt is in contact with the container for longer periods, increasing the risk of impurity pick-up. A second disadvantage is that adhesion of the solid materials to the ampoule wall or compression of the solid by the contracting container during cooling can lead to the development of stresses high enough to nucleate dislocations in the material. A further drawback of the technique is that the container wall acts as a preferential, spurious nucleation site, resulting in polycrystalline rather than single crystal growth unless the temperature gradient and liquid-solid interface shape are well controlled.

1.6.2.2. Czochralski Technique

Czochralski technique (1918) is a popular method of crystal growth because it can produce large, dislocation free crystals in a relatively short space of time [32]. The Czochralski growth geometry is shown schematically in Figure 1.6. The material to be grown is melted by induction or resistance heating under a controlled atmosphere in a
suitable non-reacting container (crucible). By controlling the furnace temperature, the material is melted. The melt temperature is then adjusted to be slightly above the melting point and seed crystal is lowered. After thermal equilibrium, the seed is contacted with the melt and the melt temperature is raised to establish the desired growth interface configuration. The seed is rotated at the same time in order to attain thermal symmetry and also to stir the melt. When the temperature of the seed is maintained very low compared to the temperature of the melt, by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed. The advantage of this method over the Bridgman method is that it can accommodate the volume expansion associated with the solidification.

The main requirements for growing good crystals by this method are that the pull and rotation rates should be smooth and that the temperature of the melt should be accurately controlled. The diameter of the crystal is dependent on both the temperature of the melt and the pull rate. To increase the diameter of the crystal being grown, the power is reduced or the pull rate decreased, the opposite applies for reducing the diameter. The maximum size of crystal that can be produced by this technique is governed by the volume of the melt, the diameter of the crucible, the distance that the pull rod can move and the strength of the crystal at its minimum diameter. It is essential for this method that the temperature distribution in the melt should be such that the temperature of the solid-liquid interface is the lowest in the liquid. If it is not, spurious
nucleation will occur. Czochralski method has gained wide recognition particularly in growing single crystals of semiconductors like silicon and other materials.

Liquid encapsulated Czochralski abbreviated as LEC technique makes it possible to grow single crystals of materials, which consists of components that produce high vapour pressure at the melting point. This refined method of Czochralski technique is widely adopted to grow III-V compound semiconductors.

1.6.2.3. Kyropoulos Technique

In Kyropoulos technique, the crystal is grown in a larger diameter. As in the Czochralski method, here also the seed is brought into contact with the melt and is not raised much during the growth, i.e. part of the seed is allowed to melt and a short narrow neck is grown [7,34]. After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power into the melt. Shallow large diameter crucibles are required in this method but little control of crystal shape is possible. The quality of the crystal is strongly dependent on the control of the cooling schedule. The major use of this method is growth of alkali halides and oxide crystals to make optical components.

1.6.2.4. Zone Melting Technique

Zone melting is a generic title given to a large family of techniques (float zone, travelling solvent zone, zone pass etc.) which have in common the following feature: “A liquid zone is created by melting a small amount of material in a relatively large or long solid charge or ingot. It is then made to traverse through a part or the whole of the charge”[7,32]. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed [35]. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. An advantage of the zone melting technique is that impurities tend to be concentrated in the melted portion of the sample. Consequently, this process sweeps them out of the sample and concentrates them at the end of the crystal boule, which is then cut off and discarded.
The main reasons for the impact of zone refining process to modern electronic industry are the simplicity of the process, the capability to produce a variety of organic and inorganic materials of extreme high purity, and to produce dislocation free crystal with a low defect density. In the case of vertical normal freezing, the solid-melt interface is moved upwards from the cold bottom to the hot top so as to get better quality crystals. Thus this method is sometimes used to purify semiconductor crystals and is more applicable in growing single crystals of materials with volatile constituents like GaAs.

1.6.2.5. Verneuil Technique

In the Verneuil technique, a fine dry powder of size 1-20 microns of the material to be grown is shaken through the wire mesh and allowed to fall through the oxy-hydrogen flame. The powder melts and a film of liquid is formed on the top of the seed crystal. This freezes progressively as the seed crystal is slowly lowered. The art of the method is to balance the rate of charge feed and the rate of lowering of the seed to maintain a constant growth rate and diameter. By this method ruby crystals are grown up to 90 mm in diameter for use in jeweled bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of high melting oxides.

1.6.3. Vapor Growth Techniques

Vapor growth techniques can be adopted for the growth of materials which lack a suitable solvent and sublime before melting at normal pressure. Vapor growth methods have been employed to produce bulk crystals and to prepare thin layers on crystals with a high degree of purity [36]. Crystals of high purity can be grown from vapor phase by sublimation, condensation and sputtering of elemental materials [37-38]. To obtain single crystals of high melting point materials this method is used. Growth from vapor phase may generally be subdivided in to:

(i) Physical vapor transport
(ii) Chemical vapor transport.
There is an increasing demand for vapor grown crystals because these crystals sometimes possess unusual properties. The crystals often have perfectly flat external faces that cannot be duplicated by other means and they often contain less substructure and imperfections than melt grown crystals.

The fundamental aspects of vapor phase crystal growth might be divided into four major areas:

(i) Thermodynamics, which controls the driving force for the chemical reaction occurring at the vapor solid interface.
(ii) Mass transport, by which the reactants reach the growing surface and products are removed.
(iii) Surface kinetics including adsorption of reactants onto the surface, surface diffusion, step generation, surface chemical reactions between adsorbed reactants at steps and desorption of products.
(iv) Structural aspects of growth, especially epitaxial growth such as defect generation and surface morphology of homo epitaxial and hetero epitaxial layers.

1.6.3.1. Physical Vapor Transport

In PVT technique the crystal is grown from its own vapors and this method does not involve any extraneous compound formation or reaction. The PVT methods are limited to materials having an appreciable vapor pressure at attainable temperatures. There are two types of techniques employed in physical vapor transport process-sublimation-condensation and sputtering [39]. The first method involves sublimation of the charge at the high temperature end of the furnace, followed by the condensation at the colder end. Sputtering techniques are preferred to low vapor-pressure substances and mainly this method has been used to prepare thin films rather than discrete crystals. The principal advantage of this technique is that film growth can be possible at lower temperature than in ordinary sublimation-condensation growth. The PVT techniques are used to prepare a variety of crystals and for the production of epitaxial films.
1.6.3.2. Chemical Vapor Transport

Chemical vapor transport technique involves a chemical reaction between the source material to be crystallized and a transporting agent [40]. The material to be crystallized is converted into one or more gaseous product, which either diffuses to the colder end or gets transported by a transporting (carrier) gas. At the cold end, the reaction is reversed so that the gaseous product decomposes to deposit the parent material, liberating the transporting agent which diffuses to the hotter end and again reacts with the charge. The commercial importance of vapor growth is in the production of thin layer by chemical vapor deposition.
1.7. References


Chapter 1

Introduction


