CHAPTER II
INTRODUCTION TO CRYSTAL GROWTH

2.1 Crystal growth

Single crystals play a very important role in the present day technology to the extent that it can be said 'single crystals are the pillars of modern technology'. In addition to the production of technologically important crystals, there is a growing realization for the importance of crystal growth in many familiar but diverse phenomenon. The requirement of good quality and well-characterized crystals for academic research has resulted in the adaptation and development of a very specialized method of crystal growth for such materials.

Crystal growth involves the phase transformation of the material of interest from solid, liquid or gaseous phase to a well ordered solid phase resulting in a crystal [19-26]. Though crystal growth is a non-equilibrium process, it requires understanding of the thermodynamics. Crystal growth takes place if the free energy of the crystal is less than that of the corresponding polycrystalline phase. This process involves solidification of a melt or precipitation from a supersaturated solution, or deposition of vapor or ordering of a solid. Depending on the physical and chemical properties of the material, an appropriate crystal growth technique is chosen [20]. Some of the elements, alloys and intermetallics except those sublime and decompose, are usually grown from melt. Compounds that melt incongruently are grown by flux method. Solution growth is employed to grow many organic compounds and inorganic complexes for which good solubility in suitable solvent exists. Materials that sublime suitably are grown by physical vapor transport method and those decompose upon melting are conveniently transported by a chemical agent and grown [21-22].

2.2 Types of crystal growth

Crystal growth technique ranges from a small inexpensive method to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. On the basis of this, crystal growth may be classified into three main categories as follows,

(i) Solid growth – solid to solid phase transformation
(ii) Liquid growth – liquid to solid phase transformation
(iii) Vapour growth – vapour to solid phase transformation

2.2.1 Growth from melt

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. Depending on the thermal characteristics, the following techniques are employed.

a) Bridgman technique
b) Czochralski technique
c) Kyropoulos technique
d) Zone melting technique
e) Verneuil technique
(a) **Bridgman technique**

In this technique the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The bottom is lowered slowly from the hot zone of the furnace in to the cold zone. The rates of movement for such processes range from about 1-30 mm/hr. Crystallization begins at the tip and continues usually by growth from the first formed nucleus. This technique cannot be used for materials, which decompose before melting. This technique is best suited for low melting point materials.

(b) **Czochralski technique**

In this method, the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container. By controlling the furnace temperature, the material is melted. A seed crystal is lowered to touch the molten charge. 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. Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals.

(c) **Kyropoulos technique**

In this 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 (part of the seed is allowed to melt and a short narrow neck is grown). After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power supplied to the melt. The major use of this method is for alkali halides to make optical components.

(d) **Zone melting technique**

In this technique, the feed material is taken in the form of sintered rod and the seed is attached to one end. A small molten zone is maintained by surface tension between the seed and the feed. The zone is slowly moved towards the feed. Single crystal is obtained over the seed. This method is applied to materials having large surface tension. 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.
(e) Verneuil technique

In this technique, a fine dry powders 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 jewelry bearings and lasers. This technique is widely used for the growth of synthetic gems and variety of oxides.

2.2.2 Growth from solution

Crystal growth from solutions is known for a long time. A solution is a homogenous mixture of two or more substances, which can be solid, liquid or gas; and the component present in excess is the solvent and the one in relatively smaller quantity is the solute. The characteristic feature of a solvent is its ability to bring into a single phase of one or more compounds. The dissolution process involves interactions of solutes and solvent molecules, which differ according to the different types of solvents. The basic process of the solution growth method involves the preparation of a supersaturated solution of the solute dissolved in suitable solvent and to make the resultant solution to be critically supersaturated. Crystal grows when this metastable state passes through a transition to go to the stable state. By suitably adjusting the growth parameters, a single good quality crystal can be grown by this method. Solution growth can be classified as,

a. Low temperature solution growth
b. High temperature solution growth

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

Low temperature solution growth consists of three categories

(i) Slow cooling technique
(ii) Slow evaporation technique
(iii) Temperature gradient technique
2.2.2.1 Slow cooling technique

Slow cooling is the technique, among others to grow bulk single crystals from solution. Here, supersaturation is achieved by a change in temperature usually throughout the crystallizer [23]. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the metastable region along the saturation curve in the direction of lower solubility. Since the volume of the crystallizer is finite and the amount of substance placed in its limited, the supersaturation requires systematic cooling. It is achieved by using thermostated crystallizer, which is selected based on the desired size of the crystals and 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.

2.2.2.2 Slow evaporation technique

This technique is similar to the slow cooling method in terms of apparatus requirements. The temperature is fixed 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 a temperature stabilization of about 0.05°C and rate of evaporation of a few ml/hr. The evaporation technique has an 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 can effectively be used for materials having moderate temperature coefficient of solubility.

2.2.2.3 Temperature gradient technique

This method involves the transport of materials from hot region containing the solute 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 change in temperature, provided both the source and the growing crystal undergo the same change
(iii) economy of solvent and solute

On the other hand, a small temperature difference between the source and the crystal zones has a large effect on the growth rate.
The low temperature solution growth technique has the following merits

(i) simple growth apparatus
(ii) growth of strain and dislocation free crystals
(iii) permits the growth of prismatic crystals by varying the growth conditions
(iv) only method which can be used for substances that undergo decomposition before melting
(v) crystals can be grown in large size

The technique has the following conditional limitations

(i) growth substance should not react with solvent
(ii) this method is applicable for substances fairly soluble in a solvent.

The advantage of the solution growth is that the crystals grow well below the melting point and hence the crystals are not exposed to steep temperature gradients resulting in better quality crystals free from thermal strains. Formation of facets in the crystals grown by this method avoids need for orientation, cutting and polishing.

The disadvantages of the solution growth are the incorporation of solvent species into the crystal lattice and slow growth rate. However, by choosing a proper solvent the incorporation of solvent ions can be minimized.

2.2.3 Gel growth

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two-component system of a semi solid rich in liquid and inert in nature. The material, which decomposes before melting, can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3-4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

2.2.4 Growth from vapour

The growth of single crystal material from the vapour phase is probably the most versatile of all crystal growth processes. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of element materials. To obtain single crystals of high melting point materials these methods are used. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method
for the growth of bulk crystals utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as volatile species to the crystallization region. Finding a suitable transporting agent is a formidable problem in this technique. It is rarely possible to grow large crystals because of multinucleation. The commercial importance of vapour growth is the production of thin layers by chemical vapour deposition (CVD), where usually irreversible reactions e.g., decomposition of silicon halides or of organic compounds are used to deposit materials epitaxially on a substrate. Doping can be achieved by introducing volatile compounds of dopant elements into the reaction region. The thickness of the doped layer can be controlled.

2.3 Choice of solvent

It is desirable to choose a solvent in which the compound is moderately soluble. If the solute is freely soluble, this will result in small crystal size [19]. In solvents where the compounds form supersaturated solutions, size of the crystals is very small. The ideal solvent should yield a prismatic habit in the crystal and also have the following characteristics

(i) high solute solubility
(ii) high positive temperature coefficient of solubility
(iii) low viscosity
(iv) low volatility
(v) density less than that of the bulk solute and
(vi) low toxicity.

Nucleation is an important phenomenon in the crystal growth and is the precursor of the overall crystallization process. Nucleation [27] is the process of generating within a metastable mother phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase. Nucleation is consequently a study of the initial stages of the kinetics of such transformation [28].

The fewer sites at which crystals begin to grow will result in fewer crystals each of larger size. This is most desirable. Conversely, many nucleation sites, which result in a smaller average crystal size, are not desirable. In many recrystallization ambient dusts in the laboratory provide site of nucleation. It is important to minimize dust or other extraneous particulate matter in the crystal growing vessel. Nucleation may occur spontaneously or it may induce artificially. These two cases are referred to as homogeneous and heterogeneous
nucleation respectively [29]. Both of these nucleation are called primary nucleation and occur in the systems that do not contain crystalline matter. On the other hand, nuclei are often generated in the vicinity of crystals present in the supersaturated system. This phenomenon is referred to as secondary nucleation [30].

The growth of crystals from solutions can occur if some degree of supersaturation or supercooling has been first achieved in the system. There are three steps involved in the crystallization process.

(i) Achievement of supersaturation or supercooling
(ii) Formation of crystal nuclei
(iii) Successive growth of crystals to get distinct faces

**Ostwald's contributions**

Ostwald appears to be the first to explain the relationship between supersaturation and spontaneous crystallization. The relationship between the concentration and temperature is schematically shown in Fig. 2.1 [31].

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**Fig. 2.1 Meir's solubility curve**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Temperature</th>
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<tr>
<td><strong>BB'</strong> - Solubility Curve</td>
<td><strong>CC'</strong> - Super Solubility Curve</td>
</tr>
<tr>
<td><strong>AB''C''</strong> - Evaporation and Cooling</td>
<td><strong>D</strong> - Crystallization Point</td>
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Labile

Metastable

Stable

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The lower continuous line is the normal solubility curve for the salt concentration. Temperature and concentrations at which spontaneous crystallization occurs are represented by the upper broken curve, generally referred to as “super solubility curve”. This curve is not as well defined as the solubility curve and its position in the diagram depends on, among other things, the degree of agitation of the solution.

The diagram is therefore divided into three zones, one well defined and the other two variables to some degree:

1. The stable (undersaturated) zone, where crystallization is impossible.
2. Metastable (saturated), between the supersolubility curve and solubility curve is called as metastable zone, where spontaneous crystallization is not possible. Seeded growth can be initiated in this region.
3. The unstable or labile (supersaturation) zone, where spontaneous nucleation is more probable.

2.4 Mechanism of crystal growth

A solution in which the concentration of the solute exceeds that of the equilibrium at a given temperature is known as supersaturated solution. A supersaturated solution is thermodynamically unstable. Supersaturation required for crystallization process can be achieved by (i) slow evaporation (ii) slow cooling and (iii) by adding any external impurity. Supersaturation achieved by slow cooling is the best method to grow bulk size crystals by solution technique [31]. In this case, crystallization takes place by lowering the temperature of the solution under a controlled cooling rate. Supersaturation can be achieved by slow evaporation of the solvent for materials, which are having very small temperature coefficient of solubility. Here crystallization takes place at a constant temperature. Supersaturation can also be achieved by the addition of some impurities. The growth proceeds by the reduction of solubility of the solute due to the presence of an impurity. The selection of suitable growth method depends mainly on the shape of the solubility curve.

The degree of supersaturation of a solution can be expressed by the ratio:

$$ S = \frac{C}{C^*} $$

(2.1)

Where, $C$ is the actual concentration of the solution and $C^*$ is the equilibrium saturation concentration of the solution at a given temperature. Thus, $S = 1$ denotes saturated solution, $S < 1$ denotes undersaturation, and $S > 1$ indicates supersaturation.
The concentration driving force $\Delta C$ is given by

$$\Delta C = C - C^*$$  \hspace{1cm} (2.2)

The relative supersaturation is defined as,

$$\delta = \frac{C - C^*}{C^*}$$

$$\delta = \frac{C}{C^*} - 1$$

Crystallization process is initiated by the formation of embryos or nuclei with number of microsize solid particles present in the solution, termed as centers of crystallization. The mechanism of formation of such embryos is the simple collision process 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.,

$$A_1 + A_{i-1} \rightarrow A_i$$  \hspace{1cm} (2.4)

The total Gibb’s free energy change, $\Delta G$ of the embryo between the two phases associated with this process is given as

$$\Delta G = \Delta G_s + \Delta G_v$$  \hspace{1cm} (2.5)

where $\Delta G_s$ is the surface free energy and $\Delta G_v$ is the volume free energy

For the spherical nucleus of radius, $r$

$$\Delta G_v = 4 \pi r^2 \gamma + 4 \pi r^3 \Delta G$$  \hspace{1cm} (2.6)

where $\gamma$ is the interfacial tension and $\Delta G_v$ is the free energy change per unit volume and is a negative quantity. These quantities are represented in Fig. 2.2. Since the surface free energy increases with $r^2$ and volume free energy decreases with $r^3$, the total net free energy change increases with increase in size and attains a critical size after which it decreases. At critical condition, the free energy of formation obeys the condition,

$$\frac{d\Delta G}{dr} = 0$$  \hspace{1cm} (2.7)

Hence the radius of the critical nucleus is expressed as

$$r^* = \frac{-2\gamma}{\Delta G_v}$$

where $\Delta G_v = -kT \ln S/v$

$$S = \frac{C}{C^*}$$

$v = \text{molar volume of the crystal}$

$k = \text{Boltzmann constant}$

$C = \text{actual concentration of the solution}$

$C^* = \text{equilibrium concentration of the solution}$

$T = \text{Temperature of the solution in K}$

$S = \text{Supersaturation ratio}$
Fig. 2.2 Change in free energy due to the formation of nucleus

Hence, the critical free energy barrier

$$\Delta G^* = 16 \pi \gamma^3 / 3 \Delta G_v^2$$  \hspace{1cm} (2.9)

The number of molecules in the critical nucleus is expressed as

$$i^* = 4/3 \pi \gamma (r^3)$$  \hspace{1cm} (2.10)

The interfacial tension, $\gamma$ can be determined experimentally.

Crystal habit

Mostly, all crystals grow approximately at equivalent rates in all dimensions. This will result in a large bulk crystal from which samples of any desired orientation can be cut. Furthermore, during growth where dislocations and other defects propagate, they do so from the nucleus or seed along specific directions into the bulk of the crystal. If the crystal is grown with a bulky habit, these imperfections usually become isolated into defective regions surrounded by large volumes of high perfection.

Changes of habit in crystals can be achieved by any one of the following ways:

(i) changing the growth temperature

(ii) changing the pH of the solution

(iii) adding a habit modifying agent

(iv) changing the solvent
Achievement in this area is of great industrial importance, where such morphological changes are induced during crystallization to yield crystals with better perfection and packing characteristics [32]. Among the different methods, the slow evaporation technique is found to be more feasible because of its relatively simple instrumentation and handling. Hence in present study the slow evaporation technique is chosen for the growth of single crystals.

2.5 Scope of the thesis

The fundamental principle and applications of nonlinear optical phenomena and an insight into different NLO materials have been discussed. The brief discussions about ferroelectrics and crystal growth techniques have been explained. In view of the potential application of nonlinear optical materials and ferroelectric crystals the present investigation aimed at

(i) growth of γ-glycine, glycerine nitrate (GN), triglycerine sulphate (TGS) and triglycerine sulphi phosphate (TGSP) crystals.

(ii) studying the effect of additives on the growth of glycine family crystals.

(iii) studying the physical and chemical properties.