

CHAPTER 1

INTRODUCTION TO CRYSTALS AND CRYSTAL GROWTH TECHNIQUES

The present thesis focuses on the study and synthesis of Semi organic nonlinear optical and ferroelectric crystals for optical device application and biomedical applications.

1.1 INTRODUCTION TO CRYSTALS

Probably the first historical references to the use of crystals come from the Ancient Sumerians (4th millennium BC), who included crystals in magic formulas. Crystals were (and are) also used for healing in traditional Chinese Medicine, which dates back to at least 5000 years. The Ancient Egyptians used lapis lazuli, turquoise, carnelian, emerald and clear quartz in their jewelry is shown in Figure1.1. They used some stones for protection and health, and some crystals for cosmetic purposes, like galena and/or malachite ground to a powder as the eye shadow. Green stones in general were used to signify the heart of the deceased and were included in burials, as it was also found at a later period in Ancient Mexico.

The actual word crystal comes from a Greek word Crystallos, from “Krysos” meaning “Ice Cold”, as it was originally thought that crystals were a type of ice that was so cold it would never melt. Around the late 1700’s this theory was superseded by the idea that crystals “grew” by the addition of layers. A short history of observations on the shapes of snow crystals in



Ancient China was summarized by Kepler in 1611. During 16th and 17th centuries Quartz to Sapphire crystal was used as a gems and precious stones.

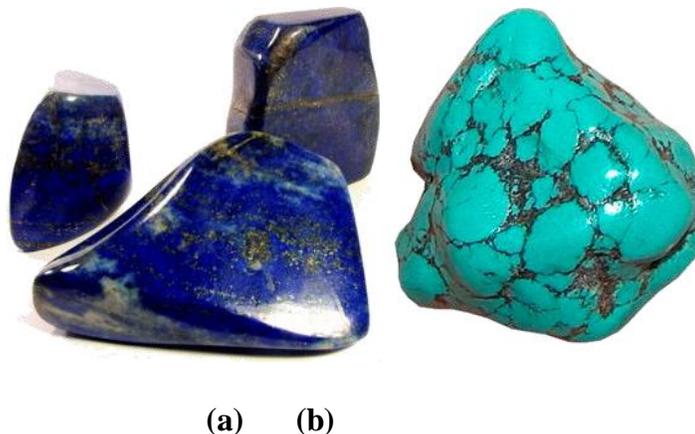


Figure 1.1 Beautiful specimens of Lapis lazuli (a) and Turquoise (b)

The first reference to crystals in Ancient Rome was reported by Pliny the Elder (I Century AD) in his “Natural History”, where he describes the windows and greenhouses of the richer inhabitants of the Roman Empire being covered by crystals of “Lapis specularis”, the Latin name for large transparent crystals of gypsum. This dehydrated form of calcium sulphate was extracted by Romans in Segobriga (Spain) because of its crystal clarity, size (up to one meter) and perfect flatness.

In general, Crystal is a small piece of a substance that has many sides and is formed when the substance turns into a solid. By terms crystal is defined as “a solid composed of atoms arranged in a periodic pattern in three dimensions”.

When we look at the human body and the structure of Quartz crystals, humans are basically liquid Quartz. Both Quartz and human body are made of silicon, water and oxygen. Both have the same atomic structure. The largest event that showed the importance of crystal was the

invention of Transistor. In the 20th century, contributions of crystal growth in the fabrication of the electronic and optical devices have shown more light on the importance of crystals.

Nowadays, crystals are produced artificially to satisfy the needs of science, technology and jewelry (Asselberghset al. 2008, Audebertet al.2003, Borduiet al. 1993). The ability to grow high quality new crystals has become an essential criterium for the competitiveness of nations. “New materials are the lifeblood of solid state research and device technology. Contrary to what many believe, new materials are not usually discovered by device engineers, solid state theorists, or research managers; they are mostly discovered by crystal chemists who are crystal growers”.

1.2 STRUCTURE OF CRYSTALS

We all knew about the natural minerals and crystals. We find them in our day today life without entering a museum. A rock and a mountain are made up of minerals, as crystalline as a lump of sugar, a bit of porcelain or a gold ring. However, only occasionally is the size of a crystal large enough to draw our attention, as is the case of these beautiful examples shown in Figure 1.2 & 1.3.

Crystal structure is characterized by groups of ions, atoms or molecules arranged in terms of some periodic repetition model, and this concept (periodicity) is easy to understand if we look at the drawings in a mosaic, or a military parade. From theseFigure 1.4 & 1.5, we can see that there is always a fraction of them that is repeated.



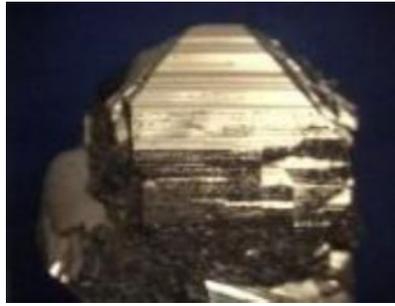


Figure1.2 Pyrite (iron sulphide)



Figure1.3 Diamond (pure carbon)

In crystals, the atoms, ions or molecules are packed in such a way that they give rise to "motifs" (a given set or unit) that are repeated over 5 Angstrom, up to the hundreds of Angstrom ($1 \text{ Angstrom} = 10^{-8} \text{ cm}$), and this repetition, in three dimensions, is known as the 'crystal lattice'.

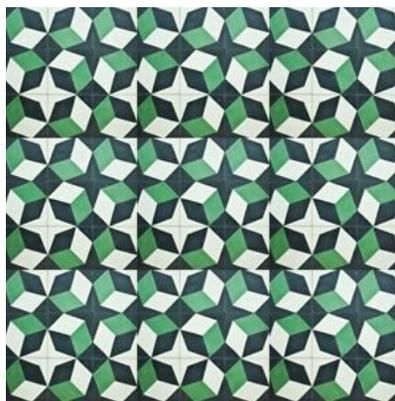


Figure1.4 Periodic repetition model in Mosaic drawing



Figure 1.5 Periodic repetition in Military parade

The unit that is repeated, by orderly shifts in three dimensions, produces the whole crystal and it is called elementary cell or unit cell. The content of the unit being repeated (atoms, molecules, ions) can also be drawn as a point (the reticular point) that represents every constituent of the unit. For example, each soldier in the Figure 1.5 could be a reticular point (Bosshardt et al. 2001).

When the repetition is broken, or it is not exact, and it will distinguish a crystal from glass, or in general, from materials called amorphous (disordered or poorly ordered) shown in Figure 1.6 & 1.7.

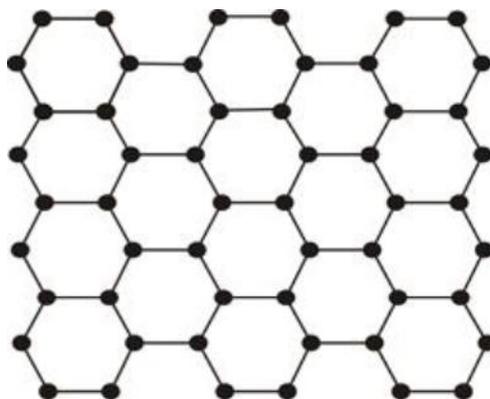


Figure 1.6 Atomic model of an ordered material (an amorphous material)

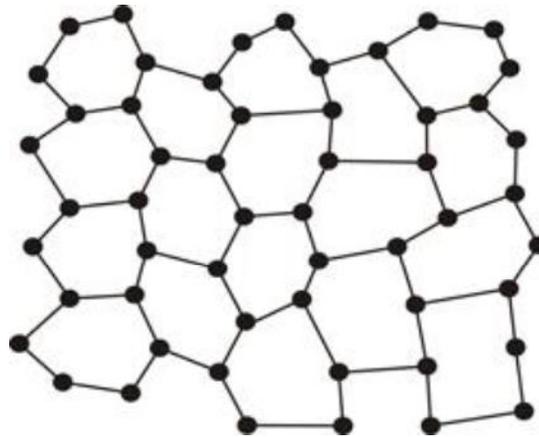


Figure 1.7 Atomic model of glass (Crystal)

1.3 SIGNIFICANCE OF SINGLE CRYSTAL

The energy of ordered atomic arrangement is lower than that of disordered one. Hence nature favours for the crystalline solids. “A microscopic piece of solid in which the regularity of atomic arrangement extends throughout is called a single crystal”. But there is an obvious limit to the extent over which the regularity of arrangement exists in the crystalline matter. The matter also exists in polycrystals. A polycrystal is the macroscopic piece of material say metal, ceramic or ionic salt; composed of an agglomerate of small single crystals separated from one another by grain boundaries. The grain boundaries are the localized regions of severe lattice disruption and dislocation. There are two principle reasons for the deliberate growth of single crystals.

- A. The presence of grain boundaries makes many physical properties of solid are more complicated.
- B. The internal symmetry of the crystal structure is maintained throughout the specimen.

1.4 EXTERNAL APPEARANCE OF CRYSTALS

The first thing we notice about a crystal is the presence of planes called faces which constitute the external boundaries of the solid. Of course, any solid, including non-crystalline glass, can be carved, molded or machined to display planar faces; examples of these can be found in any "dollar store" display of costume jewelry.

What distinguishes and defines a true crystal is that these faces develop spontaneously and naturally as the solid forms from a melt or from solution. The multiple faces invariably display certain geometrical relationships to one another, resulting in a symmetry that attracts our attention and delights the eye. Below Figure 1.8 shows the external appearance of a crystal. Figure 1.9 shows the flow chart of Seven Crystal system.

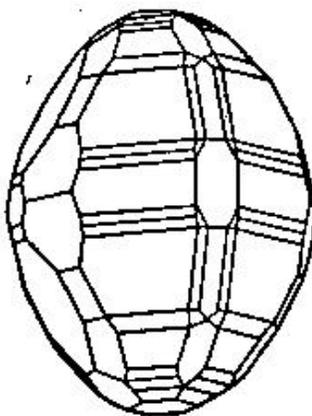


Figure 1.8 External appearance of a Crystal

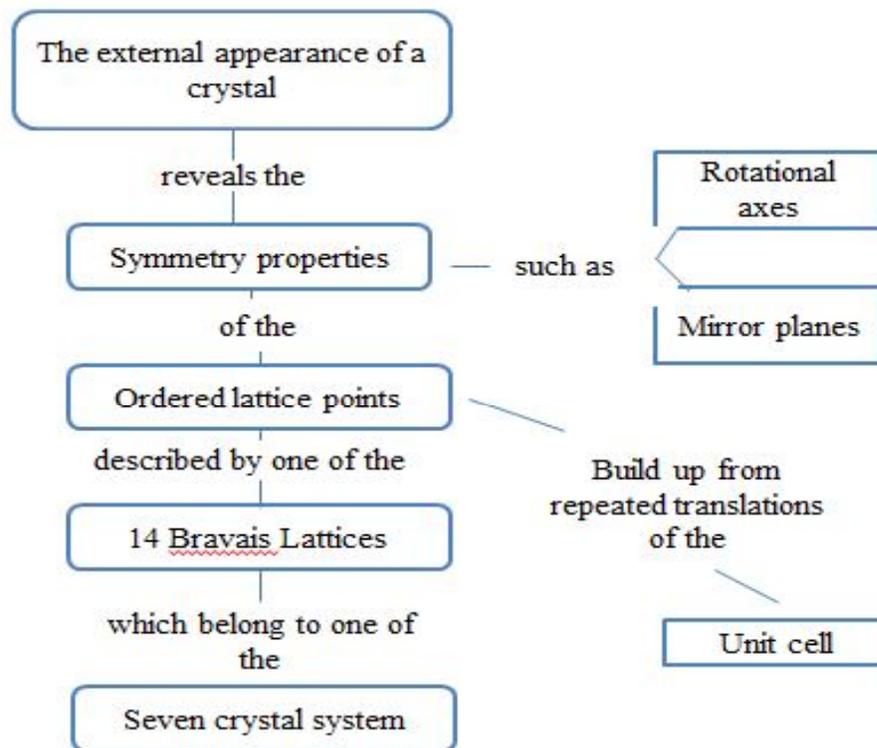


Figure 1.9 Flow chart of Seven Crystal system

1.5 EXTERNAL SYMMETRY OF CRYSTALS

The external shape of a crystal reflects the presence or absence of translation-free symmetry elements in its unit cell. While not always immediately obvious, in most well-formed crystal shapes, axis of rotation, axis of rotoinversion, center of symmetry, and mirror planes can be spotted. The symmetry observed in crystals as exhibited by their crystal faces is due to the ordered internal arrangement of atoms in a crystal structure. This arrangement of atoms in crystals is called a lattice.

Symmetry is the consistency, the repetition of something in space and/or in time, as is shown in the Figure below: a wall drawing, the petals

of flowers, the two sides of a butterfly, the succession of night and day, a piece of music, etc is shown in Figure 1.10 and Figure 1.11 (a,b,c).

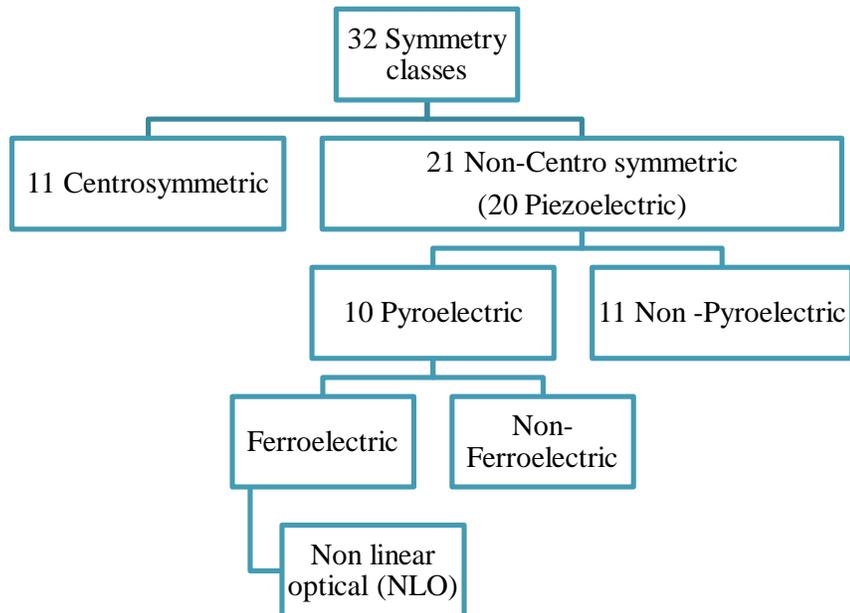


Figure 1.10 Flow chart of 32 Symmetry classes

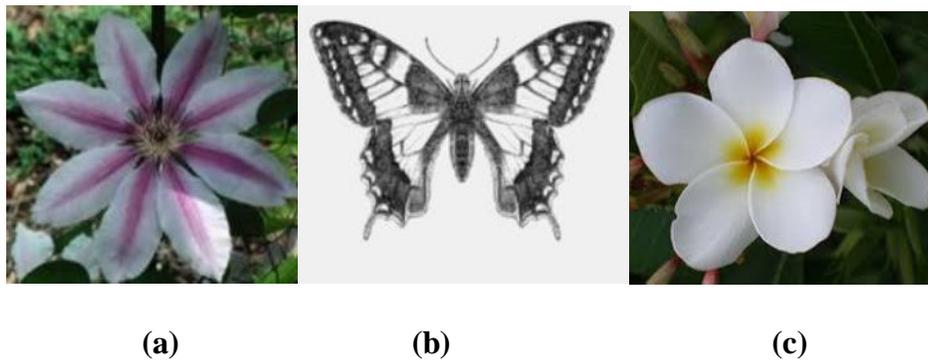


Figure 1.11 (a) A wall diagram (b) Sides of a Butterfly (c) The petals of flower

There are 32 possible combinations of symmetry operations that define the external symmetry of crystals. These 32 possible combinations result in the 32 crystal classes. These are often also referred to as the 32 point

groups. By combining the 32 crystal classes (crystallographic point groups) with the 14 Bravais lattices, we find up to 230 different ways to replicate a finite object in 3-dimensional space. These 230 ways to repeat patterns in space, which are compatible with the 32 crystal classes and with the 14 Bravais lattices, are called space groups, and represent the 230 different ways to fit the Bravais lattices to the symmetry of the objects.

$$32 \text{ crystal classes} + 14 \text{ Bravais lattices} = 230 \text{ Space groups}$$

Table 1.1 Seven Crystal System

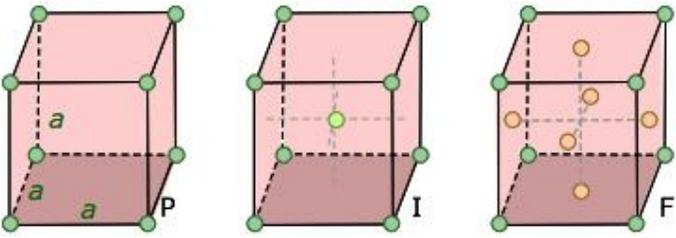
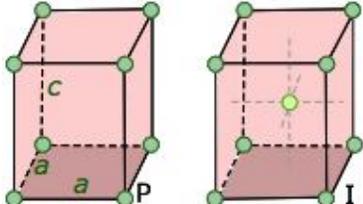
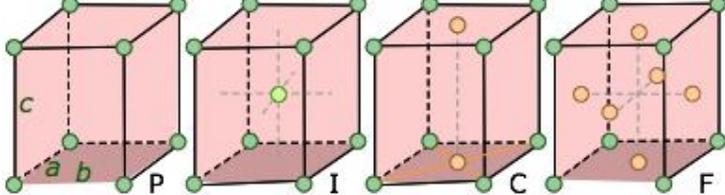
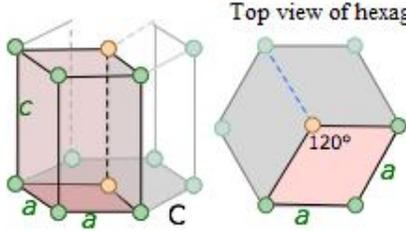
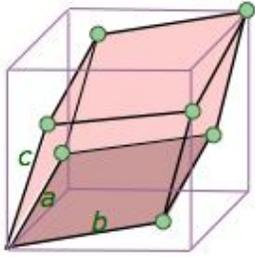
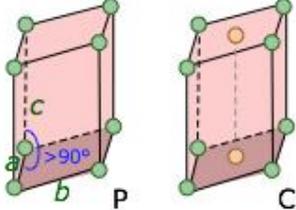
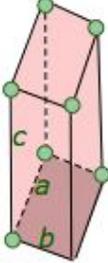
Crystal system	Bravais lattices (P = primitive, I = body-centered, F = face-centered)
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	 <p>The F cell corresponds to closest cubical packing, a very common and important structure.</p>
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	 <p>Three unequal axes at right angles. The "C" form has atoms in the two faces that cut the c-axis.</p>

Table 1.1(Continued)

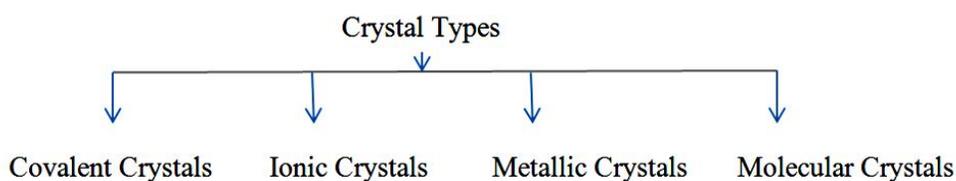
Crystal system	Bravais lattices (P = primitive, I = body-centered, F = face-centered)
Hexagonal $a = b \neq c$ $\alpha = \beta = 60^\circ,$ $\gamma = 120^\circ$	 <p>Top view of hexagon</p>
Trigonal (rhombohedral) $a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ,$	
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ,$ $\beta > 90^\circ$	
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	 <p>This is the most generalized of the crystal systems, with all lengths and angles unequal, and no right angles.</p>

Lattices can either be primitive (only one lattice point per unit cell) or non-primitive (more than one lattice point per unit cell).

If we combine the 7 crystal systems with the 2 different types of lattices, it will end up with 14 Bravais Lattices (named after Auguste Bravais who find all this out in 1850).

1.6 TYPES OF CRYSTALS

There are four types of crystals. Each type has a different type of connection, or bond, between its atoms. The type of atoms and the arrangement of bonds dictate what type of crystal is formed.



1.6.1 Covalent Crystals

Covalent crystals are crystals whose atoms are connected with covalent bonds. Covalent bonds exist where the atoms share electrons. These bonds are extremely strong and very hard to break. Because of this, the crystals themselves are also very strong and have high melting points. An example of a covalent crystal is a Diamond is shown in Figure1.12, which is one of the hardest substances known to man.



Figure1.12Diamonds - covalent crystal

1.6.2 Ionic Crystals

Ionic crystals are crystals whose atoms are held together with ionic bonds, or charged bonds. One atom is negatively charged and is attracted to other atoms in the crystal that are positively charged. They are arranged in a pattern based on the charges. These crystals are typically solid with a high melting point. An example of an ionic crystal is table salt is shown in Figure1.13.



Figure1.13 Table salt - ionic crystal

1.6.3 Molecular Crystals

Molecular crystals are crystals formed from weak bonds called hydrogen bonds. These have to do with how tiny charged particles on atoms, called electrons, are arranged between different hydrogen atoms. These bonds are very weak bond. Because of this, molecular crystals typically have lower melting points than other crystals. A familiar example is rock candy; the crystalline sugar candy on a stick is shown in Figure1.14.



Figure1.14Hydrogen bonds between sugarmolecules make rock candy

Other examples are ice crystals and dry ice, or frozen carbon dioxide. Scientists use molecular crystals to identify the shape of various microscopic proteins inside cells.

1.6.4 Metallic Crystals

Metallic crystals are crystals made of metal elements. These crystals sparkle with the lustrous sheen we think of metals having. They are extremely good conductors of heat and electricity. Copper can be extracted from copper crystals to form the copper wire used to transmit electricity in our homes. The melting point of these crystals depends on the metal used in the crystal. Gold Nuggets is the best example of Metallic Crystal shown in Figure 1.15.



Figure 1.15 Gold Nuggets - Metallic Crystals

1.7 INTRODUCTION TO CRYSTAL GROWTH

For the past five decades, crystals have been used by the physicists and engineers as the key materials for modern electronics, opto-electronics and other technical fields of application. 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.”

Crystal growth is an art of science and the subject of the growth of crystals is an interdisciplinary one which contributes many professional fields, solid state physicists, mineralogists, crystallographers, physical chemists, mathematicians, chemical engineers, metallurgists etc. Though it has been studied extensively more than 100 years, crystal growth still plays an important role in both theoretical and experimental research fields, as well as in applications (Jagannathan et al. 2007, James et al. 1975, Ravindra et al. 2008). Crystal growth plays a prominent role in the era of immense technological excellence attributing to the usefulness of many crystals in important areas of service to the humanity namely science, medicine, engineering, technology and also strategic areas of defence and space science. The solid state materials can be classified as single crystals, poly crystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. Crystals are used for devices because the charge carriers are electrons and holes which can move freely. The relevant scientific research in the field of crystal growth covers a wide spectrum of work on nucleation, growth rates, translation rates, segregation, growth interfaces, composition morphology, stability and crystalline defects (Ray 2010).

1.8 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 to crystallization. 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 (Xue & Kitamura et al. 2002).



1.9 THEORY OF NUCLEATION AND GROWTH

1.9.1 Nucleation

The formation of a new crystalline entity from a solution starts through the nucleation process. Nucleation is defined as the series of atomic or molecular processes by which the atoms or molecules of a reactant phase rearrange into a cluster of the product phase large enough as to have the ability to grow irreversibly to a macroscopically larger size. The cluster is defined as nucleus or critical nuclei.

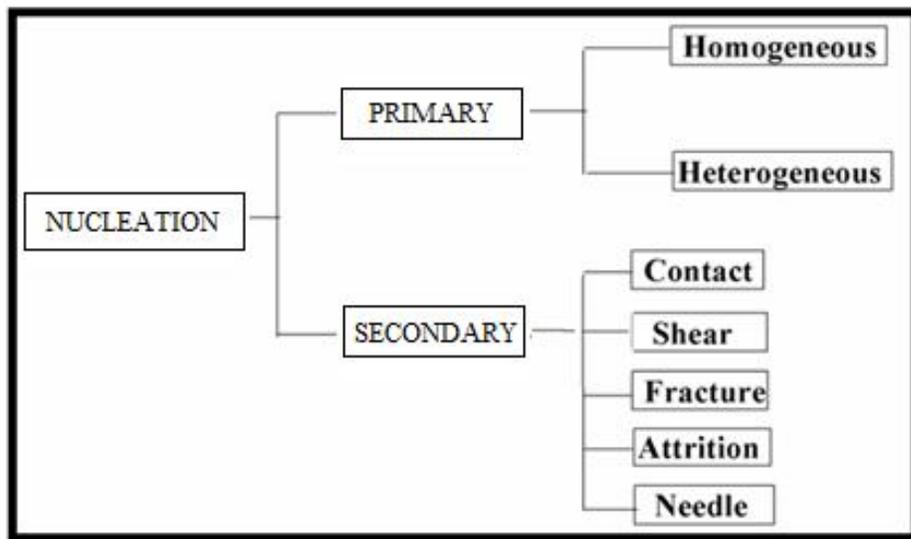


Figure 1.16 Flow chart of Nucleation

1.9.2 Heterogeneous

The new phase appears on the walls of the container, at impurity particles, etc. is shown in Figure 1.17.

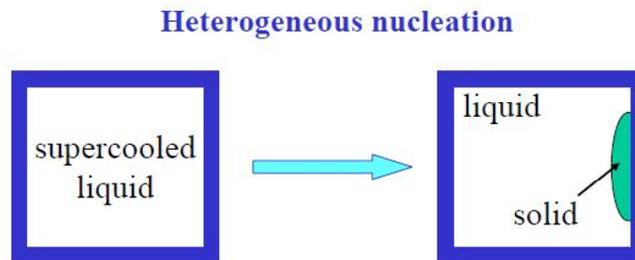


Figure 1.17 Heterogenous Nucleation

1.9.3 Homogeneous

Solid nuclei spontaneously appear within the undercooled phase. Let's consider solidification of a liquid phase undercooled below the melting temperature as a simple example of a phase transformation shown in Figure 1.18.

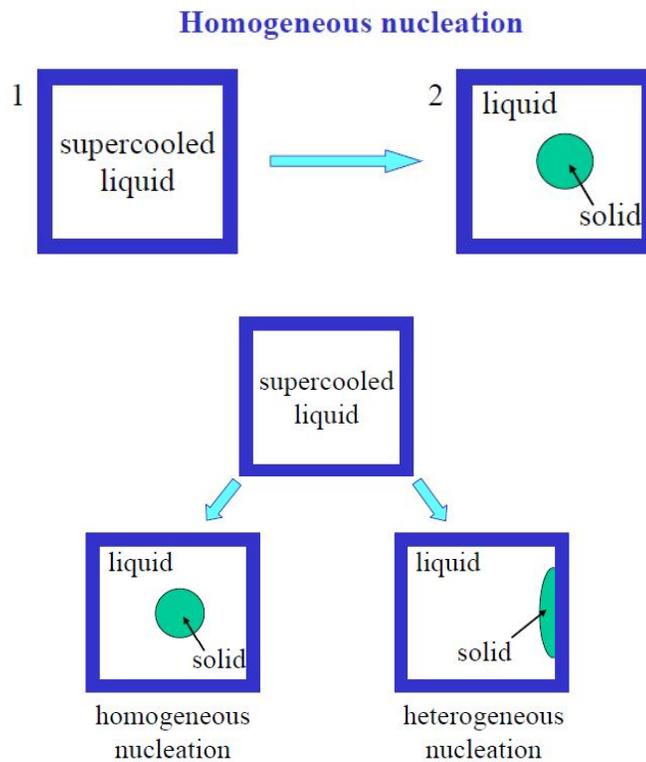


Figure 1.18 Homogenous Nucleation

1.9.4 Growth Mechanisms

The next step after the nucleation is growth. Atomically rough (diffuse) interfaces migrate by continuous growth, whereas atomically flat interfaces migrate by ledge formation and lateral growth is shown in Figure 1.19.

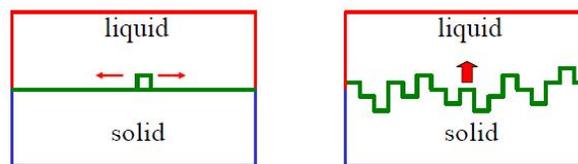


Figure 1.19 Ledge formation and lateral growth

The rate of the continuous growth (typical for metals) is typically controlled by heat transfer to the interfacial region for pure materials and by solute diffusion for alloys. Growth in the case of atomically flat interfaces can proceed from existing interfacial steps (e.g. due to the screw dislocations or twin boundaries) or by surface nucleation and lateral growth of 2D islands.

1.9.5 Supersaturation

The driving force needed for the nucleation and growth of a crystal is referred to as supersaturation and is defined as the difference in chemical potential between a molecule in solution and that in the bulk of the crystal phase:

$$\Delta\mu = \mu_s - \mu_c \quad (1.1)$$

Where μ_s is the chemical potential of a molecule in solution and μ_c is the chemical potential of the molecule in the bulk crystal (Zhou 1999). Following thermodynamics Equation (1.1) can be expressed as

$$\Delta\mu = kT \ln S \quad (1.2)$$

Where k is the Boltzmann constant, T is the absolute temperature, and S is the supersaturation ratio. When $\Delta\mu > 0$ the solution is said to be supersaturated the supersaturation ratio will change depending on the system considered (i.e., gas/solid, solution/solid, melt/solid). For nucleation and growth from solutions it takes the following form:

$$S = \frac{\pi a_i^{n_i}}{\pi a_{i,e}^{n_i}} \quad (1.3)$$

Where n_i is the number of i^{th} ions in the molecule of the crystal, and a_i and $a_{i,e}$ the actual and equilibrium activities of the i molecule in the crystal.

1.9.6 Energetics

According to nucleation theory, the work necessary to form a cluster of n number of molecules is the difference between the free energy of the system in its final and initial states (Brandle 1979, Brice 1972) plus a term related to the formation of an interface between nucleus and solution. This can be expressed by (assuming a spherical nucleus):

$$\Delta GT = -n\Delta\mu + 4\pi \cdot r^2\sigma \quad (1.4)$$

Where r is the radius of the nucleus and σ is the surface free energy. If each molecule in the crystal occupies a volume V , then each nucleus will contain $(4/3)\pi \cdot r^3/V$ molecules. Equation (1.4) will then take the following form:

$$\Delta GT = -(4/3)\pi \cdot (r^3/V)\Delta\mu + 4\pi \cdot r^2\sigma \quad (1.5)$$



Figure 1.17 (a) shows a plot of ΔG_T as a function of r ; it can be seen how the function reaches a maximum, which represents the energetic barrier that needs to be surpassed to achieve nucleation (ΔG^*). The value of r at this maximum (r^*) is defined as the critical radius or nucleus size (Chernov 1984, Davey 1976). Its value is defined by

$$r^* = 2\sigma \cdot V/kT \ln S \quad (1.6)$$

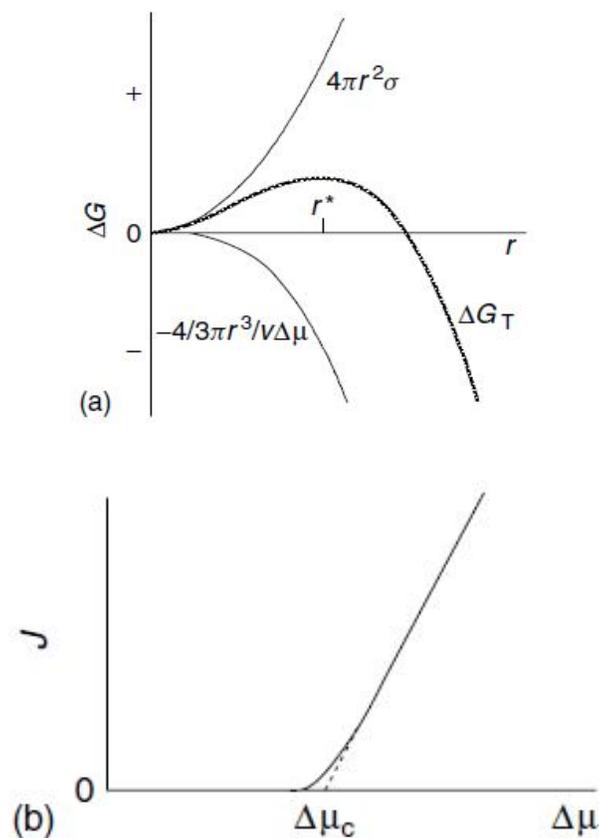


Figure 1.20 (a) Total free energy versus cluster size (b) Nucleation rate as a function of supersaturation (Showing the critical supersaturation)

It has been proved that the value of r^* decreases (as well as that of ΔG^*) as the supersaturation increases (Magesh et al. 2011), meaning that the

probability of having nucleation in a given system will be higher, the higher and the supersaturation.

1.9.7 Nucleation Rate

The rate of nucleation (i.e., the number of nuclei formed per unit time per unit volume) can be expressed by an Arrhenius-type Equation (1.5).

$$J = A \exp (-\Delta G^*/kT) \quad (1.7)$$

where A also depends on supersaturation. A typical plot of J as a function of supersaturation (S) is depicted in Figure 1.17 (b). It can be seen in this plot that the nucleation rate is virtually zero until a critical value of supersaturation is achieved, after which the rate increases exponentially. This critical supersaturation ($\Delta\mu_c$) defines the so-called metastable zone where crystal growth can proceed without concomitant nucleation taking place.

1.9.8 Heterogeneous and Secondary Nucleation

Equations (1.5) and (1.6) shows that both ΔG^* and r^* depend heavily on the surface free energy (σ), so any process that modifies this value will have an effect on the possible viability of the nucleation process. It has been proved that in the presence of a foreign substrate the decrease in the value of σ therefore reduces the values of ΔG^* and r^* at constant supersaturation (Zhanget al. 2007) that is, making nucleation more favorable. A decrease in σ will also decrease the value of the critical supersaturation ($\Delta\mu_c$), since the nucleation rate is also dependent on the surface energy Equation (1.7). This will make heterogeneous nucleation more viable than homogeneous nucleation at low supersaturation conditions. The reduction of the surface energy will be the highest when the best match between the substrate and the crystallizing substance is achieved. This



situation is created, of course, when both the substrate and the crystallizing substance are the same, referred to as secondary nucleation. This mechanism will be more favorable than both heterogeneous and homogeneous nucleation and thus produced at lower supersaturation.

1.9.9 Induction Time

Induction time is defined as the amount of time elapsed between the achievement of a supersaturated solution and the observation of crystals. Its value will thus depend on the setting of $t = 0$ and the technique used to detect the formation of crystals. The induction period can be influenced by factors such as supersaturation, agitation, presence of impurities, viscosity, and so on. Mullin (Ruiz 2008) defined the induction time as

$$t_i = t_r + t_n + t_g \quad (1.8)$$

The induction time is separated into three periods: t_r is the relaxation time, required for the systems to achieve a quasi-steady-state distribution of molecular clusters; t_n is the time required for the formation of a nucleus; and t_g is the time required for the nucleus to grow to a detectable size.

1.10 CRYSTAL GROWTH

Crystal growth is the series of processes by which an atom or a molecule is incorporated into the surface of a crystal, causing an increase in size. These different processes can be summarized into four steps (Onitsch 1947) illustrated in Figure 1.21.

- 1) Transport of atoms through solution
- 2) Attachment of atoms to the surface
- 3) Movement of atoms on the surface



4) Attachment of atoms to edges and kinks.

The first process is the so-called transport process, whereas 2–4 are referred to as surface processes (and may involve several substeps). Since these different steps normally occur in series, the slowest process will control the overall crystal growth.

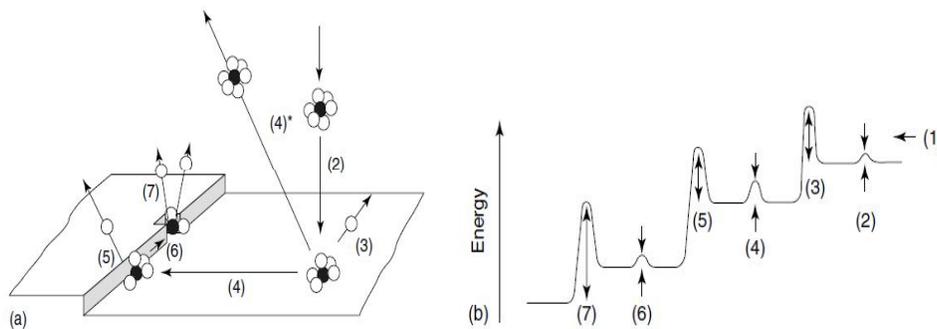


Figure 1.21 Schematic representation of processes involved in the crystal growth

(1) Transport of solute to a position near the crystal surface; (2) diffusion through boundary layer; (3) adsorption onto crystal surface; (4) diffusion over the surface; (4*) desorption from the surface; (5) attachment to a step or edge; (6) diffusion along the step or edge; (7) Incorporation into kink site or step vacancy. (b) Associated energy changes for the processes depicted in (a).

Advancement in the development of crystal growth is highly demanded in the fields of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries (Franken et al. 1961, Huang et al. 1997). The utility of crystals has been extended from the bounds of ornaments to several useful applications in optical, electrical and optoelectronic devices. This thesis presents the possibility of using organic, inorganic and semi organic materials for the fabrication of optoelectronic devices and biomedical applications.

1.10.1 Crystal Growth Methods

1.10.1.1 Single crystal growth

Solid phase must be created under the physical conditions close to the thermodynamic equilibrium (stacking “atom-by-atom” on the seed crystal surface)

Classification by Wilke:

- 1) From the dispersion phase (solutions, gases...)
- 2) From the own melt
- 3) From the solid phase

1.10.1.2 Single-crystal growth from the dispersion phase

- From the gas phase
 - 1) Sublimation
 - 2) Chemical reaction (e.g. “hot wire” method)
- From the (low temperature) solutions
 - 1) Evaporation (isothermal)
 - 2) Cooling (speed growth)
 - 3) Gradient method
 - 4) Chemical reaction
- Hydrothermal
- From the melt solutions (flux)

1.10.1.3 Single-crystal growth from the own melt



- Crucible methods
 - 1) Stationary crucible methods
 - 2) Czochralski method
 - 3) Bridgman-Stock Barger method
 - 4) Stepanov method
 - 5) Zonal melting
- Methods without crucible
 - 1) Verneuil method
 - 2) Cool crucible method

1.10.1.4 Single-crystal growth from the solid phase

- Recrystallization
 - 1) Mechanical
 - 2) By annealing

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. Accordingly the basic growth methods are

1. Growth from melt
2. Growth from vapour
3. Growth from solution

In general, the crystallization process takes place by three steps:



- (i) Achievement of supersaturation or super cooling
- (ii) Formation of crystal nuclei and
- iii) Growth of crystal.

1.11 GROWTH FROM MELT

Melt growth is the process of crystallization by fusion and resolidification of the pure material. In this technique, apart from possible contamination from crucible materials and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods. Mainly, for the latter reason, melt growth is commercially the most important method of crystal growth. The preferential role of the electrochemical process responsible for the change in composition of the crystals when they grow in melt in an applied field has been studied (Willey G.R. et al. 1985). The growth from melt can further be sub-grouped into various techniques listed below.

- i) Bridgman technique
- ii) Czochralski technique
- iii) Zone melting technique
- iv) Verneuil technique
- v) Heat exchanger method
- vi) Skull melting and
- vii) Shaped crystal growth



The major practical factors to be considered during growth of crystals from melt are:(a) volatility, (b) the chemical reactivity and (c) the melting point.

1.11.1 Bridgman Method

The original techniques after which the methods are usually named (Bridgman 1925) involved a crucible which was lowered through a furnace so that freezing started at the lowest point in the crucible and the solidification face moved slowly up the crucible.

Advantages:

- Low-cost, with the added advantage that the melt temperature increases with distance from the solid-liquid interface and the system is therefore density-stable and less prone to convection effects than Czochralski technique, though radial gradients ensure that convection cannot be eliminated entirely.

Disadvantage:

- 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 the liquid-solid interface shape are well controlled.



- If the solid has a lower density than the melt the crucible can burst. If the solid has a greater density than the melt, parts of the crystal will not have the same dimensions as the crucible.

These problems can be overcome by the use of side arms on the crucible, but this sacrifices the essential simplicity of the method. Mechanically, Bridgman systems are usually fairly simple. The necessary movements can be produced by using wires wound on to or from drums or by lead screws of the types used in machine tools (Yariv 1975). Hydraulic systems have advantage of minimal vibration. From the point of view of vibration it is better to move the furnace than the crystal. The most obvious desirable characteristic of a crucible is that its presence should not contaminate the crystals. Graphite is a useful crucible material for some covalently-bound and metallic materials. The crucible should have a smaller coefficient of thermal expansion than the crystal.

Bridgman method relied on random nucleation to produce a single crystal which then propagated to form just one crystal including the whole frozen charge. The formation of just one nucleus is more probable if the super cooled volume is small. Thus traditionally crucibles have tapered tips. To ensure that only one crystal propagates, various shapes are used. However, it is now common to use a seed crystal. It is easier to maintain the desired thermal configuration if the crucible does not conduct much heat. In order to obtain high crystalline perfection, a small radial temperature gradient is needed. The effects of the crucible are somewhat complex, but if the crucible has a higher thermal conductivity than the crystal, a thin wall is desirable. The advantage of having transparent furnace system is that the growth can be monitored continuously. Observation of the interface between the crystal and the melt during the growth is a crucial parameter and can effectively determine the quality of the final crystal obtained. The shape influences the



crystalline perfection and compositional homogeneity. A crystal that grows with a flat interface has minimal thermal stresses because the thermal changes are in one dimension only, Dutta et al observed that GaSb crystals grown with a flat melt-solid interface exhibited very low dislocation densities due to the reduction of thermal stresses at the interface. The convex interface is associated with higher lowering rate. The container should not react with the melt.

1.11.2 Czochralski Method

Crystal pulling is also the method which is likely to produce the highest quality crystal in the sense of the most perfect and homogeneous. At least half of all the high-quality crystals grown are pulled. Crystal pulling is applicable only to materials which melt congruently or nearly congruently, i.e. the compositions of the solid and the melt in equilibrium with it cannot differ much. Crystal is usually faster than Bridgman growth so that less contamination occurs. The melt is raised to a temperature a few degrees above the melting point (Zyss 1994).

In a well-designed system, temperature differences both radially and vertically are fairly small, so that the bulk of the melt is within say $\pm 20^{\circ}\text{C}$ of its mean temperature, which for a high thermal conductivity material will be about 25°C above the melting point. For a low-conductivity material the mean melt temperature will be nearer to the melting point. The seed crystal, rotating slowly, is brought slowly into contact with the melt surface, and the lowering is stopped. If the melt temperature was its optimum value, the seed melts slowly and at a decreasing rate so that the seed remains in contact with the melt.

If the seed does not remain in contact, the melt temperature was too high. If visible crystal growth occurs, the temperature was too low and must



be increased until all the grown material and bit of the seed have melted. After a short pause typically 1 to 3 minutes pulling is commenced at a slow rate, say half the final value. New crystal should grow with a diameter which is slightly less than the seed diameter. The growth rate and rotation rates are increased to their final values. The diameter of the growing crystal should decrease. If a dislocation-free crystal is required, a long narrow neck is grown. The length of this neck varies with the material and the growth direction, but 5 to 10 times the seed diameter is a usual length.

After completion of the neck, the melt temperature is lowered slowly. The diameter of the crystal increases. As determined by experience the lowering of the melt temperature is stopped and after a short time the crystal should attain its final diameter. Growth at a constant diameter is maintained until the desired length of crystal has grown. Growth is then terminated. In some cases, this is done by sharply increasing the pulling rate so that the crystal breaks contact with the melt. A better procedure is to increase the melt temperature so that the crystal diameter decreases fairly slowly to zero. After growth has been terminated, the system should be cooled slowly (Petrov et al. 1969).

1.11.3 Kyropoulos Growth

Kyropoulos method is widely used. The basic system resembles that used for Czochralski growth, but the mode of use is one in which the seed is brought into contact with the melt as in the Czochralski method but is not raised much during growth. The Czochralski process lends itself to produce crystals with length-to-diameter ratios which greatly exceed unity and the diameters of the crystals rarely exceed half the crucible diameter. However, there are many applications for which a large diameter is more important than great length. Part of the seed is allowed to melt and a short neck is grown.



After this, however, the vertical motion of the seed is stopped and growth proceeds by decreasing the power input to the melt (Kleinman 1962).

The method looks economically attractive simple inexpensive apparatus and minimal operator attentions are needed. In Czochralski system many impurities are lost from the melt by evaporation. The restricted free melt surface in a Kyropoulos system prevents this happening to any great extent. Hence the Kyropoulos method is only really attractive for a restricted range of materials destined for a limited range of uses. The major use of the method is for alkali halides to make optical components, mostly for long wavelength applications.

1.12 GROWTH FROM VAPOUR

Vapour growth techniques can be adopted for the growth of materials which lack a suitable solvent and sublime before melting at normal pressure. Vapour growth methods have been employed to produce bulk crystals and to prepare thin layers on crystals with a high degree of purity (Hari Singh Nalwa et al. 1997). Growth from vapour phase may generally be subdivided in to

- 1) Physical vapour transport (PVT)
- 2) Chemical vapour transport (CVT)

1.12.1 Physical Vapour Transport (PVT)

In PVT technique the crystal is grown from its own vapours and this method does not involve any extraneous compound formation or reaction. The PVT methods are limited to materials having an appreciable vapour pressure at attainable temperatures. There are two types of techniques employed in physical vapour transport processi) sublimation, (ii) condensation and(iii) sputtering.



The first method involves sublimation of the charge at the high temperature end of the furnace, followed by the condensation at the colder end (Jainet al. 1981, Kurtz 1968). Sputtering techniques are preferred to low vapour-pressure substances and mainly this method has been used to prepare thin films rather than discrete crystals.

Advantage

- 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.

1.12.2 Chemical Vapour Transport (CVT)

Chemical vapour transport technique involves a chemical reaction between the source material to be crystallized and a transporting agent. 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 (Jiang & Fang 1999, Li et al. 1997). 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 vapour growth is in the production of thin layer by chemical vapour deposition.

1.13 GROWTH FROM SOLUTION

Growth from solution is more widely used than growth from the melt or from the vapour phase. This method is widely used to grow the crystals, which have high solubility and have variation in solubility with temperature (Manoj et al. 2011, Dongfeng Xue et al. 2003). The method of



crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals.

The growth of materials by low temperature solution growth involves weeks, months and sometimes years. Much attention has been made to understand the growth mechanism of the process. Though the technology of crystal growth 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 mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermo dynamical parameters of the process such as temperature, pressure and solvent concentration. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control to an accuracy of $\pm 0.01^{\circ}\text{C}$. Due to the precise temperature control, supersaturation can be very accurately controlled. Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low temperature solution method. Also efficient stirring of solutions reduces fluctuations to a minimum (Xu & Xue 2008).

The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance grown by variation of growth conditions or of solvents. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and on removal from the apparatus. Crystal growth from solution is a very important process used in many applications from laboratory to industry. Materials which decompose on heating or which exhibit structural transformations while cooling from the melting point can be



grown from the solution growth method, if suitable solvents are available. This method is more widely used to grow bulk crystals (Yoshimura et al. 1999, Socrates 2001).

Growth from solution, however, is used more broadly, compared with growth from the melt technique; it requires lower temperatures and can lead to lower density of lattice defects. The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of crystal growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. Among the methods of growing single crystals, slow evaporation solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many experimental modifications and refinements, the process of solution growth now yields good quality bulk crystals for a variety of applications. The advantages of solution growth methods are as follows,

- i. The growth process occurs near the ambient temperature.
- ii. Growth apparatus is relatively simple and cheap.
- iii. The concentration of structural imperfections in solution grown crystals is relatively low.
- iv. Sometimes, impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal which changes the crystal habit.
- v. Low temperature introduces small thermal stress in the grown crystals.



- vi. The crystals obtained usually have well-developed faces which enable to investigate crystal growth process including in-situ observations and capture impurities.

Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. There are two methods in solution growth depending on the solvents and the solubility of the solute. They are

1. High temperature solution growth
2. Low temperature solution growth

1.13.1 High Temperature Solution Growth

This technique can be applied to materials with incongruent melting point. By suitable choice of growth parameters mixed crystal of solid solutions can be grown. The growth takes place well below the melting point (Rumi & Perry2010)of the solute. High temperature solution growth has two methods

- Gel growth and
- Hydrothermal growth.

In high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturated may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region. The high temperature crystal growth can be divided into two major categories:



1. Growth from single component system.
2. 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 materials dissolve. This temperature is maintained for a 'soak' period of several hours and then the temperature is lowered very slowly.

1.13.1.1 Hydrothermal growth

Hydrothermal implies conditions of high pressure as well as high temperature. Substances like calcite, quartz is considered to be insoluble in water but at high temperature and pressure, these substances are soluble. This method of crystal growth at high temperature and pressure is known as hydrothermal method (Walker Buehler 1950). 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.

1.13.1.2 Gel growth

It is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a twocomponent system of a semisolid 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 (Willard 1986). Crystals with dimensions of several milli metres can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

1.13.2 Low Temperature Solution Growth

Low temperature solution growth is found to be the best among the crystal growth methods due to its versatility and simplicity. Crystals are grown close to equilibrium condition and hence they are obtained with high perfection. Many crystals can be grown by low temperature solution growth. Advantages of low temperature solution growths are growth is possible at temperature far below the melting point of the material, so a lower crystal growth temperature leads to defects free crystals (Zernike & Midwinter 1973). The contamination of the desired material by oxidation is also reduced. Disadvantages of this method is small percentages of impurities in the solvent may produce high concentrations in the crystal. Atoms or molecules of the solvent itself may become entrapped within the rapidly growing crystal. Low temperature solution growth is the most widely used method for the growth of the large size single crystals and it demands that the materials must crystallize from solution with prismatic morphology. Generally, the method is seeded growth from a saturated solution. The driving force i.e. the super saturation is achieved either by temperature lowering or solvent evaporation. This method is widely used to grow bulk crystals, which have appreciable solubility with temperature (Wooster 1953, Shen 2003). Many modifications and refinements have been made in the solution growth process, yielding good quality crystals for variety of applications. Though the rate of crystallization is relatively low when compared with the other growth methods, crystals grown from solution at and around room temperature the structural



imperfections in the solution grown crystals are relatively very low (Bhagavannarayana et al. 2010). Low temperature solution growth can be carried out through any one of the following methods: slow-cooling method and slow evaporation method.

1.13.2.1 Slow cooling method

This is good for solute-solvent systems which are less than moderately soluble and the solvent's boiling point is less than 100°C. Prepare a saturated solution of the compound where the solvent is heated to just its boiling point or a just below it. Transfer the solution to a clean large test tube and stopper. Transfer the test tube to a Dewar flask in which hot water (heated to a temperature of a couple of degrees below the solvent boiling point). The water level should exceed the solvent level in the test tube, but should not exceed the height of the test tube. Stopper the Dewar flask with a cork stopper and let the vessel sit for a week. A more elaborate version of this involves a thermostated oven rather than a Dewar flask (Chen 1989).

1.13.2.2 Slow evaporation method

As far as the apparatus is concerned, slow cooling and slow evaporation methods are similar to each other. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. The basic apparatus used for the solution growth technique is shown in Figure 1.22. If the solvent is non-toxic 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 mm. The evaporation technique has an advantage viz. 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 very low temperature coefficient of solubility. But the



crystals tend to be less pure than the crystals produced by slow cooling technique because, as the size of the crystal increases, more impurities find place in the crystal faces. Evaporation of solvent from the surface of the solution produces high local supersaturation and formation of unwanted nuclei. Small crystals are also formed on the walls of the vessel near the surface of the liquid from the material left after evaporation. These tiny crystals fall into the solution and hinder the growth of the crystal. Another disadvantage lies in controlling the rate of evaporation (Chemla & Zyss 1997). A variable rate of evaporation may affect the quality of the crystal. In spite of all these disadvantages, this is a simple and convenient method for growing single crystals of large size.

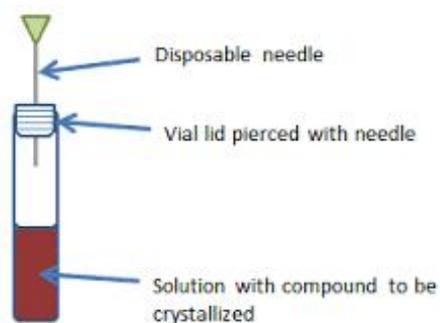


Figure 1.22 Slow evaporation technique

Advantages of low temperature solution growth

- a. Due to the precise temperature control to an accuracy of $\pm 0.01^\circ\text{C}$, the supersaturation can be very accurately controlled.
- b. Well suited for materials which suffer from decomposition in the melt or in the solid at high temperatures.
- c. Well suited to those materials which undergo structural transformations while cooling from the melting point and as a matter.

- d. Variety of different morphologies and polymorphic forms of the same substance can be crystallized by variations of growth conditions or of solvent.
- e. Reduces the possibility of major thermal shock to the crystal both during growth and on removal from the apparatus.

1.14 OPTIMIZING SOLUTION GROWTH

The growth of good quality single crystals by slow evaporation technique require the optimized conditions and the same may be achieved with the help of the following norms:

- (i) Material purification,
- (ii) Solvent selection,
- (iii) Solubility,
- (iv) Solution preparation,
- (v) Seed preparation,
- (vi) Agitation,
- (vii) Crystal habit and
- (viii) Cooling rate

1.14.1 Material Purification

An essential prerequisite for success in crystal growth is the availability of the highest purity material. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects(Laudise et al. 1970). Sometimes impurities may slow down the crystallization process by being



adsorbed on the growing face of the crystal which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

1.14.2 Solvent Selection

The water is almost exclusively used as a solvent for the growth of all inorganic crystals from solution. This was because of water can dissolve a large number of chemical compounds, readily available, cheap, odorless and harmless. For these reasons water are used as a solvent even for the crystallization of organic compounds. For a variety of reasons (like insoluble in water, organic materials, etc.) other solvents were also being used. There were several hundred organic liquids that are capable of acting as crystallization solvents, but outside the laboratory the list can be shortened to a few dozen selected from the following groups: ethyl acetate, acetic acid, ethanol methanol, ketones, ethers, chloroform, benzene, toluene, dimethylformamide and dimethyl sulfoxide (George H Stout & Lyle H Jensen 1989).

A mixture of two or more solvents will occasionally be found to possess the best properties for a particular crystallization purpose. A second liquid was sometimes added to a solution to increase or reduce the solubility of the solute, to increase the growth rate. Some of the key points that should be considered while choosing a solvent for a crystal growth are,

1. The solute to be crystallized should be readily soluble in the solvent.
2. The solute should also be quickly deposited from a solution in the desired crystalline form while cooling, evaporation, salting-out with an additive, etc.



3. Solvents may be classified as polar and non-polar; polar means the liquids which have high dielectric constants, e.g. water, acids, alcohols, and the non-polar refer to liquids of low dielectric constant, e.g. aromatic hydrocarbons.
4. A non-polar solute is usually more soluble in a non-polar solvent than in a polar solvent.
5. The close chemical similarity between solute and solvent should be avoided, because their mutual solubility is high in all probabilities, and crystallization may be difficult or uneconomical and the crystal habit can be changed by changing the solvent based on the nature of their intermolecular bonding interactions of solvents may be classified as,
 - a. Polar protic
 - b. Dipolar aprotic and
 - c. Non-polar aprotic

Water, methanol, acetic acid are some examples of polar protic solvents, in which molecules interact by forming strong hydrogen bonds. In order to dissolve, the solute must break these bonds and replace them with bonds of similar strength. To have a reasonable solubility, the solute must be capable of forming hydrogen bonds, either because the solute itself was hydrogen bonded or because it was sufficiently basic to accept a donated hydrogen atom to form a hydrogen bond. If the solute was aprotic and not basic, it cannot form strong bonds with the solvent molecules and will have a very low solubility.



1.14.3 Solubility

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and lower solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure (Tarasov 1981). Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

Low temperature solution growth is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process. The solubility test at various temperatures is essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process.

The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A sample of the clear supernatant liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analyzed. By repeating the above procedure, for different temperatures, the solubility curve can be plotted. Solubility of most substances increases with temperature.



1.14.4 Solution Preparation

Preparation of solution to grow the desired crystals by solution growth technique is an important stage of crystal growth. The solution is saturated as per the solubility data obtained from the solubility diagram (accurate solubility-temperature data). The saturated solution is filtered using the filter paper. The filtered solution is transferred into the growth beaker and placed in the Constant Temperature Bath (CTB). The desired supersaturation required is obtained by just lowering the temperature. Extreme care is to be taken to avoid under saturation, which results in the dissolution of seed crystal. Similarly, high supersaturation is also to be avoided to prevent the formation of spurious nucleation. The growth vessel is hermetically sealed to avoid the evaporation of the solvent. The solution is tested for saturation by suspending small test seed crystal in the solution. If the system is not in equilibrium, the seed crystal either dissolves or the solute will crystallize on the seed. By adjusting the temperature, the necessary equilibrium condition is achieved and the test seed crystal is removed and a fresh seed crystal is introduced for crystal growth (Madhavan et al. 2006).

1.14.5 Seed Preparation

Slow evaporation method was used to prepare the seed crystals. Using the solubility data of the chosen solute, a saturated solution was made at the desired temperature. Slow evaporation of a saturated solution was allowed to take place in a controlled temperature and clean surrounding. During this process, the surface of the seed inevitably was getting damaged. One can overcome this problem by dissolving the deformed surface layers of the seed crystal, before commencing the growth. Seeds of excellent quality with high transparency, low visible defects and free from inclusion and imperfection are selected for growth. Defects present in the seed crystal



propagate into the bulk crystal that decreases the quality of the crystal. Hence, seed crystals were prepared and selected with utmost care.

1.14.6 Agitation

To have a regular and even growth, the level of supersaturation has to be maintained equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. Moreover, the concentration gradients that exist in the growth vessels at different faces of the crystal may cause fluctuations in supersaturation, seriously affecting the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the metastable zone width, resulting in spurious nucleation. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.

1.14.7 Crystal Habit

Mostly, all crystals grow approximately equivalent rates in all dimensions. These imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystal grows with a bulk habit. 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. In the crystals, which grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect (Muller 2004). Needle like crystals have very limited applications and plate like crystals need to be favorably oriented.



Changes of habit in such crystals, which naturally grow as needles or plates can be achieved by any one of the following ways:

- (i) changing the temperature of growth
- (ii) changing the pH of the solution
- (iii) adding a habit modifying agent and
- (iv) changing the solvent

Achievement in this area is of great industrial importance where such morphological changes are induced during crystallization to yield crystal with better perfection and packing characteristics.

1.14.8 Cooling Rate

To obtain the required supersaturation, a driving force for the growth of crystal, the temperature of the growth solution is lowered. The cooling rate is to be employed according to the growth rate of the crystals. A large cooling rate changes the solubility beyond metastable limit and fluctuations in the supersaturation may encourage inclusions. A proper balance between temperature lowering rate and growth rate will yield good quality crystals.

