CHAPTER 1

INTRODUCTION TO CRYSTAL GROWTH METHODS
WITH EMPHASIS ON LOW TEMPERATURE SOLUTION GROWTH TECHNIQUE

1.1 INTRODUCTION

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications (Brice 1986, Nalwa and Miyata 1997). Atomic arrays that are periodic in three dimensions, with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly-crystalline material and extra effort is justified because of the outstanding advantages of single crystals (Laudise 1970). The reason for growing single crystals is, many physical properties of solids are obscured or complicated by the effect of grain boundaries. The chief advantages are the anisotropy, uniformity of composition and the
absence of boundaries between individual grains, which are inevitably present in polycrystalline materials. The strong influence of single crystals in the present day technology is evident from the recent advancements in the above mentioned fields. Hence, in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research.

Nonlinear optical crystals are very important for laser frequency conversion (Kurtz 1968). Potassium dihydrogen phosphate (KDP) is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also KDP has a high laser damage threshold. Potassium titanyl phosphate (KTP) is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd:YAG laser. It has high optical nonlinearity, large temperature and angular allowance and it is non hygroscopic and mechanically hard. The method of growing crystals varies widely, it is mainly dictated by the characteristics of the material and its size (Buckley 1951 and Mullin 1976). In recent years there has been considerable progress in the development of coherent UV sources based on non-linear optical processes. The demand for nonlinear optical crystals with superior properties is increasing due to quantum jump in the design of nonlinear optical devices with higher performance. With the progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at a rapid pace (Baumert et al 1987, Chemla and Zyss 1987, Gunter et al 1987 and Warren 1990). To enable a material to be potentially useful for NLO applications, the material should be available in bulk single crystal form (Bailey 1991). And so, crystal growth of new nonlinear optical materials and investigation into their properties have become most indispensable and efficacious disciplines in the field of materials science and engineering. The rapid development of optical
communication system has led to a demand for Nonlinear Optical (NLO) materials of high performance for use as components in optical devices. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers. The search for new materials has identified novel semiorganic systems of considerable potential and high performance. There are three major stages involved in this research. The first is the production of pure materials and improved equipment associated with the preparation of these materials. The second is the production of single crystals first in the laboratory and then extending it to commercial production. The third is the characterization and utilization of these crystals in devices. In this section, various methods of crystal growth with emphasis on low temperature solution growth technique are described. The solvent to be chosen to grow good quality crystals from solution, the effect of supersaturation and pH value of the solution is also discussed.

1.2 METHODS OF CRYSTAL GROWTH

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. 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 categories as follows,

Solid Growth   -   Solid-to-Solid phase transformation
Liquid Growth  -   Liquid to Solid phase transformation
Vapour Growth  -   Vapour to Solid phase transformation

Based on the phase transformation process, crystal growth techniques are classified as solid growth, vapour growth, melt growth and solution growth (Pamplin 1979).
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 (Mullin 1972). The above methods have been discussed in detail by several authors (Brice 1986, Pamplin 1980, Chernov 1984). The different techniques of each category are found in reviews and books by Faktor and Garret (1974) on vapour growth, Brice (1973) on melt, Henisch (1988) on gel growth, Buckley (1951) on solution growth and Elwell and Scheel (1975) on high temperature solution growth.

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.

In the above mentioned categories liquid growth includes both melt and solution growth. A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid and only 2% by hydrothermal methods.

In contrast to the historical work, it seems that the essential task for the crystal growers at present is to gain basic knowledge about the correlation of crystal properties and the growth conditions defined to be special parameters. This basic understanding of the deposition of atoms onto a suitable substrate surface – crystal growth – the generation of faults in the atomic structure during growth and subsequent cooling to room temperature – crystal defect structure, are the input for the design of crystal growth systems.
and control of growth parameters. Though the fundamentals are relatively simple, the complexities of the interactions involved and the individualities of different materials, system and growth process have ensured that experimentally verifiable predictions from scientific principles have met with limited success – good crystal growth remains as art. As a result, crystal growth has long had the image of alchemy. This is clearly expressed by the title of one of the first text books on crystal growth ‘The Art (!) and Science of Growing crystal’ (Gilman 1963). The recent advances which include reduction of growth temperature, the reduction or elimination of reactant transport variables and the use of better controlled energy sources to promote specific reactions, coupled with increased development and application of in-situ diagnostic techniques to monitor and perhaps the ultimate control lead to simplified growth systems and the crystal growth process has transferred and the field from an art to science, technique and to technology.

1.3 GROWTH FROM SOLUTION

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

1.3.1 High temperature solution 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.

1.3.1.1 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. 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 are 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.

1.4 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 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. Crystals with dimensions of several mm 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.

1.5 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.

1. Bridgman technique
2. Czochralski technique
3. Kyropoulos technique
4. Zone melting technique
5. Verneuil technique
In Bridgman technique the material is melted in a vertical cylindrical container, tapered conically with a point bottom. The container is lowered slowly from the hot zone of the furnace into 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 materials with low melting point.

In Czochralski 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.

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.

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. After this, the vertical motion of the seed is stopped and growth proceeds by decreasing the power
into the melt. The major use of this method is growth of alkali halides to make optical components.

In the zone melting 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.

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. The method is more applicable in growing single crystals of materials with volatile constituents like GaAs.

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.
1.5.1 Electrocry stallisation

Electrolysis of fused salts is normally used for the commercial production of metals such as aluminium and has great technological importance. The process of crystal growth from fused salts is analogous in many respects, except for the requirement of electron transfer in deposition of the metal. Fused salt electrolysis has been used to grow crystals of oxides in reduced valence states.

1.6 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 elemental materials. To obtain single crystals of high melting point materials this method is 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 a 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 multi-nucleation.

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.
1.7 LOW TEMPERATURE SOLUTION GROWTH

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures (Pamplin 1979) and also which undergo phase transformations below melting point (Hooper et al 1980). 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.

Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method (James and Kell 1975). 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 thermodynamical parameters of the process; temperature, pressure and solvent concentration (Chernov 1984). 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 of accuracy of ±0.01 °C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. 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 temperatures and which undergo structural transformations while cooling.
from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique. 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 (Hooper et al. 1979). The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

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 growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low (Brice 1973).

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. After undergoing so many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications.

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 (McArdle and Sherwood 1987). It also permits the preparation of different morphologies of the same materials by varying the growth conditions.

1.7.1 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.

1.7.2 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 stability.

### 1.7.3 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

(a) Crystal grows at a fixed temperature

(b) This method is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change.

(c) 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.

1.8 CRYSTAL GROWTH APPARATUS

The schematic diagram of the growth apparatus used for the low temperature solution growth technique is shown in Figure 1.1. It consists of a large tank (constant temperature bath) heated at the base using an infrared lamp. The IR lamps are energized through a relay switch. The control is effected by a jumo contact thermometer coupled to an on-off controller, which has a controlling accuracy of ± 0.01°C. A typical on-off controller circuit is shown in Figure 1.2. The temperature of the constant temperature bath is converted into a signal by a suitable sensor. The controller is contacted with an on-off switch. It gets activated when the process variable (bath temperature) crosses the set point. There are only two stable states in an on-off controller. “On” state is enabled when the temperature is below the set point. As the desired set point is arrived, the controller goes to the “off” state. To get change in the state, the temperature must cross the set point. Set point variations, which occur due to electrical noise interference and process disturbances, seriously affect the practical applications of the controller. Contrary to this, a proportional controller continuously manipulates the process variable so that the heat input is in balance with the heat demand. The controller consists of a power supply, processor, booster and proportional controllers. In the present investigation, the growth instrument was modified by replacing the infrared lamp using a programmable controller heater. The constant temperature bath used in the present study is shown in Figure 1.3.
Figure 1.1 Basic apparatus for solution growth

L: Heater Lamp; B: Bath; F: Flask; S: Stirrer; O: Opening; SG: Stirring Gland; T: control Thermometer; M: Motor.
Figure 1.2 A typical ON-OFF controller
1.9 NUCLEATION

Nucleation is an important phenomenon in crystal growth and is the precursor of the overall crystallization process. Nucleation is the process of generating within a metastable motherphase, 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 transformations (Santhanaraghavan and Ramasamy 2000).

Nucleation may occur spontaneously or it may be induced artificially. There are cases are referred to as homogeneous and heterogeneous nucleations respectively. Both these nucleations are called primary nucleation and occur in 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 (Mullin 1972).

Growth of crystals from solutions can occur if some degree of supersaturation or supercooling has been achieved first 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

All the above steps may occur simultaneously at different regions of a crystallization unit. However an ideal crystallization process consists of a strictly controlled stepwise program.

1.9.1 Ostwald’s Diagram

While the concept of a definite supersolubility is contained in the earliest reports on the crystal growth, 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 Figure 1.4 (Meirs and Issac 1987). Meir carried out extensive research into the relationship between supersaturation and spontaneous crystallization. The lower continuous line is the normal solubility curve for the salt concerned. Temperature and concentration at which spontaneous crystallization occurs are represented by the upper broken curve, generally referred to as the supersolubility curve. The whole concentration-temperature field is separated by the saturated-solution line (solubility curve) into two regions, unsaturated and supersaturated solutions. Saturated solutions are those mixtures, which can retain their equilibrium indefinitely.
in contact with the solid phase with respect to which they are saturated. The solubility of most substances increases with temperature (the temperature coefficient of the solubility is positive) and crystals can be grown only from supersaturated solutions, which contain an excess of the solute above the equilibrium value. The diagram is divided into three zones, which are termed as region I, II and III respectively.

(i) The stable (undersaturated) zone, where crystallization is not possible.

(ii) The second region is a metastable zone, between the solubility and supersolubility curves, where spontaneous crystallization is improbable. However, if a crystal seed is placed in such a metastable solution, growth would occur on it.

(iii) Third region is the unstable or labile (supersaturation) zone, where spontaneous crystallization is more probable.

If the solution whose concentration and temperature represented by point A in the Figure 1.4, is cooled without loss of solvent (line ABC) spontaneous crystallization cannot occur until conditions represented by point C are reached. At this point, crystallization may be spontaneous or seeding, agitation or mechanical shock may induce it. Further cooling to some point D may be necessary before crystallization can be induced, especially with very soluble substances such as sodium thiosulphate.
The evaporation of solvent from the solution may also result in supersaturation. Line AB’C’ represents an operation carried out at constant temperature. Penetration beyond the super solubility curve into the labile zone rarely happens, as the surface from which evaporation takes place is usually supersaturated to a greater degree than the bulk of the solution. Crystals, which appear on this surface eventually fall into the solution and seed it. In practice, a combination of cooling and evaporation as represented by the line AB”C” in (Figure 1.4) is adopted.

1.9.2 Expression of Supersaturation

The supersaturation of a system may be expressed in a number of ways. The basic units of concentration as well as temperature must be
specified. The concentration driving force ($\Delta C$), the supersaturation ratio ($S$) and relative supersaturation ($\sigma$) are related to each other as follows:

The concentration driving force $\Delta C = C - C^*$

where $C$ is the actual concentration of the solution at a given temperature and $C^*$ is the equilibrium concentration at a given temperature.

Supersaturation ratio $S = C / C^*$

Relative supersaturation $\sigma = (C - C^*) / C^*$

$\sigma = S - 1$

If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known, then, it is easier to calculate the supersaturation.

1.10 HABIT MODIFICATION

The growth rate of a crystal plane is a function of a set of crystal growth parameters like temperature, the degree of supersaturation of the solution, pH of the solution, concentration of impurities in the solution and the following equation can be used to express the functional relation.

$R = F(t, s, pH, c)$

where $R$ expresses the growth rate of the crystal and $t$, $s$, $c$ express the temperature, supersaturation and concentration of impurity respectively, in the solution. Different crystal faces grow at different rates under varying environmental conditions. The high index of a crystal grow faster than the low index faces.
Growth of good quality single crystals by slow evaporation and slow cooling techniques require optimized conditions. The same way may be achieved with the help of the following criteria: (i) material purification, (ii) Solvent selection, (iii) solubility, (iv) solution preparation, (v) seed preparation, (vi) agitation, (vii) crystal habit and (viii) cooling rate.

1.10.1 Material Preparation

An essential prerequisite for success in crystal growth is the availability of material of the highest purity. 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. 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.

1.10.2 Choice of Solvent and Solubility

Growth from aqueous solution provides information on the fundamental process applicable to both low and high temperature solution growth methods (Bordui 1987). Water is a popular solvent for the growth of a variety of inorganic and organic compounds. It is not toxic and is less volatile than organic solvents, which are, in general, toxic, volatile and flammable. In comparison with organic solvents, it is also easily available in the pure state and is cheap. Because of its higher boiling point than most of the organic solvents commonly used for growth, it provides a reasonably wide range for the selection of growth temperature. Moreover, it is chemically inert to a variety of glasses, plastics and metals used in crystal growth equipment. However, water is not a reversible solvent for some materials. It hydrolyzes
some materials and introduces water of crystallization to others which may be desired in the anhydrous form. Therefore, for the growth of crystals of a compound from solution, the selection of a solvent is critical. A simple rule of thumb in the proper selection of a solvent is chemical similarity between the solvent and the compound to be grown. For example, crystals of nonpolar organic compounds can be grown easily from nonpolar organic solvents. Chemical similarity also determines solute solubility in the solvent. Experiments reveal that a solvent in which the compound has a solubility between 10 and 60% at a given temperature is economically suitable for crystal growth. Very low and very high solubility of a solute provide low growth rates due to low solute concentration and increased viscosity, respectively. Therefore, in both of these cases it is desirable to use additives to change the solute solubility in a solvent or solution viscosity. Additives not only change the properties of solutions, but also lead to changes in the growth habits of crystals (Buckley 1951).

Another example of the solvent-induced change in growth morphology is the organic compound alizarin (1,2-dihydroxy-9,10-anthraquinone), which crystallizes as long needles from the vapor and organic solvents such as acetone, acetonitrile, hexane, toluene and acetic acid, while flat triangular-shaped crystals are produced by alcohols such as ethanol, methanol and propanol (Algra et al 2005). In this case, the morphology change is not caused by the direct interaction of solvent molecules with the crystal surface itself, but by the interaction of partially deprotonated alizarin molecules with the solvent. This example demonstrates that a solvent can also play an indirect role in changing the morphology of a crystal. The solvent changes the structure of the solute molecules, which subsequently adsorb on several faces of the crystal, thereby blocking their normal growth. The solvent has a strong influence on the habit of crystalline materials, because solvent molecules affect the growth rates of different faces appearing in the crystal
morphology differently. The effect of solvent on the growth rates of different faces is associated with selective adsorption of solvent molecules on them. The effect of solvent on growth rates can be explained by two approaches (Weissbuch et al 1995). The first approach considers changes in the interfacial tension due to interactions between solvent and crystal molecules of the growing crystal face. An increase in the interfacial tension leads to a decrease in the growth rate, whereas a decrease in the interfacial tension leads to an increase in the growth rate. These effects may be explained in terms of surface entropy factor. The second approach is an extension of the role played by tailormade impurities, where the growth rate of a crystal face is determined by the removal of solvent molecules adsorbed on the face (Buckley 1951). In this case, the face where solvent molecules are more strongly adsorbed than on other faces will grow more slowly than those where the solvent molecules are less strongly adsorbed. The characterization of organic materials for their nonlinear optical properties involves the use of samples in the liquid phase. The most convenient way to prepare samples for such investigations at room temperature is to dissolve the materials in a suitable solvent. However, the influence of the solvent on the measurements may depend on the physical and chemical properties of both the solvent and the solute. If the solvent effect is not properly taken into account in relating measured macroscopic quantities to the microscopic properties of solute molecules, the comparison of the experimental results of hyperpolarizabilities with the theoretical predictions may be invalid.

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. 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 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 and
(v) less corrosion
(vi) non-toxic

If the solubility is too high, it is difficult to grow bulk single crystals and too small a solubility restrict the size and growth rate of the crystals. Solubility gradient is another parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystal from solution; while the level of supersaturation could not be varied by reducing the temperature in the former, even a small fluctuation in the temperature will affect the supersaturation to a large extent in the later disabling the growth of good quality bulk crystals in both cases. 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.

Growth of crystals from solution is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transport of the growth units from the bulk solution by diffusion. Hence a solvent with less viscosity is preferable (Ohara and Reid 1973). The solubility data at various temperatures are 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 (Christian 1990).
The solubility of the solute may be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, the equilibrium concentration of the solute may be determined gravimetrically. A sample of the clear supersaturated liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analyzed. The solubility curve can then be plotted in this way by repeating the above for different temperatures. The effect of pH value on the crystals have impact on the solubility and the hardness of the crystals (Ushasree et al 1999, Rajendran et al 2003) and also on the morphology of the grown crystals in the case of L-alanine grown by us with pH value 2.0.

1.10.3 Preparation of Solution and Crystal Growth

For solution preparation, it is essential to have the solubility data of the material at different temperatures. Sintered glass fibres of different pore size are used for solution filtration. The clear solution, saturated at the desired temperature is taken in a growth vessel. For growth by slow cooling, the vessel is sealed to prevent the solvent evaporation. Solvent evaporation at constant temperature can be achieved by providing a controlled vapour leak. A small crystal suspended in the solution is used to test the saturation. By varying the temperature, a situation where neither the occurrence of growth nor dissolution is established. The test seed is replaced with a good quality seed. All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after saturation. Solvent evaporation can also be helpful in initiating the growth. The quality of the grown crystal depends on the (a) nature of seed, (b) cooling rate employed and (c) agitation of the solution.
1.10.4 Preparation of Seed and Seed Mounting

Seed crystals are prepared by self-nucleation under slow evaporation from a saturated solution. Seeds of good visual quality, free from any inclusion and imperfections are chosen for growth provided seed should be suspended in a saturated solution on a smooth support to avoid spurious nucleation. A nylon thread was used to suspend the good quality seed crystal. Since strain free refaceting of the seed crystal results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth.

1.10.5 Cooling Rate

Supersaturation is an important parameter for the solution growth process. Crystal grows by the accumulation of the solute in the solution as a degree of supersaturation is maintained. Temperature and supersaturation have to be precisely controlled for desirable results. In order to grow bulk crystals growth rate should be maintained linear. This requires an increase in the supersaturation level and hence after the initial growth, the rate of temperature lowering is increased. Also fluctuations in supersaturation may encourage solution inclusions flaw in growing crystals (Wilcox 1983). Hence, a balance between the temperature lowering rate and the growth rate has to be maintained.

1.10.6 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
exit in the growth vessels at different faces of the crystal cause fluctuations in supersaturation, which 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.

1.10.7 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 (Pamplin 1979). Needle like crystals have very limited applications and plate like crystals need to be favourably 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.

1.11 PERFECTION OF THE GROWN CRYSTAL

The perfection of the grown crystal is based on,

(i) the purity of the starting materials
(ii) the quality of the seed crystal
(iii) cooling rate employed and
(iv) the efficiency of agitation

Hence, high quality single crystals can be grown from quality seeds in an efficiently stirred solution.

1.12 THE CHEMICAL PHYSICS OF CRYSTAL GROWTH

If the crystal is in dynamic equilibrium with its parent phase the free energy is at a minimum and no growth will occur. For growth to occur this equilibrium must be disturbed by a change of the correct sign, in temperature, in pressure, chemical potential (e.g. saturation) electrochemical potential (e.g. electrolysis), or strain (solid state growth). The system may then release energy to its surrounding to compensate for the decrease in entropy occasioned by the ordering of atoms in the crystal and the evolution of heat of crystallization. In a well – designed growth process just one of these parameters is held minimally away from its equilibrium value to provide a driving force for growth.
Crystal growth then is a non-equilibrium process and thought must be given to the temperature and concentration and other gradients and the fact that heat of crystallization is evolved and must be removed to the surroundings. At the same time the crystal growth process must be kept as near equilibrium and as near to a steady state process as possible. This is why control of the crystal growth environment and a consideration of growth kinetics both at the macroscopic and the atomic levels are of vital importance to the success of a crystal growth experiment. It is particularly important to avoid constitutional supercooling and the breakdown of the crystal-liquid interface that this can cause.

In some growth techniques there is no crystal initially present. Here the nucleation problem is met which in essence is due to the fact that the surface-to-volume ratio of small particle is much higher than for a large crystal. Surfaces lose energy because of discontinuities in atomic bonding. Thus the nucleation of a new phase is a discontinuities, not a quasi equilibrium process. This is the reason why pure melts supercool and solutions become supersaturated. Thus the growth system departs considerably from equilibrium before a crystal nucleates, and when it comes the new born crystal grows very rapidly at first and is full of defects, some of which propagate on into the later stages of near equilibrium growth. Crystal growers thus seek to use methods where a seed crystal can be introduced into the system to avoid the nucleation. In the last three decades great strides have been made toward achieving crystal perfection motivated by the needs of the electronics and optics industries. While thermodynamics excludes the possibility of growing a perfect crystal, gross defect like grain boundaries, voids, and even dislocations can be eliminated with care and point defects, like impurities, vacancies, interstitials, and antistucture disorder can be minimized by attention to growth environment and purity of reagents and apparatus.