CHAPTER I
INTRODUCTION TO CRYSTAL GROWTH TECHNIQUES AND NONLINEAR OPTICS

1.1 INTRODUCTION

The history of crystal growth goes back to the seventeenth century when the Danish anatomist Nicolas Steno introduced law of the constancy of interfacial angles. Later in the nineteenth century crystals were classified into seven crystal systems due to their symmetry. Study of crystal growth at atomic level has started since 1930’s by Volmer, Kossel and Stranski who have developed the theory of growth of perfect crystals (Russel Raj, 2012). Burton, Cabrera and Frank continued their works and developed the theory of real crystals (Burton, Cabrera and Frank, 1951). Today, crystal growth is a multidisciplinary subject. It draws upon just about every field of science and engineering, providing insights for other researchers to use in their field. The strong influence of single crystals in the present day technology is evident from the recent advancements in the fields of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optics, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand for materials for technological applications (Laudise, 1970; Brice, 1986; Nalwa and Miyata, 1996). The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size (Buckley, 1951; Mullin, 1976). Method of crystal growth ranges from a simple inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months.

In optics, nonlinear effects became a subject of interest only after the invention of the laser. Nonlinear optics (NLO) is the study of phenomena that
occur as a consequence of the modification of the optical properties of a material system in the presence of high intense electromagnetic field. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. To measure the nonlinear response of matter to electromagnetic waves in the optical region, in general high fields are necessary, starting at about $10^6$ V/m and the corresponding light intensities of a few kW/cm$^2$, which can be realized with laser of 1 mW power onwards (Maiman, 1960). As laser physics started with the ruby laser with its high pulse intensities, it took only few years after the invention of the laser that many classical experiments in nonlinear optics were successfully performed. Among the first were the second order processes, like the experiments on second harmonic generation by Franken et al. (1961), on sum frequency generation by Bass et al., (1962a) and on optical rectification by Bass et al., (1962b). Since that time nonlinear optics has become a rapidly growing field in physics. Presently, many optical materials are of special interest in information technologies, photonics as supplement and extension of electronics. Nonlinearities in the properties of these optical materials are often of significant relevance for the technological applications.

1.2 NONLINEAR OPTICS

1.2.1 Introduction

The interaction of light with matter is usually characterized by several phenomena, such as light absorption, refraction, scattering and luminescence etc. All of these were regarded as properties of the material with wavelength dependence, but independent of the light intensity. The high intensities obtainable with lasers however can alter the optical properties of matter. Thus the characteristic optical properties of a material become a function of intensity. The study of such interactions is the field of nonlinear optics.

Development in non-linear optics took place dramatically, especially during the last decade due to the advancement of both experimental techniques and evolution of molecular modeling and quantum chemical theoretical
procedures. Molecules with large optical non-linearities have extensively been studied due to their potential applications in the area of materials science and various photonic technologies, including optical switching, data processing and optical communication. NLO also takes a primary part in modern technology involving lasers, sensors, interferometers, memory chips, detectors, electrical devices and optical components. Frequency conversion is one of the important and popular techniques among the nonlinear behaviour of a material to extend the useful wavelength range of laboratory laser. Some other nonlinear optical properties are as follow,

(i). Sum-Frequency Generation
(ii). Difference-Frequency Generation
(iii). Optical Parametric Oscillation
(iv). Third-Order Nonlinear Optical Processes etc.

1.2.2 Theoretical Explanation of Nonlinear Optics

When a beam of electromagnetic radiation propagates through a solid, the nuclei and associated electrons of the atoms form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, which by the classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is small, the dipoles emit radiation of the same frequency as the incident radiation. As the intensity of the incident radiation increases, the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in the generation of harmonics in the frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and indeed higher order frequency effects occur as the incident intensity is increased.

In a nonlinear medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.
At very low fields, the induced polarization is directly proportional to the electric field (Nalwa and Miyata, 1996).

\[ \mathbf{P} = \varepsilon_0 \chi \mathbf{E} \]  

(1.1)

where \( \chi \) is the linear susceptibility of the material, \( \mathbf{E} \) is the electric field vector, \( \varepsilon_0 \) is the permittivity of free space.

At high fields, polarization becomes independent of the field and the susceptibility becomes field dependent. Therefore, this nonlinear response is expressed by writing the induced polarization as a power series in the field.

\[ \mathbf{P} = \varepsilon_0 \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots \]  

(1.2)

In nonlinear terms, product of two or more oscillating fields gives oscillation at combination of frequencies and therefore the above equation can be expressed in terms of frequency as:

\[ \mathbf{P}(\omega_o) = \varepsilon_0 \chi^{(1)} (-\omega_o; \omega_1). \mathbf{E}(\omega_o) + \chi^{(2)} (\omega_o; \omega_1, \omega_2). \mathbf{E}(\omega_1). \mathbf{E}(\omega_2) \]

\[ + \chi^{(3)} (-\omega_o; \omega_1, \omega_2, \omega_3). \mathbf{E}(\omega_1). \mathbf{E}(\omega_2). \mathbf{E}(\omega_3) + \ldots \]  

(1.3)

where \( \chi^{(2)}, \chi^{(3)} \ldots \) are the nonlinear susceptibility of the medium, \( \omega_o, \omega_1, \omega_2 \ldots \) are the frequency of beam. \( \chi^{(1)} \) is the linear term responsible for material’s linear optical properties, like refractive index, dispersion, birefringence and absorption. \( \chi^{(2)} \) is the quadratic term which describes second harmonic generation in non-centrosymmetric materials. \( \chi^{(3)} \) is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bistability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients, \( \chi^{(1)}, \chi^{(2)} \) and \( \chi^{(3)} \) give rise to certain optical effects, which are listed in Table 1.1. If the molecule or crystal is centro-symmetric then \( \chi^{(2)} = 0 \). If a field \( +\mathbf{E} \) is applied to the molecule (or medium), equation (1.3) predicts that the polarization induced by the first nonlinear term is predicted to be \( +\mathbf{E}^2 \), yet if the medium is centro-symmetric the polarization should be \( -\mathbf{E}^2 \). This contradiction can only be resolved if \( \chi^{(2)} = 0 \) in centro-symmetric media. If the same argument is used for the next higher order
term, +E produces polarization +E\textsuperscript{3} and −E produces −E\textsuperscript{3}, so that \( \chi^{(3)} \) is the first non-zero nonlinear term in centro-symmetric media.

**Table 1.1 Effects of susceptibility**

<table>
<thead>
<tr>
<th>Order</th>
<th>Coefficient</th>
<th>Effects</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>( \chi^{(1)} )</td>
<td>Refraction</td>
<td>Optical fibers</td>
</tr>
<tr>
<td>2.</td>
<td>( \chi^{(2)} )</td>
<td>SHG (( \omega + \omega = 2\omega )) &lt;br&gt;Frequency mixing (( \omega_1 \pm \omega_2 = \omega_3 )) &lt;br&gt;Pockel’s effect (( \omega + 0 = \omega ))</td>
<td>Frequency doubling &lt;br&gt;Optical parametric oscillations &lt;br&gt;Electro-optical modulators</td>
</tr>
<tr>
<td>3.</td>
<td>( \chi^{(3)} )</td>
<td>4 wave mixing &lt;br&gt;Gratings &lt;br&gt;Kerr effect &lt;br&gt;Optical amplitude</td>
<td>Raman coherent spectroscopy &lt;br&gt;Real time holography &lt;br&gt;Ultra high speed optical gates &lt;br&gt;Amplifiers, choppers etc.</td>
</tr>
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</table>

In second harmonic generation,

\[
2\omega_1 = \omega_2 \quad \text{or} \quad (\lambda_1 = 2\lambda_2)
\]  

(1.4)

During this process, a polarization wave at the second harmonic frequency 2\( \omega_1 \) is produced. The refractive index, \( n_1 \) is defined by the phase velocity and wavelength of the medium. The energy of the polarizing wave is transferred to the electromagnetic wave at a frequency \( \omega_2 \). The phase velocity and wavelength of this electromagnetic wave are determined by \( n_2 \), the refractive index of the doubled frequency. To obtain high conversion efficiency, the phase vectors of input beams and generated beams are to be matched.

\[
\Delta K = \frac{2\pi}{\lambda (n_2 - n_1)} = 0
\]

(1.5)

where \( \Delta K \) represents the phase-mismatch. The phase matching can be obtained by angle tilting, temperature tuning or other methods. Hence, to select a nonlinear
optical crystal, for a frequency conversion process, the necessary criterion is to obtain high conversion efficiency. The conversion efficiency ($\eta$), is given by

$$\eta = PL^2 \left( \frac{d_{\text{eff}} \sin \Delta K \cdot L}{\Delta K \cdot L} \right)^2$$  \hspace{1cm} (1.6)

where $d_{\text{eff}}$ is the effective nonlinear coefficient, $L$ is the crystal length, $P$ is the input power density and $\Delta K$ is the phase mismatching. In general, higher power density, longer crystal, large nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency.

1.3 NONLINEAR OPTICAL CRYSTALS

Considerable work has been concentrated on developing highly transparent NLO crystals suitable for frequency conversion of high-power lasers, such as those used for inertial confinement fusion, optical data storage and optical communications. Since a large number of NLO processes exist, therefore, requirement of an individual NLO material is confined to a particular application. The materials required for the design of NLO devices must fulfill certain basic conditions, such as large nonlinear figure of merit, appropriate transparency range, high resistance to optical damage, adequate birefringence for phase matching and good environmental stability. A typical SHG active molecule must be non-centrosymmetry in nature. This symmetry requirement eliminates many materials from being SHG active and hence at the early stage of designing and synthesizing novel materials, one has to consider ways of introducing non-centrosymmetry in the molecular structures. Nonlinear optical materials are broadly classified into

(i). Inorganic crystals,

(ii). Organic crystals and

(iii). Semi-organic crystals.

1.3.1 Inorganic Crystals

Investigations on nonlinear optical phenomena in single crystals were initially focused on purely inorganics, such as quartz, lithium niobate (LiNbO$_3$, LN), potassium dihydrogen orthophosphate (KH$_2$PO$_4$, KDP), potassium
titanyl phosphate (KTiPO$_4$, KTP), lithium iodate (LiIO$_3$), borates and semiconductor crystals. Potassium dihydrogen phosphate (KDP) and its homologues (including permutations of Rb, Cs or NH$_4$ replacing K, or deuterium replacing H, or As replacing P) are among the most widely-used commercial NLO materials due to their good UV transmission, high birefringence and relatively high tolerance to laser damage (Bordui and Fejer, 1993). (LiNbO$_3$, LN) offers good transmission and it is not hygroscopic. However, when it is grown in usual congruent composition without any doping suffers from a relatively low optical damage threshold which is a major drawback (Salvestrini et al., 2004). LiTaO$_3$ (LT) crystals, which are isomorphic to LN also possess large electro optical (EO) and nonlinear optical properties and has been reported that the damage threshold is twice as large as in LN crystal. Various borate crystals including beta barium borate ($\beta$-BaB$_2$O$_4$, BBO) and lithium borate (LiB$_3$O$_5$, LBO) have been reported as promising NLO crystals. In addition, during the last few years, newly developed nonlinear optical (NLO) crystals gadolinium calcium oxoborate (GdCa$_4$O(BO$_3$)$_3$, GdCOB) and Yttrium calcium oxoborate (YCa$_4$O(BO$_3$)$_3$, YCOB) have attracted much attention due to their promising optical properties (Iwai et al., 1997). However, inorganic crystals face a ‘trade-off’ problem between response time and magnitude of optical nonlinearity. A Semiconducting nonlinear optical crystal absorb strongly the visible region and are of poor optical quality, thereby limits many possible applications.

1.3.2 Organic Crystals

Organic NLO materials offer several advantages over inorganic NLO materials, such as large nonlinear figure of merit, fast response time and their structural flexibility facilitate easy control of physical properties over very wide range. Aromatic benzene and stilbene contains electron donating and electron accepting groups with large nonlinear hyper polarizibilities (Davydov et al., 1970). As second-order nonlinear optical materials, a lot of organic compounds with polarized $\pi$-conjugation systems have been found to have potential to exceed
inorganic compounds (Bosshard et al., 1995). 4-dimethylamino-N-methyl-4-
stilbazolium tosylate (DAST) is one of the potential nonlinear optical crystals
among the organic materials. The second order nonlinear coefficient of DAST was
reported to be 72 times larger than that LiNbO$_3$ (Shoma et al., 1999) and exhibits
SHG efficiency of about 1000 times that of Urea (Marder et al., 1992). However
growth of large size DAST crystal possesses more experimental difficulties. The
lack of reasonably large and high quality DAST crystals prevents real applications.
A potential nonlinear optical organic crystal, Urea L-Malic acid (ULMA), has
been grown from aqueous solution by solvent evaporation and slow cooling
methods (Dixit et al., 2003). Most of the organic NLO crystals are constituted by
weak van der Waals and hydrogen bonds with conjugated $\pi$ electrons. So they are
soft in nature and difficult to polish and these materials also have intense
absorption in UV region. Compared with inorganic materials, the major drawbacks
of organic NLO materials are their moderate environmental stability, low
mechanical strength and a limited temperature range of operation (Adachi et al.,
1999).

1.3.3 Semiorganic Crystals

The widest search for new compounds and crystals led to the
development of many amino acid based semiorganic single crystals. Semiorganic
crystals are less hygroscopic compared to inorganic crystals and can be easily
grown as single crystals compared to organics. L-arginine phosphate monohydrate
(LAP) is one of the potential nonlinear optical crystals among the amino acid
based semiorganic materials. Monaco et al., (1987) synthesized LAP and its
chemical analogs from amino acids and various other acids. All the compounds in
this class contain an optically active carbon atom and therefore all of them form
acentric crystals. All the crystals are optically biaxial and among them several
gave second harmonic signals greater than quartz. Different organic and inorganic
acids were introduced into L-alanine and L-hystidine and many new nonlinear
optical materials were reported with a better NLO efficiency compared to
inorganic KDP crystal (Aggarwal, 2003). LAP crystal is usually grown from aqueous solution by temperature lowering technique. LAP crystals possess high nonlinearity, wide transmission range (220–1950 nm), high conversion efficiency (38.9 %) and high damage threshold (Monaco et al., 1987). Metal-organic crystals form a new class of materials under semi-organics. Compared to organic molecules, metal complexes offer a larger variety of structures, the possibility of high environmental stability and a diversity of electronic properties by virtue of the coordinated metal center (Bella, 2001). This discussion reveals that the semiorganic materials exhibiting the positive properties of both inorganic and organic materials together.

1.4 CRYSTAL GROWTH - CLASSIFICATION

Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapour phase. The methods of growing single crystals may be classified according to their phase transformation as given below:

Growth from solid -----> Solid–solid phase transformation
Growth from liquid -----> Liquid–solid phase transformation
Growth from vapor -----> Vapor–solid phase transformation

One can consider the conversion of the polycrystalline piece of a material into a single crystal by causing the grain boundaries to swept through and pushed out of the crystal in the solid–solid growth of crystals (Mullin, 1976). The crystal growth from liquid falls into five categories namely,

(i). Low temperature solution growth,
(ii). Gel growth,
(iii). Hydrothermal growth,
(iv). Melt growth and
(v). Flux growth.

There are number of growth methods in each category. Among the various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Growth from solution occurs close to equilibrium conditions and hence crystals of high
perfection can be grown. Growth of large single crystals from aqueous solution is of interest for essentially two reasons. First, there is a growing need for solution-grown crystals in the area of high-power laser technology. Second, research on this area of crystal growth and the corresponding in-depth examination of several key parameters provides fundamental case studies generating theory and technology, applicable to all of solution growth, including new aqueous growth systems and high temperature solution growth (Karl, 1980; Bordui, 1987). Low temperature solution growth has some significant properties, such as near equilibrium growth, low cost, easy handling, small working area etc. From these aspects, solution growth is one of the good methods to grow bulk crystals.

1.5 FUNDAMENTALS OF SOLUTION GROWTH

1.5.1 Supersaturation

Solution is a homogeneous mixture composed of only one phase. In such a mixture, a solute is a substance dissolved in another substance, known as solvent. Solution in which no more solvent can be dissolved is known as saturated solution. The driving force necessary for the crystallization phase transition is the supersaturation. The supersaturation of a system can be expressed in a number of ways. A basic unit of concentration as well as temperature must be specified. The concentration driving force (ΔC), supersaturation ratio (S) and relative supersaturation (σ) are related to each other as follows:

Concentration driving force, \( ΔC = C - C* \)

where \( C \) is the actual concentration of the solution and \( C* \) is the equilibrium concentration at a given temperature.

Supersaturation ratio, \( S = \frac{C}{C*} \)

Relative supersaturation, \( \sigma = \frac{C - C*}{C*} \)

i.e., \( \sigma = S - 1 \)
If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known, then the supersaturation can be estimated.

The required supersaturation can be achieved either by cooling/evaporation or addition of a precipitant. Meirs and Isaac (1987) reported a detailed investigation on the relationship between supersaturation and spontaneous crystallization. The results of their analysis are shown in figure 1.1. It shows three zones, which are termed as region I, II and III. The lower continuous line is the normal solubility curve for a particular solute concerned. Temperature and concentration, at which spontaneous crystallization occurs, are represented by the upper broken curve, generally referred to as the supersolubility curve. This curve is not well defined as the solubility curve and its position in the diagram depends on the degree of agitation of the solution.

![Meir's solubility diagram](image)

Figure 1.1 Meir’s solubility diagram

The three zones are defined as follows:

(i). The stable zone (undersaturated - region I), where crystallization is not possible.
(ii). The metastable zone (region II), where spontaneous crystallization is improbable. However, if a seed crystal is placed in such a metastable solution, growth will occur.

(iii). The unstable or labile zone (supersaturated - region III), where spontaneous crystallization is more probable.

1.5.2 Nucleation

Nucleation, is the first stage in the crystallization process which nothing but the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organisation. Simply defined, it represents the birth of a new crystal. Nucleation plays an essential role in the crystal growth and it act as the precursor of crystal growth for the overall crystallization process. The deposition of a solid crystalline phase from liquid solutions can occur only if there exits some degree of supersaturation in the system. The achievement of supersaturation is not only sufficient to initiate the crystallization. The formation of embryos (an aggregate of a small number of molecules) or nuclei, often termed as centers of crystallization, is a prerequisite. Nucleation may occur spontaneously or it may be induced artificially. Nucleation can be broadly classified into primary and secondary nucleations. All types of nucleations, homogeneous or heterogeneous in systems, which do not contain crystalline matter comes under primary. On the other hand, nucleation generated in the vicinity of crystals present in a supersaturated system is termed as secondary nucleation.

The growth units (ions or molecules) in a solution can interact with one another resulting in a short-lived cluster. Many nuclei fail to achieve maturity and simply dissolve due to their unstable nature. The formation of stable nuclei occurs only by the addition of molecule (A₁), till a critical cluster is formed.

\[ A_{n-1} + A_1 \rightarrow A_n \text{ (critical cluster)} \]  

(1.7)
Subsequent addition, even a single molecule, to the critical cluster results in nucleation which is followed by growth. The formation of a solid particle within a homogeneous solution results from the expenditure of a certain quantity of energy.

The change in Gibbs free energy ($\Delta G$) between the crystalline phase and the surrounding mother phase is a driving force, which stimulates crystallization. $\Delta G$ is the sum of surface free energy and volume free energy.

\[ \text{Gibbs free energy change} = \text{Surface free energy change} + \text{Volume free energy change} \]

For a spherical nucleus,

\[ \Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v \quad (1.8) \]

where $r$ is the radius of nucleus, $\gamma$ is the surface free energy change per unit area (interfacial tension) and $\Delta G_v$ is the free energy change per unit volume. The first term expresses the energy of formation of new surface and the second term expresses the volume free energy of the new phase.

For spontaneous crystallization, $\Delta G < 0$. At the critical condition, the free energy of formation obeys the condition, $\frac{d(\Delta G)}{dr} = 0$. Hence, the radius of the critical nucleus is expressed as

\[ r^* = \frac{-2\gamma}{\Delta G_v} \quad (1.9) \]

where,

\[ \Delta G_v = -\frac{\Delta \mu}{V} \quad (1.10) \]

\[ \Delta \mu = -\left(\frac{kT}{V}\right) \ln S \quad (1.11) \]

\[ S = \frac{C}{C^*} \quad (1.12) \]
The critical free energy barrier,

\[ \Delta G^* = \frac{16\pi \gamma^3 V^3}{3(\Delta \mu)^2} \]  

(1.13)

where \( V \) - molar volume of the crystal, \( \mu \) - chemical potential, \( S \) - supersaturation, \( k \) - Boltzmann constant and \( T \) - absolute temperature

The number of molecules in the critical nucleus is given as

\[ i^* = \left( \frac{4\pi}{3V} \right) (r^*)^3 \]  

(1.14)

The crucial parameter between a growing crystal and the surrounding mother phase is the interfacial tension (\( \gamma \)). This complex parameter can be determined by conducting the nucleation experiments.

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

(i). achievement of supersaturation or supercooling,

(ii). formation of crystal nuclei and

(iii). growth of crystal from the crystal nucleus.

1.6 LOW TEMPERATURE SOLUTION GROWTH

Crystal growth from solution is very important process used in many applications from laboratory to industry. The material which decomposes before its melting point can be grown as single crystals by aqueous solution growth method (Pamplin, 1979). This method demands that the materials must crystallize from solution with prismatic morphology. In general, low temperature solution growth involves seeded growth from a saturated solution. The driving force, i.e., the supersaturation is achieved either by temperature lowering or by solvent evaporation. This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature (James and Kell, 1975; Chernov, 1984 and Chernov, 1999). 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 near room temperature i.e., near equilibrium condition, the structural imperfections in solution grown crystals are relatively low (Brice, 1972).

1.6.1 Growth Methods

Low temperature solution growth can be subdivided into the following categories:

(i). slow cooling method,
(ii). slow evaporation method,
(iii). Temperature gradient method and
(iv). Sankaranarayanan Ramasamy (SR) or Unidirectional Method.

1.6.2 Slow Cooling Method

Slow cooling is the best method to grow good quality crystals by aqueous solution technique. However, the limitation of slow cooling method is the need to use a range of temperature. The possible range of temperature is usually narrow and hence much of the solute remains in the solution at the end of the growth run. To compensate this effect, large volume of solution is required. Wide range of temperature may not be desirable because the properties of the grown crystal may vary with temperature.

Fast Growth

Fast growth is the one of the brilliant technique to grow bulk size single crystals for the technological applications in a short duration. If the meta stable zone is so broad, the temperature can be reduced very fast without disturbing the stability of the solution and hence very high growth rate can be achieved in this technique.
1.6.3 Slow Evaporation Method

In slow evaporation method, the temperature is fixed and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05°C and rates of evaporation of a few mm$^3$/h. The evaporation technique has an advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system and difficulty of controlling the rate of evaporation still pose a major effect on the growth rate. This method can effectively be used for materials having very low temperature coefficient of solubility.

1.6.4 Temperature Gradient Method

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

(i). crystal grows at a fixed temperature,

(ii). insensitive to changes in temperature provided both the source and growing crystal undergo the same change and

(iii). economy of solvent and solute.

On the other hand, a small temperature difference between the source and the crystal zones has a large effect on the growth rate.

1.6.5 Sankaranarayanan Ramasamy (SR) or Unidirectional Method

Sankaranarayanan-Ramasamy method is one of the solution growth methods. The novel Sankaranarayanan-Ramasamy crystal growth method has more advantages when compared to conventional solution growth techniques (Sankaranarayanan and Ramasamy 2005) and this can be employed to grow unidirectional crystal from solution. Figure 1.2 shows the schematic representation of SR method apparatus. It consists of heating coils, seed-mounting pad, growth portion and top portion (made up of glass). Heating coils are placed at the top and
bottom of the ampoule and it is directly connected to thermostat to maintain the heater voltage. Heater voltage plays a major role in this novel unidirectional SR method and this is used for solvent evaporation of the growth solution. The entire SR method growth system is placed inside a constant temperature bath (CTB) (accuracy ± 0.01°C) for avoiding temperature fluctuations in the growth portion. Growth condition of this method depends on the temperatures of heating coils. Once the growth condition is optimized, it is possible to grow the crystals with different orientations at a faster rate.


Figure 1.2 Schematic experimental set up of SR method

The advantages of Sankaranarayanan-Ramasamy method are as follows:

(i). can grow single crystal with specific orientation from solution,
(ii). room temperature growth is possible,
(iii). solute-crystal conversion efficiency is almost 100 percent and
(iv). simple experimental setup.
1.6.6 Factors that Influence the Perfection of Crystal

In order to grow large size and well-faceted optically clear crystals, there are five basic factors need to be optimized, which are,

(i). the purity of the starting material,

(ii). the perfection of the seed,

(iii). cooling or evaporation rate,

(iv). pH of the growth solution and

(v). the efficiency of agitation of the seed and the solution.

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

1.6.7 Apparatus for Low Temperature Solution Growth

The basic crystallization apparatus used for the solution growth technique is shown in figure 1.3. It consists of a large tank (constant temperature bath) heated at the base by heaters. The heaters are energized through a relay switch. The temperature control is achieved by a eurotherm temperature controller, which is coupled to an on-off controller of accuracy of ± 0.01°C. The temperature of the constant temperature bath is converted into digital signal by a suitable sensor. The controller is a contactor with an on–off switch and it gets activated, when the process variable (bath temperature) crosses the set point. To effect a change in the state, the temperature must cross the set point.

Growth occurs without any secondary nucleations in the solution, if the supersaturation is fixed within the metastable zone limit. A large cooling rate may changes the solubility beyond the metastable zone width and multi nucleation occurs at the expense of the seed crystal. A balance between the temperature lowering and the growth rate has to be maintained to avoid multinucleation. Growth at a low supersaturation prevents strain and dislocation formation at the interface. Supersaturation can be increased after initial growth to arrive at a reasonable growth rate.
1.6.8 Solvent Selection

Solution is a homogeneous mixer of a solute in a solvent. Solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high purity starting materials, solution growth requires a good solvent. The solvent must be chosen taking into account the following factors:

(i). moderate solubility for the given solute,
(ii). should not react with the solute,
(iii). good solubility gradient,
(iv). low viscosity,
(v). low volatility,
(vi). low corrosion,
(vii). easily available,
(viii). low toxicity,
(ix). low cost etc.,

If the solubility is too high, it is difficult to grow bulk single crystals and too small a solubility restricts the size and growth rate of the crystals. 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. 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 crystal 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).

1.6.9 Preparation of Saturated Solution and Seed Mounting

After selecting the desirable solvent for a particular high purity solute to be crystallized, the next important part is the preparation of saturated solution. The crushed power form of the solute material has to be added step by step in the mother solvent at a particular temperature till the material stop dissolving. The test seed is tied with the nylon thread and introduced in to this saturated solution. If there is no dissolution of the seed or overgrowth then the test seed has to be withdrawn from the solution and a good quality seed is introduced. The temperature of the solution is slightly raised above the saturation temperature to dissolve any unwanted nuclei or any surface damage on the seed. The temperature is then lowered to the equilibrium temperature to induce the growth.

1.7 SCOPE OF THE THESIS

The fundamental principle and applications of nonlinear optical phenomena and an insight into different NLO materials have been discussed. The brief introduction on crystal growth and classification of crystal growth methods has been described. Various methods of crystal growth, especially the fundamental and experimental aspects of low temperature solution growth technique have been explained in detail. The importance of nucleation kinetics to optimize the growth condition for growing optically high quality bulk crystals is presented.

The present work deals about the investigation on potential organic and semi-organic materials, such as l-arginine diphenylacetate (APA), 4- bromoanilinium hydrogen phthalate (BAP), imidazole – imidazolium picrate monohydrate (IIP) and anilinium perchlorate (AP).
The present investigation is aimed at:

(i) Synthesizing high purity materials, like l-arginine diphenylacetate (APA), 4- bromoanilinium hydrogen phthalate (BAP), imidazole – imidazolium picrate monohydrate (IIP) and anilinium perchlorate (AP).

(ii) Investigating the metastable zone width for the synthesized materials.

(iii) Nucleation kinetics study of l-arginine diphenylacetate (APA).

(iv) Growth of bulk single crystals of l-arginine diphenylacetate (APA), 4- bromoanilinium hydrogen phthalate (BAP), imidazole – imidazolium picrate monohydrate (IIP) and anilinium perchlorate (AP) using various techniques of low temperature solution growth method.

(v) Confirmation of the structure and quality of the grown single crystals by X-ray diffraction technique.

(vi) Determining the thermal stability of the grown crystals to assess their suitability in device fabrication.

(vii) Understanding the mechanical behaviour of the grown crystals.

(viii) Linear optical study to reveal optical band gap, transmittance window and other optical parameters.

(ix) The experimental determination of refractive index and laser damage threshold of the crystals.

(x) Understanding the phase matchability of the title compounds by studying the size dependent second harmonic generation efficiency.