CHAPTER 1

AN INTRODUCTION TO LOW TEMPERATURE SOLUTION GROWTH TECHNIQUE AND NONLINEAR OPTICAL CRYSTALS

1.1 INTRODUCTION

Single crystal growth has a prominent role in the present era of rapid scientific and technical advancement, whereas the application of crystals has unbounded limits. Single crystal may be briefed out as the ordered array of atoms in repeated groups that shows characteristic symmetry elements by which the entire block of the material is built. The aim of the crystal growth is to understand the fundamental properties of the crystals and materials. Lot of basic science focuses the property of the crystal which depends on the production of high quality crystals with reasonable size. The field of crystal growth is interdisciplinary as it needs expertise in fields such as Physics, Chemistry, Mathematics, Electrical Engineering, Crystallography and Optics.

Modern technology is based on single crystals of nonlinear optical, ferroelectric, semiconductor, superconductor and acousto-optic materials. New materials are the lifeblood of solid state research and device technology. Nonlinear optical materials have come upon the materials science scene and are being studied by many research groups around the world. These materials operate on light in a way very analogous to the way of semiconductors which operate on electrons to produce very fast electronic switching and computing circuits. Due to the large requirement of crystals to fulfill the needs of the
current information world and emerging field of research, many methods for the growth of crystals have been a part of research in the last decades. The mission of crystal grower is to adopt suitable technique for a particular material to produce a large size single crystal from its poly-crystalline form.

1.2 CRYSTAL GROWTH TECHNIQUES

The choice of a particular crystal growth method depends on the material to be crystallized, its quality, size, growth rate, particularly its physical and chemical properties and the nature of the method. A number of crystal growth methods that were proposed based on the three main general classifications such as,

i. Growth from solutions
ii. Growth from melt and
iii. Growth from vapour phase

1.2.1 Growth from Solutions

Growth from solution is more widely used than growth from the melt or from the vapour phase. A saturated solution of the material in an appropriate solvent is used for this process. The solution is supersaturated by evaporating the solvent (isothermal methods) or by lowering the solution temperature (non-isothermal methods) and hence the growth takes place. Growth from solution is used more broadly than growth from the melt as it requires lower temperatures that lead to lower density of lattice defects.

In general, solution growth is simple and inexpensive. However, it becomes complex, when rigid specifications on the purity and size of the crystals are imposed and the properties of the solvent increases the requirements for instrumentation and control of the growth parameters.
The general classifications of the solution growth are low temperature solution growth, high temperature solution growth and hydrothermal growth.

1.2.2 Growth from Melt

In principle, all materials can be grown in single crystal form from the melt, provided when the material melt congruently, do not decompose before melting, and do not undergo a phase transformation between the melting point and the room temperature. Growth from melt is the fastest crystal growth method, as its rate does not depend on mass transport processes. Melt growth can be achieved through different techniques depending on the specific properties of the material and requirements of size and shape. In addition, the compositional requirements (e.g. dopant distribution) can be an important factor in choosing a specific technique.

1.2.3 Growth from Vapour Phase

In general, gases can be obtained at higher levels of purity than liquid and the high purity conditions can usually be maintained during gaseous processes. Thus, vapour phase growth can readily lead to high purity materials. Bulk as well as thin layers are prepared from vapour phase. As the growth rate from the vapour phase is slow, bulk crystals are prepared when their growth by other methods is not possible or leads to inferior crystals. This method is extensively used for the growth of high quality thin layers of materials such as Si (silicon) compound semiconductors, layers of metals and other inorganic compounds.

1.3 LOW TEMPERATURE SOLUTION GROWTH

The low temperature solution growth is probably the oldest method of crystal growth. However, rapid developments in the techniques of solution
growth took place in the present century due to the demands of crystals of good quality for industrial applications. The method of crystal growth from low temperature solutions is extremely popular in the production of crystals for many basic and technological applications. This method is more widely used to grow bulk crystals. Materials having moderate to high solubility in the temperature range ambient to 100 °C at atmospheric pressure can be grown by low temperature solution method. The mechanism of crystallization from solutions is governed, in addition to other factors, the interaction of the ions or molecules of the solute and the solvent that is based on the solubility of substance on the thermodynamical parameters of the process, temperature, pressure and solvent concentration (Chernov 1984).

The method of growing crystals from solutions may be used for substances fairly soluble in a solvent and not reactive with it. Despite this limitation of usability, this method is in constant use because of the following reasons:

- The method and growth apparatus are relatively simple and cheap
- Low growth temperature introduces small thermal stresses in the crystals obtained
- It leads to good quality crystals
- It lends itself to continuous operation
- The crystals obtained usually have well developed faces (growth habit), which enables to investigate crystal growth processes including in situ observations and capture of impurities
In addition, growth from aqueous solution can be visually analyzed and has been extensively used for studying the growth parameters (including convection and mass transport) by means of photography.

Other advantages of low temperature solution growth are the proximity to ambient temperature and, consequently, the degree of control which can be exercised over the growth conditions. This method is restricted not only for water soluble materials, but also for the materials which are insoluble in water. It can also be brought into solution by the uses of complexes. Supersaturation can be accurately and precisely controlled because of the stabilization of temperature up to ± 0.01 °C. In addition to these factors, ease of efficient agitation of the growing crystal and solution reduces all kinds of fluctuations to a minimum. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal during the process of growth and on removal from the apparatus. The materials which suffer from decomposition in the melt or at high temperatures in the solid and which undergo phase transformations are suited for low temperature solution growth. Large number of organic and inorganic materials falls under low temperature solution growth. Low temperature solution growth also permits the preparation of different morphologies and polymorphic forms of the same substance by variation in the growth conditions.

1.4 NUCLEATION

Nucleation is an important phenomenon in crystal growth. In a supersaturated system, when few atoms or molecules join together a change in energy takes place in the process of formation of the cluster. The cluster consisting of atoms or molecules is normally termed as embryo. An embryo
may grow or disintegrate and disappear completely. If the embryo grows to a particular size—critical size—known as critical nucleus, then there is greater probability for the nucleus to grow. Thus the birth of critical nucleus is an important event in crystal growth. There are four stages involved in the formation of the stable nucleus. First stage is the development of supersaturated stage. This may be due to a chemical reaction, changes in pressure, temperature or any other chemical or physical condition. The second stage is the generation of embryo. This may be either homogeneous where the atoms or molecules build themselves in the interior of the parent system or heterogeneous where the molecules build up on an impurity atom or dust particle or on the surface of the container or on any other imperfections. The third stage is the growth of the embryo from the unstable or metastable state to the stable state or the critical size and fourth stage is the relaxation processes where the texture of the newly born nucleus alters.

1.5 TYPES OF NUCLEATION

According to the conditions existing in a supersaturated system, nucleation processes may be represented by the following scheme:

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Nucleation
  |   
  Primary ——— Secondary
            |     |   |
        Homogeneous (spontaneous) ——— Heterogeneous (induced by foreign particles)
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The term primary will be reserved for both the case of homogeneous and heterogeneous nucleations, 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, referred to secondary nucleation. Formation of nuclei of a new phase in the mother phase (homogeneous nucleation) can occur only when supersaturation in the system is sufficiently high. In supersaturated homogeneous systems, nuclei of the new phase can appear and disappear as a result of statistical fluctuations. However, there is always a certain statistical probability that some neighboring particles acquire sufficient energy necessary for the formation of stable three dimensional nucleus (critical nucleus) of the new phase.

Considerations of homogeneous nucleation have basic significance for the general understanding of the problem of nucleation. However, in practice, one usually encounters heterogeneous nucleation. Heterogeneous nucleation involves the formation of nuclei in conditions when certain sites (e.g. impurity particles in the medium or cracks in the walls of a crystallizer) serve as the catalytic agents for the process of nucleation of the new phase. Nucleation can often be induced by the external influences like agitation, mechanical stock, friction, extreme pressure, electric or magnetic fields, spark discharge, UV, X-rays, γ-rays, sonic and ultrasonic irradiation and so on. Activation energy for heterogeneous nucleation is lower than that for homogeneous nucleation. Therefore, under the same temperature and pressure conditions, heterogeneous nucleation occurs at the lower supersaturation (supercooling) than the homogeneous nucleation.

When the pressure of a vapour is less than, equal to, or greater than the vapour pressure of the liquid phase at the same temperature known as equilibrium pressure, the vapour is described as undersaturated, saturated or supersaturated with respect to the liquid phase. The undersaturated and saturated states are thermodynamically stable. But the supersaturated state is unstable; i.e., a supersaturated vapour in contact with the bulk liquid phase will condense onto the liquid until the saturation is obtained.
In a supersaturated vapour, single molecules $A_1$ and embryos are present which are clusters of molecules bound together by their intermolecular interactions. The mechanism of formation of such embryos is the simple collision process consisting of a single molecule $A_1$ with a cluster $A_{i-1}$ consisting of $(i-1)$ molecules and thus giving rise to a cluster $A_i$: i.e.,

$$A_1 + A_{i-1} \rightarrow A_i$$  \hspace{1cm} (1.1)

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

$$A_{i+1} \rightarrow A_i + A_1$$  \hspace{1cm} (1.2)

The phase change takes place by single molecules becoming attached to embryos of various sizes; these processes predominate slightly over the reverse processes in which the various embryos lose single molecules. The size distribution of embryos changes with time, the numbers of embryos increases. There is a critical size which is in unstable equilibrium with the supersaturated vapour; the formation of this critical nucleus constitutes the bottleneck of the phase change. Once embryos achieve the critical size, there is a high probability that they will grow, relatively unhindered, to macroscopic size.

### 1.6 SOLUTION AND SOLUBILITY

The term solution is most commonly used to describe the liquid which is the result of dissolving a quantity of a given substance in a pure liquid. In solution, solute is the component, which is present in a smaller quantity. 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. For a given solute, there may be different solvents. Solubility gradient is
an another important parameter, which dictates the growth procedure. It will be seen that the saturation of a given solvent by a solid (the solute) cannot be represented by a single value, but by a series of values which can be plotted on a curve with the temperatures as ordinates and concentrations of solute as abscissae. For every given solvent, such a succession of points can be plotted for every substance soluble in it; the curves are often referred to as solubility curves or curves of saturation. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals 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 grow the good quality bulk crystals in both cases. 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. When the solubility gradient is very small, slow evaporation of the solvent is the option for crystal growth to maintain the supersaturation in the solution. If solubility of a material increases with increase in temperature, it is called positive temperature coefficient material and if it decreases with increase in temperature it is called negative temperature coefficient material. Majority of the materials are positive temperature coefficient materials.

1.7 SATURATION AND SUPERSATURATION

A solution that is in equilibrium with the solid phase is said to be saturated with respect to that solid. A solution containing more dissolved solid than that represented by saturation condition is said to be supersaturated solution. Uncontaminated solutions in clean containers, cooled slowly without disturbance in a dust free atmosphere, can readily be made to show appreciable degrees of supersaturation.
Supersaturation is an important parameter for the solution growth process. The crystal grows by the accession of the solute in the solution as a degree of supersaturation is maintained. 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. A typical solubility diagram is shown in Figure 1.1.

![Solubility diagram](image)

**Figure 1.1 Solubility diagram**

The lower continuous line is the normal solubility curve for the material concerned. Temperatures and concentrations at which spontaneous crystallization occurs are represented by the upper curve, generally referred to as the supersolubility curve. This curve is not so well defined as the solubility curve and its position in the diagram depends on the other things, such as the degree of agitation of the solution. A region of metastability exists in the supersaturated region above the solubility curve. The diagram is therefore divided into three zones:
i. Region I corresponds to the stable (unsaturated zone), where crystallization is not possible. This region is thermodynamically stable.

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

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

1.8 EXPRESSION OF SUPERSATURATION

In order to grow crystals, the solution must be supersaturated; the concentration of the solute in the solvent should be more than the equilibrium concentration. The supersaturation of a system may be expressed in number of ways. The concentration driving force (Δc), supersaturation ratio (S) and relative supersaturation (σ) are related to each other as follows:

Concentration driving force \( Δc = c - c_o \) \hspace{1cm} (1.3)

Where \( c \) is the actual concentration of the solution and \( c_o \) is the equilibrium concentration at a given temperature.

Supersaturation ratio \( S = c/c_o \) \hspace{1cm} (1.4)

Relative supersaturation \( σ = (c - c_o)/c_o \)

\( σ = S - 1 \) \hspace{1cm} (1.5)
1.9 METASTABLE ZONE WIDTH

A new crystalline phase can form and grow from the liquid phase only if the latter is supersaturated with respect to the former. In general, the degree of supersaturation may be represented by concentration–temperature diagrams. Liquid-solid phase transition is illustrated by the diagram (Sangwal 1994) shown in Figure 1.2.

Figure 1.2 Representation of the metastable zone in a concentration-temperature diagram

Cooling of the solution of composition A' leads to the point A lying on the solubility curve. The point A represents the solution in equilibrium with the solid. Further, slow decrease in the temperature leads to the point B without the formation of the solid. The solutions becomes supersaturated i.e. the solute concentration exceeds the equilibrium concentration. Despite this, the solid phase is not precipitated even after a sufficiently long time.
Further decrease in temperature, however, results in rapid crystallization. In between the points A and B, the solution is in the metastable state. The position of the boundary of the metastability state (point B) is expressed by the maximum supercooling $\Delta T_{\text{max}} = (T_2 - T_1)$ corresponding to the maximum concentration difference $\Delta c_{\text{max}} = (c_{oT2} - c_{oT1})$. These maximum values of supercooling and concentration difference are related by

$$\Delta c_{\text{max}} \approx \Delta T_{\text{max}} \left(\frac{dc_o}{dT}\right)$$  \hspace{1cm} (1.6)

By evaporating the solvent, the point A can also be reached isothermally from point A". Evaporation of the solvent result in entering into the metastable zone until the metastability boundary at point C. Further evaporation of the solvent leads to an instantaneous precipitation of the solid phase. The value of $(\Delta c_{\text{max}})T = (c_{oT3} - c_{oT2})$ obtained isothermally corresponds to the value of $\Delta T_{\text{max}} = (T_3 - T_2)$.

The metastable zone in real systems can be divided into two parts (by dashed line in Figure 1.2). In the region between the equilibrium curve and the dashed curve instantaneous nucleation, in principle, does not occur. But instantaneous nucleation (precipitation) takes place in between the dashed line and the metastability boundary. It should be pointed out that nucleation and growth processes take place in the metastable zone while precipitation in the unstable zone.

The width of the metastable zone of a supersaturated solution is affected by a number of factors, of which most important are the temperature, the physical purity of the solution, the thermal history of the solution, the cooling rate, the presence of soluble additives, mechanical effects etc. Most of these effects are closely connected with nucleation behavior of the solution.
1.9.1 Determination of Metastable Zone Width by Polythermal Method

The width of the metastable zone in aqueous solutions can be experimentally determined by polythermal method. In this method, the solution is cooled in a controlled manner from the saturation temperature (or higher) to the temperature at which visible crystals appear or where there is a discontinuity in the temperature dependence of the conductivity, refractive index etc. The difference in these temperatures is then the maximum supercooling, $\Delta T_{\text{max}}$.

The measured solution placed in a sealed ampoule or test tube is cooled either spontaneously or at a controlled rate of 2 to about 30 °C/h. The solution is either unstirred during cooling or is stirred in a suitable manner by using stirrers (Nyvlt et al 1970, Nyvlt 1971).

The determined values of $\Delta T_{\text{max}}$ depend on the experimental method used, and especially on the manner of detection of the change in the state of the solution and of preparing the solution before the measurement.

1.10 INDUCTION PERIOD

A period of time usually elapses between the achievement of supersaturation and the appearance of the crystals is generally referred as induction period. This time lag is considerably influenced by the level of supersaturation, state of agitation, presence of impurities, viscosity etc.

The induction period considered as being made up of several parts. For example, a certain relaxation time, $t_r$, is required for the system to achieve a quasi-steady-state distribution of molecular clusters. Time is also required for the formation of a stable nucleus, $t_n$, and then for the nucleus to grow to a detectable size, $t_g$. So the induction period, $t_{\text{ind}}$, may be written as
\[ t_{\text{ind}} = t_r + t_n + t_g \] (1.7)

It is difficult to isolate these separate quantities. The relaxation time depends to a great extent on the system viscosity. The nucleation time depends on the supersaturation which affects the size of the critical nucleus, but its estimation is the subject of speculation (Sohnel et al 1988). The growth time depends on the size at which nuclei are detectable and the growth rate applicable to this early stage of development.

In some systems, particularly at low supersaturations, another time lag may be observed. To distinguish it from the induction period, defined above as the point at which crystals are first detected in the system, the term latent period will be used, and is defined here as the onset of a significant change in the system, e.g. the occurrence of massive nucleation or some clear evidence of substantial solution desupersaturation. Figure 1.3 indicates some of these events diagrammatically on a typical desupersaturation curve (Mullin 1993).

Figure 1.3 Diagrammatic representation of desupersaturation curve
In the figure, $c_o$ = equilibrium concentration, $t_n$ = nucleation time, $t_{\text{ind}}$ = induction period, $t_{\text{lp}}$ = latent period. Supersaturation is created at zero time (point A) and a certain induction time $t_{\text{ind}}$ elapses before crystals are first detected (B). This point, of course, is not the nucleation time $t_n$ (B’) since critical sized nuclei cannot be detected; they need a certain time ($t_{\text{ind}} - t_n$) to grow into crystals of detectable size. However, at point B, and often for a considerable time afterwards, no significant changes in the solution may be detected until, at point C, sometimes referred to as the end of the latent period, $t_{\text{lp}}$, rapid desupersaturation occurs (D). Crystal growth predominates during the desupersaturation region. Towards the end of the gradual approach to equilibrium, E, which may take hours or days, an ageing process, may occur. At very high supersaturations, the induction time and latent period can be extremely short and virtually indistinguishable.

The presence of seed crystals generally reduces the induction period, but does not necessarily eliminate it. Even if the system is seeded at time $t = 0$, a measurable induction period $t_{\text{ind}}$ may elapse before new crystals are detected. Factors that can influence the induction and latent periods and the rate of desupersaturation are temperature, agitation, heat effects during crystallization, seed size, seed surface area and the presence of impurities.

1.11 METHODS OF CRYSTALLIZATION

Low temperature solution growth can be classified as

i. Slow cooling method

ii. Slow evaporation method

1.11.1 Crystallization by Slow Cooling of Solutions

In this method, supersaturation is produced by change in temperature usually through out the whole crystallizer. The crystallization
process is carried out in such a way that the point on the temperature
dependence of the concentration moves into the metastable region along the
saturation curve in the direction of lower solubility. Since the volume of the
crystallizer is finite and the amount of substance placed in it is limited, the
supersaturation requires systematic cooling. The main disadvantage of this
method is the need to use the 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 growth period. Volume of the crystallizer is selected based
on the desired size of the crystals. It is the best way to grow crystals from
solution technique, even though the method has technical difficulty of
requiring a programmable temperature controller.

1.11.2 Crystallization by Solvent Evaporation

In this method the temperature is fixed constant and provision is
made for evaporation. With non-toxic solvents like water, it is permissible to
allow evaporation into atmosphere. An excess of a given solute is established
by utilizing the difference between rates of evaporation of the solvent and the
solute. In this method, volume of the solution decreases, but total mass of the
system remains constant in slow cooling method. Generally vapour pressure
of the solvent above the solution is higher than the vapour pressure of the
solute and, therefore, the solvent evaporates more rapidly and the solution
becomes supersaturated (Petrov 1969). Usually, it is sufficient to allow the
vapour formed above the solution to escape freely into the atmosphere.
Careful initial filtration of the solution and the use of new, unscratched
crystallizers help to minimize the number of nucleation sites and produce
larger size crystals. The growth crystallizer should be left undisturbed in a
fairly constant temperature environment for the duration of crystallization
process which may be up to several weeks. This method is very much suited
for the materials having very small temperature coefficient of solubility or negative temperature coefficient.

1.12 SELECTION OF SOLVENT

Selection of a solvent is a critical step in crystal growth from low temperature solutions. Apart from high purity starting materials, solution growth requires a good solvent. A solvent for growth should have a number of properties such as good solubility of the material in it, good temperature coefficient of solute solubility, no corrosion of growth apparatus, low vapour pressure at the growth temperature, low toxicity and inflammability, low viscosity, non-volatality, maximum stability, cheap in pure state etc.

The proper selection of a solvent depends on the chemical similarity between the solvent and the material to be grown. For example, crystals of nonpolar organic compounds easily grow from nonpolar organic solvents. The chemical similarity also determines crystal solubility in the solvent. Consequently, because of the interaction of the surface of a growing crystal and the solvents molecules, the solvent also provides a control over crystal habit.

For growing many materials, water is a good solvent because of its low viscosity, low toxicity, easily availability in the pure state and cheapness. It is also inert a variety of glasses, plastics and metals, and provides a reasonably wide range for the selection of growth temperature in comparison with the other solvents. However, water is not a reversible solvent for some materials. It hydrolys some materials and introduces water of crystallization to other substances which may be desired in the anhydrous form. In such a situation, other solvents have to be used. Generally, organic solvents are volatile, toxic and inflammable.
A solvent in which the solute has solubility between 10 and 60% may be considered suitable for crystal growth. In the case of very high solubilities (i.e. solutions containing a large amount of solute), growth rate may be very low due to the increased solution viscosity which renders the system diffusion-controlled or the resulting crystals are of unwanted morphology. Similarly, solvents in which a solute is less soluble also provide low growth rates due to the low solubility. In both these cases it is desirable to use solution modifiers to change solubility or viscosity.

1.13 PREPARATION OF SOLUTION

For rapid preparation of solutions, stirring or vigorous shaking helps to promote a rapid mixing of the solute and solvent components. They have no influence on the amount of solid material that a given solvent can take in, but this varies from one temperature to another so that, if the temperature remains the same, a time will arrive when the solution is completely saturated for this temperature. The only way to get the solution to hold more solid is to change the temperature until, at given higher degree, another saturation value will be reached.

1.14 INTRODUCTION OF NONLINEAR OPTICS

Nonlinear optics is a study that deals mainly with various new optical effects and novel phenomena arising from the interactions of intense coherent optical radiation with matter. Second harmonic generation (SHG) was the first nonlinear optical effect ever observed in which a coherent input generated a coherent output. Nonlinear optics (NLO) covers a much broader scope. It deals in general the problems such as light-induced changes in the optical properties of a medium in the nonlinear interaction of light with matter. Each nonlinear optical process consists of two steps. The intense light first induces a nonlinear response in a medium, and then the medium in reacting
modifies the optical fields in a nonlinear way. Other NLO effects are third, fourth, and fifth harmonic generation, optical parametric oscillation, linear and quadratic electro-optic effects, acousto-optic effect, stimulated Raman scattering and self-focusing of light (Davis 2000).

In the regime of conventional optics, the electric polarization vector $P$ is simply assumed to be linearly proportional to the electric field strength $E$ of an applied optical wave, i.e.,

$$ P = \varepsilon_o \chi E $$

(1.8)

where $\varepsilon_o$ is the free-space permittivity and $\chi$ is the susceptibility of the given medium.

Maiman (1960) developed first laser in 1960, which was an opening of a new era for laser research. Franken et al (1961) successfully demonstrated harmonic generation in quartz crystal by a ruby laser light in 1961. Shortly after this discovery, several other coherent optical frequency mixing effects (such as optical sum-frequency generation, optical difference-frequency generation and optical third harmonic generation) were observed. The researchers realized that all these new effects could be reasonably explained if the linear term on the right hand side of equation (1.8) replaced by a power series

$$ P = \varepsilon_o [\chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots] $$

(1.9)

Here $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the first order (linear), second order (nonlinear) and third order (nonlinear) susceptibility and so on. They are material coefficients and in general are tensors. In the case of centrosymmetric crystal, $\chi^{(2)} = 0$ and hence the material cannot exhibit second
harmonic generation but can exhibit harmonic generation of third and fifth order.

The phenomenon of nonlinear optics is very handy in the conversion of available laser light frequency to double or triple. The usefulness of laser is extended further with this phenomenon. The discovery of nonlinear properties in quartz crystal makes the material research and crystal growth and technology more intensive.

An important development in nonlinear optical materials occurred in 1970, when Davydov et al (1970) reported a strong second harmonic generation in organic molecules having electron donor and acceptor groups connected with a benzene ring. This discovery led to an entirely new concept of molecular engineering to synthesize new materials for the SHG studies. In the 1980s, tremendous growth occurred in design and development of materials for second order nonlinear optics.

Materials having attractive NLO properties are being discovered at a rapid pace, with advances in crystal growth technology making possible the commercial development of promising materials such as potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), lithium niobate (LiNbO$_3$), potassium titanyl phosphate (KTP) etc. Currently KDP and ADP crystals are needed for laser radiation conversion in laser fusion system because of its excellent properties (Zaitseva et al 2001). LiNbO$_3$ have large values of electro-optic coefficients favourable for the applications as frequency doublers (Li et al 2010). KTP has high optical nonlinearity, large temperature and angular allowance and it is mechanically hard (Roth et al 2010). Recently, substantial progress has been made in the development of nonlinear optical materials such as 4-N, N-dimethylamino-4'-N'-methyl stilbazolium tosylate (DAST) (Ruiz et al 2008), 2-methyl-4-nitroaniline (MNA) (Okwieka et al 2008) and borate crystals (Zhang et al 2009).
1.15 CHARACTERISTICS OF NONLINEAR OPTICAL CRYSTALS

Nonlinear optical crystals play a major role in fast developing fields like photonics and optoelectronics. In the last decades major advances have been made in the development of nonlinear materials with improved optical and mechanical characteristics and high damage thresholds.

An ideal nonlinear optical crystal should possess the following characteristics:

i. Large nonlinear figure-of-merit for frequency conversion
ii. Wide phase matching angle
iii. High laser damage threshold
iv. Wide optical transparency
v. Ease of fabrication
vi. High mechanical, thermal and chemical stability

Large nonlinear optical coefficient in the phase matching direction is an important parameter for effective NLO crystal for the attainment of nontrivial gain. The effective nonlinear coefficient and the types of phase matching that are allowed can be determined from the symmetry group of the material and the sign of crystal birefringence.

An efficient NLO crystal should be phase matchable over the range of interaction frequencies. In other words, the crystal must be sufficiently birefringent to compensate for dispersion and thus allow phase matching. The degree of birefringence of the crystal and its phase-matchability can be determined from the refractive index data at appropriate wavelengths, which may be obtained from the dispersion relations called Sellmeier equations for the material.
The operation of nonlinear devices obviously involves the exposure of material to high power laser source. For harmonic generation, the efficiency of conversion is strongly dependent on the incident power level. The utility of NLO crystal depends largely on its ability to withstand high power lasers. Because of the high optical intensities involved in nonlinear processes, the materials must be able to withstand power densities typically in excess of 10 MW/cm$^2$ and often many times this value. Optical damage may be caused by several different mechanisms and can be of various types. The predominant type is irreversible damage, which can take the form of surface or bulk damage. It can be caused by thermal heating, induced absorption self focusing, stimulated brillouin scattering, dielectric breakdown or several other mechanisms. Accurate determination of the damage threshold for a given material is often difficult, as it depends on the wavelength of the radiation and the exact experimental conditions under which the measurements are performed. It is also found that the surface preparation and cleanliness as well as the presence of inclusions or impurities in the particular crystal sample can strongly affect the material damage threshold (Bass et al 1973).

A wide transmission range is desirable for a NLO crystal, as it extends the useful frequency range of the device. Certain crystals exhibit losses in the form of absorption or scattering or both. Low losses are very important as high losses can severely affect the conversion efficiency of the nonlinear process or the threshold for oscillation in parametric devices. Moreover, the absorption losses can give rise to thermal distortions in material, which drastically limit the device performance, particularly at high power levels, and can lead to premature optical damage. Thus a good NLO crystal should exhibit low optical losses at the frequencies involved.
One of the most important considerations in the choice of a material for NLO applications is its optical quality. In particular, the material must be free from optical inhomogeneities, inclusions, impurities and other imperfections. In addition, it must be available in the bulk form and large size. Other practical considerations include mechanical hardness, chemical stability, low cost and ease of device fabrication. Mechanical strength is one of the important deciding factors in selecting the processing (cutting, grinding and polishing) steps of bulk crystal in fabrication of devices based on crystals. Thermal stability of crystal determines the temperature range in which the fabricated device works. Other important parameters are non-toxicity and good environmental and chemical stability.

### 1.16 TYPES OF NONLINEAR OPTICAL CRYSTALS

There is a widespread need to have high power monochromatic optical sources at frequencies from the ultraviolet to the far infrared for a variety of device applications. The development of new lasers is a very lengthy procedure and therefore, frequency conversion using nonlinear optical single crystals has become the method of choice for frequency generation. No single material can be used over the entire wavelength range. Thus, several classes of materials have been developed for operation in specific spectral regions.

In the ultraviolet region, there are few materials with the requisite properties for generating light at wavelengths below 200 nm. Urea and β-barium borate (BBO) are, so far, the most promising crystals. Urea, although mechanically fragile and hygroscopic, has been used as an optical parametric oscillator to generate tunable radiation throughout the visible, but intrinsic absorption and phasematchability considerations makes it unsuitable for wavelengths longer than 1200 nm (Donaldson et al 1984). BBO seems much more attractive due to its better mechanical and chemical properties, a
temperature bandwidth for doubling 1064 nm larger than any other known material, high damage threshold (3 times KDP) and transparency from 200 to 3000 nm and phasematchability for fifth harmonic generation at 212 nm (Chen et al 1985).

In the visible region, a broad choice of crystals exists including phosphates, niobates, iodates and oxide materials. Phosphate materials such as KDP and its isomorphs are representative of hydrogen bonded materials which possess important nonlinear optical, piezoelectric, ferroelectric and electro-optic properties. Another phosphate material, KTP is an efficient nonlinear optical crystal in the visible spectral region with relatively low cost. It has large nonlinear coefficient. Its damage threshold is near 1 GW/cm$^2$ for 1 Hz, 10 ns pulses at 1064 nm (Villa et al 2007). In the visible region, niobate crystals such as lithium niobate (Kar et al 2008) and potassium niobate (KNbO$_3$) (Duan et al 2001) crystals possesses the largest nonlinear coefficients for wavelength conversion of all commercially available inorganic materials. Iodate crystal, lithium iodate is a uniaxial crystal with high NLO coefficients and wide transparency range in visible region (Galez et al 2002).

For infrared applications, non-oxide materials such as the chalcopyrite compounds silver gallium sulfide (AgGaS$_2$), silver gallium selenite (AgGaSe$_2$), zinc germanium diphosphide (ZnGeP$_2$) and cadmium germanium arsenide (CdGeAs$_2$) have attractive properties. AgGaS$_2$ and AgGaSe$_2$ crystals have recently attained special interest for the middle and deep infrared (IR) applications due to their large NLO coefficients and high transmission in the IR region (Atuchin et al 2006, Knuteson et al 2010). ZnGeP$_2$ and CdGeAs$_2$ single crystals are the highly-effective NLO materials for the middle IR as well as terahertz range (Petrov et al 1997, Bai et al 2005).
On the basis of three types of cohesive forces that bind the charges and polarization together, the NLO crystals can be classified into the following cases.

i. Organic crystals
ii. Inorganic crystals
iii. Semiorganic crystals

1.17 ORGANIC CRYSTALS

Organic crystals have compounds with carbon atoms as their essential structural elements. Extensive research in the last decades has shown that organic crystals often possess a higher degree of optical nonlinearity than their inorganic counterparts. Some of the advantages of organic materials include inherently high nonlinearity, high electronic susceptibility through high molecular polarizability, fast response time, the ease of varied synthesis, scope for altering the properties by functional substitutions, high damage resistance, relative ease of device processing, etc. Organic materials have another advantage over inorganic materials, in that the properties of organic materials can be optimized by modifying the molecular structure using molecular engineering and synthesis. A very large operating bandwidth modulation in organic electro-optic devices can be obtained through its low dielectric constant at low frequencies.

Many organic materials have figures-of-merit which are two to three orders of magnitude greater than that of their inorganic counterparts and exhibit substantially greater laser damage thresholds. The molecular features that give rise to large nonlinearities are now well understood and the quantitative prediction of hyperpolarizabilities is well established. The use of this predictive capability, in combination with molecular engineering methods, has enabled improvements in performance through the identification, design
and synthesis of new molecules. Tailoring of molecular structure has been utilized not only for the enhancement of second order hyperpolarizabilities but also to promote crystallization of potentially useful molecules in noncentrosymmetric crystal structures and with favourable molecular orientations for phase matching. Majority of organic crystals can be successfully grown from solution growth method. In addition to water, the organic solvents such as acetone, xylene, benzene etc. are used for the growth of organic crystals. Development of organic single crystals is one of the important emerging areas of optoelectronics and molecular engineering for advanced technology devices.

1.17.1 **Origin of Second Order Nonlinear Optical Effects in Organic Molecules**

Virtually second order NLO effects in organic molecules originate from a strong donor-acceptor intramolecular interaction. This concept was demonstrated by Davydov and co-workers in 1970 while screening SHG activity in a wide variety of substituted benzenes. They concluded that the dipolar aromatic molecules possessing an electron donor group and an electron acceptor group contribute to large second order optical nonlinearity arising from the intramolecular charge transfer between the two groups of opposite nature. Therefore, a typical SHG active molecule can be presented as shown below if it lacks a center of symmetry. On the other hand, $\pi$-conjugated molecules with a donor and an acceptor will not display SHG activity if they possess a center of symmetry. These symmetry requirements eliminate many materials from being SHG active and at the early stage of designing and synthesizing novel materials, one has to consider ways of introducing noncentrosymmetry in the molecular structures (Chemla et al 1987).
The large second order optical nonlinearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end. The $\pi$-conjugated systems could be benzene, azobenzene, stilbene, biphenyl, benzylidene, heterocycle, polyenes etc. (Nalwa et al 1996).

1.18 INORGANIC CRYSTALS

Inorganic crystals are mostly ionic bonded and it is always easier to synthesize inorganic materials. Normally inorganic crystals have high melting point and high degree of chemical inertness. High temperature oxide materials are well studied for diverse applications like piezoelectricity, ferroelectricity, and electro-optics. Examples of most useful inorganic crystals discovered are KDP and its analogues, LiNbO$_3$, KNbO$_3$, BBO, KTP and its analogues etc. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation at high efficiency in new regions of the spectrum inaccessible by other nonlinear crystals and conventional laser sources.

A major obstacle to the development many organic NLO materials and the exploitation of their full potential has been the considerable difficulty associated with the growth of large high quality single crystals of these materials. As with many other organic solids, the intermolecular forces are comparatively weak, being predominantly van der Waals or permanent dipole-dipole interactions. This typically results in low melting points and relatively high vapour pressure. Mechanical properties are, in general, rather poor with most organic solids being relatively soft. This can have important consequences for the structural perfection of the crystals.  These factors
together with the low thermal conductivities can pose substantial problems in organic crystal growth. Scientists working on laser materials realize the extreme importance, in the search for new materials having excellent properties with a thorough elucidation of the structure-property relationship between NLO effects and microstructure. This resulted in the new inorganic NLO crystals such as perovskite, phosphate, iodate, nitrate crystals etc.

1.19 SEMIORGANIC CRYSTALS

Semiorganic materials have the potential for combining high optical nonlinearity and chemical flexibility of organic with the physical ruggedness of inorganic. The inherent limitations on the maximum attainable nonlinearity in inorganic materials and the moderate success in growing large size device grade organic single crystals have made scientists adopt newer strategies. The obvious one was to develop hybrid inorganic–organic materials with little trade-off in their respective advantages. This new class of materials has come to be known as the semiorganics (Bhat 1994). A new approach to high efficiency, optical quality, and organic based nonlinear optical materials is to consider compounds in which a polarizable organic molecule can be bound within an inorganic host.

A typical case is the formation of inorganic salts of chiral organic molecules. L-arginine phosphate monohydrate (LAP) is an example of this semiorganic class discovered by Xu et al (1983). An organic chiral molecule (L-arginine), an inorganic acentric tetrahedral molecule (phosphoric acid), and a water molecule are combined by positive-negative coulomb interactions and hydrogen bonding. There are plenty of choices of organic molecules to form semiorganic salts. The examples of predominantly NLO active organic salts are amino acids, tartrates and oxalates.
An alternative and closely related strategy is to form metal-coordination complexes of highly polarizable organic molecules. The choices of the ligands are unlimited. Infact, the organic part need not be noncentrosymmetric. This is illustrated by the example of thiourea, which forms excellent complexes with zinc and cadmium. Thiourea is more polarizable than urea because of the presence of large sulphur atoms and hydrogen bonds in the NH₂ ensure the lack of center of inversion in many thiourea complexes. The other known choices of ligand are allyl thiourea, guanidium and dithiocarbamate.

The advantages of semiorganic materials are that they can be grown from aqueous solution and form large three dimensional crystals. The crystals can be easily cut and polished with specific phase-matching loci, acceptance angle, and the effective nonlinear coefficient, for frequency doubling of 1064 nm.

1.20 SCOPE OF THE THESIS

The present thesis aimed at the growth and characterization of nonlinear optical single crystals of bis(2-aminopyridinium) maleate, γ-glycine, tris(glycine) calcium(II) dichloride, bis(2-aminopyridinium) sulfate, potassium carbonate doped KDP, potassium thiocyanate doped KDP, L-arginine monohydrochloride doped ADP and L-alanine doped ADP by low temperature solution growth technique.

Single crystal X-ray diffraction analysis was performed to determine unit cell parameters of the grown crystals. The structural perfection of the crystals has been analyzed by high-resolution X-ray diffraction (HRXRD) rocking curve measurements. Fourier transform infrared (FTIR) analysis was performed to get information about the molecular structure, inter and intra molecular forces, vibrational interactions, hydrogen bonding etc. The optical transmittance window and the lower cutoff wavelength were
identified by UV–vis–NIR studies. Thermo gravimetric and differential thermal analysis (TG-DTA) studies were used to study its thermal properties. Dielectric constant and dielectric loss of these crystals were determined by the parallel plate capacitor method at different frequencies and temperatures. Mechanical strength of the grown crystals was analysed by the determination of Vickers microhardness values at different loads. Powder SHG study was carried out for the materials using Kurtz-Perry powder technique.

Nucleation studies for the determination of solubility, metastable zone width, induction period and crystal growth rate of pure and doped KDP and ADP crystals were carried out. Bulk size KDP and ADP crystals were grown by slow cooling method using microcontroller based seed rotation technique. Piezoelectric charge coefficient of doped crystals were determined by piezometer system and compared with pure.