CHAPTER 1

INTRODUCTION TO CRYSTAL GROWTH
TECHNIQUES AND NONLINEAR OPTICS

1.1 CRYSTAL GROWTH - INTRODUCTION

Crystal growth is an important field of materials science, which involves controlled phase transformation. In the past few decades, there has been a growing interest in the crystal growth process, particularly in view of the increasing demand for materials for technological applications. Crystal growth involves a variety of research fields ranging from surface physics, crystallography and material sciences to condensed matter physics. Though it has been studied extensively for more than 100 years, crystal growth still plays an important role in both theoretical and experimental research fields, as well as on applications [1]. The strong influence of single crystals in the present day technology is evident from the recent developments in the fields of semiconductor, polarizer, transducers, infrared detector, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. All these developments could be achieved due to the discovery of nonlinear optical properties in some organic and semiorganic crystals.

The main applications of crystals till the 19th century were as precious stones in jewellery, in medical prescriptions and in mysticism because of the belief in the special virtues of gemstones - a superstition still
existing in modern times. In the 17\textsuperscript{th} and 18\textsuperscript{th} centuries, crystallography became an independent branch of science. In the 20\textsuperscript{th} century, crystallography became more oriented towards physics and an increasing number of new optical, electrical, mechanical and magnetic phenomena inherent to crystals were found.

Mathematical methods began to be used in the theory of symmetry which achieved its completion in the classical space-group theory at the end of the 19\textsuperscript{th} century. The discovery of X-ray diffraction by crystals caused a complete change in crystallography and in the whole science of atomic structure of matter [2].

The growth of bulk crystalline materials remains one of the most challenging and astonishing of technical endeavors, with objectives ranging from the one-time creation of milligrams of single crystal protein pharmaceuticals to the annual production of metric tons of electronic-grade silicon. Due to this broad application, a great variety of crystals are needed and the exact quality typically required of single crystal materials. Their successful growth ranks among the most difficult challenges of modern materials processing.

Many types of crystals find application in lasers, optical components for communication, light emitting diodes, thermal imaging, piezoelectric detectors etc [3]. The fast development of solid-state physics requires single crystals of near perfection. With the absence of crystals, there would be no electronic industry. Crystals are the prime candidates for the fabrication of optoelectronic devices. New materials are always investigated and the list of applications for crystals is on the rise. Hence growth of crystals has become inevitable for any further development in material science research [4, 5].
The solid-state materials are classified into single crystals, polycrystals and amorphous depending upon the arrangement of constituent molecules, atoms or ions. An ideal crystal may be defined as the solid in which the atoms or molecules are arranged in the most ordered form. In the ordered form, infinite lattice of atoms or molecules are arranged in a pattern, which repeats itself in all three directions. However, real crystals are with finite repetitions and do contain defects.

At present, considerable research has been carried out in nonlinear optics and many useful nonlinear optical materials have been developed artificially by using various crystal growth techniques. Single crystals can be grown successfully from a melt by Czochralski, Bridgman, Kyropoulos and floating zone methods.

In this chapter, various methods of growing single crystals and in particular, the solution growth technique have been presented. The development of the nonlinear optical crystals and theory of nonlinear optics (NLO) are also briefly discussed.

1.2 CRYSTAL GROWTH TECHNIQUES

Based on the phase transformation process, crystal growth techniques are classified as given below:

- Growth from solid - solid – solid phase transformation
- Growth from vapour - vapour – solid phase transformation
- Growth from liquid - liquid – solid phase transformation
There are a number of growth methods in each category [6]. A brief outline of various important techniques of crystal growth has been discussed in this chapter.

1.2.1 Melt Growth

Crystal growth from melt is the important method for growing large single crystals with high perfections. Melt growth is the process of crystallization by fusion and resolidification of the pure material. In this technique, apart from possible contamination from crucible material and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than the other methods [7]. In principle, all materials can be grown into a single crystal from the melt, provided, they melt congruently, they do not decompose before melting and they do not undergo a phase transition between the melting point and room temperature. Growth from melt can be further sub divided into:

(i) Bridgman - Stockbarger method,

(ii) Czochralski technique,

(iii) Verneuil technique,

(iv) Kyropoulos technique and

(v) Zone melting.

The temperature gradient of the furnace plays an important role in Bridgman technique getting the single crystal. The furnace consists of two zones: the upper zone held at a temperature slightly above the melting point of the materials to be grown (T>T_m) and the lower zone at a temperature just below the melting point (T<T_m). The crucible is made of platinum, quartz or glass and has a point as lower and this is filled with the material to be grown and the crucible is lowered very slowly. The temperature gradient between the
two furnaces (I and II) is made as steep as possible. When the tip of the crucible crosses the zone corresponding to the freezing point of the material, a crystal forms at the bottom tip. As the crucible is lowered, the first nucleated seed grows as more melt cools below its melting point. The main advantage of this technique is that it is possible to grow crystals of any desired shape by choosing the appropriate shape of the crucible. Several materials such as ZnS, GaAs, PbS, AgI, CaF₂, AgCl, etc., have been grown in crystal form using this technique. Chlorine doped GaSe is also grown by this method [7, 8].

In *Czochralski method*, the melt is usually taken in a crucible. The melt is raised to a temperature of a few degrees above the melting point and the seed crystal is rotated slowly and brought into contact with the melt surface. After a short pause, pulling is commenced with a fast rate for necking. Necking is employed to minimize the defect content of the crystal being grown. After necking, the rate of pulling decreases or then the melt temperature is lowered slowly so as to have a bigger diameter crystal. The largest use of this method is for the growth of silicon. The advantage of this method is that though the crucible is used, the grown crystal is not in contact with the crucible. LiNbO₃ is the first crystal grown by this method [9, 10].

In the *Verneuil Technique*, fine dry powder of the material to be grown is taken in a container having a fine wire mesh and allowed to fall through the oxygen – hydrogen flame where it melts. The melt falls on the seed crystal which is kept just below the melting point of the substance. The melt freezes progressively and a single layer is obtained. To maintain symmetry, rotation is imparted. In this technique, care must be taken to balance the rate at which the powder feed is supplied at the rate of lowering of the growing crystal to maintain a constant growth rate and diameter. When the rate of feeding is more, the crystal grows bigger and for less feeding, it
will be smaller. Ruby crystals are grown for use in jewelled bearing and lasers. This growth is widely used for the growth of synthetic gems [11, 12].

In *Kyropoulos technique*, the crystal is grown in a larger diameter. From the larger diameter crystal, one can make windows, prisms, lenses and other optical components. 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, for alkali halides to make optical components.

Originally, *zone melting technique* was used only to purify the materials and this can also be used to grow single crystals. In this method, a small liquid zone is created by melting a small amount of materials in a long ingot and moved up or down. For doping an impurity, the ingot is repeatedly moved up and down. Germanium and silicon are a few examples of the crystals grown by this technique. One of the advantages of this method is the simultaneous purification of the materials during the growth process [13, 14].

### 1.2.2 Growth from Solution

This method is widely used to grow the crystals which have high solubility and have variation in solubility with temperature. There are two methods in the solution growth depending upon the solvent and the solubility of the solute. They are:

(i) High temperature solution growth

(ii) Low temperature solution growth
1.2.2.1 High Temperature Solution Growth

The high temperature solution growth can be further sub-divided into

(a) Flux growth method

(b) Hydrothermal growth

In the flux growth method, a solid (molten solid / flux) is used as the solvent instead of a liquid and the growth process takes place well below the melting temperature [15] of the solute. The flux growth is preferably used for the following reasons:

(i) The material melts incongruently

(ii) The melting point of the material is too high and

(iii) The material is non-stoichiometric at its melting point due to a high vapour pressure of one or more constituents.

A number of metals, metal oxides and other compounds, practically insoluble in water up to its boiling point, show an appreciable solubility when the temperature and pressure is increased well above 100 °C and 1 atmosphere respectively.

Hydrothermal growth is usually carried out in steel autoclaves with gold or silver linings. The liquids from which the process starts are usually alkaline aqueous solutions. Pressure is typically in the range of hundreds or thousands of atmospheres. The requirement of high pressure presents practical difficulties and they are only a few crystals of good quality and large size grown by this technique. Quartz is the crystal grown industrially by this technique. The criteria followed for the growth of crystals under this technique are:
(i) A combination of solvent pressure and temperature must be studied and should have sufficient solubility for reasonable supersaturation [16].

(ii) The temperature coefficient of solution density should be large and [17] the vessel must be suitable to contain the pressure temperature condition of the experiment without corrosion.

Materials like quartz, calcite, alumina and antimony sulfite can be grown by this method.

1.2.2.2 Low Temperature Solution Growth

Low temperature solution growth is the most widely used method for the growth of crystals, when the starting materials are unstable at high temperatures. This method demands that the materials must crystallize from solution with prismatic morphology. In general, this method involves seeded growth from a saturated solution. The driving force i.e. the supersaturation is achieved either by lowering the temperature or by the evaporation of the solvent. This method is widely used to grow bulk crystals, which have high solubility and have variation in solubility with temperature [18]. After introducing proper 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 [15].

Low temperature solution growth can be subdivided into the following categories:
(a) Slow cooling method

(b) Slow evaporation method

(c) Temperature gradient method and

(d) Gel method

*Slow cooling* is the best way to grow crystals by the solution growth technique. The main disadvantage of slow cooling method lies in the crystallization over 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, a 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. Even though this method has the technical difficulty of requiring a programmable temperature control, it is widely used with great success [19]. KDP crystals were grown by Rajesh et al., [20] from aqueous solutions with organic additives by this method for better nonlinear optical properties. Sweta Moitra and Tanusree Kar [21] recently reported Zinc Tris (Thiourea) Sulphate (ZTS) was grown by slow cooling method, which exhibits higher resistance to laser damage.

*Slow evaporation method* is similar to the slow cooling method in terms of the apparatus requirements. The temperature is fixed and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05 °C and rate of evaporation of a few mm³/hr. The evaporation technique has 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 can effectively be used for materials having a very low temperature coefficient of solubility.
Srinivasan et al., [22] have reported that the L-asparagininium picrate crystal can be grown by this method and it exhibits high NLO efficiency when compared to the standard KDP crystal. L-tyrosine hydrobromide, semiorganic crystals of good size were grown by slow evaporation technique [23]. Many NLO crystals are grown using this method and they exhibit good SHG efficiency. In the present work, slow evaporation technique employed to grow the nonlinear optical crystals.

*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 achieves supersaturation and the crystal starts growing. The main advantages of this method are:

(i) Crystal grows at 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.

When the growth of single crystals has a problem by conventional technique such as decomposition before melting or non-availability of suitable flux, *gel growth* serves as an excellent alternative method. In this method, aqueous solution of two suitable compounds, which give rise to the required insoluble substance, is allowed to react in a gel medium. Crystals of several millimeter dimensions can be grown in a few days by using a simple test tube apparatus. By this method, many crystals like Antimony trihalide, Cadmium hydroxides etc., have been grown. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases.
fixed frequency laser to a different spectral region. For example, Nd:YAG laser operates in the near infrared at a wavelength of 1064 nm. Second harmonic generation is routinely used to convert the wavelength of the radiation to 532 nm, in the middle of the visible region.

Second harmonic generation can be visualized by considering the interaction in terms of the exchange of photons between the various frequency components of the field. According to this picture, which is illustrated in Figure 1.1 (b), two photons of frequency $\omega$ are destroyed and a photon of frequency $2\omega$ is simultaneously created in a single quantum mechanical process. The solid line in the figure represents the atomic ground state and the dashed lines represent what are known as virtual levels. These levels are not energy eigen levels of the free atom, but rather represent the combined energy of one of the energy eigen states of the atom and of the one or more photons of the radiation field.

![Diagram](image)

**Figure 1.1**  (a) Geometry of second harmonic generation  (b) Energy-level diagram describing second harmonic generation

The second harmonic conversion efficiency is the ratio of the output power of the second harmonic signal to the input power of the fundamental beam and is given by the expression [4, 28]:

\[ \eta = \frac{P_{2\omega}}{P_\omega} \]
\[
\eta = \frac{P_{2\omega}}{P_{\omega}} = 2 \left( \frac{\mu_0}{\varepsilon_0} \right)^{\frac{1}{2}} \frac{\omega^3 d^2 l^2 \sin^2 \left( \frac{\Delta kl}{2} \right) P_{\omega}}{\left( \frac{\Delta kl}{2} \right)^2 n^3 A}
\]  

(1.5)

where \( P_{\omega} \) = power at fundamental frequency, \( P_{2\omega} \) = power at second harmonic frequency, \( d \) = nonlinear optical coefficient, \( n \) = refractive index, \( \omega \) = fundamental frequency, \( k \) = wave vector, \( \Delta k = k^{(2\omega)} - 2k^{(\omega)} \), \( l \) = length of the crystal, \( \varepsilon_0 \) = permittivity of free space, \( \mu_0 \) = permeability of free space and \( A \) = beam area.

Nonlinear effects are used to generate light at new frequencies such as frequency doubling or SHG, sum and difference frequency generation and so on. The high intensity light can generate a static DC electric field via difference of frequencies or optical rectification. Connected to this effect is the electro-optic effect, where a static field modifies the optical properties of the medium.

In the case of nonlinear laser medium if the pump beam is at the higher frequency \( \omega_1 \) and the input signal is at the slightly low frequency \( \omega_2 \) then the output laser beam contains a new frequency \( \omega_3 \) such that

\[
\omega_3 = \omega_1 + \omega_2
\]

(1.6)

This phenomenon is called parametric amplification. These kinds of parametric amplifiers are used in optical fiber communications. The subtraction of the two frequencies (\( \omega_3 = \omega_1 - \omega_2 \)) can also be obtained due to the nonlinear phase shift. By this method, very low frequencies can be generated.
1.3.4 Self-focusing

One of the processes that can occur as a result of the intensity-dependent refractive index is self-focusing. This process can occur when a beam of light having a non-uniform transverse intensity distribution propagates through a material in which \( n_2 \) (nonlinear components of refractive index) is positive. Under these conditions, the material effectively acts as a positive lens, which causes the rays to curve toward each other. This process is of great practical importance because the intensity at the focal spot of the self-focused beam is usually sufficiently large to lead to optical damage of the material.

1.4 CRITERIA FOR NLO CRYSTAL

An ideal NLO material should possess the following properties:

(i) Large nonlinear figure of merit for frequency conversion
(ii) High optical damage threshold
(iii) Fast optical response time
(iv) Wide phase matchable angle
(v) Architectural flexibility for molecular design of morphology
(vi) Ability to process into crystals/thin films
(vii) Wide transparency range
(viii) Easy fabrication
(ix) Non-toxic and good environmental stability
(x) High mechanical strength and thermal stability
(xi) Non-hygroscopic in nature.
1.5 Application of Nonlinear Optical Materials

The important applications of NLO materials are the following:

(i) Second and higher order-harmonic generation
(ii) Frequency mixing
(iii) Optical Computers
(iv) High speed telecommunication devices
(v) Extremely fast data storage technology
(vi) Optical switching, etc.

1.6 Review of Literature

Nonlinear optical materials play a major role in information technology and possess many industrial applications. The available NLO crystals are classified into three different categories such as organic, inorganic and semiorganic materials.

1.6.1 Inorganic NLO Materials

NLO materials are essential for the fabrication of electro optic modulators, which convert an electric signal to an optical signal for the transmission through fiber optic cable. Currently, such devices are made with inorganic NLO materials. Investigations of NLO effects were initially focused on pure inorganic systems and it was first demonstrated in potassium dihydrogen phosphate (KDP). The second order NLO properties were found in quartz crystal. Many efficient NLO inorganic crystals like KDP, Potassium pentaborate (KB₅), Ammonium dihydrogen phosphate (ADP), Beta barium borate (BBO), Potassium niobate (K₅NbO₃), potassium titanyl phosphate (KTP), lithium triborate (LiB₃O₅ or LBO) and lithium iodate (LiIO₃) were
developed in the past decades for NLO applications [36, 37]. Among the inorganic materials, KDP is one of the popular nonlinear optical materials used for frequency doubling phenomena. The NLO coefficient $d_{36}$ of KDP is $d_{36}$ (1064 nm) = 0.37 pm/V. Borate materials such as (LiB$_3$O$_5$) and potassium pentaborate tetrahydrate (KB$_5$O$_8$·4H$_2$O) are superior in UV laser applications to many other commonly used inorganic materials due to their high UV transmittance down to 155 nm, chemical stability and mechanical hardness [38]. Centimetre-sized single crystals of Thallium Lead Bromide (Tl$_3$PbBr$_5$) were grown by Alban Ferrier et al., [39] using Bridgman - Stockbarger method. This compound has high phase transition at 237 °C. The spectroscopic properties and SHG tests suggest that, it is a potential material for middle infrared nonlinear optics. A NLO crystal of calcium fluoroborate (Ca$_3$(BO$_3$)$_2$F) was grown by Guojun Chen et al., [40] using Lithium Fluoride (LiF) as a flux. They also reported that the UV-Vis cut off wavelength is about 190 nm. The SHG test proves that it could be phase matchable and its efficiency is two times as large as that of KDP. Xu et al., [41] have studied the chemical bond analysis for crystal growth of KDP and ADP. Good-sized with high optical quality cesium lithium borate (CLBO) crystals were obtained by Kyropoulos method [42]. Feigelson [43] has reported that the enhancement of optical transparency in Cadmium Germanium Arsenide (CdGeAs$_2$) single crystals by controlling crystalline defects. Potassium pentaborate is an important inorganic NLO crystal and it is successfully used in the conversion of laser radiation into the UV and vacuum UV wavelength region. The structure of the non-centrosymmetric borate chlorides [Ba$_2$TB$_4$O$_9$Cl (T = Al, Ga)] have been determined by Jacques Barbier [44]. The SHG efficiency for the powder sample of Barium Gallium Chloro Borate (Ba$_2$GaB$_4$O$_9$Cl) was found to be 0.95 times that of KDP standard crystal.
1.6.2 Organic NLO Materials

The 21st century is said to be an age of photonics. As one of the aspects of basic technology of photonics, improvements of the wavefront control technology using organic nonlinear optical effects are considered very important. Now research and development on the organic materials with excellent nonlinear optical properties and vigorous applied studies have been carried out.

Inorganic materials are much more matured in their applications to second order NLO materials than organics. Most commercial materials are inorganic especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long term promise than inorganics. The perfect organic material would be the one, which has a high efficiency, a very low absorption edge cut-off (to allow access into the UV), a high damage threshold and favorable crystal growth properties. The enhancement in nonlinearity in comparison to inorganic materials arises due to the existence of \( \pi \) electrons in the organic materials.

Nonlinear optical organic crystals have proved to be the interesting candidates for a number of applications: second harmonic generation, frequency mixing, electro optic modulation, optical parametric oscillation, optical bistability, etc. The superiority of organic NLO materials results from their versatility and possibility of tailoring them for many applications [4]. Recent efforts in molecular engineering suggest that organic NLO materials possess comparably better properties than inorganic materials; their tremendous practical applications are anticipated. In 1970, Davydov et al., [29] demonstrated this concept, while screening SHG activity in a wide range of substituted benzenes. A typical SHG active molecule lacks a center of
symmetry. 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. Most of the materials initially investigated are nitroaniline derivatives. 2-methyl-4-nitroaniline (MNA), methyl-(2, 4-dinitrophenyl)-aminopropanoate (MAP) and 3-methyl-4-nitropyridine-1-oxide (POM) are some of the prominent materials of these categories. Vijayan et al., [45] have grown p-hydroxy acetophenone (C₈H₈O₂), one of the potential organic NLO materials.

Recently, Anandha Babu [46] reported about the growth of 4-aminobenzophenone crystals by vertical Bridgman technique. Also reported that the single organic crystals 2,4,4'-Trimethoxybenzophenone, Benzophenone hydrazone, 4,4'-dimethylbenzophenone, 2-Amino-5-nitropyridinium toluenesulfonylate and 2-aminopyridinium 4-nitrophenolate 4-nitrophenol has been grown by low temperature solution growth technique for nonlinear optical (NLO) applications. The well known organic NLO compound, urea has three times the nonlinearity of the popular KDP and has the damage threshold of 1.5 GW/cm² which exceeds that of LiNbO₃. Conjugated donor-acceptor substituted organic molecules exhibit measurable NLO and electro-optical effects [47]. Such materials can be used for optical computing and optical telecommunication systems. Vijayan et al., [48] have reported that the benzimidazole crystal grown by vertical Bridgman technique, exhibits high nonlinear optical behavior especially SHG. A single crystal of 3-methyl 4-nitropyridine 1-oxide (POM) was grown by Boomadevi et al [49]. It was found that POM has optical transparency of 55%. A new NLO crystal 4-phenylpyridinium hydrogen squarate (4PHS) has been grown and characterized by Ramachandra Raja et al [50]. Good organic NLO crystal 1-chloro-2,4-dinitrobenzene (CDNB) was grown from low temperature solution growth technique by Sethuraman et al [51]. Arivanandhan et al., [52]
reported that the melt grown Ethyl p-aminobenzoate (EPAB) exhibit SHG higher than that of KDP crystal. However, these crystals have several unfavorable physical properties that limit their applications in nonlinear optical devices and there has not been much progress in fabricating devices out of these molecular crystals due to poor transparency, mechanical and thermal properties compared to inorganic materials. Organic nonlinear materials clearly do have some limitations. Nobody expects them to match the temperature performance of inorganic crystals, nor is there much interest in simple second-harmonic generation, which requires high optical power densities. In order to retain the merits and overcome the shortcomings of organic materials, some new complexes of NLO crystals such as metal organic or semiorganic crystals have been developed.

1.6.3 Semiorganic or Metal Organic NLO Materials

The shortcomings of aromatic crystals, such as poor physicochemical stability, low hardness and cleavage tendency hinder their device applications. In order to retain the merits and overcome the shortcomings of organic materials, a new class of NLO crystals - metal organic or semiorganic complex crystals has been developed. The relatively strong metal ligand bond permits the complex crystals to combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high nonlinearity and molecular engineering features. Current interest is centered on metal complexes of such organic ligand and among them metal complexes of thiocyanate and thiourea of special interest owing to their large nonlinearity, high laser damage threshold, low UV cut-off and good mechanical properties. Zinc Tris (thiourea) Sulfate (ZTS), Zinc Thiourea Chloride (ZTC), Bis (Thiourea) Cadmium Chloride (BTCC) has high NLO and high laser damage threshold [53-55]. Zinc Cadmium Tetra isothiocyanate (SCN)$_4$ (ZCTC), Zinc Mercury Tetra
isothiocyanate (SCN)$_4$ (ZMTC) exhibits efficient SHG at short wavelengths [56]. Zang et al., [57] have reported that tri-allythiourea cadmium chloride (ATCC) exhibits good NLO property. Petrosyan [58] discovered the L-Arginine Phosphate and it is one of the prominent NLO crystals and is being used in devices such as optical parametric amplifiers. The current trend in the scientific pursuits is on newer organic and semiorganic materials and the search is particularly focussed on materials for applications in compact blue-green lasers.

1.6.4 Amino Acid NLO Crystal

Among organic crystals for NLO applications, amino acids offer the rich choice. All amino acids have a proton-donating carboxyl and proton-accepting amino group. Among the amino acids, all except glycine are characterized by the presence of chiral carbons. Several new complexes incorporating the amino acid with different organic/inorganic acids are developed and are found to be very suitable for a number of NLO applications. In these, pure amino acids like L-arginine, L-histidine, L-alanine, etc., are good NLO materials. Among organic crystals of NLO applications, amino acids display specific features of interest as reported by Nicoud et al., [59] such as, (i) molecular chirality, which secures acentric crystallographic structures, (ii) absence of strongly conjugated bonds leading to high transparency ranges in the visible and UV spectral regions and (iii) zwitterionic nature of the molecule, which favours crystal hardness. Further amino acids can be used as a basis for synthesizing organic-inorganic compounds like L-arginine phosphate and its derivatives. L-arginine phosphate monohydrate (LAP) is a potential nonlinear optical [60] material first introduced in 1983 by Xu et al. Owing to its good transparency, chemical stability, dipolar strength, Reena Ithyachen and Sagayaraj reported [61] that the properties of L-arginine diphosphate, make it another promising material
for NLO applications. L-arginine formate (LAF) [62] possesses high NLO coefficient next to LAP reported by Packiam Julius et al. Tanusri Pal et al., [63] concentrated on L-arginine halide systems and mixed crystals of L-arginine hydrochloride (LAHCl) and L-arginine hydrobromide (LAHBr) and estimated the damage threshold of LAHCl, LAHBr and L-arginine hydrochloride bromide (LAHClBr) at about 27.72, 16.37 and 29.84 GW/cm² at 1064 nm, respectively [63].

The bulk crystals of L-arginine tetrafluoroborate (LAFB) with dimensions 78 × 50 × 35 mm³ were grown by employing temperature lowering method [64]. The experiment reveals that the useful transmission range of solution grown bulk crystal of LAFB extends from 198 to 900 nm, which makes it valuable for applications that require blue-green light. L-arginine trifluoroacetate (LATF) was grown by Xu et al., [65] from aqueous solution by employing temperature lowering method. It was reported that the optical damage threshold of LATF at 1064 nm is higher than that of LAP and KDP. The linear optical properties showed that L-alanine family crystals have lower cut-off wavelength in the UV-region. Among all L-alanine derivatives, L-alanine acetate possesses high transmittance of 80%. The powder SHG test confirmed the nonlinear optical property of the grown crystals of L-alanine derivatives is comparable with other semi organic crystals. Dhanuskodi and Ramajothi in 2004 reported about the growth, thermal and optical characterization of L-histidine tetrafluoroborate crystal [66]. It has excellent NLO properties much more than LAP. Reena Ittyachan and Sagayaraj [67] have reported about the growth of L-histidine bromide (LHB), a possible material for fabrication of photonic devices. They also studied the L-Histidine diphosphate (LHDP) semiorganic crystal and reported that LHDP have good transparency [68]. An L-threonine single crystal has been grown by slow evaporation and temperature lowering method from aqueous solution by Ramesh Kumar et al [69]. The smallest amino acid is
glycine and it has no chirality’s. However, it forms addition compounds with organic and inorganic acids and forms complexes. Such compounds of glycine [70] exhibit SHG activity. The present work is focussed on the growth and characterization of some important crystals of amino acid complexes. The SHG efficiencies of the grown crystals are comparable with that of KDP crystals, which shows their suitability for optoelectronic applications.

1.7 SUMMARY AND OBJECTIVES

The search for nonlinear optical (NLO) materials has been of great interest in the recent years because of their numerous potential applications. As far as the second order nonlinear effects in bulk crystals are concerned, both inorganic and organic materials are of much interest. Inorganic crystals have been characterized by good stability combined with a high transparency range, but their second order coefficients are limited. In contrast, organic crystals exhibit higher nonlinear second order coefficient, but their transparency domain is reduced. They also suffer from problems such as low thermal stability, mechanical weakness etc. In order to overcome these shortcomings, new classes of material called metal organic or semiorganic, which share both the properties of organic and semiorganics can be used. These materials should also possess high nonlinear coefficient as well as extended mechanical and thermal stability over a wide range of temperature. Since semiorganic NLO crystals formed with amino acid have been identified as potential candidates, they can be extensively used for the replacement of inorganic crystals such as KDP, Ammonium Dihydrogen Phosphate (ADP), etc., in nonlinear optical applications. The present work is an attempt to synthesize and characterize efficient materials for nonlinear optical applications in amino acids complexes. The main objectives are to synthesize, characterize and study the linear and nonlinear optical properties of amino acids complexes. The studies also include the mechanical, laser damage
threshold and thermal properties of the grown crystals. The present investigation deals with the growth and characterization of nonlinear optically active, some pure and metal complexes of amino acids such as L-leucinium oxalate, L-phenylalaninium maleate, L-cystine dihydrobromide, β-alanine cadmium chloride, β-alanine zinc chloride, γ-glycine and L-valine single crystals.

Therefore, the objectives of the present investigation are:

1. Synthesizing the chosen materials as single, bulk and defect free crystals

2. Identifying the crystal structure by single crystal X-ray diffraction and powder X-ray diffraction analyses

3. Confirming the protonation of the amino group and identifying the various functional groups present in the grown crystal by spectral analyses such as FTIR, FTRaman, proton NMR and $^{13}$C NMR.

4. Characterizing the grown NLO crystal by
   (i) UV-Vis-NIR analysis
   (ii) NLO study
   (iii) Thermal analyses
   (iv) Microhardness measurement
   (v) Etching studies
   (vi) Dielectric studies and
   (vii) Laser damage threshold studies.