Chapter 1

Introduction to Nonlinear Optics and Crystal Growth Methods

1.1. General

Nonlinear optics (NLO) is the branch of optics that describes the behaviours of light in non-linear media in which the dielectric polarization responds non-linearly to the electric field of the light. This nonlinearity is only observed at very high light intensities such as those provided by pulsed lasers. The coherent radiation at a few discrete frequencies can be produced by laser devices as in solid-state lasers or with narrow range of tenability as in dye lasers. Many applications require frequencies that are not readily available from such laser sources. The most effective way of converting a fundamental laser frequency to other frequencies, either to higher or lower frequencies is harmonic generation or parametric oscillation in a NLO non-centro-symmetric crystalline medium [1]. The light propagated through a crystalline solid, which lacks a centre of symmetry, generates light at second harmonics of the applied frequency. This important nonlinear property of non-centro-symmetric crystals is called second harmonic generation (SHG) and the materials in which it occurs is the subject of intense study [2].

The second harmonic generation (SHG) was observed by Franken et al., [3] in 1961 marked the birth of nonlinear optics as a new discipline in the area of laser matter interaction. Franken observed that the light of 347.15 nm could be generated when a quartz crystal was irradiated with light of 694.3 nm obtained from a ruby laser as shown in Figure 1.1.

![Figure 1.1: Schematic diagram showing the arrangement for SHG in quartz crystal](image)
The generation of coherent blue light through second harmonic generation (SHG) from near infrared (NIR) laser sources is an important technological problem that has attracted much attention in the last few years. The coherent blue and green light are important for many applications such as displaying, high-resolution printing and signal processing.

The one of the current interesting field of research is to synthesize, grow and characterize the organic and semi-organic NLO crystals. In recent years, many organic materials have been considered for the possible use in nonlinear optical applications [4-5]. Particularly semi-organic NLO materials are finding a lot of importance in the field of laser technology compared to inorganic and organic crystals, since they possess higher mechanical strength and chemical stability [6-7]. In the past, efforts have been made on amino acid mixed organic and inorganic complex crystals due to their enhanced chemical stability, laser damage threshold and nonlinear optical properties that have been considered for photonic applications [8-9]. However some of nonlinear optical crystals have failed to meet the standard required for the practical use in devices because of the great difficulty of growing crystals of sufficient size and quality. Hence, there is a need for research in the field of new nonlinear optical crystals and their characterization. In addition to the growing of novel NLO crystals, it is important to understand the radiation effects on NLO crystals since, the crystals may need to work in different radiation environments. Therefore understanding the radiation-induced degradation of the various NLO components becomes an important consideration in the system design.

1.2. Origin of Optical Nonlinearity
Nonlinear optics is a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be understood as we think about the electrons in nonlinear crystal. Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal. If an external force pulls an electron away from its equilibrium position, the spring pulls it back with a force proportional to the displacement. The spring’s restoring force increases linearly with the electron displacement from its equilibrium position. In an ordinary optical material, the
electrons oscillate about their equilibrium position at the frequency of this electronic field. According to the fundamental law of physics an oscillation charge will radiate at its frequency of oscillation; hence, these electrons in the crystal "generate" light at the frequency of the original light wave. If the light passing through the material is intense enough, its electric field can pull the electrons so far that they reach the end of their springs. The restoring force is no longer proportional to the displacement and, then, it becomes non-linear. The electrons are jerked back roughly rather than pulled back smoothly and they oscillate at frequencies other than the driving frequency of the light wave. These electrons radiate at the new frequencies, generating the new wavelength of light [6].

1.3. Theoretical Explanation of Nonlinear Optics

The charged particles in dielectric medium are bound together. When an electric field is applied, they are displaced slightly from their equilibrium positions. This small movement of positive charges in one direction and negative charges on the other, results in a collection of induced electric dipole moments [10]. The electromagnetic radiation interacts with these dipoles causing them to oscillate results in the dipoles themselves acting as sources of electromagnetic radiation. 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.

For small values of the electric field associated with the radiation, the induced polarization $P$, which is the electric dipole moment per unit volume of the medium, is linear in the field [11].

$$P = \varepsilon_o \chi E$$  \hspace{1cm} 1.1

where $\chi$ is the linear susceptibility of the material, $E$ is the electric field vector, $\varepsilon_o$ 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.

$$P = \varepsilon_o \{\chi^{(1)} E + \chi^{(2)} E E + \chi^{(3)} E E E +...\}$$  \hspace{1cm} 1.2
In nonlinear terms, a 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:

$$P(-\omega_o) = \varepsilon_o \left\{ \chi^{(1)}(-\omega_o; \omega_1). E(\omega_o) + \chi^{(2)}(-\omega_o; \omega_1, \omega_2). E(\omega_1). E(\omega_2) + \chi^{(3)}(-\omega_o; \omega_1, \omega_2, \omega_3)E(\omega_1). E(\omega_2). E(\omega_3) + \ldots \right\}$$  1.3

where $\chi^{(1)}$ is the linear term responsible for material's linear optical properties like, refractive index, dispersion, birefringence, absorption etc. and $\chi^{(2)}$, $\chi^{(3)}$ …. are the nonlinear susceptibilities of the medium. $\chi^{(2)}$ is the quadratic term which describes the second harmonic generation in non-centro-symmetric materials. $\chi^{(3)}$ is the cubic term responsible for the third harmonic generation, stimulated Raman scattering, phase conjugation and optical bi-stability. Hence, the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients of $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ give rise to certain optical effects. These are listed in Table 1.1 [6, 12].

**Table 1.1: Optical effects of nonlinear materials**

<table>
<thead>
<tr>
<th>Order</th>
<th>Crystal</th>
<th>Effects</th>
<th>Applications</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 ($\omega + \omega = 2\omega$) Frequency mixing ($\omega_1 + \omega_2 = \omega_3$) Pockels effects ($\omega + 0 = \omega$)</td>
<td>Frequency doubling, Optical parametric oscillators, Electro optical modulators</td>
</tr>
<tr>
<td>3.</td>
<td>$\chi^{(3)}$</td>
<td>Four wave mixing phase gratings Kerr effect Optical amplitude</td>
<td>Raman Coherent spectroscopy, Real time holography, Ultra high speed optical gates, Amplifiers, choppers etc.</td>
</tr>
</tbody>
</table>

The odd-orders $\chi$ in equation (1.3) are orientationally independent but the even terms vanish in a centro-symmetric environment. Hence, for centro-symmetric materials all compounds of even order $\chi$ are zero and, therefore, $\chi^{(2)} = 0$. Therefore an important
criterion for a material to exhibit SHG is that it should be a non-centro-symmetric material. This can be illustrated by considering an electric field:

\[ E(t) = E_0 \cos \omega t \]

1.4 is incident on a material, the resultant second order polarization is:

\[ P(t) = \chi^{(2)}E^2(t) \]

1.5

But if the medium is centro-symmetric and thus possesses inversion symmetry, we can write

\[-P(t) = \chi^{(2)}[-E(t)]^2 = \chi^{(2)}E^2(t) \]

1.6

Equations (1.5) and (1.6) can be simultaneously true only if the polarization field is zero. Therefore, the \( \chi^{(2)} \) is zero for a centro-symmetric medium and no SHG will occur.

In order to select a nonlinear optical crystal for a frequency conversion process, the necessary criterion is to obtain high conversion efficiency. To obtain high conversion efficiency, the phase vectors of input beams and generation beams have to be matched [13]. The conversion efficiency \( \eta \) can be expressed as:

\[ \eta = PL^2 \left( \frac{d_{\text{eff}} \sin \Delta K L}{\Delta K L} \right)^2 \]

1.7

where \( d_{\text{eff}} \) is the effective nonlinear coefficient, \( L \) is the length of the crystal, \( P \) is input power density and \( \Delta K \) is phase-mismatching. In general, higher power density, longer crystal, large nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency. Also, the input power density has to be lower than the damage threshold of the crystal.

1.4. Various Types of Second-Order NLO Effects

In a medium, several second-order NLO effects can be observed experimentally which are summarized as follows:

1.4.1 Second Harmonic Generation (SHG)

The process of transformation of light with frequency \( \omega \) into light with double frequency \( 2\omega \) is referred as SHG. This process is spontaneous and involves three photon transitions; two photons with the same energy \( h\nu \) and same frequency \( \omega \) are absorbed spontaneously to emit a photon with energy \( 2h\nu \) and frequency \( 2\omega \). The SHG is shown in Figure 1.2 schematically [8]. Among the nonlinear optical
phenomena, frequency doubling by the second harmonic generation is the most important one, because this process provides significant tool for the conversion of near infrared laser light from diode laser into visible light in the field optical image storage.

1.4.2 Sum Frequency Generation (SFG)

The sum frequency generation combines two low energy photons with frequencies $\omega_1$ and $\omega_2$ into a high energy photon with frequency $\omega_3$ ($\omega_1 + \omega_2 = \omega_3$). The SFG is shown in Figure 1.3 schematically.

1.4.3 Differential Frequency Generation (DFG)

The difference frequency generation combines two high energy photons with frequencies $\omega_1$ and $\omega_2$ into a low energy photon with frequency $\omega_3$ ($\omega_1 - \omega_2 = \omega_3$). This is shown schematically in Figure 1.4.
1.4.4 Optical Parametric Generation (OPG)
The optical parametric generation (OPG) is an inverse process of sum frequency generation. It splits one high-frequency photon (pumping wavelength $\lambda_p$) into two low-frequency photons (signal $\lambda_S$ and idler wavelength $\lambda_i$). For a fixed pump wavelength, an infinite number of signal and idler wavelengths can be generated by tilting a crystal. Therefore, OPG is an excellent source for generating a wide tunable range of coherent radiation. The OPG is shown in Figure 1.5 schematically.

![Figure 1.5: Schematic representation of optical parametric oscillator](image)

There is a three photon process in which one photon with energy $h\nu$ is absorbed and two photons with energies $h\nu_1$ and $h\nu_2$ are emitted.

1.5. Development of Nonlinear Optical Material
The advances in the development of NLO materials can be divided into three different areas [6-7]:
(i) Discovery of new NLO materials
(ii) Growth of promising NLO crystals
(iii) Improving the characteristics of NLO crystals

Nonlinear optical materials will be the key elements for future photonic technologies based on the fact that the photons are capable of processing information with the speed of light. The search for new and efficient materials has been very active since SHG was first observed in single crystal quartz by Franken and co-workers in 1961 [3]. In the initial stages, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO$_3$) and semiconductors such as cadmium sulfide, selenium and tellurium. At the end of 1968, the Kurtz and Perry powder SHG method was introduced [14]. In this method, a powdered sample is irradiated with a laser beam and scattered light is
collected and analyzed for its harmonic content with the use of suitable filters. Chemla and Zyss (1987) recorded the early NLO history more extensively [2].

1.6. Classification of Nonlinear Optical Material

The NLO materials can be classified into three different categories as inorganic, organic and semi-organic or metal-organic materials.

1.6.1 Inorganic NLO Materials

Inorganic materials are mostly ionic bonded and it is always easier to synthesize inorganic materials which have high melting point, high degree of chemical inertness, high thermal and mechanical stability. The phenomenon of SHG in inorganic materials was first reported in 1961 by Franken and co-workers. The inorganic NLO materials have some advantages like highest bulk susceptibility and compatible physical properties but on the other hand these materials suffer from disadvantages like absorption in the visible region, poor response time and degradative photorefractive effects, low laser damage threshold (~10 MW cm\(^{-2}\) ) and poor optical transparency [8]. The examples of inorganic NLO crystals are lithium niobate (LiNbO\(_3\)), potassium niobate (K NbO\(_3\)), barium titanate (Ba TiO\(_3\)), potassium titanly phosphate (K TiOPO\(_4\)), potassium dihydrogen phosphate (KH\(_2\)PO\(_4\)), ammonium dihydrogen phosphate (NH\(_3\)H\(_2\)PO\(_4\)), lithium iodate (LiIO\(_3\)), etc., [15-16]. The main inorganic materials applied in nonlinear optics are tabulated in Table 1.2 as follows:

<table>
<thead>
<tr>
<th>Title</th>
<th>Typical Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium triborate (LiB(_3)O(_5))</td>
<td>High power laser harmonics generation and pumped by Nd: YAG laser</td>
</tr>
<tr>
<td>Beta barium borate (β-BaB(_2)O(_4))</td>
<td>Solid state and dye laser harmonics generation</td>
</tr>
<tr>
<td>Potassium titanly phosphate (K TiOPO(_4))</td>
<td>Harmonics generation in UV and Vis region</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate (KH(_2)PO(_4))</td>
<td>Harmonics generation in visible region</td>
</tr>
<tr>
<td>Lithium niobate (LiNbO(_3))</td>
<td>SHG and OPO pumped by Nd: YAG laser</td>
</tr>
<tr>
<td>Silver gallium sulfide (AgGaS(_2))</td>
<td>Harmonics generation in IR region of CO(_2) laser</td>
</tr>
<tr>
<td>Bismuth silicon oxide (Bi(<em>{12})SiO(</em>{20}))</td>
<td>Photorefractive, electro-optical and acoustic-optical</td>
</tr>
<tr>
<td>Potassium pentaborate tetrahydrate (KB(_5)O(_6)(OH)(_4))</td>
<td>Second to sixth harmonics generation</td>
</tr>
<tr>
<td>Potassium titanyl arsenate (K TiOAsO(_4))</td>
<td>Harmonics generation in UV and Vis region</td>
</tr>
</tbody>
</table>
1.6.2 Organic NLO Materials

The organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak van der Waal interactions. The organic molecules which contain both conjugated bonds and acceptor group on one side and a donor group on the other side are known as nonlinear optical (NLO) materials. The NLO properties of large organic molecules have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely [4-5]. The advantages of organic nonlinear optical materials are:

(i) High second–order nonlinear optical efficiency
(ii) Much greater resistance to damage in the laser beam
(iii) Birefringent (facilitates phase–matching)
(iv) Possible to chemically “engineer” molecular properties

Moreover, organic materials have advantages like low dielectric constants, inherent synthetic flexibility and large NLO response over a broad frequency range compared to those of inorganic materials. The organic material has a very low absorption edge cut-off (to allow access into the UV) and favourable crystal growth properties. The enhancement in nonlinearity, in comparison to inorganic materials, arises due to the existence of \( \pi \) electrons in the organic materials. Organic molecules with significant nonlinear optical activity generally consist of an \( \pi \) electron-conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a (push pull) conjugated structure. Functionalization of both ends of the \( \pi \)-bond system with appropriate electron donor-acceptor groups can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to increased optical non-linearity [12]. The \( \pi \)-conjugated systems would be benzene, azobenzene, stilbine, tolans, biphenyl, benzylidene, heterocycle, polyenes, etc. The electron acceptor and donor groups, which can be attached to a \( \pi \)-conjugated system, are listed in Table 1.3.
Table 1.3: List of some acceptor and donor groups

<table>
<thead>
<tr>
<th>Donor groups</th>
<th>Acceptor groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₂, NHCH₃, N(CH₃)₂, NHR, N₂H₃, F, Cl, Br, I, SH, SR, OR, CH₃, OH, NHCOCH₃, OCH₃, SCH₃, OC₆H₅, C(CH₃)₃, COOCH₃, O⁻, S⁻ and aromatic. (R is an alkyl group)</td>
<td>NO₂, NO, CN, COOH, COO⁻, CONH₂, CONH₂, CONHR, CONR₂, CHO, SSI, SO₂R, SO₂C₅F₇, SO₂CH₃, COR, COCF₃, CF₃, COCH₃, CH=C(CN)₂, C₂(CN)₃, SO₂NH₂, N₂⁺, NH₃⁺, N(CH₃)₃⁺ and aromatic. (R is an alkyl group)</td>
</tr>
</tbody>
</table>

Both the second order optical nonlinearity and optical transparency are affected by the nature of conjugated bonds, length of π-conjugation and strength of electron donor/acceptor constituents [17]. Among organic crystals of NLO applications, amino acids display specific features of interest [2] such as, (i) molecular chirality, which secures a centric crystallographic structures, (ii) absence of strongly conjugated bonds leading to high transparency ranges in the visible and UV spectral regions and (iii) zwitter-ionic nature of the molecule, which favours crystal hardness. The importance of amino acid for NLO application lies in the fact that almost all amino acids contain an asymmetric carbon atom and crystallized in non-centro-symmetric space group. Among the amino acids, all except glycine, are characterized by chiral carbons, a proton-donating carboxyl (–COOH) group and a proton-accepting amino (–NH₂) group. In the solid state, these exist as dipolar ions in which carboxyl group is present as carboxylate ion. Due to this dipolar nature, amino acids have physical properties which make them ideal candidates for NLO applications [12, 18]. The general formula for an amino acid is given below:

![Amino Acid Structure](image)

R is the functional group of the amino acid

The shortcomings of organic crystals such as poor physicochemical stability, low hardness and cleavage tendency hinder their device application [2]. In order to retain the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semi-organic complex crystals have 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.

1.6.3 Semi-organic Materials

The semi-organic compounds share the properties of both organic and inorganic compounds. They are organic based materials in which the polarizable part is an organic molecule which is stoichiometrically bonded with an inorganic ion. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganic materials has been found to be overwhelmingly successful in the recent past. Hence, recent search is concentrated on semi-organic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [6-7].

1.6.4 Organo-metallic NLO Crystals

The metal-organic crystals form a new class of materials under semi-organics. Compared to organic molecules, metal complexes offer a large variety of structures, and a diversity of electronic properties by virtue of the coordinated metal centre. Recent interest is concentrated on metal complexes of organic compounds owing to their large non-linearity.

1.7. General Requirements of NLO Crystals

In recent years, major advances have been made in the development of nonlinear optical materials with improved optical, mechanical characteristics and damage thresholds far higher than the classical crystals.

The following properties are very important for a non-centro-symmetric crystal for device applications

(i) High NLO coefficient  
(ii) Wide phase matching angle  
(iii) High laser damage threshold  
(iv) Wide transparency range  
(v) High thermal, mechanical and chemical stability  
(vi) Moderate birefringence  
(vii) Low absorption and easy device fabrication
1.8. Applications of NLO crystals

The nonlinear optical crystals are very important for laser frequency conversion. KDP crystal is suitable for higher harmonic generation of huge laser systems for fusion experiments because it can be grown to larger sizes and also it has a higher laser damage threshold. Potassium titanly phosphate (KTP) crystal is a useful nonlinear optical crystal to get efficient green light by the frequency doubling of Nd: YAG laser. In recent years there has been considerable progress in the development of coherent UV sources based on nonlinear optical processes. The discovery of new material with enhanced second harmonic generating characteristics can significantly change the utility of the laser systems. For example the availability of KTP, has made the mode locked continuous wave YAG laser competitive with the argon ion laser in many applications. Therefore, there is a current interest in finding materials that will extend the wavelength capability of laser sources into UV region and new frequency conversion materials will have significant impact on applications such as optical communications technology and laser driven inertial confinement fusion experiment. This demands from optical and device physicists for improved and effective materials to call for world-wide research on NLO materials which is most targeted and speculative [12].

1.9. Crystal Growth

1.9.1 Introduction

The crystal defined as “a solid composed of atoms arranged in a pattern periodic in three dimensions.” For the past five decades, crystals have been used by the physicists and engineers as the key materials for modern electronics, opto-electronics and other technical fields of applications. The formation of crystal in nature, like snowflakes and minerals, as well as the preparation of the crystals in laboratories and factories for technical applications is called “crystal growth.” Crystal growth plays a prominent role in the era of immense technological excellence attributing to the usefulness of many crystals in important areas of service to the humanity namely science, medicine, engineering, technology and also strategic areas of defense and space science [7]. There is a requirement of good quality crystals for various applications and, hence, different methods are developed to grow suitable crystals. It has been found that the
crystalline property has applications in devices such as: laser resonators, acoustic-optic modulators, phase decay plates, polarizer, pyro-electric detectors, piezo-electric devices, crystal X-ray monochromatres, scintillation detectors, holographic devices, membranes of iron selective electrodes and substrate for thin films. Therefore, the growth of single crystals and their characterizations towards device fabrications are important in both basic and applied scientific research [8]. Nonlinear optical (NLO) frequency conversion materials have significant impact on laser technology. However, some special nonlinear optical problems called for crystals with improved properties like high transparency in the UV region, high nonlinearity etc. This leads to the synthesis of new NLO materials of high optical quality like LiNbO$_3$ in 1964, Ba$_2$NaNb$_5$O$_{15}$ in 1967, LiIO$_3$ in 1969 and other crystals [10, 12].

1.9.2 Crystal Growth Methods

The aim of a crystal grower is to prepare crystals of best possible quality, as quickly as possible with required specifications for the intended applications. Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. There are three main categories of crystal growth techniques based on the phase transformation process which are:

(i) **Growth from the solid**: Solid-Solid processes involving solid – solid phase transitions. One can consider the conversion of a polycrystalline piece of the material into a single crystal by causing the grain boundaries to be swept through and pushed out of the crystal in the solid-solid growth of crystals [19].

(ii) **Growth from the Liquid**: Liquid-Solid processes involving liquid-solid phase transitions. Liquid growth includes both melt and solution growth. All materials can be grown in single crystal from the melt provided they melt without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature [20].

(iii) **Growth from the vapour**: Vapour-Solid processes involving vapour – solid phase transitions. Crystals of high purity can be grown from vapour phase by sublimation, condensation and sputtering of elemental materials.
1.9.3 Method of Solution Growth

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

(i) Low temperature solution growth and
(ii) High temperature solution growth

Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low temperature solution growth method. Growth in this method can be done in two ways;

(i) Growth from solution and
(ii) Gel growth

Gel growth method is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. Gel is a two-component system of a semisolid rich in liquid and inert in nature. The material which decomposes before melting can be grown in this medium by counter diffusing two suitable reactants. Crystals with dimensions of several mm can be grown in a period of 3 to 4 weeks. The crystals grown by this technique have high degree of perfection and fewer defects since the growth takes place at room temperature.

In high temperature solution growth method, the solute is dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. This method can be divided into two categories

(i) Flux growth and
(ii) Hydrothermal growth

There are many ways of high temperature solution growth and the most widely used technique is the flux growth. The term ‘flux’ is used to describe the growth of crystals from molten solvents at high temperature i.e., it refers to the materials that reduce the melting point.

In hydrothermal growth technique, the crystals are grown from the solution at elevated temperature and pressure so that it dissolves a solute which would ordinarily be insoluble at ambient conditions. The materials to be grown is finely powdered and
taken in a vessel which is filled with a basic hydroxide solution and is kept in a furnace for heating. As temperature increases and at some temperature the vessel fills completely with the liquid phase. Under suitable conditions the solution is supersaturated and, hence, the crystallization begins. This technique is best suited for producing large quantities of single crystals with good homogeneity and high quality.

The present thesis deals with the growth of crystals from solution. Hence, in the next section, low temperature solution technique will be discussed in details.

1.9.4 Low Temperature Solution Growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. It is the most widely used method for the growth of single crystals when the initial materials are unstable at high temperatures \[21\] and also which undergo phase transformations below the melting point. The growth of crystals by low temperature solution growth involves weeks, months and sometimes years. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. The mechanism of crystallization from solutions is governed by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the solvent. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straightforward equipment design which gives a good degree of control of accuracy of ± 0.01°C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and, as a matter of fact, numerous organic and inorganic materials which fall in this category can be crystallized using this technique. The low temperature solution growth technique also allows a variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent. The proximity to ambient temperature
reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low.

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. In the low temperature solution growth, crystals can be grown from solution if the solution is supersaturated. The low temperature solution growth can be subdivided into the following methods:

(i) Slow cooling method
(ii) Slow evaporation method and
(iii) Temperature gradient method

It is possible to grow bulk crystals of high perfections as the growth occurs close to equilibrium conditions. It also permits the preparation of different morphologies of the same materials by varying the growth conditions [12].

(i) Slow Cooling Method

This is the most suitable method among the various methods of solution growth. However, the main disadvantage of slow cooling method is the need to use a range of temperatures. 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. The use of wide range of temperatures may not be desirable because the properties of the grown crystals may vary with temperature. Temperature stability may be increased by keeping the solution in large water bath or by using a vacuum jacket. Achieving the desired rate of cooling is a major technological hurdle. This technique needs only a vessel for the solution in
which the crystals grow. The height, radius and volume of the vessel are so chosen as to achieve the required thermal stability. Even though this method has technical difficulty of requiring a programmable temperature controller, it is widely used with great success. In general, the crystals produced are small and the shapes of the crystals are unpredictable.

(ii) Slow Evaporation Method
As far as the apparatus is concerned, slow cooling and slow evaporation methods are similar to each other. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. If the solvent is non-toxic like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve a temperature stabilization of about 0.05 °C and rate of evaporation of a few mm³/h. The evaporation technique has an advantage of growing crystals at a fixed temperature. This method can effectively be used for materials having very low temperature coefficient of solubility. But the crystals tend to be less pure than the crystals produced by slow cooling technique because as the size of the crystal increases, more impurities find place in the crystal faces. Evaporation of solvent from the surface of the solution produces high local supersaturation and formation of unwanted nuclei. Small crystals are also formed on the walls of the vessel near the surface of the liquid from the material left after evaporation. These tiny crystals fall into the solution and hinder the growth of the crystal. Another disadvantage lies in controlling the rate of evaporation. A variable rate of evaporation may affect the quality of the crystal. Inspite of all these disadvantages, this is a simple and convenient method of growing single crystals of large size [7].

(iii) Temperature Gradient Method
This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this technique are;
(i) Crystal grows at a fixed temperature
(ii) This technique is insensitive to changes in temperature provided both the source and the growing crystal undergo the same change
(iii) Economy of solvent and solute
On the other hand, changes in the small temperature difference between the source and the crystal zones have a large effect on the growth rate.

Out of all the methods discussed above, slow evaporation solution growth method has been used for the present study for the growth of organic and semi-organics single crystals due to its simplicity and high effectiveness.

1.9.5 Advantages of Low Temperature Solution Growth Method

The low temperature solution growth method has the following merits:

(i) Simple growth apparatus
(ii) Growth of dislocation free crystals
(iii) Permits the growth of prismatic crystals by varying the growth conditions
(iv) Only method which can be used for substances that undergo decomposition before melting
(v) Crystals can be grown in large size

This technique has the following conditional limitations:

(i) Growth substance should not react with solvent
(ii) This technique is applicable for substances fairly soluble in a solvent

1.10. Interaction of Radiation with Matter

Solid-state laser systems based in space will be required to withstand five to ten years of exposure to charged particles, such as electrons and protons, high energy cosmic rays, and bremsstrahlung photons. All these forms of radiation can damage the laser by ionizing constituent atoms in the gain medium. Additionally, protons can create damage sites by physically disrupting the laser material. Depending upon the orbit, exposure levels can reach upwards of 100 krad over a 5 year period and conceivably higher for nonearth based missions. Moderate amounts of shielding can significantly reduce exposure to electrons and low energy protons. However, high energy protons (>30 MeV), either trapped in the Van Allen belts or deriving from solar flare activity, have very long penetration depths and are thus difficult to protect against [22].

The manner in which radiation interacts with solid materials depends on the type, kinetic energy, mass and charge state of the incoming particle and the mass, atomic number and density of the target materials. In the following section, we discuss the interaction of the different types of radiations with materials [23].
1.10.1 Ionization Effects

Ionization of the target material occurs for photons, electrons, protons, and energetic heavy ions.

Photons interact with material through three different processes, namely the photoelectric (or fluorescent) effect, the Compton effect and the pair production. These processes are illustrated in Figure 1.6 for each of these processes, the primary result of the interaction is the creation of energetic secondary electrons.

Low-energy photons interact with materials predominantly through the photoelectric effect. The photoelectric effect is illustrated in Figure 1.6a. In this process, an incident photon excites an electron from an inner shell of a target atom to a high enough state to be emitted free of the target atom. For the photoelectric effect, the incident photon is completely absorbed. Thus, the photoelectric effect creates a free electron (photoelectric electron) and an ionized atom. In addition, as the photoelectric electron is emitted, an electron in an outer orbit of the atom will fall into the spot vacated by the photoelectron causing the emission of low energy photon.

For higher energy photons, Compton scattering will dominate over the photoelectric effect, Compton scattering is illustrated in Figure 1.6b. In this process, when a photon collides with an atom, it transfers a fraction of its energy to an electron of the target atom and becomes free. For Compton scattering, a photon of lower energy is created which is free to interact with other target atoms. It also creates a free electron and an ionized atom.

Pair production occurs only for very-high energy photons (E > 1.02 MeV). It is illustrated in Figure 1.6c. In pair production, the incident photon collides with a target atom creating an electron-positron pair. A positron has the same properties as an electron (charge and mass), except that the charge is positive. The incident photon is completely annihilated in pair production.
1.10.2 Displacement Effects

In addition to ionization effects, high-energy protons and ions can also cause displacement damage in materials. As a high-energy proton collides with an atom, the atom will recoil from its lattice site. If the energy transferred to the atom is high enough, the atom can be knocked free from its lattice site to an interstitial site. The minimum energy required to knock an atom free of its lattice site is called the displacement threshold energy. As the atom is displaced from its original position, it leaves behind a vacancy. The combination of the interstitial atom and its vacancy is called a Frenkel pair. If the displaced atom has sufficient energy it can in turn displace other atoms. Thus, for very high energy recoils a defect cascade can be created with large defect clusters.

1.11. Literature Survey

Nonlinear optical (NLO) materials are expected to play a major role in the technology of photonics like telecommunication, optical computing, optical data storage and optical information processing. Due to their enormous applications in the above said areas, material scientists have focussed their attention on the growth of a variety of nonlinear optical materials. Nowadays, most of the researchers are focussing on organic nonlinear optical material since, they have good nonlinear effect, which is useful for photonic applications. Historically, the optical SHG in an organic material was reported for the first time in 1964 by Rentzepis and Pao [24] and Heilmer et al.,
in 3, 4-benzopyrene and in hexamethylenetetramine single crystals. Two years later, Orlov [26] reported SHG from the hippuric acid. Further research in organic NLO was stimulated in 1970, when Davydov et al., [27] reported strong SHG from organic compounds having electron donor and acceptor groups attached to a benzene ring. The low-temperature solution growth technique is widely used for the growth of organic compounds to get bulk single crystals of good quality.

Nagaraja et al., [28] showed that benzoyl glycine (BG), an organic nonlinear crystal grown by slow evaporation has both the advantages of organic and inorganic NLO materials. Owing to its high nonlinear efficiency, high melting point, good chemical stability, less sublimation problems with improved hardness and cleavage properties (unlike other organic materials), benzoyl glycine is a promising material for NLO applications.

Lochran et al., [29] was grown organic crystal (S)-3-methyl-5-nitro-N-(1 phenylethyl)-2-pyridinamine as a promising nonlinear optical material. A large single crystal of this material was grown by temperature lowering of a seeded supersaturated solution in acetone.

Prabhu et al., [30] have grown the single crystals of N-(2-chlorophenyl)-(1 propanamide) by slow evaporation technique. The grown crystals were transparent and the chemical structure was established by NMR. The UV–visible spectrograph shows good transparency in the visible range. Owing to good quality, transparency and size, a grown crystal was found to be a promising material for NLO applications.

Vijayan et al., [31] reported that semicarbazone of acetophenone is one of the potential organic NLO materials for photonic and optoelectronic applications. This crystal has been grown by slow evaporation technique. It was found that the crystal belongs to a triclinic system with space group P1. The FTIR spectrum of the compound revealed both free and hydrogen bonded N–H stretching modes. The ultraviolet spectrum proved the highly transparent nature of the material between 950 and 325 nm.
Lakshmana Perumal et al., [32] have grown an organic nonlinear optical material, 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST), which is a derivative of stilbazolium tosylate and a new material having high NLO property. FTIR and NMR spectrums recorded identify the various functional groups present in the material. The Kurtz powder SHG measurements on MBST showed that the peak intensity is 17 times more than that of urea.

Vijayan et al., [33] have grown bulk single crystals of Methyl 4 hydroxybenzoate by slow evaporation solution growth technique. The lattice parameters have determined from the powder X-ray diffraction pattern. It was found that the compound is monoclinic crystal system. The functional groups of the compound have determined from the Fourier transform infrared spectrum. From the Raman spectrum analysis, it was found the intensity was more in powder sample compared to crystal form and is due to the molecular packing of the system. The UV spectrum revealed that the absorbance is very low between 400 and 1200 nm.

Vijayan et al., [34] investigated that the absence of absorption of benzimidazole in the region between 400 and 1200 nm is an advantage as it is the key requirement for materials having NLO properties. The bright green light emission from the sample by using Nd: YAG laser confirmed the NLO property of the sample. The relative SHG efficiency of the grown specimen is 4.5 times greater than that of the potassium dihydrogen phosphate (KDP) single crystal.

Srinivasan et al., [35] have grown good transparent single crystals of N-(2 chlorophenyl)-(1-propanamide) (NCP) by slow cooling solution growth technique. The dielectric constant was found to decrease with increase in frequency. The useful transmission range of NCP crystals is suitable for applications required in blue-green light. The damage threshold of NCP crystal is much higher than KDP.

Sethuraman et al., [36] have grown an organic nonlinear optical crystal of 1-chloro-2, 4-dinitrobenzene by low temperature solution growth technique. Good optical quality single crystals of size 28 mm × 11 mm × 5 mm were obtained. The functional groups of compound were confirmed by FT-IR and FT-Raman spectral
analyses. UV–vis studies showed the cut-off wavelength is less than 400 nm. The SHG was confirmed by the emission of green light radiation with conversion wavelength of 532 nm.

Arun and Jayalekshmi [37] have grown the bulk size single crystals of L-alanininium oxalate by the slow evaporation solution growth method at room temperature. Crystal structure was confirmed by powder XRD. Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) studies established the good thermal stability of the crystal upto its melting temperature (197°C), suggesting it to be a potential material for laser applications where crystal should withstand high temperatures. FTIR studies confirmed the various functional groups and their vibrational interactions. The UV/Vis/NIR absorption studies highlight the excellent transparency of the material in the range 318 nm to 1524 nm. The third order nonlinear optical properties of the crystals were investigated by open aperture Z scan technique.

Uma Devi et al., [38] have synthesized and grown L-valinium picrate (LVP) by solution growth method. The single crystal X-ray diffraction study revealed that the LVP crystal belongs to monoclinic system. The UV-Visible- NIR spectrum of LVP showed that the crystal is transparent in the range of 500 – 1000 nm. The band gap energy of LVP was estimated from the optical transmittance spectrum and found to be 2.24 eV. The TGA showed the good thermal stability of the material. The hardness measurement showed that the grown LVP crystal is mechanically stable only up to 50 g. The SHG was found to be 60 times greater than that of KDP.

Cyrac Peter et al., [39] reported the solubility of organic non-linear optical crystal L-phenylalanine L-phenylalaninium nitrate (LPAN) in the temperature range 30-50 ºC. Single crystals (15 x 4 x 3 mm³) have been grown by slow evaporation of the saturated aqueous solution at 30 ºC. The UV-Vis-NIR spectrum revealed the wider transmission window of LPAN and a low cut-off wavelength of 300 nm. The thermal studies proved that LPAN is thermally stable up to 168 ºC. The low dielectric loss with high efficiency implied that the sample possesses good optical quality with lesser defects. The activation energy was determined from the plots of ac and dc conductivity.
The single crystals of L-Phenylalanine-benzoic acid (LPBA) have grown from aqueous solution by solvent evaporation technique by Geetha et al., [40]. The XRD analysis confirmed that the crystal belongs to the monoclinic system with non-centro-symmetric space group P21. The LPBA was optically transparent in the entire visible region with a lower cut-off below 300 nm. The TG-DTA studies established that the compound undergoes no phase transition and is stable up to its melting point 180 °C. The emission of green radiation from the crystal confirmed the second harmonic generation in the crystal.

Single crystals of L-arginine Acetate (LAA) with good degree of transparency were grown by Suresh et al., [41] from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis revealed that the crystal belongs to monoclinic system with space group P21. The optical absorption studies showed that the crystal is transparent in the entire visible region with a cut off wavelength of 240 nm. The optical band gap was found to be 3.75 eV. The dielectric constant was found to decrease with increase in frequency at different temperatures.

Alosious Gonsago et al., [42] have synthesized amino acid organic nonlinear optical material L-histidinium maleate (LHM). Single crystal and powder X-ray crystallographic data indicated that the LHM crystal belongs to monoclinic system with the space group P21. The emission of SHG from the grown crystal was confirmed by the emission of green radiation using Kurtz and Perry powder method. The SEM analysis revealed the existence of grain boundary and striations on the surface of the grown crystal. The thermal stability of LHM crystal was analyzed by DTA and DSC techniques which indicated that the crystal is stable up to 117.5°C.

Paramasivam et al., [43] have observed that there is high transmittance in the far ultraviolet, visible and near infra red regions for grown single crystal of L-Proline Succinate (LPS) The Kurtz Perry technique for second harmonic generation showed positive results. The DTA and TGA studies revealed that the crystal is thermally stable up to 160°C.

Prabhu et al., [44] have grown a new potentially useful nonlinear optical (NLO) organic material chalcones, 1-(5-bromothiophen-2-yl)-3-(4-nitrophenyl) prop-
2-en-1-one (BTNP) by the slow evaporation technique. The compound crystallizes in triclinic system with a non-centro-symmetric space group P1, with unit cell parameters $a = 4.8093(4)$ Å, $b = 5.9428(6)$ Å, $c = 11.5153(11)$ Å, $\alpha = 94.999(4)$, $\beta = 95.780(3)$, $\gamma = 96.396(4)$ and $V = 323.79(5)$ Å$^3$. The scanning electron microscope images confirmed step-like growth of the crystal. The relatively lower refractive index of BTNP in comparison to inorganic materials makes it a better material for NLO applications. The SHG efficiency of the crystal was obtained by powder technique using Nd: YAG laser and was found to be four times that of urea. The good transparency, thermal stability (up to melting point (201.86°C)) and high second harmonic generation efficiency indicated that, the crystal is a promising candidate for NLO applications.

Coumarins are an important class of organic compounds and have been extensively studied. Various coumarin organic derivatives are known to exhibit unique photochemical and photophysical properties; hence they have useful in applications such as optical brighteners, non-linear optical chromophores, solar energy collectors, fluorescent labels and as two-photon absorption (TPA) materials [45-46].

Hara et al., [47] have investigated the effects of deoxycholic acid (DCA) and 4-tert-butylpyridine (TBP) as additives on the photovoltaic performance of coumarin-dye-sensitized nanocrystalline titanium dioxide (TiO$_2$) solar cells. It was observed that DCA improved both the photocurrent and photovoltage of the solar cells, even though it decreases the amount of dye adsorbed on the TiO$_2$ electrode. The addition of TBP to the electrolyte also markedly improved the photovoltage and fill factor of the solar cell, and consequently, the total conversion efficiency increased from 3.6% to 7.5%. The FT-IR spectroscopy indicated that a large amount of TBP was adsorbed on the dye-coated TiO$_2$ films in the presence of Li cations. This result suggests that TBP, like DCA, suppressed the dark current on the TiO$_2$ surface, which resulted in the improved photovoltage.

Wang et al., [48] reported the photophysical and electrochemical properties of new coumarin dye, cyano- \{5,5-dimethyl-3- [2-(1,1,6,6-tetramethyl-10-oxo-2,3,5,6-tetrahydro-1H,4H,10H-11-oxa-3a-aza-benzo [de] anthracen-9yl) vinyl] cyclohex-2-
enylidene}-acetic acid (NKX-2753). It was employed as a dye sensitizer in dye-sensitized solar cells and showed efficient photon-to-electron conversion properties. The photocurrent action spectrum exhibited a broad feature with a maximum incident photon-to-electron conversion efficiency (IPCE) of 84% at 540 nm.

Baharfar et al., [49] reported the crystal structure of the (E)-Dimethyl 2-(6-benzoyl-7-hydroxy- 4-methoxycarbonyl-2-oxo-2H chromen-8-yl) but-2-enedioate. It was found that this compound crystallized in orthorhombic non-centro-symmetric space group.

A series of coumarin dyes with a coumarin derivative as the electron donor, connected with methane and thiophene as the π-conjugation linkage and two -CN groups as the electron acceptor were synthesized and applied as dye sensitizers for dye-sensitized solar cells by Wang et al., [50].

Nitrophenyl hydrazones are organic compounds which form crystals in non-centro-symmetric space groups that motivated their earlier investigation for applications as non-linear optical materials [51- 54]. By contrast, we are interested in the involvement and interplay of the hydrazone moiety (–CH=N–NH–) with additional functional groups, in forming intermolecular interactions.

Owen and white [55-56] reported the discovery of strong SHG in 1-formyl 2(4-nitrophenyl) hydrazine (FNPH) and they investigated its optical and electro-optical properties.

In past several years much effort has been devoted to polymeric systems usable in nonlinear optics [57]. Kminek et al., [58] have synthesized the 4-nitrophenylhydrazone of poly (4-formylstyrene) (PFSN) by the reaction of poly (4-formylstyrene) with 4-nitrophenylhydrazine. PFSN possesses some properties suitable for NLO application and the hydrazone groups might conveniently serve as NLO-chromophores.

Organic crystals with large nonlinear susceptibilities and laser damage threshold make them attractive for application in frequency conversion and optical
processing. However their device applications have been impeded by their inadequate optical transmittance, poor optical quality, lack of robustness, low laser damage threshold and inability to be grown into large size crystals. In order to overcome these difficulties, the large nonlinearities of $\pi$-conjugated organics and the favourable crystal growth properties of ionic salts can be combined into a single NLO material called semi-organics. Semi-organic compounds share the properties of both organic and inorganic compounds.

L-arginine phosphate monohydrate (LAP) is semi-organic nonlinear optical (NLO) material first introduced by Xu et al., in 1983 [59]. LAP crystals are usually grown from aqueous solution by the temperature lowering technique. LAP crystals caught the attention of many researchers because of their high nonlinearity, wide transmission range of 220 - 1950 nm, high conversion efficiency (38.9%) and high damage threshold [60]. Monaco et al., [61] formed LAP and its chemical analogs from the strongly basic amino acid and various other acids. All the compounds in this class contain an optically active carbon atom and all of them form centric crystals. All the crystals are optically biaxial and among them several give second harmonic signals greater than quartz. Hameed et al., [62] have reported that L-arginine fluoride (LAF) possesses high NLO coefficient next to LAP. The amount of second harmonic generated in a powder LAF sample at 1064 nm was 5.6 times of quartz. Julius et al., [63] reported that the efficiency of frequency doubling of L-arginine hydrofluoride (LAHF) was 39% and was larger than KDP (22%) and LAP (33%).

L-histidine salts can display high NLO properties due to the presence of imidazole group in addition to amino-carboxylate. Among the L-histidine analogs, the low temperature solution grown L-histidine tetrafluoroborate (LHFB) [64] is a promising NLO material and has superior NLO properties than LAP. The SHG intensity of L-HFB crystal is five times that of the KDP. The single crystals of L-histidinium dihydrogen orthophosphate ortho-phosphoric acid (LHP) were grown and characterized by Madhavan et al., [65]. The SHG efficiency of LHP was found to be nearly 4 times that of KDP.

Narayan Bhat and Dharmaprakash [66] have reported the growth of the semi-organic glycine nitrate (GSN) by slow evaporation from solution. They have
determined the SHG efficiency of GSN to be 2 times that of KDP. Glycine forms the ferroelectric diglycine nitrate whose spectral transparency range is from 245 to 1900 nm.

Rajan Babu et al., [67-68] reported the growth of single crystals of L-alanine derivatives such as L-alanine tetrafluoroborate (L-AlFB) and L-arginine tetrafluoroborate (L-AFB).

The growth and properties of new semi-organic nonlinear optical crystal, tetra L-lysine alanine mono hydrochloride dihydrate (TLAMHCl) has been studied [69]. The second harmonic generation (SHG) efficiency of TLAMHCl was found to be 1.2 times that of KDP. L-lysine sulphate a semi-organic NLO material useful for frequency doubling in the IR region has been synthesized by Krishnakumar et al., [70].

Chandrasekaran et al., [71] have grown semi-organic NLO crystal thiosemicarbazide potassium chloride (K (NH₂NHCSNH₂) Cl· H₂O) (TSCPC) by slow evaporation method at ambient temperature. They found that the TSCPC is thermally stable up to 185°C and it is optically transparent in the entire visible region with 90% transparency level. The lower cut off wavelength (260 nm) shows a good optical transparency level and high melting point makes TSCPC as a new promising material for many applications. From the dielectric studies it was seen that the dielectric constant decreases with increased frequency.

Metal-organic crystals form a new class of materials under semi-organics. Several metal-organic complexes of amino acid have already been reported. Bis (thiourea) cadmium chloride (BTCC) is a promising metal-organic NLO material for second-harmonic generation [72]. BTCC crystals have very high laser induced damage threshold values. In organo-metallic category complexes of thiourea like, Bis (thiourea) cadmium zinc chloride (BTCZC) [73] exhibit good NLO property. The second harmonic generation efficiency of these crystals is higher than that of urea.

A novel NLO organo-metallic complex crystal, Cadmium mercury thiocyanate dimethyl sulphoxide (CMTD) was reported for the first time by Dong et al., [74]. The
SHG efficiency of CMTD crystal was found to be 15 times that of urea and is larger than that of a Cadmium mercury thiocyanate (CMTC) crystal. Another novel NLO crystal manganese mercury thiocyanate (MMTC) was grown by Wang et al., [75]. The thermal analysis of MMTC shows that it possesses better physicochemical stability than that of CMTC.

Recently, Sun et al., [76] have reported the crystal structure, optical and thermal characterization of tri-allyl thiourea zinc chloride (ATZC). ATZC shows powder SHG efficiency comparable to urea.

Selvaraju et al., [77] have synthesized semi-organic nonlinear optical thiosemicarbazide cadmium acetate (TSCA) material by slow evaporation method. It was observed that the grown TSCA crystal belongs to monoclinic system and the lattice parameter values are $a = 6.675 \text{ A}^\circ$, $b = 10.569 \text{ A}^\circ$, $c = 23.689 \text{ A}^\circ$ and $\beta = 109.20^\circ$. TSCA has a wide transparency window from 300 to 1200 nm, which highlights their prospects of applications as NLO materials. Thermal analysis clearly illustrated that the crystal undergoes decomposition above 163°C. NLO property was confirmed using ND: YAG laser with wavelength 1064 nm and the efficiency was estimated to be 2 times higher than KDP.

Venkatesan et al., [78] have synthesized the metal organic complex, [Zn(lp)$_2$Br$_2$] (DBPZ), (lp = L-proline). The complex DBPZ crystallizes in orthorhombic crystal system with space group P2$_1$2$_1$2$_1$. DBPZ displayed second-order nonlinear optical properties with an estimated efficiency of 1.5 times the value of KDP. Thermal study showed stability of the compound and the melting point was found to be 229 °C.

A considerable interest has been shown recently in studying the effect of impurities (both inorganic and organic) on the nucleation, growth and physical properties of some NLO crystals. The presence of impurity molecules even at lower concentrations in the parent solute may have considerable effect on growth kinetics and other properties.
Freeda and Mahadevan [79] have grown pure KDP and impurity added with ammonium chloride [NH₄Cl], ammonium nitrate [NH₄NO₃], ammonium dihydrogen orthophosphate [NH₄H₂PO₄], ammonium carbonate [(NH₄)₂CO₃] and ammonium sulphate [(NH₄)₂SO₄] KDP single crystals by the gel method using silica gels. Electrical conductivity measurements were carried by the conventional two-probe method and were found to increase with the increase in impurity concentration and temperature. Priya et al., [80] have grown pure and impurity added (with urea and thiourea) KDP single crystals by the gel method using silica gels. Deepa et al., [81] have showed that the alkali halide such as sodium chloride (NaCl)/ potassium bromide (KBr) addition reduces the DC conductivity of KDP single crystals. Ananda Kumari and Chandramani [82] have found that the KDP crystals containing alkali halides such as potassium chloride (KCl), sodium chloride (NaCl), potassium bromide (KBr), sodium bromide (NaBr), potassium iodide (KI), sodium iodide (NaI) shows appreciable increase in SHG efficiency compared to pure KDP crystals. Rajasekaran [83] investigated the impurity effects with different dopant such as lithium, sodium, rubidium and cesium on KDP crystal and compared with pure KDP. It was reported that the hardness is high for heavier metal ions (Rb and Cs) doped KDP crystals and the hardness is low for lighter ion (Li and Na) doped KDP crystals. The higher hardness value for Rb and Cs doped KDP crystals make them suitable for the fabrication of devices applicable for SHG. Assencia and Mahadevan [84] have grown pure and impurity added (with urea and thiourea) ammonium dihydrogen phosphate (ADP) single crystals by the free evaporation method. They observed the DC conductivity of ADP single crystal increases with the increase in impurity concentration and temperature.

Moitra et al., [85] reported the influence of organic impurity L-arginine on the growth and physical properties of bulk zinc tris (thiourea) sulphate ZTS single crystals. It was observed that prominent morphological changes occurred in the doped crystals. It was observed from X-ray diffractograms that there are some sort of partial amorphization of ZTS crystal due to L-arginine. Enhancement of percentage of transmission in the UV–Vis region indicated that optical damage in this region can be reduced by L-arginine doping. Also it was reported the L-arginine doped crystals are much harder than pure ZTS crystals.
Mahadevan [86] has found that the dc conductivity does not vary systematically with impurity concentration in the case of KCl added magnesium sulphate heptahydrate (MSH) single crystals. However, the conductivity is larger for impurity added crystals than the pure crystals.

Kasthuri et al., [87] have investigated the influence of rare earth cerium (Ce) on nonlinear optical crystals of potassium hydrogen phthalate (KHP) and tris (thiourea) zinc (II) sulfate (ZTS). They reported that the SHG efficiency was not influenced by Ce doping in the KHP crystals while in ZTS crystals, it is enhanced to a considerable extent correlated with moderately improved crystalline perfection.

Meana and Mahadevan [88] investigated the effect of sodium chloride, potassium chloride, glycine and urea (added separately) as impurities on the electrical properties of L-arginine acetate single crystals and showed that the organic impurities considered are able to reduce the electrical parameters (ac and dc conductivity, dielectric constant and dielectric loss). In case of inorganic impurities, sodium chloride was able to increase the electrical parameters while potassium chloride decreases the electrical parameters. Raj et al., [89] have studied the solubility, growth, microhardness, X-ray diffraction (XRD), SHG, optical transmittance, thermal and dielectric studies of grown undoped and thiourea-doped $\gamma$-glycine crystals. They observed that solubility was found to be more for the undoped $\gamma$-glycine sample than that of thiourea-doped sample. There was a slight shift in reflection peaks and change in the intensity in the powder XRD pattern of thiourea-doped sample compared to that of pure sample and they reported that thiourea doped $\gamma$-glycine crystal has slightly less thermal stability, more hardness, less melting point, and less SHG efficiency compared to the pure crystal. The shift in the lower cut-off wavelength makes the thiourea-doped crystal to find more applications in NLO devices like frequency doubler, sum frequency generator, difference frequency generator, blue laser generator, etc.

Joema et al., [90] have synthesized undoped and urea-doped L-histidine bromide (LHB) salt by solution method and found to increase in polarizability of the molecule in the presence of urea, which tends to increase the SHG efficiency.
Muthu et al., [91] have studied the effect of magnesium (Mg) doping on the properties of bis (thiourea) zinc (II) chloride (BTZC) crystals. The incorporation of Mg into the crystal lattice was confirmed by energy dispersive X-ray spectroscopy. The powder X-ray diffraction and FT-IR spectral analyses indicated that the crystal undergoes considerable stress as a result of doping. The SEM studies of pure and doped samples indicated the formation of structural defect centres in BTZC crystals. The TG–DTA studies revealed the purity of the materials, and no decomposition was observed up to the melting point. Improved crystalline perfection by doping was observed by high-resolution X-ray diffraction. The high transmittance was observed and the cut-off was found to be 295 nm.

Many of solid-state lasers are designed to work in the strong external fields of ionizing radiation for space born applications, so it is essential to know whether the used components in particular NLO crystals in these lasers sustain the exposure to space radiation.

Sorescu et al., [92] have studied the excimer laser (λ= 308 nm) and electron beam (7 MeV) irradiation effects in LiNbO3 crystal doped with iron (57Fe). Pulsed eximer laser irradiation on crystalline sample results in a significant increase in the optical absorbance over the whole visible range. The high energy electron beam irradiation on crystalline sample was shown to induce dose dependent changes to optical absorption.

Frukacz et al., [93] have investigated the influence of gamma-irradiation (Co-60 source, dose= 10^3-10^6 Gy) and electron irradiation on optical properties of LiNbO3 crystals containing rear-earth impurities (Erbium (Er^{3+}), Thulium (Tm^{3+}) and Magnesium (Mg^{3+})). They observed radiation induced colour centre in LiNbO3 crystals.

Aithal et al., [94] have reported the effect of 100 MeV Ag^{14+} ion irradiation on the electrical and optical properties of organic nonlinear crystal para-hydroxy acetophenone (HAP). They observed that SHG efficiency was marginally affected and the laser damage threshold at higher input laser intensity was found to decrease.
However, changes in refractive index and dielectric constants (13 times higher) are noticed in the irradiated HAP.

Aithal et al., [95] reported the effect of 100 MeV Ag$^{14+}$ ions on organic NLO single crystals of Methyl para-Hydroxy Benzoate (MHB). The results showed an increase in refractive index at the ion irradiated region. The dielectric constant of the irradiated crystal was found to increase more than 15 times compared to that of a unirradiated crystal. They found that the nonlinearity and conversion efficiency of MHB was not affected considerably due to heavy ion irradiation at low input energy of the laser beam. However, with increase in input energies beyond 160 mJ, the irradiated crystal was found to be damaged.

Rao et al., [96] irradiated two organic nonlinear single crystals methyl p-hydroxy benzoate (MHB) and p-hydroxy acetophenon (HAP) with 100 MeV Ag ions and 50-100 MeV Si ions. A dramatic increase in the value of the dielectric constant was observed in both MHB and HAP. The refractive index was also increased after irradiation. However the SHG efficiency of these crystals was only marginally affected.

Bhat et al., [97] have investigated the effect of Si and Ag ions on nonlinear electro-optic ammonium dihydrogen phosphate (ADP) (pure and doped with Chromium, Nickel) crystals. The high energy ion induced changes in dielectric properties was found to be increased in pure ADP when compared to the doped ADP crystals. The change was found to be more pronounced in 100 MeV Ag ion irradiated crystals than 50 MeV Si ions due to larger electronic energy loss. The observed change in dielectric properties can be understood by considering the displacement damage introduced by irradiation resulting in the increase in the dielectric constant.

Roth et al., [98] have reported the effect of different energies of proton radiation (8, 70, and 300 MeV) and different doses of gamma radiation (10 krad, 20 krad, 50 krad and 139 krad) on SHG and transmission spectrum of nonlinear optical crystals β-barium borate (BBO), lithium triborate (LBO), and potassium titanium oxide phosphate (KTP). They observed that the BBO crystal was unaffected by irradiation; only a high dose of gamma irradiation decreases the second harmonic signal about 5%, which still lies within the uncertainty margin of the measurement.
But LBO crystals were affected by 70 MeV protons and gamma irradiation; the decreases of second harmonic signal is less than 10% and KTP crystals are the most affected by irradiation. They observed slight reddish discoloration in the irradiated crystals due to the reduced transmission in the green wavelengths. The second harmonic signal decrease up to 15% for 139 krad gamma and the transmission decreases by 20% for 8 MeV protons ($7.1 \times 10^{10} \mathrm{p^+/cm^2}$). They suggested that BBO crystal is the most suitable nonlinear crystal for SHG in space applications.

Irradiation effects on nonlinear optical crystal barium strontium borate by 120 MeV silver ions of and 8 MeV electrons have investigated by Bhat et al., [99]. They found that the dielectric constant of these crystals was increased by approximately a factor of 4 due to irradiation by silver ions. Electron irradiation also causes a slight increase in the dielectric constant. Refractive indices of these crystals were found to decrease due to both ion as well as electron irradiation which shows the possibility of fabricating optical waveguides by ion and electron irradiation in barium strontium borate crystals. They observed that the change in the transmittance properties of these crystals after ion and electron irradiation was negligible.

Matkovskii et al., [100] was observed stable and transient colour centres in electron ($E = 0.25 \mathrm{MeV}$) irradiated pure and copper -doped Lithium niobate (LiNbO$_3$) single crystals.

Krishnakumar et al., [101] have studied the effect of 40 MeV lithium ions at fluences varying from $10^{10}$ to $10^{12}$ ions/cm$^2$ on NLO crystal potassium tetrakis thiourea bromide (KTTB). The micro hardness was found to decrease after irradiation and it was attributed to the ion induced amorphization. They also observed the increase in dielectric constant and decrease in dielectric loss due to the disordering of crystal lattice by ion beam.

As-ik [102] reported the effect of Co-60 gamma radiation on NLO single crystals of 3-nitroacetanilide. The irradiation of 3-nitroacetanilide by gamma radiation produces free radicals at the nitrogen atoms in the molecule.

Javidi et al., [103] compared the pure KDP crystals with KDP: LaCl$_3$ before and after Co-60 gamma irradiation with different doses (10, 20, and 30 Gray). The conductivity of the pure and doped KDP crystals was found to increase after
irradiation. Microhardness test showed the increase in degree of crystal hardness after gamma irradiation.

The behaviour of dielectric constant and ac conductivity of dimethyl-aminopyridinium-4-nitrophenolate-4-nitro-phenol (DMAPNP) after 100 MeV Ag\(^{8+}\) ion and 50 MeV Si\(^{8+}\) ion irradiation was carried out by Srinivasan et al., [104]. The dielectric constant was found to drastically increase. Greater increase in the dielectric constant was believed to be due more to Ag\(^{8+}\) ion irradiation than Si\(^{8+}\) ion irradiation and due to high fluence rather than to low fluence of irradiation. The dielectric constant and conductivity was increased with increase in fluence for both Ag\(^{8+}\) and Si\(^{8+}\) ions. There was a small shift in absorption edge towards the lower wavelength side for irradiated crystals, accounted for a decrease in the band gap of the material.

Kanagasekaran et al., [105] reported the effect of 70 MeV Li\(^{3+}\) and 100 MeV Ag\(^{7+}\) ion irradiated on M-nitroaniline NLO single crystals. They investigated the irradiation induced defect structures at the crystal surface which becomes more prominent at higher irradiation fluencies, leading to the enhancement in the optical absorption behaviour and the nonlinear property of the irradiated crystals.

Kalidasan et al., [106] have studied the irradiation effects of 120 MeV Au\(^{9+}\) ions on the structural, optical and dielectric properties of Yttrium calcium oxy borate (YCOB) single crystals. The XRD studies confirmed the structural damage induced in the ion projected range. The optical absorption was found to increase and the band edge shifts towards the lower energy side with increase in ion fluence. This is the consequence of photo-darkening effect and hence there may be permanent refractive index change induced in the ion projected layer. Laser Raman spectrum presented the most intense band due to stretching vibrations of (BO\(_3\))\(^3-\) groups from which the major contribution to nonlinearity arises. Also, they observed much reduction in the peak intensity of these modes with ion fluence.

It is evident from the literature that various researchers have extensively studied the growth and characterization of organic and semi-organic NLO crystals. However most nonlinear optical crystals have failed to meet the standards required for the practical use in devices because of the great difficulty of growing crystals sufficiently large size and quality. Hence, there is need for research in the field of new nonlinear optical crystals and their characterization. Also a large number of tests have been performed on the radiation effects on electronic equipment. However, there is
little research covering the radiation effects in the growing field of optics and photonics. In this context, an effort has been made to grow new NLO crystals and to understand the effect of Co-60 gamma and high energy ion (100 MeV O\textsuperscript{7+} ions) irradiation on some NLO single crystals.

1.12. Aim and Scope

The aim of the proposed study is to grow organic NLO crystals of 4-nitrophenyl hydrazone and 3-[(1-(2-phenylhydrazinylidene)ethyl]-2H-chromen-2-one, organic NLO crystals of pure L-alanine alaninium nitrate (LAAN) and doped with lanthanum oxide (La\textsubscript{2}O\textsubscript{3}), sodium chloride (NaCl), urea (CH\textsubscript{4}N\textsubscript{2}O), glycine (C\textsubscript{2}H\textsubscript{5}NO\textsubscript{2}) and thiourea (CH\textsubscript{4}N\textsubscript{2}S). The semi-organic NLO crystals of L-alanine cadmium chloride (LACC) and L-alanine sodium nitrate (LASN) were also grown. In addition, the inorganic NLO crystals of potassium dihydrogen orthophosphate (KDP) doped with L-alanine and L-arginine were grown. The crystals were grown from low temperature solution growth technique by slow evaporation solution method. This is the most suitable method among the various methods of solution growth due to its simplicity and it is convenient method of growing single crystals of large size. The grown crystals were characterized by different characterization techniques. The structural studies were done using single crystal X-ray diffraction (XRD), powder XRD, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. The different optical studies like UV-visible spectroscopy, Fourier transform infrared (FTIR), refractive index (RI) and electrical studies like dielectric measurement, ac and dc conductivity were done. The mechanical studies like Vickers microhardness and thermal studies such as differential scanning calorimetric (DSC), thermo gravimetric analysis (TGA), differential thermal analysis (DTA) were used to understand the mechanical properties and thermal stability of the grown crystals. The second harmonic generation (SHG) was studied using Kurtz Perry technique.

In the present investigation, the effect of Co-60 gamma radiation on the various characteristics of LACC, L-alanine and L-arginine doped KDP grown crystals were studied in the dose range from 100 krad to 6 Mrad. The effect of 100 MeV O\textsuperscript{7+} ions on the various characterizations of LASN grown crystals were also studied in the dose range from 1 Mrad to 10 Mrad. The characterizations of unirradiated and irradiated crystals were carried out to understand the radiation effects on physical and structural properties. The results of all these systematic investigations are incorporated in this thesis.