CHAPTER 1

CRYSTAL GROWTH AND ITS APPLICATIONS AND NONLINEAR OPTICS (NLO) - AN INTRODUCTION

1.1 CRYSTALS – AN INTRODUCTION

Man had admired crystals for long, as he had appreciated their beauty. The gems and crystals delivered by the earth have always attracted mankind and the belief in the virtues of gems and some minerals dates back to at least two thousand years. The use of gems for ornamental purposes appears to be in practice since the birth of mankind. Today, crystals are the pillars of modern technology. Without crystals, there would be no electronic industries, no photonics industry and no fiber optic communications. In the past few decades, there has been a growing interest in crystal growth process, particularly in view of the increasing demand of materials for technological applications.

The solid state materials can be classified as single crystals, poly crystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. An ideal crystal is one, in which the surroundings of an atom would be exactly the same as the surroundings of every similar atom. Real crystals are finite and they contain defects. However, single crystals are solids in the most uniform condition that can be attained and this is the basis for most of the uses of crystals. The uniformity of single crystals can allow the transmission without scattering of electromagnetic waves.

Crystal growth is an interdisplinary field. Modern technology requires physicists, chemists, electrical engineers, metallurgists and crystal growers to assist each other at many levels. Crystal growth is a vital and fundamental part of materials
science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other applications [1 - 3].

Progress in crystal growth is highly demanded in view of its recent advancements in the fields of semiconductors, polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. The utility of crystals has been extended from the bounds of ornaments to several useful applications in optical, electrical and optoelectronic devices. The fantasy of their external beauty was understood more thoroughly through the natural laws of mathematics, physics and chemistry. The contents of the crystals and their insides were explored, analysed and understood by modern methods of diffraction as well as with the help of spectroscopic techniques. The external shapes, planes and colours were correlated with the internal atomic content and their arrangements in unequivocal terms. Thus, grew a science, the study of “crystal growth and characterization”.

1.2 METHODS OF CRYSTAL GROWTH

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. The methods of growing crystals are very wide and mainly dictated by the characteristics of the material and its size [4].

The methods of growing single crystals may be classified according to their phase transformation as given below.

- Growth from solid → solid - solid phase transformation
- Growth from liquid → liquid - solid phase transformation
- Growth from vapour → vapour - solid phase transformation
The basic common principle in all these methods is that a nucleus is first formed and it grows into a single crystal by organizing and assembling ions or molecules with specific interactions and bonding, so that the process is slow and multiple nucleation is minimized. Crystal growth process and size of the grown crystal differ widely and are determined by the characteristics of the material. An efficient process is the one, which produces crystals adequate for their use at minimum cost. The growth method is essential because it suggests the possible impurity and other defect concentrations. Choosing the best method to grow a given material depends on material characteristics.

1.2.1 Growth from solution

The crystal growth from liquid can be classified into six categories namely,

i) Melt growth

ii) High temperature solution growth (Flux growth)

iii) Hydrothermal growth

iv) Gel growth

v) Electrocry stallization and

vi) Low temperature solution growth

There are number of growth methods in each category. Among various methods of growing single crystals, solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. Growth from solution occurs close to equilibrium conditions and hence crystals of perfection can be grown. Study of anisotropy of the properties of crystals requires specimens cut in different orientations from the same single crystal. This can be easily done from crystals of large size.
1.2.1.1 Growth from melt

Melt growth is the process of crystallization by fusion and resolidification of the pure material. In this technique, apart from possible contamination from crucible materials and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods. Mainly, for the latter reason, melt growth is commercially the most important method of crystal growth. The preferential role of the electrochemical process responsible for the change in composition of the crystals when they grow in melt in an applied field has been studied [5]. The growth from melt can further be sub-grouped into various techniques listed below.

i) Bridgman technique

ii) Czochralski technique

iii) Zone melting technique

iv) Verneuil technique

v) Heat exchanger method

vi) Skull melting and

vii) Shaped crystal growth

The major practical factors to be considered during growth of crystals from melt are: (a) volatility, (b) the chemical reactivity and (c) the melting point.

1.2.1.2 High temperature growth (Flux growth)

Flux and hydrothermal growths form the category of high temperature solution growth. In the growth of crystals from high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to
a cooler region. The high temperature crystal growth can be divided into two major categories: first one is growth from single component systems and the second one is that from multi-components. In this method, a solid (molten salt / flux) is used as the solvent instead of liquid and the growth takes place well below the melting point of the solute. The success of crystal growth from high temperature solution largely depends on the selection of the solvent system.

This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point [6]. The crystals grown from melt have lower concentration of equilibrium defects and lower dislocation density. One major disadvantage of this method is the corrosive nature of the fluxes used, which attack the common furnace materials.

1.2.1.3 Hydrothermal growth

The term hydrothermal means, literally, “hot water”. But, in the jargon of the crystal grower, hydrothermal also implies conditions of high pressure as well as high temperature. Closely related to growth from aqueous solution at ambient or near-ambient conditions is the growth from hydrothermal solution. Hydrothermal growth is usually defined as the use of an aqueous solvent at elevated temperature and pressure to dissolve a solute which would be virtually insoluble at ambient conditions. The disadvantages of the hydrothermal techniques are mainly associated with high pressure and inability to observe growth during the process. Quartz is the crystal grown industrially by this technique [7, 8].

1.2.1.4 Gel growth

The growth of variety of crystals having immense importance for their practical consideration and theoretical interest has been achieved by gel technique. The importance of the gel growth is attributed to its simplicity in technique, effectiveness in growing single crystals of compounds that cannot easily be grown by other methods. Though the origin of the method dates back to 1899 – the famous
work of Liesegang who discovered the periodic crystallization in gels, interest in gel technique received attention only after the work of Henisch and his co-workers [9 - 11]. Crystal growth in gels is a promising technique for growing single crystals of substances which are slightly soluble in water and which cannot be grown conveniently from melt or vapour. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases.

1.2.1.5 Electrocrystallization

Electrocrystallization is the basis for important fields such as corrosion, energy storage and generation, electrodeposition, electronics material development, electrorefining, electrotwinning etc. Crystallization without chemical transformation or charge transfer is the simplest case. In certain instances, the crystallization is determined by a chemical transformation occurring prior to or simultaneously with the crystallization process. The role played by the chemical reaction is to supply the material, which crystallizes. Electrocrystallization is the process, which leads to the formation of a new face at the electrode/electrolyte interface, which in turn plays a major role.

1.2.1.6 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. The growth of crystals by low temperature solution growth method involves weeks, months and sometimes years. Much attention has been paid to understand the growth mechanism of the process.

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. This method is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperature. This method is widely used to grow bulk crystals, which have high solubility and have variation in
solubility with temperature. 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.

The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance, which 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 on removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of growth, the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. After undergoing so many modification and refinements, the process of solution growth now yields good quality crystals for a variety of applications.

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

i) Slow cooling method

ii) Slow evaporation method and

iii) Temperature gradient method

1.2.1.6.1 Slow cooling method

This is the most suitable method among 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.

1.2.1.6.2 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. The basic apparatus (Manson Jar Crystallizer) used for the solution growth technique is shown in Figure 1.1. 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 mm$^3$/h. The evaporation technique has an advantage viz. 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 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. In spite of all these disadvantages, this is a simple and convenient method for growing single crystals of large size.
1.2.1.6.3   Temperature gradient method

This method involves the transport of the materials from 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 the method are that,

i)   Crystal grows at fixed temperature

ii)  This method is insensitive to changes in temperature, provided both the source and the growing crystal undergo the same change and

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.
1.3 OPTIMIZING SOLUTION GROWTH

The growth of good quality single crystals by slow evaporation and slow cooling techniques require the optimized conditions and the same may be achieved with the help of the following norms: (i) Material purification, (ii) Solvent selection, (iii) Solubility, (iv) Solution preparation, (v) Seed preparation, (vi) Agitation, (vii) Crystal habit and (viii) Cooling rate.

1.3.1 Material purification

An essential prerequisite for success in crystal growth is the availability of the highest purity material. Solute and solvents of high purity are required, since impurity may be incorporated into the crystal lattice resulting in the formation of flaws and defects. Sometimes impurities may slow down the crystallization process by being adsorbed on the growing face of the crystal which changes the crystal habit. A careful repetitive use of standard purification methods of recrystallization followed by filtration of the solution would increase the level of purity.

1.3.2 Solvent selection

A solution is homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and the one which gets dissolved in the solvent. For a given solute, there may be different solvents. The solvent must be chosen taking into account the following factors to grow crystals from solution. A solvent of choice is the one with,

i) a good solubility for the given solute

ii) a good temperature coefficient of solute solubility

iii) less viscosity

iv) less volatility

v) less corrosion and non-toxicity and

vi) cost effective
It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal, as it grows and the solvent molecules. Sometimes, this is sufficient to result in the precipitation of a new crystalline phase. Also, this effect is related to the influence of impurities or additives upon habit [4]. Solvent commonly used include light water (H₂O), heavy water (D₂O), ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many others. Solvents having all the above characteristics together, however, do not exist. Almost 90% of the crystals produced from low temperature solutions are grown by using water as solvent. Probably, no other solvent is as generally useful for growing crystals as water. Some properties that account for this are its high solvent action, which is related to its high dielectric constant, its stability, its low viscosity, its low toxicity and its availability. For crystal growth, high purity water is needed.

1.3.3 Solubility

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and lower solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

Low temperature solution growth is mainly a diffusion-controlled process, the medium must be less viscous to enable faster transfer of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process.
The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A sample of the clear supernatant liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analyzed. By repeating the above procedure, for different temperatures, the solubility curve can be plotted. Solubility of most substances increases with temperature (the temperature coefficient of solubility is positive).

1.3.4 Solution preparation and crystal growth

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

1.3.5 Seed preparation

Seed crystals are prepared by self-nucleation under slow evaporation from a saturated solution (Figure 1.2). Seeds of good visual quality, free from any inclusion and imperfections are chosen for growth. Since, strain free refaceting of the seed crystal results in low dislocation content, a few layers of the seed crystal are dissolved before initiating the growth. Defects present in an imperfect seed propagate into the
bulk of the crystal, which decreases the quality of the crystal. Hence, seed crystals are prepared with care. The quality of the bulk crystal is usually slightly better than that of the seed.

![Apparatus for the preparation of seed crystals](image)

**Figure 1.2 Apparatus for the preparation of seed crystals**

1. Perforated closed lid  2. Crystallization vessel  
3. Supersaturated solution  4. Seed crystal

### 1.3.6 Agitation

To have a regular and even growth, the level of supersaturation has to be maintained equally around the surface of the growing crystal. An uneven growth leads to localized stresses at the surface generating imperfection in the bulk crystals. Moreover, the concentration gradients that exist in the growth vessels at different faces of the crystal cause fluctuations in supersaturation, seriously affecting the growth rate of individual faces. The gradient at the bottom of the growth vessel exceeds the metastable zone width, resulting in spurious nucleation. The degree of formation of concentration gradients around the crystal depends on the efficiency of agitation of the solution. This is achieved by agitating the saturated solution in either direction at an optimized speed using a stirrer motor.

### 1.3.7 Crystal habit

The growth of a crystal at approximately equivalent rates along all the directions is a prerequisite for its accurate characterization. This will result in a large
bulk crystal from which samples of any desired orientation can be cut. Further, such
large crystals should also be devoid of dislocation and other defects. These
imperfections become isolated into defective regions surrounded by large volumes of
high perfection, when the crystal grows with a bulk habit. In the crystals which grow
as needles or plates, the growth dislocations propagate along the principal growth
directions and the crystals remain imperfect. Needle like crystals have very limited
applications and plate like crystals need to be favourably oriented.

Changes of habit in such crystals which naturally grow as needles or plates
can be achieved by any one of the following ways:

i) Changing the temperature of growth

ii) Changing the pH of the solution

iii) Adding a habit modifying agent and

iv) Changing the solvent

Achievement in this area is of great industrial importance where such
morphological changes are induced during crystallization to yield crystals with better
perfection and packing characteristics.

1.3.8 Cooling rate

Supersaturation, the driving force which governs the growth of a crystal, is
achieved by lowering the temperature of a solution. Temperature and supersaturation
have to be precisely controlled for desirable results. The growth rate is maintained
linear in order to grow large crystals. This requires an increase in the supersaturation
level and linear cooling will not provide this. Hence, after the initial growth, the rate
of temperature lowering is increased. Operation within the metastable limit occurs
without any spurious nucleation in the solution. A large cooling rate changes the
solubility beyond the metastable limit. Further, fluctuations in supersaturation may
encourage solution inclusions of flaw in growing crystal. Hence, a balance between
the temperature lowering rate and the growth rate has to be maintained.
1.3.9 Crystal perfection

The perfection of the final crystal is based on the following:

i) The purity of the starting materials

ii) The quality of the seed crystal

iii) Cooling rate employed and

iv) The efficiency of agitation

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

1.4 INTRODUCTION TO NONLINEAR OPTICS

The field of nonlinear optics emerged nearly five decades ago with the development of the first operating laser and the demonstration of frequency doubling phenomena. These milestone discoveries not only created much interest in laser science, but also set the scope for future work in nonlinear optics. The extraordinary growth and development of nonlinear optical materials during the past decade has rendered photonic technologies, an indispensable part of our daily life. With the emerging demand for information systems, nonlinear optical materials have been considered as the key elements for the future photonic technologies of optical computing, telecommunications, optical interconnects, high density data storage, sensors, image processing, switching etc.

1.4.1 Nonlinear optical phenomenon

Nonlinear optics (NLO) deals with the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude [12]. Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency. The process occurs within a nonlinear medium, usually a crystal. Such frequency doubling process is commonly used to produce green light (532 nm) from, for example, a Nd:YAG laser operating at
1064 nm. The light propagated through a crystalline solid, which lacks a centre of symmetry, generates light at second and higher harmonics of the applied frequency. This important nonlinear property of noncentrosymmetric crystals is called second harmonic generation and this phenomenon and the materials in which it occurs are the subject of intense study [13].

Nonlinear optics is completely, 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, only if the nature of the electrons in nonlinear optical crystal is studied. Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal (Figure 1.3). 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. The electric field in a light wave passing through the crystal exerts a force on the electrons and pulls them away from their 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 oscillating charge will radiate at its frequency of oscillation, hence these electrons in the crystal “generate” light at the frequency of the original light wave.

Figure 1.3  Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points in a crystal
The nonlinear material is different from the linear material in several aspects. The nonlinear optical material can be considered as the one whose electrons are bound by very short springs. 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. Then, the restoring force is no longer proportional to the displacement and then it becomes nonlinear. The electrons bounce 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. The exact values of the new wavelengths are determined by conservation of energy. The energy of the new photons generated by the nonlinear interaction must be equal to the energy of the photon used. Figure 1.4 shows the photons involved in the second harmonic generation process.

![Diagram showing second harmonic generation](image)

**Figure 1.4** Two photons are welded together to produce a single photon with the energy of both original photons

**1.4.2 Theoretical explanation of nonlinear optics**

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

In a nonlinear medium, the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.

At very low fields, the induced polarization is directly proportional to the electric field.

\[ P = \varepsilon_0 \chi \mathbf{E} \quad (1.1) \]

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

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

\[ P = \varepsilon_0 \chi^{(1)} \mathbf{E} + \chi^{(2)} \mathbf{E} \cdot \mathbf{E} + \chi^{(3)} \mathbf{E} \cdot \mathbf{E} \cdot \mathbf{E} + \ldots \quad (1.2) \]

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

\[ P (-\omega_b) = \varepsilon_0 \chi^{(1)} (-\omega_b; \omega_f) \mathbf{E}(\omega_b) + \chi^{(2)} (-\omega_b; \omega_f, \omega_2) \mathbf{E}\omega_f \mathbf{E}\omega_2 + \chi^{(3)} (-\omega_b; \omega_f, \omega_2, \omega_3) \mathbf{E}\omega_f \mathbf{E}\omega_2 \mathbf{E}\omega_3 + \ldots \quad (1.3) \]
where $\chi^{(2)}$, $\chi^{(3)}$, .... are the nonlinear susceptibilities of the medium. $\chi^{(1)}$ is the linear term responsible for material’s linear optical properties like, refractive index, dispersion, birefringence and absorption. $\chi^{(2)}$ is the quadratic term which describes second harmonic generation in noncentrosymmetric materials. $\chi^{(3)}$ is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical instability. 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, which are listed in Table 1.1. If the molecule or crystal is centrosymmetric, then $\chi^{(2)} = 0$. If a field $+E$ is applied to the molecule (or medium), equation (1.3) predicts that the polarization induced by the first nonlinear term is predicted to be $+E^2$, yet if the medium is centrosymmetric, the polarization should be $-E^2$. This contradiction can only be resolved if $\chi^{(2)} = 0$ in centrosymmetric media.

**Table 1.1 Optical effects of nonlinear materials**

<table>
<thead>
<tr>
<th>Order</th>
<th>Susceptibility</th>
<th>Optical 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>Second Harmonic Generation ($\omega + \omega = 2\omega$)</td>
<td>Frequency doubling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frequency mixing ($\omega_1 \pm \omega_2 = \omega_3$)</td>
<td>Optical parametric oscillators</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pockels effects ($\omega + \omega = \omega$)</td>
<td>Electro-optical modulators</td>
</tr>
<tr>
<td>3</td>
<td>$\chi^{(3)}$</td>
<td>Four wave mixing Phase gratings</td>
<td>Raman Coherent spectroscopy; Real time holography</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kerr effect</td>
<td>Ultra high speed optical gates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Optical amplitude</td>
<td>Amplifiers, choppers etc.</td>
</tr>
</tbody>
</table>
If the same argument is used for the next higher order term, \( +E \) produces polarization \( +E^3 \) and \( -E \) produces \( -E^3 \), so that \( \chi^{(3)} \) is the first non-zero nonlinear term in centrosymmetric media. In second harmonic generation, the two input wavelengths are the same \( 2\omega_1 = \omega_2 \) or \( (\lambda_1 = 2\lambda_2) \).

During this process, a polarized wave at the second harmonic frequency \( 2\omega_1 \) is produced. The refractive index, ‘\( n_1 \)’ is defined by the phase velocity and wavelength of the medium. The energy of the polarized wave is transferred to the electromagnetic wave at a frequency \( \omega_2 \).

The phase velocity and wavelength of this electromagnetic wave are determined by \( n_2 \), the refractive index of the doubled frequency. To obtain high conversion efficiency, the phase vectors of input beams and generated beams are to be matched [14].

\[
\Delta K = \frac{2\pi}{\lambda(n_2 - n_1)} = 0 \tag{1.4}
\]

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

\[
\eta = PL^2 \left( \frac{d_{\text{eff}} \sin \Delta K L}{\Delta K L} \right)^2 \tag{1.5}
\]

where \( d_{\text{eff}} \) is the effective nonlinear coefficient, \( L \) is the crystal length, \( P \) is the input power density and \( \Delta K \) is the phase mismatching.

In general, higher power density, longer crystal, large nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency. Also, the input power density has to be lower than the damage threshold of the crystal. Table 1.2 lists the laser and crystal parameters for selecting a NLO crystal for a particular application.
Table 1.2  Parameters for selecting a NLO crystal

<table>
<thead>
<tr>
<th>Laser parameters</th>
<th>Crystal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLO process</td>
<td>Type of phase matching</td>
</tr>
<tr>
<td>Power, Repetition rate</td>
<td>Damage threshold</td>
</tr>
<tr>
<td>Divergence</td>
<td>Acceptance angle</td>
</tr>
<tr>
<td>Band width</td>
<td>Spectral acceptance</td>
</tr>
<tr>
<td>Beam size</td>
<td>Crystal size, Walk – Off angle</td>
</tr>
<tr>
<td>Pulse width</td>
<td>Group velocity mismatching</td>
</tr>
<tr>
<td>Environment</td>
<td>Moisture, temperature acceptance</td>
</tr>
</tbody>
</table>

1.4.3  Nonlinear optical materials

Materials in crystalline form have good optical and electrical properties, by and large improved properties over randomly oriented materials. Many organic and inorganic materials are highly polarizable and are good candidates for NLO study. However, the net polarization of a material depends on its symmetry properties, with respect to the orientation of the impinging fields. It can be shown that the odd order terms in Equation (1.2) are orientationally independent, but the even terms vanish in a centrosymmetric environment. Thus, materials for second order NLO application must be orientationally non-centrosymmetric to be functional. No such restriction applies to third order materials.

Advances in the development of NLO materials can be divided into three different areas:

i) discovery of new NLO materials

ii) growth of promising NLO crystals and

iii) improving the properties of NLO crystals.
Nonlinear optical materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. In the beginning, 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 designed in order to find the SHG efficiency of nonlinear optical materials [15]. 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. For the first time, rapid, qualitative screening for second order NLO effect was possible. The stage was set for a rapid introduction of new materials, both inorganic and organic [13].

Second order NLO materials are used in optical switching (modulation), frequency conversion (SHG, wave mixing) and electro-optic applications, especially in electro-optic modulators. All of these applications rely on the manifestation of the molecular hyper polarizability of the materials.

Inorganic materials are much more matured in their application to second order NLO materials than organics. Most commercial materials are inorganics 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. Recent studies indicate that new crystals possess superior NLO properties and thus they have opened a era in this area of research.

For optical applications, a nonlinear material should have the following characteristics [16]:

i) a wide optical transparency domain

ii) large nonlinear figure of merit for frequency conversion

iii) high laser damage threshold
iv) be readily available in large single crystals

v) wide phase matchable angle

vi) ability to process into crystals, thin films, etc.

vii) ease of fabrication

viii) nontoxicity and good environmental stability

ix) high mechanical strength and thermal stability and

x) fast optical response time.

1.5 REVIEW OF LITERATURE

The emergence of new materials with superior quality is often responsible for major advances in new technologies. New techniques applied to the fabrication of ultra-pure silica glass that enabled the fabrication of fibers with ultra-low loss provided the main stimulus to optical fiber communication. The recent emergence of Erbium doped glasses and the fabrication of fiber amplifiers, another major milestone in this area, enabled 50 gigabits per second transmission rates. Such high amplification rates can not be achieved with standard electronic amplifiers. The high speed, high degree of parallelism of optics will lead gradually to optoelectronic systems where an increasing number of functions will be implemented optically. However, the development of photonic technology relies largely on the progress achieved in fabricating new optical materials with better performance. In that respect, materials with a nonlinear optical response are expected to play a major role in enabling optoelectronic and photonic technologies.

Today, organic nonlinear optical materials are widely used for a variety of photonic technologies. Many NLO organic single crystals have been identified as potential candidates in optical and electro-optical devices. Nonlinear optical materials have acquired new significance with the advent of large number of devices utilizing solid-state laser sources.
1.5.1 Inorganic materials

The search for novel crystals with nonlinear optical properties is still a big challenge for scientists. To fulfill the “molecular engineering” of nonlinear optical crystals, two theoretical models suitable respectively for the studies of the absorption edge and birefringence of a nonlinear optical crystal have been set up [17]. The following parameters are critically important for an NLO crystal: (i) nonlinear optical coefficients, (ii) birefringence, (iii) absorption edge on the UV side, (iv) damage threshold, (v) optical homogeneity and (vi) physicochemical stability and mechanical properties. As a useful ultraviolet (UV) NLO material, Potassium pentaborate (K[B$_5$O$_6$(OH)$_4$]·2H$_2$O) is the first NLO crystal discovered in the series of borates [18]. Many borate crystals such as β-barium borate, lithium borate, strontium beryllium borate, bismuth borate and the latest Ca$_4$LnO (BO$_3$)$_3$ (CLnOB, where Ln = Gd, La, Y) have been studied as promising NLO crystals. The family of the various borate crystals thus plays a very important role in the field of nonlinear optics [19].

Potassium dihydrogen Phosphate (KH$_2$PO$_4$), an inorganic crystal, is a classical ferroelectric and has variety of applications. KDP crystals are widely used in modern short wavelength laser techniques, nonlinear and integrated optics. Takatomo Sasaki et al., [20] have grown KDP crystals, with 40 × 40 cm$^2$ cross sectional area by conventional temperature reduction method (TRM) and three-vessel method using constant-temperature and constant supersaturation technique. Owezarek et al., [21] have reported the results of the dependence of the tapering angle $\theta$ and micromorphology of tapered faces of KDP on the concentration of Fe$^{3+}$ and Cr$^{3+}$ impurities at various supersaturations. Surface topographies of the (1 0 0) and (1 0 1) faces of as grown KDP crystals were observed ex situ by atomic force microscopy by Mariusz et al [22]. de Vries et al., [23] have studied the surface atomic structure of KDP crystal using X-ray scattering. Ravi et al., [24] have reported the optimized growth condition of tetragonal phase DKDP with higher deuterium concentration for growing large size crystals. Xun Sun et al., [25] have proved that light scattering in KDP crystal aggravates with the increasing concentration of EDTA in the growth solution. Pritula et al., [26] have grown KDP single crystals with different molar values of urea as dopants. It is found that 0.2 – 2.0 mole of the urea additive enhances
the laser damage threshold and second harmonic efficiency more than by 25% respectively. Zheshuai Lin et al., [27] have performed the first principle calculations of the linear and nonlinear optical properties of KDP crystal. The electronic band structure is obtained from pseudopotential method. It is found that for KDP, the contribution from the virtual electron process to nonlinear optical responses are dominant. Pritula et al., [28] have grown KDP crystals doped with the organic xylenol orange (XO) dye. Analysis of the IR absorption spectra reveals a strong interaction between the incorporated dye molecules and the hydrogen subsystem of the matrix.

The effect of swift heavy ions on the dielectric properties of doped and undoped ADP crystals was studied by Bhat et al [29]. Xue et al., [30] have studied the second-order nonlinear optical (NLO) properties of doped lithium niobate (LN) crystals (abbreviated as M:LN, where M = Mg$^{2+}$, Zn$^{2+}$ and In$^{3+}$ respectively). It was observed that the second order NLO response of doped LN crystals decreases with increasing dopant concentration in the crystal.

Zhang et al., [31] have grown Ga and Ce doped Potassium acid phthalate (KTP) crystals by flux method. KTP has wide applications as waveguides, electro-optical and periodic poling structures. In this context, KTP crystals should possess low conductivity. By doping the KTP with Ga or Ce, it was found that the conductivity of KTP crystals is reduced.

Feigelson et al., [32] has predicted the enhancement of optical transparency in CdGeAs$_2$ single crystals by controlling crystalline defects. Successful growth of new nonlinear LiKB$_4$O$_7$ single crystal was achieved by Adamiv et al., [33] using Czochralski technique. The Mohs hardness of the crystal was found to be equal to 5. Xin Yuan et al., [34] have obtained a high optical quality Cesium lithium borate (CLBO) crystal with dimensions of 146 × 132 × 118 mm$^3$ by Kyropoulos method. Centimetre-sized single crystals of TI$_3$PbBr$_5$ were grown by Alban Ferrier et al., [35] using the Bridgman-Stockbarger method. This compound undergoes phase transition at 237 °C. The spectroscopic properties and second harmonic generation tests suggest that it is a potential material for middle infrared nonlinear optics. Enhancement of crystalline perfection by organic dopants in tris(thiourea) zinc(II) sulfate (ZTS),
ammonium dihydrogen phosphate (ADP) and potassium hydrogen phthalate (KHP) crystals were investigated using High resolution X-Ray diffraction (HRXRD) and Scanning electron microscope (SEM) by Bhagavanarayana et al [36]. Zhoubin Lin et al., [37] have reported that the SHG efficiency of YCa$_{9}$ (VO$_{4}$)$_{7}$ single crystal is 4.7 times as large as that of KDP crystal. The absorption edge of the crystal was found at 360 nm. The structures of the non-centrosymmetric borate chlorides Ba$_{2}$TB$_{4}$O$_{9}$Cl (T = Al, Ga) have been determined by Jacques Barbier et al [38]. The second harmonic generation efficiency ($d_{eff}$) for a powder sample of Ba$_{2}$GaB$_{4}$O$_{9}$Cl was found to be 0.95 relative to a KH$_{2}$PO$_{4}$ standard. Many inorganic NLO materials were reported for various applications.

1.5.2 Organic materials

For the past two decades, the search for new NLO materials has concentrated primarily on organic compounds owing to their large nonlinearity. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electro-optic effect and large second or third-order hyperpolarizabilities compared to inorganic NLO materials.

The low-temperature solution growth technique is widely used for the growth of organic compounds to get quality single crystals. Vijayan et al., [39] have grown p-hydroxy acetophenone (C$_{8}$H$_{8}$O$_{2}$), one of the potential organic NLO materials. It has been grown by slow evaporation technique. Nagaraja et al., [40] showed that benzoyl glycine (BG), an organic nonlinear crystal grown by slow evaporation from Dimethyl Formamide solution has the advantages of both the organic and inorganic NLO materials and is nondeliquescent. Owing to high nonlinear efficiency, high melting point, good chemical stability, less sublimation problems and improved hardness and cleavage properties (unlike other organic materials), benzoyl glycine is found to be a promising material for NLO applications. Lakshmana Perumal et al., [41] further extended the effort in synthesizing 4-methoxy benzaldehyde-N-methyl-4-stilbazolium tosylate (MBST), which is a derivative of
stilbazolium tosylate and a new material having high NLO property. The Kurtz powder SHG measurements on MBST showed that the peak intensity is 17 times more than that of urea. Methyl p-hydroxybenzoate (p-MHB) is a para-substituted aromatic compound with a molecular formula $C_8H_8O_3$.

Urea has been used in an optical parametric oscillator to generate tunable radiation throughout the visible region but intrinsic absorption and phase matchability considerations make it unsuitable for wavelengths longer than 1000 nm, as reported by Rosker et al [42]. The efforts made to resolve the problems associated with urea have not been successful. The newly grown binary UNBA crystal by Rai et al., [43], is thermally and mechanically harder than the crystal of the parent components. It is quite transparent almost in the entire the UV region and hence it can be used for producing green/blue laser light. Lin et al., [44] have synthesized two component urea-mNBA systems and urea-L-malic acid systems with different urea compositions. Jun Shen et al., [45] have grown single crystals of L-tartaric acid-nicotinamide and D-tartaric acid-nicotinamide by the temperature lowering method from aqueous solution. Single crystal of 3-methyl 4-nitropyridine -1-oxide (POM) was grown by Boomadevi et al [46]. Manivannan et al., [47] have grown 3-[(1E)-N-ethylethanimidoyl]-4 hydroxy-6-methyl-2H-pyran 2-one, by slow evaporation technique and found that the SHG efficiency is close to that of urea. A chiral mixed carboxylate, $[Nd_4(H_2O)_2(OOC(CH_2)COO)_4(C_2O_4)_2]$ was grown by Vaidhyanathan et al [48]. It was found to possess about 1.1 times the SHG activity of urea. Lakshmanaperumal et al., [49] have reported single crystals of 4-hydroxy-benzaldehyde-N-methyl-4-stilbazolium tosylate grown using solution growth technique and confirmed the irregular cut chunk and irregular pyramid morphology. Single crystals of N-methylldutidone trihydrate $[C_8H_11NO\cdot3H_2O]$ (NM) were grown by slow evaporation technique by Dhanuskodi et al., [50] and their SHG was 0.51 times of that of urea. NLO single crystals of benzimidazole have been reported by Vijayan et al [51]. Solution grown single crystals of bis-2,7-diethylaminohepta-2, 5-dien-4-one (BEDO) have produced SHG efficiency of 0.51 times that of urea as reported by Dhanuskodi et al [52]. However, the shortcomings of aromatic crystals, such as poor physico–chemical stability, low hardness and cleavage tendency hinder their device application.
A new ligand N-(3-fluorophenyl) naphthaldimine has been synthesized by Unver et al [53]. The electric dipole moment ($\mu$) and the first hyperpolarizability ($\beta$) values of the N-(3-fluorophenyl) naphthaldimine have been computed and the results reveal that the synthesized molecule might have microscopic nonlinear optical (NLO) behaviour with non-zero values. L-arginine acetate (LAA) is an organic nonlinear optical material which has a wide optical transmission window between 220 and 1500 nm. Its laser damage threshold and SHG efficiency are comparable with that of KDP. Vickers microhardness measurement was done for different crystallographic planes of LAA by Tanusri Pal et al [54]. LAA was also grown by Tanusri Pal et al., [55] from its aqueous solution with pH of 6. Morphological analysis reveals that LAA is a polyhedron with 16 developed faces with major face forms (1 0 0), (0 0 1), and (1 0 2) (pinacoids) parallel to the polar axis. The N-(3-nitrophenyl) phthalimide (N3NP) is a phase-matchable NLO crystal and can be used as an efficient frequency doubler and optical parametric oscillator due to its high SHG conversion efficiency, which was grown by slow evaporation technique using DMF solvent by Ravindra et al [56]. Single crystals of pure, benzophenone and iodine doped benzoyl glycine (BG) were grown and characterized by Prem Anand et al [57]. Its hardness anisotropy is confirmed by the microhardness study. Shaokang Gao et al., [58] have synthesized the N-(4-nitrophenyl)-N-methyl-2-aminoacetonitrile (NPAN) material and their single crystals of dimensions $36 \times 8 \times 8$ mm$^3$ were harvested in the size using 2-butanone as the solvent and in the size $21 \times 15 \times 15$ mm$^3$ with nitromethane as the solvent. Second harmonic generation (SHG) in the NPAN crystal was observed using Nd:YAG laser with a fundamental wavelength of 1064 nm. Haja Hameed et al., [59] have obtained DAST crystals by the two-zone growth technique and the crystal surfaces were analyzed with help of optical and scanning electron microscopic results. Ramachandran et al., [60] have employed photoacoustic spectroscopy (PAS) method to determine the thermal diffusivity and conductivity of the gel-grown nonlinear optical single crystals of hippuric acid. Optical absorption of the specimen was studied using its PA spectrum and compared with UV-visible absorption spectra. An organic NLO material, 4-OCH$_3$-4'-nitrochalcone (MNC), has been synthesized and grown by Patil et al., [61] which has NLO efficiency 5 times more than that of KDP.
A new organic crystal of semicarbazone of 2-amino-5-chloro-benzophenone (S2A5CB) has been grown and characterised by proton nuclear magnetic resonance by Sethuraman et al., [62] and its second harmonic generation property was confirmed by Kurtz powder method. Vibrational spectral analysis of the nonlinear optical material, L-prolinium tartrate (LPT) was carried out using NIR-FT Raman and FTIR spectroscopy by Padmaja et al., [63]. Also the single crystals of LPT were grown by Martin Britto Dhas et al., [64] using submerged seed solution growth method. An organic electro-optic and nonlinear optical (NLO) crystal, L-alaninium oxalate (LAO) was grown and its physicochemical properties was studied by Dhanuskodi et al [65] and Vimalan et al [66].

Jagannathan et al., [67] have synthesized the organic material 4-Ethoxybenzaldehyde-N-methyl 4-Stilbazolium Tosylate (EBST), a new derivative in Stilbazolium Tosylate family. It has NLO efficiency 11 times greater than urea. Studies on the nucleation kinetics of Sulphanilic acid (SAA) single crystals were reported by Mythili et al [68]. The laser damage threshold values of the SAA crystals are found to be 7.6 and 6.6 GW/cm² for single and multiple shots, respectively. Single crystals of pure and Cu²⁺ and Mg²⁺ doped L-arginine acetate (LAA) were grown by Gulam Mohamed et al., [69] using slow evaporation method. It is observed that both Cu²⁺ and Mg²⁺ dopants have increased the percentage of transmission in LAA. Investigation on the nucleation studies of L-arginine acetate single crystals were reported by Selvaraju et al [70]. Modified hippuric acid (HA) single crystals have been grown from aqueous solution of acetone by doping with NaCl and KCl, with the vision to improve the physicochemical properties of the sample. It is noted that the dopants have increased the thermal stability and mechanical strength of the crystal as reported by Suresh Kumar et al [71]. The influence of isoelectric pH (PI) on the growth, linear and nonlinear optical and dielectric properties of L-threonine single crystals has been studied. The crystalline powder SHG efficiency of L-threonine crystals grown at PI (Isoelectric pH) was found to be 1.2 times that of KDP. High quality bulk crystals of L-threonine grown at different pH values were tested using high resolution X-ray diffractometry by Ramesh Kumar et al [72, 73]. Melt grown Ethyl P-amino benzoate (EPAB) single crystal was recently identified as new organic nonlinear optical material, with nearly six times higher SHG efficiency than that of
KDP was reported by Arivanandhan et al [74]. Recently, a new nonlinear optical organic single crystal, 4-phenylpyridinium hydrogen squarate (4PHS) has been grown and characterized by Ramachandra Raja et al [75]. Good optical quality single crystals of organic nonlinear material 1-chloro-2, 4-dinitro benzene (CDNB) were successfully grown by low temperature solution growth technique by Sethuraman et al [76].

In order to retain the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semiorganic 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.

1.5.3 Organo-Metallic Complex Materials

Inorganic materials are much more matured in their applications to second-order NLO 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 inorganic materials. Growth of inorganic single crystals has been a subject to perennial concern in order to use these materials for device applications. However, to enable a material to be potentially useful for nonlinear optical applications, the material should also be available in bulk form.

The search for new frequency conversion materials over the past decade has led to the discovery of many organic NLO materials with high nonlinear susceptibilities. The approach of combining the high nonlinear optical coefficients of the organic molecules with the excellent physical properties of the inorganics has been found to be overwhelmingly successful in the recent past. Hence, recent search is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness. Recently, metal complexes of urea and urea analogs have been explored.
These crystals have better nonlinear optical properties than KDP. Bis (thiourea) cadmium chloride (BTCC) is a promising semiorganic NLO material for SHG as reported by Xing et al [77]. BTCC crystals have the highest laser induced damage threshold values among the other solution grown NLO crystals. In general, crystals of the type M[tu]$_2$X$_2$, where M = Cd, Co, Hg, Pb, Ti and Zn, tu is thiourea and X is a halogen, have been found to exhibit good NLO properties. Bis(thiourea) zinc chloride (BTZC) single crystals have been grown by slow evaporation technique at room temperature. The metal thiocyanates and their Lewis-base adducts are one of the interesting themes of structural chemistry. As second order nonlinear optical (SONLO) materials, bimetallic thiocyanates: Zinc cadmium thiocyanate (ZCTC), Zinc mercury thiocyanate (ZMTC), Cadmium mercury thiocyanate (CMTC), Manganese mercury thiocyanate (MMTC) exhibit efficient SHG at short wavelengths. Spectroscopic and thermal properties of iron mercury thiocyanate (FMTC) crystals were studied by Wang et al [78]. Its SHG efficiency was found to be 0.6 times that of urea. Single crystals of cadmium thiourea acetate (CTA) have been grown by slow evaporation technique at ambient temperature. CTA has good optical transmission in the entire visible region as reported by Rajesh et al [79]. Kannan et al., [80] have grown bisthiourea-zinc Acetate (BTZA) by slow evaporation technique and observed that BTZA has better SHG efficiency than CTA. A new metal-organic co-ordination nonlinear optical crystal, tri-allyl thiourea zinc chloride (ATZC) was synthesized in water and recrystallized in ethanol by Sun et al [81]. The powder SHG efficiency of ATZC was found to be comparable with urea. Single crystals of pure, Mg$^{2+}$ and Zn$^{2+}$ doped nonlinear optical BTCC have been conveniently grown by slow evaporation technique and subjected to NLO test by Selvakumar et al [82].

Metal (Cd$^{2+}$ and Cu$^{2+}$) substituted single crystals of bis (thiourea) zinc chloride (BTZC) were grown by slow evaporation technique by Selvakumar et al. [83]. Selvakumar et al., [84] have grown yet another variety of organometallic nonlinear optical crystal bis (thiourea) cadmium formate (BTCF) and characterized by optical and mechanical studies. Vickers hardness measurements show that BTCF has a high Vickers hardness number (VHN) value of 109.7 kg mm$^{-2}$. Bis(dimethylsulfoxide) tetrathiocyanato-cadmium(II) mercury(II) (CMTD), a promising organometallic NLO crystal was grown and characterized by
Rajarajan et al., [85] and the SHG efficiency of the crystal was found to be 15 times that of urea. A highly efficient nonlinear optical crystal of tetrathiourea mercury (II) tetrathiocyanato zinc (II) (TMTZ) was grown by Rajarajan et al [86]. The lower cut-off wavelength of TMTZ is at 330 nm. A spectroscopic investigation on the single crystal of thiocyanato manganese mercury-\(N,N\)-dimethylacetamide (MMTWD) reveals that MMTWD belongs to the two-dimensional layer net structure. The water and DMA molecules present in the layers induce large nonlinearity and higher environmental stability. Optically clear manganese mercury thiocyanate (MMTC) crystals have been grown by Ginson P. Joseph et al [87]. The high second harmonic efficiency of nearly 18 times that of urea and the wide optical transmittance window (373 - 2250 nm) of MMTC indicate that this material is an excellent candidate for photonics device fabrication. Siddheswaran et al., [88] have grown ATMC crystal which is a new nonlinear optical material (NLO) having high optical quality and its second harmonic generation (SHG) efficiency is thrice that of urea. Complex degradation of ATMC compound takes place above 230 °C. Single crystals of BTZA have been grown by low temperature solution growth method using slow cooling process at an optimized pH of 3.5. Transmission spectrum reveals that the crystal has a low UV cut off of 434.5 nm and has a transmittance of 100%. The Vickers hardness value was estimated as to be 108.36 kg/mm\(^2\).

The influence of metallic substitution (Mg\(^{2+}\) and Cd\(^{2+}\)) on the physical properties of MMTC was studied by Joseph et al., [89] and it was found that metallic substitution has improved the physicochemical properties. Highly efficient single crystals of zinc cadmium thiocyanate (ZCTC) with SHG efficiency 12 times that of urea was grown by Joseph et al [90]. ZCTC has a UV cut-off wavelength of 290 nm and a high thermal stability of 350 °C. Nisha Santha Kumari et al., [91] have also grown Zinc Cadmium Thiocyanate (ZCTC) single crystals with dimensions upto \(12 \times 2 \times 1.3\) mm\(^3\) in Silica gel.

Effect of different metal ions on the physical properties of tri-allylthiourea cadmium chloride (ATCC) and tri-allylthiourea mercury chloride (ATMC) single crystals were studied by Perumal et al [92]. It was reported that the presence of the different central metal (Cd and Hg) atoms have changed the thermal
properties of the materials when formed with the common ligand allylthiourea. A novel second order nonlinear optical co-ordination complex crystal tris allylthiourea zinc bromide (ATZB) was synthesized and grown from ethanol as solvent by Sun et al [93]. It was found that the crystal exhibited no temporal degradation due to the hygroscopic or efflorescent effects at room temperature. Recently, new metal complexes of urea such as potassium thiourea iodide (PTI) and potassium thiourea chloride (PTC) have been grown by solution growth technique by Selvaraju et al [94, 95]. Both crystals show good optical transmission in the entire visible region. Growth and characterization of pure and Zn$^{2+}$ doped bis(thiourea) cadmium acetate (BTCA), a nonlinear optical single crystal was reported by Selvakumar et al [96]. Growth aspects of nonlinear optical material cadmium zinc thiourea acetate (CZTA) have been studied by Kirubavathi et al [97]. The optical transmission studies and second harmonic generation (SHG) efficiency studies justified the device quality of the grown crystals. Semiorganic nonlinear optical thiosemicarbazide cadmium chloride monohydrate (TSCCCM) single crystals were grown from aqueous solution by slow evaporation method by Sankar et al [98]. The SHG conversion efficiency of TSCCCM crystal was found to be 14 times higher than that of KDP crystal. In TSCCCM crystal structure, the planar $\pi$-organic molecules combine harmonically with inorganic distorted polyhedrons. The chlorine atoms in TSCCCM must be involved in the coordinate polyhedral and have promoted the NLO property. The organometallic complex crystals generally are of good NLO activity and have good thermal stability and are suited for applications.

### 1.6 SCOPE OF THE THESIS

The search and design of high efficient nonlinear optical (NLO) crystals for visible and Ultraviolet (UV) regions are extremely important for laser and material processing. The inorganic, organic nonlinear optical materials have their advantages and disadvantages. The inorganic nonlinear optical crystals are easy to grow. They can be grown in to large sized crystals using the conventional solution growth technique. But the efficiency of the inorganic crystals are lower compared to their organic counterparts. The mechanical strength of inorganic crystals is high generally. The organic materials are difficult to grow and have less mechanical strength. Inspite
of these drawbacks, the organic materials have high nonlinear activity. In order to combine the advantages of organic and inorganic materials, semiorganic crystals were grown.

In the present work, crystals of pure and doped hippuric acid, 4-Nitrophenol Urea, Glycine Oxalate, L-Histidine Bromide, pure and doped Triglycine Sulphate (TGS) and pure and doped crystals of Potassium Di hydrogen Phosphate (KDP) were grown using slow evaporation method.

The present investigation is aimed at:

i) Growing bulk sized crystals.

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

iii) Analysing the grown crystal for its optical transmission/absorption, NLO property, laser damaged threshold, hardness, dielectric property, A.C. Conductivity and refractive index.

iv) Studying the thermal behaviour of the grown crystals.