CHAPTER I

INTRODUCTION, REVIEW OF LITERATURE AND OBJECTIVES

1.1 INTRODUCTION

Solids can be broadly classified as either crystalline or non-crystalline. In a crystal the atoms are arranged in a periodic manner in all three directions, whereas in a non-crystalline solid the arrangement is random. A crystalline solid can either be a single crystal, or polycrystalline. A single crystal is a crystalline solid in which the crystal lattice of the entire sample is continuous with no grain boundaries. Polycrystal is an aggregate of many small crystals separated by well defined boundaries.

Non-crystalline substances are called amorphous and they have no directional properties and therefore they are called isotropic substances. They do not possess any regular shape and they have wide range of melting point. A crystal has regular shape and when it is broken, all broken pieces have the same regular shape. A crystal has sharp melting point. Since the crystals may have different periodic arrangements in all three directions, the physical properties vary with direction and therefore they are called anisotropic substances.

Solid crystals can be divided into four categories. (i) Metallic crystals (ii) Ionic crystals (iii) Covalent crystals and (iv) Molecular crystals. In metallic crystals, atoms are joined together by metallic bond. Metallic crystals are very hard. They have high melting point and boiling point. They have shiny surface. They conduct electricity and heat. They are ductile.
Solids that contain ionic bond in their structure are ionic crystals. In ionic
crystals, oppositely charged ions are joined together by strong electrostatic forces.
They are hard substances. They have high melting and boiling points. They conduct
electricity in molten state and in the form of solution. They are brittle. They are not
ductile. Solid substances in which atoms are held together by covalent bond are
known as covalent crystals. These crystals are very stable. In molecular crystals,
molecules are joined together by weak Vander Walls forces. These substances have
low melting and boiling points.

Crystals are classified into seven crystallographic systems based on their
symmetry: cubic, trigonal, hexagonal, tetragonal, orthorhombic, monoclinic and
triclinic.

Crystals are divided into macro, micro and nano crystals. Macro crystals are
ordered crystals of mm (10^{-3} m and above) size. They are visible crystals. Micro
crystals are microscopically small crystals (of the order of 10^{-6} m). Nano crystals are
crystals of dimensions \sim 10^{-7} m and below.

1.2 SIGNIFICANCE OF CRYSTALS

The colours, the smooth surfaces with scintillating reflections of light, the
definite and varied shapes with sharp edges, the transparency of some perfect crystals,
all together aroused the aesthetic sense of the early man who used them as ornaments.
Behind every new solid state device there stands a single crystal and many new
crystals have to be grown and fabricated in order to assess their device properties.
The ever increasing application of electronics creates an enormous demand for high
quality semiconducting, ferroelectric, piezoelectric, nonlinear optical and oxide single
crystals.
A variety of crystals are needed to meet some very important gaps in conventional production engineering. Many types of crystals find application in lasers, optical components for communication, light emitting diodes (LED’s), thermal imaging, pyroelectric detectors etc. Semiconductor lasers, piezoelectric, ferroelectric and infrared sensitive crystals are part of several solid state devices in use today. With the absence of crystals, there would be no electronic industry and fibre optic communications. New materials are always investigated and the list of crystals is on the rise. Hence, the growth of single crystals has become inevitable for any further developments in material science research. Modern technology is largely based on materials such as semiconductors, superconductors, piezoelectric, ferroelectric, infrared sensitive crystals and nonlinear optical materials.

Nonlinear Optical (NLO) crystals are very important for laser frequency conversion. Potassium Dihydrogen Phosphate (KDP) is a suitable material for higher harmonic generation of huge laser systems for fusion experiments. In recent years, there has been considerable progress in the development of coherent UV sources, based on nonlinear optical processes. Various types of organic, inorganic and semi-organic NLO crystals have been developed because of the possibility of extreme high optical nonlinearity. Large size crystals are essential for device fabrication and efforts are taken to grow large crystals in short duration by fast growth techniques (Santhana Raghavan and Ramasamy 2000).

Apart from pure crystals, mixed and impurity-added ones are also involved in the above mentioned devices. The demand for storage and processing of data has encouraged interest in photo-refractive crystals. The interaction of laser light with crystals like barium titanate produces a small change in the refractive effect and it is exploited for recording holograms and the development of phase-conjugate optics.
Photonic crystals are attractive optical materials for controlling and manipulating the flow of light. One-dimensional photonic crystals are already in widespread use in the form of thin-film optics with applications ranging from low and high reflection coatings on lenses and mirrors to colour changing paints and inks. Higher dimensional photonic crystals are of great interest for both fundamental and applied research and the two-dimensional ones are beginning to find commercial applications. The first commercial products involving two-dimensional periodic photonic crystals are already available in the form of photonic-crystal fibers which use a nanoscale structure, to confine light with radically different characteristics compared to conventional optical fibers for applications in nonlinear devices and guiding exotic wavelengths.

Progress in crystal growth and epitaxy technology is highly demanded in view of its essential role for the development of several important areas such as production of high efficiency photovoltaic cells and detectors for alternative energy and medicine and the fabrication of bright and long-life light emitting diodes for saving energy by wide use in illumination and traffic lights. The most exciting and at the same time widely anticipated contribution to molecular biology made by crystallographers in the recent years has been the direct insulation, at atomic resolution of nucleic acid and variety of proteins with which it interacts. Indeed it appears likely that the structural basis is now making interpretation of protein acid interaction, the highest level of details. This will emerge an understanding in the molecular, biological and classical chemical terms, of the process by which genetic events are initiated, mediated and ultimately regulated. Attempts are made to replace the naturally available crystals by artificially grown crystals and this has been going on for a long time. Crystals play an important role in the development of high
temperature super conductors. In the field of optics, new materials like titanium doped sapphire are being developed as tunable lasers which promise longer life and more stable output than the present dye lasers (Chernov and Komatsu 1995; Bhagavantam 1966; Morrison 1966; Zyss 1994; Anukrum 1971).

Ferroelectric crystals utilize the unique dielectric, piezoelectric, pyroelectric and electro-optic properties for device fabrication. Ferroelectric crystals have attracted attention for applications in many electronic and electro-optic devices. Some of the most important electronic applications of ferroelectric and pyroelectric crystals include non-volatile memories, thin film capacitors, pyroelectric sensors, Surface Acoustic Wave(SAW) substrates, Ferroelectric Random Access Memories(FRAMs), transducers, switching devices etc. The electro-optic devices are optical wave guides, optical memories and displays. The main advantages offered by FRAMs include non-volatile and radiation hardened compatibility with CMOS and GaAs circuitry, high speed (30 ns cycle time for read / erase / rewrite) and high density. Data is stored by localized polarization switching in the microscopic regions of ferroelectric thin films. The FRAMs are non-volatile because the polarization remains in the same state after the voltage is removed (as ferroelectrics have a non-linear hysteresis curve). The radiation hardness of FRAMs allows for the use of devices containing these memories in harsh environment like outer space (Lines and Glass 1997; Xu 1991; Tareev 1979).

1.3 AN OVERVIEW ON NONLINEAR OPTICS AND NONLINEAR OPTICAL MATERIALS

Nonlinear optical (NLO) effects are analyzed by considering the response of the dielectric material at the atomic level to the electric fields of an intense light beam (Armstrong et al 1962). The propagation of a wave through a material produces changes in the spatial and temporal distribution of electrical charges as the electrons
and atoms interact with the electromagnetic fields of the wave. The main effect of the forces exerted by the field on the charged particles is displacement of the valence electrons from their normal orbits. This perturbation creates electric dipoles whose macroscopic manifestation is the polarization (Narasimhamurty 1981). Thus nonlinear Optics (NLO) is the study of interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude (Firdous Anwar 1988; Bloembergen 1965; Munn and Ironside 1994; Zernike and Midwinter 1973). 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. The light propagated through a crystalline solid, which lacks a center of symmetry, generates light at second and higher harmonics of the applied frequency. Such frequency doubling processes commonly produce green light (532 nm) from, for example, an Nd:YAG (yttrium-aluminium-garnet) laser operating at 1064 nm. 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 (Chemla and Zyss 1987).

1.3.1 Nonlinear Optics

Nonlinear optics is given increasing attention due to its wide application in the area of laser technology, optical communication and data storage technology (Gambino 1990). 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 best 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 (Figure 1.1).
Figure 1.1: Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points

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 electric field. According to the fundamental law of physics an oscillation change will radiate at its frequency of oscillation, hence these electrons in the crystal generate light at the frequency of the original light wave.

An NLO material is a compound in which a nonlinear polarization is invoked on application of an intense electric field. This electric field results from the external application of an intense laser-source. The nonlinear material is different from the linear material in several aspects. A nonlinear material is 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. The restoring force is no longer proportional to the displacement and then it becomes nonlinear. 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. The exact values of the new wavelengths are determined by conservation of energy. The energy of the new photon generated by the nonlinear interaction must be equal to the energy of the photons used. Figure 1.2 shows the photons involved in the second harmonic generation process.

![Figure 1.2: Two photons are welded together to produce a single photon with the energy of both original photons](image)

In linear materials, the response is always proportional to the stimulus. The induced polarization is proportional to the field and the susceptibility is independent of the field. In practice, this is always the case at low fields. However at high fields, the polarization is proportional to the field and hence the susceptibility starts depending on the field. It is called Nonlinear Optics (NLO) because, at high intensity, the graph representing the dependence of optical polarization on the light field amplitude has curvature and deviates from straight line. When a string is bowed with much force or a wind instrument is blown hard, many overtones may be generated; similar thing happens to the electrons in matter when they are violently
excited by high intensity light; overtones of light are created. This has the dramatic effect that a red light beam may be changed to a UV beam with twice or thrice the frequency or one half or one third of the wavelength.

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 noncentrosymmetric crystalline medium (Bhawalkar et al 1965). Now, after 40 years of research with NLO materials, it is possible to cover almost continuously the range from 170 nm to 180 nm. As a result, further extension of applications to the ultraviolet (UV) and far-infrared regions will be possible. However, materials limitations are significantly slowing the development of required optical devices.

One of the obvious requirements for a nonlinear crystal is that it should have excellent optical quality. This means that for new materials, for which single crystal specimens are not available, it is necessary to grow single crystal specimens of optical quality. Thus in many cases the search for new and better nonlinear optical materials is very largely a crystal growing effort. It is realized that the requirements of optical quality for a useful nonlinear optical material are more stringent than even the most exciting requirements on optical quality for materials used in linear optics. For a device to succeed it is vital that it meets a number of other criteria and these other criteria should receive greater emphasis. The relevant issues include reliable crystal growth techniques, ready availability, optical nonlinearity, birefringence, moderate to high transparency and optical homogeneity for high conversion
efficiency, mechanical strength, chemical stability, polishing and coating technology for ease of fabrication, low absorption temperature phase matching bandwidth, fracture toughness, thermo-mechanical properties for high average power, damage threshold, nonlinear absorption and brittleness index for lifetime and system capability.

1.3.1.1 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 an electric dipole. 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 intensity of the incident radiation increases and amplitude of vibration becomes nonlinear resulting in the generation of harmonic in the frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and indeed higher order frequency effect occurs as the incident intensity is increased. In a nonlinear medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such a way that a polar orientation is maintained throughout the crystal.

At very low fields, the induced polarization is directly proportional to the electric field (Nalwa and Miyata 1997).

\[ P = \varepsilon_0 \chi E \]  

(1.1)
Where \( \chi \) is the linear susceptibility of the material, \( E \) 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.

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

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:

\[
P (-\omega_0) = \varepsilon_0 \left\{ \chi^{(1)} (-\omega_0; \omega_1) \cdot E (\omega_0) + \chi^{(2)} (-\omega_0; \omega_1, \omega_2) \cdot E \omega_1 \cdot \omega_2 + \chi^{(3)} (-\omega_0; \omega_1, \omega_2, \omega_3) \cdot E \omega_1 \cdot \omega_2 \cdot \omega_3 + \ldots \right\} \quad (1.3)
\]

Where \( \chi^{(2)}, \chi^{(3)} \ldots \) 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 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.
Table 1.1: Optical effects of nonlinear materials

<table>
<thead>
<tr>
<th>Order</th>
<th>Susceptibility</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 ($\omega + \omega = 2\omega$)</td>
<td>Frequency doubling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frequency mixing ($\omega_1 + \omega_2 = \omega_3$)</td>
<td>Optical parametric oscillators</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pockels effects ($\omega + 0 = \omega$)</td>
<td>Electro optical modulators</td>
</tr>
<tr>
<td>3</td>
<td>$\chi^{(3)}$</td>
<td>4 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 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.

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

$$2\omega_1 = \omega_2 \quad (\lambda_1 = 2 \lambda_2 ).$$

During this process, a polarization wave with the second harmonic frequency $2\omega_1$ is produced. The refractive index, $n_i$, is defined by the phase velocity and wavelength of the medium. The energy of the polarization 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 vectors of input beams and generated beam are to be matched.

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

(1.5)

Where \( \Delta K \) represents the phase-mismatching. The phase-mismatch can be obtained by angle tilting, temperature tilting 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, \( \eta \) can be expressed as

\[
\eta = PL^2(d_{\text{eff}} \sin(\Delta KL)/\Delta KL)^2
\]

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 is to be lower than the damage threshold of the crystal. Table 1.2 lists the laser and crystal parameters for selecting an NLO crystal.

**Table 1.2: Parameters for selecting an 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</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>
1.3.2 Nonlinear Optical Materials

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response and high damage threshold. But in addition to the processability, adaptability and interfacing with other materials improvements in nonlinear effects in devices, led the way to the study of new NLO effects and the introduction of new concepts. Optical solitons, optical switching and memory by NLO effects, which depend on light intensity, are expected to result in the realization of pivotal optical devices in optical fibre communication (OFC) and optical computing which make the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed.

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 materials
(iii) Improving the characteristics of NLO materials
Many organic and inorganic materials are highly polarizable and thus are good candidates for study. However, the net polarization of a material depends on its symmetric properties, with respect to the orientation of the impinging fields. It can be shown that the odd order terms in equation (1.2) are orientation independent, but the even terms vanish in a centrosymmetric environment. Thus materials for second order NLO must be orientationally noncentrosymmetric to be functional. No such restriction applies to third order materials.

1.3.2.1 General Requirements of NLO Crystals

The following properties are very important for a noncentrosymmetric crystal for device applications.

(i) High transparency in the entire visible region
(ii) Wide phase matching angle
(iii) Non hygroscopic nature
(iv) High mechanical and thermal stability
(v) High laser damage threshold
(vi) High NLO coefficient
(vii) Moderate birefringence
(viii) Low absorption and
(ix) Ease of device fabrication

1.3.2.2 Classification of NLO Crystals

Nonlinear optical crystals are broadly classified into (i) inorganic crystals, (ii) organic crystals and (iii) semi-organic crystals.
(i) Inorganic Crystals

Inorganic crystals are mostly ionic bonded. It is always easier to synthesize inorganic materials. Often these have high melting point and high degree of chemical inertness. High-temperature oxide materials are well studied for diverse applications like piezoelectricity, ferroelectricity and electro-optics. Some of the most useful crystals discovered are LiNbO$_3$, KNbO$_3$, Potassium Dihydrogen Phosphate (KDP) and its analogues, Potassium Titanyl Phosphate (KTP) and its analogues, β-Barium Borate. Potassium dihydrogen orthophosphate (abbreviated as KDP) is an excellent inorganic NLO material with different device applications. Single crystals of KDP and its isomorphs are representatives of hydrogen bonded materials which possess important piezoelectric, ferroelectric, electro-optic, mechanical and nonlinear optical properties (Shirsat et al 2008). KDP is a model system for nonlinear device application therefore it is used as a standard to characterize the nonlinear optical response of other crystal samples (Dhanaraj et al 2009). Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation at high efficiency in new regions of the spectrum inaccessible by other nonlinear crystals and conventional laser sources.

Growth and characterization of sulphamic acid single crystals, a nonlinear optical material is reported by Valluvan et al (2006). Feigelson (2006) has predicted the enhancement of optical transparency in GdGeAs$_2$ single crystals by controlling crystalline defects. A nonlinear optical crystal of calcium fluoroborate (Ca$_5$(BO$_3)_3$F) was grown by Guojun Chen et al (2006) using LiF as a flux. Transmission spectrum showed that the UV cut off wavelength for Ca$_5$(BO$_3)_3$F crystal was about 190 nm. Successful growth of new nonlinear LiKB$_4$O$_7$ single crystal was achieved by Adamiv et al (2006) using Czochralski technique. Centimeter-sized single crystals of Tl$_3$PbBr$_5$
were grown by Alban Ferrier et al (2006) using the Bridgeman-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.

Zhoubin Lin et al (2007) have found 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 noncentrosymmetric borate chlorides Ba$_2$TB$_4$O$_9$Cl (T=Al, Ga) have been determined by Jacques Barbier (2007). The second harmonic generation (SHG) 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.

The growth and characterization of a nonlinear inorganic crystal, alpha-lithium iodate is reported. The growth of single crystals of alpha-lithium iodate was accomplished by slow evaporation technique. The Kurtz Perry SHG test confirms the NLO property of the grown crystal and the relative efficiency is 0.78 times greater than KDP (Ashok Kumar et al 2010). Growth of negative solubility lithium sulphate monohydrate crystal by slow evaporation and Sankaranarayanan–Ramasamy method is reported by Boopathi et al (2012).

The growth of a new inorganic non-linear optical (NLO) borate crystal, tris lead tris barium borate (TLTBB) material has been reported by Prabha et al (2011). The second harmonic generation (SHG) efficiency of the sample is found to be nearly three times that of the standard KDP and its laser damage threshold value is 1.32 GW cm$^{-2}$. The growth of a new inorganic mixed borate of barium strontium borate (BSB) is reported by solution growth technique for the first time by
Prabha et al (2010). The NLO efficiency of the crystal is found to be 1.25 times higher than that of KDP crystal.

(ii) Organic Crystals

Organic NLO materials offer several advantages over inorganic NLO materials such as large nonlinear figure of merit, fast response times and their structural flexibility facilitates easy control of physical properties over very wide range. Aromatic benzenes and stilbenes contain electron donating and electron accepting groups with large nonlinear hyper-polarizabilities (Davydov et al 1970).

As second order nonlinear optical materials, a lot of organic compounds with polarized \( \pi \)-conjugation systems have been found to have potential to exceed inorganic compounds (Bosshard et al 1995). 4-dimethylamino-N-methyl-4-stilbazolium tosylate (DAST) is one of the potential nonlinear optical crystals among the organic materials. The second order nonlinear optical coefficient of DAST was reported to be 72 times larger than that of LiNbO\(_3\) (Sohma et al 1999) and exhibits SHG efficiency about 1000 times that of urea (Marder et al 1994).

Various efficient organic crystals include 3-methyl 4-nitro pyridine 1-oxide (POM) (Boomadevi et al 2004a), L-pyrrolidone-2-carboxylic acid (L-PCA) (Boomadevi and Dhanasekaran 2004b) etc.

Most of the organic NLO crystals are constituted by weak Vander Walls forces and hydrogen bonds with conjugated \( \pi \)-electrons. So they are soft in nature, difficult to polish and also have intense absorption in the UV region. Compared with inorganic materials, the major drawbacks of organic NLO materials are their moderate
environmental stability, low mechanical strength and a limited temperature range of operation.

The low temperature solution growth technique is widely used for the growth of organic compounds to get quality single crystals. Vijayan et al (2003) have grown p-hydroxy acetophenone (C₈H₆O₂), one of the potential organic NLO materials. It has been grown by slow evaporation technique. Cyrac Peter et al (2010) have grown L-Phenylalanine L-Phenylalaninium Nitrate, an active NLO crystal by slow evaporation technique and its SHG efficiency was found to be 1.7 times that of KDP. Ammonium maleate (AM) is an organic nonlinear optical material and it belongs to the noncentrosymmetric space group Cc (Anandha babu et al 2008). Nagaraja et al (1998) showed that benzoyl glycine (BG), an organic nonlinear crystal grown by slow evaporation from DMF 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 (2002) further extended the effort in synthesizing 4-methoxy benzaldehyde-N-methyl-4-stabazolium tosylate (MBST), which is a derivative of stilbazolium tosylate and a new material having high NLO property. The Kurtz powder SHG measurement on MBST showed that the peak intensity is 17 times more than that of urea.

L-arginine acetate (LAA) is an organic nonlinear optical material which has a wide optical transmission window between 220 nm and 1500 nm. Its laser damage threshold and SHG efficiency are comparable with that of KDP (Tanusri Pal and Tanusree Kar 2005). 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 (Ravindra et al 2006). Shaokang Gao et al (2006) have synthesized the N-4-nitrophenyl-N-methyl-2-aminoacetonitrile (NPAN) material and their single crystals of dimensions 36 x 8 x 8 mm$^3$ were harvested using 2-butanone as the solvent and crystal of size 21 x 15 x 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.

Ramachandran et al (2006) have employed photo acoustic 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 spectrum. An organic NLO material, 4-OCH$_3$-4'-nitrochalcone (MNC), has been synthesized and grown by Patil et al (2006) 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 characterized by proton nuclear magnetic resonance by Sethuraman et al (2006) and its second harmonic generation property was confirmed by Kurtz powder method. Vibrational spectral analysis of the nonlinear optical material, L-prolinium tartarate (LPT) was carried out using NIR-FT-Raman and FTIR spectroscopy by Padmaja et al (2006). Also the single crystals of LPT were grown by Martin Britto Dhas et al (2007) using submerged seed solution growth method.
Jagannathan et al (2007) 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 (2007). The laser damage threshold values of the SAA crystals are found to be 7.6 GW/cm² and 6.6 GW/cm² for single and multiple shots, respectively.

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 (Arivanandhan et al 2007). Recently, a new nonlinear optical organic single crystal, 4-phenylpyridinium hydrogen squarate (4PHS) has been grown and characterized by Ramachandra Raja et al (2008). 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 (Sethuraman et al 2007).

Bulk single crystal of L-arginine maleate dihydrate (LAMD) of size 48 x 33 x 7 mm³ was grown by slow cooling technique in a period of 3 weeks, whose SHG efficiency was found to be 1.4 times that of KDP crystal and investigated its physicochemical properties (Kalaiselvi et al 2008; Sun et al 2008). Single crystals of L-arginine trifluoroacetate (LATF) were grown by employing low temperature solution growth method and its thermal and nonlinear optical properties were studied (Sun et al 2007). L-nitroarginine and its salts show better nonlinear optical properties in comparison with L-arginine and its salts because of the presence of electron acceptor nitro group (NO₂) in addition to existing electron donor amino group (NH₂) (Apreyan et al 2007).
An organic second order nonlinear optical single crystal 2, 4, 5-trimethoxy-4’chlorochalcone was grown and characterized by powder X-ray diffraction and UV-Vis-NIR analysis. The second harmonic generation of this crystal was confirmed by using the Kurtz powder technique (Patil et al 2008). Single crystals of organic nonlinear optical (NLO) materials L-histidine nitrate and L-cysteine tartrate monohydrate were grown by submerged seed solution method (Martin Britto Dhas and Natarajan 2008). Bis glycine maleate, an NLO material is grown and studied by Balasubraminium et al (2010). An organic NLO active crystal 4 hydroxy-N-Methyl 4 stilbazolium besylate was synthesized and studied by Rutkis et al (2010). Anandha Babu et al (2010) have grown and studied the NLO active 2, 4, 4-tri methoxy benzophenone. Pure and deuterated L-alanine crystals have been grown by slow evaporation as well as slow cooling techniques (Suriya Kumar et al 2008).

Single crystals of the organic NLO material, benzaldehyde thiosemicarbazone (BTSC) monohydrate were grown by slow evaporation method by Santhakumar et al (2011). Second harmonic generation efficiency of the powdered BTSC monohydrate was tested using Nd:YAG laser and it is found to be ~5.3 times that of KDP. Organometallic NLO crystals of Bis (thiourea) cadmium formate (BTCF) were grown and studied by Ravi Kumar et al (2011). Significant wider optical transparency and lower cut off wavelength down to 290 nm makes it a promising material for NLO applications. A new organic crystal Dimethylammonium picrate was grown by Anandha Babu et al (2010) by slow evaporation method with dimensions 25 x 15 x 10 mm³ whose SHG efficiency was found to be 2.02 times that of KDP crystal.

A novel organic nonlinear optical crystal ninhydrin having good optical quality was grown by solution technique using aqueous solution (Uma Devi
et al 2009). Optical transmission studies confirm that ninhydrin is transparent in the entire visible region and the band gap energy is 2.5 eV. The Kurtz powder studies on the NLO property showed that the second harmonic generation efficiency is about 5 times that of KDP. A novel organic NLO material bis (2-amino pyridinium) maleate (B2AM) was synthesized and crystals were grown from aqueous solution (Dhanaraj et al 2010). The second harmonic conversion efficiency of B2AM was determined using the Kurtz and Perry powder technique. It was observed to be greater than that of KDP.

Synthesis and growth of N-Methyllutidone trihydrate (NM), an organic NLO single crystal, following the slow evaporation technique is reported by Dhanuskodi et al (2004). The powder SHG efficiency of NM is found to be 0.51 times that of urea. Growth and characterization of organic NLO crystal β-Naphthol have been reported by Janarthanan et al (2011). Tamilselvan et al (2011) have reported the growth and electrical properties of a new semi-organic NLO crystal of L-Asparaginium nitrate (LAsN) whose SHG efficiency is about two times that of the standard KDP.

Growth and characterization of organic NLO material meta nitro aniline (mNA) is reported by Thomas Joseph Prakash et al (2010). The SHG efficiency of mNA is higher than KDP. Growth, thermal and optical studies of a new organic NLO material L-methionine L-methioninium hydrogen maleate have been reported by Natarajan et al (2010). Its SHG efficiency was found to be about 90% of that of the standard KDP. Synthesis, crystal growth and characterization of nonlinear optical organic crystal, p-Toluidinium p-toluenesulphonate is reported by Vijayakumar et al (2012). Second harmonic conversion efficiency of p-TTS has been found to be 1.3 times higher than that of KDP.
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 crystal 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.

(iii) Semi-organic crystals

The widest search for new compounds and crystals led to the development of many amino acids based semi-organic single crystals. Semi-organic crystals are less hygroscopic compared to inorganic crystals and can be easily grown as single crystals compared to organic crystal. The advantage of semi-organic materials is that the crystals can be grown from aqueous solutions and they form three dimensional crystals which can be easily cut and polished (Min-hua Jiang and Qi Fang 1999). Now-a-days the organic and inorganic materials are being replaced by semi-organic materials because they share the properties of both organic and inorganic materials. Also the semi-organic materials show large nonlinearity, low angular sensitivity and good mechanical hardness (Velsko 1990; Warren 1990; Xing et al 1987).

Different organic and inorganic acids were introduced into L-alanine, L-arginine and L-hystidine and many new nonlinear optical materials were reported with a better NLO efficiency compared to inorganic KDP crystals (Aggarwal et al 2003). L-arginine phosphate monohydrate (LAP) is one of the potential nonlinear optical crystals among the amino acid based semi-organic materials. LAP crystals are usually grown from aqueous solution by temperature lowering technique. LAP crystals possess high nonlinearity, wide transmission range (220 nm - 1950 nm), high
conversion efficiency and high laser damage threshold (Monaco et al. 1987). Semi-organic NLO crystals involve the combination of a metal with an organic ligand. Metal-organic crystals form a new class of materials under semi-organics. Allyl thiourea cadmium chloride (ATCC) (Sun et al. 2003), Bis-glycine sodium nitrate (BGSN) (Sankar et al. 2007) are some examples of semi-organic crystals which are employed in devices. L-arginine diiodate, a new semi-organic nonlinear optical (NLO) crystals were grown by the slow evaporation and slow cooling methods with maximum size of $20 \times 10 \times 10 \text{ mm}^3$ and the crystals were characterized by single crystal XRD, FTIR, FT-Raman, TG-DTA, microhardness study and UV-Vis-NIR studies. NLO efficiency of this crystal is 1.3 times higher than that of the KDP crystal. Laser damage threshold studies revealed that the grown crystals possess high damage threshold values (Sankar et al. 2008). Semi-organic NLO crystals of L-Proline Cadmium Chloride Monohydrate (L-PCCM) were grown by slow evaporation solution growth technique at room temperature. Thermal study indicates that the L-PCCM crystal is thermally stable up to its melting point of 200 °C and is moderately softer substance (Thomas Joseph Prakash et al. 2008).

A semi-organic NLO material Bis glycine lithium molybdate (BGLM) crystal has been grown by slow evaporation technique by Balu et al. (2009). The SHG efficiency measured by the Kurtz powder test was about 1.3 times that of KDP. A semi-organic NLO single crystal L-argininium perchlorate was grown by slow solvent evaporation technique in a period of 15 days by Aruna et al. (2007). The SHG efficiency was found to be nearly 0.2 times that of urea. A new semi-organic nonlinear optical crystal, Bis thiourea zinc acetate (BTZA) has been grown and characterized by Kannan et al. (2004). The SHG efficiency was better than that of KDP. Single crystal of Bis glycine hydrogen chloride (BGHC), a semi-organic
nonlinear optical (NLO) material, has been grown by slow solvent evaporation technique by Ambujam et al (2006). The SHG efficiency in the BGHC crystal was evaluated by the Kurtz and Perry powder technique and it was found to be 5.6 times that of KDP.

Glycine lithium sulphate (GLS) single crystals of size 12 x 6 x 4 mm$^3$ have been grown by slow evaporation technique at ambient temperature from aqueous solution of glycine and lithium sulphate by Suresh Kumar et al (2007). The GLS crystallizes in noncentrosymmetric structure which is an essential criterion for second harmonic generation. The second harmonic conversion efficiency of GLS was determined using Kurtz and Perry technique and was found to be two times greater than that of KDP.

A new semi-organic NLO single crystal tris glycine zinc chloride (TGZC) has been grown by slow cooling technique (Sugandhi et al 2010). Its SHG efficiency was found to be 0.75 times that of the standard KDP. Single crystals of semi-organic materials tris glycine calcium dibromide (TGCB) were grown from aqueous solution by Dhanaraj et al 2010. The second harmonic conversion efficiency of TGCB was determined using the Kurtz and Perry powder technique and it was found to be greater than that of KDP.

Good optical quality single crystal of L-histidine hydrochloride monohydrate (LHC) a novel semi-organic NLO material was grown by slow solvent evaporation technique and characterized by Madhavan et al (2007). The SHG efficiency is found to be higher than that of KDP crystal. A semi-organic nonlinear optical single crystal of cadmium thiosemicarbazide bromide (CTSB) has been grown from solution growth
method by slow evaporation technique at room temperature by Maadeswaran et al (2009). The result shows that SHG conversion efficiency is 1.9 times that of KDP.

Single crystals of semi-organic materials Glycine Sodium Nitrate (GSN) with very high degree of transparency were grown from aqueous solution by slow evaporation technique by Suresh et al (2010). The result obtained for GSN shows the SHG efficiency is about 2 times that of KDP crystal. A semi-organic nonlinear optical material, L-lysine L-lysinium dichloride nitrate was synthesized at room temperature and it was grown by slow cooling solution growth technique (Vasudevan et al 2011). The SHG efficiency of the L-LLDN crystal is about 1.06 times that of the standard KDP crystal.

A new semi-organic nonlinear optical bis (thiourea) cadmium zinc chloride (BTCZC) crystal was synthesized by Kirubavathi et al (2008). The crystals were grown from aqueous solution by the slow evaporation technique. The crystals were thermally stable up to 201 °C. Zinc Tris-Thiourea Sulphate (ZTS) is one of the semi-organic nonlinear materials for type II second harmonic generation (SHG). It has a high damage resistance and a low UV cut off wavelength of about 260 nm and hence is useful for frequency conversion of high power lasers. SHG relative efficiency of ZTS has been found to be about 1.2 times that of KDP (Krishnan et al 2009).

Single crystals of new semi-organic nonlinear optical zinc guanidinium sulphate have been grown from solution by slow evaporation technique. The nonlinear optical property of the grown crystal was confirmed by Kurtz-Perry powder technique (Siva Sankar et al 2009). Growth and characterization of tetramethyl ammonium tetrachlorozincate (II) whose SHG efficiency is 1.3 times that of KDP,
have been reported by Devashankar et al (2009). Karthick et al (2009) have reported
the synthesis, growth and characterization of semi-organic nonlinear optical bis
(thiourea) antimony tribromide (BTAB) single crystals. Lydia Caroline et al (2009)
have reported the growth and characterization of pure and Cd$^{2+}$ doped bis (thiourea)
zinc acetate (BTZA). Krishnan et al (2009) have reported the growth and
characterization of pure and potassium iodide doped zinc tris (thiourea) sulphate
(ZTS) single crystals. A novel organometallic nonlinear optical crystal, namely,
thiourea complex of tetrakisthiourea iodide (TTPI) has been grown by slow
SHG efficiency of TTPI was found to be higher than that of KDP. It is a potential
material for frequency conversion.

Uma Devi et al (2010) have reported the synthesis, growth and
characterization of a semi-organic nonlinear optical L-Cystine Dihydrochloride single
crystal whose SHG efficiency is 0.35 times that of KDP. Crystal growth and
characterization of semi-organic nonlinear optical single crystals L-histidine
hydrochloride monohydrate have been reported by Anandan et al (2012).

1.4 REVIEW ON L-ALANINE DERIVATIVE CRYSTALS

An interesting class of materials receiving wider attention in recent past
includes, the analogues of amino acids like L-alanine, L-arginine, L-histidine etc.
Among organic crystals of NLO applications, amino acids display specific features of
interest such as (i) molecular chirality which secures acentric crystallographic
structures, (ii) absence of strongly conjugated bonds leading to high transparency
ranges in the visible and UV spectral regions and (iii) zwitterionic nature of the
molecule which favours crystal hardness. Further, amino acids can be used as the base for synthesizing organic-inorganic compounds.

An organic electro-optic and nonlinear optical (NLO) crystal, L-alaninium oxalate (LAO), was grown and its physicochemical properties were studied by Dhanuskodi et al (2004), Arun et al (2009) then by Vimalan et al (2007). L-alanine oxalate crystal was grown and its structure was solved by Subha Nandhini et al (2001).

A new nonlinear optical organic single crystal L-alaninium fumarate (LAF) belonging to the amino acid group was grown from aqueous solution by employing slow evaporation solution technique (SEST) by Ramachandra Raja et al (2009). It was observed that LAF crystal was conveniently transparent in the region from 300 nm to 1100 nm. Its SHG efficiency is comparable with that of KDP.

Good optical quality bulk single crystals of NLO material L-alanine formate were grown successfully by modified Sankaranarayanan-Ramasamy (SR) method and characterized by Justin Raj et al (2008). The SHG efficiency was found to be 0.75 times that of KDP crystal. The nonlinearity, transparency, wide band gap, high mechanical strength, low dielectric constant and loss confirms that L-AlFo crystals are considered to be a potential candidate for the fabrication of SHG and optoelectronic devices.

L-alanine alaninium nitrate (LAAN), an organic nonlinear optical material was grown by slow evaporation technique at room temperature from aqueous solution at pH value of 2.5 by Lydia Caroline et al (2008). Transmittance spectrum of LAAN crystal reveals that the crystal has a low UV cut off wavelength of 320 nm and has good transmittance in the entire visible region. The FTIR spectrum confirmed the
protonation of the amino group and the presence of NO₃⁻ in the compound. The TG-DTA studies establish that the compound undergoes no phase transition and is stable up to its melting point (ie) 149 °C. A comparative study on the properties of L-alanine (LA) and LANN crystals has been made and discussed by Aravindan et al (2008). The relative SHG efficiency of LAAN crystal was found to be 7.01 times higher than that of KDP and 1.3 times lesser than that of urea and 12.89 times greater than its parent material (L-alanine).

L-alanine Cadmium Chloride (LACC), a semi organic nonlinear optical material has been synthesized by Dhanuskodi et al (2007). The LACC single crystals were grown from an aqueous solution by solvent evaporation technique. The TG-DTA studies establish that the compound undergoes no phase transition and is stable up to its melting point (ie) 110 °C. Powder SHG study shows that LACC is 1.5 times efficient than KDP. Its optical transparency goes down to 200 nm comparable to the typical borate crystals like potassium pentaborate.

New nonlinear optical material, L-alanine acetate (L-AlAc) single crystals have been grown by slow cooling method by Mohan Kumar et al (2005). The grown crystals were subjected to various characterization studies such as chemical etching, dielectric measurement, Vickers microhardness analysis, UV-visible spectral analysis and powder SHG test. Etching studies were carried out on the {011} face of L-alanine acetate crystal using water as etchant. Triangular etch pits were observed when L-AlAc single crystal was etched with water for 5 sec. There was no change in etch pits with varying etching time (10 sec – 20 sec). The morphology of L-AlAc is similar to that of pure L-alanine with slight elongation along the c-axis. FTIR analysis indicates protonation of alanine carboxyl group by acetic acid. The dielectric constant gradually increases at low frequency and becomes constant with a further increase in
frequency. The increase in frequency is attributed to the space charge distribution. SHG studies reveal that L-AlAc crystal is a promising candidate for NLO application.

Single crystal of L-alaninium maleate (LAM), an organic nonlinear material has been successfully grown by slow evaporation technique and characterized (Vasantha et al 2004; Natarajan et al 2006; Vimalan et al 2010). The powder SHG efficiency analysis reveals that the efficiency of this material is about 1.1 times that of KDP. A comparative study was made by Urit et al (2010) on L-alaninium maleate (LAM) single crystal grown by slow evaporation technique and by SR method.

An organic nonlinear optical material, L-alanine maleate (LALM) was synthesized by Balasubramanian et al (2009). Bulk single crystals of LALM have been grown by slow cooling method with a solution of pH value 5. Etching studies were carried out for LALM crystal using various etchants. Mechanical behaviour of grown crystal was studied on {011} using mirohardness measurements and the hardness values are found to be comparable with pure L-alanine. TG-DTA studies reveal that the material starts decomposing at 162.2 °C. The UV-Vis spectrum establishes the good transmittance window and the lower cut off wavelength are found to be as low as 320 nm, allowing for frequency conversion down to UV-region. From the Kurtz-Perry powder technique, the second harmonic generation efficiency of the grown LALM crystal was found to be 1.2 times that of KDP crystal.

A new and efficient semi-organic nonlinear optical crystal (NLO) from the amino acid family L-alanine lithium chloride (LAL) has been grown by slow evaporation technique from aqueous solution by Redrothu Hanumantharao et al (2012). The relative SHG efficiency is measured by Kurtz and Perry method and
found to be about 0.43 times that of standard potassium dihydrogen phosphate (KDP) crystals.

A novel organic nonlinear optical (NLO) material, L-alaninium succinate (LAS) was synthesized by standard method by Ramachandra Raja et al (2009). Single crystals were grown by slow evaporation technique using water as solvent. The grown crystals were characterized by FTIR, FT-NMR, UV-Vis-NMR techniques. The SHG efficiency was determined as 23% of that of standard KDP. Functional groups present in the crystal and production of NH$_3^+$ ion are studied by FT-IR spectrum. The optical absorption studies confirm that the crystals have very good transmission in the entire visible region, with lower UV cut off wavelength around 190 nm, which is an essential consideration for NLO crystals. The chemical structure of L-alaninium succinate was established by $^1$H- and $^{13}$C NMR studies.

Optical quality crystals of semi-organic L-alanine terafluoroborate (L-AIFB) have been grown from aqueous solution by slow evaporation method (Rajan Babu et al 2002). Well-defined etch pits were observed on the {001} plane of the crystal. The grown crystals possess higher optical transmittance than those of other semi-organic NLO crystals. The output radiation for L-AIFB in Kurtz powder technique shows a higher output power than that of L-alanine, which confirms higher SHG efficiency. The enhancement of transmittance and NLO properties of the grown L-AIFB crystal proves it to be a potential material for SHG device applications.

A new nonlinear optical material, thiourea L-alanine acetate (TLAA), has been synthesized, grown and characterized. Single crystals of TLAA have been grown by slow evaporation method (Neelam Singh et al 2008). The structure analysis reveals that it belongs to the orthorhombic crystallographic system with space group P2$_1$2$_1$2$_1$. 
Optical transparency of the grown crystals was investigated by UV-Vis-NIR spectrum. The lower optical cut off wavelength for this crystal was observed at 300 nm and energy band gap is 3.74 eV. TG and DTA have been performed to show that TLAA is thermally stable up to 206.22 °C. Capacitance and dielectric loss measurements were carried out and the dielectric constant was calculated at room temperature in the frequency range 100 Hz – 2 MHz. The dielectric constant has a high value of 190.92 at 100 Hz and decreases to 54.69 at 2 MHz.

Jaikumar et al (2009) discussed in detail the growth of single crystals of L-alanine DL-malic acid from aqueous solution by slow cooling technique. Structural, optical, thermal and mechanical properties of the crystals have been analyzed. Single crystal XRD reveals the structure of the crystal to be orthorhombic. The HRXRD study shows the crystalline perfection of the grown crystal to be reasonably good. The presence of functional groups has been confirmed by FTIR analysis. The grown LADLMA crystal is found to be thermally stable up to 224 °C. Kurtz powder SHG test confirms the frequency doubling of the grown crystal and its efficiency is nearly equal to that of KDP. Hence LADLMA can act as a promising material for NLO applications and it can also possibly be used for the fabrication of electro-optic devices. From the Knoop hardness test the Young’s modulus of the grown crystal is calculated to be 0.7018 x 10¹⁰ Nm⁻².

A new organic nonlinear optical crystal L-alaninium tartrate (LAT) has been grown by slow evaporation method at room temperature by Vimalan et al (2010). Single crystal X-ray diffraction studies reveal that the crystal has monoclinic structure with space group P2₁. From FT-IR spectrum, the CH vibrations of tartaric acid generate peaks at 2977 cm⁻¹ and 2960 cm⁻¹. The thermal studies indicate that the grown LAT is stable up to 118 °C. Photoconductivity studies of LAT reveal its
negative photoconducting nature. The second harmonic generation efficiency of LAT
crystal is found to be 174 mV. The laser damage threshold is found to be
8.16 GW/cm².

Recep Biyik (2009) has reported EPR and Optical absorption studies of VO²⁺
doped L-alanine single crystals. Two new L-alanine compounds (alanine alaninium
triiodide and alanine SrCl₂.3H₂O) have been grown and characterized by X-ray
single crystal analysis by Michel et al (2008). Growth and characterization of pure
and lithium doped L-alanine single crystals for NLO devices are reported by
Suresh Kumar et al 2008.

1.5 REVIEW ON UREA DERIVATIVE CRYSTALS

Urea has been used in optical parametric oscillators to generate tunable
radiation throughout the visible region but intrinsic absorption and phase matchability
considerations make it unsuitable for wavelengths longer than 1000 nm (Rosker and
and mechanically harder than the crystal of the parent components. It is quite
transparent almost in the entire UV region and hence it can be used for producing
green/blue laser light. Lin et al (2002) have synthesized two components urea-mNBA
systems and urea-L-malic acid systems with different urea compositions.

Meng et al (1997) described a method, organic inclusion complex, to design
materials without center of inversion for application in quadratic nonlinear optics in
the ultraviolet region. The characterization of linear and nonlinear properties of such
an inclusion complex crystals, urea-(d) tartaric acid (UDT), were also presented by
them.
The crystallographic and thermal properties including thermal expansion coefficients and specific heat as well as differential scanning calorimetry (DSC), thermogravimetric analysis (TG) curves for a single crystal of a new organic nonlinear optical material, urea-(d) tartaric acid (UDT) were reported by Meng et al (1998). The second harmonic generation (SHG) of UDT, based on powder measurement, is three times higher than that of KDP. Its transparency range is from 240 nm to 1395 nm.

A new nonlinear optical organic crystal, viz. Urea L-malic acid, has been grown from aqueous solution employing the techniques of solvent evaporation and slow cooling by Dixit et al (2003). The grown crystals were subjected to various studies. Preliminary measurements indicate that the second harmonic generation efficiency at a fundamental wavelength of 1064 nm is roughly three times that of KDP.

Uma Devi et al (2009) have synthesized, grown and characterized Urea Ninhydrin monohydrate single crystal for the first time from aqueous solution employing slow evaporation method. Preliminary z-scan measurement indicates that nonlinear refractive index of this crystal is $-4.1 \times 10^{-8}$ cm$^2$/W.

Krishnan et al (2008c) have reported growth and characterization of novel ferroelectric urea succinic acid single crystals. A new second order nonlinear optical organic crystal Urea L-threonine has been grown from aqueous solution by slow cooling technique by Jaikumar et al (2008). The second order nonlinear optical property was examined by Kurtz-Perry powder technique and found that the second harmonic generation efficiency is 1.2 times that of KDP at wavelength 1064 nm.
1.6 OBJECTIVES OF THE PRESENT WORK

The search and design of low $\varepsilon_r$ crystals are extremely important for microelectronics industry. Organic and semi-organic NLO crystals formed with L-alanine and urea have been identified as potential candidates for replacing KDP in nonlinear optical applications. Pure and doped L-alanine hydrogen chloride monohydrate, inorganic acids and salts admixed L-alanine crystals and urea based single crystals are promising NLO materials for device fabrication. Keeping this in view, attempts have been made to grow and study various properties of L-alanine based and urea based single crystals.

The objectives of the present investigation are

(i) Synthesizing the chosen materials for the growth of single crystals.
(ii) Determining the solubilities of the materials.
(iii) Growing single crystals by employing slow evaporation solution growth technique at ambient temperature.
(iv) Identifying the crystals structure by single crystal and powder X-ray diffraction analysis.
(v) Measuring density of all the grown crystals by floatation method.
(vi) Performing the energy dispersive analysis of X-rays (EDAX) to determine the chemical composition.
(vii) Finding the functional groups present in the grown crystals by Fourier Transform Infrared (FTIR) spectral analysis.
(viii) Studying the transmittance behaviour of the crystals by UV-visible transmission spectral analysis.
Confirming the nonlinear optical (NLO) property of the grown crystals by Kurtz – Perry powder technique.

Determining the hardness number and work hardening coefficient of the grown crystals by Vickers microhardness measurement.

Measuring the dielectric constant, dielectric loss and AC conductivity of the grown crystals by the parallel plate capacitor method using LCR meter.

Carrying out thermogravimetric and differential thermal analysis (TG/DTA) to investigate the thermal stability of the crystals.

1.7 SCOPE OF THE THESIS

In this thesis the first chapter deals with general introduction, a brief review of various studies made on L-alanine and urea based single crystals in the recent past, objectives of the present investigation and scope of the present work. The second chapter explains the experimental details for different growth methods and characterization techniques. Growth and studies on various properties of undoped and doped L-alanine Hydrogen Chloride (LAHC) monohydrate single crystals are covered in the third chapter. The fourth chapter provides growth and characterization of L-alanine single crystals admixed with alkali halides NaCl and NaI. The fifth chapter gives growth and studies of phosphoric acid admixed L-alanine single crystals. Growth and characterization of ZnSO₄ admixed L-alanine single crystals are reported in the sixth chapter. The seventh chapter provides growth and characterization of L-alanine single crystals admixed with LiCl and BaCl₂. The eighth chapter contains growth and studies of novel urea based NLO crystals – Urea Glycine (UG) and Urea Lithium Sulphate (ULS). The summary and conclusions derived out of the present study along with the scope for future work in the same area of research are presented in the ninth chapter. Finally the references cited are listed in
the bibliography. The resume of the candidate, list of publications and list of seminars/conferences attended/presented papers are provided in the Appendixes section. The mentioned twelve objectives are actualized by the various studies and the reports of them are provided in this thesis.