CHAPTER 2

AN OVERVIEW ON NON-LINEAR OPTICS AND NONLINEAR OPTICAL MATERIALS

2.1 INTRODUCTION

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 are commonly used to
produce green light (532 nm) from, for example, a 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).

2.2 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). 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 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 non-linear. The electrons are jerked back roughly rather than pulled back smoothly and they oscillate at frequencies other than the driving frequency of the light wave. These electrons radiate at the new frequencies, generating the new wavelength of light. 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.

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 Non-linear 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 noncentro-symmetric 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 non-linear 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 non-linear optical materials is very largely a crystal growing effort. It is realized that the requirements on optical quality for a useful non-linear 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 non-linearity, 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, non-linear absorption and brittleness index for lifetime and system capability.
2.3 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 the relationship between irradiance 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).

\[ P = \varepsilon_0 \chi E \]  
(2.1)

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.

\[ P = \varepsilon_0 \{ \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \ldots \} \]  
(2.2)
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:

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

(2.3)

**Figure 2.1** Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points.

**Figure 2.2** Two photons are welded together to produce a single photon with the energy of both original photons.
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 noncentro-symmetric 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 2.1.

**Table 2.1 Optical effects of nonlinear materials**

<table>
<thead>
<tr>
<th>Order</th>
<th>Crystal</th>
<th>Effects</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>$\chi^{(1)}$</td>
<td>Refraction</td>
<td>Optical fibers</td>
</tr>
</tbody>
</table>
| 2.    | $\chi^{(2)}$ | SGH ($\omega + \omega = 2\omega$)  
Frequency mixing ($\omega_1 \pm \omega_2 = \omega_3$)  
Pockels effects ($\omega + 0 = \omega$) | Frequency doubling  
Optical parametric oscillators  
Electro optical modulators |
| 3.    | $\chi^{(3)}$ | 4 wave mixing phase gratings  
Kerr effect  
Optical amplitude | Raman Coherent spectroscopy  
Real time holography  
Ultra high speed optical gates  
Amplifiers, choppers etc, |

If the molecule or crystal is centro-symmetric then $\chi^{(2)} = 0$. If a field $+E$ is applied to the molecule (or medium), equation 2.3 predicts that the polarization induced by the first nonlinear term is predicted to be $+E^2$, yet if
the medium is centro-symmetric the polarization should be \(-E^2\). This contradiction can only be resolved if \(\chi^{(2)} = 0\) in centro-symmetric 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 centro-symmetric media. In second harmonic generation, the two input wavelengths are the same

\[
2\omega_1 = \omega_2 \text{ (or) } (\lambda_1 = 2\lambda_2).
\]  

(2.4)

During this process, a polarization wave with 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 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 are to be matched.

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

(2.5)

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, \(\eta\) 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 a NLO crystal.

**Table 2.2 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</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>

**2.4 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. The goal is to find and develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, high damage threshold but also processability, adaptability and interfacing with other 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
(iii) Improving the characteristics of NLO crystals

On the basis of the three types of cohesive forces that bind the charges and polarization together, the NLO materials can be classified into the following cases: ionic crystals, which essentially consist of oxygen-polyhedra based solids, Covalent crystals essentially dealing with semiconductors and molecular crystals that with organic materials, disordered and amorphous solids, in particular glasses and polymers and composites and inhomogeneous artificial solids.

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 symmetry properties, with respect to the orientation of the impinging fields. It can be shown that the odd order terms in equation (2.2)
are orientation independent, but the even terms vanish in a centro symmetric environment. Thus materials for second order NLO must be orientationally noncentrosymmetric to be functional. No such restriction applies to third order materials.

2.4.1 NLO Polymers Materials

The widespread use of fiber optics in today’s communications transmission systems is the first stage in a revolution of data processing and communications technologies based on optics rather than electronics. Current systems are expected to soon be drastically redesigned to include faster optical and hybrid optical/electrical components. Basic research into the properties of the materials as well as applied research into the optimal use of these materials is greatly needed and is an important part of the activities for photon induced processes. NLO polymeric and liquid crystalline materials have been identified as strong candidates for emerging photonic data processing technologies. These materials consist in general of molecular fragments displaying NLO activity, or highly coloured chromophores, dissolved in or covalently attached to a polymeric host material. NLO polymers/liquid crystals possess vast potential for use in a variety of photonic systems, including high-speed optical modulators, ultra-fast optical switches, and high-density optical data storage media. These devices are essential for continued advancement in the effort to transform information storage and transmission from the electrical to the optical regime. The promise of NLO polymers lies in their fortuitous combination of exceptional optical qualities, low cost, and ease of fabrication into device structures. These technologically favorable characteristics have led to considerable research into the development of NLO polymers for commercial applications. A material suitable for widespread industrial use has yet to be synthesized, however. One of the most interesting and technologically promising phenomena applicable
to some of these materials is the light-induced modulation of the index of refraction of the material through the photorefractive effect. Photorefractive materials combine photoconductivity and the electro-optic effect. Photorefractive nonlinear optics is by far the most efficient technique for causing beams of light to interact. Holograms can be written and erased in photorefractive media with low power lasers, and the intrinsic phase shift in the holographic grating can lead to energy exchange between the writing beams. With the growing use of fiber optics and optical communications technologies, photorefractive materials have become prime candidates for all-optical data processing applications. They are expected to be used for high density optical data storage, associative image processing techniques including dynamic holography and image amplification, spatial light modulation, programmable interconnections in integrated optics and simulations of neural networks and associative memories with parallel signal processing. Polymers and liquid crystals have emerged in recent years as exceptional candidates for photo-refraction but much work in material development and characterization remains to be done.

2.4.2 Thin Film NLO Materials

The optical signal processing appears to be better in a number of ways. The signal carried by light is superior, in a certain sense, to that carried by an electric current. Electrons, which move in an electric circuit, are tiny charged particles, and as such they are attracted and repelled by other charges. Light also needs much less power to be transmitted through optical fiber lines, than electrical current does for transmission through coaxial lines. Light is a much ‘finer’ carrier that interacts very little with an appropriate transmission environment. Consequently, it is much less attenuated and distorted during transmission. This fact has been realized a while ago, and most of the communication nowadays relies on fiber optics. Optical data storage had an
impressive take-off with CDs, however, there is still a noticeable gap in data processing, mostly due to the lack of reliable electro-optic devices. Many types of signals are genuinely optical, like in photo and video cameras, binoculars, photocopiers, spectrometers and overhead projectors. Optical processing seems only natural for these signals. Now the interest lies in thin-film NLO materials to be able to meet the huge demand in the years to come with the onset of IOCs as an alternative to silicon chips. The important premier NLO materials, like KTiOPO4 (KTP), RbTiOPO4 (RTP) and their derivatives have excellent chemical stability, ease of obtaining in crystalline form, wide working ranges of wavelength and temperature, high optical damage threshold and conversion efficiency ability to take the output of a number of widely used solid state lasers such as Nd:YAG and InGaAs.

2.4.3 Single Crystals for EO, AO and Nonlinear Applications

KDP(KH₂PO₄), DKDP(KD₂PO₄), ADP(NH₄H₂PO₄), lithium iodate BBO, LBO, CLBO, KTP, KTA, KB₅, tellurium dioxide, lead molybdate, silver thiogallate and silver selenogallate, zinc germanium phosphide, gallium selenide, BGO, BSO, LNB, LTA lithium tetraborate, barium nitrate. KDP, DKDP and ADP are widely used as the second, third and fourth harmonic generators for Nd:YAG and Nd:YLF lasers. Crystals are also widely used for electro-optical applications such as Q- switches for Nd:YAG, Nd:YLF, Ti:sapphire and alexandrite lasers and as well as for Pockel’s cells. The most commonly used electrooptical crystal is DKDP with deuterium more than 98%. These crystals are grown by a solution growth method and can be grown into very large sizes. Therefore, these crystals are available as low-cost and large-size, finished nonlinear components. For frequency doubling (SHG) and tripling (THG) of Nd:YAG laser at 1064 nm, both type I and type II phase-matchings can be employed for KDP and DKDP. For frequency quadrupling (4HG, output at 266 nm) of Nd:YAG laser KDP crystal is normally used.
2.4.4 Organic NLO Crystals

Conjugated DA substituted organic molecules exhibit measurable NLO and electro-optical effects. Such materials can be used to double or triple the frequency of laser light and are of considerable interest for the high-speed processing of data, which is essential for numerous modern technologies like optical computing and optical telecommunication systems. Some major applications are optical data storage, optical information processing, electro-optic switching and all-optic switching. Generally DA substituted compounds, where D and A are separated by an aromatic spacer group, represents the basis for all organic NLO compounds.

The optical nonlinearity of organic molecules can be enhanced by adding strong electron donating and withdrawing entities as well as optimizing the distance between D and A. This generates a highly polarizable charge transfer compound with an asymmetric electron distribution. Optical storage and optical processing applications span interests from photochromics through spectral hole-burning materials, and to a particularly new class of materials called photorefractive polymers, where the light-induced generation of mobile charges, transport, and trapping are combined with second-order optical nonlinearity in a polymeric composite to form dynamic holograms. Charge separation produces internal electric fields, which locally alter the refractive index through the second-order optical nonlinearity. Polymer photorefractives are expected to be cheaper, easier to modify, and easier to fabricate into novel geometries than inorganic crystals. Both the polarizability anisotropy and the hyperpolarizability of the nonlinear chromophores are essential for the creation of strong holograms. The rationalization, computation, and prediction of NLO properties is thus a major field of interest in the research field of organic, physical, and theoretical chemistry as well as for the materials scientist. In spite of theoretical efforts, there is still no
reliable way to predict first or even second order hyperpolarizabilities of organic DA compounds. There is great demand for non centrosymmetric molecular crystals with large second order nonlinearities and with wide transparency range between the highest vibrational and lowest electronic transitions. The latter requirement is very restrictive regarding organic molecules and excludes the majority of them for further consideration in nonlinear optics. Among the remaining ones a large proportion is also excluded because they cannot form stable noncentrosymmetric crystals. This is mainly because asymmetric molecules most frequently carry a dipole moment in their ground electronic state and in order to reduce the dipole-dipole interaction, which is dominant over the van der Waals in the lattice, a head to tail antiparallel configuration will be favored when forming the crystal most frequently resulting in centrosymmetric crystalline structures and consequently vanishing $\chi^2 E$ unless certain precautions are taken to prevent this from happening.

Recently organic compounds with delocalized conjugated p-electrons have gained much attention because of their large NLO properties and quick response. Organometallic and coordination complexes materials exhibit novel NLO behavior. Second order NLO materials have the ability to double the frequency of incident light and have important commercial applications. Typical NLO molecules must have a dipole and be polarizable. In practice conjugated molecules with donor and acceptor groups on opposite ends of a conjugated chain are often used. Second order NLO materials must also have the correct alignment of molecules in the solid state. This is necessary to
avoid having the individual molecular dipoles pairing up and effectively canceling each other out. Amino acid crystals such as L-threonine, L-alanine, L-phenylalanine, L-arginine have been grown by slow evaporation and temperature lowering methods from aqueous solution and reported (Ramesh Kumar et al 2004, Razetti et al 2002, Mahalakshmi et al 2006, Tapati Malik et al 2005). Optical properties of L-alanine single crystals was reported by Misoguti et al (1996). Also Banfi et al (2001) have grown high optical quality organic crystal N-(4-nitrophenyl)-L-prolinol (NPP) in methanol solution starting from toluene nucleated seeds. Also several people reported good quality organic NLO materials such as 3-methyl 4-nitropyridine 1-oxide (POM), γ-glycine, 4-methoxybenzaldehyde-N-methyl-4-stilbazolium tosylate (MBST), 4-dimethyl-4-stilbazolium tosylate (DAST), L-lysine monohydrochloride dehydrate (L-LMHCL), 2-amino-5-chlorobenzophenone (2A-5CB) and L-alaninium maleate Boomadevi et al 2004, Ambujam et al 2006, Lakshmana Perumal et al 2002, Shunichi et al 1999, Ramesh Babu et al 2006, Ramesh Babu et al 2004, Martin Britto Das et al 2007).

2.4.5 Inorganic NLO Materials

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. The search for new and efficient materials in which to carry out nonlinear optical processes has been very active since SHG was first observed in single crystal quartz by Franken and co-workers in 1961. In the beginning, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO₃), and its analogues, potassium titanyl phosphate (KTP) and its analogues, Beta Barium Borate (Dewey et al 1975) and semiconductors such as cadmium sulfide, selenium, and tellurium. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric
generators to provide coherent laser radiation with high frequency conversion efficiency in the new region of the spectrum inaccessible by other nonlinear crystal conventional sources. After that various borate crystals including \( \beta\)-BaB\(_2\)O\(_4\) (BBO), LiB\(_3\)O\(_5\) (LBO), Sr\(_2\)B\(_2\)Be\(_2\)O\(_7\) (SBBO), BiB\(_3\)O\(_6\) (BiBO) and the latest Ca\(_4\)LnO (BO\(_3\))\(_3\) (CLnOB, where Ln = Gd, La, Y) have been reported as promising NLO crystals. In the last few years, newly developed nonlinear optical (NLO) crystals GdCa\(_4\)O(BO\(_3\))\(_3\) (GdCOB) and YCa\(_4\)O(BO\(_3\))\(_3\) (YCOB) have attracted much attention due to their promising optical properties (Iwai et al 1997). The family of various borate crystals thus plays a very important role in the field of nonlinear optics (Becker 1998).

The following parameters are critically important for NLO crystal: (i) nonlinear optical coefficients \( X_{ijk} \), (ii) birefringence, (iii) absorption edge on the UV side for the UV and VUV crystals, (iv) damage threshold, (v) optical homogeneity and (vi) physico-chemical stability and mechanical properties. Inorganic crystals are ionic bonded, it is always easier to synthesize inorganic materials. However, inorganic crystals face a ‘trade-off’ problem between response time and magnitude of optical nonlinearity. High temperature oxide materials are studied for device application like piezoelectric, ferroelectric and electro-optics.

2.4.6 Semiorganic NLO Single Crystals

Presently, inorganic and organic materials are being replaced by semi-organics. They share the properties of both organic and inorganic materials. Recent interest is concentrated on metal complexes of organic compounds owing to their large non-linearity (Newman et al 1990). 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 (Velsko 1990, Warren 1990, Xing et al 1987). The $\pi$ conjugated network, in organic system with large nonlinearity, has significant absorption in the visible region. Hence for the Second Harmonic Generation (SHG) in the blue – near – UV region, more transparent and less extensively delocalized organics like urea or its analogs have been considered (Newman et al 1990).

Another interesting class of semiorganic crystals, which receive wider attention in the recent past includes, the analogs of L-arginine, L-histidine, L-alanine, L-proline, L-phenylalanine etc. Among organic crystals of NLO applications, amino acids display specific features of interest (Nicoud et al 1987) 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) zwitter-ionic nature of the molecule, which favours crystal hardness. Further amino acids can be used as a basis for synthesizing organic-inorganic compounds like L-arginine phosphate and its derivatives. L-arginine phosphate monohydrate (LAP) is a potential nonlinear optical (NLO) material first introduced by Chinese in 1983 (Xu et al 1983).

LAP crystals are usually grown from aqueous solution by the temperature lowering technique. LAP crystals possess high nonlinearity, wide transmission range (220–1950 nm), high conversion efficiency (38.9%) and high damage threshold (Monaco et al 1987). Yokotani et al (1990) have reported the synthesis and growth of deuterated LAP (DLAP) crystal with a higher harmonic generation (Sasaki et al 1989). Monaco et al (1987) synthesized LAP and its chemical analogs from the strongly basic amino acid and various other acids. All the compounds in this class contain an optically
active carbon atom, and therefore all of them form acentric crystals. All the crystals were optically biaxial and among them several gave second harmonic signals greater than quartz.

Petrosyan et al (2000) reported a special class of compounds having the Arg-2Ax composition (Ax is one of several inorganic or organic acids). Such compounds (Arg-2H$_3$PO$_4$, Arg-2HF, Arg-2HCl·H$_2$O, and Arg-2HBr·H$_2$O) have been synthesized and single crystals were grown. Later crystal structure and characterization studies were carried by Petrosyan et al (2005) on salts of arginine with chloric (HClO$_3$) and bromic (HBrO$_3$) acids. L-arginine dihydrogen phosphate (LADP), another analog of LAP was grown by slow solvent evaporation technique. Owing to its good transparency, chemical stability, dipolar strength, L-arginine diphosphate seems to be a promising material for NLO applications (Reena Ittyachan and Sagayaraj 2002). It has been reported that L-arginine fluoride (LAF) possesses high NLO coefficient next to LAP. LAF has a very strong type I position i.e., angularly insensitive compared to LAP, which makes LAF crystal attractive for certain cascade scheme for producing third harmonic. Tanusri Pal et al (2002) concentrated on L-arginine halide system and mixed crystals of LAHCl and LAHBr and estimated the damage threshold of LAHCl, LAHBr and LAHClBr as about 27.72, 16.37 and 29.84 GW/cm$^2$ at 1064 nm, respectively.

Owens et al (2001) have grown bulk crystals of L-arginine tetrafluoroborate (L-AFB) with dimensions 78 x 50 x 35 mm$^3$ by employing temperature lowering method. Their experiments reveal that the useful transmission range of solution grown bulk crystal of L-AFB extends from 198 to 900 nm, which makes it valuable for applications that require blue-green light. Rajan Babu et al (2003) reported that L-AFB has higher SHG efficiency
than KDP. L-arginine trifluoroacetate (LATF) was grown by Xu et al (2003) from the aqueous solution by employing temperature lowering method. It was reported that the optical damage threshold of LATF at 1064 nm is higher than that of LAP and KDP. Single crystals of L-arginine acetate (LAAC) were grown by Muralidharan et al (2003) by employing low temperature solution growth technique. LAAC has lower UV cut-off wavelength at 240 nm and hence suitable for frequency conversion applications. Single crystals of L-arginine maleate were grown by slow evaporation of the saturated aqueous solution at 30°C. The UV-Vis-NIR transmission spectrum shows that L-arginine maleate has lower cut off at 300 nm (Vasantha et al 2004). Packiam Julius et al (2004a) reported that L-arginine hydrofluoride (LAHF) single crystal has higher transmission in the wavelength range 800-2000 nm. Studies on the growth and characterization of L-arginine formate (LAF) single crystals have been carried out by Packiam Julius et al (2004b) and also by Haussuhl et al (2006). Preema Thomas et al (2005) have grown single crystals of L–argininium dinitrate (LADN) by the slow evaporation technique.

L-histidine salts can display higher NLO properties due to the presence of imidazole group in addition to amino-carboxylate. Among the L-histidine analogs, the low temperature solution grown L-histidine tetrafluoroborate (LHFB)\{[(C$_3$N$_2$H$_4$)CH$_2$CH(NH$_3$)(CO$_2$)]$^+$BF$_4$:HFB\} is a promising NLO material and has better NLO properties than LAP. The power threshold figure-of-merit compares favourably with BBO and LBO single crystals (Marcy et al 1992). Reena Ittyachen and Sagayaraj (2003a) studied the growth of L-histidine bromide (LHB), a semiorganic NLO material with molecular formula C$_6$H$_{12}$N$_3$O$_3$Br by slow evaporation technique. with molecular formula C$_6$H$_{15}$N$_3$O$_{10}$P$_2$ is a new semiorganic NLO crystal, which possesses good transparency, dipolar strength and is regarded as a promising material for NLO applications (Reena Ittyachen and Sagayaraj 2003b). Single crystals of L–histidinium perchlorate (LHPC), a semiorganic
NLO crystals have been grown by solvent evaporation method at room temperature (Reena Ittyachan et al 2005). Also bulk crystals of L-histidine tetrafluoroborate (L-AFB) and L-arginine tetrafluoroborate (L-AFB) have been grown by temperature lowering methods were proved to be good NLO materials makes them suitable for applications that require blue-green light (Aggarwal et al 2003). Also another amino acid based semiorganic material L-tyrosine hydrobromide with the molecular formula C₉H₁₂₃NO₃Br which is found to have SHG efficiency 1.2 times that of KDP has been reported by Narayana Moolya and Dharmaparakash (2006).

The linear optical properties showed that L-alanine family crystals have lower cut-off wavelength in the UV-region. The growth aspects of L-alanine acetate was studied by Mohankumar et al (2005). Dhanuskodi and Vasantha (2004c) have reported the structural, thermal and optical characterization of L-alaninium oxalate (LAO). LAO has its transparency window from 230 nm onwards, suggesting the suitability of LAO for SHG of the 1064 nm radiation and for other applications in the blue violet region. Rajan Babu et al (2002 and 2003) reported the growth of single crystals of L-alanine derivatives such as L-alanine tetrafluoroborate (L-AlFB) and L-arginine tetrafluoroborate (L-AFB) and studied their fundamental growth properties. Metal-organic crystals form a new class of materials under semiorganics. Several metal-organic complexes of amino acid have already been reported (Balakrishnan et al 2008, Dhanuskodi et al 2007). Compared to organic molecules, metal complexes offer a large variety of structures, and a diversity of electronic properties by virtue of the coordinated metal centre. (Bella and Fragala 2001).

Also several analogs of L-proline based materials have been reported. L-prolinium picrate, prolinium tartrate, L-proline cadmium chloride materials have been grown by slow evaporation and slow cooling techniques
Jin et al 2003, Uma Devi et al 2008, Kandasamy et al 2007). They found to exhibit very good SHG response. We tried to grow an analog of L-proline with zinc chloride, a metal-organic NLO crystal in mixed solvent. The structure of dichlorobis L-proline Zn (II) was already reported by Yukawa et al (1985).

2.4.7 Apparatus for SHG Measurement

The first observation of SHG in organic material (benzopyrene) was made in 1965 by Rentzepis and Pao.

At the end of 1960, the Kurtz and Perry powder SHG method was introduced. In this method, a powdered sample irradiated with a laser beam emits scattered light, which 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. Early NLO history has been chronicled more extensively by Chemla and Zyss (1987).

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

Inorganic materials are much more matured in their application to second order NLO materials than organics. Most commercial materials are inorganic especially for high power use. However, organic materials are perceived as being structurally more diverse and therefore are believed to have more long-term promise than inorganics. Organic NLO materials are often superior to inorganics in terms of their response speed, optical clarity,
and the magnitude of their third-order susceptibility Chang (1981). For a material to exhibit NLO activity it should be noncentrosymmetric.

![Apparatus used for the study of second harmonic generation in powders](image)

**Figure 2.3  Apparatus used for the study of second harmonic generation in powders**

For optical applications, a nonlinear material should have the following characteristics (Nalwa and Miyata 1997).

(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.

For exhibiting SHG, in materials, there are two factors, which determine the existence or absence of efficient SHG. Firstly, and fundamentally, the material should crystallize with a non-centrosymmetric crystal structure. Secondly, for maximum SHG efficiency, crystals should possess phase matching properties (i.e., the propagation speeds of the fundamental and harmonic waves should be identical in the crystal).

The advantages of organic optical materials are:

i) high second-order nonlinear optical efficiency
ii) much greater resistance to damage in the laser beam
iii) they are birefringent (facilitates phase-matching)
iv) possible to chemically “engineer” molecular properties

Ideally, the perfect organic material would be one which has a high efficiency, a very low absorption edge cut-off (to allow access into the UV), a high damage threshold and finally has favourable crystal growth properties. The enhancement in nonlinearity in comparison to inorganic materials arises due to the existence of $\pi$ electrons in the organic materials. Large second-order optical nonlinearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end (Devydov et al 1970).

A comparison of general crystal growth characteristics of organic and inorganic compounds is shown in Table 2.3.
Table 2.3 Comparison of organic and inorganic compounds

<table>
<thead>
<tr>
<th>Sl.No.</th>
<th>Property</th>
<th>Organic compounds</th>
<th>Inorganic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Chemical nature</td>
<td>Covalently bonded molecules</td>
<td>Ionic bonded molecules</td>
</tr>
<tr>
<td>2.</td>
<td>Solubility</td>
<td>Soluble in a wide variety of organic solvents</td>
<td>Soluble in water</td>
</tr>
<tr>
<td>3.</td>
<td>Sensitivity to pH and ionic strength</td>
<td>None</td>
<td>Sensitive</td>
</tr>
<tr>
<td>4.</td>
<td>Thermal properties</td>
<td>Thermally stable up to melting point (commonly between 50-150°C)</td>
<td>Highly thermally stable</td>
</tr>
<tr>
<td>5.</td>
<td>Crystal size</td>
<td>0.1-10 mm³, from common crystal growth methods</td>
<td>No size limit for many inorganic compounds</td>
</tr>
<tr>
<td>6.</td>
<td>X-ray diffraction quality</td>
<td>Good</td>
<td>Excellent</td>
</tr>
<tr>
<td>7.</td>
<td>Mechanical strength</td>
<td>Fair-good</td>
<td>Extremely good</td>
</tr>
</tbody>
</table>

Growth of single crystals of semi-organics has been a subject of perennial concern in order to use the materials for device application. However, to enable to be potentially useful for nonlinear optical applications, the material should also be available in bulk form.

Hence, in the present thesis growth aspects of amino acid based nonlinear optical crystals such as LA, LAAN, LPN and DBLPZ have been investigated. These materials have been identified as potentially useful materials for frequency doubling (SHG).
2.5 NLO CRYSTALS CHOSEN FOR INVESTIGATION

2.5.1 L-alanine family single crystals

L-Alanine is an efficient organic NLO compound under the amino acid category. The title compound was first crystallized by Bernl (1931) and later by Simpson et al (1966). It belongs to the orthorhombic crystal system (space group $P2_12_12_1$) with a molecular weight of 89.09 and has a melting point of 297 °C. The carboxyl group is present as a carboxylate ion and amino group as ammonium ion. The structural arrangement (head to-tail hydrogen-bond sequence) and the occurrence of the $\pi-\pi^*$ transition in the carboxylic group account for the nonlinearity in this crystal.

The grown single crystals were characterized by various methods. The NLO response and laser damage threshold were tested by using an Nd:YAG laser. Among organic crystals for nonlinear optics (NLO) applications, amino acids exhibit some specific features of interest which favors their becoming very promising materials (Razzetti et al 2002, Nicoud et al 1987, Fuchs et al 1989). Efforts have been made on the amino acid mixed complex crystals in order to make them suitable for device applications. In recent years, amino acids are mainly used as a basis for synthesizing organic inorganic compounds. Amino acid family crystals exhibit excellent nonlinear and electro-optical properties. L-alanine alaninium nitrate (LAAN) single crystal belonging to the amino acid group was grown by slow cooling solution growth technique. It is found to possess a good optical quality and laser damage threshold study proves it to be good candidate for NLO applications.
2.5.2 Metal Complex of L-proline Single Crystals

In metal organic complexes, the organic ligand is usually more dominant in the NLO effect. As for the metallic part, focus is on the group (II B) metal (Zn, Cd and Hg) as these compounds usually have a high transparency in the UV region, because of their closed d\textsuperscript{10} shell configuration. Dichloro bis L-proline zinc (II) (DBLPZ) is a promising semiorganic NLO material for efficient SHG of Nd: YAG laser. DBLPZ crystals have been grown by slow evaporation method at room temperature. Second harmonic generation conversion efficiency of DBLPZ is 0.5 times of KDP and hence it can be a potential material for frequency doubling process.

2.6 SCOPE OF THE THESIS

An overview on different methods of crystal growth techniques and experimental aspects of low temperature solution growth method have been explained in chapter 1. The basic principle and applications of nonlinear optical phenomena and an insight into the different NLO materials have been discussed in this chapter. 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. In the present investigation it was aimed at the

i) growth of single crystals of L-Alanine (LA), L-alanine alaninium nitrate (LAAN), L-phenylalanine nitric acid (LPN) and Dichlorobis L-proline Zn(II) (DBLPZ) and have been identified as efficient NLO candidates for device fabrication.

ii) Crystal has been grown by low temperature solution growth method. The grown crystals have been characterized by single
crystal and powder XRD study, EDAX and FTIR, Thermal and NMR studies. Kurtz powder NLO test, laser damage threshold and optical transmission / absorption reveal the linear and nonlinear optical properties. The thermal behaviour of the grown crystals was investigated. Measurement of dielectric constant and dielectric loss of the grown crystals were carried out for L-alanine crystal and the laser damage studies were also carried out for both LA and LAAN crystals.