CHAPTER I

INTRODUCTION TO NONLINEAR OPTICS AND CRYSTAL GROWTH

1.1 Nonlinear optics:

Nonlinear optics (NLO) deals with the interaction of electromagnetic fields with materials to generate modified electromagnetic fields of changed frequency, phase, amplitude etc [1, 2]. NLO has been a subject of much interest and study since Franken et al., [3] first observed frequency doubling in the year 1961. It was observed that when a quartz crystal was illuminated by a high power Ruby laser of wavelength 694.2 nm, a weak signal of wavelength 347.1 nm was generated [3,4]. This phenomenon was called second harmonic generation (SHG). The invention of high power lasers intensified the investigations in the field of NLO, and also the demand for high quality NLO materials increased because of the large number of applications such as SHG, third harmonic generation (THG), self focusing, frequency mixing, electro optical effect etc. SHG is applied in solid state frequency doubled laser pointers and also in the field of optical computing, optical information processing, optical disk data storage, laser driven fusion, color displays, laser remote sensing, medical diagnostics known as endocardial detection etc [5].

THG was observed by New and Ward in 1967 [6]. In THG the photons interacting with a nonlinear material are effectively combined using two processes. At first a second harmonic wave is produced (SHG) and is followed by sum frequency generation (SFG) of the original and the second harmonic waves. THG finds application in ozone sensing (308 nm to 320 nm), OH and SO2 sensing.
(308 nm to 300 nm), biological detection (290 nm) etc. Fifth and higher order harmonic generations were observed by Reintjes and co-workers [7].

Frequency change in the output radiation occurs due to the ability of the material to change its refractive index and thus altering the frequency of the light passing through it [8]. This phenomenon of alteration of frequency of light by a medium on application of an applied electric field is called Pockels effect [9]. An example of this is the conversion of the commercial infrared laser with the wavelength of 1064 nm, to green light of wavelength 532 nm, when passed through second-order nonlinear media. This transformation is useful because it quadruples the amount of information the laser can write on an optical disc [10].

The interaction of light with nonconducting and nonmagnetic media can be generally regarded as dielectric subjected to an electric field. Due to the effect of the field the medium gets polarized. Each atom behaves as a dipole and the dipole moment \( \mu_{\text{ind}} \) is given by

\[
\mu_{\text{ind}} = -er \quad (1-1)
\]

Where \( e \) is the electronic charge and \( r \) is the field-induced displacement of the charge centers of the atom.

The developed dipole moment per unit volume of the material is called the polarization ‘\( P \)’ and is given by

\[
P = -Ner \quad (1-2)
\]

Where \( N \) is the electron density in the medium.

The field strength of the conventional light source is around \( 10^3 \) V/cm that is very small compared to the atomic or interaction field strength, which is around \( 10^7 \) V/cm to \( 10^{10} \) V/cm. For low field strengths the polarization is linear which is given by

\[
P = \chi^{(1)}E \quad (1-3)
\]
Where the susceptibility $\chi^{(1)}$ is related to the dielectric constant $\varepsilon$ of the medium by the equation [11].

$$\varepsilon = 1 + 4\pi\chi^{(1)} \quad (1-4)$$

When the medium is subjected to a strong electric field as that due to an intense laser pulse which has a field strength of $10^7$ V/cm to $10^{10}$ V/cm, the polarization becomes nonlinear and is given by [12-14]

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \cdots \quad (1-5)$$

$\chi^{(2)}$, $\chi^{(3)}$ etc. are tensors of second, third and higher order ranks representing the non-linear susceptibilities of the medium.

Using the field equation $E = E_0 \cos \omega t$

The polarization equation can be expressed as

$$P = \chi^{(1)} E_0 \cos (\omega t - kz) + (1/2) \chi^{(2)} E_0^2 \left[ 1 + \cos (2\omega t - 2kz) \right]
+ \chi^{(3)} E_0^3 \left[ (3/4) \cos (\omega t - kz) + (1/4) \cos (3\omega t - 3kz) \right] \quad (1-6)$$

The term with $2\omega$ represents the SHG and $3\omega$ the THG.

The term $\chi^{(2)} E^2$ represents the second order polarization field [15]. The coefficient $\chi^{(2)}$ is the second order nonlinear susceptibility tensor with 27 elements. The number of independent elements is reduced to 18 using crystal symmetry conditions. Hence the susceptibility tensor can be represented as a $3 \times 6$ matrix.

Since the susceptibility tensor and the piezoelectric tensor have the same form the induced polarization is expressed using the piezoelectric ‘$d$’ tensor as

$$P_i = d_{ijk} E_j E_k \quad (1-7)$$

A noncentrosymmetric media only will be able to give a contribution from $\chi^{(2)}$ where as $\chi^{(3)}$ contribution can be regardless of the symmetry of the compound
Fig. 1.1 represents the response of the linear and nonlinear optical media on electromagnetic radiation.

That means noncentrosymmetry is an essential requirement for second order nonlinear optical behavior [17]. Photons interacting with a second order nonlinear material are effectively combined to produce photons with twice the energy and therefore twice the frequency and hence half the wavelength.

In order to observe noticeable SHG all the wavelets must combine constructively along the propagation path of the incident wave. This is possible only if the fundamental (ω) and SHG (2ω) waves are in phase, which is generally the condition needed for phase matching. In non-centro symmetric materials even though both the quadratic and cubic terms will be present they will be negligibly small compared to the second harmonic term and can be ignored. For such materials,

\[ P = \chi^{(1)} E + \chi^{(2)} E^2 \quad (1-8) \]

In second harmonic generation, at first a polarization wave of the second harmonic 2ω is produced with a phase velocity and wavelength determined by the refractive index \( n_1 \) of the material corresponding to the fundamental wave given by \( \lambda_1 = \frac{c}{2n_1} \). Then energy of the polarization wave is transferred to an
electromagnetic wave at frequency $2\omega$. The phase velocity and the wavelength of the electromagnetic wave are determined by the refractive index at the second harmonic wavelength $n_2$ given by $\lambda_2 = c/2tn_2$. The energy transfer will be effective if both the waves are in phase and the condition needed is

$$n_1 = n_2.$$

Since the electromagnetic wave lags behind the polarization wave due to dispersion there will be a phase mismatch. It is represented as

$$k^{(2\omega)} - k^{(\omega)} = \Delta k \quad \text{(1-9)}$$

SHG intensity will be a maximum when $\Delta k = 0$ or $n_1 = n_2$.

The second harmonic intensity grows and decays as a function of distance with the period given by $\Delta k l/2 = \pi$

$1/2 = l_c$ is the coherence length and $l$ is the length of the crystal.

The conversion efficiency, for a given material and wavelength, depends on

(i) Interaction length $l$, which can be increased using large size crystals.

(ii) Crystals of lesser angular sensitivity are required for efficient device operation.

(iii) The power density. The laser beam can be focused into the crystal to increase the power density of the input beam and this increase can enhance the conversion efficiency. For this the crystal should have high resistance to laser damage.

Hence for device applications large single crystals with high laser induced damage threshold are required. This encourages the search for better quality crystals.
1.1.1 Non-linear Optical Materials

The properties needed for an efficient NLO material are

(i) Wide transparency range
(ii) Large NLO coefficient in the phase matchable direction
(iii) Moderate birefringence
(iv) High laser induced damage threshold
(v) Large angular, spectral and temperature bandwidth
(vi) Good chemical stability
(vii) Good mechanical stability
(viii) Low optical losses at the frequencies involved and
(ix) Ease of growth and low cost.

1.1.1.1 Inorganic Materials

The classical NLO materials are inorganic crystals. The first crystal used for this purpose was quartz in 1961. Lithium niobate (LiNbO₃) became important due to its non-hygroscopic and easily polishable natures [18-20], potassium dihydrogen phosphate (KDP) [21] and ammonium dihydrogen phosphate (ADP) [22,23] replaced quartz due to the large conversion efficiency and phase matching property, potassium niobate (KNbO₃), β-barium borate (BBO) [24,25], lithium triborate (LBO) [26-28], potassium titanyl phosphate (KTiOPO₄)[29], silver gallium selenide (AGSe) [30], lithium iodate (LiIO₃)[31] etc are some of the important inorganic NLO materials.

In order to improve the SHG efficiency of inorganic materials, doping of these materials with active trivalent ions such as Nd³⁺ and Yb³⁺ had been undertaken. They possessed the property known as self-frequency doubling. These crystals generate infrared radiation and simultaneously double the frequency of the fundamental radiation. Some example of self frequency doubling crystals are neodymium-doped yttrium aluminum tetraborate (NYAB), ytterbium-doped...
yttrium aluminum tetraborate (Yb:YAB), neodymium–and magnesium-oxide–doped lithium niobate (NdMgLN), neodymium-doped gadolinium calcium oxyborate (Nd:GdCOB) and neodymium-doped yttrium calcium oxyborate (Nd:YCOB) [32-34]. The optical properties of some of the important inorganic materials are listed in Table 1.1 [35].

<table>
<thead>
<tr>
<th>Material</th>
<th>Point group</th>
<th>Transparency range nm</th>
<th>η SHG Compared to KDP</th>
<th>d_{eff} pm/V</th>
<th>Re refractive Index At 1064 nm</th>
<th>Damage threshold GW/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n₀=1.493</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₑ=1.458</td>
<td>5</td>
</tr>
<tr>
<td>KDP</td>
<td>42m</td>
<td>180-1800</td>
<td>1.0</td>
<td>0.35</td>
<td></td>
<td>(1 ns)</td>
</tr>
<tr>
<td>LiB₃O₅</td>
<td>mm2</td>
<td>160-2300</td>
<td>8</td>
<td>0.85</td>
<td>nₓ=1.565</td>
<td>1-4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nᵧ=1.591</td>
<td>(12 ns)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₜ=1.605</td>
<td>0.3</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>3m</td>
<td>350-5000</td>
<td>105</td>
<td>5.1</td>
<td>n₀=2.232</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₑ=2.156</td>
<td>(10 ns)</td>
</tr>
<tr>
<td>β-B₃BO₄</td>
<td>3m</td>
<td>198-2600</td>
<td>---</td>
<td>1.6</td>
<td>n₀=1.655</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₑ=1.543</td>
<td>(14 ns)</td>
</tr>
<tr>
<td>KTP</td>
<td>mm2</td>
<td>350-4500</td>
<td>215</td>
<td>3.2</td>
<td>nₓ=1.573</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nᵧ=1.739</td>
<td>(20 ns)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₜ=1.830</td>
<td></td>
</tr>
<tr>
<td>LiIO₃</td>
<td>6m</td>
<td>340-4000</td>
<td>---</td>
<td>1.8</td>
<td>n₀=1.857</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nₑ=1.717</td>
<td>(0.1 ns)</td>
</tr>
<tr>
<td>KNbO₃</td>
<td>mm2</td>
<td>400-5500</td>
<td>---</td>
<td>13</td>
<td>nₓ=2.119</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>nᵧ=2.219</td>
<td>(10 ns)</td>
</tr>
</tbody>
</table>

Inorganic materials have high melting point, mechanical strength and high degree of chemical inertness but have only low nonlinearity, low damage threshold and only a low probability of the materials crystallizing in non-centrosymmetric structure. Most of the commercial frequency doublers used presently are made up of inorganic materials.
1.1.1.2 Organic Materials

Organic materials are more optically nonlinear than inorganic materials due to the high degree of delocalisation possessed by them because of the weak Vander Waals and hydrogen bonds present in them [35]. Following are some of the advantages of organic materials [36,37].

(i) Flexibility in the method of synthesis
(ii) Scope of property alteration by functional substitution
(iii) High nonlinearity
(iv) High damage thresholds to laser radiation
(v) Thin film processing properties.

There will be one or more delocalized bonds in the organic nonlinear optical materials. Donor/acceptor substitution in it will induce large dipole moments under the influence of electromagnetic fields. These materials tend to crystallize in centrosymmetric structure. But in centrosymmetric crystals the dipole moments vanishes. Only in noncentrosymmetric crystals a macroscopic non-vanishing dipole moment exists. A large number of organic materials crystallizing in the noncentrosymmetric structure are shown to exhibit second order nonlinear efficiencies that are several orders of magnitude higher than that of LiNbO$_3$. Organic materials exhibit significant nonlinearity across the visible and infrared spectral region [38]. They show flexibility in modification and optimization of linear and nonlinear properties [39]. Organic NLO materials have their limitation in device applications due to [40,41]

(i) Poor mechanical hardness
(ii) Low melting point
(iii) Poor chemical inertness
(iv) Inadequate transparency
(v) Poor optical quality
(vi) The inability to grow large size crystals

Some of the organic materials identified with good nonlinear optical properties are methyl-(2,4-dinitrophenyl)-amino-2-propanate (MAP) [42], 3-methyl-4-nitro-pyridine-1-oxide (POM) [43], urea [44], n-(4-nitrophenyl)-l-prolinol (NPP) [45], sulphonyl group compounds [46], 3-methyl-4-methoxy-4'-nitrosteilbince (MMONS) [47] 5-nitro-uracil [48], organometallic compounds [49], organic polymers [50], 2-\(\alpha\)-methylbenzyl-amino)-5-nitropyridine (MBANP) [51], (-)-1-(4-dimethylaminophenyl)-2-(2-hydroxypropylamino)cyclobutene-3,4-dione (DAD) [52], L-N-(5-nitro-2-pyridyl)leucinol [53] p-nitroaniline [54] 2-methoxy -5-nitro phenol (MNP) [55], 2-Amino-5-Nitropyridinium chloride [56]. 2-methyl-4-nitroaniline (MNA) and 2-dimethyl amino-5-nitroacetanilide (DAN) are used for fiber production because of their suitable melting temperatures [57,58]. N-(4-nitro-2-pyridyl) phenylalalinol (NPPA) [59] is used for the fabrication of nonlinear optical films by depositing a layer of it on a substrate. In Table 1.2, some of the properties of selected organic materials are tabulated [35].

In organic materials the polarizability is the contributions from the atoms and molecules due to the weak intermolecular bonding. NLO effect in molecular crystals depends on the polarizability of the electrons in the \(\pi\) bonding orbits. The optical nonlinearity can be increased by adding conjugated bonds or substituting donors that donate electrons to the \(\pi\) electron system and acceptors that accept electron into the \(\pi\) electron system. This addition at the ends of the \(\pi\) system can enhance the asymmetric electronic distribution [60]. \(\sigma\) bond and \(\pi\) bond are the two types of bonding with the carbon atom and other elements. \(\sigma\) bond is along the carbon-carbon inter-nuclear axis and \(\pi\) bonds are regions of delocalized electronic charge distribution above and below the inter-atomic axis [61].
Table 1.2 NLO characteristics of some standard organic materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Point group</th>
<th>Transparency Range (nm)</th>
<th>NLO Coefficient $NLO_{\text{Coefficient}} \times 10^{-9}$ esu</th>
<th>Refractive index (n) at 1064 nm</th>
<th>Laser damage threshold (GW/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MNA</td>
<td>mm2</td>
<td>480-2000</td>
<td>$d_{11}=60$ $d_{12}=90$</td>
<td>$n_x=1.800$ $n_y=1.600$ $n_z=1.621$</td>
<td>0.2 (20 ns)</td>
</tr>
<tr>
<td>POM</td>
<td>222</td>
<td>500-1700</td>
<td>$d_{14}=23$ $d_{25}=23$ $d_{36}=23$ $d_{22}=12.4$</td>
<td>$n_x=1.663$ $n_y=1.829$ $n_z=1.625$</td>
<td>2 (0.02 ns)</td>
</tr>
<tr>
<td>DAN</td>
<td>2</td>
<td>485-2700</td>
<td>$d_{24}=55$ $d_{32}=41$ $d_{33}=184$</td>
<td>$n_x=1.530$ $n_y=1.630$ $n_z=1.961$</td>
<td>5 (10 ns)</td>
</tr>
<tr>
<td>MMONS</td>
<td>mm2</td>
<td>510-2100</td>
<td></td>
<td>$n_x=1.650$ $n_y=1.714$ $n_z=1.688$</td>
<td>---</td>
</tr>
<tr>
<td>MBANP</td>
<td>2</td>
<td>420-1900</td>
<td>$d_{22}=8.3$</td>
<td>$n_x=1.507$ $n_y=1.59$ $n_z=1.843$</td>
<td>1 (12 ns)</td>
</tr>
<tr>
<td>MAP</td>
<td>2</td>
<td>500-2500</td>
<td>$d_{21}=40$ $d_{22}=44$ $d_{23}=8.8$</td>
<td>$n_x=1.507$ $n_y=1.59$ $n_z=1.843$</td>
<td>3 (10 ns)</td>
</tr>
</tbody>
</table>

Conjugated organic molecules with large delocalized \(\pi\) electron systems have very large nonlinear optical effects. The second order nonlinearity can be increased by attaching functional groups with electron accepting and donating characters at opposite ends of the conjugation bridge leading to a one dimensional charge transfer.

1.1.1.3 Amino acids

Amino acids are the basic structural units of proteins. Amino acids contain chiral carbon atom and crystallize in noncentrosymmetric space groups. Hence they are potential candidates for optical second harmonic generation. Due to the absence of strongly conjugated bonds amino acids have a wide transparency range...
in the visible and UV spectral regions. Single crystals of amino acids are more stable compared to other organic crystals due to the proton donor carboxylic acid group (-COOH) and the proton acceptor amino (NH$_2$) group present in them. In amino acids the carboxylic acid group donates one proton to amino group to form a salt of the form R-NH$_3^+$CHCOO$^-$. Thus, in solid state, all amino acids exist as dipolar ion and hence have net dipole moment. This causes the second harmonic generation in these materials.

Alanine, arginine, asparagine, aspartic acid, cysteine, glutamine, glutamic acid, glycine, hystidine, isoleucine, leucine, lysine, phenylalanine, praline, myhionine, serine, threonine, tryptophan, tyrosine and valine are the basic amino acids. Amino acids possess interesting features such as [62]

(i) Molecular chirality, which possess non-centro symmetric crystallographic structures
(ii) Absence of strongly conjugated bonds, leading to wide transparency range in the visible and UV spectral regions
(iii) Zwitterionic nature of the molecule, which favors crystal hardness.

Due to the proton donor carboxylic acid group (-COOH) and the proton acceptor amino (NH$_2$) group, they provide a push-pull mechanism. Hence these amino acids posses significant SHG efficiency compared to KDP. Amino acid crystals are more stable compared to other organic crystals.

1.1.1.4 Semiorganic Materials

High efficiency optical quality NLO materials are prepared by stoichiometrically bonding a polarizable organic molecule to an inorganic host, combining the advantages of both organic and inorganic materials. The properties can be improved by forming metal coordination complexes of organic materials. Even if the organic part is centrosymmetric there is a possibility of the metal
complex of it crystallizing in noncentrosymmetric structure. Like metal complexes of thiourea. Many thiourea complexes ensure the lack of center of inversion due to the presence of large sulphur atoms and the hydrogen bonds in NH₂ [35].

The nonlinear optical L-arginine phosphate (LAP) was first reported by D. Xu et.al., [63] and its deuterated analogue (dLAP) which is more efficient than LAP was reported by D. Eimerl et.al., [64]. Microbe inhibition growth of L-arginine phosphate monohydrate and its thermal and electrical properties were reported [65,66]. A.S. Haja Hameed et.al., reported the study on L-arginine fluoride [67]. Bulk growth of L-arginine tetrafluoroborate (L-AFB) of size 78 X 50 X 35 mm³ was grown by temperature lowering technique [68]. Its growth aspects were studied and reported by D. Rajan Babu et.al., [69]. Potassium fluoride mixed L-arginine phosphate was reported [70]. D.Xu et.al., reported the characterization of L-arginine trifluoroacetate [71]. L-arginine hydrofluoride was reported by Tanusri Pal and Tanusree Kar [72]. L-arginine diphosphate (LADP) of size 30 x 6 x 4 mm³ grown by slow evaporation method was reported by R. Ittyachan et.al., [73]. Rajan Babu et.al., reported L-alanine tetrafluoroborate (L-AFB) grown by solvent evaporation method [74].

Marcy et.al reported zinc (tris) thiourea sulphate (ZTS) [75], bis (thiourea) cadmium chloride (BTCC) [76] and triallyl thiourea cadmium chloride (ATCC) [77] are reported to exhibit excellent NLO properties. Triallyl thiourea mercury bromide (ATMB), thiosemicarbazide cadmium bromide [78, 79], cadmium mercury thiocyanate (CMTC) [80], cadmium mercury thiocyanate dimethyl sulphoxide (CMTD), and cadmium mercury thiocyanate glycol monomethyl ether (CMTG) [81] are reported to exhibit NLO properties.
Table 1.3 NLO characteristics of some standard semiorganic crystals

<table>
<thead>
<tr>
<th>Material</th>
<th>Point group</th>
<th>Transparency Range(nm)</th>
<th>Nonlinear coefficient $(x10^{-9}$ esu)</th>
<th>Refractive Index</th>
<th>Damage threshold (GW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dLAP</td>
<td>2</td>
<td>250-1300</td>
<td>$d_{14}=0.22$ $d_{16}=0.48$ $d_{22}=0.68$ $d_{31}=0.31$</td>
<td>$n_x=1.4977$ $n_y=1.5595$ $n_z=1.5686$</td>
<td>13 (1 ns)</td>
</tr>
<tr>
<td>ZTS</td>
<td>mm2</td>
<td>300-2000</td>
<td>$d_{32}=0.35$ $d_{33}=0.23$ $d_{31}=1.5$ $d_{22}=0.7$ $d_{33}=1.9$</td>
<td>$n_y=1.6936$ $n_z=1.6984$ $n_0=1.6996$</td>
<td>40 (32ps)</td>
</tr>
<tr>
<td>ATCC</td>
<td>3m</td>
<td>300-1500</td>
<td>$d_{31}=0.27$ $d_{22}=0.7$ $d_{33}=1.9$</td>
<td>$n_0=1.6400$ $n_z=1.6400$ $n_c=1.6400$</td>
<td>0.32 (40 ns)</td>
</tr>
<tr>
<td>ATMB</td>
<td>3m</td>
<td>300-1500</td>
<td>$d_{22}=8.2$ $d_{33}=2.7$ $d_{31}=2.75$</td>
<td>$n_x=1.6341$ $n_y=1.6936$ $n_z=1.7046$</td>
<td>---</td>
</tr>
<tr>
<td>BTCC</td>
<td>mm2</td>
<td>300-2000</td>
<td>$d_{32}=0.2$ $d_{33}=2.7$ $D_{13}=0.5$</td>
<td>$n_y=1.7902$ $n_z=1.8600$ $n_x=1.7200$</td>
<td>32 (32ps)</td>
</tr>
<tr>
<td>TSCCB</td>
<td>M</td>
<td>330-1420</td>
<td>$D_{15}=2.8$</td>
<td>$n_y=1.7180$ $n_x=1.8120$</td>
<td>---</td>
</tr>
</tbody>
</table>

Single crystals of L-histidine nitrate, L-cysteine tartrate monohydrate[82], L-alanine oxalate[83], L-tyrosine hydrochloride[84], L-prolinium tartrate[85], L-cystine hydrochloride[86], L-hystidine hydrofluoride dihydrate[87], L-alanine-alaninium nitrate[88] are some of the recently reported materials with NLO properties. Some of the optical properties of selected semiorganic materials are tabulated in Table1.3 [35].

According to the hard and soft acid and bases concept the harder metals show affinity for coordination with harder ligands while softer metals prefer coordination with soft ligands [89].
1.1.2 Applications of NLO materials:

NLO materials play an important role in electro-optical modulators, high density optical memories, colour displays, signal processing devices, signal amplification and emission or oscillation [90]. This is because optical techniques for modulating, amplifying, transforming and transmitting signal information can, in principle, be much faster than electrical techniques.

NLO materials utilized for opto-electronic applications such as optical computing, optical data storage and optical communications have been developed enormously. Parallel image processing and integrated optics are now established as an alternative field to electronics for the future photonic technologies.

Some of the optical phenomena using nonlinear optical materials are

1) Second Harmonic Generation (SHG) or Frequency doubling – by passing a high intense laser beam through a NLO crystal, a light with a doubled frequency i.e. half the wavelength of the incident light is generated.

2) Sum Frequency Generation (SFG) – Light with a frequency that is the sum of two other frequencies is generated. SHG or optical frequency doubling is just a special case of sum frequency generation. A light wave of frequency \( f \) incident on the NLO material generates a wave of twice the frequency. Sum frequency and SHG are standard techniques to create a new coherent output from existing laser systems and especially to access the short wavelength range towards the ultraviolet region.

3) Difference Frequency Generation (DFG) – Generation of light with a frequency that is the difference between the frequencies of two incident waves.

4) Optical Parametric Generation (OPG) – The photon of an incident laser pulse is divided into two photons by a nonlinear optical crystal. One of the laser pulse generated is called the signal and the other the idler. The sum of
the energies of these two photons is equal to the energy of the incident laser photon. The wavelengths of the two laser pulses generated are determined by the phase matching condition, which can be changed by adjusting the angle between the incident laser ray and the axes of the crystal.

5) Optical Parametric Amplification (OPA) – The signal light from the OPG output is separated and the idler is passed through a nonlinear optical crystal collinearly with the light of the same wavelength as the pump producing stronger output of the same wavelength as the signal and idler.

6) Parametric Oscillation – In a resonator signal and idler waves are generated.

7) Spontaneous Parametric Down Conversion (SPDC) - Amplification of the vacuum fluctuations in the low gain regime.

8) Optical Rectification – Generation of quasi-static electric fields.

9) Third Harmonic Generation (THG) – Generation of a light with a tripled frequency i.e. one third the wavelength of the incident light. This is usually done in two steps. A SHG followed by SFG of original and the frequency doubled waves.

10) Optical Kerr effect – Intensity dependant refractive index, self focusing, Kerr-lens mode locking, self phase modulation, optical solitons, cross phase modulation, four wave mixing [91].


13) Two-photon absorption – simultaneous absorption of two photons and transfer of energy to a single electron.

14) Multiple photonisation – Near simultaneous removal of many bound electrons by one photon. etc.
1.2 Crystal Growth

Crystals are materials in which atoms/molecules are symmetrically arranged in three dimensional space. The fundamental building block of a crystal is the unit cell. During the crystal growth the unit cells are arranged symmetrically in three dimensional periodic arrays. Depending on the unit cell parameters a, b, c, α, β, γ and the number of atoms/molecules in a unit cell, there are 14 crystal structures identified. It is difficult to grow perfect crystals. The grown crystals will be containing different types of crystal defects, imperfections, polycrystalline nature, twinning etc. Good single crystals are essential for a variety of scientific and commercial purposes [92]. Crystal formation may take place when a substance undergoes phase transition to solid phase [93]. The crystal growth process is very complex as it is influenced by numerous independent parameters. The method used for the growth of the crystal and the conditions maintained during the growth process are essentially crucial factors when the perfection, size and the orientation of the crystal are important. So it is very important to select the best suited method and optimum values of the growth parameters for growing good quality crystals.

1.2.1 Theory of Crystal Growth

The crystal growth process consists of two phases:

1. Nucleation and
2. Growth.

Nucleation is the formation of the first nucleus of the crystal. The driving force that stimulates nucleation is the change in Gibbs free energy (ΔG) between the crystalline phase and the surrounding mother liquid. The total change in free energy is the sum of the free energy change involved in the phase transition (ΔG_v), the free energy change involved in the formation of the free surface (ΔG_s) and the free energy change due to the elastic strain (ΔG_e).

\[ \Delta G = \Delta G_v + \Delta G_s + \Delta G_e \]  \hspace{1cm} -(1-10)
$\Delta G_e$ is negligibly small compared to the other two terms. Hence the free energy change associated with the formation of a spherical nucleus of radius $r$ is

$$\Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta g_v \quad (1-11)$$

Where $\gamma$ is the interfacial energy per unit surface area formed and $\Delta g_v$ is the free energy change per unit volume of the solid formed.

During the conglomeration of atoms or molecules to form the nucleus for the growth, the energy value of the surface area term increases with $r^2$ and that of the volume term decreases with $r^3$ in a supercooled or supersaturated system. Hence $\Delta G$ increases gradually with $r$, reaches a maximum $\Delta G^*$ up to a radius $r^*$ and then decreases. The size of the crystal with radius $r^*$ is called the critical nucleus. If the size of the cluster is greater than that of the critical nucleus the crystal grows. Fig 1.2 represents the formation of critical nucleus.

Nucleation kinetics control the rate at which new crystals are formed and the growth kinetics controls the rate at which existing crystals grow. The knowledge of the crystallization process is useful in selecting the growth techniques. Crystal growth occurs due to the transition of the material in to the solid phase from solid,
liquid or vapour phase. If the free energy is minimum in the mother phase, crystallization will not take place. Changing the temperature, pressure, chemical potential, electrochemical potential or strain can disturb the dynamic equilibrium.

### 1.2.2 Crystal Growth Techniques

The growth method selected should be appropriate for the material used for crystallization. The crystal growth techniques are generally classified into the following major groups.

1. **Solid growth** - Change from one solid phase to another.
2. **Vapour growth** - Change from gaseous phase to solid.
3. **Melt/solution growth** - Change from liquid phase to solid.

The growth process has a greater influence on the quality as well as the physical properties of the grown crystals. Vapour deposition is most commonly used technique to grow thin crystalline films. Melt growth and solution growth are used to grow bulk crystals.

#### 1.2.2.1 Solid Growth

In the solid growth method a polycrystalline rod or compressed powder of the material that is to be grown as a single crystal is maintained at a higher temperature below its melting point. After several hours grains start growing.

This is observed in compressed powder of tungsten and in the devitrification of quartz. It is not a suitable method for growing large single crystals [92].

#### 1.2.2.2 Vapour Growth

Vapour growth yields crystals with low concentration of point defects and dislocations compared to melt growth because the growth temperature is considerably lower than the melting temperature of the material. Vapour growth is mainly used to grow thin films and in the field of semiconductor technology. It is a
three-stage process, which involves vaporization, transport and deposition of the material.

At high temperature the material vaporizes and the kinetic energy of vaporization helps the transportation of the vapour to the crystal-growing surface. Deposition of the vapour occurs due to condensation or chemical reaction. In the simplest method a sealed tube is used. At one end of it the source material is heated to high temperature and the vapour is transported to the cooler end of the tube where it crystallizes. The transport process is controlled with the help of an inert carrier gas.

1.2.2.3 Melt Growth

In this method the crystal is grown by the solidification of the melt. Bulk crystals of any size weighing from few grams to few kilograms can be grown with a good yield and relatively high growth rate. The material to be grown as a single crystal is placed in a suitable container and heated in a furnace above the melting point of the material. The growth is initiated by cooling the melt from a temperature above the equilibrium melting point. When the temperature reaches slightly below the equilibrium melting point, if a seed is formed, the crystal growth begins. In order to avoid the crystal imperfections a uniform temperature gradient is to be maintained between the growing crystal and the feed melt. The parameters, which are anisotropic, are orientation dependant. Seeded growth is preferred for growing crystals with a growth orientation. Melt growth is applicable to materials, which do not decompose and do not undergo phase transition before melting. Different techniques used for the melt growth are

(i) Czochralski crystal pulling.
(ii) Bridgeman – Stockbarger technique.
(iii) Zone melting/zone refining technique.
(iv) Vemuolli method.
(i) **Czochralski method:**

In this method a heater capable of melting the material surrounds the crucible containing the material to be crystallized. A pull rod is coaxially mounted above the crucible. A chuck is attached at the end of the pull rod. With the seed crystal fixed at the chuck, the pull rod is lowered until the end of the seed is dipped into the melt. Once the thermal steady state is achieved the pull rod is slowly lifted and rotated which results in the growth of the crystal at the end of the seed. The pull rate as well as the rotation rate is adjusted suitably. The whole crystal growth assembly is isolated from the ambient temperature fluctuations by using an envelope. The Czochralski method of crystal growth is shown in Fig 1.3.

![Fig. 1.3 Czochralski method of crystal growth](image)

The inorganic crystals like Ruby, Sapphire, compound semiconductor crystals like Gallium Arsenate, Gallium Phosphate [94-97] and organic crystals like benzophenone, urea [98,99] are among many crystals grown by this technique. Major part of the silicon used in electronic Industry is grown by this method. Since the growth is from the free surface, it accommodates the volume expansion during the solidification of the material.

By adjusting the parameters of the growth the size of the crystal can be varied as per the requirement. By using proper melt composition doping can be
performed effectively. Uniform distribution of dopant can be maintained by rotating the crystal. The process is comparatively faster and high structural perfection can be obtained during the growth, as the crystal is not constrained as it cools. Since the crystallization can be observed during the growth, the crystal can be melted back if the growth is found to be defective. This method does not support the growth of materials high vapour pressure at the melting point. Contamination from the crucible cannot be avoided in this method.

(ii) Bridgeman – Stockbarger Technique

In Bridgeman- Stockbarger technique the material to be grown is taken in a closed cylindrical container that can be mounted vertical or horizontally. It is tapered conically with a point bottom and the material is made to melt using a furnace. The container is lowered slowly from the hot zone of the furnace to the cold zone. Crystallization begins at the tip and usually continues to grow from the first nucleus formed. To grow the crystals with a particular orientation a seed crystal can be placed at the end of the container to activate the growth in that direction [100]. This method is also known as normal freezing method and is extensively used for the growth of single crystals of materials containing volatile constituents.

(iii) Zone melting

In zone melting the molten zone, heated by an r.f.induction coil is moved along the ingot. A separate boat at a lower temperature contains a volatile component and the temperatures are adjusted to prevent any net transport to or from the molten zone. In the growth using zone melting simultaneous purification of the material also is performed. Addition of dopants can be effectively performed using this method. Due to the small volume of the melt used, a homogeneous distribution of the dopants can be achieved in this technique. Zone melting was
developed for the purification of semiconductors. It is also used for the growth of several organic materials.

(iv) Vernoulli’s Method

Vernoulli in 1902 achieved control of nucleation using flame-fusion growth method. Industrial crystal growth was benefited by this to a greater extent. Single crystals of ruby and sapphire with melting points above 2000°C are grown by this method. For this growth, at first a sinter cone and a central melt droplet is formed on an alumina rod. By adjusting the power supply and the hydrogen-oxygen flame a neck is grown and the diameter is increased without overflow of the molten cap. This results in the growth of the single crystal boule [101].

(v) Heat Exchanger Method (HEM)

The Heat Exchanger Method (HEM) for growing large sapphire boules was invented by Fred Schmid and Dennis Viechnicki in 1967[102]. A diagram of the modern furnace used to grow large size sapphire boules with heat exchanger method is shown in Fig.1.4. In this unit a seed crystal of sapphire is placed at the bottom of a molybdenum crucible, which is then loaded with pure alumina crackle. The furnace is evacuated and resistively heated to melt the crackle. The seed crystal is kept just below its melting point by passing helium gas through the heat exchanger. Alumina gets purified as some impurities vaporizes due to the heat and vacuum. When the seed crystal is partially melted, crystallization of alumina onto the seed is initiated by further cooling the crystal by increasing the helium flow. The furnace is held at constant temperature during growth of the crystal. The growth proceeds out from the seed in 3 dimensions. When the crystallization is completed, the furnace temperature and the helium flow are decreased and the boule is slowly annealed. Sapphire of highest crystal quality is produced using long slow cooldown. Sapphire boules with a diameter of 38 cm and a mass of 84 kg have been grown using this method[103].
Fig. 1.4 Furnace used to grow sapphire by the Heat Exchanger Method.

Sapphire is an infrared transparent material and most durable with respect to thermal stress and particle impact. Hence it is used in the fabrication of infrared windows for the seeker dome on an infrared-guided missile [104].

In 1977 Chandra Khattak had grown crack-free polycrystalline silicon ingots in high purity silica crucibles using the heat-exchanger method. Silicon ingots weighing 240 kg with a cross section of 69 cm × 69 cm are produced using heat exchanger method [104]. Multicrystalline silicon solar cells are used for terrestrial photovoltaic application because of relatively low material cost and potential for high efficiencies [105].
1.2.2.4 Solution Growth

The crystal is grown from a saturated solution of the material in a proper solvent, by supersaturating it either by evaporating the solvent or by lowering the solution temperature. This method is very simple and less expensive. Since the growth is at a lower temperature the lattice defects will be minimum. Materials that melt or undergo phase transition before the melting point can be grown using solution growth method. The growth process can be inspected hence it is used for studying growth parameters. But the growth rate is slow and chances of inclusion of the solvent in the growing crystal is also high.

The quality of the grown crystals depend on several factors such as
(i) The purity of the starting materials
(ii) Quality of the seed crystal selected for the growth
(iii) The growth rate maintained etc.

Solution growth is a simple and less expensive method, which is the most commonly used technique for the production of medicines, fertilizers, pesticides, dyestuffs and some of the materials of technological importance.

1.2.2.4.1 Theory of solution growth

In the solution growth method at first a nucleus has to be formed which grows into a crystal. The driving force needed for this is the chemical potential $\Delta u$. It is represented by the equation

$$\Delta u = RT \ln \left( \frac{C}{C_e} \right) \quad -----(1-12)$$

Where $R$ is the gas constant
$T$ is the absolute temperature
$C$ is the concentration of the solution and
$C_e$ is the equilibrium concentration.
C/ $C_e$ is called the supersaturation.

When the supersaturation crosses a critical value, the nucleation starts. This supersaturation needed for the formation of a nucleus can be arrived at by cooling the solution, vaporizing the solvent or by adding solute. To form a stable nucleus the surface energy should be a minimum. The stability of the crystal will depend on the structure and size of the crystal.

The free energy $G_n$ needed for the formation of a nucleus with $n$ molecules is given by

$$G_n = (n-1)G_v + \frac{n^{2/3}-1}{(36)^{1/3}}$$

The critical size of the nucleus for stability is

$$n^* = \left(\frac{2m}{3G_v}\right)^{3/2}$$

Where $G_v$ is the free energy per atom and $\lambda$ is the latent heat.

The probability of the nucleus to grow is more when its size is more than the critical size. The rate of formation of stable nuclei is given by the equation

$$N^* = NkT/h \ exp \left(\frac{G^* + G_d}{kT}\right)$$

Where $k$ is the Boltzmann constant

$T$ is the absolute temperature

$N$ is the monomer density per unit volume

$G^*$ is the maximum free energy for the formation of monomer

$G_d$ is activation energy for dissolution and

$h$ is the Planck’s constant.

If the growth occurs with out the formation of new nuclei, the crystal grows to large size. This happens at low supersaturation below the critical value.
1.2.2.4.2 Solution Growth Techniques

There are different techniques used for the growth of crystals in solution growth. The important methods used are

(i) Low temperature solution Growth.
(ii) High temperature solution Growth.
(iii) Growth from gel.
(iv) Hydrothermal growth and
(v) Rapid growth.

(i) Low temperature solution Growth.

In this method the growth of the crystal is performed well below the boiling point of the solvent. The solubility of a material in a solvent depends on the temperature at constant pressure. The solubility is also influenced by the impurity and the pH of the solvent. A solvent in which the compound is moderately soluble is to be chosen for the growth. Crystallization of the material takes place when a saturated solution is cooled. It involves three stages

1. Attainment of super saturation
2. Formation of the critical nucleus and
3. Growth of the crystal

Super saturation of a solution with respect to a salt is a stage when the actual concentration becomes greater than the equilibrium concentration. Super saturation may be obtained by cooling or evaporation. In most of the solution growth techniques initially the solution is allowed to undergo slow evaporation or cooling to grow small crystals. In evaporation the solvent is allowed to evaporate and in cooling method solubility is reduced resulting in the crystallization. Using these small crystals as seed larger bulk crystals are grown. If the seed is introduced
into the meta stable zone it will continue to grow without causing spontaneous nucleation. The seed crystal may be rotated if necessary during the growth.

Many inorganic nonlinear optical crystals like sodium nitrate (NaNO₂), ammonium di hydrogen phosphate (ADP), potassium di hydrogen phosphate (KDP), KTP, barium nitrate (Ba(NO₃)₂), Lithium formate, strontium formate, sodium formate etc.[106-115] and organic nonlinear crystals like POM, MBA-NP, DAD, COANP, m-NA, DAN, MNA, MAP, MMONS, Benzophenone, Urea, NPPA, PNP, LAP, NMBA, NPP, APDA, Indole 3-aldehyde etc.[116-132] are grown using this technique. Commonly used solution growth techniques are

(a) Isothermal solvent evaporation
(b) Temperature lowering and
(c) Temperature difference

(a) Isothermal solvent evaporation

This is the simplest way to grow crystals for compounds, which are not sensitive to ambient conditions. And is suitable where there is sufficient material to prepare a few milliliters of saturated solution. To grow crystals a saturated or nearly saturated solution of the compound in a suitable solvent is to be prepared. The solution is stirred well and filtered. This is transferred into a petri dish or a glass beaker and is covered to avoid dust particles. The covering should not be airtight so that the evaporation takes place. This is then kept undisturbed for evaporation under ambient conditions. As the solvent evaporates nucleation takes place and the crystal grows.

(b) Temperature lowering technique

This method is applicable for materials that are less than moderately soluble in a solvent and the boiling point of the solvent is less than 100°C [133,134]. In this method a saturated solution of the compound is prepared at a temperature just
below the boiling point of the solvent. The solution is transferred to a clean vessel and is kept in a water bath with a temperature just below the boiling point of the solvent. The temperature of the water bath is slowly decreased by using an infrared lamp and contact thermometer set up. The crystal grows as the solution is slowly cooled. The apparatus used for the growth by temperature lowering method is shown in Fig. 1.5.

![Apparatus for crystal growth by temperature lowering](image)

(c) **Temperature difference.**

In this technique the solution is filled in two tanks and they are maintained at different temperatures. Super saturation for the growth is produced due to the difference in temperatures between the tanks. Saturated solution from the tank, which is kept at a higher temperature, is pumped into the growth tank, which is at a lower temperature for which the super saturation is maintained. It is then circulated to the first tank where it is re-saturated.
(ii) High Temperature Solution Growth

High temperature solution growth is also known as Flux growth. In this method crystals are grown at high temperature from molten salt solutions known as flux.

![Diagram of furnace used for high temperature solution growth](image)

Some of the single crystals grown by high temperature solution growth method are BaTiO₃ [135], KTP [136], PbTiO₃ [137], Fe₂ZnO₄, βBaB₂O₄ and LiB₃O₅ [138]. A diagram of the furnace used for high temperature solution growth is shown in Fig. 1.6.

Liquid phase epitaxy is another method of high temperature growth. This method is used for the deposition of material layers of micrometer thickness on substrates. The crystalline films produced by this method are used in devices for microwave, opto-electronics, magnetic bubble memory applications etc.

(iii) Growth from Gel

Gel is a highly viscous semi solid medium with micro pores in it. Crystal growth from various gels such as silica, gelatin, agar etc. had been studied [139]. For the growth of good quality single crystals silica hydro gel is found to be more suitable [140]. The turbulence and convection currents are very much less in gel medium. It is chemically inert and harmless and it allows a strain free crystal
growth. Precipitation is reduced as the nuclei are spatially separated. Growth stages can be observed and the method produces nearly defect free crystals [141]. Moreover the method is simple and inexpensive. Various types of crystals can be grown using this method [142-144].

(iv) Hydrothermal Growth

Hydrothermal Growth is a typical solution growth technique used for producing quartz crystals. It is very difficult to grow quartz crystals using melt or flux techniques because of its high melting point of 1670°C. Moreover it is having high chemical resistivity. To avoid twinning of the crystal, the growth process to produce single crystals of quartz must be done below its curie temperature. Hence the solution growth is conducted at high pressure and is called hydrothermal growth. Hydrothermal growth is conducted in steel pressure vessels called autoclaves. Typical operating temperature is between 300 and 400°C and pressure is between 700 to 1000 bars. The conditions are set to give the same effect under which naturally occurring materials are grown.

Potassium titanyl phosphate (KTiOP04), an interesting material with high resistance to laser damage and large NLO coefficient comparable to that of lithium niobate, is grown using hydrothermal method [145]. For the growth hydrothermal solution of 1.5 parts of KH2PO4 to 1 part TiO2 is prepared at 1250°C in platinum container. Crystals are grown in silver or gold cans in autoclaves at 1.5 to 1.8 kilo bars pressure and 520 °C to 560°C temperature at the rate of 0.2 to 1.8 mm per week. Using excellent solvents the growth is possible in the temperature range of 375°C to 425°C. At these temperatures steel autoclaves can be used.

Hydrothermal method is also used to grow crystals of gold, silver, platinum, cobalt, nickel, arsenic etc., which are used for electronic materials, and crystals of oxide superconductors. This method is useful to prepare refractory
materials at relatively low temperatures and also some of the most difficult to prepare materials.

High-pressure solution growth is used in recent years for the growth of crystals useful for the fabrication of light emitting diodes of blue, green and yellow colours [146,147]. GaN/GaInN diode has been developed [148,149]. The method can be used for the development of red nitride based diodes that are needed for the production of highly effective semiconductor sources of three basic colours of light red, green and blue manufactured on a single substrate [150].

(v) Rapid Growth

The rapid growth technique was initiated in the early 1980s with a view to grow very large single crystals of KDP and DKDP. The growth rate in this method is found to be more than an order of magnitude larger than that obtained by using traditional methods. Moreover the grown crystals are found to be of high optical quality. A pyramidal shaped seed crystal is used for the growth. The advantage in this method is that the crystal grows uniformly on both prismatic (100) and pyramidal (101) faces [151].

The apparatus used for the growth process is shown in Fig 1.7. It consists of a glass tank of 1000 L capacity placed in a controlled temperature bath. A square acrylic platform of size 60 x 60 cm² is used for the growth. The platform is rotated alternately in the clockwise and anticlockwise directions with a controlled acceleration, deceleration and rotation rates. A seed protector is also attached with the platform shaft. The system can be operated within a temperature range of 20°C to 80°C.
1.3 Aim and Objectives of the present work

There are various qualities required for a good NLO material. Since, it is highly difficult to get crystals that satisfy all the requirements needed for a good NLO material, the search for new materials satisfying most of these conditions needed for an efficient NLO material is still continuing. Amino acids are organic materials, which crystallizes in noncentrosymmetric structure. The wide transparency range in the UV and visible region due to the absence of strongly conjugated bonds, make them useful for NLO applications. Amino acids are more stable compared to other organic materials due to the proton donor carboxylic acid group and the proton acceptor amino group. They are potential candidates for harmonic generation. Most of the organic NLO crystals have weak Vander Walls and hydrogen bonds with conjugated electrons. Hence they are soft and difficult to process.

The physical properties of materials can be improved by forming their complexes. Glycine is the simplest amino acid and many complexes of glycine have been studied and reported. L-threonine is another amino acid, which
crystallizes in noncentrosymmetric structure with comparatively higher hardness and can be grown into large size. The mechanical hardness of glycine can be improved by forming suitable metal complexes.

The important objectives of the present investigation are:

(i) to grow metal complexes of amino acid glycine and pure L-threonine crystals in solution.
(ii) to characterize the solution grown crystals employing the techniques: powder XRD, FTIR, TG/DT and microhardness measurement.
(iii) to investigate the linear and nonlinear optical properties of glycine complexes and L-threonine crystals.
(iv) to investigate the electrical characteristics of glycine complexes and L-threonine crystals.
(v) to study the Raman absorption spectral characteristics.
(vi) to study the effect of high energy electron irradiation on the structure, electrical and optical characteristics.