CHAPTER 1

CRYSTAL GROWTH TECHNIQUES AND NONLINEAR OPTICS (NLO) – AN INTRODUCTION

1.1 A JOURNEY TO THE LAND OF CRYSTALS: HISTORY TO MODERN CIVILIZATION

Man had admired crystals for long, as he had appreciated their beauty. The gems and crystals have always attracted mankind and belief in the virtues of gems and some minerals, dates back to at least two thousand years. A crystal is a solid in which the constituent atoms, molecules, or ions are packed in a regularly ordered, repeating pattern extending in all three spatial dimensions. Crystals are the unacknowledged pillars of the world of modern technology.

Crystal growth can be regarded as an ancient subject, owing to the fact that the crystallization of salt and sugar was known to the ancient Indian and Chinese civilizations. There are examples of crystals grown in nature, which are the famous Amarnath Shivalinga of ice in Himalayan cave, large crystals grown around Dead Sea in Israel and gigantic mineral crystals in Naica caves, Chihuahua State of Mexico. Systematic studies of the symmetries of crystal with flat facets began in the 1700s, and the relationship to internal structure was confirmed by X-ray crystallography in the 1920s. However, the scientific approach to the field of crystal growth started in 1611 when Kepler correlated crystal morphology and structure, followed by Nicolous Steno, who explained the origin of variety of external forms.

Crystal growth is a highly interdisciplinary subject that demands the collaboration of physicists, chemists, biologists, engineers, crystallographers, process engineers, material scientists, and material engineers. The significance
of the beauty and rarity of crystals is now well knitted with their symmetry, molecular structure, purity and the physicochemical environment of their formation

Crystals grown nowadays find places ranging from microelectronics, optoelectronics, medical instruments, radar systems, communication systems, defence, and laser sources to the space vehicles viz., satellites. Progress in crystal growth and epitaxial technology is highly demanded in view of its essential role for the development of several important areas such as production of high efficient photovoltaic cells and detectors for alternative energy and the fabrication of bright long-lifetime light emitting diodes, for saving energy by wide use in illumination and traffic lights. The success of laser fusion depends on the timely development of high-power laser crystals and radiation-resistant frequency multiplying crystals of oxide compounds.

Buckley (1951) has elegantly put the matter, “It should be remembered that, in the preparation of large crystals, the touch of the artist is about as important as the application of established scientific principles”

The solid state materials can be classified as single crystals, polycrystals and amorphous materials depending upon the arrangement of constituent molecules, atoms or ions. Single crystals form the foundation for modern technology. The ordered array of atoms in repeated groups, showing characteristic symmetry elements, by which entire block of the material is built is called single crystal.

The pie chart in Figure 1.1 shows the overview of the worldwide crystal production. Many of the present-day instruments and devices used in various areas of science and technology, e.g., in electronics, optics, acoustics, and lasers incorporate single crystals of various materials in the shape of plates, fibers, tubes or rods of different cross sections.
1.2 TECHNIQUES OF CRYSTAL GROWTH

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

- Growth from solid $\rightarrow$ solid - solid phase transformation
- Growth from liquid $\rightarrow$ liquid - solid phase transformation
- Growth from vapour $\rightarrow$ vapour - solid phase transformation

The basic common principle in all these methods is that a nucleus is first formed and it grows into a single crystal by organizing and assembling ions or molecules with specific interactions and bonding, so that the process is slow and multiple nucleations is minimized. Figure 1.2 represents the various crystal growth methods.
Figure 1.2 Classification of crystal growth techniques

A survey of the methods of growth suggests that almost 80% of the single crystals are grown from the melt compared with roughly 5% from vapour, 5% from low temperature solution, 5% from high temperature solution, and 3% from the solid and only 2% by hydrothermal methods.
1.3 GROWTH FROM MELT

Growth from melt is by far the fastest of the growth methods, as its rate does not depend on mass transport process. All materials can be grown in single crystal form from the melt provided they melt congruently without decomposition at the melting point and do not undergo any phase transformation between the melting point and room temperature. The growth from melt can be further subdivided into the following techniques:

- Bridgman technique
- Czochralski technique
- Kyropoulos technique
- Zone melting and Normal Freezing technique
- Verneuil technique

1.4 GEL GROWTH

The growth of single crystals in gel is a self-purifying process free from thermal strains which are common in crystals grown from the melt. Crystal growth in gels is a promising technique for growing single crystals of substances which are slightly soluble in water and which cannot be grown conveniently from melt or vapour. The gel method has also been applied to study the crystal formation in urinary calculi and rheumatic diseases. Based on the nature of physical changes and chemical reactions involved in the growth process, gel method can be classified into four categories:

- Chemical reaction method
- Chemical reduction method
- Solubility reduction method
- Complex dilution method
1.5 GROWTH FROM VAPOUR

This is a method by which single crystals and epitaxial layers of high chemical purity and crystalline perfection may be obtained. The thickness and the doping of the layers can be closely controlled and the process can be recycled. But since the growth is slow, the method is not practical for bulk single crystals. Growth from vapour phase may generally be subdivided into two categories:

- Physical vapour transport
- Chemical vapour transport

1.6 GROWTH FROM SOLUTION

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

- High temperature solution growth
- Low temperature solution growth

1.6.1 High temperature solution growth

Flux and hydrothermal growths form the category of high temperature solution growth. In the growth of crystals from high - temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The supersaturation may be promoted by evaporation of the solvent, by cooling the solution or by a transport process in which the solute is made to flow from a hotter to a cooler region. The high temperature crystal growth can be divided into two major categories: first one is growth from single component systems and the second one is that from multi-components.
This technique can be used for the crystallization of oxide compounds which generally have high melting points as well as for materials which have phase transitions below the melting point. One major disadvantage of this method is the corrosive nature of the fluxes used, which attack the common furnace materials.

1.6.2 Low temperature solution growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. It is the most widely used method for the growth of single crystals, when the starting materials are unstable at high temperatures and also which undergo phase transformations below melting point. Materials having moderate to high solubility in temperature range, ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method. The mechanism of crystallization from solutions is governed, in addition to other factors, by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of ±0.01 °C. Due to the precise temperature control, supersaturation can be very accurately controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be
grown by variations of growth conditions or of solvent. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low. Three principal methods are used to produce the required supersaturation.

- Slow cooling of the solution
- Slow evaporation of the solvent
- The Temperature gradient method.

1.6.2.1 Slow cooling technique

This is the most suitable method among various methods of solution growth. The main limitation is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Even though the method has technical difficulty of requiring a programmable temperature control, it is widely used with great success. The temperature at which crystallization can begin is usually within the range 45 - 75 °C and the lower limit of cooling is the room temperature.
1.6.2.2 Slow evaporation method

This method is similar to the slow cooling method in view of the apparatus requirements (Figure 1.3). The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ± 0.005 °C and rates of evaporation of a few ml /hr. The evaporation techniques of crystal growth have the advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one, which can be used with materials, which have very small temperature coefficient of stability.

Figure 1.3 Slow evaporation crystal growth

1.6.2.3 Temperature gradient method

This method involves the transport of the materials from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are:

- Crystal grows at a fixed temperature
- This method is insensitive to changes in temperature provided both the
source and the growing crystal undergo the same change.

- Economy of solvent and solute

On the other hand, changes in the small temperature differences between the source and the crystal zones have a large effect on the growth rate. Excellent quality crystals of ferroelectric and piezo-electric materials such as Ammonium dihydrogen phosphate (ADP), Potassium dihydrogen phosphate (KDP) and Triglycine sulphate (TGS) are commercially grown for use in devices by the low temperature solution growth method.

1.7 OPTIMIZING SOLUTION GROWTH

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

1.7.1 Material purification

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

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and the one which gets dissolved in the solvent. For a given solute, there may be different solvents. The solvent must be chosen taking into account the following factors to grow crystals from solution: (i) a good solubility for the given solute, (ii) a good temperature coefficient of solute solubility, (iii) less viscosity and less volatality, (iv) less corrosion and non-toxicity and (v) cost effective.

It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Solvents commonly used include light water (H$_2$O), heavy water (D$_2$O), ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many others. Almost 90% of the crystals produced from low temperature solutions are grown by using water as solvent as water has high dielectric constant, stability, low viscosity, low toxicity and abundant availability.

1.7.3 Solubility

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and lower solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution. Low temperature solution growth is mainly a diffusion-controlled process; the medium must be less viscous to enable
faster transfer of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process.

The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. The solubility of the solute can be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. On reaching saturation, equilibrium concentration of the solute can be determined gravimetrically. A sample of the clear supernatant liquid is withdrawn by means of a warmed pipette and a weighed quantity of the sample is analyzed. By repeating the above procedure for different temperatures, the solubility curve can be plotted. Solubility of most substances increases with temperature (the temperature coefficient of solubility is positive).

1.7.4 Solution preparation and crystal growth

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

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

1.7.6 Agitation

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

1.7.7 Crystal habit

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

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

1.8 INTRODUCTION TO NONLINEAR OPTICS

Before the advent of lasers, it was assumed that the optical parameters of the medium were independent of the intensity of the light propagating in that medium. The electric field strength generated by the non laser light sources is of the order of $10^3$ V/cm, which is very much smaller than the inter-atomic fields of the order of $10^7$ to $10^{10}$ V/cm. Therefore, normal light source is unable to affect the atomic fields of the medium and thereby the optical properties of the medium. On the other hand, lasers generate electric field strength of the order of $10^5$ to $10^9$ V/cm, which is able to commensurate to that of the atomic electric fields of the medium. This affects the optical properties of the medium and thus generates new electromagnetic fields altered in phase, frequency and amplitude. The first demonstration of Nonlinear Optical (NLO) frequency conversion took place as early as 1961 by
Franken et al. They used quartz crystal to double the frequency of 694 nm light of Ruby laser.

1.9 NONLINEAR OPTICAL PHENOMENON

Nonlinear optics is completely a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be understood, only if the nature of the electrons in nonlinear optical crystal is studied. Electrons in a nonlinear crystal are bound in potential well, which acts like a spring, holding the electrons to lattice point in the crystal (Figure 1.4). 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 springs’ restoring force increases linearly with the electron displacement from its equilibrium position. The electric field in a light wave passing through the crystal exerts a force on the electrons and pulls them away from their equilibrium position. In an ordinary optical material, the electrons oscillate about their equilibrium position at the frequency of this electronic field. According to the fundamental law of physics, an oscillating charge will radiate at its frequency of oscillation, hence these electrons in the crystal “generate” light at the frequency of the original light wave.

The nonlinear optical material is different from the linear one in several aspects. The nonlinear optical material can be considered as the one whose electrons are bound by very short springs as shown in Figure 1.4. If the light passing through the material is intense enough, its electric field can pull the electrons so far that they reach the end of their springs. Then, the restoring force is no longer proportional to the displacement and then it becomes nonlinear. The electrons bounce back roughly rather than pulled back smoothly and they oscillate at frequencies other than the driving frequency of the light wave. These electrons radiate at new frequencies, generating new
wavelength of light. The exact values of the new wavelengths are determined by conservation of energy. The energy of the new photons generated by the nonlinear interaction must be equal to the energy of the photon used. Figure 1.5 shows the photons involved in the second harmonic generation process.

Figure 1.4 Electrons in a nonlinear crystal are bound in a potential well, holding the electrons to lattice points in a crystal

Figure 1.5 Two photons are welded together to produce a single photon with the energy of both original photons
1.10 THEORETICAL EXPLANATION OF NONLINEAR OPTICS

In a nonlinear medium, the induced polarization is a nonlinear function of the applied field \( \varepsilon \). 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 \( P \) is directly proportional to the electric field as shown in equation (1.1):

\[
P = \varepsilon_0 \chi \varepsilon
\]  

(1.1)

where ‘\( \chi \)’ is the linear susceptibility of the material, ‘\( \varepsilon \)’ 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 as shown in equation (1.2).

\[
P = \varepsilon_0 \chi^{(1)} \varepsilon + \chi^{(2)} \varepsilon \varepsilon + \chi^{(3)} \varepsilon \varepsilon \varepsilon + \ldots \]

(1.2)

In nonlinear terms, product of two or more oscillating fields gives oscillation at combination of frequencies and therefore, the above equation can be expressed in terms of frequency as shown in equation (1.3):

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

(1.3)

Where \( \chi^{(2)} \), \( \chi^{(3)} \) ........ are the nonlinear susceptibilities of the medium. The induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients of \( \chi^{(1)} \), \( \chi^{(2)} \), and \( \chi^{(3)} \) give rise to certain optical effects, which are listed in Table 1.1.

At the molecular level equation (1.2) is expressed as,
\[
P = \sum_{j} \alpha_{ij} E + \sum_{j<k} \beta_{ijk} E^2 + \sum_{j<k<l} \gamma_{ijkl} E^3 + \ldots \quad (1.4)
\]

Where, \( \alpha_{ij} \) = Polarizability, \( \beta_{ijk} \) = First hyper-polarizability (second order effects), \( \gamma_{ijkl} \) = second hyper-polarizability (third order effects) and \( i, j, k, l \) corresponds to the molecular coordinates. Table 1.1 shows the various optical effects of nonlinear materials.

**Table 1.1 Optical effects of nonlinear materials**

<table>
<thead>
<tr>
<th>Order</th>
<th>Susceptibility</th>
<th>Optical effects</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \chi^{(1)} )</td>
<td>Refraction, dispersion, Birefringence, absorption</td>
<td>Optical fibers</td>
</tr>
<tr>
<td>2</td>
<td>( \chi^{(2)} )</td>
<td>Second Harmonic Generation ((\omega + \omega = 2\omega))</td>
<td>Frequency doubling</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Frequency mixing ((\omega_1 + \omega_2 = \omega_3))</td>
<td>Optical parametric oscillators</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pockels effects ((\omega + 0 = \omega))</td>
<td>Electro-optical modulators</td>
</tr>
<tr>
<td>3</td>
<td>( \chi^{(3)} )</td>
<td>Third harmonic generation Four wave mixing phase gratings</td>
<td>Raman coherent spectroscopy; Real time holography</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kerr effect</td>
<td>Ultra high speed optical gates</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Optical amplitude</td>
<td>Amplifiers, choppers etc.</td>
</tr>
</tbody>
</table>

If the molecule or crystal is centrosymmetric, then \( \chi^{(2)} = 0 \). If a field \( +E \) is applied to the molecule (or medium), equation (1.3) predicts that the polarization induced by the first nonlinear term is predicted to be \( +E^2 \), yet if the medium is centrosymmetric, the polarization should be \( -E^2 \). This contradiction can only be resolved if \( \chi^{(2)} = 0 \) in centrosymmetric media.
If the same argument is used for the next higher order term, $+E$ produces polarization $+E^3$ and $-E$ produces $-E^3$, so that $\chi^{(3)}$ is the first non-zero nonlinear term in centrosymmetric media. In second harmonic generation, the two input wavelengths are the same, $2\omega_1 = \omega_2$ or $(\lambda_1 = \lambda_2)$. During this process, a polarized wave at the second harmonic frequency $2\omega_1$ is produced. The refractive index, $n_1$ is defined by the phase velocity and wavelength of the medium. The energy of the polarized wave is transferred to the electromagnetic wave at a frequency $\omega_2$.

In order to obtain high conversion efficiency, the phase vectors of input beams and generated beams have to be matched,

$$\Delta k = k_3 - k_2 - k_1 = 2\pi (n_3/\lambda_3 - n_2/\lambda_2 - n_1/\lambda_1) = 0$$  \hspace{1cm} (1.5)

Where, ‘$\Delta k$’ is phase mismatching, ‘$k_i$’ is phase vector at ‘$\lambda_i$’ and ‘$n_i$’ is refractive index at ‘$\lambda_i$’. In low power case, the relationship between conversion efficiency and phase mismatching is given in equation (1.6):

$$\eta \propto P L^2 (d_{\text{eff}} \sin (\Delta k L)/\Delta k L)^2$$  \hspace{1cm} (1.6)

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. The parameters for selecting a NLO crystal are depicted in Table 1.2.

<table>
<thead>
<tr>
<th>Laser parameters</th>
<th>Crystal parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>NLO process</td>
<td>Type of phase matching</td>
</tr>
<tr>
<td>Power, Repetition rate</td>
<td>Damage threshold</td>
</tr>
<tr>
<td>Divergence</td>
<td>Acceptance angle</td>
</tr>
<tr>
<td>Bandwidth</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 mismatch</td>
</tr>
<tr>
<td>Environment</td>
<td>Moisture, temperature acceptance</td>
</tr>
</tbody>
</table>
1.11 NONLINEAR OPTICAL MATERIALS

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

• Discovery of new NLO materials
• Growth of promising NLO crystals
• Improving the characteristics of NLO crystals

For an NLO crystal device to work well without degradation of its performance over the lifetime of its assignment, the following criteria are required to be fulfilled:

• Wide optical transparency domain
• Large nonlinear figure of merit for frequency conversion
• High laser damage threshold
• Ready availability in large single crystals, thin films, etc.
• Wide phase matchable angle
• Ease of fabrication
• Nontoxicity and good environmental stability
• High mechanical strength and thermal stability and
• Fast optical response time.

1.12 SCOPE AND OBJECTIVES OF THE THESIS

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

In recent years, efforts have been made to synthesize amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold, linear and nonlinear optical properties.

In the present work the amino-acid L-valine has been selected and its organic-inorganic complexes have been synthesized using slow evaporation solution growth technique at low temperature. The aim of the present study is to identify novel NLO materials using L-valine.

Dicarboxylic oxalic acid has been incorporated with potassium hydroxide to explore their NLO properties. Semiorganic crystals of Potassium hydrogen oxalate and Magnesium sulphate doped in Potassium borooxalate have been grown using slow evaporation solution growth technique at low temperature.

The present investigation is aimed at:

- Growing bulk sized crystals.
- Identifying and solving the crystal structure by XRD single crystal diffraction analysis.
- Analysing the grown crystal for its percentage elemental composition, optical transmission/absorption, NLO property, laser damage threshold, hardness, dielectric property, and photoconductivity.
- Studying the thermal behaviour of the grown crystals.