Chapter 1

CRYSTAL GROWTH, NON LINEAR OPTICAL PHENOMENON AND CHARACTERISATION TECHNIQUES
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1.1 INTRODUCTION

The regular surface geometry, the shining faces and often colourful appearance have made crystals from the mineral kingdom fascinating objects for everybody. Nowadays crystals are produced artificially to satisfy the needs of science and technology. The ability to grow high quality crystals has become an essential criterion for the competitiveness of nations. Crystal growth specialists have been moved from the periphery to the centre of the material based technology.

Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, crystallography, electrical engineering, mineralogy, metallurgy etc. Large size single crystals are essential for the development of material science research. Several important fields like microelectronics, optoelectronics, lasers and biosensors require single crystals.

New crystalline materials are the life blood of solid state research and device technology. New materials are not usually discovered by device engineers or solid state researchers but are mostly discovered by crystal chemists [1]. Nonlinear optics remains unexplored until the discovery of second harmonic generation in 1961 by Peter Franken [2].
Prospects of crystal growth in the twenty first century led to the discovery of new nonlinear optical (NLO) materials. NLO materials have a great impact on information technology and on industrial applications and they have become an alternative field to electronics for the future photonic technologies. NLO materials typically have a distinct crystal structure which is anisotropic with respect to electromagnetic radiation. Initially, investigations were made on inorganic materials, which were the first solids to show NLO properties. Later the attention shifted towards organic materials due to their low cost, large nonlinear response over a broad frequency range, fast optical response time, architectural flexibility for molecular design, high laser damage threshold and ease of fabrication.

These molecular organic compounds with one or more aromatic systems in conjugated positions have been intensely studied [3]. Kerkoc [4] and Dmitriev [5] have investigated the nonlinear behavior of organic NLO materials theoretically and experimentally. The conjugated π electron system provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the π conjugated system with appropriate electron donor and acceptor groups can increase the asymmetric electron distribution in either or both the ground and excited states leading to an increased optical nonlinearity [6], but the nonlinearity in inorganic crystals is poor. Due to the various technological applications of NLO crystals, it is essential to synthesize new NLO materials in bulk form.
Amino acids are interesting materials for NLO applications [7-9], this is because of the presence of chiral carbon atom and non centrosymmetric space groups in the structure [10,11]. Amino acids in general have carboxylic group (COO\(^-\)) and amine group (NH\(_2\)^+). Due to this dipolar nature amino acids possess peculiar physical and chemical properties making them an ideal candidate for NLO applications. Amino acids and their organic complexes were studied extensively and they were found to have high SHG property.

Hence, good quality single crystals are needed to achieve better performance from the devices. The growth of single crystals and their characterisations towards device fabrication have assumed great impetus due to their importance for both academic and applied research. In the present work crystals of L-Aspartic acid have been grown by slow cooling method and the crystals of L-Histidinium 2 Nitrobenzoate, 4 Carboxyanilinium bromide and Ammonium hydrogen oxalate hemihydrate were grown using slow evaporation method.

1.2 METHODS OF CRYSTAL GROWTH

The choice of suitable methods of crystal growth is mainly influenced by simple, inexpensive and the crystallization time. It is a two stage process, the first step is the formation of microscopic nucleus in the supersaturated solution and the second stage is the successive growth on this nucleus yielding bulk crystal.

The growth of crystals can be achieved by controlling the phase change and is classified as,
1) Solid growth (solid to solid phase transition)

2) Vapour growth (vapour to solid phase transition)

3) Liquid growth – melt & solution (liquid to solid phase transition)

Growth of defect free crystals is an art and it essentially involves heat and mass transfer phenomena as well as convection effects. Therefore, appropriate control of fluid dynamics and a good understanding of the convection phenomena are very important for the growth of good quality crystals.

**Solution Growth**

Growth from solution can be achieved using appropriate solvent, in which crystals can grow after the solution is supersaturated by lowering the temperature. In all the growth methods, the nucleus forms first and it grows into a single crystal by coordinating and assembling molecules and ions by suitable interactions and bondings. Among the various techniques of crystal growth, solution growth technique is simple and inexpensive. In solution growth technique, materials can undergo a phase transformation between the melting point and room temperature.

Solution growth can be classified into,

1) High temperature solution growth (Flux growth)

2) Hydrothermal growth

3) Gel growth and

4) Low temperature solution growth.
In the present work, low temperature solution growth method is employed to grow the crystals by considering its importance.

1.2.1 Low Temperature Solution Growth

Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versatility and simplicity. A variety of crystals can be grown by this technique at room temperature. Though the technology of crystal growth from solution has been well perfected, it involves meticulous work and much patience.

In this method, a saturated solution of the material is prepared in a suitable solvent and crystallization is initiated by slow cooling of the solution or by slow evaporation of the solvent. Crystals grown by this method has many advantages, due to the slow rate of crystallization the structural imperfections are relatively low [12]. In the low temperature solution growth, crystals can be obtained by supersaturation through any one of the methods.

1) Slow cooling of the solution
2) Slow evaporation of the solvent
3) Temperature gradient method.

1.2.2 Slow Cooling Method

The slow cooling method is the most suitable method to grow bulk crystals. The supersaturation of the systematic cooling requires the volume of
the crystallizer to be finite and the amount of substance in it is limited. However, the limitation of the slow cooling method is the need to use a range of temperatures. The possible range of temperature is usually small and hence much of the solute remains in the solution at the end of the growth run. To compensate, large volumes of solution is required. Though the method has technical difficulty of requiring a programmable temperature control, yet it is widely used with great success. The temperature at which such crystallization can begin is usually within the range 45 °C – 75 °C and the lower limit of cooling is the room temperature.

1.2.3 Slow Evaporation Method

Substances that are either moderately soluble at room temperature or unstable at higher temperatures are good candidates for crystal growth by slow evaporation technique. Slow cooling and slow evaporation methods are similar according to their apparatus requirements. In this method, the saturated solution is kept at a particular temperature and provision is made for evaporation. In this method, an excess of given solute is established by utilizing the difference between the rate of evaporation of the solvent and the solute. In slow evaporation method, the solution losses particles which are weakly bound to other molecules and therefore, the volume of the solution decreases. The solvent evaporates more rapidly and the solution becomes super saturated.
1.2.4 Temperature Gradient Method

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

a) the growth of crystal at a constant temperature

b) the minimum quantity of solvent and solute

c) it is insensitive to changes in temperature

1.3 OPTIMIZATION OF GROWTH PARAMETERS

The growth of good quality single crystals by slow evaporation and slow cooling techniques require the optimized conditions. Crystallization from the solution exists in two steps. The first step involves in phase separation and second step involves the growth of the crystal of large size. It is also a particle formation process by which molecules in solution or vapour are transformed into a solid phase of a regular lattice structure, which is reflected on the external crystal faces. Crystallization may be further described as a self-assembly molecular building process [13].

Nucleation

Nucleation occurs through the formation of small clusters of the new phase inside the large volume of the old phase. Nucleation can be pushed by agitation, shearing action, crystal breakage and pressure changes. Nucleation is classified into two types namely primary and secondary nucleation. The term
‘primary’ nucleation can be reserved for all cases that do not contain foreign particles. On the other hand, secondary nucleation process involves the dislodgement of nuclei from the parent crystal at supersaturation in which the primary homogeneous nucleation would not occur.

1.4 SOLVENT AND SOLUBILITY

The solution is a homogeneous mixture of solute in a solvent. The solubility of a substance in a solvent is the maximum concentration that can exist in equilibrium at a given set of conditions. An ideal solution should possess significant solubility, low volatility, low viscosity, good solubility gradient, no corrosion of growth apparatus and low vapour pressure at the growth temperature. If the solubility is too high, it is very difficult to grow bulk size crystals and since the solution is directly related to the solubility of the substance and the selection of solvent are very important. Changes in the degree of supersaturation, solvent, etc., may lead to dramatic habit modifications in crystal morphology [14]. The solubility of a substance mostly increases with respect to solution temperature and rarely decreases. The state of supersaturation is an essential requirement for all crystallization processes. The terms ‘labile’ and ‘metastable’ supersaturation are introduced by Ostwald [15] to classify the supersaturated solutions in which spontaneous nucleation may or may not occur.
The equilibrium phase diagram or solubility–super solubility diagram shown in Figure 1.1 provides a useful starting point for crystallization. It can be divided into three zones as region I, region II and region III. Region I corresponds to the undersaturated region where crystallization is not possible. The region between the super solubility curve and solubility curve is termed as metastable zone (region II) and seeded growth may be initiated in this region. The unstable or labile zone (region III) is the region where the spontaneous nucleation takes place. If a solution, whose concentration and temperature are represented by point A in Figure 1.1 is cooled without loss of solvent (line ABC), spontaneous crystallization cannot occur until the conditions represented by point C are reached.

At this point, crystallization may be spontaneous or it may be induced by seeding, agitation or mechanical shock. Further, cooling to point D may be necessary before crystallization, especially with very soluble substances. Supersaturation can also be achieved by removing some of the solvent from the solution by evaporation. Line $AB'C'$ represents such that an operation can be carried out at a constant temperature. Penetration beyond the supersolubility curve into the labile zone rarely happens, as the surface from which evaporation takes place is usually supersaturated to a greater degree than the bulk of the solution. Crystals which appear on this surface eventually fall into the solution and seed it, often before conditions represented by point $C'$ are reached in the bulk of the solution. In practice, a combination of cooling and evaporation is employed (line $AB'C'$).
Figure 1.1 Solubility–Super solubility diagram
Expression for Supersaturation

The degree of supersaturation ($\alpha$) of a solution is defined using the concept of absolute supersaturation.

$$\alpha = C - C_o$$  \hspace{1cm} (1.1)

Where, $C$ is the solution concentration and $C_o$ is its solubility limit. If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known then it is easier to calculate the degree of supersaturation from the relative supersaturation ($\beta$) as,

$$\beta = \frac{C - C_o}{C_o} = \frac{\alpha}{C_o}$$  \hspace{1cm} (1.2)

or the coefficient of supersaturation ($\gamma$) is given as

$$\gamma = \frac{C}{C_o} = \beta + 1 = \frac{\alpha}{C_o} + 1$$  \hspace{1cm} (1.3)

the quantities $\alpha$, $\beta$ and $\gamma$ are obviously interrelated.

1.5 THE PHENOMENON OF NONLINEAR OPTICS

Nonlinear optics is the study of phenomena that occur as a consequence of the modification of the optical properties of a material system in the presence of light. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. In fact, the beginning of the field of nonlinear optics is often taken to be the discovery of second harmonic generation by Franken et al in 1961, shortly after the demonstration of the first working laser by Maiman in 1960 [16].
The process of two photons of same frequency, converted into a single photon of doubled frequency is known as second harmonic generation. Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied field depends in a nonlinear manner upon the strength of the field. Nonlinear optics (NLO) is the branch of science dealing with nonlinear action of light coupling to matter leading to polarization. Polarization (P) or macroscopic polarization can be achieved if low electric field (E) is applied on the bulk medium, which is linearly related with susceptibility ($\chi$).

At high fields, the contribution of nonlinear (second and higher order) terms becomes significant. Another inception of potential nonlinear response on optical material to light depends on the density of the optical field. The most commonly used nonlinear optical effects are frequency doubling and electro-optic modulation. For second order nonlinear optical effects, including sum and difference frequency generations, optical parametric amplification and of photorefractive effects, the medium should be an asymmetric system.

The phenomenon of nonlinear optical effect is understood by considering the process of the dielectric material at the atomic level to the electric fields of an intense light beam. The propagation of the wave through a material produces the spatial and temporal distribution of electrical charges as electrons and atoms react with electromagnetic field of the wave. In linear optics, the induced polarization (P) is directly proportional to the applied electric field (E).

$$P = \varepsilon_0 \chi^{(1)} E^{(1)}$$  \hspace{1cm} (1.4)
where the constant of proportionality $\chi^{(1)}$ is known as the linear susceptibility and $\varepsilon_0$ is the permittivity of free space. In nonlinear optics, the optical response can often be described by generalizing Eq. (1.4) by expressing the polarization $P(t)$ as a power series in the field strength $E(t)$ as [17]

$$P(t) = \varepsilon_0 \left[ \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \ldots \right] \quad (1.5)$$

The quantities $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second order and third-order nonlinear optical susceptibilities. The electric field in Equation (1.5) is $E = E_0 \cos \omega t$ where $\omega$ is the angular frequency of the light. Equation (1.5) then becomes,

$$P(t) = \varepsilon_0 \left[ \chi^{(1)} E_0 \cos \omega t + \chi^{(2)} E_0^2 \cos^2 \omega t + \chi^{(3)} E_0^3 \cos^3 \omega t + \ldots \right] \quad (1.6)$$

Trigonometric substitution can be made for the $\cos^2 \omega t$ and $\cos^3 \omega t$

$$\cos^2 \omega t = \frac{1}{2} + \frac{1}{2} \cos 2\omega t \quad (1.7)$$

$$\cos^3 \omega t = \frac{3}{4} \cos \omega t + \frac{1}{4} \cos 3\omega t \quad (1.8)$$

So that equation (1.6) becomes

$$P(t) = \varepsilon_0 \left[ \chi^{(1)} E_0 \cos \omega t + \frac{1}{2} \chi^{(2)} E_0^2 \cos 2\omega t + \frac{3}{4} \chi^{(3)} E_0^3 \cos 3\omega t + \frac{1}{4} \chi^{(3)} E_0^3 \cos 3\omega t \right] \quad (1.9)$$

This leads to an interesting conclusion since the third term in equation (1.9) contains a term with an order of $2\omega$, one component of the charge polarization equation is at twice the fundamental frequency of the original laser.
beam. As the incident beam falls on the crystal, oscillating electric dipoles absorb light at a frequency $\omega$ and reradiate it at the same frequency $\omega$ and at twice the original frequency $2\omega$. The total energy of the beam is not altered much, but is now split into two components. This is the second harmonic of the original beam and the effect is called second-harmonic generation [18].

The fifth term in equation (1.9) describes a response at frequency $3\omega$, that is created by an applied field at frequency $\omega$. This term leads to the process of third-harmonic generation (THG). The fourth term in equation (1.9) describes a nonlinear contribution to the polarization at the frequency of the incident field, this term hence leads to a nonlinear contribution to the refractive index experienced by a wave at frequency $\omega$. The variation of refractive index with respect to intensity is called optical Kerr effect.

The propagation characteristics of the incident light beam are affected by self-action nonlinear effects. They are due to nonlinear polarizations that are at the same frequency as that of the incident light wave. Depending on the particular effect, they can change the direction of propagation, the degree of focusing, the state of polarization or the bandwidth of the incident radiation. Self-action effects can also change the amount of absorption of an incident radiation. The most common self-action effects arise from third order interactions. The various types of self-action effects depend on whether the susceptibility is real or imaginary and on the temporal and spatial distributions of the incident light. The real part of the nonlinear susceptibility gives rise to the spatial effects of self-focusing and self-defocusing. The imaginary part of
the susceptibility causes nonlinear absorption. The important self-action effects are self-focusing, self-defocusing and saturable absorption.

a) Self-focusing is one of the processes that can occur as a result of the intensity dependent refractive index, when a beam of light having a non-uniform transverse intensity distribution propagates through a material for which nonlinear refractive index is positive. Under these conditions, the material effectively acts as a positive focal lens, which causes the rays to curve toward each other. This process is of great practical importance because the intensity at the focal spot of the self-focused beam is usually sufficiently large due to decrease in the beam radius.

b) Self-defocusing is a process that results from a combination of a negative value of nonlinear refractive index and a beam profile that is more intense at the center than at the edge. The refractive index is smaller at the center of the beam than at the edge, resulting in a short optical path for rays at the center than for those at the edge. This same condition can exist for propagation through a negative focal lens and the beam gets defocused.

c) Saturable absorption involves a decrease in absorption at high optical intensities and it is usually observed in materials that are strongly absorbing at low light intensities. The dependence of the measured absorption coefficient $\alpha$ on the intensity $I$ of the incident laser radiation is given by the expression:
\[ \alpha \frac{\alpha_s}{1 + I/I_s} \]  \hspace{1cm} (1.10)

Where \( \alpha_o \) is the low-intensity absorption coefficient and \( I_s \) is a parameter known as the saturation intensity. The saturable absorption occurs when the upper state of the absorbing transition gains enough population to become filled, preventing the transfer of any more population into it [19].

1.5.1 Experimental technique used for second and third order NLO studies

a) Second order nonlinear optical study

The Kurtz powder technique [20] is a convenient method for screening large number of powdered materials for the second harmonic generation efficiency of crystals. A schematic diagram of second harmonic generation setup is shown in Figure 1.2. The Nd:YAG laser source with 1064 nm is directed onto a powdered sample and the emitted light is collected, filtered and detected with a photo multiplier tube. The pulse energy of 5.65 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used in the present investigation. At high fields, polarization becomes independent of the field and the susceptibility becomes field dependent. Therefore, the nonlinear response can often be described by generalizing the Equation (1.9) and expressing the polarization \( P(t) \) as a power series in field strength \( E(t) \) [21].

b) Third order nonlinear optical study

The Z-scan method is a standard technique for the accurate measurement of intensity dependent nonlinear susceptibilities, nonlinear
refractive index (NLR) $n_2$ and the nonlinear absorption coefficient (NLA) $\beta$. The schematic diagram of Z-scan technique is as shown in Figure 1.3. In this method, the sample is translated in the Z-direction along the axis of a focused Gaussian beam from the He-Ne laser at 632.8 nm and the far field intensity is measured as a function of the sample position. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), one can be able to determine the amplitude of the phase shift. By moving the sample through the focus, the intensity dependent absorption of the sample without placing an aperture at the detector (open aperture) can be measured. When both the methods (open and closed) are used for the measurements, the ratio of the signals determines the nonlinear refraction of the sample.

A typical closed aperture Z-scan output for a thin sample exhibiting nonlinear refraction, is shown in Figure 1.4 (solid line). From the Figure 1.4 (solid line), a self-focusing nonlinearity, $\Delta n>0$, results in a valley followed by a peak in the normalized transmittance as the sample is moved away from the lens. The normalization is performed in such a way that the transmittance is unity for the sample at far from focus where the nonlinearity is negligible. The positive lensing in the sample placed before the focus moves the focal position closer to the sample resulting in a greater far field divergence and a reduced aperture transmittance. On the other hand, with the sample placed after focus, the same positive lensing reduces the far field divergence allowing for a larger aperture transmittance. The opposite side of curve occurs for a self-defocusing nonlinearity, $\Delta n<0$ (Figure 1.4, dotted line) [22].
Figure 1.2 Schematic diagram of SHG experimental set up

Figure 1.3 Schematic diagram of Z-scan technique
Figure 1.4 A typical Z-scan curve for positive (solid line) and negative (dashed line) third-order nonlinear refraction.
1.6  A REVIEW ON THE DEVELOPMENT OF NONLINEAR OPTICAL CRYSTALS

After the invention of lasers, the investigation towards optical properties of materials has been drastically increased. A typical SHG material must have a noncentrosymmetric crystal system. The symmetry requirement eliminates many materials as SHG active and hence the modification of crystal structure by synthesis may be important. Nonlinear optical crystals can be classified according to the composition of materials as inorganic, organic and semiorganics.

1.6.1 Inorganic NLO crystals

Inorganic materials possess high mechanical and thermal stability, but most of them have low nonlinear efficiency. After the invention of lasers, research on nonlinear optical phenomena in crystalline materials emerged highly and the nonlinear effect in inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO₃), potassium titanyl phosphate (KTP) and semiconductor crystals have been observed. Potassium dihydrogen phosphate is one of the most widely used crystal for second harmonic generation due to the wide transparency range, good birefringence and moderate optical damage density. However, the less hygroscopic nature of KDP limits the applications. After many attempts, good nonlinear borate crystals have been discovered with wide transparency window and the first nonlinear optical borate series crystal is potassium pentaborate (KB₅) [23]. As the consequence of this, many number of crystals have been grown and
investigated in this family and among them, calcium gadolinium oxoborate $\text{GdCa}_4\text{O(BO}_3\text{)}_3$ (GdCOB) and yttrium calcium oxoborate $\text{YCa}_4\text{O(BO}_3\text{)}_3$ (YCOB) have attracted more attention due to their promising optical properties [24].

The family of various borate crystals thus plays a very important role in the field of nonlinear optics. Halasyamani and Poeppelmeier [25] have reported the series of polar oxide inorganic materials synthesized in noncentrosymmetric structure with cations susceptible, known as Second Order Jahn Teller (SOJT) distortions. Though inorganic materials posses good mechanical and thermal stabilities, the optical nonlinearity is relatively lower than organic materials. The growth of inorganic crystals is usually more difficult and typically adopts high temperature growth techniques.

1.6.2 Organic NLO crystals

The search for new NLO materials over the past two decades has concentrated primarily on organic compounds owing to their large nonlinearity. The organic compounds with the delocalized conjugated electrons have excellent nonlinear optical property and high-speed responsiveness due to high mobility of electrons.

The advantages of organic nonlinear optical materials are,

i) High nonlinear optical efficiency

ii) Birefringence used for phase matching and

iii) Possibility to chemically engineer the molecular properties.
The superiority of organic NLO materials result from their versatility and possibility of tailoring them for a particular device application. Organic NLO materials have high figure of merit for frequency conversion, high laser damage threshold (LDT) and fast optical response time as compared within organic NLO materials [26]. Recently, Saravana Kumar et al have grown N, N′ – Diphenyl guanidinium nitrate one of the potential organic NLO material by slow evaporation method and its SHG efficiency is 4.2 times that of KDP. The SHG efficiency of 4-methylanilinium p-toluenesulfonate single crystals grown using ethanol as solvent was found to be higher than urea and KDP. Single crystals of p-toluidinium p-toluenesulphonate are grown by slow evaporation technique and its SHG efficiency is 1.8 times than that of KDP.

With the progress in crystal growth technology, organic materials having attractive nonlinear properties are being discovered at a rapid pace [27]. However, there are some drawbacks with organic NLO materials. The growth of large size single crystal is of great challenge and in general, the mechanical properties of organic solids are poor.

1.6.3 Semiorganic NLO crystals

Organic and inorganic materials have increased attention due to its rapid technological advances in various fields, such as laser technology, ultrafast phenomena, fiber optics, optical communication and data storage technology. The advantage of semiorganic crystals is that the bonding schemes are three dimensional, unlike polar organic crystals. L-Arginine phosphate monohydrate (LAP) crystals have attracted many researchers because of their high
nonlinearity, wide transmission range, high conversion efficiency and high damage threshold. The SHG efficiency of L-Arginine fluoride single crystal is 5.6 times greater than that of KDP [28]. The SHG efficiency of L-lysine 4-nitrophenolate monohydrate is 1.4 times greater than that of standard KDP [29].

Recent investigation shows that inorganic and organic materials have been replaced by semiorganic materials. In recent years, the crystal research is concentrated on semiorganic materials due to their large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [30,31].

1.7 CHARACTERISATION TECHNIQUES

1.7.1 Single and Powder crystal X-ray diffraction

X-rays used as a tool for investigating the crystal structure was first suggested by Von Laue in 1912 and further developed by Bragg. X-ray diffraction has provided a wealth of information to science and technology because it is based upon the fact that an X-ray diffraction pattern is unique for each crystalline substance.

Single crystal X-ray diffraction is a powerful technique, used to study the structure of solids (organic, inorganic, Semiorganic), which provides accurate and precise measurements about the internal lattice of crystalline substances, including unit cell dimensions, structure of the crystal, bond-lengths, bond-angles, molecular orientation, morphology and packing of
molecules. Single crystal X-ray diffractometer (MESSRS ENRAF CAD4 single crystal X-ray diffractometer) collects intensity data required for structure determination. In the present study, the single crystal X-ray diffraction analysis was performed using MESSRS ENRAF CAD-4 single crystal X-ray diffractometer with graphite monochromated MoKα radiation.

The principle of powder X-ray diffraction is a tool for accurate determination of lattice parameters in crystals of known structure and for the identification of elements and compounds. It involves the diffraction of monochromatic X-rays by a powder specimen. The focusing monochromatic geometry results in narrower diffracted peaks and low background at low angles. It is possible to record the diffracted beam from 2 degrees to 160 degrees. The diffractometer is connected to a computer for data collection and analysis. A high resolution diffractometer, Siemens D 500 X-ray diffractometer was employed for the characterisation. The peaks of the X-ray diffraction pattern can be compared with the standard available data for the confirmation of the structure. It is powerful and rapid (< 20 min) technique for identification of an unknown mineral. In most cases, it provides an unambiguous mineral determination.

1.7.2 Fourier transform infrared (FT-IR) analysis

The infrared region of the electromagnetic spectrum is divided into three regions, the near, mid, and far infrared. In order to examine the functional group and their interactions, Fourier Transform Spectroscopy of both the far-infrared and infrared regions was introduced in the late 1960s. Fourier
Transform Spectroscopy is a simple mathematical technique to resolve a complex wave into its frequency components. FTIR is more accessible in the mid–infrared (4000 cm\(^{-1}\) - 400 cm\(^{-1}\)) region. Conventional spectroscopy, called the frequency domain spectroscopy, records the radiant power as a function of frequency. In time domain spectroscopy the change in radiated power is recorded as a function of time, whereas in Fourier Transform Spectrometer, a time domain plot is converted into a frequency domain spectrum. The actual calculation of the Fourier transform of such systems is done by means of high speed computers. One of the most important advantages of IR spectroscopy over the other usual methods of structural analysis (X-ray diffraction, electron spin resonance and nuclear magnetic resonance) is that it provides useful information about the structure of the molecule quickly.

1.7.3 UV-Vis-NIR spectroscopy

UV-Vis-NIR spectroscopy is used to characterise the absorption, transmission, and reflectivity of variety of compounds associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are valence or bonding electrons and they can be excited by absorption of UV or visible or near IR radiation. Excitation of a bound electron from the highest occupied molecular orbital increases the spatial extent of the electron distribution, making the total electron density larger and more diffuse, and often more polarizable. Electronic transitions are possible for a wide range of vibrational levels within the initial and final electronic states. Ultraviolet and
visible light are energetic enough to promote outer (valence) electrons to higher energy levels.

There are three types of valence electrons that are found in electron orbital namely $\sigma$ - bonding orbitals, $\pi$ - bonding orbitals and non-bonding orbitals (n lone pair electrons). Sigma ($\sigma$) bonding orbits have lower energy than $\pi$ - bonding orbital, which in turn have lower energy than non-bonding orbital. The unoccupied or anti bonding orbital ($\pi^* \alpha\nu\delta \sigma^*$) are the orbits of highest energy. The region between 10 nm - 200 nm is termed as vacuum ultraviolet region, which can be studied in evacuated systems. The region between 200 nm - 380 nm is called quartz ultraviolet region or ultraviolet region. The region or spectral range most accessible for 200 nm to 800 nm includes the visible region lying between 380 nm - 780 nm. In the present work, UV-Vis-NIR studies were carried out using Varian carry 5E model dual beam spectrophotometer.

1.7.3.1 Optical band gap

A study on ionic crystals absorbing strongly in the ultra-violet region, was first made on semiconductors [32]. In the case of crystalline materials, the absorption edge is observed in the short wavelength range [33]. This low wavelength data are related to inter band transitions (i.e. Excitation of an electron from the valence band to the conduction band). This study helps to precisely identify the allowed direct and indirect transitions in the crystal. The optical energy gap ($E_g$) can be calculated from the well-known quadratic equation which is often called Tauc law [34].
\[ \alpha h\nu = A (h\nu - E_g)^n \]  

(1.11)

Where, \( h\nu \) is the incident photon energy, \( \alpha \) the absorption coefficient, \( E_g \) the band gap of the material, \( A \) is a constant that depends on the electronic transition probability and \( n \) is the exponent that characterises the type of electronic transition responsible for optical absorption process. For direct allowed transition \( n = \frac{1}{2} \), and indirect allowed transition the value of \( n = 2 \).

1.7.4 High resolution X-ray diffraction

The crystalline perfection of the grown crystals was analyzed by high resolution X-ray diffraction (HRXRD) by employing a multicrystal X-ray diffractometer [35]. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm x 8 mm; 2kW Mo) was first reduced by a long collimator fitted with a pair of fine slit assemblies. The fore shortening angle of the emerging beam from the target was kept at 3 degrees instead of the usual value of 6 degrees, though the intensity is expected to be lesser in view of having better resolution. Mo target has been chosen instead of commonly used Cu as the wavelength of \( \text{MoK}_{\alpha 1} \) (0.70926 Å) is less than half of that of \( \text{CuK}_{\alpha 1} \) (1.54056 Å) and hence the expected resolution for HRXRD experiments is more.

This collimated beam is diffracted twice by two Bonse-Hart type of monochromator crystals and the thus diffracted beam contains well resolved \( \text{MoK}_{\alpha 1} \) and \( \text{MoK}_{\alpha 2} \) components. The \( \text{MoK}_{\alpha 1} \) beam is isolated with the help of fine slit arrangement and allowed to further diffract from an independent third Si monochromator crystal set in dispersive geometry (+,−,−). All the three
Si monochromator crystals are plane crystals and set for diffraction for (111) planes in symmetrical Bragg geometry. The specimen crystal is aligned in the (+,−,−,+ ) configuration, wherein the specimen crystal is in non-dispersive geometry with respect to the third monochromator.

Due to dispersive configuration of the third monochromator crystal with respect to the second monochromator, the spectral quality of the diffracted beam emerging from the third monochromator is perfectly high. The advantage of dispersion configuration (+,−,−) over the non-dispersive configuration (+,−,+ ) of monochromators was established [36].

All the monochromators are symmetrical cut crystals and aligned for symmetrical Bragg diffraction for crystal planes. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The diffraction or rocking curves (RCs) are recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak, so that all the meaningful scattered intensities on both sides of the peak are included in the diffraction curve.

In the present study, the rocking curves (RC) were recorded by the omega ($\omega$) scan wherein the detector was kept at the fixed angular position $2\theta_B$ ($\theta_B$ being the Bragg diffraction angle) with wide opening for its slit. The slit width was kept around 1 mm through which the intensity distribution for an
angular range upto around 500 arc sec on both sides of the 2θ position (of the detector which was at a distance of around 165 mm from the sample) can be received which could cover all the peaks due to various grain boundaries or the meaningful scattered intensity for the specimens studied in the present investigation. When the residual direct beam which may emerge through the crystal is stopped, and even if the slit width is much more than 1 mm, the observed RC along with the scattered intensity along the tails of the RC does not change as observed experimentally.

The omega scan is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries [36]. In case of 2 theta-theta or 2 theta-omega scan, the experimentally obtained RC contains the information about a single grain and rocking curve is expected to be very sharp as the detector with narrow slit will not receive diffracted intensities from the other grains which are misoriented to the grain under investigation (i.e.aligned for diffraction) or the diffuse scattering from point defects and their aggregates. Whereas in the relatively simple omega scan, with sufficiently wide slit for the detector, if the crystal contains structural grain boundaries, all the peaks in the RC are obtained. On the other hand a single sharp peak can be obtained in omega scan, it really confirms that the specimen crystal has a single domain with single orientation. The schematic diagram of HRXRD is shown in Figure 1.5.
Figure 1.5 Schematic diagram of the multi-crystal X-ray diffractometer
1.7.5 Laser damage threshold (LDT)

The development of higher damage threshold optics is an important task, as it would result in less expensive laser components for high power lasers and overall smaller systems. It leads to several research groups to develop such a system which benefits scientific progress in the field of laser-matter interaction. Laser damage threshold is a significant parameter, to use the crystal as an NLO element in various applications involving large laser input power, like frequency doubling, optical parametric processes etc. Optical damage may be caused by thermal heating, induced absorption, self-focusing and dielectric breakdown. When performing LDT testing, the sample is irradiated numerous times using a small beam over the whole clear aperture of the sample [37].

The schematic diagram of the LDT setup is shown in Figure 1.6. The laser damage threshold value was measured using a Q-switched Nd:YAG laser source of pulse width 10 ns and repetition rate of 10 Hz operating in TEM$_{00}$ mode. The energy per pulse of 1064 nm laser radiation attenuated using appropriate neutral density filters was measured using an energy meter (Coherent EPM 200). For surface damage observation, the sample was placed at the focus of a planoconvex lens with focal length of 20 cm.

The laser damage threshold was calculated using the relation,

$$ P = \left( \frac{E}{\tau A} \right) $$

(1.12)

Where $E$ is the energy required to break the crystal, $\tau$ is the response time in nanosecond and $A$ represents the beam area.
The laser beam of diameter 4 mm was focused on to the crystal sample. During laser irradiation, the power meter records the energy density of the input laser beam by which the crystal gets damaged. For both single and multiple shot experiments, the sample was mounted on a translator which facilitates in bringing different areas of the sample for exposure.

### 1.7.6 Thermal studies

The thermal analysis is a method to study the thermal behavior of materials and it also finds widespread applications in diverse industrial and research fields. Thermal analysis is a tool to study the physical property of a substance as a function of temperature. This method not only provides valuable information on the thermal stability of the compounds and the decomposition products, but also provides an insight into their mode of decomposition. Among the thermal methods, the most widely used techniques are thermogravimetry analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) which find extensive use in all fields of inorganic and organic chemistry.

#### 1.7.6.1 Thermogravimetric analysis (TGA)

Thermogravimetry analysis involves monitoring the weight of the sample while varying the temperature or time while the substance is subjected to a controlled temperature program. The curve obtained in a thermogravimetric analysis is called a thermogram (TG) and its first derivative is called as derivative thermogram (DTG). The inflection point in the program corresponds to the peak point in the derivative thermogram.
Figure 1.6 Schematic diagram of the setup used for Laser damage threshold measurement
Here, the furnace is normally an electrical resistive heater and the temperature range for most of the furnace is from 1000 °C – 2000°C. Thermogravimetry analysis is used to study the thermal degradation/decomposition/dehydration and to check the sample’s purity, temperature of desorption and drying, oxidative stability etc.

1.7.6.2 Differential thermal analysis (DTA)

Differential thermal analysis (DTA) technique is primarily used for the detection of transition temperature. DTA is involved in the measurement of temperature difference between the sample and inert reference materials. The energy difference occurred is manifested as enthalpy changes - either exothermic or endothermic. The differential thermal curve would be parallel to the temperature axis till the sample undergoes any physical or chemical change of state. However, as the sample reached the temperature of the change of state, the additional heat flux reaching the sample will not increase the sample temperature at the same rate as that of the reference and this differential signal appear as a peak. The DTA apparatus consists of a furnace, linear temperature – programme controller, sample holder, differential temperature detector with preamplifier and a recorder.

1.7.7 Microhardness studies

Hardness is an important factor in the choice of ceramics for abrasives, bearings, tool bits, wear resistance coatings etc. Hardness measurement enables to resist plastic deformation, by penetration and is also referred as resistance to bending, scratching, abrasion or cutting. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or
damage. It is a non-destructive method to determine the mechanical behavior of the materials. For hard and brittle materials, the hardness test has proved to be a valuable technique in the general study of plastic deformation [38]. Hardness properties are basically related to the crystal structure of the material and the bond strength.

Among the different methods adopted for hardness measurement, the static indentation test is preferred for hardness measurement due to its popularity and simplicity. An indenter of specific geometry is pressed on to the surface of a test specimen under known load. The indenter may be a ball or diamond cone or diamond pyramid. By measuring the cross sectional area or the depth of the indentation and knowing the applied load, the empirical hardness may be calculated. This method is followed by Brinell, Meyer, Vickers, Knoop and Rockwell tests [39-41].

**Vickers hardness test**

Vickers hardness method is the reliable and most common among the various methods of hardness measurement. In this method, micro-indentation is made on the surface of a specimen with the help of diamond pyramidal indenter. Smith and Sandland [42] have proposed that a pyramid be substituted for a ball in order to provide geometrical similitude under different values of load. The Vickers pyramid indenter whose opposite faces contained an angle ($\alpha = 136^\circ$) is the most widely accepted pyramid indenter and is shown in Figure 1.7. A pyramid indenter is well suited for hardness tests due to the following reasons [43].
1. The contact pressure for a pyramid indenter is independent of indent size.

2. Pyramid indenters are less affected by elastic release than other indenters.

The base of the Vickers pyramid is a square and the depth of indentation corresponds to \( \frac{1}{7} \) of the indentation diagonal. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vickers hardness number \( (H_v) \) of Diamond Pyramid Number (DPN) is defined as,

\[
H_v = 2 \frac{P \sin (\alpha/2)}{d^2}
\]  

(1.13)

Where \( P \) is the applied load in kg, \( d \) is the diagonal length of the indentation mark in mm and \( \alpha \) is the apex angle of the indenter \( (\alpha = 136^\circ) \). The Vickers hardness number relation is thus reduced as,

\[
H_v = 1.8544P/d^2 \text{ kg/mm}^2
\]  

(1.14)

1.7.8 Dielectric studies

One of the useful characterisations of electrical response of solids is the dielectric measurement. Since every material has a unique set of electrical characteristics such as dielectric properties like permittivity, permeability, resistivity, conductivity etc. The dielectric properties of solids also provide information about the electric field distribution within the solid and the dielectric characteristics of the material are important to study the lattice dynamics in the crystal. It is important to note that permittivity and permeability are not constant and changes with frequency, temperature, orientation, mixture, pressure, and molecular structure of the material. The different polarization mechanisms in solids can be understood from the study of dielectric constant as a function of frequency and temperature.
Figure 1.7 The schematic of Vickers diamond pyramidal indenter
In the present investigation, the dielectric measurement was carried out by measuring different parameters such as capacitance and dielectric loss of the pressed pellets of samples with known dimension at room temperature using HIOKI 3532-50 LCR HITESTER meter. The relative dielectric constant is defined as the ratio of the permittivity of the dielectric material ($\varepsilon$) to the absolute permittivity ($\varepsilon_0$). It can also be defined as

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}$$  \hspace{1cm} (1.15)

where A is the area of the sample, d is its thickness and C the capacitance of the parallel plate capacitor. The relative permittivity ($\varepsilon_r$) is usually known as permittivity and is always greater than unity.

The dielectric loss is a measure of the energy absorbed by dielectric when subjected to frequency. The ratio of imaginary part to the real part of the relative permittivity is known as dielectric loss or the dissipation factor $D$. The dissipation factor is measured along with the capacitance at room temperature using the LCR meter.

1.7.9 Photoconductivity studies

Photoconductivity is an important property of solids, which reveal the conductivity of the sample due to incident radiation. In short, photoconductivity is due to the absorption of photons (either by an intrinsic process or by impurities with or without phonons), leading to the creation of free charge carriers in the conduction band or in the valence band. Photoabsorption followed by photoconduction takes place by one of the following mechanisms.
1. Band-to-band transitions
2. Impurity levels to band edge transitions
3. Ionization of donors
4. Deep level (located in the valence band) to conduction band transitions.

The experimental set up used for measuring photocurrent is shown in Figure 1.8. When electrons from a filled band are injected into vacant impurity levels for the applied d.c value of current, the number of holes increases in the conduction band, thus the photo current ($I_p$) of the material increases, this is referred as ‘positive photo conductivity’.

The dark current $I_d$ is the amount of current that flows through the material or device without radiation and it changes with operating temperature and applied voltage. The average d.c value of the current is generally mentioned as dark current. In few cases, it has been observed that when radiation of certain energy is incident on a photoconductor, decrease in current is observed instead of the expected increase, this phenomenon is called “negative photoconductivity”.

This is explained by Stockmann model [44]. According to this model, the forbidden band gap contains two types of centers with energies $E_1$ and $E_2$. One type lies between the Fermi level and the conduction band, while the other is situated close to the valence band. The function of these types of centers in the presence of radiation is to create holes (by accepting electrons from the valence band) but at the same time not to increase the number of free electrons. Thus, the net number of mobile charge carriers is reduced due to incident radiation, giving rise to negative photoconductivity.
Figure 1.8 Experimental setup for photoconductivity study
1.8 SCOPE OF THE THESIS

The search and design of high efficient nonlinear optical (NLO) crystals for visible and Ultraviolet (UV) regions are extremely important for laser material related applications. The inorganic, organic nonlinear optical materials have their own advantages and limitations. The inorganic nonlinear optical crystals are easy to grow in large size using the conventional solution growth technique. Though mechanical strength of inorganic crystals is high, the NLO efficiency is low as compared to their organic counterparts. The organic materials have large nonlinearity but have less mechanical and thermal strength.

Organic materials have a massive range of interesting properties that are almost continuously tunable. The prerequisite of good quality crystals can be fulfilled by the development and implementation of wide range of methods. Understanding the fundamentals and features of crystal growth and its practical applications, it was aimed to synthesize and grow bulk crystals. A special emphasis on organic materials and its characterisation has been made in the present work. Synthesis of materials and growth of crystals and the study of their physical properties are essential to utilize them for future applications.

In the present work, L-Aspartic acid single crystal was grown by slow cooling method and L-Histidinium 2 nitrobenzoate, 4 Carboxyanilinium bromide and Ammonium hydrogen oxalate hemihydrate crystals were grown by slow evaporation method.
The present investigation is aimed towards,

(i) Growing bulk sized crystals with good optical quality.

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

(iii) Analysing the grown crystal for its optical transmission, hardness, dielectric property, HRXRD and photoconductivity.

(iv) Studying the thermal stability of the grown crystals.

(v) Finding the nonlinear behaviour and laser damage threshold of the grown crystals.