

CHAPTER-1

INTRODUCTION

Non-linear optics (NLO) is the branch of optics that describes the behavior of light in non-linear media, that is, media in which the dielectric polarization (P) responds non-linearly to the electric field (E) of the light. This non-linearity is typically observed at very low intensities such as those provided by pulsed lasers. The understanding of the non-linear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably developed in the field of research. Many significant achievements have occurred in the field of non-linear optics because of the development of laser technology and new NLO materials of both inorganic and organic types. Most of the scientific developments applied to the organic materials were borrowed from their counterpart inorganic materials and, by the virtue of its nature. NLO materials have a great impact on information technology and industrial applications. The aim is to develop materials presenting large non-linearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. An ideal non-linear optical material should possess the following characteristics:

- Large non-linear figure of merit for frequency conversion.
- High laser damage threshold.

- Fast optical response time.
- Wide phase matchable angle.
- Architectural flexibility for molecular design and morphology.
- Ability to process into crystals, thin films.
- Optical transparency (no absorption at fundamental and SHG wavelengths).
- Ease of fabrication.
- Non toxicity and good environmental stability.
- High mechanical strength and thermal stability.

1.1 CLASSIFICATION OF NON-LINEAR OPTICAL CRYSTALS

On the basis of three types of cohesive forces that bind the charges and polarization together, the NLO materials can be classified into the following cases:

- Organic crystals
- Inorganic crystals
- Semi-organic crystals.

1.1.1 Organic Crystals

Organic crystals have large non-linear responses, inherent synthetic flexibility, high optical damage threshold intrinsic tailorability (Wang *et al.*, 2002). Organic crystals exhibit excellent NLO properties because of their electronic structure with π conjugated systems between donors and acceptors

(Patil *et al.*, 2014, Prakash *et al.*, 2013). This is due to non-centrosymmetry leading to huge NLO efficiency, exhibited by organic materials in the order of 10 to 100 times larger than that of inorganic NLO materials through macroscopic second-order NLO response (Periyasamy *et al.*, 2007). These materials exhibit excellent properties such as optoelectric coefficients, large second-order NLO coefficients, small dielectric constants, molecular designing, faster optical responses, and ultrafast responses to external electric fields (Goel *et al.*, 2013). Hence, organic materials are superior to their inorganic counterparts in terms of crystal preparation, device fabrication, and production of better devices with large non-linearities. They have wide applications in areas such as information storage, optical communication, optical data storage, optoelectronics, laser technology and telecommunications (Sudhahar *et al.*, 2013).

1.1.2 Inorganic crystals

Inorganic crystals are mostly ionic bonded which has high melting point, high degree of chemical, thermal and mechanical stability. Some of the familiar properties of inorganic host materials are large mechanical strength, excellent thermal stability, good transmittance, high phase matching angle, large damage threshold, chemical stability and high electro-optic coefficients as well as high degree of chemical inertness. The search for new and efficient materials in which to carry out non-linear optical processes has been very active since second-order non-linear (SHG) was first observed in single crystal

quartz by Franken and co-workers in 1961. In the beginning, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate (LiNbO₃), and its analogues, potassium titanyl phosphate (KTP) and its analogues, beta barium borate (Dewey *et al.*, 1975) and semiconductors such as cadmium sulfide, selenium, and tellurium. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation with high frequency conversion efficiency in the new region of the spectrum inaccessible by other non-linear crystal conventional sources.

1.1.3 Semi-organic crystals

The inability of organic crystals to grow to larger sizes impedes device fabrication, which has led to the discovery of a new class of crystals called semi organics to satisfy technological requirements (Sivakumar *et al.*, 2014, Vetrivel *et al.*, 2013). In semi-organic crystals, the organic ligand is ionic bonded with the inorganic host, which promotes exceptional mechanical strength and chemical stability (Sun *et al.*, 2005). The semi-organic crystals are promising for many other applications such as frequency conversion, light amplitude, phase modulation and phase conjugation (Dhanabal and Amirthaganesan, 2014). Further the metal-organic compounds have attracted researchers in recent years due to their various properties such as NLO response, magnetism, and luminescence, as well as applications in

photography (Murugan *et al.*, 2008). Semi-organic crystals have shown large NLO behavior and also favourable properties such as high optical transparency over the entire visible region, a large laser damage threshold value, low deliquescence, high resistance, and low angular sensitivity (Chithambaram and Krishnan, 2014, Muthu *et al.*, 2014).

1.2 THEORETICAL EXPLANATION OF NON-LINEAR OPTICS

In 1962, theoretical investigations dealing with the behavior of light waves by solving Maxwell's equation in a non-linear dielectric and at the boundary of non-linear media were performed by Bloembergen (Bloembergen and Pershan, 1962, Bloembergen, 1999) respectively. The explanation of non-linear optics lies in the way in which a beam of light propagates through a solid. The nuclei and the associated electrons of the atoms in the solids form electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate, by classical laws of electromagnetism, results in the dipoles themselves acting as sources of electromagnetic radiation. As the intensity of the incident radiation increases, the relation between the radiation and the amplitude of the vibration becomes non-linear, which results in the generation of frequencies that are different from those of incident fields. Thus, second and higher harmonic generation occurs.

In a non-linear medium the induced polarization is a non-linear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules with asymmetric charge distributions arranged in the crystal in such

a way that a polar orientation is maintained throughout the crystal. At very low fields, the induced polarization is directly proportional to the electric field.

$$P = \epsilon_0 \chi E \quad (1.1)$$

where χ is the linear susceptibility of the material, E is the electric field vector, ϵ_0 is the permittivity of free space. At high fields, polarization becomes independent of the field and the susceptibility becomes field dependent. Therefore, this non-linear response is expressed by writing the induced polarization as a power series in the field.

$$P = \epsilon_0 \{ \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \dots \} \quad (1.2)$$

In non-linear terms, product of two or more oscillating fields gives oscillation at combination of frequencies and therefore the above equation can be expressed in terms of frequency as:

$$P(-\omega_0) = \epsilon_0 \{ \chi^{(1)}(-\omega_0; \omega_1) \cdot E(\omega_0) + \chi^{(2)}(-\omega_0; \omega_1, \omega_2) \cdot E(\omega_1) \cdot E(\omega_2) + \chi^{(3)}(-\omega_0; \omega_1, \omega_2, \omega_3) \cdot E(\omega_1) \cdot E(\omega_2) \cdot E(\omega_3) + \dots \} \quad (1.3)$$

where $\chi^{(2)}$, $\chi^{(3)}$ are the non-linear susceptibilities of the medium. $\chi^{(1)}$ is the linear term responsible for the linear optical properties of the materials like, refractive index, dispersion, birefringence and absorption. $\chi^{(2)}$ is the quadratic term which describes second harmonic generation in non-centrosymmetric materials. $\chi^{(3)}$ is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bistability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The

coefficients of $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ give rise to certain optical effects. If the molecule or crystal is centro-symmetric 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 non-linear term is predicted to be $+E^2$, yet if the medium is centro-symmetric the polarization should be $-E^2$. This contradiction can only be resolved if $\chi^{(2)} = 0$ in centro-symmetric media. If the same argument is used for the next higher order term, $+E$ produces polarization $+E^3$ and $-E$ produces $-E^3$, so that $\chi^{(3)}$ is the first non-zero non-linear term in centro-symmetric media. In second harmonic generation, the two input wavelengths are the same

$$2\omega_1 = \omega_2 \text{ (or) } (\lambda_1 = 2\lambda_2) \quad (1.4)$$

During this process, a polarization wave with the second harmonic frequency $2\omega_1$ is produced. The refractive index, n_1 is defined by the phase velocity and wavelength of the medium. The energy of the polarization wave is transferred to the electromagnetic wave at a frequency ω_2 . The phase velocity and wavelength of this electromagnetic wave are determined by n_2 , the refractive index of the doubled frequency. To obtain high conversion efficiency, the vectors of input beams generated are to be matched.

$$\Delta K = \frac{2\pi}{\lambda(n_1 - n_2)} \quad (1.5)$$

where ΔK represents the phase-mismatching. The phase-mismatch can be obtained by angle tilting, temperature tuning or other methods. Hence, to select a non-linear optical crystal, for a frequency conversion process, the

necessary criterion is to obtain high conversion efficiency. The conversion efficiency η can be expressed as:

$$\eta \propto PL^2 (d_{\text{eff}} \text{Sin } \Delta K L / \Delta K L)^2 \quad (1.6)$$

where d_{eff} is the effective non-linear coefficient, L is the crystal length, P is the input power density and ΔK is the phase – mismatching. In general, higher power density, longer crystal length, large non-linear coefficients and smaller phase mismatching will result in higher conversion efficiency. Also, the input power density is to be lower than the damage threshold of the crystal.

NLO effects can be classified into two types:

Second-order effects that dependent on the first hyperpolarizability tensor term $\chi^{(2)}$ and third-order effects that dependent on the second hyperpolarizability tensor term $\chi^{(3)}$. Other higher order effects are difficult to observe. For a medium to exhibit second-order non-linear susceptibility it should not possess a center of symmetry, i.e. it should be non-centrosymmetric. All media and molecules exhibit third-order response. Basically all forms of matter exhibit NLO phenomena. But to be useful in a device, the material must exhibit a high degree of non-linearity at a reasonable power level.

1.2.1 Second Harmonic Generation

Second harmonic generation (also called frequency doubling) is a non-linear optical process in which photons interacting with a non-linear material

are effectively "combined" to form new photons with twice the energy, and therefore twice the frequency and half the wavelength of the initial photons. This is also known as frequency doubling effect (Zyys and Chemla, 1987).

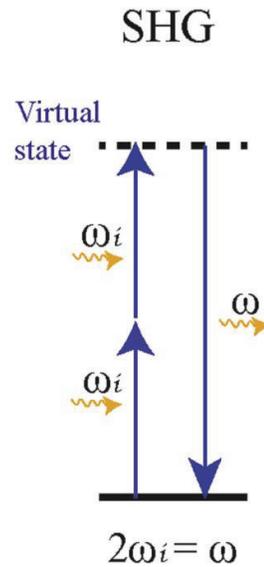


Fig. 1.1: Second Harmonic Generation.

Here ω_i and ω are the frequency of the absorbed photons and the emitted photon respectively. The process is spontaneous and involves three-photon transitions i.e., two photons with a frequency ω_i per each photon are absorbed spontaneously to emit a photon with a frequency ω . The dashed (-----) line corresponds to the virtual level. Fig. 1.1: shows the second harmonic generation.

1.2.2 Theory of Second harmonic generation

Second harmonic generation is a non-linear optical process that results in the conversion of an input optical wave into an output wave of twice the input

frequency. The process occurs within a non-linear medium, usually a crystal. The light propagated through a crystalline solid, which lacks a centre of symmetry, generates light at second and higher harmonics of the applied frequency. Such frequency doubling processes are commonly used to produce green light (532 nm), for example, a Nd:YAG (Neodymium-doped yttrium aluminium garnet) laser operating at 1064 nm. This important non-linear property of non-centrosymmetric crystals is called second harmonic generation and this phenomenon and the materials in which it occurs are the subject of intense study (Zyss and Chemla, 1987).

As the general expression for the non-linear optical polarization is quite complicated, a very simplified way (for the related second order processes with the time domain expansion of the second order term only) is shown in the description (Butcher & Cotter 1990).

According to Maxwell's consideration, for a non-magnetic media with no free charges or no free currents, the electrical displacement field (D) is the total electric field within the material and is given by

$$D = E + 4\pi P \quad (1.7)$$

where E is the incident electric field and P is the polarization field generated from the electric field induced dipoles within the medium. For a linear isotropic media, the polarization field will be having a linear relationship with the applied electric field as shown in eqn. 1.7

The power series expansion of dielectric polarization $P(t)$ at time t in a medium can be written as,

$$P(t) \propto \chi^{(1)}E(t) + \chi^{(2)}E^2(t) + \chi^{(3)}E^3(t) + \dots \quad (1.8)$$

Here, the coefficients $\chi^{(n)}$ are the n^{th} order susceptibilities of the medium. For any three wave mixing process, the second-order term is crucial and must be non-zero. In other words, a medium exhibiting such an NLO response might consist of a crystal composed of molecules with asymmetric charge distribution, i.e., if the molecule is centrosymmetric. The second order non-linear optical susceptibility [or first hyperpolarizability (β)] is zero, indicating that centrosymmetric media does not show second order non-linear effects. In general, in a material with inversion symmetry, for example, many isotropic media such as glasses, liquids and gases, for symmetry reasons there can be no even powers of the field in the expansion of the polarization (Butcher & Cotter 1990)

Consider a material having inversion center (i.e. centrosymmetric). On interaction of such a material with an incident field, the resultant second order polarization field will be

$$P_2(t) = \chi^{(2)}E^2(t) \quad (1.9)$$

Due to inversion symmetry, the following relations exist:

$$-P_2(t) = \chi^{(2)}[-E^2(t)] = \chi^{(2)}E^2(t) \quad (1.10)$$

This can be true only if the polarization is zero and ultimately this can be possible if second-order coefficient ($\chi^{(2)}$) is zero. Assuming that the material

is non-centrosymmetric, and if we write the expression only for the second order term, the equation will look like (Butcher & Cotter 1990).

$$\begin{aligned}
 P_2(t) &= \chi^{(2)} E^2(t) \\
 &= \chi^{(2)} \left[\frac{1}{2} E_\omega e^{i\omega t} + \frac{1}{2} E_\omega e^{-i\omega t} + E_0 \right]^2 \\
 &= \chi^{(2)} \left[\frac{1}{4} E_\omega^2 (e^{i2\omega t} + e^{-i2\omega t}) + E_0 E_\omega (e^{i\omega t} + e^{-i\omega t}) + E_0^2 \right] \\
 &= \chi^{(2)} \left[\frac{1}{2} E_\omega^2 \cos(2\omega t) + 2 E_0 E_\omega \cos(\omega t) + E_0^2 \right] \quad (1.11)
 \end{aligned}$$

As shown in Eq.1.11, the resulting polarization field contains components oscillating at various frequencies. The first term in the equation represents SHG, the second term the Pockels effect and the third term, the process for optical rectification (Butcher & Cotter 1990).

1.2.3 Third Harmonic Generation

The third order susceptibility in THG is $\chi^{(3)}$ ($-3\omega: \omega, \omega, \omega$) and it forms an idea for the parameter, the index of refraction. This nonlinear susceptibility is completely originated by electronic effects. When a single or two or three photons of the fundamental beam are in resonance with the excited states of NLO material, a strong frequency dependent enhancement of harmonic intensity is observed (McKinnon JJ, 2007). Similar to SHG, the phase matching between all generated harmonic waves can influence the harmonic intensity which arises due to the dispersion of NLO material. The fig.1.2 shows the third harmonic generation. The dashed lines show the virtual levels.

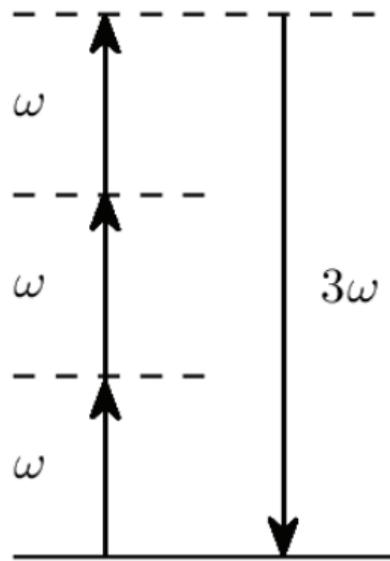


Fig. 1.2: Third harmonic generation

1.2.4 Theory of third harmonic generation.

The third-order nonlinear polarization is given by

$$P^{(3)}(t) = \epsilon_0 \chi^{(3)} E^3(t) \quad (1.12)$$

The field $E(t)$ is made up of different frequency components and the expression for $P(t)$ is very complicated. Consider the simplified case in which the applied field is monochromatic which is given by

$$E(t) = E \cos(\omega t) \quad (1.13)$$

Then, through use of the identity

$$\cos^3(\omega t) = \frac{1}{4} \cos(3\omega t) + \frac{3}{4} \cos(\omega t) \quad (1.14)$$

Applying in the third-order nonlinear polarization gives

$$P^{(3)}(t) = \frac{1}{4} \epsilon_0 \chi^{(3)} E^3 \cos(3\omega t) + \frac{3}{4} \epsilon_0 \chi^{(3)} E^3 \cos(\omega t) \quad (1.15)$$

The first term in Equation (1.15) describes a response at frequency 3ω created by applied field at frequency ω . This leads to the process of third harmonic generation. The second term in Equation (1.15) describes a non-linear contribution to the polarization at the frequency of the incident field. This term leads to a non-linear contribution to the refractive index experienced by a wave at frequency ω . The refractive index in the presence of this type of non-linearity can be represented as

$$n = n_0 + n_2 I \quad (1.16)$$

where I is the intensity of the incident wave, n_0 is the linear index of refraction, n_2 is the third-order non-linear refractive index which characterizes the strength of the optical non-linearity is given by

$$n_2 = \frac{12 \pi^2}{n_0^2 c} 10^7 \text{ (esu)}$$

1.2.4.1 Self-focusing and Self-defocusing

The process that occurs as a result of intensity dependent refractive index of the medium is called as Self-focusing. It is also called self-action because the non-linear polarization induced by the incident beam changes the propagation or other properties of the same incident beam. It can occur when a beam of light having a non-uniform transverse intensity distribution propagates through a material for which n_2 is positive. The material will

effectively acts as a positive lens under such conditions and causes the rays to curve towards each other as shown in Fig 1.3(a). This process is of significant importance because the intensity at the focal spot of the self-focused beam is usually sufficiently large to lead to optical damage of the material. Self-defocusing occurs when a beam of light having non-uniform transverse distribution propagates through a material in which n_2 is negative and the material start behaving like a negative lens and tend to diverge as shown in Fig 1.3(b).

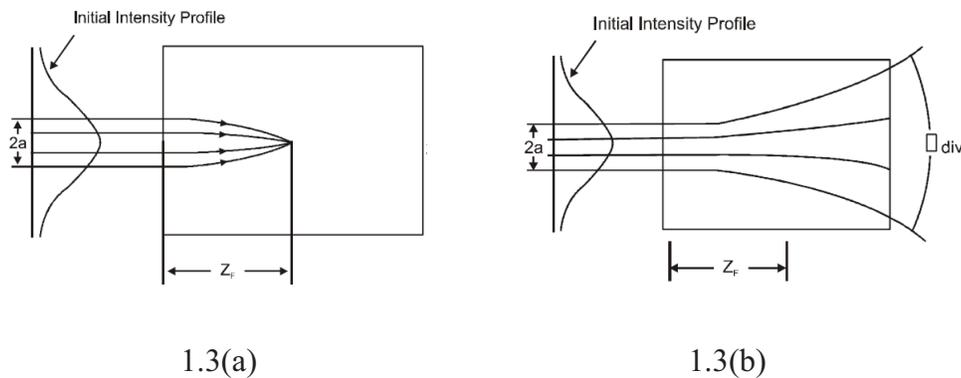


Fig. 1.3: (a) Self-focusing and (b) Self-defocusing of light beam in a non-linear medium

1.2.4.2 Saturable absorption

Saturable absorption is a nonparametric non-linear optical process in which the absorption coefficient of the material decreases when a very high intensity laser beam propagates through it. The absorption coefficient α depends on the intensity I of the incident laser radiation and is given by the expression,

$$\alpha = \frac{\alpha_0}{1 + I/I_s} \quad (1.17)$$

where I is low intensity absorption coefficient and I_s is known as the saturation intensity.

1.2.4.3 Two-photon absorption

The transition of an atom from its ground state to an excited state by the simultaneous absorption of two laser photons is called as two photon absorption. The absorption cross-section σ describing this process increases linearly with laser intensity according to the relation

$$\sigma = \sigma^{(2)} I \quad (1.18)$$

where $\sigma^{(2)}$ is a coefficient and it describes the strength of two photon absorption process. The atomic transition rate R due to two-photon absorption depends on the square of the laser intensity, i.e.

$$R = \frac{\sigma^{(2)} I^2}{\omega \hbar} \quad (1.19)$$

where ω is the frequency and \hbar is reduced Planck constant. Two-photon absorption is an effective tool to determine the positions of energy levels that are not connected to the atomic ground by a one-photon transition. Suppose a single input beam is incident on a non-linear material that displays linear absorption. Then, the non-linear phase shift (ϕ_{NL}) is given by,

$$\phi_{NL} = n_2 \frac{\omega}{c} I_0 L_{eff} \quad (1.20)$$

where $L_{\text{eff}} = (1 - e^{-\alpha L})/\alpha$, is the effective length of the material, L is the path length and c is the velocity of light. For a strongly absorbing nonlinear optical material, the effective interaction length can be much shorter than the physical length of the non-linear medium. When the optical material exhibits two-photon absorption as well as linear absorption, the absorption coefficient in the Equation (1.17) should be replaced by

$$\alpha = \alpha_0 + \beta I$$

where β is the two-photon absorption coefficient. Two-photon absorption is often a significant problem in the design of all optical switching devices because it occurs at the same order of non-linearity as the intensity dependent refractive index n_2 (because these processes are proportional to the imaginary and real parts of $\chi^{(3)}$ respectively).

1.3 CRYSTAL GROWTH PHENOMENA

1.3.1 Nucleation

Nucleation is an important phenomenon in crystal growth and is the precursor of crystal growth and of the overall crystallization process. The condition of supersaturation alone is not sufficient for a system to begin crystallization. Before crystals can grow, there must exist in the solution a number of minute solid bodies known as centers of crystallization, seeds, embryos or nuclei. Nucleation may occur spontaneously or it may be induced artificially and they are usually referred to as homogeneous and heterogeneous

nucleations, respectively. As shown in Fig. 1.2, the term primary is used for both homogeneous and heterogeneous nucleation even in systems that do not contain crystalline matter.

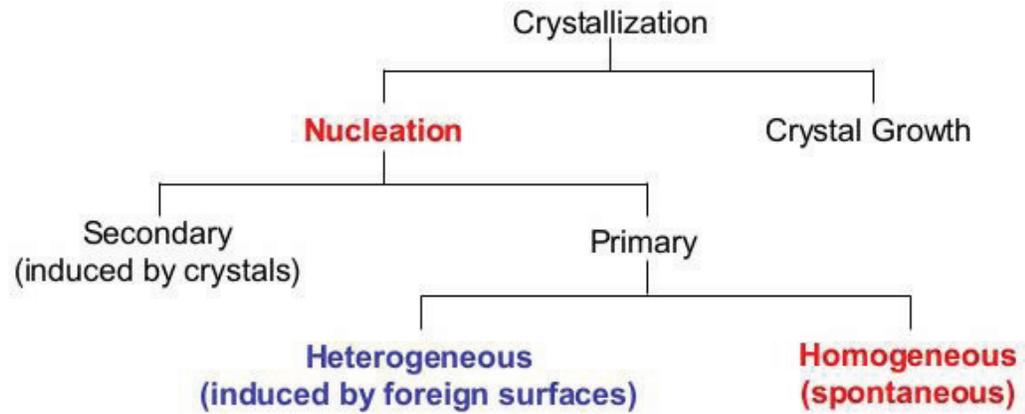


Fig. 1.4: Classification of Nucleation

On the other hand, during secondary nucleation, nuclei are often generated in the vicinity of the crystals present in the supersaturated system. This process involves the dislodgement of the nuclei from the parent crystal at supersaturation in which primary homogeneous nucleation cannot occur. When a supersaturated solution is disturbed by agitation, friction or mechanical stimulus in the presence of the crystalline substance of the solute, embryos are formed at the surfaces of the parent crystal. These embryos give rise to secondary nucleation. If the nuclei form homogeneously in the interior of the phase, it is called homogeneous nucleation. If the nuclei form heterogeneously around ions, impurity molecules or on dust particles, on surfaces or at structural singularities such as imperfections or dislocations, it is

known as heterogeneous nucleation. Further, the creation of a new phase in the homogeneous solution, demands for the expenditure of certain quantity of energy.

1.4 CRYSTAL GROWTH TECHNIQUES

Crystal growth is a highly complex phase change phenomenon. The phase change may occur from the solid, liquid or vapour state. With regard to the phase transitions, the crystal growth methods are broadly classified into four main categories (Buckley, 1951, Laudice, 1970, Pamplin, 1975, Brice, 1986).

- Solid growth techniques (solid solid)
- Growth from vapour (vapour solid)
- Melt growth techniques (liquid solid)
- Growth from solution (liquid solid)

1.4.1 Solid Growth Techniques

In solid growth technique, single crystals are developed by the preferential growth of a polycrystalline mass. This can be achieved by straining the material and subsequent annealing. Large crystals of several materials, especially metals have been grown by this method (Barrett and Massalski, 1966). The main advantage of solid growth method is that this technique permits the growth at low temperatures without the presence of additional component. But as the growth takes place in the solid, density of sites for nucleation is high and it is difficult to control nucleation.

1.4.2 Growth from Vapour

Vapour growth techniques can be adopted for the growth of materials which lack a suitable solvent and sublime before melting at normal pressure. Vapour growth methods have been employed to produce bulk crystals and to prepare thin layers on crystals with a high degree of purity. Growth from vapour phase may generally be subdivided into

- Physical vapour transport (PVT)
- Chemical vapour transport (CVT)

1.4.2.1 Physical Vapour Transport (PVT)

In PVT technique the crystal is grown from its own vapours and this method does not involve any extraneous compound formation or reaction. The PVT methods are limited to materials having an appreciable vapour pressure at attainable temperatures. There are two types of techniques employed in physical vapour transport process; sublimation-condensation and sputtering. The first method involves sublimation of the charge at the high temperature end of the furnace, followed by the condensation at the colder end (Faktor and Garrett, 1974, Piper and Polich, 1961). Sputtering techniques are preferred to low vapour-pressure substances and mainly this method has been used to prepare thin films rather than discrete crystals. The principal advantage of this technique is that film growth can be possible at lower temperature than in ordinary sublimation-condensation growth. The PVT techniques are used to

prepare a variety of crystals (Bremer, 1963, Bradley, 1963, Reynolds, 1963) and for the production of epitaxial films (Holland, 1956, Archibald and Parent, 1976).

1.4.2.2 Chemical vapour transport (CVT)

Chemical vapour transport technique involves a chemical reaction between the source material to be crystallized and a transporting agent. The material to be crystallized is converted into one or more gaseous product, which either diffuses to the colder end or gets transported by a transporting (carrier) gas. At the cold end, the reaction is reversed so that the gaseous product decomposes to deposit the parent material, liberating the transporting agents which diffuses to the hotter end and again reacts with the charge. The commercial importance of vapour growth is in the production of thin layer by chemical vapour deposition (Schafer, 1964, Kaldis, 1972, Kulkarni, 1994, Arivuoli *et al.*, 1986).

1.4.3 Melt Growth Technique

Melt growth is the process of crystallization by fusion and resolidification of the pure material. It is the fastest of all crystal growth methods and is widely used for the preparation of large single crystals. Melt growth methods are limited to materials which melt congruently and have an experimentally viable vapour pressure at its melting point. This method requires only simple systems. The material to be grown is melted and after that

it may progressively be cooled to yield the crystalline matter. This method has been generally employed for the growth of metals, semiconductors, and laser host crystals. Single crystals with high degree of perfection and purity can be obtained by this method. Usually melt growth methods are grouped into two categories.

1) Normal freezing method

- Bridgman technique
- Czochralski technique

2) Zone-growth method

- Zone melting method
- Floating zone method

There are two versions for Bridgman's method; Horizontal Bridgman method (Chalmer's technique) and Vertical Bridgman method (Bridgman-Stockbarger technique). In these techniques, directional solidification is obtained by slowly withdrawing a boat containing molten material through a temperature gradient (Bridgman 1925, Stockbarger 1936). The Bridgman technique is most frequently applied for the growth of metals, semiconductors and alkaline earth halides (Shah, 1993, Bhatt *et al.*, 1989, Beny *et al.*, 1963). But this method cannot be used for materials having high melting point and high expansion coefficient. Czochralski method is the most powerful method for growing single crystals and is basically a crystal pulling system. The

advantage of this method over the Bridgman method is that it can accommodate the volume expansion associated with the solidification. Czochralski method has gained wide recognition particularly in growing single crystals of semiconductors like silicon (Dash, 1959) and other materials (Howe and Elbaum, 1961, Furukawa *et al.*, 1990).

Zone melting is mainly considered as a purification technique. However, it may be used as a method for the growth of single crystals. In this method, a zone or part of the solid material is melted and this molten zone travels together with the heating elements. The advantage of zone melting is that it offers a relatively simple way of producing doped crystals containing deliberately admixed additives in a given concentration in uniform distribution (Pfann, 1966). Floating zone technique developed by Keck and Golay (Keck and Golay, 1953) is a variant of the zone melting technique in which no crucible is used. This method is especially suitable for the preparation of high purity silicon and germanium.

1.4.4 Growth from Solution

Another method of growth of crystals is the precipitation technique from solution. In this method, the crystals are prepared from a solution at a temperature well below its melting point. This may help to grow crystals even at room temperature, and it will turn out to be more advantageous. Here the crystallisation takes place from the critically supersaturated solution. The supersaturation may be achieved by lowering the temperature of the solution

or by slow evaporation or by giving continuous supply of materials to compensate for the material that precipitates out. The present work utilises this method. The solution growth methods are classified according to the temperature range and the nature of the solvents used. The main methods commonly used in this process are:

- High temperature solution growth.
- Hydrothermal growth
- Low temperature solution growth

1.4.4.1 High temperature solution growth

High temperature solution growth includes a number of related techniques (Udea and Mullin, 1975). The flux method and liquid phase epitaxy are the two widely used methods (Brice, 1973, Hartmann, 1973). A high temperature solvent, which reduces the melting temperature of the solute, is referred as flux (Elwell and Scheel, 1975). The main advantage of the flux growth is the reduction of high temperature. The materials to be crystallised are dissolved in proper solvent at a temperature slightly above the saturation temperature; slow cooling of the container allows the growth of crystals. Slow cooling of the flux is also effective in obtaining slightly bigger crystals.

1.4.4.2 Hydrothermal growth

This is a well-known and widely used technique to grow crystals of certain class or species of materials, which are insoluble in water at standard temperature and pressure. This is more imitative to the natural growth of certain important minerals. Almost all metals and oxides show an appreciable increase in solubility due to the increase in temperature and pressure. It can be treated as aqueous solution growth at elevated temperature and pressure. Autoclaves with gold or silver linings are usually utilised for the growth purpose. The hot saturated solution is directed towards the upper (colder) part, where it becomes cold and supersaturated and hence the growth takes place. The solution simply acts as a transporting agent for the solid phase. Synthetic quartz crystals are grown by this technique (Laudise, 1959). The natural process of crystallisation beneath the earth resembles this growth technique.

1.4.4.3 Low temperature solution growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. 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 (Chernov, 1984).

Low temperature solution growth can be further subdivided as

- Crystallization by Slow Cooling
- Crystallization by Solvent Evaporation
- Gel method

1.4.4.3.1 Crystallization by Slow Cooling

This is one of the best suited methods of growing bulk single crystals. In this method, supersaturation is attained by a change in temperature usually throughout the whole crystallizer. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the metastable region along the saturation curve in the direction of lower solubility. Since the volume of the crystallizer is finite and the amount of substance placed in it is limited, the supersaturation requires systematic cooling. It is achieved by using a thermostated crystallizer and volume of the crystallizer is selected based on the desired size of the crystals and the temperature dependence of the solubility of the substance. The temperature at which such crystallization can begin is usually within the range of 45 °C to 75 °C and the lower limit of cooling is the room temperature.

1.4.4.3.2 Crystallization by Solvent Evaporation

In this method, an excess of a given solute is established by utilizing the difference between rates of evaporation of the solvent and the solute. In contrast to the cooling method, in which the total mass of the system remains constant, in the solvent evaporation method, the solution loses particles which are weakly bound to other components, and, therefore, the volume of the solution decreases. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore, the solvent evaporates more rapidly and the solution becomes supersaturated. Usually, it is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This is the oldest method of crystal growth and technically, it is very simple. Typical growth conditions involve temperature stabilization of about $\pm 0.005^\circ \text{C}$ and the rate of evaporation of a few mm^3/hr .

1.4.4.3.3 Gel method

Gel growth is an alternative technique to solution growth with controlled diffusion and the growth process is free from convection. This technique has gained considerable importance due to its simplicity and effectiveness in growing single crystals of certain compounds. Gel technique is a simple and elegant method of growing single crystals under controlled growth and at room temperatures. Here, solutions of two suitable compounds,

which give rise to the required insoluble crystalline substance by mere chemical reaction between them, are allowed to diffuse into the gel medium and chemically react as follows:



where AX and BY are the solutions of two compounds, AB is the insoluble substance and XY is the waste product. This method can be useful for substances having very high solubility (Buckley, 1995, Henisch, 1970). The gel medium prevents turbulence and helps the formation of good crystals by providing a frame work of nucleation sites. Moreover, the convection is absent in gel growth experiments.

1.5 LITERATURE SURVEY

Literature survey plays an important role in any research work. Some of the relevant materials connected to the topic are given below. The design of efficient materials for applications in non-linear optical effect is based on asymmetric polarization, induced by electron donor and electron acceptor groups on either side of the molecule at appropriate positions in the molecular systems. Due to their commercial importance in the fields of optical communication, signal processing, sensing and instrumentation, non-linear optical materials capable of producing second harmonic generation, have been studied (Eaton, 1991, Xu and Xue, 2008). In order to understand the microscopic origin of non-linear behavior of organic NLO materials,

considerable theoretical and experimental investigations have also been made (Kerkoc *et al.*, 1990, Dmitriev *et al.*, 1991). These efforts have brought its fruits in applied aspects of non-linear optics. To obtain information on the behavior of normal modes, the effect of various types of intermolecular forces and the nature of hydrogen bonding on these non-linear optical materials, IR and Raman spectroscopy has been used. Information about electronic transitions can be achieved by the analysis of UV-visible spectrum (Rao, 1975). Since atoms or molecules absorb UV-visible radiation at different wavelength, spectroscopy is often used in physical and analytical chemistry for the identification of substances through the spectrum emitted from or absorbed by them. Both the experimental and theoretical techniques are necessary for the accurate measurement of the properties of NLO materials. Furthermore, for the systematic analysis of the properties of these NLO materials, designing of optimization strategies are also important and this can be enhanced by understanding the relationship between electronic and geometric structure. In this regard, quantum chemical computations which are particularly useful for the determination of molecular properties and interpretation of experimental data those are inaccessible experimentally has to be carried out. Keeping these in mind, efforts were made to grow five non-linear optically active crystals by slow evaporation technique and were characterized using FT-IR, FT-Raman and UV-visible spectral techniques and

interpreted by quantum chemical computations using Gaussian'09 program package.

Amino acid crystals such as L-threonine, L-alanine, L-phenylalanine, L-arginine have been grown by slow evaporation and temperature lowering methods from aqueous solution, and reported (Ramesh *et al.*, 2004, Razzetti *et al.*, 2002, Mahalakshmi *et al.*, 2006, Mallik and Kar, 2005). Optical properties of L-alanine single crystals were reported by (Misoguti *et al.*, 1996). Also (Banfi *et al.*, 2001) have grown high optical quality organic crystal N-(4-nitrophenyl)-L-prolinol (NPP) in methanol solution starting from toluene nucleated seeds. Leucine derivatives have potential non-linear optical applications from the amino acid family. The IR spectroscopy, X-ray diffraction (XRD) analysis, morphology, solubility test, metastable zone width, DTA–TGA analysis, optical transmittance and second harmonic generation efficiency of L-Leucine has been studied (Adhikari and Kar, 2012), L-Leucinamide hydrogen Squarate (Kolev *et al.*, 2009), L-Leucine L-Leucinium Picrate (Bhagavannarayana *et al.*, 2011) l-leucyl-L-leucyl-L-Leucine (Go and Parthasarthy, 1995). L-Leucine hydro bromide (Subramanian, 1967), L-Leucyl-L-Leucine (NathMitra and Subramanian, 1994), DL-Leucine (Di Blascio *et al.*, 1975), L-Leucine nitrate (Beulah *et al.*, 2000) etc have been explored as non-linear crystals.

Salicylic acid is a versatile ligand with benzene ring, displaying a variety of bonding modes. The salicylate ion $C_7H_5O_3^-$ – contains both the

carboxylic and hydroxyl functional groups and with this ion represents a bonding typical of the more complicated natural materials. Some metal salicylate complexes have been used as additives in medicine. Zinc which is one of the most abundant trace elements in the body is an important component of many proteins. Zinc carboxylates with organic ligands are interesting because of their potential biological activity. A zinc complex based on salicylic acid derivatives is a powerful charge-control agent for toners used in electro photography. Many of the zinc complexes are luminescent materials with potential applications in opto-electronic devices (Boaz *et al.*, 2005). The luminescent property of Tb³⁺ doped zinc salicylates and the relationship between the luminescent property and crystal structures have been reported earlier (Ding *et al.*, 2011).

The 4-nitrophenol (4NP) derivatives are interesting candidates, due to their typical one-dimensional (1D) donor-acceptor π system, and the presence of phenolic OH favors. The formation of materials with various organic and inorganic bases results in an enhancement of the hyperpolarizability of both species. The triphenylphosphine oxide (TPPO) is very important in both organic and inorganic chemistry. Also it has a great conformational flexibility and the ability to form the hydrogen bond (Khalid and Al-Farhan, 1992). Especially the oxygen atom of TPPO can act as a single, double or triple hydrogen bond acceptor, and the orientation of the phenyl groups is not restricted to certain torsion-angle values (Lamas *et al.*, 1991). These properties

make TPPO as versatile hydrogen-bond acceptor and a very useful crystallization aid (Etter and Baures, 1988).

There are many reports available about the 3,5-dinitrobenzoic acid bonded to the metals like sodium (Rathika and Raman, 2014), lithium (Yang and Ng, 2007, Gillon *et al.*, 2005, Tiekink *et al.*, 1990), manganese (Yang *et al.*, 2001), magnesium (Smith, 2013), potassium (Du and Hu 2006), cerium (Tahir *et al.*, 1996), calcium (Hundal *et al.*, 1996), strontium (Kanters and Harder, 1987), zinc and cobalt (Yang *et al.*, 2000). Further, (Miminoshvili *et al.*, 2003), report the complexes of Co, Ni, Cu and Zn obtained by the reaction of dialkylammonium 3,5-dinitrobenzoates with hydrated metal sulfates in dimethyl sulfoxide. The nitro-substituted aromatic acid of 3,5-dinitrobenzoic acid has been used to synthesise chiral crystalline adduct materials with physical properties potentially useful in applications such as non-linear optics. The 3,5-dinitrobenzoate anion satisfies the push-pull requirement and it can be approximated to a dipolar NLO chromophores. Also, it has a relatively strong proton donor-acceptor due to the presence of the COOH carboxylic group.

Benzoic acid, $C_7H_6O_2$, is the simplest aromatic carboxylic acid. The name is derived from gum benzoin, which was for a long time the only source for benzoic acid. Benzoic acid is also a common food preservative. Benzoic acid helps to prevent infection caused by bacteria. Among such agents, metal complexes of biologically active ligands are attractive as metal ions can interact with different steps of pathogenic life cycles (Bury *et al.*, 1987). Zinc

is an essential element in human growth. This element is known to regulate activity in over 300 metalloenzymes and as a component of “zinc fingers” participates in the reliable transfer of genetic information (Vallee and Auld, 1990). In addition to physiological functions, zinc and its compounds have important roles in clinical medicine. Certain zinc salts are biologically active ingredients useful to counter bacterial attachment. Zinc and its compounds have anti-bacterial and anti-viral activity and the wound-healing effect of zinc containing ointments has been known for several centuries.

1.6 AIM AND SCOPE OF THE THESIS

The fundamental principle and applications of non-linear optical phenomena and an insight into different NLO materials have been discussed. The brief introduction on crystal growth and classification of crystal growth methods has been described. Various methods of crystal growth, especially the fundamental and experimental aspects of low temperature solution growth technique have been explained in detail. The importance of nucleation kinetics to optimize the growth condition for growing optically high quality bulk crystals is presented. Computational methods play an important role in the crystal design process since they do not only supplement experimental approaches but also contribute directly to the design and discovery of new crystals. Special care has to be taken on the application of theoretical and experimental methods on selected molecules which will give clear insight into the matter. A comparison of theoretical (DFT) and experimental (FT-IR, FT-

Raman, FT-NMR and UV-visible) spectra leads to an in depth knowledge of the physical and chemical structure of the investigated crystal structures. Vibrational spectroscopy encompasses the techniques of infrared (IR) and Raman spectroscopy which are now extensively used in most of the vibrant research areas including photonics, medical diagnosis, material science, planetary science, biochemical analysis, pharmaceutical industry etc. It deals with the measurement and interpretation of absorption and emission of electromagnetic radiations, when atoms or molecules or ions move from one energy level to the other. Spectroscopic investigations in different regions of electromagnetic spectrum provide information regarding rotational, vibrational and electronic energy levels of molecules, thereby obtaining the complete vibrational characteristics of the molecule and can be used to derive valuable information regarding the structure of the molecule, nature of chemical bonding, vibrational interactions, symmetry of molecular groups or ions in crystals, H-bonding, the nature of co-ordination between atoms etc. IR and Raman spectroscopy combined with quantum chemical computations has been used as an effective tool in the vibrational analysis of NLO compound. The present work deals about the investigation on potential organic and semi-organic materials, such as L-Leucinium Squarate Monohydrate, Zinc salicylate Dihydrate, Triphenyl Phosphine oxide-4-nitrophenol, Potassium 3,5-dinitrobenzoate, Zinc Benzoate.