CHAPTER 1

INTRODUCTION TO SOLUTION GROWTH TECHNIQUE, NONLINEAR OPTICS AND IRRADIATION

1.1 INTRODUCTION

“New materials are the lifeblood of solid state research and device technology. Contrary to what many believe, new materials are not usually discovered by device engineers, solid state theorists, or research managers; they are mostly discovered by crystal chemists who are crystal growers. Some physical phenomena are only exhibited in single crystals and can only be studied and understood in single crystals. Thus the crystal grower - especially if he/she develops a proficiency in relating structure, bonding and other chemo-physical considerations to properties of interest – is in a key position in determining the direction and success of solid state research and ultimately – technology” (van Bueren 1960).

The study of crystals has had an influence on society through the ages, both in an abstract ideological and in a practical technological sense. The importance and need for single crystals for the fabrication of any solid state devices has never ceased since the invention of transistor in 1948. Crystals are used in much advanced equipment because in a crystal the charge carriers (electrons and holes) can move freely; the wavelength assorted with moving charge carriers which is inversely proportional to its momentum is in general large when compared with lattice spacing. Since there is a vast demand for solid-state devices, efforts have been directed towards producing
larger size crystals in recent years. Even in the present era of scientific team work, successful research on crystal growth can be accomplished by individuals with relatively modest approach and apparatus.

The invention of the pulsed ruby laser in 1960 provided a revolutionary new light source, of exceedingly high intensity. The amazing high power, high brightness, good coherence, highly directional, narrow bandwidth and short pulses of laser beam enable new technologies which is profoundly changing our way of life. Thus it opened new frontiers in science and optics. One of the new horizons opened by laser is the field of nonlinear optics. Now it has become a vast and mystifying complex field of research. Exciting materials known as nonlinear optical (NLO) materials have come upon the materials science scene and are being studied by many research groups around the world. These new materials operate on light in a way very analogous to the way semiconductors operate on electrons to produce very fast electronic switching and computing circuits. It is imagined that the successful production of these materials will lead to computing machines operating on light and yielding the ultimate speed in information processing, as electrons typically move only at about one tenth to one half the speed of light. Such devices will require much less heat dissipation and may lead to further miniaturization of computing circuits. Thus the nonlinear optical crystals have played an important role in laser science and technology, and the search for new NLO crystals, particularly for the ultraviolet (UV) and infrared (IR) spectral regions, is still very active, even though intensive efforts in this field have been in progress for nearly forty years. Scientists working in this field realize the extreme importance, in the search for new NLO crystals, of a thorough elucidation of the structure–property relationship between NLO effects and its microstructure. The development of these materials has gained much impact from its wide application ever since the first observation of optical second harmonic generation (SHG). A microscopical expression of the
NLO susceptibility was given in the classical treatise by Bloembergen and co-workers and was well documented (Bloembergen 1965; Bloembergen and Pershan 1962).

1.2 TECHNIQUES USED TO GROW CRYSTALS

Methods of crystal growth can be classified according to various criteria; we can use phase change; we may consider ‘pure’ or ‘impure’ systems, or the idea of conservative or non-conservative systems. The technique of crystal growth can be:

(a) growth from solution  
(b) growth from melt and  
(c) growth from the vapour phase.

In general, the crystallization process takes place by three steps:

(i) achievement of supersaturation or supercooling  
(ii) formation of crystal nuclei and  
(iii) growth of crystal.

1.3 GROWTH FROM SOLUTION
1.3.1 Solution, Solubility and Supersolubility

Solution is a homogeneous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity. Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. Solubility gradient is another important parameter, which dictates the growth procedure. Neither a flat nor a steep solubility curve will enable the growth of bulk crystals from solution;
while the level of supersaturation could not be varied by reducing the temperature in the former, even a small fluctuation in the temperature will affect the supersaturation to grow the good quality bulk crystals in both cases. If the solubility gradient is very small, slow evaporation of the solvent is the other option for crystal growth to maintain the supersaturation in the solution.

Growth of crystals from solution is mainly a diffusion-controlled process; the medium must be viscous to enable faster transference of the growth units from the bulk solution by diffusion. Hence, a solvent with less viscosity is preferable. Supersaturation is an important parameter for the solution growth process. The crystal grows by the accession of the solute in the solution as a degree of supersaturation is maintained. The solubility data at various temperatures are essential to determine the level of supersaturation. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process. The diagram is divided into three zones, which are termed as region I, region II and region III. Region I corresponds to the undersaturated zone, where crystallisation is not possible. This region is thermodynamically stable. The region II between the supersolubility curve and the solubility curve is termed as metastable zone where spontaneous crystallization is improbable. Seeded crystal growth can be achieved in this region. The unstable or labile zone where the spontaneous nucleation is more probable which is termed as region III (Figure 1.1).

1.3.2 Expression for Supersaturation

In order to grow crystals, the solution must be supersaturated; the concentration of the solute in the solvent should be more than the equilibrium concentration. Supersaturation is the driving force, which governs the rate of crystal growth. The supersaturation of a system may be expressed in number
of ways. The degree of supersaturation of a solution is defined using the concept of absolute supersaturation.

\[ \alpha = C - C_0 \]  

(1.1)

where \( C \) is the concentration of the dissolved substance at a given moment and \( C_0 \) is its solubility limit. The degree of supersaturation can also be defined as the relative supersaturation given by

\[ \beta = \frac{C - C_0}{C_0} = \frac{\alpha}{C_0} \]  

(1.2)

or as the coefficient of supersaturation

\[ \Gamma = \frac{C}{C_0} = \beta + 1 = \frac{\alpha}{C_0} + 1 \]  

(1.3)

Figure 1.1 Solubility diagram showing different levels of saturation
The quantities $\alpha$, $\beta$ and $\Gamma$ are obviously inter related (Khamsii 1969). The relation between supersaturation and spontaneous crystallization was reported by Meirs and Issac (1987).

1.3.3 Methods of Crystallisation

Low temperature solution growth method can be subdivided as

1) Slow cooling method
2) Slow evaporation method
3) Temperature gradient method

1.3.3.1 Crystallization by slow cooling of solutions

This is one of the best methods to grow bulk single crystals. In this method, supersaturation is produced by a change in temperature usually throughout the whole crystalliser. The crystallisation 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 crystalliser is finite and the amount of substance placed in it is limited, the supersaturation requires systematic cooling. It is achieved by using a thermo stated crystalliser and volume of the crystalliser 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 crystallisation can begin is usually within the range 45 to 75°C and the lower limit of cooling is the room temperature.
1.3.3.2 Crystallisation 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 (Petrov 1969). 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 to about ± 0.05°C and the rate of evaporation of a few mm³/hr.

1.3.4 Solvent Selection

After choosing the solution method for growth, suitable choice of solvent is necessary. The solvent must be chosen, taking into account the following factors:

a) a good solubility for the given solute
b) a good temperature co-efficient of solute solubility
c) less viscosity
d) less volatility
e) less corrosion and non-toxicity
f) small vapour pressure and
g) cost advantage
It is known that the choice of solvent provides some control over crystal habits and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Sometimes this is sufficient to result in the precipitation of a new crystalline phase. Also this effect is related to the influence of impurities or additives upon habit (Buckley 1951).

1.3.5 Preparation of Solutions

Preparation of solution to grow the desired crystals by solution growth technique is an important stage of crystal growth. The solution is saturated as per the solubility data obtained from the solubility diagram (accurate solubility–temperature data). The saturated solution is filtered using the filter paper. The filtered solution is transferred into the growth beaker and placed in the Constant temperature bath (CTB). The desired supersaturation required is obtained by just lowering the temperature. Extreme care is to be taken to avoid undersaturation, which results in the dissolution of seed crystal. Similarly high supersaturation is also to be avoided to prevent the formation of spurious nucleation. The growth vessel is hermetically sealed to avoid the evaporation of the solvent. The solution is tested for saturation by suspending small test seed crystal in the solution. If the system is not in equilibrium, the seed crystal either dissolves or the solute will crystallize on the seed. By adjusting the temperature, the necessary equilibrium condition is achieved and the test seed crystal is removed and a fresh seed crystal is introduced for crystal growth.

1.3.6 Seed Preparation

The quality of the crystal grown very much depends on the quality of the seed crystals used. Small seed crystals can be obtained by spontaneous nucleation in the labile region of the supersaturated solution. A seed used to
grow a large uniform crystal must be single crystal free of inclusions, cracks, block boundaries, sharp cleaved edges, twinning and any other obvious defects. It should be of minimum size, compatible with other requirements. When larger crystals of the same material are already available, they can be cut in the required orientation to fabricate the seed crystal. Since the growth rate of the crystal depends on the crystallographic orientation, the seed crystal must be cut in such a way that it has larger cross-section in the fast growing direction.

1.3.7 Cooling Rate

To obtain the required supersaturation, a driving force for the growth of crystal, the temperature of the growth solution is lowered. The cooling rate is to be employed according to the growth rate of the crystals. A large cooling rate changes the solubility beyond metastable limit and fluctuations in the supersaturation may encourage inclusions (Wilcox 1983). A proper balance between temperature lowering rate and growth rate will yield good quality crystal.

1.4 DEFINITION OF NONLINEAR OPTICS

Nonlinear Optics (NLO) deals with the interactions of applied electromagnetic fields in various materials to generate new electromagnetic field altered in phase, frequency, amplitude or other physical properties (Williams 1984). The nonlinear behaviour will begin once the perturbation to the interatomic field becomes significant. At fields very much below that of the atomic field, the perturbation is not sufficient to generate a measurable nonlinear effect.
The field of NLO and photonics are rapidly emerging as the technology for the twenty first century (Prasad and Reinhardt 1990). Photonics is the technology in which a photon instead of an electron is used to acquire, store, process and transmit information. A photonic circuit is equivalent to electronic circuit, in which photons are conducted through channels. Light can be switched from one channel to another at certain junction points. For optical switching at these junctions, one needs to use a material that allows the manipulation of an electric field or laser pulse. The materials which manipulate the light at these junction points are known as NLO materials and these are gaining importance in technologies such as optical communication, optical computing and dynamic image processing (Boyd 1992, Bloembergen 1965). Photonics has many distinct merits over electronics. The most important advantage is the gain in speed due the fact that a photon travels much faster than an electron. Other advantages are that there is no electrical and magnetic interference, there by the photonic circuits are fully compatible with the existing fiber optics networks (Prasad and Williams 1991).

Before the advent of the lasers, optics assumed that optical parameters of the medium are independent of the intensity of the light propagating in these medium. The reason is that, the electric field strength generated by the non-laser light sources is of the order of $10^3$ V/cm, is very much smaller than the interatomic field strength i.e. $10^7$ to $10^{10}$ V/cm of the medium, which is unable to affect the atomic fields of the medium and there by the optical properties of the medium. Lasers have drastically changed the situation as they generate electric field strength varying from $10^5$ to $10^{10}$ V/cm, which is able to commensurate to that of the atomic electric fields of the medium and there by affect the optical properties of the medium and thus generate new electromagnetic fields altered in phase, frequency, amplitude. This is the domain of NLO. NLO processes can be viewed as
dielectric phenomena. Electric fields such as an applied dc field or a propagating electromagnetic wave when passes through the medium induces electron displacement. Electrons that are bound to the nearby nuclei in the medium gets slightly perturbed by the external applied electromagnetic field and begins oscillating at the applied frequency. The magnitude of such an induced polarization ($P$) at modest field strengths will be proportional to the applied field and expressed as (Zernike and Midwinter 1973)

$$P = \chi^{(1)} E$$  \hspace{1cm} (1.4)

where $E$ is the magnitude of the applied electric field and $\chi^{(1)}$ is the polarizability of the material.

The NLO phenomena occur at sufficiently intense fields. As the applied field strength increases (e.g., lasers) the polarization response of the medium is no longer linear as shown by the Equation (1.4). The induced polarization ($P$) becomes a function of the applied field and given by (Shen 1984)

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \ldots$$  \hspace{1cm} (1.5)

where the $\chi^{(2)}$ and $\chi^{(3)}$ coefficients represent the second and third order susceptibilities of the medium respectively.

At the molecular level Equation (1.5) is expressed as (Prasad and Reinhardt 1990)

$$P = \sum_j \alpha_{ij} E_j + \sum_{j<k} \beta_{ijkl} E_{ij} E_{kl} + \sum_{j<k<l} \gamma_{ijkl} E_{ijkl} + \ldots$$  \hspace{1cm} (1.6)
where
\[
\alpha_{ij} \quad - \quad \text{Polarizability}
\]
\[
\beta_{ijk} \quad - \quad \text{First order hyperpolarizability (second order effects)}
\]
\[
\gamma_{ijkl} \quad - \quad \text{Second order hyperpolarizability (third order effects)}
\]
and i, j, k, l corresponds to the molecular coordinates.

A medium (crystal) exhibiting such a NLO response might consist of molecules with asymmetric charge distribution. If the medium (or molecule) is centrosymmetric, then first order hyperpolarizability (\(\beta\)) is zero, indicating that centrosymmetric media do not show second harmonic generation. This can be explained as follows. If a field +\(E\) is applied to the medium, Equation (1.6) predicts the first nonlinear term as +\(\beta E^2\). If a field −\(E\) is applied, the polarization is still predicted to be +\(\beta E^2\). Yet if the medium is centrosymmetric the polarization should be −\(\beta E^2\). This contradiction can be resolved only if \(\beta=0\). Thus the centrosymmetric medium has zero \(\beta\)-value. In the case of third order NLO susceptibility, if +\(E\) field produces polarization +\(\gamma E^3\) and −\(E\) field produces −\(\gamma E^3\), so the second order hyperpolarizability (\(\gamma\)) is the first non-zero nonlinear term in centrosymmetric media (Williams 1984).

Williams (1984) and Yariv (1975) put forth a chemically oriented picture to describe the connection between the nonlinear propagation response and applied electric field in medium. This description considers an individual molecular unit rather than a collection of molecular units to describe the NLO optical phenomena. The applied electric field compete with the interatomic binding forces, there by permitting the electrons to move further away from the equilibrium positions giving rise to microscopic polarizability.
1.4.1 Theoretical Background

In 1962, theoretical investigations dealing with the behavior of light waves by solving Maxwell’s Equation in a nonlinear dielectric and at the boundary of nonlinear media were performed by Armstrong et al (1962) and Bloembergen and Pershan (1962) respectively.

The explanation of nonlinear 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 solid 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 nonlinear, which results in generation of frequencies that are different from those of incident fields. Thus second and higher harmonic generation occur. The properties like processibility and interfacing ability with other materials led to the way of study of NLO effects and introduction of new concepts. The development of nonlinear optics during the decade of the sixties was followed by a decade with relatively little activity. Since 1980, the subject has experienced a period of continuous growth. As described by Bloembergen (1999) in a historical overview paper, for this topic one may designate the decade of the sixties as the period of “classical antiquity”, the seventies as the Middle Ages, with the renaissance starting in 1980. Downer (2002) described that today’s nonlinear optics is probably in “a new law” and a new era is about to begin.

1.4.2 Mathematical Background

Light propagating through a medium or through vacuum may be described by a transverse wave, where the oscillating electric and magnetic
field components are solutions to the Maxwell Equations. The NLO material is a compound, in which nonlinear polarization (P) is invoked on the application of electric field, which results from the application of intense laser source. The nonlinear polarization induced in the medium has to obey these Equations.

\[ \nabla \times E = -\frac{\partial}{\partial t}(B) \]  
(1.7)

\[ \nabla \times H = j + \left( \frac{\partial}{\partial t} \right) D \]  
(1.8)

\[ \nabla . D = P \]  
(1.9)

\[ \nabla . B = 0 \]  
(1.10)

with relations connecting to the polarization of the medium to displacement vector (D).

\[ D = \varepsilon_0 E + P \]  
(1.11)

\[ j = \sigma E \]  
(1.12)

where \( \sigma \) - conductivity

The induced polarization P may be taken to include both linear and nonlinear part (\( P_{NL} \)).

\[ P = \varepsilon_0 \chi E + P_{NL} \]  
(1.13)

Substituting this in Maxwell’s Equation (1.8) for the curl of the magnetic field yields with \( \varepsilon = \varepsilon_0(1+\chi) \)
\( \nabla \times H = \sigma E + \varepsilon \left( \frac{\partial}{\partial t} \right) E + \left( \frac{\partial}{\partial t} \right) P^{NL} \) \hspace{1cm} (1.14)

Taking the curl of electric field component the starting form of first Equation (1.7) can be written as

\[
\nabla \times \nabla \times E = -\left( \frac{\partial}{\partial t} \right) \nabla \times B
\]
\[
= -\mu \left( \frac{\partial}{\partial t} \right) \nabla \times H
\]
\[
= -\mu \frac{\partial}{\partial t} \left[ \sigma E + \varepsilon \left( \frac{\partial}{\partial t} \right) E + \left( \frac{\partial}{\partial t} \right) P^{NL} \right]
\] \hspace{1cm} (1.15)

Also the general vector relation holds

\[
\nabla \times \nabla \times E = \nabla (\nabla \cdot E) - \nabla^2 E
\] \hspace{1cm} (1.16)

By taking \( \nabla \cdot E = 0 \) (for a charge free medium)

\[
\nabla^2 E = \mu \sigma \left( \frac{\partial}{\partial t} \right) E + \mu \varepsilon \left( \frac{\partial^2}{\partial t^2} \right) E + \mu \left( \frac{\partial^2}{\partial t^2} \right) P^{NL}
\] \hspace{1cm} (1.17)

This is the wave Equation that describes the light propagation in a medium, provided the medium is dispersion free.

### 1.5 Various Types of Second-Order NLO Effects

#### 1.5.1 Second Harmonic Generation (SHG)

The first break through of SHG was achieved in 1961, when pulsed laser beam was sent into a piezoelectric crystal sample.
Peter A Franken (Franken et al 1961) and several coworkers at the University of Michigan were the first to observe SHG experimentally. They focused a 3 kW pulse of red ruby laser light onto a quartz crystal. Just about one part of $10^8$ of the incident wave converted to the 347.15 nm UV second harmonic. Thus the frequency of the incident light gets doubled which enables one to extend the range of laser wavelength into the blue and UV parts of the spectrum. This is called frequency doubling. Two waves each of frequency $\omega$ simultaneously superimposed constructively. The resulting wave excites an electron from the ground state to a virtual excited state. On relaxation, one wave of frequency $2\omega$ is emitted. To optimize SHG effect, one must optimize $\chi^{(2)}$. $\chi^{(2)}$ is influenced by various structural features. Crystallographically, the compound must be noncentrosymmetric by nature.

The process of transformation of light with frequency into light with double frequency is referred as SHG (Tarasov 1981) (Figure 1.2).

The $p_1$ and $p_2$ are the momenta of the absorbed photons, and $p$ is the momentum of the emitted one. The process is spontaneous process and involves three-photon transitions

\[ h\nu + h\nu = 2h\nu \]  \hspace{1cm} (1.18)

\[ p_1 + p_2 = p \]  \hspace{1cm} (1.19)

**Figure 1.2 Second harmonic generation**
i.e., two photons with an energy of $hv$ per each photon are absorbed spontaneously to emit a photon with an energy $(2hv)$. The dashed (-----) line corresponds to the virtual level.

1.5.2 Sum Frequency Generation or Parametric Generation

The transformation of the light wave with frequency $\nu$ into two new light waves with frequencies $\nu_1$ and $\nu_2$ is termed as parametric generation (Tarasov 1981) (Figure 1.3).

$$hv = h\nu_1 + h\nu_2 \quad (1.20)$$

$$p = p_1 + p_2 \quad (1.21)$$

**Figure 1.3 Optical parametric generation**

This also represents a three-photon process in which one photon with energy $hv$ is absorbed and two photons, one with energy $h\nu_1$ and the other with $h\nu_2$, are emitted.

The coupled Equations (Sum and difference frequency generation) can be explained by the following
Consider an input wave with electric field components at frequencies $\omega_1$ and $\omega_2$. Recalling the Equation (1.17)

$$\nabla^2 E = \mu_0 \left( \frac{\partial}{\partial t} \right) E + \mu_e \left( \frac{\partial^2}{\partial t^2} \right) E + \mu_i \left( \frac{\partial^2}{\partial t^2} \right) P^{NL}$$

This is a vectorial expression that may be used in three fold for the three vector components. In the simple case of frequency mixing with two incoming plane waves propagating along $Z$-axis, the assumption of a linear polarization in a single transverse direction is

$$E_1(z,t) = E_1(z) \exp(\text{i}\omega_1 t - \text{i}k_1 z)$$
$$E_2(z,t) = E_2(z) \exp(\text{i}\omega_2 t - \text{i}k_2 z)$$

(1.22)

The incoming fields induce a nonlinear polarization at frequency $\omega = \omega_1 + \omega_2$ that may be written as

$$P^{NL}(z,t) = dE_1(z)E_2(z)\exp[\text{i}(\omega_1+\omega_2)t - \text{i}(k_1+k_2)z]$$

(1.23)

and we assume that the new field is created at frequency

$\omega_3 = \omega_1 + \omega_2$ with a field.

$$E_3(z,t) = E_3(z) \exp(\text{i}\omega_3 t - \text{i}k_3 z)$$

(1.24)

Substituting these fields into the wave Equation, for plane waves traveling in the $z$-direction the field gradient may be written as

$$\nabla^2 E_3(z, t) = \frac{\partial^2}{\partial z^2} E_3(z, t)$$

(1.25)
Left side of the above Equation becomes

\[
\frac{\partial^2}{\partial z^2} E_3(z, t) + \mu \sigma \frac{\partial}{\partial t} E_3(z, t) - \mu \varepsilon \frac{\partial^2}{\partial t^2} E_3(z, t) =
\]

\[\frac{d^2}{dz^2} E_3(z, t) + 2i k_3 \frac{d}{dz} E_3(z, t) - k_3^2 E_3(z, t) + i \omega_3 \mu \sigma
\]

\[E_3(z, t) + \mu \varepsilon \omega_3^2 E_3(z, t)
\]  

(1.26)

Applying the assumption the variation of amplitude over the distance of one wavelength will be small.

\[\left| \frac{d^2}{dz^2} E_3(z, t) \right| << \left| 2i k_3 \frac{d}{dz} E_3(z, t) \right|
\]  

(1.27)

The relation between the dielectric constant \( \varepsilon \) and magnetic susceptibility \( \mu \) is

\[\mu \varepsilon \omega_3^2 - k_3^2 = 0
\]  

(1.28)

\[2i k_3 \frac{d}{dz} E_3(z) \exp(i \omega_3 t - i k_3 z) + i \omega_3 \mu \sigma E_3(z) \exp(i \omega_3 t - i k_3 z)
\]  

(1.29)

The right side is evaluated as

\[\mu \frac{\partial^2}{\partial t^2} P_{NL}(z, t) = \mu \frac{\partial^2}{\partial t^2} dE_1(z)E_2(z) \exp[i(\omega_1 + \omega_2)t - i(k_1 + k_2)z]
\]

\[= -\mu(\omega_1 + \omega_2)^2 dE_1(z)E_2(z) \exp[i(\omega_1 + \omega_2)t - i(k_1 + k_2)z]
\]  

(1.30)
Equating two results

$$\frac{d}{dz} E_3(z) = -\frac{\sigma}{2} \sqrt{\frac{\mu}{\varepsilon_3}} E_3(z) - \frac{i\omega_3}{2} \sqrt{\frac{\mu}{\varepsilon_3}} dE_1(z)E_2(z) \exp\left[-i(k_1 + k_2 - k_3)z\right]$$

(1.31)

This basic equation found implies that the amplitude of the newly produced wave is coupled through the nonlinear constant d to the incoming wave. At the same time inverse processes will also take place where the newly generated frequency \(\omega_3\) mixes with one of the two incoming waves in a difference frequency mixing process like \((\omega_3 - \omega_2 = \omega_1)\). By inserting the fields in the Maxwell’s wave Equation in a similar fashion one can derive two more coupled amplitude Equations:

$$\frac{d}{dZ} E_1(z) = -\frac{\sigma}{2} \sqrt{\frac{\mu}{\varepsilon_1}} E_1(z) - i\frac{\omega_1}{2} \sqrt{\frac{\mu}{\varepsilon_1}} dE_3(z)E_2(z) \exp\left[-i(k_3 - k_2 - k_1)z\right]$$

$$\frac{d}{dZ} E_3(z)^* = -\frac{\sigma}{2} \sqrt{\frac{\mu}{\varepsilon_2}} E_3(z)^* + i\frac{\omega_2}{2} \sqrt{\frac{\mu}{\varepsilon_2}} dE_1(z)E_2(z)^* \exp\left[-i(k_1 + k_2 - k_3)z\right]$$

(1.32)

One application of sum frequency generation is to produce tunable radiation in the ultraviolet spectral region by choosing one of the input waves to be the output of a fixed frequency visible laser and the other to be the output of a frequency tunable visible laser. Difference frequency generation (DFG) will convert one high-energy photon and one low energy photon into another low energy photon. DFG has several forms like optical parametric generation and optical parametric oscillation.
1.5.3 Linear Electro-Optic Effect or Pockels Effect

The Pockels effect is a linear change in the refractive index of a medium in the presence of an external electric field. Here a dc field is applied to a medium through which an optical wave propagates. The change in the polarization due to the presence of these two interacting field components effectively alters the refractive index of the medium (Williams 1984).

1.5.4 Optical Rectification

The optical rectification is defined the ability to induce a dc voltage between the electrodes placed on the surface of the crystal when an intense laser beam is directed into the crystal (Williams 1984).

1.6 THIRD HARMONIC GENERATION (THG)

In the case of centrosymmetric materials, the expression (1.5) will lack terms in even powers of E and it will reduce to

\[ P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} EEE + \ldots \quad (1.33) \]

Or in vector notation

\[ P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(3)} E^2 E + \ldots \quad (1.34) \]

Thus we find the important relation for (inversion) symmetric media. All even powers in the susceptibility expansion are zero \( \chi^{(2n)} = 0 \).
As a consequence all even orders of the nonlinear polarization cancel:

\[ P^{(2n)} = 0 \]  \hspace{1cm} (1.35)

\[ P^{\text{NL}} = \varepsilon_0 \chi^{(3)} \text{ EEE} \]  \hspace{1cm} (1.36)

\( \chi^{(3)} \) is a material property that governs the nonlinear response of a medium and all nonlinear processes occurring in that medium. But the third order nonlinear processes are generally weak.

1.7 APPLICATIONS OF NLO EFFECTS

Various susceptibility functions and frequency arguments with their applications in various fields (Williams 1984) are given in Table 1.1 for \( \chi^{(2)} \) and \( \chi^{(3)} \).

Table 1.1 Various susceptibility functions with their applications

<table>
<thead>
<tr>
<th>Susceptibility</th>
<th>Effect</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi^{(2)}(0; \omega, -\omega) )</td>
<td>Optical rectification</td>
<td>Hybrid bistable device</td>
</tr>
<tr>
<td>( \chi^{(2)}(-\omega; \omega, 0) )</td>
<td>Electro-optic (Pockels) Effect</td>
<td>Modulators, variable phase retarders</td>
</tr>
<tr>
<td>( \chi^{(2)}(-2\omega; -\omega, \omega) )</td>
<td>Frequency doubling</td>
<td>Harmonic generation device</td>
</tr>
<tr>
<td>( \chi^{(2)}(-\omega_a; \omega_a, \omega_b) )</td>
<td>Frequency mixing</td>
<td>Parametric amplifiers, IR up convertors</td>
</tr>
<tr>
<td>( \chi^{(3)}(-\omega; \omega, \omega, -\omega) )</td>
<td>ac electro optic effect ac kerr effect</td>
<td>Optical bistability Phase conjugation</td>
</tr>
<tr>
<td>( \chi^{(3)}(-3\omega; \omega, \omega) )</td>
<td>Frequency tripling</td>
<td>Deep UV conversion</td>
</tr>
</tbody>
</table>
1.8 MATERIALS FOR NONLINEAR OPTICS

Applications of the nonlinear effects demand sufficient knowledge of the nonlinear properties of possible materials. The development of nonlinear optics is also intimately connected with the progress in NLO materials. The fast developments in photonics and optoelectronics necessitate the search for novel materials for NLO applications. Hence the progress in this area would be greatly enhanced by the availability of processed materials with sufficiently large NLO responses. With progress in crystal growth technology, materials having attractive nonlinear properties are being discovered at rapid pace (Baumert et al. 1987a; Chemla and Zyss 1987; Gunter et al. 1987). This has enabled the commercial development of single crystals with promising NLO properties.

1.8.1 Conversion Efficiency (\(\eta\))

To select a suitable nonlinear optical crystal, for a frequency conversion process, it is necessary to obtain high efficiency.

The conversion efficiency for SHG is

\[
\eta_{\text{SHG}} = \frac{P^{(2\omega)}}{P^{(\omega)}} \times \alpha \omega^2 d^2 L^2 \cdot \frac{\sin^2 \left( \frac{\alpha L}{2} \right) P^{(\omega)}}{\left( \frac{\alpha L}{2} \right)^2 A} \quad (1.37)
\]

From the derivation, it may be concluded that the conversion efficiency is proportional to the power density, so the total amount of generated light at the second harmonic is proportional to \([P^{(\omega)}]^2\).
1. thus second harmonic generation is a process that is nonlinear in the power dependence.

2. the efficiency is equal to the square of the nonlinear coefficient \( d \), or in other terms proportional to \( |\chi^{(2)}|^2 \).

3. the efficiency is proportional with \( L^2 \) and a "sine"-function involving \( L \); it seems that longer crystals will produce more second harmonic.

4. the efficiency is optimal if \( \Delta k = 0 \) and this is a condition that generally cannot be met in ordinary media. In birefringent media this condition can be written as \( k^{(2\omega)} = 2k^{(\omega)} \) and also the breakdown of inversion symmetry can be met at the same time.

The condition of \( \Delta k = 0 \) is referred to as the phase-matching condition. With the use of \( k = n\omega/c \) the phase matching relation is given by \( \Delta k = k^{(2\omega)} - 2k^{(\omega)} \).

1.8.2 General Considerations

Nalwa and Miyata (1996) have formulated a set of characteristics of a nonlinear optical material for optical applications. The nonlinear optical material must be highly transmitting at the fundamental and harmonic wavelengths and must have a laser induced damage threshold high enough to allow optical intensities that will provide adequate conversion efficiency. Phase matching must be possible in the material. The harmonic generation process requires that the phase velocities of the fundamental and harmonic radiation be matched. The material also needs to be of good optical quality to provide optical transmission without distortion. Above all, the crystal must
be accentric for SHG and have large refractive indices. Further, the materials must be non-hygroscopic to introduce it into demonstrable applications and must have mechanical and thermal stability. The magnitude and speed of the nonlinearities (Fast optical response time) are essential characteristics of the materials for NLO applications.

NLO materials can be broadly classified in two different categories as inorganic and organic materials. Each category (i.e. inorganic and organic) possesses its own set of advantages and disadvantages (Blau 1987) as shown in Table 1.2.

**Table 1.2 Advantages and disadvantages of Inorganic and Organic nonlinear materials**

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inorganic materials</strong></td>
<td></td>
</tr>
<tr>
<td>Highest bulk susceptibility</td>
<td>Absorption in visible region</td>
</tr>
<tr>
<td>Compatible physical properties</td>
<td>Poor response time</td>
</tr>
<tr>
<td></td>
<td>Degradative photorefractive effects</td>
</tr>
<tr>
<td><strong>Organic materials</strong></td>
<td></td>
</tr>
<tr>
<td>Efficient molecular nonlinearity</td>
<td>Bulk susceptibility relies on non-symmetric crystal packing</td>
</tr>
<tr>
<td>Ultra fast response</td>
<td>Thermal degradation due to laser radiation</td>
</tr>
<tr>
<td>Lower dielectric constant</td>
<td>Absorption of visible light due to conjugation</td>
</tr>
<tr>
<td>Better processability</td>
<td></td>
</tr>
<tr>
<td>Increased transparency</td>
<td></td>
</tr>
<tr>
<td>Fine tuning of activity through structural variation</td>
<td></td>
</tr>
</tbody>
</table>
1.8.3 Organic Materials

Organic materials are molecular materials that consist of chemically bonded molecular units interacting in the bulk media through weak van der Waal interactions. Organic materials are emerging as the alternative materials because of their low cost, ease of fabrication and integration into devices, and intrinsic tailorability (Lipscomb et al 1981; Baumert et al 1987b; Dehu et al 1993) which allow one to fine tune the chemical structure and properties for a given NLO process. The organic materials possess inherent synthetic flexibility, high optical damage thresholds, and large NLO response over a broad frequency range comparable to those of inorganic materials (Williams et al 1984; Prasad and Williams 1991; Eaton 1991). The NLO property of these molecule-based materials is governed by the NLO characteristics of the constituent individual molecular chromophores. It is observed that chromophores containing donor (D) and acceptor (A) substituents linked through an intervening π-backbone such as Figure 1.4 (a and b) shows larger NLO response.

![Figure 1.4 (a) and (b) Chromophores containing donor and acceptor](image)

A prototypical noncentrosymmetric electron donor (D) / acceptor (A) molecule, which exhibits an asymmetric polarization response to the symmetric applied electric field (e.g. Lasers) is shown in Figure 1.5. The polarization takes place from D (electron rich substituent) to the A (electron deficient substituent). The asymmetric polarization can be described as a
summation of the Fourier components of frequencies $\omega$, $2\omega$, and $3\omega$ etc., as shown in Figure 1.5. The harmonic components of polarization, such as $P(2\omega)$, will produce a photonic electric field of harmonic frequency $E(2\omega)$. Thus an ensemble of microscopic units each contributing to the macroscopic polarization in a similar way produces a macroscopic harmonic response.

Figure 1.5  (a) Plot of the polarization response $P$ to an incident electromagnetic wave of field strength $E(\omega)$ at frequency in a noncentrosymmetric medium. (b) to (d). Fourier components of $P$ at frequencies for $2\omega$, $\omega$ and 0

The large second order optical nonlinearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end. The $\pi$-conjugated systems could be benzene, azobenzene, stilbene, tolans, biphenyl, benzylidene, hetrocycle, polyenes etc. The electron acceptor and donor groups that can be attached to a $\pi$-conjugated system are as follows: (1) Acceptors groups: NO$_2$, NO, CN, COOH, COO$^-$, CONH$_2$, CONHR, CONR$_2$, CHO, SSI, SO$_2$R, SO$_2$C$_3$F$_7$, SO$_2$CH$_3$, COR,
COCF₃, CF₃, COCH₃, CH=CN(CN)₂, C₂(CN)₃, SO₂NH₂, N₂⁺, NH₃⁺, N(CH₃)₃⁺ and aromatic (R is an alkyl group).

(2) Donor Groups NH₂, NHCH₃, N(CH₃)₂, NHR, N₂H₃, F, Cl, Br, I, SH, SR, OR, CH₃, OH, NHCOCH₃, OCH₃, SCH₃, OC₆H₅, C(CH₃)₃, COOCH₃, O⁻, S⁻ and aromatic (R is an alkyl group).

The absorption band of an organic dye can be tailored by either increasing the π-conjugation length or by substituting donor-acceptor groups to a conjugated system. As a result the absorption band of the UV-visible spectrum can be shifted and will have either bathochromic (red shift towards a longer wavelength) or hypsochromic (blue shift towards a shorter wavelength) features. The position of an absorption band could be changed among stilbene, azobenzene, benzylidene, heterocycle and tolan π-backbones. Electron donor-acceptor groups are of particular interest because they tend to cause bathochromic shifts which also increase the intensity of absorption bands. A donor group can provide additional electrons into the π-conjugated system leading to a strong interaction from a donor-acceptor combination. The donor-acceptor interaction is not only affected by the length of conjugation but also by the relative positions at the π-conjugated system. Because organic structures offer tremendous possibilities of chemical modification, their optical and nonlinear optical properties can be tailored. The strong donor-acceptor charge transfer interactions contribute large β values for organic molecules. For example β is larger for para-nitroaniline molecule because the donor-acceptor charge-transfer intramolecular interactions are prominent by attaining the most desirable resonance structure. The para-nitroaniline exhibits very large first order hyperpolarizability due its highly asymmetric charge-correlated excited states of the π-electronic structure of the molecule (Lalama and Garito 1979).
Though p-nitroaniline exhibits high molecular hyperpolarizability, due to centrosymmetric nature it cannot display SHG activity. But substitution of CH$_3$- group at the second carbon atom of a p-nitroaniline molecule changes the whole physical aspects of optical nonlinear activity by introducing non-centrosymmetry. Therefore, the molecular engineering approach offers an avenue to design and tailor second order NLO materials of interest.

1.9 FACTORS AFFECTING SECOND ORDER OPTICAL NONLINEARITY

The hyperpolarizability of an organic molecule is related to charge-transfer characteristics eventually governed by the increasing conjugation length and strength of donor-acceptor groups. Therefore a trade-off should exist between hyperpolarizability and optical transparency such as large $\beta$ values can be obtained from highly polar molecules but that leads to a loss in optical transparency. Both second-order optical nonlinearity and optical transparency are affected by the nature of the conjugated bonds, length of $\pi$-conjugation, strength of electron donor and acceptor substituents.

1.9.1 Conjugation Length

Huijts and Hesselink (1989) performed a systematic study on a series of disubstituted conjugated organic molecules to establish a relationship between the conjugation length and hyperpolarizability (Hari Singh Nalwa et al 1997). The substituent groups for all molecules were the same; the methoxy (CH$_3$O) group as a donor and the nitro (NO$_2$) group as an acceptor. It was observed that as the conjugation length increases the hyperpolarizability increases. Therefore the length of $\pi$-conjugation has a very significant effect
on the magnitude of hyperpolarizability. From the viewpoint of an efficiency–transparency trade-off, although hyperpolarizability increases remarkably as the length of $\pi$-conjugation increases, increased conjugation length causes a loss in optical transparency.

### 1.9.2 Strength of Acceptor and Donor Groups

The effects of various factors such as strength of donor and acceptor groups, nature of conjugated systems and $\pi$-conjugation length on polarizabilities and hyperpolarizabilities have been investigated using solution-phase dc Electric field induced second harmonic (EFISH) and THG techniques (Cheng et al 1991). The following conclusions can be drawn from these experimental results

1. The para disubstituted benzenes show significant increase in $\beta$ over the sum of mono-substituted benzenes due to charge-transfer
2. The efficacies of acceptor groups increase in the order of $\text{SO}_2\text{CH}_3$, $\text{CN}$, $\text{CHO}$, $\text{COCF}_3$, $\text{NO}$, $\text{NO}_2$, $\text{CHC(CN)}_2$ and $\text{C}_2(\text{CN})_2$
3. With nitro acceptor group, relative effectiveness of various donor groups in an increasing order are: $\text{OCH}_3<\text{OH}<\text{Br}<\text{OC}_6\text{H}_5<\text{OCH}_3<\text{SCH}_3<\text{N}_2\text{H}_3<\text{NH}_2<\text{N(CH}_3)_2$ and the juliiodine amine
4. The magnitude of optical nonlinearities depends on the strength of donor-acceptor groups and the best combination of donor acceptor groups provides about 10 times enhancement (Hari Singh Nalwa et al 1997).
1.9.3 Non-Centro Symmetric Structure

In particular, most achiral organic molecules possessing large ground state dipole moments tend to crystallize into a centrosymmetric space group restricting their use for second order nonlinear optics. To generate SHG active organic structures, different techniques have been used to remove the center of symmetry. The various strategies that have been used to form acentric crystal structures are as follows:

1. Chirality
2. Hydrogen bonding (Zyss et al 1984)
3. Steric hindrance
4. Langmuir Blodgett (LB) Technique
5. Guest-host systems (Bierlein et al 1990)
6. Electrical poling
7. Co-crystallisation
8. Crystal growth technique
9. Solvents for recrystallisation
10. Lambda (Λ)-type conformation
11. Reduced dipole-dipole interaction and

1.10 Z-SCAN TECHNIQUE

The Z-scan technique is a method, which can rapidly measure both nonlinear absorption and nonlinear refraction in solids, liquids and liquid solutions. Several experimental techniques were developed to measure the nonlinear refractive index such as nonlinear interferometry, degenerate four wave mixing, ellipse rotation and beam distortion are sensitive but they require complex experimental apparatus. In that fete, the Z-scan technique has
been a very authoritative technique to measure the nonlinearity because of its high sensitivity and simplicity. This technique was first introduced by Sheik-Bahae (Sheik-Bahae et al 1989 and Sheik-Bahae et al 1990). The essential geometry is shown in Figure 1.6. Using a single focused laser beam, one measures the transmittance of a sample through a partially obscuring circular aperture placed in the far field. The transmittance is determined as a function of the sample position (Z) measured with respect to the focal plane.

Assume for example, a material with a positive nonlinear refractive index. Starting the Z-scan far from the focus at a large value of negative Z (i.e. close to the lens), the beam irradiance is low and negligible nonlinear refraction (NLR) occurs; the transmittance remains relatively constant near this sample position. The transmittance is normalized to unity in this linear regime. As the sample is brought closer to focus, the beam irradiance increases leading to self-focusing. This positive NLR moves the focal point closer to the lens causing greater beam divergence in the far field. The transmittance through the aperture is reduced. As the sample is moved fast the focus, self-focusing increasingly collimates the beam resulting in enhanced transmittance through the aperture. Translating the sample further towards the
detector reduces the irradiance to the linear regime and the normalized transmittance returns to unity.

Reading the data right to left, a valley followed by peak is indicative of positive NLR. In negative NLR, one finds exactly the opposite: a peak followed by a valley. This is due to laser-induced self-defocusing. Characteristic curves for both types of NLR are shown in Figure 1.7.

![Characteristic curves depicting both positive and negative nonlinear refraction as measured by Z-scan](image)

**Figure 1.7**  Characteristic curves depicting both positive and negative nonlinear refraction as measured by Z-scan

An easily measurable quantity $\Delta T_{pv}$ i.e. the difference between the normalized peak and valley transmittance ($T_p - T_v$) is linearly-dependent on the temporally averaged induced phase distortion, defined here as $\Delta \Phi_o$. If the experiment is capable of resolving transmission change $\Delta T_{pv} \approx 1\%$, the Z-scan will be sensitive to wavefront distortion of less than $\lambda/250$. 
So for, all the above description holds for purely refractive nonlinearity with no Nonlinear Absorption (NLA). If NLA and NLR are present simultaneously, a numerical fitting procedure can extract both nonlinear refractive and absorptive coefficients. Alternatively, a second Z-scan with the aperture removed (all the transmitted light collected) can independently determine the NLA. Considering TPA only and a Gaussian input beam, the Z-scan traces out a symmetric Lorentzian shape. The so-called open aperture Z-scan is sensitive only to NLA. One can then divide the partially obscuring Z-scan data by the open aperture data to give a curve that shows only nonlinear refraction (Said et al. 1992a). By performing these two types of Z-scans, one can isolate NLR and NLA without the need for a complicated numerical analysis of a single data set obtained with an aperture.

The required scan range in an experiment depends on the beam parameters and the sample thickness (L). A critical parameter is the diffraction length, \( Z_0 \), of the focused beam defined as \( \pi \omega_0^2/\lambda \) for a Gaussian beam where \( \omega_0 \) is the focal spot size (half-width at the 1/e^2 maximum in the irradiance). For “thin” samples i.e. when \( L \ll Z_0 \), it is preferable to scan the sample for \( \approx \pm 5Z_0 \) or more. This requirement simplifies data interpretation when the sample’s surface roughness or optical beam imperfections introduce back ground “noise” into the measurement system. In many practical cases where considerable laser power fluctuations may occur during the scan, a reference detector can be used to monitor and normalize the transmittance. To eliminate the possible noise due to spatial beam fluctuations, this reference arm can be further modified to include a lens and an aperture identical to those in the nonlinear arm (Ma et al. 1991). The position of the aperture is rather arbitrary as long as its distance from the focus is much greater than \( Z_0 \). Typical values range from 20 \( Z_0 \) to 100 \( Z_0 \). The size of the aperture is signified by its transmittance (S) in the linear regime, i.e. when the sample has been placed far away from the focus. Obviously, the S=1 case corresponds to
collecting all the transmitted light and therefore is insensitive to any nonlinear beam distortion due to nonlinear refraction. Such a scheme, referred to as an “open aperture” Z-scan, is studied for measuring nonlinear absorption ($\Delta\alpha$) in the sample.

### 1.10.1 Nonlinear refraction ($\Delta\alpha=0$)

The change in transmittance between the peak and valley in a Z-scan is given by $\Delta T_{pv} = T_p - T_v$, where $T_p$ and $T_v$ are the normalized peak and valley transmittance. The empirically determined relation between the induced phase distortion $\Delta\Phi_o$, and $\Delta T_{pv}$ for a third-order nonlinear refractive process in the absence of NLA is,

$$\Delta T_{pv} \approx 0.406(1-S)^{0.25} |\Delta\Phi_o|$$  \hspace{1cm} (1.38)

where

$$\Delta\Phi_o = \frac{2\pi}{\lambda} n_2 I_0 L_{\text{eff}}$$  \hspace{1cm} (1.39)

with, $L_{\text{eff}} = (1-e^{-\alpha L})/\alpha$, and $S$ is the transmittance of the aperture in the absence of a sample. $\Delta\Phi_o$ and $I_0$ are the on-axis ($r=0$),peak ($t=0$) nonlinear phase shift and the irradiance with the sample at focus ($Z=0$) respectively. The sign of $\Delta\Phi_o$ and hence $n_2$ are determined from the relative positions of the peak and valley with $Z$. This relation is accurate to within $\pm3\%$ for $\Delta T_{pv}<1$. Use of $S=0.4$ is a good compromise between having a large signal which averages possible beam non uniformities, thus reducing background signals and loss of sensitivity.

A useful feature of the Z-scan trace is that the Z-distance between peak and valley, $\Delta Z_{pv}$, is a direct measure of the diffraction length of the
incident beam for a given nonlinear response. In a standard Z-scan (i.e. using a Gaussian beam and a far-field aperture), this relation for a third-order nonlinearity is given by,

\[ |\Delta Z_{pv}| \approx 1.7 Z_0 \]  \hspace{1cm} (1.40)

For small \( \Delta \Phi_0 \), peak and valley are equidistant \((\pm 0.856 Z_0)\) from the focus \((Z=0)\). As \( \Delta \Phi_0 \) increases, the peak and valley positions do not remain symmetric; the valley moving towards the focus and the peak moving away so that \( \Delta T_{pv} \) remains nearly constant as given above. Being independent of the irradiance, this relation is quite helpful in estimating \( Z_0 \) and hence the beam waist \( w_0 \), of the focused beam. The above relation is valid only for closed aperture Z-scan involving third-order nonlinearity, a good quality Gaussian beam and thin nonlinear samples. Any departure from these conditions will give rise to a different characteristic \( \Delta T_{pv} \).

### 1.10.2 Higher Order Nonlinearities

For higher order effects, change in refractive index \( \Delta n \propto I^n \), with \( \eta > 1 \), for example, a fifth order NLR, (a X-type nonlinearity where \( \eta = 2 \)) becomes the dominant mechanism in semiconductors when \( \Delta n \) is induced by two-photon generated free-carriers (Said et al 1992b). For this type of nonlinearity, where \( \Delta n = n_4 I^2 \) is assumed, the Z scan relations are given by (for a Gaussian beam and far-field aperture),

\[ \Delta T_{pv} \approx 0.21(1-S)^{0.25} \Delta \Phi_0 \] \hspace{1cm} (1.41)

\[ |\Delta Z_{pv}| = 1.2 Z_0 \] \hspace{1cm} (1.42)

where \( \Delta \Phi_0 = k n 4 I_o^2 L_{eff} \) with \( L_{eff} = [1-exp(-2\alpha L)] / 2\alpha \)
In certain cases where competing $\chi^{(3)}$ and $\chi^{(5)}$ processes are simultaneously involved, the data analysis becomes more complicated. A procedure is given by Said et al (1992a) for separating the two processes using a number of Z-scan at different irradiances. This procedure make use of Equations 1.30 and 1.32 to estimate the nonlinear coefficients associated with both $\chi^{(3)}$ and $\chi^{(5)}$ processes.

1.10.3 Nonlinear Absorption

While nonlinear absorption can be determined using a two parameter fit to a closed aperture Z-scan i.e. fitting for both change in refractive index ($\Delta n$) and change in absorption $\Delta \alpha$ it is more directly and more accurately determined in an open aperture Z-scan. For small third order nonlinear losses, i.e. $\Delta \alpha L = \beta I L_{\text{eff}} << 1$ with responses times much less than the pulsewidth (e.g. two photon absorption), and for a Gaussian temporal shape pulse, the normalized change in transmitted energy is given by (Sheik-Bahae et al 1990)

$$\Delta T(Z) \approx \frac{q_o}{2\sqrt{2}} \frac{1}{[1 + Z^2 / Z_o^2]}$$

where $q_o = \beta I_o L_{\text{eff}}$ ($|q_o| << 1$). If the response time of the material is much longer than the pulsewidth used, the factor $2\sqrt{2}$ is replaced by 2. This is independent of the temporal pulse shape. Of course, in this case, the interpretation of $\beta$ changes. For example, in the case of reverse-saturable absorption (van Stryland et al 1993), $\beta I_o$ is replaced by $\sigma F / 2 \hbar \omega$, where $F$ is the fluence (energy per unit area) and $\sigma$ is the excited state absorption cross section.
1.11 DENSITY FUNCTION THEORY (DFT) CALCULATIONS

GAUSSIAN is a computational chemistry software program (Generally the word GAUSSIAN means pertaining to Carl Friedrich Gauss or his ideas). The Gaussian package was first written by John pople and the name originates from Pople's use of Gaussian orbital to speed calculations over those using Slater-type orbital. The practice improved performance on slower computer hardware and facilitated the growth of computational chemistry, particularly ab initio methods such as Hartree-Fock.

The programs used in computational chemistry are based on many different quantum-chemical methods that solve the molecular Schröedinger equation. The methods that do not include empirical or semi-empirical parameters in their equations are called ab initio methods. The most popular classes of ab initio methods are: Hartree-Fock, Moller-Plesset perturbation theory, configuration interaction, coupled cluster, reduced density matrices and density functional theory. Each class contains several methods that use different variants of the corresponding class, typically geared either to calculating a specific molecular property, or, to application to a special set of molecules. The abundance of these approaches shows that there is no single method suitable for all purposes.

1.11.1 Description of the Theory

Traditional methods in electronic structure, like Hartree-Fock theory are based on the complicated many-electron wave function. The main objective of density functional theory is to replace the many-body electronic wave functions with the electronic density as the basic quantity. Whereas the many-body wave functions are dependent on $3N$ variables, three spatial variables for each of the $N$ electrons, the density is only a function of three
variables and is a simpler quantity to deal with both conceptually and practically.

1.11.2 Basis Set

A basis set is a mathematical description of the orbital within a system (which in turn combines to approximate the total electronic wave function) used to perform the theoretical calculations. Larger the basis sets, more accurately approximate the orbital by imposing a fewer restrictions on the locations of the electrons in space. In the true quantum mechanical picture, electron has finite probability of existing anywhere in space.

Standard basis sets for electronic structure calculations use linear combinations of Gaussian functions to form the orbital. Gaussian offers a wide range of pre-defined basis sets, which may be classified by the number of basis functions that they contain. Basis sets assign a group of basis functions to each atom within a molecule to approximate its orbital. These basis functions themselves are composed of a linear combination of Gaussian functions referred as “contracted functions”, and the component Gaussian functions are referred as primitives. A basis function consisting of a single Gaussian function is termed as uncontracted function.

1.11.3 Geometry Optimization

Generally structural changes within the molecule produce differences in its energy and other properties. Its Potential Energy Surface (PES) specifies the way the energy of a molecular system varies with small changes in its structure. Geometry optimizations usually attempt to locate minima on the PES, there by predicting the equilibrium structure of the
molecular system. After finding the energy and gradient in some number of cycles, finally optimization gets completed when it has converged.

Figure 1.8 explicits the flowchart for the developments involved in calculation of NLO response.

![Flow chart for the calculation of NLO response](image)

**Figure 1.8 Flow chart for the calculation of NLO response**
1.12 FACTOR GROUP ANALYSIS

Analysis of the internal motions of the crystal depends heavily upon the symmetry of the unit cell and they are best treated on the basis of group theoretical methods. Bhagavantham and Venkatarayudu (1969) developed the method of factor group analysis for the study of all vibrations of unit cell including the lattice modes.

The application of group theoretical concepts helps chiefly in two aspects of vibrational spectroscopy. First, it helps in the classification of normal vibrations according to irreducible representations of the point group of the molecule. Second, it helps in finding out qualitatively the infrared and Raman spectral activities. The factor group and unit cell group lead to identical predictions but are only relevant when there is coupling between corresponding transitions in different molecules. For a crystal having \( p \) atoms in each molecule and with \( Z \) molecules per unit cell, the total number of vibrations is \( 3Zp \). Of these \( 3Zp \) vibrations 3 vibrations refer to acoustic modes that propagate sound waves through the crystal. The remaining modes are divided into external and internal modes. There will be \( 3Z \) rotational and \( 3Z-1 \) translational lattice modes. The remaining \( Z(3p-6) \) modes are internal vibrations. In the factor group analysis the symmetry property of the crystal is determined by studying the effect of each of the symmetry operations of the factor group on each type atom in the unit cell. The classification of the vibrational modes among the symmetry species of the unit cell group and hence the derivations of the selection rules for infrared and Raman activity can be made in the same manner as for isolated molecules. The results of the factor group analysis carried out for the crystals are presented in the thesis.
1.13 IRRADIATION

The energy deposition by particle-solid interactions was described in the early work of Bohr (1913) and since then, theoretical and experimental and theoretical treatments were refined continuously. High-energy ion accelerators used to be dedicated to nuclear / particle physics. Practical applications for radiation processing of materials have been evolving since the introduction of this technology nearly fifty years ago (Cleland et al 2003). Since 1960's, ion accelerators have been used for basic research of solid state physics and material technologies. Energetic ion beams play a vital role in the field of research in materials science. Ion beam effect on the materials depends on the ion energy, fluence and ion species. In 1970's, ion implanters were fabricated for the purpose of shallow-impurity doping into semiconductors. The ion implantation technique dominated conventional thermal-diffusion methods in the semiconductor-IC processes. The initial and running costs for ion accelerators are considerably high, especially for material applications. The main reason for the vast usage of high-energy ions is due to its good controllability of doping levels and spatial distribution of impurity, when the ion energy, current density and the implantation period are well controlled. The good controllability was very much favorable for the industrial processes.

Besides the technological merit, an attractive point for materials science is the non-equilibrium nature. For instance, 1 eV (electron volt) corresponds to $10^4$ degrees (K) and 1 MeV is $10^{10}$ K. Of course, the comparison may not directly be applicable to materials effects, since the energy stored is rapidly relaxed. However, the highly non-equilibrium states, which are never obtained under thermal equilibrium conditions, create unusual material processes and novel material properties. Non-equilibrium materials science has unlimited possibilities for undeveloped future. There are
higher energy-accelerators of energy more than GeV ($10^9$ eV) in the world, mostly for the purposes of nuclear/particle physics, but a meaningful energy range for materials science is from 1 keV to 10 MeV. Particularly, heavy ions which cause physical / chemical effects are technologically important and attractive.

Depending upon the radiation behaviour, materials can be generally divided into two, first being sensitive to the energy deposited in their electronic system and the second being insensitive to the electronic part of the energy deposition. Organic solids can be corresponded into the first type and metals can be fitted into the second type (Narasimha et al 1998; Harris and Vella 1993). During the passage through the material, energetic ions lose energy, which is quantitatively governed by the ion mass and its energy. Most of the primary excitation and ionization processes occur close to the ion trajectory in a cylindrical core region with a radius of a few nanometers. Some of the electrons gets ejected with higher kinetic energies and can cause further ionizations at some hundreds of nanometers from the primary ion path (Kramer 1995; Katz et al 1990). The incident ion loses its energy along its path in two ways, one by means of the inelastic collisions of the energetic ion with the atomic electrons of the material and other by elastic scattering from the nuclei of the atoms of the material. The latter process is responsible for displacing atoms of the medium from their lattice positions. At high energy, the changes due to electronic energy loss become predominant. Radiation effects due to electronic energy deposition by Swift Heavy Ions (SHI) in condensed matter are closely related to the consequent electron transport and secondary electron cascade multiplication where the deposited energy is distributed along and around the ion track. After relaxation and thermalisation, the energy initially deposited in electronic excitation may result in creation of defects, nuclear tracks, damage and even modification of material properties (Angert et al 1996). During the passage through the
material, energetic ions lose energy, which is quantitatively governed by the ion mass and its energy. Energy loss in the material can be either by elastic collisions or by in-elastic collisions.

Energetic ions in general are of use to materials science as given in Figure 1.9 (Avasthi 2005) in different energy regions. They play a crucial roles in the synthesis, modification and characterization of materials.

**Figure 1.9 Energetic ions in materials science**

### 1.14 SCOPE OF THE THESIS

This thesis presents the growth and characterisation of promising organic crystals like L-asparaginium picrate (LASP), Dimethyl amino pyridinium 4-nitrophenolate 4-nitrophenol (DMAPNP), L-valinium picrate
(LVAP), L-argininium-4-nitro phenolate monohydrate (LAPM), N-2 chlorophenyl 1-propanamide (NCP) single crystals and Benzaldehyde 4-nitro phenyl hydrazone crystals (BPH).

DFT calculations using finite field approach were carried out for calculating the hyperpolarisabilty ($\beta$) of the compounds at the molecular level. Powder SHG study was carried out for the materials using Kurtz-Perry powder technique. Vibrational spectroscopic studies like FTIR, FT-Raman analyses were performed to get information about the molecular structure, inter and intra molecular forces, crystalline environments, vibrational interactions, distortion of molecules, hydrogen bonding etc. Factor group analysis was performed to predict the possible modes of vibrations. The effect of swift heavy ion irradiation on the dielectric and optical properties of the crystals was studied. The third order nonlinear optical properties were studied using Z-scan technique.