CHAPTER - 1
INTRODUCTION TO NONLINEAR OPTICS, LOW
TEMPERATURE SOLUTION GROWTH AND SCOPE OF PRESENT
WORK

1.1 INTRODUCTION

The LASER (Light Amplification by Stimulated Emission of Radiation) is one of the greatest inventions in the history of science. It is a source which emits a kind of light of unrivalled purity and intensity not found in any of the previously known sources of electromagnetic radiation. Its arrival a half century ago, created many fascinating new fields, among which nonlinear optics undoubtedly has the broadest scope and most influential proponents. The field of nonlinear optics (NLO) is almost fifty years old and the interest in the field has grown continuously and now it ranges from fundamental studies (formulating basic theories) in interaction of light with matter to exciting applications such as frequency conversion and optical limiting [1]. The impact of NLO on science and technology has been twofold. First, it has enhanced the understanding of fundamental light-matter interactions. Second, it has been a driving force in rejuvenating optical technology in several areas of science and engineering. The second and the third order phenomena and devices are now at understanding and development [2], stage.

Under normal conditions, the response of a medium to light is linear and as a consequence most optical phenomena can be described with a linear refractive index. It is found that at sufficiently high light intensities, the response of the material depends on the light intensity. This led to an entirely new field of nonlinear optics. Nonlinear optics
describes the behaviour of light in a medium in which the dielectric polarization responds nonlinearly to the electric field (values of the electric field comparable to interatomic electric fields, typically $10^8$ V/m) of the light. This nonlinearity is only observed at very high light intensities that are provided by lasers [3]. The field of nonlinear optics begins with observation of second-harmonic generation by Franken and coworkers in 1961, shortly after the demonstration of the first working laser by Maiman in 1960 [4, 5].

The design, synthesis, characterization and understanding of new molecular assemblies with suitable optical nonlinearities represent an active field of research at the interface of modern Physics, Chemistry and Materials Science. Challenges in this area of materials typify an important theme in contemporary subject: to know the exact influence of a molecule in deciding the required properties of the material for various device applications. The early forays by synthetic chemists into the NLO arena were most likely motivated by academic curiosity. The multidisciplinary chain of developments from a new molecule with interesting properties to a functioning NLO device is inevitably long and convoluted; the majority of studies to date in this field have focused on chromophore design and elucidation of molecular structure-activity correlations. While this is clearly a scientifically rewarding endeavor, a greater emphasis on the properties of materials will be necessary if continued progress is to be made. This thesis highlights the structural and characterization of certain phenolate based organic and semiorganic NLO materials for various NLO applications such as frequency conversion and optical limiting in detail.

1.2 BASICS OF NONLINEAR OPTICS

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of the atoms in the solid form an electric dipole. The electromagnetic radiation interacts with these dipoles causing them to oscillate which by the classical laws of electromagnetism, result in the dipoles
themselves acting as sources of electromagnetic radiation. If the amplitude of vibration is smaller, the intensity of the incident radiation increases the relationship between irradiance and amplitude of vibration becomes nonlinear resulting in generation of harmonic frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and indeed higher order frequency effect occurs as the incident intensity is increased. In a nonlinear medium, the induced polarization is a nonlinear function of the applied field.

The optical response of a material is expressed in terms of the induced polarization \( P \). For a linear material, the relationship between the polarization and the electric field \( E \) of the incident radiation is linear. At very low fields, the induced polarization is directly proportionate to the electric field \([6, 7]\).

\[
P = \varepsilon_0 \chi E \tag{1.1}
\]

Where

\( \chi \) - Linear susceptibility of the material

\( E \) - Electric field vector

\( \varepsilon_0 \) - Permittivity of free space.

At high fields, polarization becomes independent of the field and the susceptibility becomes field dependent. Therefore, this nonlinear response is expressed by writing the induced polarization as a power series in the field.

\[
P = \varepsilon_0 \left\{ \chi^{(1)} E + \chi^{(2)} EE + \chi^{(3)} EEE + \ldots \right\} \tag{1.2}
\]

The relations are basically tensor relations but, we have used them in scalar form. In nonlinear terms, the 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:

\[
P(-\omega_0) = \varepsilon_0 \left\{ \chi^{(1)}(-\omega_0;\omega_1) \cdot E(\omega_0) + \chi^{(2)}(-\omega_0;\omega_1,\omega_2) \cdot E(\omega_1 \cdot \omega_2) + \chi^{(3)}(-\omega_0;\omega_1,\omega_2,\omega_3) \cdot E(\omega_1 \cdot \omega_2 \cdot \omega_3) \ldots \right\} \tag{1.3}
\]
where $\chi^{(2)}$, $\chi^{(3)}$, ... are the nonlinear susceptibilities of the medium.

$\chi^{(1)}$ - Linear term responsible for material's linear optical properties like, refractive index, dispersion, birefringence and absorption.

$\chi^{(2)}$ - Quadratic term which describes second harmonic generation in noncentrosymmetric materials.

$\chi^{(3)}$ - Cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bi-stability.

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.

The nonlinear molecular polarization is expressed by the relation,

$$ P = \sum \alpha_{ij} E + \sum \beta_{ijkl} E.E + \sum \gamma_{ijkl} E.E.E $$

Thus, the second order polarization is represented as,

$$ P^{(2)}_i = e_0 \sum_{j,k} \chi^{(2)}_{ijk} E_j E_k $$

where $i, j, k$ represent the coordinates $x, y, z$.

It must be noted that the second harmonic generation occurs only in certain type of crystals. For a material that is centrosymmetric, the nonlinear susceptibility $\chi^{(2)}$ vanishes. Since 11 of 32 crystal classes possess inversion symmetry, this rule is very powerful. In order to understand the above mentioned case, an isotropic crystal with inversion symmetry ($x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$) is considered. Then

$$ -P^{(2)}_i = e_0 \sum_{j,k} \chi^{(2)}_{ijk} (-E_j) (-E_k) $$

Thus $P^{(2)}_i = 0$ and hence $\chi^{(2)} = 0$. This result can be understood intuitively by considering the motion of an electron in a non parabolic potential well. Because of the nonlinearity of the associated restoring force, the atomic response will show significant
harmonic distortion (Figure 1.1). Part (a) shows the waveform of the incident monochromatic electromagnetic wave of frequency $\omega$. Under linear response (Part (b)), there is no distortion with the polarization of the medium. Part (c) shows the induced polarization for the case of a nonlinear medium with inversion symmetry. Although significant waveform distortion is evident, only odd harmonics of the fundamental frequency are present. In a nonlinear medium with noncentrosymmetric arrangement, both odd and even harmonics are present (Part (d)) in the waveform associated with the atomic response.

![Waveforms](image_url)

Figure 1.1 Waveforms associated with the atomic response
1.3 SECOND HARMONIC GENERATION (SHG) AND PHASE MATCHING

Nonlinear properties in the optical region have been strikingly demonstrated by the harmonic generation of light observed for the first time by Franken and coworkers in 1961. Harmonic generation has found variety of applications to extend the coherent light sources to shorter wavelengths. When the radiation from a ruby laser ($\lambda = 694.3\text{nm}$) is traversed through a quartz crystal, they observed the ultraviolet light ($\lambda = 347.15\text{nm}$) at half the wavelength (twice the frequency) of ruby laser. This second order process is the second harmonic generation [8].

In this process, an intense laser beam of angular frequency $\omega_1 = 2\pi v_1$ is passed through a crystal having a non-zero value of $\chi^{(2)}$ in such a manner that the beam emerging from the crystal contains the angular frequencies $\omega_1$, of the input beam and also $\omega_2 = 2\omega_1$, twice the frequency of the input beam. This can be shown to occur by considering the field incident on a nonlinear medium that has the form

$$E = E_o \cos \omega t$$

substituting this in eqn (1.2)

$$P = \varepsilon_o \left( P_o + \chi^{(1)} E_o \cos \omega t + \chi^{(2)} E_o^2 \cos \omega t + \chi^{(3)} E_o^3 \cos \omega t + \ldots. \right)$$

Using the following relations

$$\cos^2 \omega = (1 + \cos 2\omega) / 2; \quad \cos^3 \omega = (\cos 3\omega + 3\cos \omega) / 4$$

the equation (1.8) can be written as

$$P = \varepsilon_o \left( P_o + \left( \frac{1}{2} \chi^{(2)} E_o^2 + \chi^{(1)} E_o \cos \omega t + \frac{1}{4} \chi^{(3)} E_o^3 \right) \cos \omega t \right) +$$

$$\frac{1}{4} \chi^{(3)} E_o^3 \cos 3\omega t + \ldots.$$  

The first term is a constant term. It gives rise to a dc field across the medium, the effect of which is comparatively lesser in practical importance. The second term, the external polarization is called the first or fundamental harmonic of polarization. The third
oscillates at a frequency \(2\omega\) and is called the second harmonic of polarization; the fourth is called the third harmonic of polarization and so on. The polarization oscillating at a frequency \(2\omega\) radiates an electromagnetic wave of the same frequency, which propagates with the same velocity as that of the incident wave. The wave, thus produced, has the same characteristics of directionality and monochromaticity as the incident wave and is emitted in the same direction. This phenomenon is known as the Second Harmonic Generation (SHG).

In general, crystals which show second harmonic generation are doubly refracting or they exhibit birefringence property. Hence, it is possible to cut the crystal so that the velocity of the ordinary beam of one harmonic is equal to the velocity of the extraordinary beam of the other harmonic. Both the harmonics can then travel along a particular direction with the same velocity and maintain a constant phase relation through the crystal. This arrangement is known as phase matching. Phase matching plays a crucial role in determining what nonlinear processes will predominate in any given experimental arrangement [3, 9].

Figure 1.2 Phase Matching – Second Harmonic Generation.
It is observed that the efficiency of the generation of harmonics depends not only on the intensity of the exciting radiation, but also on its direction of propagation in crystals. Figure 1.2 shows the second harmonic generation. Suppose a plane wave at a frequency $\omega$ and its second harmonic at $2\omega$ are propagating in the $z$ direction through a nonlinear optical crystal of length $L$, then the SHG efficiency ($SHG_{\text{eff}}$) is given by,

$$SHG_{\text{eff}} \propto \frac{\sin[(\sqrt{2})(2k_1 - k_2)L]}{(\sqrt{2})(2k_1 - k_2)}$$  \hspace{1cm} 1.10

where $k_1$ and $k_2$ are the propagation wavenumbers at frequencies $\omega$ and $2\omega$ respectively, $(k = 2\pi n/\lambda)$, $n$ being the refractive index of the medium which characterizes the spatial variation or the phase of the fundamental and harmonic radiations respectively.

This will be maximum when,

$$\frac{[(2k_1 - k_2)L]}{2} = \frac{\pi}{2}, \quad \text{(i.e.)} \quad L = \pi/(2k_1 - k_2) = \lambda/[4(n_{2\omega} - n_{2\omega})]$$  \hspace{1cm} 1.11

where $n_{\omega}$ and $n_{2\omega}$ are the refractive indices at $\omega$ and $2\omega$ respectively. The magnitude of $L$ given by the above equation is called the coherence length for the second harmonic radiation. The expression for intensity is given by

$$I \propto \frac{\sin^2[(\sqrt{2})(2k_1 - k_2)L]}{[(\sqrt{2})(2k_1 - k_2)]^2}$$   \hspace{1cm} 1.12

for the intensity $I$ to be maximum $(2k_1 - k_2)L = 0$ (i.e.) $k_2 = 2k_1$. For efficient frequency doubling, this relation must be satisfied. This requirement is called the phase matching criterion which follows that $n_{2\omega} = n_{\omega}$. Thus phase matching condition becomes the refractive index criterion [9].

8
1.4 OPTICAL LIMITING AND INTENSITY DEPENDENCE OF NONLINEAR REFRACTION (NLR)

There is a considerable interest in finding materials having large yet fast nonlinearities. This interest is driven primarily by the search for materials for all optical switching and sensor applications concerned with both nonlinear absorption (NLA) and nonlinear refraction (NLR) [10]. NLA refers to the change in transmittance of a material as a function of intensity or fluence. At sufficiently high intensities, the probability of a material absorbing more than one photon before relaxing to the ground state can be enhanced. This phenomenon is manifested optically in reduced (saturable) or increased (reverse saturable) absorption. One of the most important applications obtained by this phenomenon is optical limiting. NLR is defined as a change in the refractive index or spatial distribution of the refractive index of a medium due to the presence of optical waves. Again the most important phenomenon that can arise from NLR is optical limiting.

The refractive index of many materials can be related as the sum of weak-field refractive index \( n_0 \) (linear) and intensity dependent refractive index \( n_2 \) (nonlinear). The intensity dependent refractive index is defined as (optical Kerr effect)

\[
n = n_0 + n_2 I
\]

where \( I \) denotes the time averaged intensity of the optical field, given by

\[
I = \frac{n_0 C}{2\pi} |E(\omega)|^2
\]

The nonlinear refractive index is related to the third order susceptibility by the relation

\[
n_2 = \frac{12\pi^2}{n_0^2 C} \chi^{(3)}
\]
The physical processes that can produce a nonlinear change in the refractive index are listed in Table 1.1. A small change in the refractive index, even in the order of $10^{-8}$ can lead to dramatic nonlinear optical effects. One such effect is self-focusing. The origin of thermal nonlinear optical effect is the same fraction of the incident laser power absorbed while passing through an optical material. The temperature of the illuminated portion of the material consequently increases, which leads to a change in the refractive index of the material [2].

Thermal effects can be described by the power / intensity in a continuous wave (cw) laser and by the pulse energy (fluence) in a pulsed laser. In case of a cw laser beam, thermal effects are usually more dominant. The maximum temperature at the center of the laser beam with radius R is

$$T_{i}^{\text{max}} = \frac{\alpha I_{i}^{\text{max}} R^2}{k}$$

where $I_{i}^{\text{max}}$ is the laser intensity at the center of the laser beam and $k$ is the thermal conductivity.

In case of a pulsed laser, the maximum that can be attained is given as

$$T_{i}^{\text{max}} = \frac{\alpha I_{i}^{\text{max}} t_p}{\rho_o C}$$

where $t_p$ is the pulse duration and $\rho_o C$ is the heat capacity per unit volume. Thus it is interesting to note that the pulse duration is an important factor that decides the nature of nonlinear response. For laser pulses that are shorter ($t_p \ll 30 \text{ ps}$) thermal effects in making contribution, however the electronic polarization is also expected in this case [2, 3].
Table 1.1 Typical values of Nonlinear Refractive Index

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$n_2$ (cm$^2$/W)</th>
<th>$\chi^{(3)}$ (esu)</th>
<th>Response Time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic polarization</td>
<td>$10^{-16}$</td>
<td>$10^{-14}$</td>
<td>$10^{-15}$</td>
</tr>
<tr>
<td>Molecular orientation</td>
<td>$10^{-14}$</td>
<td>$10^{-12}$</td>
<td>$10^{-12}$</td>
</tr>
<tr>
<td>Electrostriction</td>
<td>$10^{-14}$</td>
<td>$10^{-12}$</td>
<td>$10^{-9}$</td>
</tr>
<tr>
<td>Saturated atomic absorption</td>
<td>$10^{-10}$</td>
<td>$10^{-8}$</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>Thermal effects</td>
<td>$10^{-6}$</td>
<td>$10^{-4}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Photorefractive effect</td>
<td>Large</td>
<td>Large</td>
<td>Intensity-dependent</td>
</tr>
</tbody>
</table>

Self focusing occurs when a laser beam of non uniform intensity falls on a medium with a nonlinear index of refraction. Since the nonlinear index follows the shape of the beam, an index gradient is induced in the medium. For a positive nonlinearity ($n_2 > 0$), the beam has a larger phase retardation along the on-axis than in the wings. This has the effect of creating a positive lens that tends to focus the beam. This is called beam collapsing. In case of media with negative nonlinearity ($n_2 < 0$), the beam will not collapse and rather it will diverge due to the negative lens effect. Thus in a media that absorbs part of a Gaussian beam, the index on-axis is smaller than in the wings and the beam thus diverges. This is called thermal blooming.

Often self focusing is undesirable, since it may lead to laser damage. However the phenomenon has some device applications like optical limiting. This is illustrated in Figure 1.3 [2]. The nonlinear medium is situated between two lenses. For positive nonlinearity, the beam collapses and thus the light is defocused in the aperture plane of
the second lens. Thus the power transmitted is limited and such optical limiter is constructed by using CS₂. In the negative nonlinearity, the beam diverges more rapidly rather than collapsing. However, it also results in defocused beam. The advantage of this type of limiter over the previous case is that it is self protecting. Such limiter is constructed using ZnSe [11, 12].

![Figure 1.3 Self Focusing and Self defocusing – NLR](image)

Figure 1.3 Self Focusing and Self defocusing – NLR
1.5 INTRODUCTION TO CRYSTAL GROWTH

A solid which consists of atoms or molecules arranged in a periodic manner is called crystal. Crystals are pillars of modern technologies. Modern technology depends on the availability of new materials/crystals for the semiconductors, super conductors, polarisers, transducers, radiation detectors, solid state lasers, non-linear optics, microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, materials science, chemical engineering, metallurgy etc.. The root of the concept of crystal structure is the various dendritic forms of snow flakes, which are considered as snow crystals by Kepler in 1611. During 16th – 19th centuries, quartz to sapphire crystals were used as gems and precious stones. The invention of transistor showed the importance of crystals. In the 20th century, contributions of crystal growth in fabricating electronic and optical devices have thrown more light on the importance of crystals.

Crystal growth is a controlled phase of transformation, either from solid or liquid or from gaseous phase to solid phase. The choice of a particular method for growing a desired single crystal critically depends on the physical and chemical properties of the substances. The consistency in the characteristics of devices fabricated from the crystals depends mainly on homogeneity and defect present in the crystals. Thus, the process of producing single crystals from homogeneous media with directional properties attracts more attention and gains more importance than any other process. The method of crystal growth may range from a small inexpensive technique to a complex sophisticated technique.

Fundamental aspects of crystal growth had been derived from early crystallization experiments in the 18th and the 19th century [13, 14]. Theoretical understanding started with the development of thermodynamics in late 19th century (Gibbs, Arrhenius,
Van’t Hoff) and with the development of nucleation and crystal growth theories and the increasing understanding of the role of transport phenomena in the 20th century. The phenomena of undercooling and supersaturation and the heat of crystallization were already recognized in 18th century by Fahrenheit and by Lowitz. The corresponding metastable region, the existence range of undercooled melts and solutions, was measured and defined in 1893/1897 by Ostwald and in 1906 by Miers, whereas the effect of friction on the width of this Ostwald–Miers region was described in 1911 and 1913 by Young. The methods of growing crystals are very wide and they mainly depend on the characteristics of the material and its size [15, 16]. In this part, the fundamentals of the various methods to grow quality single crystals in general and the solution growth method is discussed.

Crystal growth is a highly complex phase change phenomenon. It is concerned with physics and chemistry of heat and mass transfer. It deals with technology of controlling phase transition that leads to solids. The phase change may occur from solid, liquid or vapour state. The crystal growth methods are broadly classified into four main categories depending on the phase transition involved in the process [17-21].

- Solid state growth (Solid → Solid)
- Melt growth (Liquid → Solid)
- Vapour growth (Vapour → Solid)
- Solution growth (Liquid → Solid)

1.5.1 Solid state growth

In solid state growth technique, the growth of single crystal takes place from the polycrystalline mass of that particular material which we intend to grow. Usually, the straining of the material with subsequent annealing is utilized for crystallization. Metallic
crystals of larger size have been grown by this method [22]. The growth will take place at low temperature without the presence of additional component, which is the advantageous feature of this technique. But the control of growth rate and quality is very difficult because of the lack of control on nucleation rate.

1.5.2 Melt growth

This is the fastest of all crystal growth methods and is widely used for preparation of bigger and larger quantity of crystals. It is the process of crystallization by fusion and re-solidification of the pure material. Melt growth technique is commonly used in case of materials which melt congruently and have an experimentally viable vapour pressure at its melting point. One of the foremost advantages of this technique is the requirement of simple systems. Primarily, the material to be grown is melted and afterwards progressively cooled to yield crystalline form. This method has been utilised to produce commercially important semiconductors, metals and laser host crystals. The availability of pure and perfect crystals is the main advantage of this technique.

1.5.3 Vapour growth

The vapour growth is usually employed to grow crystals of the materials for which suitable solvents are not readily available and they have satisfactorily higher vapour pressure at ambient condition. This method is utilised to grow bulk crystals and for preparing thin layers on crystals with a high degree of purity. Generally the growth from vapour phase is subdivided into two; physical vapour transport (PVT) and chemical vapour transport (CVT).

1.5.4 Solution growth

Another method for growth of crystals is through precipitation technique applied to solutions. In this method, the crystals are prepared from a solution at temperature well
below its melting point. This may help in growing crystals even at room temperature and it will turn out to be more advantageous [23]

Here, the crystallization 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 utilizes this method. The solution growth methods are classified according to the temperature range and to the nature of the solvents used. The main methods commonly used in this process are; High temperature solution growth, low temperature solution growth, hydrothermal growth and gel growth [24-27].

1.5.5 Low temperature solution growth (LTSG) method

This is the easiest and most effective way for growing a variety of crystals at ambient condition or even at room temperature [28]. Materials having low to high solubility in the temperature range ambient to 70 °C and at atmospheric pressure can be grown by using low temperature solution growth method. In this method, saturated solution of the material is prepared in a suitable solvent and crystallization is initiated by slow cooling of the solution or by the slow evaporation of the solvent. The crystals grown by this technique are larger in size and relatively free from defects. This method has many advantages compared to other growth methods and they produced largest crystals. Several industrially and technologically important materials are grown by this method.

1.5.5.1 Supersaturation

Crystallization is a separation and purification technique employed to produce a wide variety of materials. Crystallization may be defined as a phase change in which a crystalline product is obtained from a solution. A solution is a mixture of two or more species that form a homogenous single phase. Solutions are normally thought of in terms
of liquids; however, solutions may include solids suspension. Typically, the term solution has come to mean a liquid solution consisting a solvent which is a liquid and a solute, which is a solid, at the conditions of interest. The solution to be ready for crystallization must be supersaturated. A solution in which the solute concentration exceeds the equilibrium (saturated) solute concentration at a given temperature is known as a supersaturated solution. There are four main methods to generate supersaturation that are the following:

- Temperature change (mainly cooling),
- Evaporation of solvent,
- Chemical reaction and changing the solvent composition.

### 1.5.5.2 Ostwald’s diagram

While the concept of a definite supersolubility is contained in the earliest reports on the crystal growth, Ostwald appears to be the first to explain the relationship between supersaturation and spontaneous crystallization. The relationship between the concentration and temperature is schematically shown in Figure 1.4 (Meirs and Issac 1987). Meir carried out an extensive research into the relationship between supersaturation and spontaneous crystallization [29].

The lower continuous line is the normal solubility curve for the salt concerned. Temperature and concentration at which spontaneous crystallization occurs are represented by the upper broken curve, generally referred to as the supersolubility curve. The whole concentration-temperature field is separated by the saturated-solution line (solubility curve) into two regions, unsaturated and supersaturated solutions. Saturated solutions are those mixtures which can retain their equilibrium indefinitely in contact with the solid phase with respect to which they are saturated. The solubility of most substances
increases with temperature (the temperature coefficient of the solubility is positive) and crystals can be grown only from supersaturated solutions which contain an excess of the solute above the equilibrium value. The diagram is divided into three zones, which are termed as region I, II and III respectively.

(i) The stable (undersaturated) zone, where crystallization is not possible.

(ii) The second region is a metastable zone, between the solubility and supersolubility curves, where spontaneous crystallization is improbable. However, if a crystal seed is placed in such a metastable solution, the growth would occur on it.

(iii) Third region is the unstable or labile (supersaturation) zone, where spontaneous crystallization is more probable.

If the solution whose concentration and temperature are represented by point A in the Figure 1.4, is cooled without loss of solvent (line ABC) spontaneous crystallization cannot occur until conditions represented by point C are reached. At this point, crystallization may be spontaneous or seeding, agitation or mechanical shock may induce it. Further cooling to some point beyond C may be necessary before crystallization can be induced, especially with very soluble substances. The evaporation of solvent from the solution may also result in super saturation. Line AB’C’ represents an operation carried out at constant temperature. Penetration beyond the super solubility curve into the labile zone rarely happens, as the surface from which evaporation takes place is usually supersaturated to a greater degree than the bulk of the solution. Crystals, which appear on this surface eventually fall into the solution and seed it. In practice, a combination of cooling and evaporation as represented by the line AB”C” shown in Figure 1.4 is adopted.
1.5.5.3 Expression for supersaturation

The super saturation of a system may be expressed in number of ways. The basic units of concentration as well as temperature must be specified. The concentration driving force $\Delta C$, the super saturation ratio ‘$S$’ and relative super saturation ‘$\sigma$’ are related to each other as follows:

The concentration driving force

$$\Delta C = C - C^*$$  \hspace{1cm} (1.18)

Where, $C =$ Actual solution concentration and $C^* =$ Equilibrium concentration at a given temperature.

Super saturation ratio $S$,

$$S = \frac{C}{C^*}$$  \hspace{1cm} (1.19)
Relative super saturation $\sigma$, 

$$
\sigma = \frac{(C - C^*)}{C^*} 
$$

1.20

$$
\sigma = \frac{\Delta C}{C^*};
$$

$$
\sigma = S - 1 
$$

1.21

Conditions $S=1$, $S>1$, $S<1$ refers to saturation, super saturation and under saturation of the solutions respectively. If the concentration of a solution can be measured at a given temperature and the corresponding equilibrium saturation concentration is known, then it is easier to calculate the super saturation.

1.5.5.4 Various methods of LTSG

The various methods of low temperature solution growth are briefly explained as follows

A. Slow cooling method

It is the best way to grow crystals by solution technique. Its main disadvantage is the need to use a range of temperature. The possible range of temperature is usually small so that much of the solute remains in the solution at the end of the run. To compensate this effect, large volumes of solution are required. The use of a range of temperatures may not be desirable because the properties of the grown material may vary with temperature. Eventhough, this method has technical difficulty of requiring a programmable temperature controller; it is widely used with greater success.

B. Slow evaporation method

This method is similar to the slow cooling method in terms of the apparatus requirements. The temperature is fixed constant and provision is made for evaporation. With non-toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about $\pm 0.01$ °C and rates of evaporation of a few mm$^3$/hr. The evaporation techniques of crystal
growth have an advantage that the crystals grow at a fixed temperature. But inadequacies of the temperature control system still have a major effect on the growth rate. This method is the only one which can be used with materials having very small temperature coefficient of solubility.

C. Temperature gradient method

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

- Crystal grows at fixed temperature
- This method is insensitive to changes in temperature provided. Both the source and the growing crystal undergo the same change.
- Economy of solvent and solute.

On the other hand, changes in the small temperature difference between the source and the crystal zones have a larger effect on the growth rate.

1.5.5.5 Advantages and disadvantages

The advantages of crystal growth from low temperature solution nearer to the ambient temperature result in simple and straight forward equipment design which gives a good degree of control accuracy at ± 0.02 °C. Due to the precise temperature control, the supersaturation can be very accurately controlled. Also efficient stirring of solution reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at higher temperatures and the materials which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized by using this technique. The low
temperature solution growth technique also allows variety of different morphologies and the polymorphic forms of the same substance can be grown by varying the growth conditions of a solvent [30]. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

Slow growth rate in many cases and the ease of solvent inclusion into the growing crystal are the major disadvantages in this method. Under the controlled conditions of growth, the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. After many modifications and refinements, the process of solution growth now yields good quality crystals for a variety of applications. Growth of crystals from solution at room temperature has many advantages over other growth methods though the rate of crystallization is slow. Since growth is carried out at room temperature, the structural imperfections in solution grown crystals are relatively low [31].

1.6 SCOPE OF PRESENT WORK

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in general they have made a greater impact on information technology and industrial applications, in particular. Eimerl et al. (1989) have introduced new group of nonlinear materials called semiorganic. These metal complexes satisfy very different demands of second order NLO materials such as switchable, tunable and multi dimensional properties depending on the suitable interplay of structure property relationships. It offers a wide range of metals with different oxidation states and ligands, which can give rise to tunable electronic properties. Semiorganic NLO crystals are expected to possess the advantages of both inorganic and organic materials. The metal-organic coordination complexes can
provide enhancement in physico-chemical stability, breaking up of the centrosymmetry of the ligand in the crystal and an increase in NLO intensity via the metal-ligand bridging interactions. The central metal ion not only offers a certain anisotropic field to keep the NLO-active chromophore ligands in a favourable acentric arrangement, but is also involved in the NLO process. The hyperpolarizability value can drastically vary with the electronic configuration of metal ions.

Nonlinear organic materials have proved to be interesting candidates for a number of applications like, second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation etc. The superiority of organic NLO materials results from their versatility and the possibility of tailoring them for a particular end use [7]. The optical nonlinearity of organic molecules can be enhanced by adding strong electron donating and withdrawing entities as well as optimizing the distance between donor and acceptor. This generates a highly polarizable charge transfer compound with an asymmetric electron distribution. Studies show that conjugated organic molecules with large delocalized π electron systems exhibit measurable nonlinear optical and electro-optical effects. The ideal material that can have potential applications in nonlinear optical devices should possess a combination of physico chemical properties such as high laser damage threshold, fast optical response, flexible for molecular design, optical transparency, mechanical stability, thermal stability and ease of fabrication [32]. Compared with inorganic NLO materials, organic materials may fulfill many of these requirements, but there are also some drawbacks in organic NLO materials, such as environmental stability, mechanical strength and performance at low and high temperatures. Since organic materials offer a very wide range of chemical modification, some of these problems can be overcome [33]. Recent growing efforts in molecular engineering suggest that organic NLO materials possess comparably better NLO
properties than inorganic and hence, their tremendous practical potentials have been anticipated.

As second order nonlinearity is the most commonly occurring nonlinear optical phenomenon, it is necessary to know some of the basic requirements of materials to exhibit second order nonlinear (SONLO) effects [34]. As a general rule, the basic requirements apart from the noncentrosymmetry of the crystal structure are,

i) The material should be polarizable (the electrons need to be greatly perturbed from their equilibrium positions)

ii) Asymmetric charge distribution (incorporation of donor – acceptor molecule)

iii) A pathway of π-conjugated electrons (β value increases with increasing conjugation length)

iv) Relatively large $d_{ijk}$ coefficient ($d_{ijk} = \chi_{ijk}/2$)

v) Moderate birefringence

vi) Wide transparency range for operating wavelengths

vii) High laser induced damage threshold

viii) Ease of growth

ix) Low materials cost

x) Good mechanical, thermal and chemical stability

An optical limiter must provide protection over a wider range of incident intensity or fluence. Thus if the input-output slope is nonzero, at some point above the threshold, the device will fail to provide protection. In some cases, the material itself may be damaged if its damage threshold is below this point. Any of these situations will define a maximum input for which the device will provide effective limiting. The ratio of this input value to threshold is called the dynamic range of the limiter. In consolidation, the desirable attributes that are essential for an optical limiter are [34],

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i) Low threshold
ii) Wide dynamic range
iii) Fast optical response
iv) Broad band response
v) Low insertion loss / high linear transmittance
vi) Optical clarity / low optical scattering
vii) Color neutrality
viii) Robustness

The main interest in this work is focused on synthesis and growth of certain phenolate based organic and metal organic nonlinear optical crystals and characterize their structural, functional, thermal, linear optical, second and third order nonlinear optical properties.

Therefore, in the present investigation, the following materials are chosen as samples for investigation:

**Organic NLO materials**

- Ethylenediamminium di(2-nitrophenolate) (EDA2NP)
- Ethylenediamminium di(3-nitrophenolate) (EDA3NP)
- Ethylenediamminium di(4-nitrophenolate) (EDA4NP)

**Semiorganic NLO materials**

- Lithium p-nitrophenolate trihydrate (LPNP)
- Sodium p-nitrophenolate dihydrate (SPNP) and
- Potassium p-nitrophenolate monohydrate (PPNP)
1.7 REVIEW OF LITERATURE

Plenty of works on the phenolate based NLO materials are available in the literature. In particular, nitrophenol derivatives are interesting candidates, as they are typical one-dimensional (1D) donor–acceptor π systems, and the presence of phenolic OH favours in formation of salts with various organic and inorganic bases. Mahadevan et al. [35] have successfully grown single crystals of L-arginine 4-nitrophenolate 4-nitrophenol dihydrate (LAPP) from the solution of L-arginine and 4-nitrophenol by slow evaporation technique. It is reported that the grown crystal has no absorption in green wavelength region and the SHG efficiency is found to be 2.66 times that of the standard KDP. Srinivasan et al. (2008) reported the synthesis, growth, crystal structure determination, and hyperpolarizability studies of L-argininium-4-nitro phenolate monohydrate (LARP) single crystals. First order hyperpolarizability of LARP has been computed by using density functional theory [36]. The morphology, thermal stability and NLO activity of L-arginine 4-nitrophenolate 4-nitrophenol dehydrate (LAPP) crystal were investigated by Wang et al. (2011) [37].

Mahadevan et al. [38] have synthesized L-Lysine 4-nitrophenolate monohydrate (LLPNP) by applying solution growth method at room temperature as well as using deionised water as a solvent. Second harmonic generation (SHG) efficiency of the material has been determined by Kurtz and Perry technique and the efficiency was found to be 4.45 and 1.4 times greater than that of standard KDP and urea samples, respectively. Bulk single crystals of L-histidine-4-nitrophenolate 4-nitrophenol (LHPP), a new organic material, have been successfully grown by using slow evaporation solution growth technique at room temperature by Dhanalakshmi et al. [39]. Chen et al. (2012) have grown the good-quality single crystals of L-histidinium-4-nitrophenolate 4-nitrophenol (LHPP) by applying slow cooling method [40].

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Chen et al. (2012) investigated the SHG efficiency, specific heat and dielectric properties of 2, 6-diaminopyridinium 4-nitrophenolate 4-nitrophenol (DAPNP) [46]. Dielectric and micro hardness studies of (DAPNP) was analysed by Krishnakumar et al. (2012) [42]. 2-Aminopyridinium 4-nitrophenolate 4-nitrophenol (2APNP), with molecular formula C_{17}H_{16}N_{4}O_{6} having D–π–A type, has been synthesized and grown as single crystals by slow evaporation solution growth technique using acetone as solvent at constant temperature (32 °C) by Anandha Babu et al. [43]. The relative second harmonic efficiency of the compound is found to be 17 times greater than that of KDP. Biilab Mondal et al. [44] reported that 5-Nitro-2-hydroxybenzaldehyde condenses with benzylamine to yield a Schiff base that exists in the solid state as zwitter ionic form as 2-benzyliminiomethylene-4-nitrophenolate. A new piperazinium 4-nitrophenolate monohydrate single crystal was grown by employing the solution growth technique with piperazine and 4-nitrophenol as the source material as reported by Subhashini et al. [45].

Novel PcCo(CN)₃ monomeric complexes were synthesized from [PcCoCN]ₙ compounds and bidentate axial ligands (L) such as ethylenediamine, 1,4-diaminebutane, 1,12-diaminedodecane and 2,6-diamineanthraquinone by Morales-Saavedra et al. These complexes were implemented to fabricate pellets and thin films by the vacuum thermal evaporation technique. Additionally, cubic nonlinear optical (NLO) characterizations of the film samples were performed with the Z-Scan and third harmonic generation (THG) techniques, with all samples exhibiting outstandingly high nonlinear activity [46]. Single crystals of Ethylenediamine Ditartrate Dihydrate (EDADTDH) [2(C₄H₈O₆)⁻] [(C₂H₁₀N₂)²⁺]·2H₂O, which is organic in nature and showing non-linear optical, ferroelectric and piezoelectric properties was grown by slow evaporation technique at room temperature by Subhashini et al. [47]. Jian-Han Zhang et al. [48] reported the preparation and characterization of a new Cd-4,4'-bpy co-ordination
framework formulated as \([\text{Cd(en)}(\text{NO}_3)_2(4,4'-\text{bpy})]_n\). The polymer also exhibits strong NLO refraction behavior, its \(n_2\) value is \(6 \times 10^{-18} \text{ m}^2 \text{ W}^{-1}\) in a \(2.2 \times 10^{-4} \text{ mol dm}^{-3}\) DMF solution, and gives self-focusing effect. The susceptibilities \(\chi^{(3)}\) and the hyperpolarizability \(\beta\) value were calculated to be \(1.5 \times 10^{-11} \text{ esu}\) and \(1.7 \times 10^{-29} \text{ esu}\), respectively. The \(\beta\) is comparable to those of the known cluster compounds, and they are better than those observed in other compounds, such as ferrocene derivatives, Group 10 metal alkynyl polymers and some octopolar alkynylruthenium complexes. Muthu et al. (2011) have studied the proton transfer complex of 2,4,6-trinitrophenol as an electron acceptor with p-toluidine as electron donor [49].

A series of organic salts based on ethylenediaminium divalent cation, \([\text{C}_2\text{H}_{10}\text{N}_2]_X\) \(X\) (where \(X = 2\)-nitrophenolate, 3-nitrophenolate, 4-nitrophenolate, 2,4-dinitrophenolate, 2,6-dinitrophenolate and 2,4,6-trinitrophenolate respectively have been prepared. Additionally, crystal structures of compounds 2-nitrophenolate and 4-nitrophenolate were determined with X-ray single crystal diffraction. The IR and Raman spectra of 2-nitrophenolate and 4-nitrophenolate were interpreted and the assignments of bands to the corresponding vibrations were proposed based on the data calculated by the B3LYP/6-311G (d, p) level. Finally, the influence of molecular structure on both the densities and thermal stabilities of synthesized compounds have been discussed [50].

The growth and properties of semi organic lithium para nitrophenolate trihydrate single crystals and their SHG efficiencies have been studied by Milton Boaz et al. (2004) [51]. Milton Boaz et al. (2005) demonstrated the increase of NLO activity due to the presence of sodium ions in sodium substituted lithium para nitrophenolate trihydrate single crystal and also studied thermal and mechanical properties [52]. Dinakaran et al. (2008) reported the uniaxial growth of lithium para-nitrophenolate trihydrate single crystal by Sankaranarayanan-Ramasamy (SR) method and carried out mechanical and
frequency dependent dielectric studies [53]. The optical band gap and third order nonlinear response of lithium para nitrophenolate trihydrate crystals were determined by Dhanuskodi et al. (2011) [54].

Minemato et al. (1992, 93 & 94) solved the crystal structure, SHG efficiency of deuterated sodium para nitrophenolate [55-57]. The defect content, topography hardness of sodium para nitrophenolate dihydrate was studied by Brahadeeswaran et al. (1998) [58]. The NLO activity of anhydrous and hydrated sodium p-nitrophenolate was reported by Brahadeeswaran et al. (1999) [59]. Vanishri et al. (2005) have reported the growth of sodium p-nitrophenolate dihydrate by slow cooling method using water as solvent and compared the properties with methanol grown crystal [60]. Photoconductivity and dielectric studies on sodium p-nitrophenolate dihydrate and lithium p-nitrophenolate trihydrate have been reported by Milton Boaz et al. (2007) [61].

Dinakaran et al. (2007) estimated solubility, metastable zonewidth and induction period for sodium p-nitrophenolate dihydrate crystal [62]. A laser damage study on sodium para-nitrophenolate dihydrate was reported by Vanishri et al. (2007) [63]. Growth and characterization of potassium p-nitrophenolate dihydrate was studied by Milton Boaz et al. (2005) and they estimated microhardness and SHG efficiency [64]. Vesta et al. (2007) have reported about the growth, structural and micro hardness studies on calcium p-nitrophenolate dihydrate [65]. The crystal and molecular structures of potassium 4-nitrophenolate monohydrate, potassium 2-chloro-4-nitrophenolate monohydrate, ammonium 2-chloro-4, 6-dinitrophenolate sesquihydrate and potassium 2, 6-dinitrophenolate were studied by Krogh Andersen et al. (1989) [66]. Muthuraman et al. (1999) discussed the herring bone structure and NLO efficiency of sodium 4-nitrophenolate 4-nitrophenol dihydrate crystal [67].
The idea of forming semiorganic ionic crystals by using Group (I) elements like sodium, potassium, lithium, rubidium etc., with p-nitrophenol have drawn the attraction of many. Also, addition of organic chromophores such as ethylenediamine with nitrophenol and changing the functional groups positions in the various positions of the phenyl ring results in a wider range of new NLO compounds. Hence, a series of semiorganic and organic NLO compounds were selected as subjects of investigation. Also its second and third order NLO properties will be intensively discussed their possible usage in frequency conversion and optical limiting applications.

1.8 CHARACTERIZATION TECHNIQUES

In the present study, the chemical composition of synthesized materials was analysed by Elemental Vario EL III CHNS analyser in the Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Cochin - 682 022, Kerala. Single crystal X-ray diffraction of the grown crystals was carried out by using Bruker Kappa Apex II diffractometer, with MoKα radiation (\(\lambda = 0.71073 \text{ Å}\)) in STIC, Cochin. Powder X-ray diffraction of the grown crystals was performed in a PANalytical Xpertpro diffractometer (Netherlands) using CuKα radiation (\(\lambda = 1.5418 \text{ Å}\)) in the Department of Physics of Alagappa University, Karaikudi. FT-IR spectra were recorded by using Thermo Nicolet 380 FTIR spectrophotometer (USA) and by applying KBr pellet technique in the Department of Physics of Alagappa University, Karaikudi. Laser Raman studies were carried out using Imaging spectrograph STR 500 mm focal length laser Raman spectrometer (SEKI, Japan) in the Department of Physics in Alagappa University, Karaikudi. \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra were recorded by using a Bruker Avance III, 400MHz FT-NMR spectrometer in STIC, Cochin.
The optical properties of the grown crystals were determined from UV-Vis spectra recorded with a Varian, Cary 5000 spectrophotometer in STIC, Cochin. Thermal property of the samples was studied by TG-DTA and differential scanning calorimetry (DSC) analyses by using a Perkin Elmer, Diamond TG/DTA and Mettler Toledo DSC 822e available at STIC, Cochin. Non-linear optical properties of the grown crystals were analysed by Kurtz Perry powder second harmonic generation (SHG) test using Nd: YAG laser (λ = 1064nm) at the Department of Inorganic and Physical Chemistry, IISc, Bangalore. The Z- scan studies were performed by using cw diode pumped Nd:YAG laser at 532 nm in the Department of Physics, Madras University, Chennai.

In order to realize the practical applications of the materials selected for investigations, it is essential to predict the second and the third order NLO properties. Hence to find the suitable materials for frequency conversion and optical limiting applications, the following experiments were performed.

1.8.1 Powder SHG Test

To find suitable materials with desired NLO properties in the crystal engineering, one can utilize the theories and the experiments to predict the magnitude of the NLO coefficients of the newly synthesized substances. It is difficult, time consuming and expensive endeavor to develop single crystal growth methods for new materials. However for effective analysis, it is important that the NLO coefficients of the crystals are somehow estimated before hand to optimize the conditions for single crystal growth towards the practical applications. Therefore a relatively rapid and simple method of screening new candidates for frequency conversion applications prior to crystal growth is needed.
In this context, Kurtz and Perry powder technique represents the first real means of screening the materials for second order NLO applications [7]. The advantage of this method is that it not only provides nonlinear coefficient (d<sub>ij</sub>) values but also determines whether the material is phase matchable or not. Although the accuracy of this method is not so high (~ 25%) it has proved to be a very useful method for screening new materials that can occur in powder form.

Kurtz and Perry developed a semi quantitative approach to the theory of SHG from powders. Boyd et al. [8] have shown that the SHG intensity by a single particle can be related by assuming no absorption and low dispersion,

\[ I_{2\omega} \alpha \left[ d^2 L^2 \sin^2 \left( \frac{\pi r}{2 L_c} \right) \right] \]

where \( d \) is the nonlinear coefficient, \( r \) is the particle size and \( L_c \) is the coherence length.

The powder SHG measurements were performed by applying a modified Kurtz-Perry method. The experimental setup for Kurtz-Perry powder technique used in the present investigation is shown in Figure 1.5. In this, the particles are initially ground and sieved to obtain a desired particle size range. Then the powder sample is packed tightly in a capillary tube and is illuminated by using a Q-switched Nd: YAG laser (1064 nm, 8 ns, 10Hz). The low energy (~ 9mJ) beam is used for illumination. A photo diode is used as a reference to monitor pulse-to-pulse fluctuations in the input beam. The fundamental transmitted wave, IR (1064 nm) is blocked by using RG850.
To ensure low dispersion and absorption, all the crystalline powder samples were graded by using standard sieves and a desired range of particle sizes are prepared. For obtaining qualitative results and to test the phase matching property, the graded powders having particles sizes in the range <53, 53-106, 106-125, 125-150, 150-212, 212-250, 250-300 and >300 \( \mu m \) are taken. The generated SHG signal from the randomly oriented crystallites is focused at the slit of the monochromator and is monitored by a photomultiplier tube and a duel beam digitalized storage cathode ray oscilloscope assembly. For each range of particle size, the average of SHG output for 20-30 pulses are measured.

1.8.2 Laser Induced Surface Damage Study

In frequency conversion phenomenon of NLO materials, when the power density of the fundamental beam is higher, more will be the harmonic conversion efficiency. Hence, a convenient way to increase the efficiency is to focus the beam into the crystal.
But this often leads to damage of the crystal and so it is useful to describe the maximum permissible power for a particular crystal, defined as damage threshold.

It is worthwhile to note that the surface of a material often tends to get damaged at power levels, in an order of magnitude lower than the bulk. Hence this necessitates an independent definition of surface and bulk damage resistances. The minimum power levels that cause damage to at least 50% of the sites irradiated is defined as the single shot (1-on-1) damage threshold (P1). However, power levels much lower than this are detrimental to the material under continuous exposure. According to Nakatni et al., the multi-shot (n-on-1) damage threshold is the minimum power level below which the crystal does not suffer damage even after 2000 pulses. However, the origin of laser damage is complex [10].

The experimental setup for evaluating the laser induced surface damage of the grown crystals was developed by Indian Institute of Science (IISC), Bangalore, India. A Q-switched Nd:YAG laser (1064 nm, 10 ns,10 Hz) was used as a source (Fig.1.6). An IR reflector (IR) and a prism (P) combination are used to generate a laser beam with low pulse energies below 2mJ. The beam is focused by using a focusing lens of focal length 400 mm through eyrics. The diameter used for this experiment is 8mm and 3mm and their corresponding focusing spot sizes are 129 mm and 346 mm respectively. The crystal under study is mounted on a rotating sample holder and the selected surface of the crystal is irritated with the laser beam. The energy of the laser beam incident on the crystal is increased step by step by an attenuator until the damage occurred (by observing the audible crack sound /visual crack). The energy required to cause the catastrophic damage is measured by using a power meter.
During the experiments, to measure n-on-1 damage resistance values, the occurrence of damage is monitored on the CRO. Irrespective of whether the damage had occurred or not, the samples are moved on to a new site. The distance between the two sites is so kept apart at least 5 times the spot size on the crystal surface. Thus cumulative effect is avoided and this facilitated accurate measurement, eliminating the possibility of sample getting damaged at lesser fluence. It is well known that the defect content of the crystal has a lot of influence on the damage resistance; care is taken to avoid crystals with high density of dislocations in the statistical testing. The elimination process consisted of visible examination for macroscopic inclusions and imperfections, testing the samples with He-Ne laser for light scattering from defects. Based on the observations, the surface damage threshold of the grown crystals is evaluated by using the expression,

\[ P.D = \frac{E}{\tau \pi \omega_0^2} \]  \hspace{1cm} (1.23)

where \( E \) is the energy (mJ), \( \tau \) is the pulse width (ns), and \( \omega_0 \) is the radius of the spot.
1.8.3 Z-Scan Study

The intense monochromatic radiation from a laser can induce profound changes in the optical properties of a material. Nonlinear absorption refers to the change in transmittance of a material as a function of input intensity or fluence. For effective performance of all optical switches and limiting devices, a strong nonlinear absorption is an essential criterion. Nonlinear absorption has also been employed to enhance the optical spectroscopic study of materials. The nonlinear index of refraction or the third order susceptibility is an important parameter in the optical limiting applications. Measurement techniques include degenerate four-wave mixing, Z-scan, optical Kerr effect and ellipse rotation interferometric methods, two-beam coupling, beam self-bending and third-harmonic generation [10].

Z-scan is a popular technique that is particularly useful for simultaneous measurement of both the nonlinear refractive index and nonlinear absorption coefficient. The Z-scan method has gained rapid acceptance as a standard technique due to its simplicity in technique and interpretation through the nonlinear optics community. However, it must always be recognized that this method is sensitive to all nonlinear mechanisms that give rise to a change in the refractive index and/or nonlinear absorption coefficient. Various Z-scan methods for data analysis include single beam Z-scan, eclipsing Z-scan, two color Z-scan, time resolved excite probe Z-scan and top hat beam Z-scan [11].

The study of nonlinear refraction by using the single beam Z-scan method is based on intensity dependence of the thin sample along a focused Gaussian laser beam. The sample causes additional focusing due to a positive nonlinear refraction or defocusing due to a negative refraction. A Gaussian beam is focused by a spherical lens onto the sample and the variation in the beam profile is observed at the far field as the sample is taken
through the focus of the lens. The beam propagation direction is taken as the $Z$ direction and the sample is moved along that direction, and hence this technique is known as the $Z$-scan technique. By properly monitoring the transmittance change through a small aperture placed at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus and without placing an aperture at the detector, (open aperture), one can measure the intensity-dependent absorption as the change of the transmittance through the sample. When both methods (closed and open ones) are used for the measurements, the ratio of the signals determines the nonlinear refraction in the sample [12].

Sheik-Bahae et al. [68] and David J. Hagan et al. [11] developed a sensitive self-focusing measurement technique that involves focusing a laser beam through a thin sample and detecting the light transmitted by a small aperture in the far-field. If $E$ is the peak electric field of a Gaussian beam traveling in the $+Z$ direction, then

$$E(z,r,t) = E_0(t) \frac{\omega_0}{\omega(z)} \exp \left( -\frac{r^2}{\omega^2(z)} - \frac{ikr^2}{2R(z)} \right) e^{-i\phi(z,r)}$$  \hspace{1cm} (1.24)$$

where $\omega^2(z) = \omega_0^2 \left( 1 + \frac{z^2}{z_0^2} \right)$ is the beam radius with beam waist as $\omega_0$ and $R(z) = z \left( 1 + \frac{z^2}{z_0^2} \right)$ is the radius of curvature of the wave front at $Z$, $Z_0$ ($= k\omega_0^2 / 2$) is the diffraction length of the beam, ($k=2\pi/\lambda$) is the wave vector and $\lambda$ is the wavelength of the laser.

It is important to note that, if the sample length is smaller enough to change the beam diameter within the sample either due to diffraction or nonlinear refraction that can be neglected, the medium is regarded as thin media, in which case the self-refraction process is referred as external self action. For linear diffraction, this implies that $L \ll z_0$. 

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while for nonlinear refraction, $L \ll z_0 / \Delta \Phi_0$. In most cases $\Delta \Phi_0$ is small and eventually $L \ll z_0$ is an essential criterion to be achieved.

A diode pumped Nd:YAG laser (532 nm) is used as the excitation source for the Z-scan technique. The Gaussian profile laser beam is focused on a 1 mm cuvette containing the 1 mM concentration solution by a lens of focal length 3.5 cm to produce a beam of waist ($\omega_0$) 15.35 μm. The condition for diffraction length ($z_0 = \pi \omega_0^2 / \lambda > L$) was satisfied so that the sample is considered as a thin medium. The transmission of the beam through an aperture placed in the far field is measured using a photo detector fed to the digital power meter. For the open aperture Z-scan, a lens is used to collect the entire laser beam transmitted through the sample that replaced the aperture.

![Z-scan setup](image)

Figure 1.7 General experimental setup for Z-Scan measurement

The nonlinear parameters under cw laser illumination were determined by the well known closed Z-scan set up formulated by Sheik-Bahae et al. [68] and David J. Hagan et al. [11]. The difference between the normalized peak and valley transmission ($\Delta T_{p-v}$) is written in terms of the on axis phase shift $|\Delta \Phi|$ at the focus as,

$$\Delta T_{p-v} = 0.406(1 - S)^{0.25} |\Delta \Phi|$$  1.25

where $S$ is the aperture linear transmittance and is calculated by using the relation

$$S = 1 - \exp \left(-2 \frac{r_a^2}{\omega_a^2}\right)$$  1.26
where \( r_a \) is the aperture and \( \alpha_a \) is the beam radius at the aperture. The nonlinear refractive index is given

\[
n_2 = \frac{\Delta \phi}{KL_0L_{\text{eff}}} \tag{1.27}
\]

where \( K = 2\pi / \lambda \) \((\lambda \text{ is the wavelength of laser})\), \( I_0 \) is the intensity of the laser beam at the focus \((Z=0)\), \( L_{\text{eff}} \) is the effective thickness of the sample \((L_{\text{eff}} = [1-\exp(-\alpha L)]/\alpha)\), \( \alpha \) is the linear absorption coefficient and \( L \) is the thickness of the sample.

From the open aperture Z-scan data, the nonlinear absorption coefficient \( \beta \) is estimated

\[
\beta = \frac{2\sqrt{2}\Delta T}{I_0L_{\text{eff}}} \tag{1.28}
\]

where \( \Delta T \) is the one valley value at the open aperture Z-scan curve. The value of \( \beta \) will be negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of the third order nonlinear optical susceptibility \( \chi^{(3)} \) are defined as

\[
\text{Re} \chi^{(3)} = \frac{10^{-4} \left( \varepsilon_0 C^2 n_0^2 n_2 \right)}{\pi} \text{ (cm}^2 / \text{W}) \tag{1.29}
\]

\[
\text{Im} \chi^{(3)} = \frac{10^{-2} \left( \varepsilon_0 C^2 n_0^2 \lambda \beta \right)}{4\pi^2} \text{ (cm} / \text{W}) \tag{1.30}
\]

where \( \varepsilon_0 \) is the permittivity of vacuum, \( n_0 \) is the linear refractive index of the sample and \( c \) is the velocity of light in vacuum.

The third order nonlinear optical susceptibility is thus

\[
\chi^{(3)} = \sqrt{\left( \text{Re} \chi^{(3)} \right)^2 + \left( \text{Im} \chi^{(3)} \right)^2} \tag{1.31}
\]

The applications of NLO materials are many and hence the demand and search for materials seem to be never ending. Especially with a need for compact, maintenance free all-solid-state devices to produce short wavelength (Blue-Green) lasers along with urgent
attention in producing safeguarded photosensitive components from intense laser beam,
the discussion presented in the upcoming chapters will be very essential for research
community.

REFERENCES

5. R.W. Munn and C.N. Ironside, *Principles and applications of nonlinear optical
   Limited, New Delhi, 2007.
    315.


64. B.Milton Boaz, J.Mary Linet, Babu Varghese, M.Palanichamy, S.Jerome Das.
65. C.Vesta, R.Uthrakumar, C.Justin Raj, A.Jonie Varjula, J.Mary Linet, S.Jerome Das,