CHAPTER - 1

An Overview of Nonlinear Optics, Crystal Growth and Characterization Techniques
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1.1 Introduction

In the pre-laser era the field strengths of the conventional light sources used (<10³ V/cm), was much smaller than the field strengths of atomic and inter-atomic fields. It is known that the light wave with such a low intensity does not alter the atomic fields to the extent of changing optical properties. The field strength of lasers (10⁷ – 10¹⁰ V/cm) is comparable with the atomic and inter-atomic fields. So it alters the optical properties of the medium. At such high field strength, the electric polarization and the field strength ceases to be linear and some interesting nonlinear effects come to the fore.

Nonlinear optics (NLO) is the study of the phenomena that occur as a consequence of the modification of the optical properties of a material system by the presence of light [1]. Bloembergen played an active role in establishing the theoretical model of nonlinear optics. The invention of optical second harmonic generation in crystals by Franken and his coworkers [2] in 1961 gained rapid progress in nonlinear optics (NLO).

Photonics is the branch of technology in which a photon is used to acquire, store, process and transmit information. Nonlinear optics and photonics are emerging as the technology for the 21st century. Photonics has many distinct merits over electronics. The most important advantage is the gain in speed due to the fact that a photon travels much faster than an electron. Nonlinear optical materials are gaining importance in technologies such as electro-optics and laser industry, medicine, entertainment, remote sensing, optical data storage, laser frequency conversion, laser radar, optical communication, optical computing and dynamic image processing [3, 4].

In the last few decades photonics has developed into a new branch of science with plethora of applications [5]. The major progress that has been achieved in this field over these years is mainly due to the progress in two branches of science, i.e., lasers and materials, since only lasers can provide sufficiently intense coherent radiation to produce nonlinear effects. Any practical applications of NLO would depend on the addition of new materials [6].
Accordingly, a large number of NLO crystals were searched from known piezoelectric, ferroelectric and electro-optic crystals and their NLO properties were investigated [7]. With the availability of a large amount of experimental data efforts have been on, to study the relationship between macroscopic properties and their microscopic structures in order to understand the structure property relationships [8], which lead to the development of a number of theoretical models. This has provided a feedback to materials researchers to search for newer NLO and Electro Optic (EO) materials under the guidelines of structural criteria. This feedback in turn has led to the invention of newer NLO materials with high nonlinear optical coefficients with ultra fast response for ultimate use in photonic applications, and the search for them is still continuing. Although the first nonlinear optical effects were observed in crystalline structures, they were soon extended to organic molecular materials and polymers. The area of organic nonlinear optics has been extremely active in the past three decades. Nonlinear optical activity in organic materials lies in the polarizability of electrons at the molecular level; hence these materials are preferred for NLO applications [9]. The intrinsically electronic nature of response in organic materials gives rise to a very fast response for non resonant optical excitations and has great advantage for photonic devices over some of the inorganic analogues. Moreover, organic materials are easier to produce, more versatile and potentially cheaper. The biggest advantage of these materials is the synthesis of virtually infinite number of molecules [10, 11]. The great versatility of organic synthesis indicates a wealth of potential strategies for the optimization of the nonlinear response. However, there is a need for a theoretical and experimental model that provides guidelines in the search for optimal structures for NLO applications.

In the present work, the emphasis is on the latter aspect viz., the materials development. This thesis contains a systematic study of the synthesis, growth and characterization of five new organic NLO crystals and its theoretical origin of nonlinearity at the molecular level. As a preface to the work described in the main body of the thesis, this chapter gives a brief introduction to the NLO phenomena, materials requirement for a good NLO device and their technological applications, basic mechanisms of crystal growth and growth process, crystal growth techniques, experimental methods in characterization. Since a major portion of the thesis deals with the growth and characterization of NLO crystals, some fundamental concepts of crystal growth are also given.
1.2 Nonlinear optical phenomena

When a material is subjected to electromagnetic radiation, the atoms / molecules of the medium tend to be polarized. For small values of the electric field \( E \) associated with the radiation, the induced polarization \( P \), which is the electric dipole moment per unit volume of the medium, is linear in the field. I.e.,

\[
P = \varepsilon_0 \chi^{(1)} \cdot E
\]  

(1.1)

where \( \chi^{(1)} \) is the linear optical susceptibility-tensor of the medium and \( \varepsilon_0 \) is the permittivity of free space. The linear polarization is responsible for the linear optical phenomena of reflection and refraction.

For large values of the optical electric field, such as those available from laser sources, the induced polarization can be represented as a series expansion

\[
P = \varepsilon_0 \left[ \chi^{(1)} E + \chi^{(2)} E E + \chi^{(3)} E E E + \cdots \right]
\]  

(1.2)

where \( \chi^{(2)} \), \( \chi^{(3)} \), etc, are the non-linear optical susceptibility-tensors of the medium and are responsible for a large variety of non-linear optical phenomena [2].

If the electromagnetic field, \( E = E_0 \cos \omega t \), substituting it in the above equation gives

\[
P = \varepsilon_0 \left[ \chi^{(1)} \cdot E_0 \cos \omega t + \chi^{(2)} \cdot E_0^2 \cos^2 \omega t + \chi^{(3)} \cdot E_0^3 \cos^3 \omega t + \cdots \right]
\]  

(1.3)

This equation can be written as

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

(1.4)

{Using trigonometric relations, \( \cos^2 \theta = (1 + \cos 2 \theta) / 2 \) and \( \cos^3 \theta = (\cos 3 \theta + 3 \cos \theta) / 4 \) }.

Here, the first term represents a dc field, the second term is the fundamental harmonic, the third term causes a polarization, which oscillates at twice the incident frequency and is called the second-harmonic, and the fourth term gives rise to the third-harmonic.

The second-harmonic polarization \( P^{(2\omega)} \) can be written in terms of the nonlinear coefficient as

\[
P^{(2\omega)} = d^{(2\omega)} E^{(\omega)} E^{(\omega)}
\]  

(1.5)
\[ d^{(2\omega)} = \frac{\varepsilon_0 \chi^{(2\omega)}}{2} \quad (1.6) \]

\(d^{(2\omega)}\) is a third rank tensor with elements \(d^{(2\omega)}_{ijk}\), where the variables \(i, j, k\) range among the directions X, Y, Z.

Some important nonlinear optical interactions, their effects and applications are listed in Table 1.1 [1].

**Table 1.1: Nonlinear optical interactions**

<table>
<thead>
<tr>
<th>Susceptibility</th>
<th>Effect</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi^{(1)} (\omega=\omega))</td>
<td>Refraction</td>
<td>Lenses, Optical fibres</td>
</tr>
<tr>
<td>(\chi^{(2)} (2\omega=\omega+\omega))</td>
<td>Frequency doubling</td>
<td>Second harmonic generation</td>
</tr>
<tr>
<td>(\chi^{(2)} (\omega_s=\omega_a+\omega_b))</td>
<td>Frequency mixing</td>
<td>Frequency up converters, Optical parametric oscillators, Spectroscopy</td>
</tr>
<tr>
<td>(\chi^{(2)} (\omega=\omega+0))</td>
<td>Electro-optic effect</td>
<td>Q-Switching, Modulators, Beam defectors</td>
</tr>
<tr>
<td>(\chi^{(3)} (3\omega=\omega+\omega+\omega))</td>
<td>Frequency tripling</td>
<td>Third harmonic generation, Spectroscopy</td>
</tr>
<tr>
<td>(\chi^{(3)} (\omega=\omega+0+0))</td>
<td>dc Kerr Effect</td>
<td>Variable Phase retarder</td>
</tr>
<tr>
<td>(\chi^{(3)} (\omega_a=\omega_a+\omega_b-\omega_b))</td>
<td>ac Kerr Effect, Optical Kerr Effect, Raman scattering, Brillouin scattering</td>
<td>Fast switching, Time resolved experiments, Generation of different wavelengths</td>
</tr>
<tr>
<td>(\chi^{(3)} (\omega=\omega+\omega-\omega))</td>
<td>Intensity dependent refractive index, Self focussing, Phase conjugation</td>
<td>Optical limiters, Optical bistability, Real time holography</td>
</tr>
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</table>

### 1.3 Second harmonic generation

In second harmonic generation, a pump wave with a frequency of \(\omega\) generates a signal at the frequency \(2\omega\) as it propagates through a medium with a quadratic nonlinearity [12]. A polarization oscillating at 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 SHG (second harmonic generation).
The second harmonic generation in a crystalline powder can easily be observed by using an intense fundamental beam ($\lambda = 1064$ nm) of a pulsed Nd: YAG laser. For the incident intense IR (infrared) beam on the powder, the SHG occurs as scattered green light ($\lambda = 532$ nm). Optical nonlinearities have an electronic origin and, in the electric dipole approximation, only the valance electrons contribute to the second order nonlinear susceptibility. The magnitude of the nonlinear coefficient depends upon the direction of the electronic wave functions and the asymmetry of the electron clouds [13, 14]. Therefore, noncentrosymmetric crystals exhibit good SHG. For efficient second harmonic conversion, the wave vector mismatch $\Delta k$ between the interacting waves should be zero. This is termed as phase matching. Because of the dispersion of the refractive index between the fundamental and the second harmonic wavelengths ($n^{(1)}$, $n^{(2)}$), it is difficult to achieve phase matching in isotropic crystals. However, in anisotropic crystals it is possible to obtain $\Delta k = 0$ by a suitable choice of direction of propagation along which $n^{(1)} = n^{(2)}$; [15, 16].

The Kurtz and Perry powder technique was devised in 1968. It is a convenient method and remains an extremely valuable tool for initial screening of materials for SHG activity. The output of a laser, commonly a Nd:YAG at 1064 nm is split into two beams. One beam passes through the sample, while the other passes through a similarly mounted reference of known SHG efficiency. Filters behind the samples are used to remove the fundamental and leave only the second harmonic signals. The second harmonics are detected with photomultipliers, and the ratio of sample to reference signal is then produced and measured.

The experimental setup for measuring SHG efficiency is shown in the Figure 1.1.A fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate is made to fall normally on the sample. The power of the incident beam is measured using a power meter. The green light was detected by a PMT (photomultiplier tube) and displayed on a CRO cathode ray oscilloscope. In the NLO process that taking place in the sample, it converts the 1064 nm radiation into green light ($\lambda=532$ nm) when Nd:YAG laser light is passed into the sample and this confirms the SHG [17, 18]. The powder SHG observed for any given sample will vary with a number of parameters, including laser wavelength, bandwidth, particle size, temperature, crystallisation solvent and sample preparation, amongst others.
1.3.1 Phase matching

The advancement of research work on the mechanism of generation of optical harmonics in crystals and media in which such generation of harmonics is effectively realizable, has indicated the significance of phase relation between the fundamental and generated harmonics, as they propagate in crystals having optical dispersion. It was 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.

For a crystal to be useful as a second harmonic generator, the fundamental and the generated second harmonic beam should stay in phase throughout the interaction length. To satisfy the above condition, the refractive indices at both the wavelengths should be same. This can be achieved by exploiting the birefringence present in uniaxial or biaxial crystals [19]. A birefringent crystal has different refractive indices for different polarization of light.

Figure 1.1: Experimental setup to determine the SHG efficiency
The behavior of the refractive index is usually described in terms of refractive index surface, i.e., the indicatrix. In the case of the ordinary ray it is a sphere; for extraordinary ray it is an ellipsoid. Therefore, a material in which the refractive index for the extraordinary ray at $2\omega$, is equal to that of the ordinary ray at $\omega$, has to be chosen. This points to the fact that effective frequency conversion in the second harmonic is possible only in a limited number of crystals.

Consider a negative uniaxial crystal, i.e., a crystal for which the refractive index for the ordinary ray is greater than that for the extraordinary ray. Figure 1.2 shows a section through the refractive index surfaces (indicatrix) for one such crystal.

![Figure 1.2: Indicatrix for a negative uniaxial crystal](image)

The dotted curve represents the surface corresponding to the frequency $2\omega$ and the solid curve for frequency $\omega$. OX is the optic axis of the crystal. The refractive index surface of the ordinary wave and that for the extraordinary wave intersects at A. This means, that for the waves propagating in the direction OA

$$n_0(\omega) = n_e(2\omega)$$

(1.7)
i.e., the fundamental and the second harmonic waves propagating in this direction are phase matched. The cone angle $\theta$ is the phase matching angle. The phase matching condition is satisfied for all directions lying on the cone.

### 1.3.2 Laser induced damage

Laser induced damage is a phenomenon of interaction of high power laser radiation with matter and various physical, chemical, mechanical, optical and other aspects of materials come into play.

The second harmonic conversion efficiency ($\eta$) is the ratio of the output power of the second harmonic signal to the input power of the fundamental beam and is given by the expression:

$$\eta = \frac{P_{2\omega}}{P_{\omega}} = \frac{2\left(\frac{N}{\varepsilon_0}\right)^{3/2} a^2 l^2 \sin^2 \left(\frac{\Delta k l}{2}\right) P_{\omega} \omega^2}{n^3 \left(\frac{\Delta k l}{2}\right)^2 A}$$  \hspace{1cm} (1.8)

where $P_{\omega}$ is the power at fundamental frequency, $P_{2\omega}$ is the power at second harmonic frequency, $d$ is the nonlinear optical coefficient, $n$ is the refractive index, $\omega$ is the fundamental frequency, $k$ is the wave vector, $\Delta k = k_{2\omega} - 2k_{\omega}$, $l$ is the length, and $A$ is the area of cross-section of the crystal.

From the equation (1.8) it is clear that the harmonic conversion efficiency is proportional to the power density of the fundamental beam. Hence, a convenient way to increase the efficiency is to focus the beam into the crystal. But this often leads to breakdown of the materials, catastrophically damaging the crystal. It is then useful to prescribe the maximum permissible power for a particular crystal, defined as damage threshold.

The experimental setup used for measurements of laser damage threshold is shown in Figure 1.3. A Q-switched Nd: YAG laser of pulse width 6 ns and 10 Hz repetition rate operating in the TEM$_{00}$ mode is used as the source. The energy per pulse of 1064 nm laser radiation attenuated using appropriate neutral density filters, is measured using an energy ratiometer [Rj-7620, Laser Probe Inc.] which is externally triggered by the Nd: YAG laser. All the experiments are performed on as grown crystals.
For each experiment, the sample (S) is mounted on an X-Y translator which facilitates in bringing different areas of the sample for exposure accurately. For surface damage, the sample is placed at the focus of a plano-convex lens (L). To determine single shot damage threshold, the laser beam is irradiated at different spots on the same crystal at different pulse energies. This is done to avoid the cumulative effects resulting from multiple exposures. The onset of damage can be determined by various means viz. by observing it with microscope, by visual incandescence or by observing the scattering of He–Ne laser beam passing through the damaged volume. The laser damage threshold power density is calculated using the formula:

\[ P = \frac{E \tau}{A} \]  

where \( E \) is the laser energy per pulse, \( \tau \) is the pulse width and \( A \) is the area of the focused spot on the crystal.

### 1.4 Third order NLO processes

Processes originating from \( \chi^{(3)} \) are described in this section. \( \chi^{(3)} \) is a fourth rank tensor which contains 81 elements which get reduced to 15 under the Kleinman symmetry condition [20, 21]. Regardless of spatial symmetry, \( \chi^{(3)} \) is nonvanishing in any material and is responsible for a number of optical phenomena [1, 22–23]. The third order contribution to the nonlinear polarization is given by

\[ P^{(3)}(\omega_4) = \chi^{(3)}(\omega_4; \omega_1, \omega_2, \omega_3) E(\omega_1) E(\omega_2) E(\omega_3) \]  

(1.10)
Based on the values of frequencies $\omega_1$, $\omega_2$, and $\omega_3$, the interaction with an NLO material can give rise to third order NLO processes such as third harmonic generation, quadratic electro-optic effect (or Kerr effect), four wave mixing, two photon absorption, intensity dependent refractive index etc.

When $\omega_1 = \omega_2 = \omega_3 = \omega$ and $\omega_4 = 3\omega$, the polarization, $P^{(3)} (\omega_4 = 3\omega)$, is the source of third harmonic generation (THG) and is given by

$$P^{(3)} (3\omega) = \chi^{(3)} (-3\omega; \omega, \omega, \omega) E^3(\omega)$$  (1.11)

When $\omega_1 = 0$ (dc or low frequency ac field) and $\omega_2 = \omega_3 = \omega$, the process is known as electric field induced second harmonic generation (EFISHG) and is represented by

$$P^{(3)} (2\omega) = \chi^{(3)} (-2\omega; 0, \omega, \omega) E(0) E^2(\omega)$$  (1.12)

One of the incident fields is a d.c field and the second harmonic generation can be induced by this technique even in materials having inversion symmetry.

When $\omega_1 = \omega_2 = \omega$, $\omega_3 = \omega$ and $\omega_4 = -\omega$, the process is referred to as degenerate four wave mixing and it can be represented by

$$P^{(3)} (\omega) = \chi^{(3)} (-\omega; \omega, \omega, \omega) E^3(\omega)$$  (1.13)

Four-wave mixing involves the interaction of four coherent optical beams in a nonlinear medium. Three of them are input waves and the fourth one is generated due to third order process. If the frequencies of the incident fields are different from each other then the process is known as non-degenerate four wave mixing. The four wave mixing process leads to the important phenomenon like optical phase conjugation.

Two photon absorption (TPA), a third order NLO process, corresponds to the simultaneous absorption of two photons of the same energies (degenerate TPA) or different energies (non-degenerate TPA), in the presence of intense radiation. The TPA process is characterized by $\chi^{(3)} (-\omega_1; -\omega_2, \omega_2, \omega_1)$. At sufficiently high intensities, the probability of a material absorbing more than one photon before relaxing to the ground state can be greatly enhanced. Two-photon absorption involves a transition from the ground state of a system to a higher-lying state by the simultaneous absorption of two photons from an incident radiation field.
The third order process in which the refractive index of the medium changes with respect to the intensity of the incident optical field and the total refractive index of such medium is given by

\[ n = n_0 + n_2I \]  \hspace{1cm} (1.14)

where \( n_0 \) is the linear refractive index and \( n_2 \) is the field-dependent part. Depending on the sign of \( n_2 \), the laser beam inside the material experiences a focusing or a defocusing effect leading to the self-focusing or the self-defocusing phenomenon. The refractive index of a material is related to the dielectric susceptibility by the relation

\[ n = \sqrt{1 + \chi} \]  \hspace{1cm} (1.15)

Since the susceptibility \( \chi \) is a function of the field \( E \), \( n \) depends on \( E \). This dependence of \( n \) on \( E \) gives rise to self-focusing of intense light beams. Therefore, we can consider the second term in the equation (1.4) that describes the fundamental harmonic, viz.

\[ P^{(1)} = \varepsilon_0 \left( \chi^{(1)} + \frac{3}{4} \chi^{(3)} \varepsilon_0^2 \right) E \]  \hspace{1cm} (1.16)

Then, the expression (1.15) becomes

\[ n = \sqrt{1 + \left( \chi^{(1)} + \frac{3}{4} \chi^{(3)} \varepsilon_0^2 \right)} \]  \hspace{1cm} (1.17)

We can write \( n \) as \( n = \sqrt{\varepsilon_l + \varepsilon_{nl}} \) where \( \varepsilon_l = 1 + \chi^{(1)}, \varepsilon_l \) is the linear dielectric permittivity of the medium, and \( \varepsilon_{nl} \) is a nonlinear increment in the expression for dielectric permittivity. Therefore one can write

\[ n = \sqrt{\varepsilon_l} \sqrt{1 + \frac{\varepsilon_{nl}}{\varepsilon_l}} \approx \sqrt{\varepsilon_l} \left( 1 + \frac{\varepsilon_{nl}}{2\varepsilon_l} \right) \quad \text{(because } \varepsilon_{nl} < \varepsilon_l) \]  \hspace{1cm} (1.18)

\[ n = n_l \left( 1 + \frac{\varepsilon_{nl}}{2n_l^2} \right) = n_l \left( 1 + \frac{3}{8n_l^2} \chi^{(3)} \varepsilon_0^2 \right) \]

\[ n = n_l \left( 1 + n_{nl} \varepsilon_0^2 \right) \]  \hspace{1cm} (1.19)

where \( n_l = \sqrt{\varepsilon_l} \) is the linear refractive index of the medium, and \( n_l n_{nl} \varepsilon_0^2 \) is the nonlinear increment in the expression for the refractive index. We thus, see that the refractive index of a
nonlinear medium is proportional to the square of the amplitude of the field (intensity). Now the intensity of a laser beam peaks at the axis of the beam and falls off gradually away from the axis. The speed of the light wave is given by \( v = \frac{c}{n} \). Since \( n \) decreases owing to the falling of the intensity of the light beam, the velocity increases with the distance away from the axis. Consequently, a plane wave-front incident on material becomes concave as it propagates through the medium and contracts towards the axis. In other words, it self focuses. The distance \( L_0 \) over which the beam self-focuses can be approximately estimated to be

\[
L_0 = \frac{D}{\sqrt{n_0 E_0^2}}
\]

where \( D \) is the diameter of the beam [25].

### 1.4.1 Z-scan theory

The structure-NLO property relationship in materials under present investigation are studied using this technique, therefore a brief theory of the Z-scan is described. Let us consider the case of a material having cubic nonlinearity. The index of refraction \( n \) may be expressed as,

\[
n = n_0 + \frac{n_2}{2} |E|^2 = n_0 + \gamma I
\]

where \( n_0 \) is the linear index of refraction, \( n_2 \) (esu) and \( \gamma \) (m^2/W) are the nonlinear refractive index coefficients, \( E \) is the peak electric field and \( I \) is the irradiance of the laser beam within the sample. The \( n_2 \) (esu) and \( \gamma \) (m^2/W) are related through the conversion formula,

\[
n_2 \text{ (esu)} = \frac{cn_0^{40 \pi}}{40} \gamma \text{ (m}^2 / \text{W})
\]

where, \( c \) (m/s) is the speed of light in free space.

For a Gaussian laser beam of waist radius \( \omega_0 \), traveling in +z direction, we can express the wave electric field, \( E \) as,

\[
E(z, r, t) = E_0(t) \frac{\omega_0}{\omega_0(z)} \exp \left( -\frac{r^2}{\omega_0^2(z)} - \frac{ikr^2}{2R(z)} \right) e^{-i\phi(z, t)}
\]

where \( \omega^2(z) = \omega_0^2 \left( 1 + \frac{z^2}{z_0^2} \right) \) is the beam radius, \( \omega_0 \) is the beam radius at the focus, \( R(z) = z (1 + z_0^2 / z^2) \) is the radius of curvature of the wavefront, \( z_0 = k\omega_0^2 / 2 \) is the diffraction limit (Rayleigh length) of the beam, \( k = 2\pi / \lambda \) is the wave vector, \( \lambda \) is the wavelength of the laser beam, all in free space. \( E_0(t) \) denotes the laser electric field at the focus and contains the
temporal envelope of the laser pulse. The term $e^{-i\phi(z,t)}$ contains all the radially independent phase variations. The nonlinear medium is considered to be optically “thin” if the sample thickness is small enough that changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected. In most of the experimental situations, the nonlinear sample could be considered “thin” if its thickness $L$, equal to the thickness of the cuvette in our experiments, is much less than the Rayleigh length, $z_o$.

For nonlinearities which are not too strong, one may employ the slowly varying envelope approximation (SVEA). In such cases, the radial phase variation and the propagating laser beam intensity are governed by,

$$\frac{d\Delta \phi}{dz'} = \Delta n(I) k$$  \hspace{1cm} (1.24)

$$\frac{dI}{dz'} = -\alpha(I) I$$ \hspace{1cm} (1.25)

where $z'$ is the propagation length in the sample, $\alpha(I)$ in general includes linear and nonlinear absorption terms.

In the case of cubic nonlinearity with negligible nonlinear absorption, equation (1.24) and (1.25) are solved to obtain the phase shift $\Delta \phi$ at the exit surface of the sample, which is seen to simply follow the radial variation of the incident laser beam. Thus,

$$\Delta \phi(z,r,t) = \Delta \phi_o(z,t) \exp(-2r^2/\omega^2(z)) \text{ with } \Delta \phi_o(z,t) = \Delta \phi_o(t) / (1+z^2/z_o^2)$$   \hspace{1cm} (1.26)

$$\Delta \phi_o(t), \text{ the on-axis phase shift at the focus is given by,}$$

$$\Delta \phi_o(t) = k\gamma I_o(t) L_{\text{eff}}$$ \hspace{1cm} (1.27)

where $L_{\text{eff}} = (1-e^{-\alpha L})/\alpha$ with the sample length $L$ and the linear absorption coefficient $\alpha$, and $I_o(t)$ is the on-axis irradiance at the focus ($z = 0$).

$$I_o = \frac{4(\sqrt{\ln2})E_{\text{tot}}}{\sqrt{\pi^3} \omega_o^2 \tau}$$ \hspace{1cm},

where, $\tau$ is the pulse width, $E_{\text{tot}}$ is the incident energy on the sample.
The complex electric field exiting the sample may now be expressed as,

$$E_e(z,r,t) = E_i(z,r,t)e^{-\alpha L/2}e^{i\Delta \phi(z,r,t)}$$  \hspace{1cm} (1.28)

where $E_i(z,r,t)$ is the field of the beam incident on the sample.

Employing Kirchoff’s diffraction theory, one can obtain the far field pattern of the beam at the aperture plane as the Fraunhofer diffraction pattern of $E_e(r,z,t)$ at the diffraction plane. For this purpose we may employ the Taylor series expansion of the nonlinear phase term, $e^{i\Delta \phi(z,r,t)}$, which is given by,

$$e^{i\Delta \phi(z,r,t)} = \sum_{m=0}^{\infty} \frac{[i\Delta \phi_0(z,t)]^m}{m!} e^{-2mr^2/\omega_m^2(z)}$$  \hspace{1cm} (1.29)

Each gaussian beam can now be simply propagated to the aperture plane where they can be superposed to reconstruct the beam. Taking into account of the initial curvature for the focused beam, the resultant electric field pattern at the aperture is,

$$E_a(r,t) = E(z,r = 0,t)e^{-\alpha L/2} \sum_{m=0}^{\infty} \frac{[i\Delta \phi_0(z,t)]^m \omega_m}{\omega_m} \exp \left( -\frac{r^2}{2\omega_m^2} - \frac{ikr^2}{2R_m} + i\theta_m \right)$$  \hspace{1cm} (1.30)

Defining $d$ as the propagation distance (in air) from the sample to the aperture plane and $g = 1 + d/R(z)$, the remaining parameters in the equation (1.30) are expressed as,

$$\omega_m^2 = \frac{\omega_m^2}{2m+1}, \hspace{1cm} d_m = \frac{k\omega_m^2}{2}, \hspace{1cm} \omega_m^2 = \omega_m^2 \left[ g^2 + \frac{d^2}{d_m^2} \right]$$

$$R_m = d \left[ 1 - \frac{g}{g^2 + \frac{d^2}{d_m^2}} \right]^{-1}$$

$$\theta_m = \tan^{-1} \left[ \frac{d/d_m}{g} \right]$$

This method is applicable for small phase distortions, detected with Z-scan method, and can be applied to higher order nonlinearities.

The optical power transmitted through the aperture is obtained by spatially integrating $E_a(r,t)$ at the aperture as follows:

$$P_t(\Delta \phi_0(t)) = c\varepsilon_0n_0\pi \int_0^{r_a} |E_a(r,t)|^2 r dr$$  \hspace{1cm} (1.31)
Taking into account the temporal profile of the pulse intensity, the normalized Z-scan transmittance $T(z)$ can be calculated as,

$$T(z) = \frac{\int_{-\infty}^{\infty} P_r(\Delta \phi_0(t))dt}{\int_{-\infty}^{\infty} P_l(t)dt}$$  \hspace{1cm} (1.32)

where $P_l(t) = \pi \omega_0^2 I_o(t)/2$ is the instantaneous input power within the sample,

$S=1-\exp(-2r_a^2/\omega_a^2)$ is the aperture linear transmittance with $\omega_a$ denoting the beam radius at the aperture in the linear regime and $r_a$ is the aperture radius.

For a given $\Delta \phi_0$ the magnitude and profile of $T(z)$, i.e., Z-scan trace do not depend on the wavelength or laser beam geometry as long as the far field condition for the aperture plane ($d>>z_o$) is satisfied. The aperture size $S$, however, is an important parameter since a larger aperture reduces the variation in $T(z)$. This reduction is more prominent at the peak of the Z-scan trace, where beam narrowing occurs. For very large aperture $(S=1)$, the effect vanishes and $T(z) = 1$ for all $z$ and $\Delta \phi_0$. For small $|\Delta \phi_0|$, the peak and valley occur at the same distance with respect to the focus and for a cubic nonlinearity, this distance is found to be $\approx 0.86 z_o$ [24]. With larger phase distortions $|\Delta \phi_0|>1$, numerical evaluation of equations, (1.30) - (1.32) shows that this symmetry no longer holds and the peak and valley both move towards $\pm z$ for the corresponding sign of nonlinearity ($\pm \Delta \phi_0$) such that their separation remains nearly constant, given by,

$$\Delta T_{p-v} \approx 1.7 z_o$$ \hspace{1cm} (1.33)

where $\Delta T_{p-v}$ as the difference between the normalized peak and valley transmittance.

For small phase distortion and small aperture $(S\approx0)$,

$$\Delta T_{p-v} = 0.406|\Delta \phi_0|$$ \hspace{1cm} (1.34)

Numerical calculations show that this relation is accurate within 0.5% of the experimental value for $|\Delta \phi_0|<\pi$. For larger aperture the linear coefficient becomes smaller than 0.406. For $S=0.5$, it becomes $\approx 0.34$ and at $S=0.7$ it reduces to $\approx 0.29$. Based on the numerical curve fitting, the following relationship can be used to account for such variations within $\pm2\%$ accuracy:
Equations (1.34) and (1.35) are used to estimate the coefficient of nonlinear index ($n_2$) with good accuracy after a Z-scan is performed. This steady state result can be extended to pulsed radiation by using the time averaged index change ($\Delta n_0(t)$), defined by,

$$\langle \Delta n_0(t) \rangle = \frac{\int_{-\infty}^{\infty} \Delta n_0(t) I_0(t) dt}{\int_{-\infty}^{\infty} I_0(t) dt}$$

The time averaged $\langle \Delta \phi_0(t) \rangle$ is related to $\langle \Delta n_0(t) \rangle$ through the equation (1.27). For a material having instantaneous nonlinear response, one obtains for a temporally gaussian pulse,

$$\langle \Delta n_0(t) \rangle = \frac{\Delta n_0}{\sqrt{\pi}}$$

where $\Delta n_0$ represents the peak-on-axis index change at the focus.

These equations were obtained for a material showing cubic nonlinearity. A similar analysis can be made for higher order nonlinearities. The above theoretical discussions were based on the fact that the material has no nonlinear absorption. Practically, large refractive nonlinearities in materials are commonly accompanied by a resonant transition which may be of single or multiphoton nature. The nonlinear absorption in such materials, arising from either direct multiphoton absorption, saturation of the single photon absorption or dynamic free carrier absorption, have strong effects on the measurements of nonlinear refraction using the Z-scan technique. In such cases, a Z-scan with a fully open aperture ($S=1$), is insensitive to nonlinear refraction (thin sample approximation). Such open aperture Z-scan traces, with no aperture, are usually symmetric with respect to the focus ($Z=0$) where they have a minimum transmittance for mechanisms such as multiphoton absorption. The coefficients of nonlinear absorption can be easily calculated from the open aperture transmittance curves.

The third order nonlinear susceptibility is generally a complex quantity and is written as,

$$\chi^{(3)} = \chi_R^{(3)} + j\chi_I^{(3)}$$

where the imaginary part is related to TPA coefficient $\beta$ through,

$$\chi_I^{(3)} = \frac{n^2 \varepsilon_0 c^2}{\omega} \beta$$
and the real part is related to \( n_2 \) through,
\[
\chi_R^{(3)} = 2n_c^2 \varepsilon_o c \ n_2 
\]

We now express the total absorption coefficient as,
\[
\alpha (I) = \alpha + \beta(1) 
\]

where \( \alpha \) is the linear absorption coefficient.

Using this expression in equations (1.24) and (1.25), and solving them we obtain the intensity at the exit plane of the sample as,
\[
I_e(z, r, t) = \frac{I(z, r, t) e^{-\alpha L}}{1 + q(z, r, t)}
\]

and the corresponding phase shift as,
\[
\Delta \phi(z, r, t) = \frac{kr}{\beta} \ln[1 + q(z, r, t)]
\]

where \( q(z, r, t) = \beta I(z, r, t) L_{\text{eff}} \)

Combining above two equations, we obtain the complex field at the exit surface of the sample to be [24],
\[
E_e = E(z, r, t) e^{-\alpha L/2}(1 + q)^{(ikr / \beta - 1/2)}
\]

The above equation reduces to equation (1.28) in the absence of TPA. In general, using the zeroth-order Hankel transform, the above equation yields the field distribution at the aperture which can then be used in (1.31) and (1.32) to obtain the transmittance. For \( |q| < 1 \), following a binominal series expansion in powers of \( q \), equation (1.44) can be expressed as a sum of infinite gaussian beams as in the purely refractive case
\[
E_c = E(z, r, t) e^{-\alpha L/2} \sum_{m=0}^{\infty} \frac{q(z, r, t)^m}{m!} \prod_{m=0}^{\infty} (ikr \beta - 1/2 - n + 1)
\]

where the gaussian profile is implicit in \( q(z, r, t) \) and \( E(z, r, t) \). The complex field pattern at the aperture plane can be obtained in the same manner as before. The result can again be represented by equation (1.30) if we substitute \( i\Delta \phi_o (z, t) [m! / m!] \) terms in the sum by,
The Z-scan transmittance variations can be calculated following the same procedure as described earlier. As evident from equation (1.46), the absorptive and refractive contributions to the far-field beam profile, and hence to the Z-scan transmittance, are coupled. When the aperture is removed, however, the Z-scan transmittance is insensitive to beam distortion and is only a function of the nonlinear absorption. The total transmitted fluence in that case (S=1) can be obtained by spatially integrating equation (1.44) without having to include free space propagation. Integrating equation (1.42) at z over r, we obtain the transmitted power P(z,t) as follows,

\[ P(z, t) = P_i e^{-\alpha L} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \]  

(1.47)

where \( q_0(z, t) = \beta I_0(t) L_{eff}/(1 + z^2/z_0^2) \) and \( P_i(t) \) was defined in equation (1.32). For a temporally gaussian pulse, equation (1.30) can be time integrated to give the normalized energy transmittance

\[ T(z, S = 1) = \frac{1}{\sqrt{\pi q_0(z, 0)}} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{-r^2}] \, dr \]  

(1.48)

For \( |q_0| < 1 \), this transmittance can be expressed in terms of the peak irradiance in the following form more suitable for numerical evaluation:

\[ T(z, S = 1) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}} \]  

(1.49)

Thus, once an open aperture (S=1) Z-scan is performed, the nonlinear absorption coefficient \( \beta \) can be unambiguously deduced. Next, a Z-scan with aperture in place (S<1) can be used to extract the nonlinear refraction coefficient \( n_2 \).

By performing the on axis Z-scan experiment using a gaussian beam in the low irradiance limit, the two nonlinear terms viz., nonlinear refraction and the nonlinear absorption can be expressed as [25, 26],
Synthesis and Characterization of Nonlinear Optical Crystals of Chlorine and Bromine Substituted Chalcone Derivatives

Chapter 1

An Overview of Nonlinear Optics, Crystal Growth And Characterization Techniques

\[ T_{\Delta \phi}(x) = \frac{4x}{(x^2 + 9)(x^2 + 1)} \Delta \phi_0 \] (1.50)

\[ T_{\Delta \psi}(x) = -\frac{2(x^2 + 3)}{(x^2 + 9)(x^2 + 1)} \Delta \psi_0 \] (1.51)

and the total transmittance,

\[ T(x) = 1 + T_{\Delta \phi}(x) + T_{\Delta \psi}(x) \] (1.52)

where \( \Delta \phi_0 \) is the on–axis phase shift due to nonlinear refraction and \( \Delta \psi_0 \) is the on–axis phase shift due to nonlinear absorption. \( x = z/z_0, z_0 = k\omega_0^2/2 \) is the Rayleigh length or diffraction limit of the beam, \( \omega_0 \) is the beam radius at the focus. The ratio of \( \Delta \psi_0 \) and \( \Delta \phi_0 \) is known as the coupling factor. It also relates to the real and imaginary parts of the third order susceptibility.

Once \( \Delta \phi \) is known, the nonlinear refractive index can be calculated by using the formula,

\[ n_2 = \frac{\Delta \phi \lambda \alpha}{2\pi I_0 (1 - e^{-\alpha x})}, \]

where \( \alpha \) is the linear absorption coefficient, \( L \) is the length of the sample, \( I_0 \) is the on-axis irradiance at the focus (\( z = 0 \)). The linear absorption coefficient can be determined by fitting the data from the transmission measurement at low input intensities to the expression,

\[ \ln(I_0/I) = (\alpha x) \] (1.53)

where \( x \) is the sample length, and \( \ln (I_0/I) \) is defined to be the optical density.

### 1.4.2 Z-scan experimental technique

Z-scan technique is a sensitive measurement technique based on self focusing effect. Since its establishment, it has become a popular technique for characterizing third order nonlinear optical materials. This technique is particularly useful when the optical nonlinearity in a material is caused by both nonlinear absorption and nonlinear refraction. This technique enables simultaneous measurement of nonlinear index of refraction \( n_2 \), and nonlinear absorption coefficient \( \beta \), which are related to the real and imaginary parts of third order nonlinear optical susceptibility \( \chi^{(3)} \), respectively. Basically, in this technique a gaussian laser beam is focused using a lens on the sample and by translating the sample through the focus, the change in the far-field intensity pattern is monitored. Here, the sample is translated along...
the axis of the laser beam, taken to be the $Z$-axis, from the left to the right of the focal point. The transmitted intensity is first measured keeping an aperture in front of the detector thus obtaining closed aperture $Z$-scan data. Next, the transmittance is measured without aperture as the sample is translated along the $Z$-direction in order to obtain the open aperture $Z$-scan data. The sample itself behaves as a thin lens for the laser beam propagating through it. When the sample is translated along the beam path, its effective focal length changes depending on the intensity of the converging laser beam. This results in a change in the intensity distribution in the far-field zone and is measured by the closed aperture $Z$-scan technique. In addition to this refraction due to nonlinearity, the medium also possesses nonlinear absorption, which is significant in the open aperture measurement. Thus, collectively, the closed aperture and the open data allows us to calculate values of both $n_2$ and $\beta$.

**Nonlinear refraction**: A nonlinear optical material exhibit either positive nonlinear refraction or negative nonlinear refraction. Let us first consider a material possessing positive nonlinear refraction. The sample thickness is assumed to be smaller than the Rayleigh length of the focused laser beam, i.e., the sample is “thin”. Nonlinear refraction measurement process involves translation of the sample from about $Z = -20$ mm to $Z = +20$ mm, $Z = 0$ being the focal point without the sample. At $Z = \pm 20$ mm, the intensity of the laser beam incident on the sample is very low, and hence negligible nonlinear refraction occurs. Therefore the sample behaves as a linear medium. As the sample approaches the focal point, $Z = 0$, the beam intensity increases rapidly, leading to self-lensing in the sample. A negative self-lensing prior to the focus will tend to collimate the beam causing a beam narrowing at the aperture. The consequence of this nonlinear refraction on the laser beam propagation is a shift in the focal point of the beam from $Z = 0$ towards $+ve$ $Z$-values, which results in an increase in the measured transmitted intensity. As the translation of the sample is continued further beyond $Z = 0$, the same self-defocusing effect occurs which increases the beam divergence, leading to beam broadening at the aperture. Consequently, the transmitted intensity of the laser beam decreases rapidly. Further translation towards $Z = +20$ mm leads to rapid reduction in the beam intensity in the sample and the nonlinearity disappears. Consequently, the transmittance returns to the linear value corresponding to the initial sample position $Z = -20$ mm. When the sample is close to the focal point $Z = 0$, the nonlinearity is very strong and it
can be regarded as thin lens. The measured transmitted intensity as a function of sample position (Z) shows a pre-focal peak for Z < 0 followed by post-focal valley for Z > 0, which is the signature of negative nonlinear refractive index (i.e., n_2 < 0). A typical Z-scan plot of negative nonlinear refractive index is shown in the Figure 1.4. Similarly for a material having positive nonlinear refractive index, the measured transmitted intensity as a function of sample position (Z) shows a pre-focal valley for Z < 0 followed by post-focal peak for Z > 0.

![Figure 1.4: Closed aperture Z-scan curve](image)

**Nonlinear absorption:** From the open aperture Z-scan data, the measured values of nonlinear absorption coefficient β, and the imaginary part of third order nonlinear optical susceptibility χ^(3) of the sample can be calculated. The sensitivity to nonlinear refraction is entirely due to the presence of the aperture in front of the detector, the removal of the aperture completely eliminates this effect. The open aperture Z-scan trace exhibits decrease in the transmittance close to the focus Z = 0 of the laser beam. A typical open aperture Z-scan plot is shown in the Figure 1.5. The sample may possess absorptive nonlinearities due to mechanisms, such as multiphoton absorption and saturable absorption. Qualitatively, multiphoton absorption suppresses the peak and enhances the valley in the closed aperture Z-scan plot. On the other hand, saturation effect does the opposite. Usually the nonlinear refraction is accompanied by nonlinear absorption. To estimate the pure nonlinear refraction, a simple division of closed aperture Z-scan data by open aperture Z-scan data yields the normalized Z-scan curve which is free from nonlinear absorption. A typical normalized Z-scan plot corresponding to pure nonlinear refraction is shown in the Figure 1.6. One can calculate both...
nonlinear absorption coefficient $\beta$, and nonlinear refractive index $n_2$, by utilizing graphs shown in Figures 1.5 and 1.6 respectively.

**Figure 1.5: Open aperture Z-scan curve**

![Open aperture Z-scan curve](image)

**Figure 1.6: Pure nonlinear refraction Z-scan curve**

![Pure nonlinear refraction Z-scan curve](image)

**Z-scan experimental details:** The schematic experimental set up for Z-scan is shown in Figure 1.7. Basically, in this technique a gaussian laser beam is focused, using a lens (L) of 25 cm focal length. The experiments were performed using a Q-switched, frequency doubled Nd:YAG laser (Spectra-Physics GCR170) which produces 7 ns pulses at 532 nm and at a
pulse repetition rate of 10 Hz. The resulting beam waist radius at the focus, calculated using
the formula $\omega_0 = 1.22\lambda f / d$, where $f$ is focal length of the lens and $d$ is the diameter of the
aperture, was found to be 18.9 mm. The corresponding Rayleigh length, calculated using the
formula $z_0=\pi\omega_0^2 / \lambda$, was found to be 2.11 mm. For solution Z-scan measurements, cuvette
of 1 mm thickness was used. The sample (S) was moved along the laser beam axis using a
computer controlled (PC) translation stage. The detector (D) was placed at a distance of about
30 cm from the focal spot, i.e., $Z = 0$. A circular aperture (I) of diameter 5 mm was placed in
front of the detector and the detector output was monitored as the sample was translated along
the laser beam axis from $Z= -15$ mm to $Z= +15$ mm. The Z-scan experiment was performed
at an input peak-intensity of 2.39 GW/cm$^2$. The nonlinear transmission of the sample, with
and without the aperture in front of the detector was measured in the far-field using Laser
Probe Rj-7620 Energy Meter with Pyroelectric detectors.

![Figure 1.7: Schematic representation of Z-scan experimental setup](image)

1.5 Material requirement for NLO

In the initial stages, material scientists working on novel nonlinear optical materials had given
importance only to the optical nonlinearity, without worrying much about the other properties.
However, it was understood later that high conversion efficiency alone was not sufficient for
any device fabrication.

Other intrinsic and extrinsic parameters should also be specified for comparison of different
nonlinear optical crystals. The elastic constants and mechanical properties like fracture
toughness and microhardness can be specified. The physico-chemical properties that are
worth considering are the presence of ferroelectric phase transitions which may lead to
domain formation, compositional inhomogeneity, melting point and resistance to moisture.
Thermal expansion of the crystals can play considerable role in laser damage threshold especially in high average power applications.

1.5.1 Second order NLO materials

Over the past half a century a huge amount of research work has been devoted to the design and synthesis of novel materials for second order NLO applications. Second order NLO materials have wide variety of applications in frequency doubling, parametric amplification, parametric oscillation, frequency up conversion, difference frequency generation etc (Table 1.1). A number of researchers have paid their attention towards understanding and controlling the factors that will lead to an acentric crystal structures of inorganic, organic and semi organic compounds with superior NLO characteristics. It is a challenging task to arrange the molecules in a noncentrosymmetric structure with molecules arranged in head-to-tail fashion. To have such an arrangement of molecules in crystal structure one requires a very sound knowledge of crystal engineering to tailor molecules for SHG applications as well as combination of chemical intuition and theoretical understanding of intermolecular hydrogen bonding forces. In general, an ideal NLO material should possess the following characteristics:

- Ease of synthesis and low production cost
- Architectural flexibility for molecular design
- Ability to process into large size single crystals / thin films
- Ability to tune the surface morphology
- High SHG efficiency and figure of merit
- Wide optical transparency
- High thermal stability
- High mechanical strength
- Nontoxicity and good environmental stability
- Phase matchable in the entire transparency range
- Ultra fast response
- High laser damage resistance

The entire set of above requirements is not yet fulfilled by any of the single crystals developed so far. Therefore, there is a need to search for new materials that can simultaneously fulfill most of the above requirements.
In early days of the development of second order NLO materials, most of the materials studied for the NLO applications were inorganic crystals. Single crystals of inorganic materials were found to have moderate SHG efficiency, wide transparency, chemical inertness, thermal and mechanical stability, high laser damage threshold, and were adopted for developing NLO devices. The classical inorganic materials often used for frequency doubling applications are potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), deuterated potassium dihydrogen phosphate (DKDP), cesium lithium borate (CLBO) and potassium niobate (KN) [27]. The efficiency of the inorganic materials is poor compared to that of organic materials and they have only 20% probability of forming noncentrosymmetric crystal structures [28]. Therefore, it has become a necessity to search for a new category of materials which has significantly high SHG efficiency.

Apart from inorganic materials, materials which are extensively studied for second order NLO activity are the organic materials. The synthetic flexibility of these molecular systems offers one to fine tune the optical properties at the molecular level to enhance the SHG efficiency at the macroscopic level. SHG in these materials was first observed in 1964 [29]. In 1970, Davydov et al. [30] reported SHG efficiency in number of substituted benzenes. In their report, they proved that the dipolar aromatic molecules possessing an electron donor group and an electron withdrawing group contribute largely to the SHG efficiency arising due to strong intramolecular charge transfer between the two groups of opposite nature.

A typical SHG active molecule is shown in Figure 1.8. The groups listed on the left side of the \( \pi \)-conjugation bridge are electron donors and those listed on the right side are electron acceptors.
acceptor groups. The combination of electron donor / acceptors works only when they have noncentrosymmetric crystal structure. Generally, the materials which possess inversion symmetry do not show SHG efficiency. As a consequence the crystallographic noncentrosymmetry requirement rejects many of the materials from being SHG active. Therefore it is more important to introduce noncentrosymmetry in materials to make them SHG active. The D-π-A-π-A molecular systems show large NLO responses because of the delocalized nature of the π-electrons resulting in low-energy excitonic levels with high oscillator strength [31, 32]. However, these dipolar molecules tend to pack in an anti-parallel arrangement in the crystal structure and usually crystallize in centrosymmetric class and therefore the SHG response in these systems becomes zero [31]. The best examples for dipolar organic NLO system are nitroaniline derivatives. Zyss et al. reported the first hyperpolarizability of p-nitro aniline (PNA) [31, 32].

The PNA crystal does not possess SHG activity due to its centrosymmetric crystal packing. The high intramolecular interactions usually force the molecule to crystallize in centrosymmetric structure to satisfy the electrostatic interactions between the molecules. However, a modification in the PNA molecule resulted in a noncentrosymmetric packing and exhibited large SHG activity. One example for modified PNA structure which resulted in a noncentrosymmetric structure and large SHG efficiency is m-nitro aniline (mNA) [33]. Some of the derivatives of PNA such as 2-methyl-4-nitroaniline (MNA) and N-(4-nitrophenyl)-(L)-prolinol (NPP) also crystallized in noncentrosymmetric structure and displayed high SHG efficiency [32].

The chiral molecules, e.g., methyl-(2,4-dinitrophenyl)aminopropanoate, have more probability to crystallize in noncentrosymmetric structures and hence have chances to show SHG [32, 34]. Another strategy to obtain noncentrosymmetric SHG active materials is the lambda (Λ) shape design concept. In a Λ shape molecule, two independent hyperpolarizable moieties are linked by a σ bond so that the intramolecular charge transfer contributing to β has almost a two-dimentional character [35]. The nearly optimized geometry of such Λ-shaped molecule in the most stable conformation has an Λ-angle of 120ο between the two charge transfer axes, predicted to coming close to an optimal molecular orientation for phase matching [32, 35]. Among Λ-shaped molecules, N,N′-bis-(4-ethylcarbosyphenyl)-
methanedianime (ECPMDA) exhibited large SHG activity of 25 times greater than that of urea and good optical transparency down to 330nm. Therefore, the search for more efficient novel SHG active materials full filling all the requirements for device applications is still continued.

1.5.2 Third order NLO materials

Third order NLO materials finds applications in optical switching, optical data processing, optical communications, optical logic gates, nonlinear spectroscopy, coherent UV-light generation, optical limiting, passive laser mode-locking, waveguide switches and modulators [36]. For generating UV-light through third harmonic generation (THG) one requires optical transparency of the materials in that region. For optical switches, the molecules should show ultra fast NLO response while for optical limiting applications a material should have low optical absorption at low intensities of laser light and high optical absorption at high intensities of laser light. In this section, different types of materials that are used for third order NLO applications are reviewed briefly.

The inorganic materials are largely used to generate the frequencies of coherent light which are in the UV region. The major advantage of these materials is the transparency that allows one to obtain a coherent UV radiation by THG.

The materials which are extensively studied for third order NLO properties are organic materials. Although organic materials are less applicable for UV-coherent light generation due to the lack of transparency in the UV region, they are essential for other third order NLO applications. In these materials the origin of nonlinearity is electronic in nature and hence they show ultra fast response. A number of charge transfer compounds have been studied for their third order nonlinearities [37-40]. By choosing an appropriate π-conjugation bridge and a donor-acceptor pair, several organic molecular crystals such as stilbene [38] and azobenzene derivatives, which exhibit $\chi^{(3)}$ larger than $10^{-12}$esu, have been developed [41]. The $\chi^{(3)}$ of 4-(N,N-diethylamino)-4'-nitrostilbene (DAENS) has been reported in a solution, in a polymer host and in a crystalline state and the maximum value of the $\chi^{(3)}$ obtained is $6 \times 10^{-12}$esu[42, 43]. The third order NLO properties of a novel charge transfer compound, 4-(N,N-diethylamino)-4'-nitrostyrene (DEANST), have been investigated by means of the optical
Kerr shutter experiment and $\chi^{(3)}$ value of $7.4 \times 10^{-12}\text{esu}$ has been calculated in DEANST crystals [44, 45]. Several new symmetrical short $\pi$-conjugated molecules such as benzylidene aniline derivatives that are symmetrically substituted by donor groups at both ends of the $\pi$-conjugated bridge have been studied in the off-resonant regions and the $\chi^{(3)}$ value in these molecules is measured to be as high as $4 \times 10^{-11}\text{esu}$ [46].

Various types of organic materials have been investigated for optical limiting applications. Phthalocyanines and their derivatives [47–50], porphyrins and their derivatives [51–53], and fullerenes ($C_{60}$) and their derivatives [54–57] have been extensively investigated for their optical limiting properties owing to the applications in sensor and eye protection in optical systems such as direct viewing devices, night vision systems etc.

The materials which are highly explored for third order NLO application are polymers. The major advantage of polymers is that they can be obtained in different forms: amorphous powders, single crystals, semicrystalline, polycrystalline thin films and Langmuir-Blodgett films [58].

In order to improve the TPA cross section in organic molecules, Albota et al. [59] gave a strategy for designing the molecules with large TPA cross section on the basis of the concept of symmetric charge transfer. They suggested that the third order nonlinearity of these organic compounds can be enhanced by (i) increasing the distance over which charge can be transferred (increasing the conjugation length); (ii) increasing the extent of charge transfer from the ends of the molecule to the center by creating a donor-acceptor-donor motif and (iii) reversing the sense of symmetric charge transfer by substituting electron acceptors and electron donors and thereby creating acceptor-donor-acceptor compounds.

### 1.6 Applications of nonlinear optical crystals

The nonlinear optics is one of the few modern scientific frontiers occurring under intense laser fields, surges in recent interest of potential technological applications. Some of the applications such as second harmonic generation, optical limiting, image analysis, and high density data storage. The origin of nonlinear processes is well understood and progress now depends on the development of material technology.
1.6.1 Frequency conversion

Devices in this category will be utilized mainly for second harmonic conversion of coherent laser radiation. There are two main wavelength regions and laser power regimes of interest. The first category applications is the conversion of low or moderate power diode laser light sources from 830 nm region to the 415 nm region. The driving force of this application is the improvement of packing density in the optical memories, associated with improvements in focusing shorter wavelength. This is because the limit of the resolution of the lens which is directly proportional to the wavelength of light and hence in principle, four fold amount of information can be stored or detected from the memory. The second type of applications include frequency doubling and mixing of high power laser light sources.

1.6.2 Frequency up conversion

Frequency up conversion is another special case of sum-frequency generation in which two different frequencies are added to form the sum. There are now available very efficient low noise detectors of visible radiation such as human eye or photo multiplier, whereas most IR detectors are very inefficient by comparison. The attractive feature of this method of detecting IR is that the up converter crystal, the laser pump and the photomultiplier all operate normally at room temperature, whereas the competitive detectors in IR commonly operate between 4.2K to 77 K. Developments in this area seem to await the discovery of more stable nonlinear material that will allow the mixing crystal to be operated inside the laser cavity. The various device applications of frequency up-conversion are discussed in detail by Zernike and Midwinter [60].

1.6.3 Parametric amplification

SHG can also be used to amplify weak optical signals. The basic configuration involves an input signal at $\omega_1$ that is incident on a nonlinear optical crystal together with an intense pump wave at $\omega_3$, where $\omega_3 > \omega_1$. The amplification of the $\omega_1$ wave is accompanied by the generation of an idler wave at $\omega_2 = \omega_3 - \omega_1$. Using parametric amplification, it is possible to produce a new class of light called “squeezed light” [61]. The squeezed state is characterized by noise reduction in one of its quadrature phase field amplitudes below that of ideal laser light (a coherent state) or the normal vacuum state. These new quantum states of light have been shown to allow precision in measurement below the shot noise limit for
interferometric measurement [62–63]. It is possible to envision optical networks or computers that operate in the quantum noise limit where these new states of light could minimize the fundamental limits on noise and energy consumption. If novel crystals with larger nonlinearities and lower loss than those presently available are possible, these non classical light effects may become common place in optical switching, laser stabilization, interferometric measurement and optical communication [64].

1.6.4 Parametric oscillation

If the nonlinear optical crystal is placed within an optical resonator that provides resonances for the signal or idler waves (or both), the parametric gain will at some threshold pumping intensity, causes simultaneous oscillation at both the signal and idler frequencies. The threshold for this oscillation corresponds to the point at which the parametric gain just balances the losses of the signal and idler waves. This is the physical basis of the optical parametric oscillator. Its practical importance derives from its ability to convert the power output of a pump laser to a coherent output at the “signal” and “idler” frequencies which can be tuned continuously over large ranges. These parametric oscillators can act as ideal power limiters [65].

1.6.5 Optical power limiting

Optical power limiters are the nonlinear optical materials, which can lead to reduced transmittance when exposed to intense optical radiations. Optical limiting can be used for pulse shaping and pulse compression, but its main applications are sensor and eye protection against the high intensity lasers. Photonic sensors, including the human eye, have a threshold intensity above which they can be damaged. By using the suitable optical limiters, one can extend the dynamical range of the sensors, making them to function at higher incident intensities. An optical limiter, in order to use it in practical applications, should have low input threshold, wide dynamic range, fast optical response (<10 μs), broadband response, high linear transmittance, low optical scattering and good mechanical, thermal and chemical stability. An ideal optical limiter is perfectly transparent at light intensities below a threshold level, and above this level the transmitted intensity gets clamped at a constant value. The output energy transmittance versus input intensity for an ideal optical limiter is shown in Figure 1.9.
Figure 1.9: Schematic diagram represents the optical limiting behaviour of the linear and nonlinear optical materials

The most important instantaneous process associated with optical power limiters is two-photon absorption (TPA) [66], and two examples for accumulative nonlinearities in optical limiting are excited state absorption [67] and nonlinear refraction [68]. The optical limiting can be achieved through a number of different NLO mechanisms such as TPA, RSA (reverse saturable absorption), nonlinear refraction due to molecular reorientation, electronic Kerr effect, excitation of free carriers, photo refraction, optically induced heating in the material, thermal blooming and induced scattering. [69].

1.7 Crystal growth and its significance

A crystal is a solid material having regular arrangements of atoms, ions, or molecules characterized by periodicity. In a crystal, one can distinguish a motif that can be an atom or a cluster of atoms or ions, or one or more molecules. The crystal differs from gases and liquids because of the periodic arrangement of atoms or molecules in it and in the latter they do not possess the periodicity. All solids are not crystals and some solids exist in amorphous phase where the interior arrangements of atoms are not regular.

In this chapter a brief review on different crystal growth theories and the crystal growth techniques are outlined. Many magnificent developments in the science of solid state have
been achieved through the physical properties of single crystals [70]. Well characterized single crystals are necessary in the fundamental research as well as device applications. The present day solid state industry greatly depend on the high quality large size single crystals of NLO, semiconductor, ferroelectric, piezoelectric etc., crystals with minimum defect density. To grow high quality single crystals for above technological requirement one has to achieve control over the supersaturation, large growth rates, which ultimately lead to the large size single crystals in short period. Crystal growth is a complex process which requires sophisticated instruments that are capable of controlling growth parameters during the crystal growth to optimize the growth condition for growing device quality single crystals.

1.7.1 Crystal growth process

The three distinct important stages in the crystallization process are achievement of supersaturation, nucleation and growth. The formation of an initial crystal is for all self-seeding techniques an important process. The creation of only one nucleus can be achieved by a sufficiently slow increase of super-saturation, for example by a slow cooling of the fluid. For the case of homogeneous nucleation, seeds of the new crystalline solid are dispersed uniformly through the volume of the melt or solution. The formation of these nuclei is a dynamic process where, due to statistical accident, a significant number of atoms or molecules can come together to form microscopic crystallites. But these crystallites will dissolve again through thermal fluctuations. The growth of atomic clusters of the crystalline phase is favoured by its lower bulk free energy, but inhibited by the unfavourable positive free energy associated with the surface of the cluster. Since the surface-to-volume ratio decreases with the increase in cluster size, cluster size greater than some critical radius are stable and can grow and become the nuclei of the solid phase [71].

The presence of interfaces or foreign particles in the liquid enhances the nucleation process. Such heterogeneous nucleation occurs when the seed of the solid phase forms around these defects, offsetting the positive surface energy of the cluster with decrease in free energy associated with removing of the defect [72].
1.7.2 Earlier theories of crystal growth
The first theory of crystal growth was provided by Gibbs [73] on thermodynamic grounds. He made use of the analogy between the growth of a liquid droplet in a mist and that of a crystal and said that only those faces which would lead to a minimum total surface energy for a given volume would develop in the crystal. However, Gibbs realized the essential difference between the random arrangement of molecules or atoms in a liquid drop and the regular arrangement of them in a crystal. Curie [74] calculated the shape and end forms of the crystal in equilibrium with solution or vapour, consistent with the conditions of possessing a minimum total of surface free energies. Wulff [75] further extended Curie’s theory and deduced a simple relation between the velocities of growth of different faces in the direction of their normals and the appropriate specific surface free energies. Marc and Ritzel [76] modified Curie’s theory by considering the influence of surface tension and solution pressure (solubility) and proposed that the crystals will assume an equilibrium form which takes into account both these tendencies.

1.7.3 Growth by surface nucleation and repeatable step mechanism
Figure 1.10 represents the surface of a grown crystal. The crystal will grow by the addition of molecules at kink (K), the so called repeatable step, because the binding energy is the greatest at this point; the molecule joining the surface at any other position terrace (H) or surface vacancy (A) will be held by a smaller number of bonds. When a whole line of molecules has been added to the monomolecular ledge, starting of a new line will be a difficult process, since the first molecule to be added will be held by only two bonds. Finally, when a whole monomolecular layer has been completed the next molecule will be held by only one bond and launching of a new layer will involve an even longer delay than the starting of a fresh line. The process of starting a new layer is known as surface nucleation and involves the simultaneous arrival of a number of molecules on a small group of adjacent sites.
1.7.4 Screw dislocation theory of growth

Frank [77] in an attempt to explain the large difference between the theory and experiment drew attention to the probable role of screw dislocation in furthering the growth process, retaining many features of the older theory. Frank pointed out that the emergence of a screw dislocation on a face of a crystal produces on that face, a ledge of height equal to the Burgers vector. If the crystal is pictured as growing by the attachment of molecules to the edge of this ledge then no surface nucleation is necessary, since the ledge in question is self-perpetuating and continues to be present on the surface so long as the dislocation line intersects the surface. The ledge winds itself up into a close spiral centred on the dislocation and as growth proceeds the spiral apparently revolves as shown in Figure 1.11. Further, since the turns of this spiral will be close together, a large proportion of the molecules adsorbed on the surface will reach the ledge before re-evaporating.
1.7.5 Dendritic growth

Dendrites are normally single crystals; the branches follow definite crystallographic directions. The branches are often regularly spaced and the opposite sides of dendrites show marked symmetry. Even though the cause of this abnormal growth is known to be high supersaturation (rapid deposition), no definite explanation regarding the regularity of dendritic branching has been arrived at so far. However, it has been suggested that the spacing of the branches is decided by the supersaturation of the solution. At times dendrites whose limbs are not related to definite crystallographic directions are also observed.

One of the common modes by which crystals of every possible internal symmetry and chemical composition grow is by the formation of dendrites. They are almost invariably a rule in metals and are common in crystals grown from solution, melt and vapour. A typical dendrite consists of a primary stem onto which secondary branches grow and on these the tertiary branches grow. This commonly occurs in one plane but three dimensional dendrites are also observed [78].

Figure 1.11: Different stages of the formation of spiral from a screw dislocation
1.8 Crystal growth techniques

Crystal growth has been a subject of absorbing interest for many years and the recent development of technology has stimulated the commercial importance of the subject. A crystal starts growing once the nucleus attains the critical size. As the size of the crystallites increases, neighbouring crystallites of different orientations will come in contact. At relatively fast cooling rates polycrystalline material results. However, under equilibrium conditions the grains can be made to grow into single crystals using certain crystal growth techniques. The choice of crystal growth method depends mainly on thermodynamic properties of the material such as structural changes below the melting point, decomposition, sublimation and also on reaction of the material with different solvents and containers [79, 80].

The crystal growth techniques are classified as:
1. Growth from solid
2. Growth from vapour
3. Growth from liquid

In the case of crystal growth from solid, the conversion of a polycrystalline piece of a material into a single crystal takes place by causing the grain boundaries to be swept through and pushed out of the crystal. Crystal growth from liquid falls into four categories namely melt growth, low temperature solution growth, flux growth and hydrothermal growth. There are number of growth methods in each category. A brief outline on various important techniques of crystal growth has been presented below. Within each of these categories, there are many possible methods, so that the choice appears difficult. However, the nature of the material and its ultimate application can be used as a guide to the most suitable methods.

1.8.1 Growth from solid

Solid growth techniques are rarely used and of less significance for the production of large size single crystals. This technique is often used in metallurgical processes for tuning the materials properties. Annealing, strain annealing, deformation growth and polymorphic phase transitions are some of the methods employed in solid growth to tailor the material properties [72].
1.8.2 Vapour growth

The growth of single crystal from the vapour phase is probably the most versatile of all crystal growth processes, although the large number of variables involved tends to make it a relatively difficult process to control. Crystals of high purity can be grown from vapour phase by condensation, sublimation, and sputtering of elemental materials. Molecular beam techniques have also been applied recently to crystal growth problems. The most frequently used method for the growth of bulk crystals from vapour phase utilizes chemical transport reaction in which a reversible reaction is used to transport the source material as a volatile species to the crystallization region. Finding a suitable transporting agent is a formidable problem in this technique. It is rarely possible to grow large crystals because of multinucleation.

1.8.3 Melt growth

About 80% of the global requirement of crystals is grown by the melt growth technique. Melt growth is the process of crystallization by fusion and resolidification of the pure material. In this method, apart from possible contamination from crucible material and surrounding atmosphere, no impurities are introduced in the growth process and the rate of growth is normally much higher than the other methods. In principle, all materials can be grown into a single crystal from the melt, provided they melt congruently, they do not decompose before melting and they do not undergo a phase transition between the melting point and room temperature. The melt growth can be classified as follows.

i) Bridgman – Stockbarger technique

ii) Czochralski technique

iii) Kyropoulos technique

iv) Zone melting technique

v) Verneuil technique
1.9 Growth from solution

Solution growth technique is widely used to grow the crystals which have high solubility and have variation in solubility with temperature. There are two methods in solution growth depending upon the solvents and the solubility of the solute. They are (i) High temperature solution growth (flux growth, hydrothermal growth) (ii) Low temperature solution growth.

The growth of crystals from molten salts at high temperatures is called flux growth. The growth proceeds at a temperature well below the melting point of the solute phase. In this technique, a solid is used as the solvent instead of liquid and the growth process takes place well below the melting temperature \[72\] of the solute.

In hydrothermal growth, an aqueous solvent crystallizes on ordinarily difficult soluble material at high temperature and high pressure.

Among the various techniques of crystal growth, low temperature solution growth occupies a prominent place owing to its simplicity and versatility. Materials which decompose on heating or which exhibit any structural transformation while cooling from the melting point can be grown by solution growth if suitable solvents are available. Of all the methods of crystal growth, low temperature solution growth is perhaps the most widely practiced method. The process is easy when in fact the production of large, pure and perfect crystals is not easy by any other technique.

Low temperature solution growth are mainly of two types: (i) Slow evaporation method (ii) Slow cooling method. It is worth noting that in the case of slow evaporation technique, the growing crystal is at a fixed temperature. This provides an additional degree of choice which can be extremely useful; growth at a high temperature is often more stable than at a lower one and the habit (i.e., shape) of a crystal may well be a function of the growth temperature so that the most useful habit can be obtained by a correct selection \[71\]. The choice of the solvent is probably the most critical step in low temperature solution growth. It is virtually impossible to overcome the effects of an unsuitable solvent, so that considerable care should be taken. For some materials, it is necessary to use mixed solvents to reduce solubility or to change the viscosity.
The slow cooling solution growth technique is widely used to grow all inorganic and organic crystals. The use of slow cooling is in some ways the easiest method for the growth of crystals from solution. Its principal disadvantages all originate from the need to use a range of temperatures. The possible range is usually small so that much of the solute remains in the solution at the end of a run. To compensate for this effect, large volumes of solution are required. The use of a range of temperatures (\( \partial T/\partial t \)) may also not be desirable because, for example, the properties of the grown crystal may vary with temperature and the amount of solute incorporated will almost certainly vary. The method also has the technical difficulty of requiring a programmed temperature (which ideally should be non-linear). However, in spite of these disadvantages, the method is widely used with great success [72].

In this technique a glass flask of half or one litre capacity containing the saturated solution is kept at the center of the water bath of 20 litres capacity. The temperature of the bath, which is heated by an infrared lamp situated at the base of the unit, is controlled by a “temperature controller” employing a long range electrical contact thermometer. The large volume and continuous stirring of the bath improves the stability and homogeneity. The temperature control accuracy is \( \pm 0.02^\circ \)C. Slow cooling can be achieved by driving the contact of the electrical thermometer to lower the temperature at the required rate. The schematic diagram of the growth apparatus for slow cooling solution growth technique is shown in Figure 1.12 [81].

The type of growth conditions used, obviously vary with the material being grown, its temperature coefficient of solubility, the area of the growing face and the volume of the solution. A reasonable aim is a linear growth rate of 0.5 to 1 mm per day. In the initial stages this might require a rate of cooling of 0.02°C per day but the final rate might be 0.1 to 0.2°C per day. Typical growth runs are several months long so that the apparatus must be extremely reliable: in particular, great care should be taken that all the motors used are much under run.
The basic apparatus requirements for slow evaporation solution growth methods are similar to those for slow cooling except that a fixed temperature is used and provision must be made for evaporation. In this technique a saturated solution is kept in temperature controlled water bath and a controlled vapour leak is included in the system. The supersaturation can be achieved by evaporation of solvent by opening directly to the atmosphere or have a slow gas flow through the flask over the solution. In the initial stage for the preparation of small seed crystals this level of sophistication is not employed. The crystal growth can be performed at ambient temperature by controlling the evaporation rate of the solvent. Often this method is used to obtain seed crystals by evaporation of solvent from solutions in small, partially or fully covered dishes. This is the simplest method which requires minimum instrumentation to grow crystals and works best for compounds which are insensitive to ambient conditions of the laboratory. This method have the advantage that the crystals grow at a fixed temperature but inadequacies of the temperature control system still have a major effect on the growth rate.
1.9.1 Criteria for solution growth of crystals

Growth of crystals from solution mainly depends on the supersaturation. High supersaturation of the solution leads to spontaneous nucleation. In order to grow good crystals of perfect morphology, seeded growth is selected. In solution growth, for any material to be grown, the equilibrium concentration of the solution at different temperature must be known. The concentration of the solution must be slightly greater than its equilibrium concentration.

In solution growth, the solute molecules will be dissolved in a suitable solvent. The influence of solvent on crystal growth can be understood by crystal-medium interface. The solution can be maintained in the metastable region by maintaining the accurate temperature. A seed crystal is introduced in the solution, for the growth to proceed. On attachment of the molecule to the crystal surface, partial desolvation occurs. Solvation and desolvation of solute molecules are therefore integral parts of the growth process and will, to some extent, influence the kinetics and thermodynamics of crystal growth.

1.9.2 Solubility and supersaturation

The solubility of a solute may be determined by dissolving the solute in the solvent maintained at a constant temperature with continuous stirring. The solution growth method is mainly depends on the solubility of the material, the choice of solvent is important. If the solubility is too high, it is very difficult to grow bulk single crystals. Solution is a homogenous mixture of a solute in a solvent. Solute is the component which is present in a smaller quantity. For a given solute, there may be different solvents. An ideal solvent yields prismatic crystals; it has significant, but no successive solubility. The solubility data at various temperatures are essential to determine the level of supersaturation. Changes in supersaturation, solvent etc., may lead to dramatic modifications in the crystal morphology. As the growth of crystals from solution is mainly a diffusion controlled process, the medium must be less viscous to enable faster transference of the growth units from the bulk solution by diffusion.
1.10 Morphology of grown crystals

The morphology of the crystals depends on the growth conditions. The relative sizes of the faces vary between different crystal individuals of the same material due to different growth conditions. Crystals are defined as chemically homogenous materials with anisotropic physical properties [82]. The faces display the symmetry elements inherent in the crystal type. The crystal habit, size of the crystal, and relative dimensions of its faces strongly depend on the external conditions during crystal growth. However, the interfacial angles and the orientation of the faces remain constant as they are material constants and are characteristic of the given chemical composition [83].

Primarily, the morphology of grown crystals, i.e., the macroscopic shape, is determined by the density of free bonds at the surface. There are three types of interfaces, namely kinked, stepped and flat faces [79]. Kinked faces contain no periodic bond chains and are rough, hence fast growing and unlikely to appear. Stepped faces contain one type of periodic bond chain and provide the surface with parallel growth steps. Flat faces contain at least two types of periodic bond chains, need step sources, grow slowly, and are therefore most likely to appear. Flat faces have the highest lateral atom density, lowest Miller indices, and lowest surface energy. Reaction of free bonds with neighbouring free bonds can lead to the growth of other faces. In the case of crystal growth from solution, the final morphology is strongly polyhedral, composed of flat faces and the growth morphology consists of slowly growing faces.

The inter-atomic distances in densely packed planes are often smaller than the inter-planar distances, indicating stronger bonds in the planes than between them. Thus, the energy required for cleaving a crystal parallel to such a set of planes is smaller than for cleaving it in any other directions [84].

1.11 Experimental methods of characterization

The first step in the characterization of a material is to determine its composition and purity. Crystal structure and material properties are intimately related. For example, ferroelectric, piezoelectric, nonlinear optical properties are exhibited only by materials possessing anisotropic structures. For a deeper fundamental understanding of materials and their
properties, it is necessary to know, why different materials behave in their characteristic manner and what are the basic parameters, which control the properties. Materials characterization provides answers to these questions and helps in solving technological problems [85]. A large number of techniques are available for composition and purity analysis, some of them being destructive and others non-destructive.

1.11.1 Infrared spectroscopy

Infrared (IR) spectroscopy is sensitive to changes of the dipole moments of vibrating groups in molecules [86]. The energy of IR photons is suitable for the excitation of molecular vibrational energy levels. Thus, the absorption spectrum in the infrared is often used as a fingerprint of the molecular species and for the identifications of organic compounds.

In normal IR spectrometers, a broadband infrared radiation is generated in a source and dispersed by a dispersing element such as a grating or prism. An appropriately located slit selects a narrow band of wavelengths of the dispersed radiation. This band of wavelengths is incident on the sample, and a detector measures the amount of the radiation that is transmitted through the sample. The wavelengths of radiation that is passed through the slit can be controlled by rotating the dispersing element, so the detector will measure a spectrum of transmitted radiation as a function of wavelength that is varied over the region of interest. The transmittance (T) of the sample at a given wavelength is given by Beer’s law:

\[ T = \frac{I}{I_0} = \exp(-abc) , \]  

(1.54)

where \( I_0 \) is the intensity of radiation incident on the sample at a given wavelength and \( I \) is that after passing through the sample, \( a \) is the molar absorptivity, \( b \) is sample thickness, and \( c \) is the concentration of the absorbing species [87]. The absorbance \( A \) is then defined by

\[ A = \ln(1/T) = abc \]  

(1.55)

Recently, Fourier transform infrared (FT-IR) spectroscopy, which uses a Michelson’s interferometer, is more common than the conventional one. This is a computer-supported IR technique for rapidly scanning and storing infrared spectra. Multiple scan and Fourier transformation of the infrared spectra enhance the signal-to-noise ratio and provide improved spectra for interpretation.
In the case of organic compounds, the IR spectrum is used to identify the various functional groups and thereby to confirm the structure of the molecule. The frequency region from 4000 to 1500 cm\(^{-1}\) is called the functional group region. In this region, the peaks indicate the functional groups present in the molecule. The frequency region corresponding to 1500 to 600 cm\(^{-1}\) is considered as fingerprint region, which is characteristic of the sample.

### 1.11.2 Mass spectroscopy

When analyzing an organic compound, mass spectroscopy is useful firstly, to know the exact molecular weight and to confirm the molecular formula of the complex molecules. Secondly, the points of fragmentation of the molecules can be indicated. The molecule gives a unique fragmentation pattern that distinguishes it from all other substances. This allows the identification of certain structural units. Together with other analytical techniques, mass spectroscopy is helpful in establishing the molecular structure and purity of organic compounds.

The physics behind mass spectrometry is that a charged particle passing through a magnetic field \(B\) is deflected along a circular path of a radius \(R\) that is proportional to the mass to charge ratio, \(m/z\). At a given potential \(V\) each ion will have a kinetic energy \(\frac{1}{2} mv^2 = zV\), where \(m\) = mass of ion, \(v\) = speed, \(V\) = potential difference and \(z\) = charge on the ion. As the ions enter a magnetic field, their path is curved; the radius of curvature is obtained by equating the centrifugal force \(F = mv^2/R\) and force due to applied magnetic field \(F = Bzv\), i.e., \(R = \frac{mv}{zB}\). If the two equations are combined to factor out velocity:

\[
\frac{m}{z} = \frac{B^2 R^2}{2V} \tag{1.56}
\]

\(\frac{m}{z}\) can be changed by changing \(V\) or \(B\). If \(B\), \(V\) and \(z\) are constants then \(R \propto \sqrt{m}\).

At a given potential, only one mass would have the correct radius path to pass through the magnet towards the detector. By varying the applied potential difference that accelerates each ion, different masses can be discerned by the focusing magnet. The detector is basically a counter, that produces a current proportional to the number of ions that strike it. This data is sent to a computer interface for graphical analysis of the mass spectrum.
In mass spectroscopy, the sample is ionized in the source, and the ion beam is focussed by a magnetic field where the ions are separated according to their mass to charge ratio and collected in a detector.

A typical mass spectrum is a plot of the mass / charge of the ionized compound versus the abundance. The most intense peak in the spectrum is called base peak [88, 89].

### 1.11.3 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) can be used for structural and purity confirmation of an organic compound. By means of NMR, it is possible to study the environment of all commonly occurring functional groups as well as fragments such as hydrogen atoms attached to carbon, which are otherwise not accessible to spectroscopic or analytical techniques. NMR may also be utilized for quantitative determination of compounds in mixtures. NMR spectroscopy involves the change of the spin state of a nuclear magnetic moment when the nucleus absorbs electromagnetic radiation in a strong magnetic field [88, 90].

NMR is based on the fact that many atomic nuclei oscillate like tiny gyroscopes when in a magnetic field. In NMR, a sample is placed in a powerful magnetic field (1–14 tesla), which forces the nuclei into alignment. The sample is bombarded with radio waves and, as the nuclei absorb the radio waves, they topple out of alignment with the magnetic field. Hence, the nuclei lose the energy absorbed from the radio waves and re-align themselves again to the magnetic field. By measuring the specific radio frequencies (RF) that are emitted by the nuclei and the rate at which the realignment occurs, the spectroscopists can obtain detailed information about the molecular structure and the molecular motion within the sample being studied. NMR imaging is a technique to create maps, which relies on placing the sample in a spatially inhomogeneous magnetic field whose nuclear resonance frequency is matched to the radio frequency signal in a small region [91]. In general, the RF field is fixed and the magnetic field is varied over a range of a few gauss until the resonance is observed [90].

In NMR, the resonance depends on the chemical environment of the protons. The intensity of an ensemble of protons is directly proportional to the number of protons in it. The frequency, at which a proton resonates with respect to a standard sample is called chemical shift.
Chemical shifts expressed in ppm versus the standard are usually given in a dimensionless unit called delta (δ). Since the chemical shift reflects the molecular structure, it can be used to determine the structures of unknown compounds and since hydrogen is an almost universal constituent of organic compounds, the proton NMR is widely applicable.

### 1.11.4 Thermal properties of crystals

The thermal stability of a crystal over a large range of temperatures is important for many applications. On the other hand, the change in the properties of the material as a function of temperature is also interesting, as many materials exhibit transitions in conductivity, phase, magnetic behaviour, and so on. Common techniques for thermal analysis are thermogravimetry and differential scanning calorimetry. These techniques permit the evaluation of thermal stability, reaction processes, kinetics, phase diagrams, etc. Differential scanning calorimetry (DSC) measures the rate of heat evolution or enthalpy absorption (dH/dt) of the specimen relative to a reference. The thermal changes can be measured as (i) a function of temperature with both the specimen and reference material heated at the same heating rate (dynamic) or (ii) a function of time with both the specimen and reference material held at the same temperature (isothermal).

Chemical reactions liberate or absorb heat according to \( \frac{dQ}{dt} = (-\Delta H) \frac{dn_p}{dt} \), where \( n_p \) is the number of moles of product formed. When \( \Delta H \) is positive, the sample heater is energized and a positive signal is obtained. When \( \Delta H \) is negative, the reference heater is energized and a negative signal is obtained [92].

DSC is run in dynamic mode with the weighed sample in an aluminium specimen holder and empty holder used as the reference [83]. DSC measures the difference in energy inputs into a substance and a reference material as a function of temperature while the substance and reference are subjected to a controlled temperature program [93]. The DSC curves are commonly recorded over a temperature range by heating or cooling a sample with a constant rate. DSC can be applied to evaluate the phase change, solvent of crystallization, latent heat of fusion, and melting point. It can also be used to estimate the degree of crystallinity.
The height of the peaks is directly proportional to the rate of reaction, and the area A under this is proportional to the heat evolved or absorbed by the reaction. This can be written as

$$A = -m \Delta H/gc,$$  \hspace{1cm} (1.57)

where, $g$ is a constant related to the geometry of the sample, $c$ is a constant related to thermal conductivity, and $m$ is the amount of reactive component in the sample in moles.

### 1.11.5 Mechanical properties of crystals

The mechanical property plays a vital role in device fabrication. The mechanical strength of crystals is concerned primarily with the response of crystals to forces or loads. The hardness of a crystal depends on its plastic and elastic properties. The applicability of a crystal depends on its mechanical strength also. Harder crystals do not pose much problem while cutting and polishing whereas the soft crystals need great care while handling.

The mechanical strength of a crystal can be judged by measuring its hardness, which can be done by “Vicker’s hardness test” or “Knoop hardness test”. In Vicker’s hardness test an indentation is made on the smooth surface of the test material, by means of applying a load ($P$), on the surface, for about 10 seconds, through a pyramid-shaped diamond-indentor of top angle $\theta$. Then the diagonal length ($d$) of the indentation is a measure of the hardness\[94, 95]. The hardness is proportional to Vicker’s hardness number,

$$VHN = \frac{2 P \sin (\theta/2)}{d^2}, \text{kg/mm}^2.$$ \hspace{1cm} (1.58)

In microhardness measurement a microscope with a calibrated eyepiece is used to observe the indentation mark on the crystal surface and measure the diagonal length (in $\mu$m) of the indentation mark.

### 1.11.6 Dielectric properties of crystals

When a dielectric medium is inserted between the charged plates of a capacitor, dipoles are formed whose electric moment is given by

$$\mu_e = q \cdot r$$ \hspace{1cm} (1.59)

where, a positive charge separated from a negative charge of the same magnitude ($q$) by the distance ($r$). The total dipole moment per unit volume is called the polarization $P$, which is
The field at a molecule in the interior of a dielectric between the plates of a charged capacitor is larger than the applied field \( E \). The induced dipole moment in the molecule depends on the local field because of polarization that occurs within and on the surfaces of the dielectric. Polarization occurs due to several atomic mechanisms. Electronic polarization is due to the displacement of electron cloud and nucleus on application of an electric field. In an ionic solid, cations and anions are being displaced by the applied electric field. This gives rise to ionic polarization. The orientation occurs in the asymmetric molecules possessing a permanent electric dipole moment. Space-charge polarization occurs because of the accumulation of charges at the structural interfaces [96].

The dielectric constant can be determined by measuring the capacitance of a dielectric enclosed between two parallel plates. If \( A \) is the area of the plate, and \( d \) is the separation between the plates, then

\[
C = \left( \frac{A}{d} \right) \varepsilon_0 \varepsilon_r \tag{1.61}
\]

The dielectric constant \( \varepsilon_r \) of a dielectric medium is the ratio of its permittivity \( \varepsilon \) to the permittivity of free space \( \varepsilon_0 \). The dielectric constant of a crystal varies with temperature, frequency, its phase constitution, and structural defects. When the polarization lags behind the external field, an electrical energy loss occurs, which appears as dissipated heat. It is proportional to the product of the relative permittivity and the tangent of the lag angle \( \delta \). The dissipation factor is given by

\[
\tan \delta = \frac{\varepsilon_1}{\varepsilon_2}, \tag{1.62}
\]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are given by the complex electrical permittivity function

\[
\varepsilon^* = \varepsilon_1 + i \varepsilon_2, \tag{1.63}
\]

where \( \varepsilon_1 \) is the real part and \( \varepsilon_2 \) is the imaginary part.
1.11.7 Linear optical properties

Crystals of cubic system are optically isotropic. Non-cubic crystals are optically anisotropic. i.e., in non-cubic crystals the speed of light of a particular wavelength depends on the direction of its propagation. This means that the refractive index for a particular polarized light depends on its direction of electric vibration. The “optical indicatrix” describes this optical anisotropy of crystals completely [97]. In this, the length of the radius vector from the center of the indicatrix to its surface gives the index of refraction of light with vibration in the direction of the radius vector. In cubic crystals the indicatrix is a sphere of radius equal to the refractive index. In crystals of hexagonal, tetragonal and trigonal systems (uniaxial crystal), the indicatrix is an ellipsoid of revolution with the axial radius equal to the extraordinary refractive index (n_E) and the equatorial radius equal to the ordinary refractive index (n_O). In crystals of orthorhombic, monoclinic and triclinic systems (biaxial crystals), the indicatrix is a triaxial ellipsoid with the half-axis-length along the three mutually perpendicular axes (X, Y, Z) being equal to the three principal indices of refraction (n_X, n_Y, n_Z; n_Z>n_Y>n_X). In biaxial crystals the two optic axes are in the optic plane, perpendicular to the Y–axis of the indicatrix, making an angle (optic angle) with each other.

The indices of refraction of the crystals undergo dispersion with the wavelength of the light. With an intense beam of light the crystals show optical nonlinearity. Optical second harmonic generation can be observed for an intense light beam through the crystals having noncentrosymmetric structures.

1.11.8 Ultraviolet-visible spectroscopy

Ultraviolet-visible spectroscopy is one of the simplest and yet most useful optical techniques for studying optical and electronic properties of organic materials. This technique is based on the measurement of light absorption by a sample, typically using commercially available spectrometers.

The molecular spectra in the UV and visible regions arise due to the transitions from one electronic state to another and therefore, absorption depends on the electronic structure of the molecule. The electronic excitations of a molecule are accompanied by the vibrational and rotational excitations. Hence, the transitions result in a band [92].
Single crystals, are often transparent or semi-transparent in the visible region, but the optical transmission of these materials is limited due to the scattering at grain boundaries. The presence of defects, which is quite normal for laboratory grown crystals can also affect this.

The UV-visible absorption spectra of the crystals have been recorded in the region 200 nm to 800 nm using spectrophotometer. Crystal plates with parallel surfaces and thickness of about 1 mm can be used here. The optical density (OD) of the crystal is related to the incident beam intensity ($I_o$) and the transmitted beam intensity ($I$) by the relation,

$$OD = \ln \left( \frac{I_o}{I} \right)$$  \hspace{1cm} (1.64)

### 1.11.9 Refractive index measurement

The refractive index is one of the important parameters in determining the non linear optical properties. The linear refractive indices can be measured at laboratory temperature, using Brewster’s angle method. Brewster’s angle method calls for extremely precise intensity measurements as a function of crystal angle [98, 99]. The sources of monochromatic light used will be He-Ne laser of 632.8 nm and 543.5 nm. The block diagram of experimental setup (Home made) is shown in Figure 1.13.

The laboratory grown single crystals have been cut along different crystallographic directions and the surfaces are polished. These polished surfaces are used to reflect the He-Ne laser beam for Brewster’s angle measurement. The reflected beam is scanned by means of a photodetector. The observations are repeated with different angles of incidence ($\theta$). At the Brewster’s angle ($\theta_B$), the difference in intensity of the two polarized lights reflected from the surface, is maximum. Refractive index (n) can be calculated using the relation,

$$n = \tan \theta_B$$  \hspace{1cm} (1.65)
1.12 Scope of the present work

Laser is one of the remarkable inventions in the history of science and technology. It created many fascinating new fields, among which nonlinear optics has the highest scope. Organic crystals are increasingly being recognized as the “materials of the future” because their molecular nature combined with the versatility of synthetic chemistry can be used to alter and optimize their molecular structure in order to maximize their nonlinear optical properties. The design and synthesis of organic molecules showing nonlinear optical properties have received tremendous interest recently due to their applications in areas like optical communication, optical computing, data storage, dynamic holography, harmonic generators, frequency mixing, optical switching and optical limiting [9, 58].

Advantages of using organic molecules as NLO materials arise due to the availability of various design options by selecting appropriate reactants for carrying out chemical reactions and introduction of the desired substituents. It has been observed that extended π systems with terminal donor-acceptor substituents have been extensively investigated for the last few decades due to their unique structure, structure-NLO property tailarability, large second and third order nonlinear optical response, chemical and thermal stability, processibility and their application in ultra fast nonlinear optics [58, 32]. Molecules which are easily polarizable by low intensity optical fields are the subject of current research interest. In organic materials
delocalization of $\pi$-electrons provide unusually good nonlinear optical responses. Various strategies have been proposed to enhance the NLO response of materials and several classes of materials have been tested for the NLO properties and for the concept of molecular engineering for developing efficient NLO materials. Therefore, one requires the basic knowledge of designing molecules having high nonlinear optical properties and then fabricating such molecular materials in the form of single crystals or thin films required for NLO applications. In terms of transparency cut off and SHG efficiency, chalcones are regarded as excellent second order NLO materials [32]. Several types of chalcone have been reported in the literature for their SHG activity much higher compare to standard urea crystals.

Few reported chalcone contains nitro ($\text{NO}_2$) and cyano (CN) groups as acceptors [100, 101] and shows good SHG efficiency compared to urea. These molecules are efficient when electron acceptor group is placed on the benzoyl group rather than at the phenyl group. Fischuo and his co-workers [102] showed that the strong electron acceptor group such as NO$_2$ and CN on the benzoyl group was not necessary and the withdrawing effect of the sole carbonyl (C=O) group is sufficient to enhance the SHG activity. Substitution of an electron donor group at both the phenyl ring also resulted in high SHG. Based on the donor substitution, two molecules emerged with high SHG efficiency namely 4-bromo-4'-methoxychalcone and 4-methoxy-4'-ethoxychalcone. The SHG efficiencies of these two compounds are 11U (U= SHG efficiency of urea) and 5U, respectively. A series of chalcones were studied for SHG activity by Ravindra et al. [103, 104], Rajesh Kumar et al. [105, 106], D’silva et al. [107] and Zhao et al. [108]. Highest reported value of SHG efficiency (16U) for the chalcone co-crystals was reported by D’silva et al. Zhao and co-workers showed that chalcones substituted with Br exhibited significant SHG efficiency and good optical transparency.

A very few research groups have tried to understand the structure and property relationship by theoretical hyperpolarizability calculations [109, 110]. Zhao et al. [109] suggested that CH$_3$, OCH$_3$, Br and Cl are the suitable electron donors taking into account of hyperpolarizability and transparency cut-off in chalcones.
Despite many reports on second order NLO properties of chalcone derivatives, relatively major work has been reported in the literature on their third order NLO properties. The first report on the third order NLO properties of chalcones was given by John Kiran et al. [111]. They studied the structure-NLO property relationship in dibenzylideneacetone molecules. They also reported the third order properties of 1,3-diaryl-propenones containing 4-methylthiophenyl moieties [112]. The third order NLO properties of bis-chalcones doped in polymer matrix have been investigated by Shettigar et al. [113] and John Kiran et al. [114]. These molecules show good optical limiting due to reverse saturable absorption (RSA) mechanism. The first report on the third order NLO properties of chalcone co-crystal was given by Ravindra et al. [115]. Thus, chalcones have been interesting materials due to both second and third order NLO properties.

Among some new chalcone crystals reported for their NLO, chlorine and bromine substituted chalcone derivatives are noticeable materials for their excellent NLO properties and relatively good crystal quality. This thesis presents a detailed study of synthesis, crystal growth, characterization and second and third order nonlinear optical properties of chlorine and bromine substituted chalcone derivatives. In view of this, we have considered three molecules from chlorine series and two molecules from bromine series, to understand the effect of substituent on the crystal growth, thermal, chemical and mechanical stabilities and on linear and nonlinear optical properties of these conjugated intramolecular charge transfer molecules. Slow evaporation solution growth technique was employed to grow single crystals of these molecules. The Elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), Mass Spectroscopy and Single crystal X-ray diffraction techniques were employed to confirm the synthesized materials. The NLO properties were characterized by Kurtz and Perry powder technique, Z-scan and optical power limiting experimental techniques. Besides the crystal growth and characterization, main goal is to understand the relationship that exists between these molecular structures and their NLO properties. More importance is given to tailoring the structure by making simple modification through functional substitution in the basic structure of these chalcones. We paid special interest to those crystals which could be easily crystallized. Five varieties of good quality chalcone crystals were fully characterized and were identified as promising NLO materials. Efforts are also made to understand the structure property relationship based on semiempherical hyperpolarizability calculations and experimental results.
Brief objectives of the present investigation are as follows:

The primary interest of this PhD thesis is to carry out a systematic study on synthesis and characterization of nonlinear optical crystals of chlorine and bromine substituted chalcone derivatives

(i) The synthesis of the new organic nonlinear optical materials.

(ii) Study on growth of single crystals by solution growth technique.

(iii) Study on molecular and crystal structure of the grown single crystals.

(iv) Study on mechanical, thermal, electrical and optical properties of the grown single crystals.

(v) Comparison of the properties of the new crystals with that of the standard crystals like urea.