1.1 Introduction

Today's advanced technologies rely on sophisticated materials. Single crystals have numerous scientific and technological applications such as laser active media, semiconductor memories, infrared detectors, electro-optic modulators, piezoelectric oscillators, optical communication devices etc. The availability of appropriate crystalline materials is a crucial factor for the development of sophisticated tools for the advanced technologies as well as for a breakthrough in applied and basic sciences [1,2]. Nonlinear optical materials play an important role in the emerging photonic and optoelectronic industries. The need for high power and high intensity coherent laser radiations in the UV region for optical switching, optical computing and optical communication have kindled the search for newer and newer crystalline materials. Since such laser sources are not easily available, the alternate way is to produce the harmonics of the fundamental laser radiations through frequency doubling phenomena using nonlinear
optical materials [3,4]. This thesis deals with the synthesis, single
crystal growth and characterization of certain organic and semiorganic
nonlinear optical materials.

1.2 Nonlinear Optical Phenomena

The invention of the laser gives rise to the study of optics at high
intensities, leading to the new phenomena not seen with ordinary light
such as the generation of new colors from monochromatic radiation in a
transparent crystal, or the self-focussing of an optical beam in a
homogeneous liquid. At high intensities, the optical parameters of
materials can not be considered as constants but, become the functions
of the light intensity. The science of optics in this regime is called
nonlinear optics (NLO). Nonlinear optical properties in the optical region
have been strikingly demonstrated by Franken and his coworkers in
1961 [5] shortly after the invention of the ruby laser by Theodore
Maiman in 1960 [6]. They observed ultraviolet light (\(\lambda = 347.1\) nm) at
twice the frequency of ruby laser when the radiation from ruby laser
(\(\lambda = 694.1\) nm) traversed through a quartz crystal. This experiment
attracted widespread attention, marked the beginning of the
experimental and theoretical investigations on nonlinear optical
properties of materials.
Before the advent of lasers, the field strengths obtainable from the conventional light sources were of the order of $10^3 \text{ V/cm}$, much lower than the strength of atomic and inter-atomic fields, that are in the range $10^7$ to $10^{10} \text{ V/cm}$. But, the laser with its high degree of coherence and field strength, in the order of $10^8 \text{ V/cm}$, comparable to that of the above said inter-atomic fields, is in the right quantum to affect the optical properties of the materials. At such high fields, the relationship between the electric polarization $P$ and the field strength $E$ ceases to be linear and the nonlinear phenomena are more prominently observed [7,8].

1.2.1 Harmonic Generation

When a dielectric medium is placed in an a.c. electric field, it is polarized, if the medium does not have a transition at the frequency of the field. Each constituent molecule acts as a dipole with the dipole moment $p_i$. The polarization $P$ is given by

$$P = \sum_i p_i$$

where the sum is over all the dipoles per unit volume. The orientation effect of the external field on the molecular dipoles depends both on the properties of the medium and on the field strength. Hence, it can be written as

$$P = \varepsilon_0 \chi E$$

(1.2)
where $\chi$ is called the polarizability or dielectric susceptibility of the medium, $E$ is the electric field component of the electromagnetic radiation and $\varepsilon_0$ is the permittivity in vacuum ($8.854 \times 10^{-12} \, \text{C}^2 \, \text{N}^{-1} \, \text{m}^2$).

This relation is valid only for the field strength of ordinary light sources. The quantity $\chi$ is a constant as long as it is independent of the field strength $E$.

With intense laser radiation, the above relation does not hold good. It has to be generalized as

$$P = \varepsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \ldots \right) \quad (1.3)$$

where $P$ and $E$ are vectors and the $\chi$'s are tensor quantities. The coefficients $\chi^{(2)}$ and $\chi^{(3)}$ are the third and fourth order tensors respectively, representing the second and third order nonlinear susceptibilities. If the field is low, the first term alone will exist in eqn. (1.2). It is for this reason that the pre-laser optics is known as linear optics. Higher the values of the electric field, the more significant become the higher order terms. It is to be noted that the optical characteristics of a medium such as dielectric permittivity, refractive index etc., which depend upon susceptibility, also become functions of the field strength $E$, if it is sufficiently high. The medium for which the polarization is described by a nonlinear relation of the type (1.3) is called a “nonlinear optical medium”.

Suppose that the field incident on a nonlinear optical medium has
the form
\[ E = E_0 \cos \omega t \]  
then, equation (1.3) takes the form,
\[ P = \varepsilon_0 \left( \chi^{(1)} E_0 \cos \omega t + \chi^{(2)} E_0^2 \cos^2 \omega t + \chi^{(3)} E_0^3 \cos^3 \omega t + \ldots \right) \]  
Applying \( \cos^2 \omega t = \frac{1}{2} (1 + \cos 2\omega t) \) and \( \cos^3 \omega t = \frac{1}{4} (\cos 3\omega t + 3 \cos \omega t) \)
equation (1.5) can be transformed into
\[ P = \left( \frac{1}{2} \varepsilon_0 \chi^{(2)} \right) E_0^2 + \varepsilon_0 \left( \chi^{(1)} + \frac{3}{4} \chi^{(3)} \right) E_0^2 \cos \omega t + \left( \frac{1}{2} \varepsilon_0 \chi^{(2)} \right) E_0^2 \cos 2\omega t + \left( \frac{1}{4} \varepsilon_0 \chi^{(3)} \right) E_0^3 \cos 3\omega t + \ldots \]  
The first term is a constant term giving rise to a d.c. field response
referred to optical rectification across the medium. This field is of little
practical importance. The second follows the external polarization and is
called the first or fundamental harmonic of polarization. The third term
oscillates at frequency \( 2\omega \) and is called the second harmonic of
polarization, the fourth term is called the third harmonic of polarization
and so on. In addition, there are other effects such as frequency mixing,
optical rectification, optical phase conjugation etc., which manifest at
higher fields. However, frequency conversion is the most studied
nonlinear optical phenomena and it is particularly important in device
applications.
1.2.2 Second Harmonic Generation

A polarization oscillating at frequency $2\omega$ in eqn. (1.6) radiates an electromagnetic wave with frequency $2\omega$ 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 Second Harmonic Generation (SHG). In most of the crystalline materials, the nonlinear polarizability $\chi^{(2)}$ depends on the direction of propagation, polarization of the electric field and the orientation of the optic axis of the crystal. In such a crystalline material the $P$ and $E$ vectors are not necessarily parallel. The second order polarization must therefore be represented by the type

$$P_i^{(2)} = \varepsilon_0 \sum \chi^{(2)}_{ijk} E_j E_k$$

where $i, j, k$ represent the co-ordinates $x, y, z$. It must be emphasized here that the second harmonic generation occurs only in a noncentrosymmetric crystal. For an isotropic crystal, $\chi^{(2)}_{ijk}$ is independent of direction and hence it is a constant. Upon reversing the direction of the axes, $(X \rightarrow -X, Y \rightarrow -Y, Z \rightarrow -Z)$ leaving the electric field and dipole moment unchanged in direction, then the sign of these two must be changed.
\[ -P_i^{(2)} = \varepsilon_0 \sum \chi_{ijk}^{(2)} (-E_j) (-E_k) = + P_i^{(2)} \] (1.8)

i.e. \( \chi_{ijk}^{(2)} = 0 \)

Therefore, SHG can not occur in centrosymmetric crystals. Only crystals that lack inversion symmetry exhibit SHG. In noncentrosymmetric crystals although the quadratic and cubic terms are present, the cubic term is substantially smaller than the second order term and hence may be ignored.

1.2.3 Sum and Difference Frequency Generation

The sum - frequency generation process is illustrated in Fig 1.1.

![Diagram of sum-frequency generation](image)

\( \omega_1 \) \( \omega_2 \) \( \omega_3 = \omega_1 + \omega_2 \)

(a) (b)

**Fig 1.1 Sum-frequency generation.**
(a) Geometry of interaction (b) Energy level description.

The complex amplitude of the nonlinear polarization describing this process is given by the expression

\[ P (\omega_1 + \omega_2) = 2 \chi_{ijk}^{(2)} E_i E_j \] (1.9)

In many ways, the process of sum frequency generation is analogous to that of second harmonic generation, except that in sum frequency generation the two input waves are of different frequencies. One application of sum frequency generation is to produce tunable
radiation in the ultraviolet spectral region by choosing one of the input waves to be the output of a fixed-frequency visible laser and other to be the output of a frequency-tunable visible laser.

The process of difference-frequency generation is described by a nonlinear polarization of the form

\[ P(\omega_1 - \omega_2) = 2\chi^{(2)}E_1E_2^* \]  

(1.10)

![Diagram of difference-frequency generation](image)

Fig. 1.2 Difference-frequency generation. (a) Geometry of the interaction (b) Energy level description.

Fig. 1.2 illustrates the difference frequency generation. Here, the frequency of the generated wave is the difference of those of the applied fields. Difference frequency generation can be used to produce tunable infrared radiation by mixing the output frequency of the tunable visible laser with that of a fixed frequency visible laser.

Specifically, difference and sum frequency generations appear to be very similar processes. However, an important difference between the two processes can be deduced from the description of difference frequency generation in terms of photon energy level diagram (Fig.1.2b). The conservation of energy requires that for every photon...
that is created at the difference frequency $\omega_3 = \omega_1 - \omega_2$, a photon at the higher input frequency $\omega_2$ must be created, thus the lower frequency input field is amplified by the process of difference frequency generation. This is also known as optical parametric amplification.

According to photon energy-level description of difference frequency generation, the atom first absorbs a photon of frequency $\omega_1$ and jumps to the higher virtual level. This level decays by a two photon emission process that is stimulated by the presence of the $\omega_2$ field, which is already present. Two photon emission can occur even if the $\omega_2$ field is not applied. The generated fields in such a case are very much weaker. Since, they are created by spontaneous two-photon emission from a virtual level, the process is known as parametric fluorescence.

1.3 Phase Matching

In general, crystals exhibiting second harmonic generation are double refracting. It is possible to cut the crystal so that the velocity of the ordinary beam of one harmonic is equal to the velocity of the extraordinary beam for the other harmonic. The first and second harmonics can then travel at the same velocity and maintain a constant phase relation through the crystal. This phenomenon is known as phase matching [9].
It is observed that the efficiency of the generation of harmonics depends not only on the intensity of the exciting radiation, but also on its direction of propagation in crystals. Suppose a plane wave at frequency $\omega$ and its second harmonic $2\omega$ are propagating in the $z$-direction, through a nonlinear material of length $L$, then the SHG efficiency, $\text{Eff.}_{(\text{SHG})}$, is given by

$$\text{Eff.}_{(\text{SHG})} \propto \sin\left[\left(\frac{1}{2}\right)(2K_1-K_2)L\right] / \left(\frac{1}{2}\right)(2K_1-K_2)$$

where $K_1$ and $K_2$ are the propagation wavenumbers at frequencies $\omega$ and $2\omega$ respectively, $(K=2\pi n/\lambda)$, $n$ being the refractive index of the medium, which characterizes the spatial variation of the fundamental and harmonic radiations respectively. This will be maximum when $(2K_1-K_2)L/2$ is $\pi/2$,

$$L=\frac{\pi}{(2K_1-K_2)} = \frac{\lambda}{4(n_\omega - n_{2\omega})}$$

where $n_\omega$ and $n_{2\omega}$ are the refractive indices at $\omega$ and $2\omega$ respectively. The magnitude of $L$ given by (1.12) is called the coherence length for the second harmonic radiation. The expression for intensity is given by

$$I \propto \sin^2\left[\left(\frac{1}{2}\right)(2K_1-K_2)L\right] / \left(\frac{1}{2}\right)^2(2K_1-K_2)^2$$

For $I$ to be maximum $(2K_1-K_2)L = 0$ i.e., $K_2 = 2K_1$. For efficient frequency doubling, this relation must be satisfied. This requirement is called the phase matching criterion which follows that $n_{2\omega} = n_\omega$. Thus phase matching condition becomes refractive index criterion.
1.3.1 Types of Phase Matching

The fundamental wave interacting with a nonlinear medium may either be polarized in the parallel or perpendicular direction, and accordingly two types of phase matching can be accomplished in solid state optical materials. Type I phase matching is that in which both the interacting waves $\omega_1$ and $\omega_2$ have the same polarization and the generated harmonic will be polarized perpendicular to them. For a positive uniaxial crystal ($n_e > n_o$), the condition for type I phase matching will be

$$n_{o3}\omega_3 = n_{o3}\omega_1 + n_{o3}\omega_2$$ \hspace{1cm} (1.14)

where $n_o$ and $n_e$ are the refractive indices of ordinary and extraordinary beams respectively. For a negative uniaxial crystal $n_e < n_o$ and the condition would be

$$n_{e3}\omega_3 = n_{o3}\omega_1 + n_{o3}\omega_2$$ \hspace{1cm} (1.15)

Type II phase matching occurs when the polarization of $\omega_1$ and $\omega_2$ are orthogonal to each other as might be the case for sum and difference frequency generation. Here, the conditions for phase matching would be

$$n_{o3}\omega_3 = n_{e1}\omega_1 + n_{e2}\omega_2$$ \hspace{1cm} (1.16)

and

$$n_{e3}\omega_3 = n_{e1}\omega_1 + n_{o3}\omega_2$$ \hspace{1cm} (1.17)

for positive and negative uniaxial crystals respectively.
1.4 The Need for Compact Blue-green Lasers

Laser is described as a remarkable tool in search of an application. However, a variety of applications have emerged that are limited in their implementation by the lack of a suitable laser. The common thread running through these applications is the need for a powerful, compact, rugged, inexpensive source of light in the blue-green portion of the spectrum. The details varied greatly depending on the application such as some required tunability, some a fixed wavelength, some required a miniscule amount of optical power, some required continuous wave (cw) oscillation and others rapid modulation.

Argon-ion or helium-cadmium lasers were initially used to produce blue-light. However, they could not satisfy the requirements for every applications. The lasing wavelengths available from these lasers are fixed by the atomic transition of the gas species, and some applications required a laser wavelength that is simply not available from an argon-ion and helium cadmium laser. Other applications require a degree of tunability that is unavailable from a gas laser. In many of them, the limited lifetime, mechanical fragility, and relatively a large size of the gas laser were a problem. The new option for generation of blue-green radiation began to appear, due to the developments in other areas of laser science and technology. The development of highly efficient, high-power semiconductor diode lasers at wavelengths around
810 nm opened up the possibility of diode-pumping solid state lasers, such as those based on neodymium doped crystals and glasses. New and improved nonlinear optical materials made it practical to apply second harmonic generation to the infrared outputs of these diode-pumped solid-state lasers to generate wavelengths in the blue-green regions of the spectrum. The compact blue-green lasers are mainly used in the advanced technologies such as optical data storage, reprographics, submarine communications and biotechnology [10,11].

1.5 Applications of NLO Materials

NLO materials are used to generate new laser sources that cannot be obtained directly from the available lasers through frequency doubling phenomenon. Second harmonic generation provides the conversion of IR laser light from GaAlAs diode laser (\(\lambda = 809\) nm) into deep blue light (\(\lambda = 404.5\) nm), or output of Nd:YAG laser (\(\lambda = 1064\) nm) into green laser light (\(\lambda = 532\) nm). Optical communication and optical computing are the most appealing applications of this nonlinear phenomenon. The increase in the number of frequencies available for use with optical fibers increases the information carrying capacity of such systems. Since, the size of the focused spot of light is inversely proportional to its wavelength, SHG can increase the capacity of stored information on compact disks immensely. In all the above devices,
photons are used to acquire, store, transmit and process the information. Photonic switching can take place with femto second speed, thus providing a gain in speed, many orders of magnitude over that of electronic processes. Devices for these applications require new and improved NLO materials in order to achieve their potential. Although many inorganic and organic single crystals showing strong SHG effects are known for some years, there is a demand for newer and improved crystalline materials. The discovery of a material with enhanced second harmonic generation characteristics can significantly change the utility of, and hence the market for a particular laser system. For example, the availability of potassium titanyl phosphate has made the mode locked CW YAG laser competitive with the argon ion laser in many applications. Therefore, there is a current interest in finding materials that will extend the wavelength capacity of laser sources into the UV region and new frequency conversion materials will have significant impact on applications such as optical communication technology and laser driven inertial confinement fusion experiments. The demand from optical and device physicists for improved and effective materials calls for world-wide research on NLO materials which is most targeted and speculative.
1.6 Materials Requirement for Second Harmonic Generation

The progress in nonlinear optics has always been dictated by the availability of better and newer materials. Conversion efficiency of the second harmonic generation process is given by

\[
E_{\text{SHG}} = \frac{P_{\omega}}{P_{2\omega}} = \frac{[8(\mu_0/\epsilon_0)^3 \omega^2 d^2 L^2 \sin^2(\Delta KL/2)]}{n(\pi \omega_0^2)(\Delta KL/2)^2}
\]  

(1.18)

where \(d\) is the effective nonlinear optical coefficient and \(K\) is the wavevector [12]. For a given material and for a given frequency (\(\omega\)), the conversion efficiency is dependent on the square of the coherence length \(L\). Hence, it is imperative that large crystals are needed. As a result of the interference from the input fundamental polarization wave and the driven harmonic polarization wave, the maximum usable length of the crystal is limited to a few microns. However, this problem can be overcome by decreasing \(\Delta K\) to zero (phase matching). The quotient \((d^2/n^3)\) is called the figure of merit for SHG. This is a material limited parameter, and is given the top priority while considering new materials. In a chosen material, conversion efficiency can be further increased by increasing the power density \((P_{\omega}/A)\) of the input beam focussed into the crystal to the tolerance limit called the damage threshold. The above discussion on the parameters are for the plane wave approximation of the incident beam and is valid essentially when the crystal acceptance widths are much broader than those of the laser beam. A more detailed
consideration of the beam and crystal parameters give the phase matching parameter $\Delta s$ as

$$\Delta s = (K_1(\Delta \theta.L) + (K_2(\Delta T.L) + (\Delta \lambda.L))$$

(1.19)

where $(\Delta \theta.L)$, $(\Delta T.L)$ and $(\Delta \lambda.L)$ are defined as the angular, temperature and spectral band widths of the crystals respectively. Hence, it is essential that temperature and spectral band widths are also considered while opting for a crystal for an NLO device. In addition to the above parameters, a few other physical properties of the crystals are to be considered.

As a general rule, the basic criteria for second harmonic generation apart from the noncentro symmetry of the crystal structure include (i) relatively large $d_{ijk}$ coefficients (ii) moderate birefringence (iii) wide transparency window (iv) wide phase matching range (v) high damage threshold (vi) high melting point (vii) good chemical stability (Viii) ease of growth and (ix) low material cost [13]. There are few materials which satisfy most of these requirements. Hence, the search for new materials seems to be unending.

1.7 A Brief Review of Second Order NLO Materials

The available nonlinear optical materials can be classified into three categories viz., inorganic, organic and semiorganic materials.
1.7.1 Inorganic NLO Materials

Investigations of nonlinear optical effects were initially focussed on pure inorganic systems and the first solid to demonstrate the second order NLO properties was a quartz crystal. Many efficient inorganic materials such as potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), β-barium borate (BBO), potassium niobate (KNbO₃), lithium niobate (LiNbO₃), lithium iodate (LiIO₃), potassium titanyl phosphate (KTP), lithium triborate (LBO) and potassium pentaborate were developed in the past decades for NLO applications [11,14,15]. More recently, Xu et al. [16] have studied the chemical bond analysis for crystal growth of KDP and ADP. Zhen et al. [17] have reported that the optical damage threshold of Sc:Er:LiNbO₃ is much higher than that of Er:LiNbO₃. Inorganic NLO materials are mostly ionic bonded and have high melting point and high degree of chemical inertness. Indeed most of the commercial frequency doublers use these inorganic materials. Among the inorganic materials, KDP is one of the popular nonlinear optical materials used for frequency doubling phenomena. The NLO coefficient $d_{eff}$ of KDP is $d_{36} (1064 \text{ nm}) = 0.37 \text{ pm/V}$ [11]. Borate materials such as LiB₃O₅ and KB₅O₈ .4H₂O are superior in UV laser applications to many other commonly used inorganic materials due to their high UV transmittance down to 155 nm, chemical stability and mechanical hardness [18]. Recently, mixed borate crystals with
improved characteristics have been reported. One among them is BiB₃O₆ with exceptionally large NLO coefficient (d₁₁ = 2.53, d₁₂ = 2.3 and d₂₆ = 2.8 pm/V), a high laser damage threshold (5 GW/cm²) and a conversion efficiency of 67.7% of the Nd:YAG fundamental (1064 nm) [19]. It has a transmittance window in the range 190-3200 nm. LiKB₄O₇ has been used for frequency doubling of Ti:Al₂O₃ laser for its fundamental wavelength (720-780 nm). K₂Al₂B₂O₇ is reported to be a promising material for the generation of the fourth harmonic (266 nm) and the fifth harmonic (213 nm) [20].

The origin of nonlinearity in most of the oxide materials has been identified to be their distorted octahedron. In the borate crystals, the boron atom usually coordinates with either three or four oxygen atoms forming (BO₃)³⁻ and (BO₄)⁵⁻ groups. Accordingly, the electronic orbitals are hybridized to a planar sp² or a three-dimensional sp³ structure. There are also other structures like (B₃O₆)³⁻ and (B₃O₇)⁵⁻. These various structural possibilities for the boron atom are among the reasons for the attractive versatility of borates in nonlinear optics. The nonlinear coefficient, optical transmittance, laser damage threshold and refractive index of some of these remarkable materials are presented in table 1.1.
Table 1.1 Physico-chemical properties of some prominent inorganic NLO materials.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>KDP</th>
<th>ADP</th>
<th>KTP</th>
<th>KNbO₃</th>
<th>LiNbO₃</th>
<th>LBO</th>
<th>BBO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point group</td>
<td>42m</td>
<td>42m</td>
<td>mm2</td>
<td>mm2</td>
<td>3m</td>
<td>mm2</td>
<td>3m</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>252</td>
<td>190</td>
<td>1152</td>
<td>1060</td>
<td>1257</td>
<td>834</td>
<td>1095</td>
</tr>
<tr>
<td>Transparency range (nm)</td>
<td>180-1800</td>
<td>180-1530</td>
<td>350-4500</td>
<td>400-4000</td>
<td>350-5000</td>
<td>150-3200</td>
<td>198-2600</td>
</tr>
<tr>
<td>Refractive index</td>
<td>n₀ = 1.4931, nₑ = 1.4582</td>
<td>n₀ = 1.6259, nₑ = 1.5673</td>
<td>nₓ = 1.7371, nᵧ = 1.7345, nₑ = 1.8805</td>
<td>nₓ = 2.4974, nᵧ = 2.4145, nₑ = 2.2771</td>
<td>n₀ = 2.2322, nᵧ = 2.1560, nₑ = 1.6792</td>
<td>nₓ = 1.6335, nᵧ = 1.6582, nₑ = 1.6792</td>
<td>n₀ = 1.655, nₑ = 1.542</td>
</tr>
<tr>
<td>Nonlinear coefficient dₑff (pm/V)</td>
<td>d₃₁ = 0.37, d₃₆ = 0.47</td>
<td>dₑff = 3.2</td>
<td>d₃₁ = -11.9, d₃₂ = -13.7, d₃₃ = -20.6</td>
<td>dₑff = 5.1</td>
<td>d₃₁ = 0.67, d₃₂ = 0.85, d₃₃ = 0.04</td>
<td>dₑff = 1.6</td>
<td></td>
</tr>
<tr>
<td>Mohs Hardness</td>
<td>1.5</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.5</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>Laser damage threshold (GW/cm²)</td>
<td>14.4 (15 ns)</td>
<td>4.5 (10 ns)</td>
<td>20 (1 ns)</td>
<td>100 (0.1 ns)</td>
<td>0.1 (10 ns)</td>
<td>45 (1.1 ns)</td>
<td>23 (14 ns)</td>
</tr>
</tbody>
</table>
1.7.2 Organic NLO Materials

For the past two decades, extensive investigations have been carried out on organic NLO materials for their higher nonlinear susceptibilities compared with the inorganic materials [21]. Large molecular first order susceptibilities ‘β’ are associated with structures that have a large difference between the ground and excited state dipole moments and low energy charge transformation [22]. The preparation of organic crystals is less expensive, nonlinear susceptibilities are high, and birefringence is sufficient for use in frequency converters. In general, organic molecules exhibit very special properties originating from the versatility of the carbon atom, which is capable of engaging in various types of covalent bonds and in a wide range of combinations. Organic molecules are built up primarily from the atoms of the second row of the periodic table and they give rise to two types of orbitals with contrasting properties, the σ and π orbitals. The π orbitals overlap less than σ-orbitals and form weaker and more polarizable bonds. In certain classes of organic molecules (conjugated carbon compounds) some electrons are completely delocalized in the sense they can move over large distances under the influence of weak perturbations. These electrons are termed as π delocalized electrons. This kind of molecules owing to their complex charge distribution may
give rise to dipole moments when they lack a centre of symmetry. The molecules in pure organic crystals are often bonded by weak Van der Waals force or hydrogen bonds which result in a high degree of delocalization of charge. The prototype organic NLO material contains one or more delocalized bonds, typically a ring structure like benzene. When substituted with a donor and acceptor at para positions, the bonds get the influence of the electromagnetic fields. P-nitroaniline is a typical example for the above strategy.

It has been often found that such molecules, when packed as crystals turn out to be centrosymmetric, leading to macroscopically vanishing dipole moment. However, when substituted with a CH₃ at meta position, the resulting crystal is acentric. Thus, while perturbing the microscopic dipole moments by a small amount, a suitable addition at another site can ensure a macroscopically non-vanishing dipole moment for the donor-acceptor substituted systems. It has been found that the efficiency increases with conjugation length (the distance between donor and acceptor) and the strength of the substituents [23,24]. Most of the materials initially investigated are nitroaniline derivatives. 2-methyl-4-nitroaniline (MNA) [25], methyl-(2',4-dinitrophenyl)-amino propanate (MAP) [26], (N-(4-nitrophenyl-(L)-prolinol) (NPP) [27], 4-(N,N-Dimethylamino)-acetamidonitrobenzene
(DAN) [11] and 3-methyl-4-nitropyridine-1-oxide (POM) [28] are some of the prominent materials of this category. The well-known organic NLO material, urea has three times the nonlinearity of the popular KDP and has a damage threshold of 5 GW/cm² which exceeds that of LiNbO₃ [11,29]. An example of an efficient (SHG efficiency 30 times greater than KDP) organic material is 3-methoxy 4-hydroxy benzaldehyde (MHBA) [30]. The 2-methyl-4-nitroaniline (MNA) [25] crystals have also found extensive applications in nonlinear optics. The highest powder SHG efficiency reported so far is from the material 3-methyl-4-methoxy-4-nitrostilbene (MMONS) (3000 times that of KDP) [31]. The 4-methoxy benzaldehyde-N-4-stilbazolium tosylate (MBST) [32] is a recently reported organic material with a powder SHG efficiency 17 times that of urea. Table 1.2 gives a collective picture of the physico-chemical features of some of the prominent organic NLO materials.

However, these crystals have several unfavorable physical properties that limit their applications in nonlinear optical devices, and there has not been much progress in fabricating devices out of these molecular crystals. Most of the organic molecular crystals have poor transparency due to the presence of conjugated bonds. This will result in the absorption of the generated harmonic waves, leading to poor conversion efficiency. Also these materials have poor thermal and
Table 1.2 Physico-chemical properties of some prominent organic NLO materials.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>MAP</th>
<th>DAN</th>
<th>MMONS</th>
<th>NPP</th>
<th>MHBA</th>
<th>POM</th>
<th>MNA</th>
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</thead>
<tbody>
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<td>2</td>
<td>2</td>
<td>mm2</td>
<td>2</td>
<td>2</td>
<td>222</td>
<td>mm2</td>
</tr>
<tr>
<td>Transparency range (nm)</td>
<td>500-2200</td>
<td>480-2270</td>
<td>510-2100</td>
<td>510-2000</td>
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<td>400-2300</td>
<td>500-2000</td>
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<td>$n_x = 1.692$</td>
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<td>$n_y = 1.756$</td>
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<td>$n_z = 2.243$</td>
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<td>$n_z = 1.491$</td>
<td>$n_z = 1.808$</td>
<td>$n_z = 2.114$</td>
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<td>Linear absorption coefficient $\alpha$ (cm$^{-1}$)</td>
<td>3.7</td>
<td>3.4</td>
<td>1.5</td>
<td>3.4</td>
<td>1.42</td>
<td>1.88</td>
<td>4.0</td>
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<td>Nonlinear coefficient $d_{\text{eff}}$ (pm/V)</td>
<td>$d_{21} = 23.9$</td>
<td>$d_{21} = 56.5$</td>
<td>$d_{32} = 25$</td>
<td>$d_{21} = 56.5$</td>
<td>$d_{21} = 3.9$</td>
<td>$d_{21} = 6.0$</td>
<td>$d_{31} = 35.1$</td>
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<td>$d_{22} = 26.3$</td>
<td>$d_{22} = 18.7$</td>
<td>$d_{33} = 111$</td>
<td>$d_{22} = 18.7$</td>
<td>$d_{22} = 9.8$</td>
<td>$d_{33} = 0.30$</td>
<td>$d_{33} = 35.1$</td>
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<tr>
<td></td>
<td>$d_{23} = 5.30$</td>
<td></td>
<td></td>
<td></td>
<td>$d_{23} = 13.0$</td>
<td></td>
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<tr>
<td>Laser damage threshold (GW/cm$^2$)</td>
<td>3.0</td>
<td>10</td>
<td>5.0</td>
<td>10</td>
<td>20.0</td>
<td>2.0</td>
<td>0.2</td>
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<tr>
<td></td>
<td>(10 ns)</td>
<td>(0.0001 ns)</td>
<td>(0.1 ns)</td>
<td>(0.001 ns)</td>
<td>(10 ns)</td>
<td>(0.02 ns)</td>
<td>(25 ns)</td>
</tr>
</tbody>
</table>
mechanical properties compared to the inorganic materials. However, with intelligent planning and high degree of perseverance, scientists have grown bulk crystals by using different solvents and by judicious control of the growth at various stages.

1.7.3 Semiorganic NLO Materials

To overcome the practical difficulties encountered in fabricating devices using organic NLO single crystals, the inherent limitations on the maximum attainable nonlinearity and the tedious methods followed to grow single crystals of inorganic materials, it was suggested that a combination of the favourable properties of these classes would be ideal so that the following advantages could be realized in practice.

(i) Moderate nonlinearity
(ii) Large transparency window to avoid absorption in the blue-green region
(iii) Ease of crystal growth at moderate expenses
(iv) High thermal stability and mechanical hardness to withstand the laser power and temperature
(v) Nonhygroscopic and nondeliquescent to promote the stability

Crystal engineering and molecular design in this direction have led to the discovery of a new class of materials called semiorganics [31-34], in which a polarizable organic molecule is stoichiometrically
bonded to an inorganic host. In this class, the large nonlinearities of 
\( \pi \) - conjugated organic and the favorable crystal growth properties of 
ionic salts are combined into a single matrix.

**Classes of Semiorganic NLO Materials**

There are two broad classes in semiorganic NLO materials

1. Organic – inorganic salts like L-arginine phosphate [35,36],
   L-histidine tetrafluoroborate [37,38] and 2-amino 5-nitropyridinium
   phosphate [39,40].

2. Metal – organic coordination complexes such as Tris(thiourea) zinc
   sulphate [41,42], Bis (thiourea) zinc chloride [43], Bis(thiourea)
   cadmium chloride [44] and the tetrathiocyanate complexes [45,46].

**1.7.3.1 Organic – Inorganic Salts (Type I)**

L-arginine phosphate (LAP) is the best example of this type. In
LAP, an organic chiral molecule (L-arginine), an inorganic acentric
tetrahedral molecule (phosphoric acid) and water molecules are
combined by positive-negative coulomb interactions and hydrogen
bonding. Here, planar guanidinium and carboxylate groups at the two
 terminals of L-arginine are responsible for the SHG. In many respects
LAP can match the inorganic NLO crystal KDP. Moreover, it possesses
a larger nonlinear coefficient \( d_{21} = 2.14d_{36}(\text{KDP}) \) and is characterized by
an extremely high laser damage threshold (15 J/cm\(^2\)) [34]. DLAP is the
deuterated form of LAP, in which the protons have been replaced. The absorption around 1000 nm, due to the overtones of vibrations associated with hydrogen-containing groups in LAP, is effectively reduced in DLAP.

1.7.3.2 Metal-Organic Coordination Complexes (Type II)

These kinds of semiorganic NLO crystals are characterized by various polyhedra with a central metal ion surrounded by a number of organic and/or inorganic ligands [34]. They can be formulated as MM'L_nL'_m, where M, M' stand for different metal ions and L, L' for organic and/or inorganic ligands. The II (B) group metals (Zn, Cd, Hg) usually have a high transparency in the UV region because of their closed d^{10} shell. For the organic ligands, they can be a small \( \pi \)-electron system such as thiocyanate SCN\(^-\), urea CO(NH\(_2\))\(_2\), and thiourea CS(NH\(_2\))\(_2\). These ligands and their metal (IIB) complexes are always colorless. The ligands can be medium-sized \( \pi \)-electron systems such as benzene derivatives with the potential SHG efficiency of one order of magnitude higher than that of urea. Most of these ligands are pale yellow in colour. The ligand can also be a large \( \pi \)-electron system such as the stilbene derivatives, which have the largest potential for SHG. In view of the structural prototypes, the complexes can be classified into three categories:
i. The island type

ii. The chain type and

iii. The network type.

i. The Island Type NLO Complexes

In this type of materials, the individual coordination polyhedra are held together only by the relatively weak intermolecular interactions. The first reported complex - NLO crystal is BTCC [44]. It belongs to Pmn2₁ space group, transparent 300-1450 nm and has nonlinear coefficient d₁₁ = 2.75 d₃₆(KDP). In BTCC two Cl atoms and two S atoms form a distorted tetrahedron around the center Cd atom. The individual polyhedra are connected by relatively strong hydrogen bonding. Although the NLO property of BTCC is not very remarkable, the architecture of introducing an inorganic component into an organic crystal to break the centrosymmetry is noticeable. Thiourea itself crystallizes in a centrosymmetric Pbnm space group and is SHG inactive.

ii. One-Dimensional Chain Type Complexes

In this type of materials, coordinate polyhedra are connected via chemical bonds, corner to corner or edge to edge forming one-dimensional polymers in the crystal. A weak intermolecular packing
cohesion may exist between chains. Thiosemicarbazide cadmium chloride monohydrate (TSCCC) and Thiosemicarbazide cadmium bromide monohydrate (TSCCB) are the best examples of this type. Both TSCCC and TSCCB belong to the Cc space group with similar cell parameters and similar molecular packing style. TSCCC has an SHG efficiency of 14 times that of KDP, which is much larger than that of TSCCB. This means that the chlorine atom must be involved in the coordination polyhedra and somehow, has promoted the NLO effect. In TSCCC, the distorted coordinate octahedron consists of one Cd in the center and three Cl, two S and one N at six vertices. In the crystal structure, the planar π-organic molecules combine harmonically with the inorganic distorted polyhedra in TSCCC and TSCCB [34].

iii. The Network Type

In this type, two or three-dimensional coordinative chemical bonds link all polyhedra together. Cadmium mercury thiocyanate (CMTC) and manganese mercury tetrathiocyanate (MMTC) are the best examples of this type. It is an effective SHG crystal for the 1064 nm Nd:YAG laser with a NLO coefficient $d_{31} = 13 \times d_{33}$ (LiIO$_3$). The crystal consists of two kinds of slightly flattened tetrahedra. One is CdN$_4$ and the other is HgS$_4$. The central atoms Hg and Cd of the flattened tetrahedra are localized at the centre of the fourfold inversion axis. The
SCN$^-$ bridges between Hg and Cd ions leading to the formation of an infinite 3D Hg-SCN-Cd network. The network provides the crystal with a large domain for polarization, and induces a larger macroscopic nonlinearity of an individual dipolar group. The SCN$^-$ group may be the smallest SHG chromophore. It is also a kind of intrinsic semiorganic group. The 3D network is very significant as it offers a unique high physicochemical stability to the crystal. Both CMTC and MMTC possess exactly the same structural features of the 3D network and bond parameters. The SHG efficiency of MMTC and CMTC is 18 times and 13 times that of urea. The difference in NLO activity may be due to their difference in electronic structure [34]. The physico-chemical properties of some prominent semiorganic NLO materials are presented in table 1.3.
### Table 1.3 Physico-chemical properties of some prominent semiorganic NLO materials.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>LAP</th>
<th>DLAP</th>
<th>TSCCB</th>
<th>2A5NPDP</th>
<th>BTCC</th>
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<td>Point group</td>
<td>2</td>
<td>2</td>
<td>m</td>
<td>mm2</td>
<td>mm2</td>
</tr>
<tr>
<td>Melting point (°C)</td>
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<td>-80</td>
<td>98</td>
<td>160</td>
<td>185</td>
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<tr>
<td>Transparency range (nm)</td>
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<td>220-1300</td>
<td>400-1400</td>
<td>420-1600</td>
<td>300-2000</td>
</tr>
<tr>
<td>Refractive index</td>
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<td>$n_y = 1.559$</td>
<td>N.A</td>
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<td>$n_y = 1.718$</td>
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<td>Nonlinear coefficients d$_{eff}$ (pm/V)</td>
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<td>0.93</td>
<td>0.90</td>
<td>2.00</td>
<td>1.65</td>
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<tr>
<td>Laser damage threshold (GW/cm$^2$)</td>
<td>13</td>
<td>9.0</td>
<td>N.A</td>
<td>0.7</td>
<td>32</td>
</tr>
</tbody>
</table>

N.A – Not available
1.8 Conclusions

The relative merits of the three classes of NLO materials presented are to be considered from the device point of view and the feasibility of growth techniques. Hence a choice of a material for a particular application and the growth procedure are to be dictated in the light of specific conditions. The current trend in the scientific pursuits is on newer organic and semiorganic materials and the search is particularly focussed on materials suitable for applications in compact blue-green lasers.
References


