Chapter 1

Introduction

1.1 Introduction

Materials have always played a significant and defining role in human development, from the Stone Age to the material world of today. Materials are central to our prosperity and new materials hold the key for our future development. Material-related issues can be found in all areas of life and engineering e.g. in biomedical, telecommunications, aeronautical, construction, chemical and mechanical, and in all aspects of a products life, from an idea or discovery to a prototype or finished product and recycling. In the puzzle of innovation, material engineers focus on the application of materials, where they test, develop and modify materials that are used in a wide range of products, from jet engines and snow skis to smartphones and diapers.

Modern information technology requires new methods for data processing to save acquired data and to transfer these rapidly. One approach to meet this goal is the development of materials with non-linear optical (NLO) properties. Recently, materials having good second harmonic generation (SHG) efficiency have attracted much attention because of their potential applications in many fields. Advanced laser-based imaging, optical computers, optical switching, optical communication and data storage systems require improved non-linear optical materials. Single crystals of large sizes of various materials are needed for several applications in industries. In our laboratory, several NLO materials have been grown using submerged seed and hanging seed solution methods and reported previously.
1.2 Non-linear optics

Light is a prima donna in the nature’s opera! Light signifies knowledge and life. Light played the crucial role, when the life evolved on the Mother Earth. The first optical instrument bestowed upon vertebrates and invertebrates was eye by the Mother Nature. Pre-historic humans were thrilled by natural optical phenomena like rain-bow and mirage. As the civilizations developed, the optics and optical instruments started taking shape gradually right from common spectacles to complicated equipments like telescopes, microscopes, interferometers, etc. Moreover, the study of various optical phenomena, for example, diffraction, interference, dispersion, polarization, etc. has added either new branches or new dimensions to optics. Optics, the study of light, is usually divided into three branches, each of which employs different method of theoretical treatment; these are (1) geometrical optics (2) physical optics and (3) quantum optics [Jenkins and White, 1957]. Later on, the new fields like magneto-optics and electro-optics were developed. The optical phenomena, which depends on an applied magnetic field are called magneto-optics and, similarly, which depends on applied electric field are called electro-optics. Nowadays, extended fields of optics such as singular optics, non-imaging optics, non-linear optics, statistical optics, etc, are available.

Non-linear Optics (NLO) is the branch of optics that describes the behavior of light in non-linear media, that is, the media in which the dielectric polarization \( P \) responds to the electric field \( E \) of light non-linearly. This non-linearity is only observed at very high intensity of light having values of the electric field comparable to the inter-atomic electric fields, viz., \( 10^8 \) V/m, which is provided by pulsed laser. In non-linear optics, the superposition principle no longer holds [Newell and Monoley, 1992, He and
After the discovery of lasers, the dimension of optics changed completely. A review has been written by Rao (2010), on the completion of 50 years of the discovery of lasers.

**1.3 Basics and formulation of NLO**

Before the advent of the lasers, it was assumed that the optical parameters of the medium were independent of the intensity of the light propagating in that medium. The electric field strength generated by the non-laser light sources is of the order of $10^3$ V/cm, which is very much smaller than the inter-atomic fields; whereas, the inter-atomic electric field strength of the medium is of the order of $10^7$ to $10^{10}$ V/cm. Therefore, normal light source is unable to affect the atomic fields of the medium and thereby the optical properties of the medium. On the other hand, lasers generate electric field strength of the order of $10^5$ to $10^9$ V/cm, which is able to commensurate to that of the atomic electric fields of the medium. This affects the optical properties of the medium and thus generates new electromagnetic fields altered in phase, frequency and amplitude.

The first demonstration of non-linear optical (NLO) frequency conversion took place as early as in 1961 by Franken et al. They used quartz crystal to double the frequency of 694 nm light of Ruby laser. Inasmuch as the interaction was not phase matched, the ultraviolet output power was so small that the editors of the journal mistook for a blemish the spot on spectrograph plate that demonstrated the new effect. However, at the end of 1962, a classical paper appeared in which Armstrong et al., (1962) had given the theoretical explanation for both microscopic origin of the non-linear susceptibilities and the propagation effects governing macroscopic non-linear interactions between electro-magnetic waves. Later on, Bloembergen won the Nobel Prize in 1981 for his
contribution to laser spectroscopy. Also, the selected papers of Bloembergen were published under the title, “Encounters in the Non-linear Optics” [Bloembergen, 1996]. Then the quest began for identifying various non-linear optical materials and had gathered momentum in the past more than a decade.

In a dielectric medium when an electric field is applied, the charges are displaced slightly from their usual positions. This small movement of positive charge in one direction and negative charge in the other, results in a collection of induced dielectric dipole moment [Dimitriev, 1991]. A light wave consists of electric and magnetic fields which vary sinusoidally at optical frequencies. The motion of charged particles in a dielectric medium in response to an optical electrical field also oscillates and forms oscillatory dipoles. At very low fields, the induced polarization is directly proportional to the electric field [Zernike and Midwinter, 1973].

\[ \mathbf{P}(t) = \chi^{(1)} \mathbf{E}(t) \]  

(1.1)

where, \( \mathbf{E} \) is the magnitude of the applied electric field, \( \chi^{(1)} \) is the linear susceptibility of the material and \( \mathbf{P} \) is the polarization.

The NLO phenomena occur at sufficiently intense fields. As the applied field strength increases (e.g. in lasers) the polarization response of the medium is no longer linear as given in the equation (1.1). The induced polarization (\( \mathbf{P} \)) becomes a function of the applied field and is given by the equation [Shen, 1984]:

\[ \mathbf{P}(t) = \chi^{(1)} \mathbf{E}(t) + \chi^{(2)} \mathbf{E}^2(t) + \chi^{(3)} \mathbf{E}^3(t) + \ldots \]  

(1.2)
where the quantities $\chi^{(2)}$ and $\chi^{(3)}$ are known as the second- and third-order non-linear optical susceptibilities, respectively.

Then, equation 1.2 can also be written as follows:

$$\mathbf{P}(t) = \mathbf{P}^{(1)}(t) + \mathbf{P}^{(2)}(t) + \mathbf{P}^{(3)}(t) + \ldots$$  

(1.3)

Each term is modified by the susceptibility, $\chi$, a tensor quantity. The susceptibility tensor for second-order effects, $\chi^{(2)} = \chi_{ij}$ relates each of the three components of the polarization – $P_x$, $P_y$ and $P_z$ to the nine products of the two applied light fields, for a total 27 terms. For convenience, the second order susceptibility is converted into non-linear optical coefficient $d_{ijk}$. Different definitions and dimensions are used; therefore, absolute value of $d_{ijk}$ should be used with care. The most common second order effect and the most important NLO phenomenon is the second harmonic generation (SHG). In a similar manner the third order susceptibility, a fourth-rank tensor and the third order coefficients are responsible for the third harmonic generation, parametric conversion, stimulated scattering, etc. and there are 81 possible third order terms.

The net polarization of a material depends on its symmetry properties with respect to the orientation of the applied field. A careful examination of the symmetries in a material is indispensable in understanding its non-linear optical properties. For instance, eleven of the point groups are “centrosymmetric”, meaning that the structure of the crystal remains unchanged along a direction reversed by 180°. No second order effects can take place in centrosymmetric crystals as all components of even order of $\chi$ are zero. Obviously, an important criterion for a material to exhibit SHG is that it should be a non-centrosymmetric material.
1.4 Various types of second order NLO effects

In a medium, several second-order NLO effects can be observed experimentally which are summarized in the following sections.

1.4.1 Second Harmonic Generation

Suppose a laser beam whose electric field strength is represented as

\[ E(t) = E_0 e^{-i\omega t} + c.c \]  \hspace{1cm} (1.4)

(where, c.c-complex conjugate of the E(t)) is incident upon a crystal for which the second-order susceptibility \( \chi^{(2)} \) is nonzero. The non-linear polarization that is created in such a crystal is given (according to Eq. 1.2) as \( P^{(2)}(t) = \chi^{(2)} E^2(t) \), or as

\[ P^{(2)}(t) = \chi^{(2)} E E^* + \chi^{(2)} E^2 e^{-2i\omega t} + c.c \]  \hspace{1cm} (1.5)

We see that second-order polarization consists of a contribution at zero frequency (the first term) and a contribution at frequency \( 2\omega \) (the second term). Note that the contribution of the first term in Eq. (1.5) does not lead to the generation of electromagnetic radiation (because its second time derivative vanishes); it leads to a process known as optical rectification in which a static electric field is created within the non-linear crystal.

Under proper experimental conditions, the process of second-harmonic generation can be so efficient that nearly all of the power in the incident radiation at frequency \( \omega \) is converted to radiation at the second-harmonic frequency \( 2\omega \). One common use of second-harmonic generation is to convert the output of a fixed-frequency laser to a different spectral region. For example, the Nd:YAG laser operates in the near infrared at a
wavelength of 1.06 μm. Second-harmonic generation is routinely used to convert the wavelength of the radiation to 0.53 μm, in the middle of the visible region. Second-harmonic generation can be visualized by considering the interaction in terms of the exchange of photons between the various frequency components of the field. Two photons of frequency \( \omega \) are destroyed and a photon of frequency \( 2\omega \) is simultaneously created in a single quantum-mechanical process.

1.4.2 Sum and Difference Frequency Generation

Let us next consider the circumstances in which the optical field incident upon a non-linear optical medium characterized by a non-linear susceptibility \( \chi^{(2)} \) consists of two distinct frequency components, which we represent in the form

\[
E(t) = E_1 e^{i\omega_1 t} + E_2 e^{i\omega_2 t} + c.c
\]  

Then, assuming as in Eq. 1.2 that the second-order contribution to the non-linear polarization is of the form

\[
P(t) = \chi^{(2)} E^2(t)
\]  

We find that the non-linear polarization is given by the equation:

\[
P^{(2)}(t) = \chi^{(2)} [E_1^2 e^{-2i\omega_1 t} + E_2^2 e^{-2i\omega_2 t} + 2E_1E_2 e^{-i(\omega_1 + \omega_2)t} + 2E_1E_2^* e^{-i(\omega_1 - \omega_2)t} + c.c]
\]  

+ 2 \chi^{(2)} [E_1E_1^* + E_2E_2^*]  

It is convenient to express this result using the notations

\[
P^{(2)}(t) = \Sigma \ P(\omega_n)e^{-i\omega_n t}
\]
where the summation extends over positive and negative frequency $\omega_n$. The complex amplitudes of the various frequency components of the non-linear polarization are hence given by the following equations:

\begin{align}
\text{P}(2\omega_1) &= \chi^{(2)} E_1^2 \text{ (SHG)} \quad (1.10) \\
\text{P}(2\omega_2) &= \chi^{(2)} E_2^2 \text{ (SHG)} \quad (1.11) \\
\text{P}(\omega_1 + \omega_2) &= 2\chi^{(2)} E_1 E_2 \text{ (SFG)} \quad (1.12) \\
\text{P}(\omega_1 - \omega_2) &= 2\chi^{(2)} E_1^* E_2 \text{ (DFG)} \quad (1.13) \\
\text{P}(0) &= 2\chi^{(2)} (E_1 E_1^* + E_2 E_2^*) \text{ (OR)} \quad (1.14)
\end{align}

Here we have labeled each expression by the name of the physical process that it describes, such as second harmonic generation (SHG), sum-frequency generation (SFG), difference-frequency generation (DFG) and optical rectification (OR). Note that, in accordance with our complex notation, there is also a response at the negative of each of the nonzero frequencies given above:

\begin{align}
\text{P}(-2\omega_1) &= \chi^{(2)} E_1^{*2} \quad (1.15) \\
\text{P}(-2\omega_2) &= \chi^{(2)} E_2^{*2} \quad (1.16) \\
\text{P}(-\omega_1 - \omega_2) &= 2\chi^{(2)} E_1^* E_2^* \quad (1.17) \\
\text{P}(\omega_2 - \omega_1) &= 2\chi^{(2)} E_2 E_1^* \quad (1.18)
\end{align}

However, since each of these quantities is simply the complex conjugate of one of the quantities given in Eq. (1.10 - 14), it is not necessary to take explicit account of both the positive and negative frequency components. We see from Eq. (1.10 - 14) that four different nonzero frequency components are present in the non-linear polarization.
However, typically no more than one of these frequency components will be present with any appreciable intensity in the radiation generated by the non-linear optical interaction. The reason for this behavior is that the non-linear polarization can efficiently produce an output signal only if a certain phase-matching condition is satisfied, and usually this condition cannot be satisfied for more than one frequency component of the non-linear polarization. Operationally, one often choose which frequency component will be radiated by properly selecting the polarization of the input radiation and orientation of the non-linear crystal [Boyd, 2006].

1.4.3 Optical Parametric Generation

We have just seen that in the process of difference-frequency generation, the presence of radiation at frequency $\omega_2$ or $\omega_3$ can stimulate the emission of additional photons at these frequencies. If the non-linear crystal used in this process is placed inside an optical resonator, the $\omega_2$ and/or $\omega_3$ fields can build up to large values. Such a device is known as an optical parametric oscillator. Optical parametric oscillators are frequently used at infrared wavelengths, where other sources of tunable radiation are not readily available. Such a device is tunable because any frequency $\omega_2$ that is smaller than $\omega_1$ can satisfy the condition $\omega_2 + \omega_3 = \omega_1$ for some frequency $\omega_3$. In practice, one controls the output frequency of an optical parametric oscillator by adjusting the phase matching condition. The applied field frequency $\omega_1$ is often called the pump frequency, the desired output frequency is called the signal frequency, and the other, unwanted, output frequency is called the idler frequency.
1.4.4 Phase matching

Many of the practical problems associated with optical frequency mixing come from the distributed nature of the mixing process. Particularly, the difference in the phase velocities of the interacting waves of different frequencies in the non-linear medium produces a phase difference that accumulates along the length of the device and significantly limits the efficiency of the mixing process. In order to obtain high conversion efficiency, the phase vectors of input beams and generated beams have to be matched. In mathematical terms, one can write,

\[ \Delta K = k_3 - k_2 - k_1 = 2\pi \left( \frac{n_3}{\lambda_3} - \frac{n_2}{\lambda_2} - \frac{n_1}{\lambda_1} \right) = 0 \]  

(1.19)

where, \( \Delta K \) is the phase mismatching, \( k_i \) is phase vector at \( \lambda_i \) and \( n_i \) is the refractive index at \( \lambda_i \). In low power case, the relationship between conversion efficiency and phase mismatching is as given below:

\[ \eta \propto P L (d_{\text{eff}} \sin(\Delta KL)/\Delta KL)^2 \]  

(1.20)

where, \( d_{\text{eff}} \) is the effective non-linear coefficient, \( L \) is the crystal length, \( P \) is the input power density and \( \Delta K \) is the phase mismatching.

1.5 Criteria for selecting NLO materials

For an NLO crystal device to work well without degradation of its performance over the life time of its assignment, the following criteria are required to be fulfilled [Adhav, 2001]: (1) Reliable crystal growth technique for adequate size, (2) Large non-linear figure of merit for frequency conversion, (3) Fast optical response time, (4) Moderate to high transparency, (5) Good optical homogeneity, (6) Good mechanical strength, (7) Chemical stability, (8) Temperature phase-matching band width, (9) High

1.6 Materials for Non-linear Optics

Advances in the development of NLO materials can be divided into three different areas, as given below:

(i) Discovery of new NLO materials

(ii) Growth of promising NLO crystals

(iii) Improving the characteristics of NLO crystals

From materials point of view, the NLO materials can be broadly classified into three different categories viz., inorganic, organic and semi-organic or metal-organic materials. Inorganic and organic materials possess their own set of advantages and disadvantages [Blau, 1987], while in semi-organic or metal-organic materials, the aim is always to combine the advantages of the both.

1.7 Organic NLO crystals

Second order NLO effects in organic molecules originate from a strong donor-acceptor intramolecular interaction. This was experimentally demonstrated by Davydov and co-workers in 1970 while screening SHG activity in a wide variety of substituted benzenes. They concluded that dipolar aromatic molecules possessing an electron donor group and an electron acceptor group contribute to large second-order optical non-linearity arising from the intramolecular charge transfer between the two groups of opposite nature. On the other hand, \[\pi\]-conjugated molecules with a donor and an acceptor
will not display SHG activity if they possess a center of symmetry. This symmetry requirement eliminates many materials from being SHG active and at the early stage of designing and synthesizing novel materials, one has to consider ways of introducing non-centrosymmetry in the molecular structures. The large second order optical non-linearity originates from organic conjugated molecules having an electron acceptor group at one end and a donor group at the opposite end. The π-conjugated systems could be benzene, azobenzene, stilbene, tolans, biphenyl, benzylidene, heterocycle polyenes, etc.

1.8 **Salient features of amino acid NLO materials**

Among organic crystals for NLO applications, α-amino acids display the following specific features of interest:

(i) Molecular chirality, which results in acentric crystal structures

(ii) Absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions

(iii) Zwitterionic nature of the molecule, which favours crystal hardness

(iv) As chiral auxiliaries for nitro-aromatics and other donor-acceptor molecules with large hyperpolarizabilities

1.9 **Kurtz powder technique**

A widely used method for screening materials to determine second-harmonic generation activity is the powder technique developed by Kurtz and Perry (1968). This technique was first used in the study of organo-metallic materials. A laser is directed onto a powdered sample and the emitted light at the second harmonic frequency is collected and compared to that of a reference sample, such as quartz or urea, to obtain a measure of the SHG efficiency. It is an excellent method for testing large number of powdered
materials, but is recognized as semi-quantitative, and minor variations in relative efficiencies are probably not significant.

This technique derives information concerning angular averages of second-order non-linear tensor components, coherence lengths and phase-matching behavior. It is of most value as a screening technique to identify materials with non-centrosymmetric crystal structures and the capability for phase matching. Taking other factors into account, it might be used as a guideline for single-crystal growth. Results are dependent on the particle size, and recrystallization from a range of solvents can lead to different SHG efficiencies. The efficiency measured depends upon both the molecular ($\beta$) and bulk ($\chi^{(2)}$) polarizabilities, and powder testing is not a reliable probe of structure-property relationship.

1.10 Scope of the present work

Development of good quality non-linear optical crystals of large sizes are of great interest for various applications such as piezoelectric sensors, electro optic modulators, fiber optic communications, infrared (IR) detectors and the production of laser sources with different wavelengths. Hence, attempts were made to identify some organic NLO materials, especially for applications in second harmonic generation (SHG). Since non-centrosymmetry is the basic requirement for the SHG, efforts were made to crystallize several organic compounds, selected from the Cambridge Structural Data base (CSD) and the literature survey.

In this chapter a general introduction about materials with special reference to non-linear optical (NLO) materials and their applications is given. Chapter 2 contains the main contribution of the author, in crystal growth, viz., the design of a home-made crystal
growth setup (Moovendaran-Kalyanasundar-Natarajan setup) to conduct several crystal growth experiments simultaneously, using slow evaporation solution method. Bulk-sized single crystals of the NLO materials, viz., L-tartaric acid, D-alanine, L-threonine and L-prolinium tartrate were grown using this setup. The above crystals were also grown by slow evaporation solution technique (SEST). The comparison of the qualities of the crystals grown using SEST and the MKN setup were made using the results of several characterization techniques.

The techniques used for the characterization viz., single crystal X-ray diffraction, high resolution X-ray diffraction, infrared, UV-vis-NIR and circular dichroism spectroscopy and the results obtained are given in Chapter 3. Measurements of the second harmonic generation efficiency, laser damage threshold value, birefringence, microhardness, dielectric constants and dielectric loss were also made. Thermo gravimetric analysis and differential thermal analysis were also carried out and reported in Chapter 4. The results show that some of the crystals grown using the MKN setup may have some possible applications as NLO materials.

Synthesis and structure elucidation of L-histidinium 2-nitrobenzoate - a new NLO material are reported in chapter 5. Chapter 6 includes the detailed literature survey carried out to find the list of amino acid compounds possessing NLO properties reported till date. It is observed that for many of the compounds (among the 92 compounds possessing NLO property), the grown crystals were of very small sizes and their characterization was also not complete. The summary of the work carried out, results obtained and possible future work in this direction are given in the final chapter (Chapter 7).