Chapter 2

Nonlinear Optics and Materials

2.1 Non-Linear Optics

Nonlinear optics has gained increased interest of researchers across the discipline due to its wide applications in the areas of laser, photonics and optoelectronics technologies. Before the invention of laser, it was thought that the optical properties of the medium does not depend upon the intensity of radiation because the field strengths of the conventional light sources used were much smaller than the field strength of the atomic and inter-atomic fields. But this was proved wrong once the laser was invented, which field strengths of the order of $10^7$ to $10^{10}$ V/cm. At such a high field, the relationship between the electric polarization $P$ and the field strength $E$ ceases to be linear and some nonlinear effects come into force. Nonlinear properties in the optical region have been strikingly demonstrated by the harmonic generation of light observed for first time by Franken and his co-worker in 1961. They observed the ultraviolet light at twice the frequency of a ruby laser light, when the light was made to traverse through a quartz crystal. The existence of harmonic light waves at the boundary of a nonlinear dielectric medium was predicted by Bloembergen and Pershan in 1962.
Nonlinear optics is the study of interaction of intense electromagnetic fields with materials to produce modified fields that are different from the input fields in phase, frequency and amplitude. The light propagated through a crystalline solid which lacks the centre of symmetry, generates light at second and higher harmonics of the applied frequency [1]. The generation of light which is twice integral multiple of incident radiations is an important nonlinear property of noncentrosymmetric crystals and called as second harmonic generation (SHG). New nonlinear optical (NLO) frequency conversion materials have a significant impact on the laser technology, optical communication and optical data storage [2-9]. Nonlinear optics has wide applications in the areas such as optical modulation, optical switching, optical logic, frequency shifting etc. The NLO material has significant impact on the electro-optic effect and also useful in the UV region. The NLO crystals find applications in frequency doubling, frequency mixing and electro-optic modulation [10-32]. Nonlinear optical materials are used in abundance for EO modulators, high-density optical memories, color display, signal amplification, emission or oscillation and optical information processing [33, 34]. With the invention of nonlinear optical properties in some crystals, tunable lasers have been realized. There is vast market for solid state devices in the field of computers, telecommunication etc. Therefore, efforts are being made in recent years on producing larger single crystals. With
this progress in the crystal growth technology, materials with attractive nonlinear properties are being explored rapidly [35-40].

Nonlinear optics is a useful technology because it extends the usefulness of laser by increasing the number of wavelength available. Nonlinear optical (NLO) phenomenon is a material phenomenon and process occurs within a nonlinear medium, usually a crystal [41, 42]. This phenomenon result due to interaction of intense electromagnetic radiations with matter producing magnified fields that is different from input field in frequency, phase or amplitude. Each NLO process consist of two parts viz (1) the intense light first induces a nonlinear response in a medium (2) then the medium in reaction modifies the optical fields in a nonlinear way.

2.2 Theoretical Explanation of Nonlinear Optics

The explanation of nonlinear effects lies in the way in which a beam of light propagates through a solid. The nuclei and associated electrons of the atoms (in the solid) forms electric dipoles. The electromagnetic radiation interacts with these dipoles causing them to oscillate. According to the classical laws of electromagnetism these dipoles act a source of electromagnetic radiation. If the amplitude of vibration is small, the dipole emits radiation of same frequency as the incident radiation. When intensity of incident radiation increases, the relationship between the irradiance and the amplitude of vibration becomes nonlinear, resulting in the generation of harmonics in the
frequency of radiation emitted by the oscillating dipoles. Thus frequency doubling or second harmonic generation (SHG) and also higher order frequency effects occur as the incident intensity is increased [43-47].

In nonlinear medium the induced polarization is a nonlinear function of the applied field. A medium exhibiting SHG is a crystal composed of molecules, with asymmetric charge distributions arranged in crystal in such a way that polar orientation is maintained throughout crystal. At very low field the induced polarization is directly proportional to electric field [48].

\[ P = \varepsilon_0 \chi E \quad \text{------- (2.1)} \]
\[
\chi \text{ - linear susceptibility of the material} \]
\[
E \text{ - Electric field vector,} \]
\[
\varepsilon_0 \text{ - Permittivity of free space.} \]

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

\[ P = \varepsilon_0 \chi^{(1)} E + \varepsilon_0 \chi^{(2)} E.E + \varepsilon_0 \chi^{(3)} E.E.E + \ldots \quad \text{------- (2.2)} \]

Where \( \chi^{(2)}, \chi^{(3)} \ldots \) are the nonlinear susceptibilities of the medium.

\( \chi^{(1)} \) is the linear term responsible for the refractive index, dispersion, birefringence and absorption. \( \chi^{(2)} \) is the quadratic term
which describes second harmonic generation, optical mixing and optical parametric oscillation. \( \chi^{(3)} \) is the cubic term which is responsible for observing phenomenon such as stimulated Raman scattering, third harmonic generation, phase conjugation and optical instability. Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients of \( \chi^{(1)} \), \( \chi^{(2)} \) etc give rise to certain optical effects, for example, \( \chi^{(1)} \) gives refraction is denoted, where as for \( \chi^{(2)} \) gives SHG \((\omega + \omega = 2\omega)\) is denoted. This may be used for different applications [49].

In case of centrosymmetric crystal \((\chi^2 = 0)\), the material can not exhibit second harmonic generation but can exhibit harmonic generation of third and fifth order. In harmonic generation two processes occur, in the first step, a polarization wave at second harmonic \((2\omega_1)\) is produced which has a phase velocity and wavelength in the medium which are determined by refractive index \((n_1)\) of the fundamental wave and in the second stage transfer of energy from the polarization wave to electromagnetic wave occurs at frequency \(2\omega_2\). The index of refraction \((n_2)\) defines the phase velocity and wave length for the doubled frequency. For efficient energy transfer, two waves should remain in phase, that is \(n_1 = n_2\). Due to normal dispersion occurring in the material in the optical region, the
radiation will generally lag behind the polarization wave. The phase mismatch between the polarization and electromagnetic wave is given by following relationship [50].

\[ \Delta K = \left( \frac{4 \pi}{\lambda} \right) \left| n_1 - n_2 \right| \] \quad (2.3)

A suitable medium is required to realize the nonlinear effect. A noncentrosymmetric crystal exhibits the following properties:

I. wide optical transparency domain
II. large nonlinear figure of merit for frequency conversion
III. high laser damage threshold
IV. readily available in large single crystal
V. wide phase matchable angle
VI. ability to process into crystal and thin films
VII. ease of fabrication
VIII. nontoxicity and good environmental stability
IX. high mechanical strength and thermal stability
X. fast optical response time.

2.3 Nonlinear Optical Materials

Advancements in the development of NLO materials can be divided into the following different areas.

I. Discovery of new model NLO materials.
II. Growth of promising NLO crystals
III. Improving the characteristics of NLO crystal

Many organic and inorganic materials are highly polarizable and thus are good candidates for study. However the net polarization of a material depends on its symmetry properties, with respect to the orientation of the impinging fields. It can be seen that the odd order terms in equation (2.2) are orientationally independent, but even terms vanish in a centrosymmetric environment. Thus the materials for second order NLO must be orientationally non centrosymmetric. Nonlinear optical materials are the key elements for photonics technology as photons are capable of processing information with the speed of light.

The second order nonlinear optical effect known as second harmonic generation (SHG) was observed by Franklin and co workers in 1961 by excitation of a quartz crystal with light of wavelength $\lambda = 694 \text{ nm}$ from a ruby laser, resulting the creation of $\lambda = 347 \text{ nm}$ light, since then, the utilization of SHG and related phenomenon from crystal has been of great interest, including the ability to convert the light from a laser to a different wavelength via optical parametric oscillation discovered in 1968.

There are three different classes of NLO materials as follows:

- Organic NLO Materials
- Inorganic NLO Materials
- Semi organic NLO Materials
2.3.1 Organic NLO Materials

The development of highly efficient nonlinear optical materials for opto-electronic applications such as high speed information processing, optical communication and optical data storage have been the subject of intense research activity throughout the world over the past few decades. Organic NLO materials are more nonlinear than inorganic NLO materials since they are often formed by weak Vander Waals and hydrogen bonds and hence possess high degree of delocalization. The organic compound apart from inherent increased nonlinearity possess amenability for synthesis, scope for introducing desirable characteristics by multi functional substitution, higher resistance to optical damage and so on. The chirality and hydrogen bonds which contribute substantially for remarkable SHG activity can be identified from material properties. The organic NLO materials are soft in nature; also have intense absorption in UV region [51, 52]. The organic NLO materials play an important role in SHG, frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability etc. The organic NLO materials have higher second harmonic generation efficiency and also exhibit substantially greater laser damage thresholds. Considerable amount of work has been done to understand the microscopic origin of nonlinear behavior of organics. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental
investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electro-optic effect and large second or third order hyperpolarizibilities compared to inorganic NLO materials [53, 54]. A large number of organic compounds with non localized $\pi$ electron system and larger dipole moment have been synthesized recently to realize the nonlinear susceptibilities larger than inorganic optical materials, however their potential applications are limited by poor chemical stability, high cut-off wavelength caused by a large organic non conjugated system and poor phase matching properties caused by large birefringence which result from the layer stacking of the structure and the other factor. The basic structure of organic NLO materials is based on the $\pi$ bond systems. Due to the overlap of $\pi$ orbital, delocalization of electronic charge distribution leads to a high mobility of electron density. Functionalization of both ends of the $\pi$ bond system with appropriate electron donor and acceptor groups can enhance the asymmetric electronic distribution in either or both the ground and excited states, leading towards an increased optical nonlinearity [55].

The organic NLO materials usually have hyperpolar molecule, but most typical organic solvents have a dipole moment less than about 3 Debye. High polar materials suffer from decomposition at elevated temperature, both in melt and solid state. Hence, normally the
solution growth is adopted for growth of organic NLO materials [56, 57]. Due to the high nonlinearity much attention has been given to organic NLO materials. These materials have promising applications including telecommunication, optical computing and optical data storage applications [58]. Generally successful and popular approach towards such materials is achieved in two steps which first imply the synthesis of extended conjugated systems with donor and acceptor groups that can ensure the largest known second and third order molecular hyperpolarizability \( \beta \) of any class of materials compared to inorganic nonlinear optical (NLO) materials. The nonlinearity associated with chromophores in the organic materials leads to observable bulk nonlinearity \( \chi^2 \) only if the chromophores are oriented in a noncentrosymmetric environment [59].

### 2.3.2 Inorganic NLO Materials

The inorganic materials are efficient NLO materials, having thermal stability and mechanical robustness. The pure inorganic NLO materials have excellent mechanical and thermal properties but possess' relatively modest optical nonlinearity due to the lack of extended \( \pi \) electron delocalization. These materials possess excellent transmittance in the visible region which is advantageous for optoelectronics applications. The inorganic materials have the ionic bonded molecules; they are highly soluble in water. These inorganic materials are very
sensitive to pH and ionic strength. The inorganic NLO materials crystals do have high thermal stability, while the organic NLO crystals are thermally stable up to the melting point only. Therefore, the Potassium Dihydrogen Phosphate (KDP) which belongs to inorganic class of NLO material has been widely used for laser applications in past decades. The inorganic NLO crystals grown from any common method of growth has no limitation on size of grown crystal as in case of organic crystals. The crystals of inorganic materials have an excellent X-ray diffraction quality among all types of NLO materials. The inorganic NLO crystals got nonlinear optical and electro-optical property and they are widely used in X-ray monochromators [60-62]. The potassium dihydrogen phosphate(KDP), ammonium dihydrogen phosphate(ADP), sodium dihydrogen phosphate (DSHP), potassium tetanyl phosphate (KTP) are some of the well acclaimed inorganic NLO material crystals used for different nonlinear and optoelectronics applications.

2.3.3 Semi Organic NLO Materials

In recent years there has been tremendous development in the field of semi organic nonlinear optical materials. These materials have the property of combining on one hand the high optical non-linearity and chemical flexibility of organic compound and on the other hand the mechanical properties and chemical inactivity of inorganic materials. These materials are applicable for high power frequency
conversion and possess the better non linearity and more SHG efficiency than KDP [63-65].

Presently inorganic and organic crystals are being replaced by this new semiorganic class of NLO materials. The semiorganic materials possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity, good mechanical hardness and wide transmission window [66, 67]. Recent interest is concentrated on metal complexes of thiourea and the crystals of amino acids owing to their large nonlinearity [68-69]. The $\pi$-conjugated network in organic system with large nonlinearity has significant absorption in the visible region. Hence, for second harmonic generation (SHG) in the blue-near-UV region, more transparent and less extensively delocalized organic materials like urea or its analogs such as thiourea have been considered. Thiourea is one such organic material which is coplanar in structure and is a resonance hybrid of three resonance structure with each contributing roughly an equal amount. The $\pi$-orbital electron delocalization in thiourea arising from the mesomeric effect is responsible for their nonlinear optical response and the absorption in the near ultraviolet region. Growth of single semi organic NLO crystal has been a subject of perennial concern in order to use these materials for device application. However, to enable a material to be a potentially useful for nonlinear optical applications, the material should also be available in bulk form.
2.4 KDP Family Crystals

Potassium dihydrogen phosphate (KDP) crystals exhibit excellent electro-optical and nonlinear optical properties and is commonly used in frequency conversion applications such as second, third and fourth harmonic generation and in electro-optic modulation. Easy growth of large single crystals, a broad transparency range, a high optical damage threshold, and relatively low production cost are all qualities that make this phosphate crystal suitable for variety of optical applications.

2.5 Crystals of Thiourea Metal Complexes

Nonlinear optical (NLO) properties of organometalllic complexes are recently under great research due to their potential applications in optoelectronics. Molecules resulting from charge transfer between electron donating and withdrawing groups are good candidates owing to their large dipole moment and in transition dipole moment. Some intuitive understanding of the advantages of NLO properties of co-ordination compounds (Thiourea complexes) was reported in the literature [4-7]. There is small energy gap between ground and excited states and more optical absorption transitions, such as ligand to metal and metal to ligand charge transfer bands in UV-Visible region takes place. The intensities of these bands are associated with their transition dipole moment. The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form the
extensive network hydrogen bonds. Some of the reported thiourea metal complexes are Zinc thiourea chloride (ZTC), Zinc thiourea sulfate (ZTS), Bis cadmium thiourea chloride (BTCC), Copper thiourea chloride (CTC), Bis thiourea cadmium acetate (CTA) etc. In the present investigation Zinc thiourea chloride (ZTC), Zinc (tris) thiourea sulfate (ZTS) and Bis thiourea cadmium chloride (BTCC) single crystals have been grown from the aqueous solution and their dielectric study has been carried out using microwave bench employing transmission line wave guide method at frequency of 8 and 12GHz. In order to improve the SHG efficiency, an amino acid L-Alanine and Glycine was doped in mole% with of Zinc (tris) thiourea sulfate (ZTS) and Bis thiourea cadmium chloride (BTCC). Also L-Alanine was doped with Zinc thiourea chloride (ZTC). We observed enhancement in SHG efficiency after addition of L-Alanine and Glycine. The structural, thermal and optical properties were also studied.

2.6 Role of Amino Acids in Nonlinearity

The amino acids play most important role in the nonlinear optical crystals. The importance of amino acids in NLO applications is due to the fact that in most of the amino acids chiral carbon atom and zwitterionic ion is present. The grown crystal possesses the combined advantages of the organic amino acid (such as high optical nonlinearity of organic materials and favorable mechanical and thermal properties of the inorganic materials) because of the presence of amino acids.
Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG). The salts of amino acids like L-arginine, L-histidine are reported to have high second harmonic conversion efficiency [70-74]. Glycine is natural and simplest amino acid. According to the structural analysis of ferroelectric, triglycine sulphate there are two kinds of glycine groups, glycinium ions and zwitter ion. This structure is responsible for NLO property of Glycine. L-Alanine is another simplest amino acid having four different groups about $\alpha$-carbon atom, this tetrahedral structure of L-Alanine confers the optical activity on amino acid. The L-Alanine has SHG efficiency of about one third of that well-known KDP [75]. There are many reports in the literature about the crystals of amino acids and amino acid doped crystals which may be used as better alternative of KDP for laser fusion experiments. In the present investigation L-Alanine and Glycine are used as dopant for Zinc (tris) thiourea sulfate (ZTS), Bis thiourea cadmium chloride (BTCC) and L-Alanine for Zinc thiourea chloride (ZTC) crystal in order to enhance their nonlinearities. The new nonlinear optical crystal Bis glycine hydrogen bromide (BGHB) was also grown. The thermal, optical and the structural properties were also studied.
References


33. N Vijayan, R Rajasekaran, G Bhagavannarayana, R Ramesh Babu, R Gopalakrishnan, M Palanichamy and P Ramasamy. “Growth and


62. Guohui Li, Liping Xue, Genbosu, Zhengdong Li, XinXin Zhuang and Youping He. “Rapid growth of KDP crystal from aqueous


