CHAPTER 2

NON LINEAR OPTICAL (NLO) MATERIAL & ITS APPLICATIONS

2.1 NON LINEAR OPTICAL (NLO) MATERIAL

Linearity is one of the basics of classical optics. Light waves usually do not interact. In other fields of electricity and magnetism, yet nonlinearities are known since scientists have begun to study the phenomena in more detail. Nonlinear optics (NLO) deals with the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude (Sauter 1996). Second harmonic generation (SHG) is a nonlinear optical process that results in the conversion of an input optical wave into an output wave of twice the input frequency.

In the field of optics, however, nonlinear effects became a subject of interest only after the invention of the laser. As laser physics started with the ruby laser with its high pulse intensities, it took only few years after the invention of the laser (Prasad et al. 1991) that many classical experiments in nonlinear optics were successfully performed. Among the first were the second order processes like the experiments on second harmonic generation (Chemla 1987)on sum frequency generation (Pal et al. 2003) and on optical rectification by Bass et al.(1962).

The growth of single crystals and their characterizations towards device fabrications are important in both basic and applied scientific research (Marcy et al. 1995). NLO frequency conversion materials have significant impact on laser technology. However, some special nonlinear optical problems called for crystals with improved properties like high transparency in the UV region, high nonlinearity etc. This leads to the synthesis of new NLO materials of high optical quality.

There is a current interest in finding materials that will extend the wavelength capability of laser sources into UV region and new frequency conversion materials will have significant impact on applications such as optical communications technology and laser driven inertial confinement fusion experiment. This demands from optical and device physicists for improved and effective materials to call for world-wide research on NLO materials which is most targeted and speculative.

2.2 WORKING PRINCIPLE

NLO effects belong to a broader class of electromagnetic phenomena described within the general framework of macroscopic Maxwell equations. The Maxwell equations not only serve to identify and classify nonlinear phenomena in terms of the relevant nonlinear optical susceptibilities or, more generally, nonlinear terms in the induced polarization, but also govern the NLO propagation effects.

At very low fields, the induced polarization is directly proportional to the electric field.

$$P = \varepsilon_0 \chi E \qquad (2.1)$$

Where, χ is the linear susceptibility of the material, E is the electric field vector, ε_0 is the permittivity of free space.

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

$$P = \varepsilon_0 \{\chi^{(1)} E + \chi^{(2)} E \,.\, E + \chi^{(3)} E \,.E \,.\, E + \ldots\} \qquad (2.2)$$

In nonlinear terms, product of two or more oscillating fields gives oscillation at combination of frequencies and therefore the above equation can be expressed in terms of frequency as

$$P(-\omega_0) = \varepsilon_0 \{\chi^{(1)}(-\omega_0; \omega_1).\, E(\omega_0) + \chi^{(2)}(-\omega_0; \omega_1, \omega_2).\, E\omega_1.\, \omega_2 +$$

$$\chi^{(3)}(-\omega_0; \omega_1, \omega_2, \omega_3).\, E\omega_1.\, \omega_2.\, \omega_3 + \ldots.\} \qquad (2.3)$$

where $\chi^{(2)}$, $\chi^{(3)}$ .... are the nonlinear susceptibilities of the medium. $\chi^{(1)}$ is the linear term responsible for material's linear optical properties like, refractive index, dispersion, birefringence and absorption. $\chi^{(2)}$ is the quadratic term which describes SHG in non-centro-symmetric materials. $\chi^{(3)}$ is the cubic term responsible for third harmonic generation, stimulated Raman scattering, phase conjugation and optical bistability.

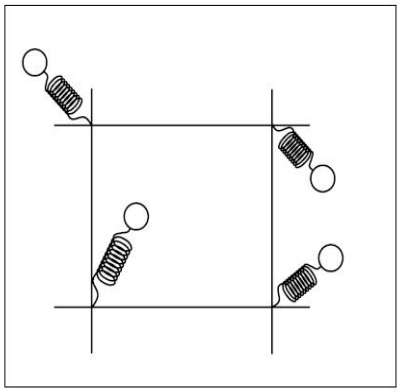

Figure2.1Electrons in a nonlinear crystal are bound in a potential well,holding the electrons to lattice points

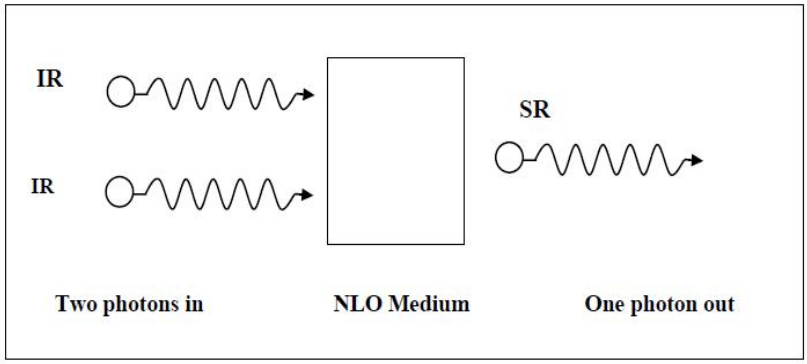

Figure2.2Two photons are welded together to produce a single photonwith the energy of both original photons

Hence the induced polarization is capable of multiplying the fundamental frequency to second, third and even higher harmonics. The coefficients of $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ give rise to certain optical effects. These are listed in Table 2.1.

If the molecule or crystal is centro-symmetric then $\chi^{(2)} = 0$. If a field +E is applied to the molecule (or medium), Equation 2.3 predicts that the polarization induced by the first nonlinear term is predicted to be $+E^2$, yet if the medium is centro-symmetric the polarization should be $-E^2$. This contradiction can only be resolved if $\chi^{(2)} = 0$ in centro-symmetric media.

Table 2.1 Optical effects of nonlinear materials

Order	Crystal	Effects	Application
1.	$\chi^{(1)}$	Refraction	Optical fibers
2.	$\chi^{(2)}$	SGH ($\omega + \omega = 2\omega$)Frequency mixing ($\omega_1 \pm \omega_2 = \omega_3$) Pockels effects ($\omega + 0 = \omega$)	Frequency doubling Optical parametric oscillators Electro optical modulators
3.	$\chi^{(3)}$	wave mixing phase gratings Kerr effect Optical amplitude	Raman Coherent spectroscopy, Real time holography, Ultra high speed optical gates Amplifiers, choppers etc,

If the same argument is used for the next higher order term, +E produces polarization $+E^3$ and – E produces $-E^3$, so that $\chi^{(3)}$ is the first non-zero nonlinear term in centro-symmetric media. In SHG, the two input wavelengths are the same

$$2\omega_1 = \omega_2 \text{ (or) } (\lambda_1 = 2\lambda_2) \qquad (2.4)$$

During this process, a polarization wave with the second harmonic frequency $2\omega_1$ is produced. The refractive index, n_1 is defined by the phase velocity and wavelength of the medium. The energy of the polarization wave is transferred to the electromagnetic wave at a frequency ω_2 .The phase velocity and wavelength of this electromagnetic wave are determined by n_2, the refractive index of the doubled frequency. To obtain high conversion efficiency, the vectors of input beams and generated are to be matched.

$$\Delta K = 2\pi/\lambda(n-n) \qquad (2.5)$$

where ΔK represents the phase–mismatching. The phase–mismatch can be obtained by angle tilting, temperature tilting or other methods. Hence, to select a nonlinear optical crystal, for a frequency conversion process, the necessary criterion is to obtain high conversion efficiency. The conversion efficiency, (η) where d_{eff} is the effective nonlinear coefficient, L is the crystal length, P is the input power density and ΔK is the phase – mismatching. In general, higher power density, longer crystal, large nonlinear coefficients and smaller phase mismatching will result in higher conversion efficiency. Also, the input power density is to be lower than the damage threshold of the crystal. Table 2.2 lists the laser and crystal parameters for selecting a NLO crystal.

Table 2.2 Parameters for selecting a NLO crystal

Laser parameters	Crystal parameters
NLO process	Type of phase matching
Power, Repetition rate	Damage threshold
Divergence	Acceptance
Band width	Spectral acceptance
Beam size	Crystal size, Walk – Off angle
Pulse width	Group velocity mismatching
Environment	Moisture, temperature acceptance

2.3 LIFETIME OF NONLINEAR CRYSTALS

In many cases, a nonlinear crystal used for nonlinear frequency conversion has a very long life time, which is longer than that of the whole laser system. The crystal material is essentially not modified during operation (Agarwal et al. 1999). However, a reduced crystal lifetime can occur under various circumstances:

- Excessive optical intensities during operation may instantly damage a crystal. Unfortunately, nonlinear crystals often need to be operated not far from their optical damage threshold in order to achieve sufficiently high conversion efficiency. This implies a trade-off between conversion efficiency and crystal lifetime. Note that even if the nominal intensity is below the nominal damage threshold, there may be problems due to fluctuations of the beam power or local intensity (e.g., if a beam profile has “hot spots”), or due to isolated defects in a crystal, which are more sensitive than the regular crystal material.

- Even well below the threshold for instant damage, some crystal materials exhibit a continuous degradation within the used volume, e.g. in the form of "gray tracking". Such phenomena are particularly common for operation with ultraviolet light. Note that a gradual degradation can also lead into instant catastrophic damage via excessive heat generation.

- Hygroscopic crystal materials deteriorate when they are not always kept in sufficiently dry air (or a dry purge gas). This applies e.g. to KDP and BBO, and in a lesser extent to LBO. It can be helpful to keep such a crystal at a somewhat elevated temperature, which makes it easier to keep it dry.

- Operation of nonlinear crystals at temperatures below room temperature (in order to achieve phase matching) is generally problematic, as it may lead to condensation of water on the crystal surfaces if the surrounding air is not very dry. Even if the crystal material or coating is not sensitive to water, small water droplets may focus laser radiation more tightly than under normal operation, and thus damage the crystal material.

- Crystals which are non-critically phase-matched in a crystal oven may exhibit problems when the crystal temperature is changed too rapidly or too often. In particular, anti-reflection coatings may be damaged due to different thermal expansion coefficients of the involved materials.

Crystal lifetime can also be strongly dependent on the material quality, although certain degradation phenomena appear to be intrinsic limitations of the material.

For high-power UV generation, nonlinear crystals may become consumables they need to be replaced quite often within the lifetime of the whole laser system (e.g., every few hundred hours of operation). Often, several problematic aspects come together in the regime UV generation: crystal materials are generally more sensitive to ultraviolet light (having high photon energies), exhibit a higher absorption in that regime, and in case of ultra-short pulses the high group velocity mismatch enforces the use of a shorter crystal, which requires high optical intensities for a given conversion efficiency.

Nonlinear Optical (NLO) materials have long been known to interact with light, to produce a nonlinear response and the composition of these materials, generally falls into one of two classes, either inorganic or organic.

2.4 ORGANIC CRYSTALS

During the past two decades, many materials chemists have focused on the development of organic molecules that can serve as the basis of cost-effective and flexible electronic, optical and energy conversion devices. Among the potential candidate molecules, metal-free or metal-containing conjugated organic molecules offer high-order electronic conjugation levels that can directly support fast charge carrier transport, rapid optoelectric responses, and reliable exciton manipulation. In recent years, significant efforts have been made in the field of organic nonlinear optical materials because of their potential applications in SHG, frequency mixing, and electro optic modulation and photorefractive properties. The extensive investigations are carried out on organic materials due to their high nonlinearity compared to inorganic material. The origin of nonlinearity in the NLO material is due to the presence of delocalized π-electron system connecting donor and acceptor groups which enhance the asymmetric polarization.

Recently, an extremely large number of organic compounds with non-localized 3-electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the inorganic optical materials (Chandrasekaran et al. 2012). The SHG efficiency of Benzoyl glycine is much higher than that of KDP (Lydia Caroline M et al. 2009). Many organic molecules have been reported to have larger nonlinear optical susceptibilities within the 0.5-2.0 μm transparency domain. Organic materials have another advantage that the properties of organic materials can be optimized by modifying the molecular structure using molecular engineering and synthesis (Bhat et al. 2002). A very large operating bandwidth modulation in organic electro-optic devices can be obtained through its low dielectric constant at low frequencies. The organic materials exhibit extremely large nonlinear optical and electro-optic effects. The Electronic nonlinearities are essentially based on the molecular units. Due to the important advantages of the organic materials, they will be widely used in the field of organic chemistry, materials science, physics and electrical engineering.

2.4.1 Pros of Organic Crystals

- Low cost
- Ease of fabrication
- Integrating in to a single devices
- Easy to do fine tuning of its NLO properties by turning its chemical structure
- Low dielectric constant
- Inherent synthetic flexibility
- High optical damage threshold

2.4.2 Cons of Organic Crystals

- Poor physico-chemical stability
- Low hardness and cleavage tendency
- Poor thermal strength obstructs their device applications.

2.5 INORGANIC CRYSTALS

Inorganic crystals are mostly ionic bonded. It is always easier to synthesize inorganic materials. These are covalent and ionic bulk materials where the optical nonlinearity is a bulk effect. The phenomenon of SHG in inorganic materials was first reported in 1961. The examples of this type of crystals are lithium niobate ($LiNbO_3$), potassium niobate ($KNbO_3$), barium titanate ($BaTiO_3$), potassium Titanyl phosphate (KTiOPO4, KTP), potassium dihydrogen phosphate ($KH2PO_4$,KDP), potassium deuterium phosphate (KD*P), ammonium dihydrogen phosphate ($NH3PO_4$, ADP), lithium iodate ($LiIO_3$), etc. In the beginning, studies were concentrated on inorganic materials such as quartz, potassium dihydrogen phosphate (KDP), lithium niobate ($LiNbO_3$), and its analogues, potassium titanyl phosphate (KTP) and its analogues (Khandpekar et al. 2011, Bellamy 1995). KDP is used as a base material to compare second harmonic generation and laser damage threshold values for all crystals. Many of these materials have been successfully used in commercial frequency doublers, mixers and parametric generators to provide coherent laser radiation with high frequency conversion efficiency in the new region of the spectrum inaccessible by other nonlinear crystal conventional sources. Lithium niobate ($LiNbO_3$) crystals are one of the most investigated materials for widespread and promising applications in nonlinear optics, e.g., for parametric amplification and SHG, holographic data storage, optical information processing, phase conjugation, and wavelength filters (Raja Shekar et al. 2011). Often these materials have high melting point and

high degree of chemical inertness. High temperature oxide materials are well studied for diverse applications like piezoelectric, ferroelectricity and electro-optics. Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively moderate optical nonlinearity (Chithambaram et al. 2011).

2.5.1 Pros of Inorganic Crystals

- High melting point,
- High mechanical strength and
- Compatible physical properties

2.5.2 Cons of Inorganic Crystals

- Modest optical nonlinearity due to the lack of extended 3-electron dislocation
- Absorption in the visible region,
- Poor response time and
- Degradative photorefractive effects, low laser damage threshold (~10 MW cm^{-2})
- Poor optical transparency

2.6 SEMI ORGANIC CRYSTALS

In recent years the need of NLO materials is much more than other materials because of their applications in optoelectronics and photonics. Materials with large second order optical nonlinearities, short transparency cutoff wavelength and stable physico thermal performance are needed in order to realize many of these applications. To overcome the problems in

organic and inorganic crystals, the research of combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semi-organic materials.

In semi-organic materials the organic ligand is ionically bonded with inorganic host, because of this the new semi-organic crystals are having higher mechanical strength and chemical stability (Aggarwal et al. 1999). The semi-organic crystals possess several attractive properties such as high damage threshold, wide transparency region and high nonlinear coefficient. The contribution from the delocalized π electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro optic coefficients. Many device applications of NLO require single crystals in the bulk form. This is achieved only with the semiorganic crystals, which exhibit wide transparency, large and bulky crystal morphologies. It offers a wide range of metals with different oxidation states and ligands, which can give rise to tunable electronic properties. Metal co-ordination complexes provide the following

2.6.1 Pros of Semi Organic Crystals

1. Enhancement of physicochemical stability.

2. Breaking of Centro symmetry of the ligand in the crystal.

3. Increase in NLO intensity via metal-ligand bridging interactions.

4. The central ion not only offers a certain anisotropic field to keep NLO active chromophores but also involved in NLO process.

5. Hyper polarizability value can also be drastically varied with electronic conFigureuration of metal ions.