Rev. Adv. Mater. Sci. 30 (2012) 175-183

REVIEW ON THEORETICAL ASPECT OF NONLINEAR OPTICS

S. Suresh[1], A. Ramanand[1], D. Jayaraman[2] and P. Mani[3]

[1]Department of Physics, Loyola College, Chennai-34, India
[2]Department of Physics, Presidency College, Chennai-05, India
[3]Department of Physics, Hindustan University, Padur, India

Received: August 25, 2011

Abstract. Nonlinear optical (NLO) materials play a major role in the field of photonics including optical information processing, sensor protector applications, data storage etc. Some organic compounds exhibit large NLO response, in many cases, orders of magnitude larger than widely known inorganic materials. The importance of amino acid in NLO application is due to the fact that all the amino acids, except glycine contain chiral carbon atom and crystallizes in non-centrosymmetric space group. Another added advantage of NLO active material is the presence of namely amino group and carboxyl group, which make it transparent in the UV-Visible region. Hence, this review paper presents theoretical aspect of nonlinear optics, solution growth of nonlinear crystals and the analysis of second order and third order NLO properties using Kurtz powder and Z-Scan technique.

1. INTRODUCTION

Non-linear optics has been a rapidly growing scientific field in recent decades. It is based on the phenomenon related to the interaction of intense coherent light radiation with mater. Non-linear optics is the study of the interactions of light with matter under conditions in which the non-linear response of the atoms plays an important role. During the past three decades optics has secured a good place in application areas previously dominated by electronics. Developments in the field of non-linear optics hold promise for important applications in optical information processing, telecommunications and integrated optics. Because of the emergence of this field from solid – state physics in which inorganic semiconductors, insulators, and crystals have constituted a major part of the scientific base, the early experimental and theoretical investigations were primarily concerned with materials from these classes.

Photonic crystals are expected to play an important role in the development of new optical devices [1,2]. The device possibilities for photonic crystals will be greatly enhanced by the addition of optical nonlinearity; such possibilities include ultrafast optical switching for communication and even optical computing [3-9].Nonlinear optics (NLO) has been an active field of research since the late 1960s' with the advent of lasers followed by the demonstration of harmonic generation in quartz [10].

The non-linear terms in the interaction of light with atoms give rise to a variety of optical processes, in addition to multiphoton absorption (which is also a non-linear phenomenon arising because of the excitation of an atom by processes in which two or more photons are absorbed). A beam of monochromatic light in interaction with atoms can be partially converted into light, whose frequencies are harmonics of the fundamental frequency. Similarly beams of two or more different frequencies

Corresponding author: S.Suresh, e-mail: sureshsagadevan@yahoo.co.in

can combine to produce light beam and can alter the refractive index of a medium through which it passes, by an amount proportional to the intensity of the beam. Scattering of light changes its nature for sufficiently strong incident light, where stimulated scattering becomes important.

Non-linear optics thus embraces a wide variety of phenomenon and is an extensive field theory. The key that opened the door to Non-linear optics was the availability of high-power lasers of hundreds of varieties. These lasers produce highly monochromatic beams, which can be concentrated to extremely high intensities. A peculiar property of the laser beam, essential to non-linear optics, is its high degree of coherence, because the stimulated emissions of different radiating atoms are synchronized. Coherence enables one to combine the weak contributions of non- linear interaction from widely separated parts of an excited medium, so as to produce an appreciable resultant.

2. CONCEPT OF NONLINEAR OPTICAL PHENOMENON

While the first nonlinear effects were seen in the 1960s' with the invention of lasers followed by the demonstration of harmonic generation in quartz, the effects themselves have been postulated during 1930s'. Only with the invention of laser, it has been possible to attain the high intensities required to experiment in this new field.

One of the most intensively studied nonlinear optical phenomenon and specifically the NLO property studied in the present paper is second harmonic generation. 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. The process occurs within a nonlinear medium, usually a crystal. Such frequency doubling processes are commonly used to produce green light (532 nm) from, an Nd: YAG (Yttrium-Aluminium-Garnet) laser operating at 1064 nm. The light propagated through a crystalline solid, which lacks a center of symmetry, generates light at second and higher harmonics of the applied frequency. This important nonlinear property of noncentrosymmetric crystals is called Second Harmonic Generation (SHG) and this phenomenon and the materials in which it occurs are the subject of intense study.

NLO materials are usually divided into different classes that refer to the order *n* of the nonlinear susceptibility $\chi^{(n)}$ that describes the response of the material, to the electric field associated with the light radiation. NLO materials are usually divided into two main classes:

For instance, $\chi^{(2)}$ materials are used for second harmonic generation. These materials must have an asymmetrical structure. Their refractive index can also be controlled with an external electric field, a property that is referred to as the electro-optic effect. This property is of principal importance for many applications and is currently used in electro-optic modulators. It also plays a major role in the photorefractive effect. $\chi^{(3)}$ materials are expected to play a key role in all optical switching devices since their optical properties can be controlled by light. However, due to the higher order of the nonlinearity these materials are usually less efficient and have not reached the maturity of $\chi^{(2)}$ materials for device applications. A number of research efforts are underway to improve their performance and to optimize their efficiency in new device geometry.

In the case of centrosymmetric crystal $\chi^{(2)} = 0$, the material cannot exhibit second harmonic generation but can exhibit harmonic generation of third and fifth order. Two stage processes occur during harmonic generation. A polarization wave at the second harmonic $2\omega_1$ is produced in the first stage. The phase velocity and wavelength in the medium are determined by n_1, the index of refraction. 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 wavelength for the doubled frequency.

3. Z-SCAN TECHNIQUE

The crystals like Aluminium Ammonium SulphateDodecahydrate (AASD) and Potassium AluminiumSulphateDodecahydrate (PASD) belong to centrosymmetric class ($\chi^{(2)} = 0$) and hence Second Harmonic Generation (SHG) is found to be absent Z-Scan technique can be employed to investigate the third order NLO properties in centrosymmetric class of crystals. It is a single beam technique developed by Sheik Bahae to measure the magnitude of nonlinear absorption as well as the sign and magnitude of nonlinear refraction.

A laser beam propagating through a nonlinear medium will experience both amplitude and phase variations. If transmitted light is measured through an aperture placed in the far field with respect to focal region, the technique is called closed aperture Z-Scan. In this case, the transmitted light is sensitive to both nonlinear absorption and nonlinear refraction.

On the other hand without an aperture, the mode of measurement is referred to as open aperture Z-Scan. Z-Scan methods yield the real and imaginary parts of nonlinear susceptibility $\chi^{(3)}$ respectively. Usually closed aperture Z-scan data are divided by open aperture data to cancel the effect of nonlinear absorption contained in the closed aperture measurements. The new graph called divided Z-scan contains information on nonlinear refraction alone.

In Z-Scan setup a He-Ne laser of wavelength of 632.8 nm will be used. A plane polarized Gaussian laser beam propagating in the Z-direction is focused on a narrow waist of 40 μm with the help of a convex lens of focal length 12 cm to give the intensity 6.25 x 10^7 N/m^2 at the focus. The crystals used should be grounded to 1 mm thickness. The intensity of transmitted beam can be measured as a function of the sample position Z, measured with respect to focal plane both in OA (Open aperture) and CA(Closed aperture) Z-Scan method.

If the transmitted beam is maximum/ minimum it is referred to as peak/valley. The peak to valley configuration of the CA (Closed aperture curves of AASD and PASD) crystals shows that the refractive change is negative, exhibiting a self-defocussing effect. In the case of L-lysine hydrochloride dehydrate (LHCL) crystal, the valley to peak configuration is obtained showing a positive change in nonlinear refractive index with self-focussing effect.

Therefore, the crystals AASD, PASD and LHCL can be used in optical limiter, broad band Optical windows, all optical switching devices, Two Photon Absorption (TPA) microscopy, Photonic (negative nonlinearity) devices and holographic applications (negative refractive index). It is concluded that the crystals AASD and PASD are not exhibiting SHG due to centrosymmetric nature of the materials.

4. THEORY OF NONLINEAR OPTICS

When the electromagnetic field of a laser beam is acting on an atom or a molecule, it induces electric polarization, which gives rise to many of the unusual and interesting properties that are optically nonlinear. In a dielectric material, the influence of an electric field causes distortion in the spatial distribution between the electrons and the nucleus. These distortions cause electric dipoles, which in-turn manifest as polarization. At very low fields, the induced polarization is directly proportional to the electric field. However, at intense electric fields, polarization becomes independent of the field and the susceptibility becomes field dependent. The induced polarization is capable of multiplying the fundamental frequency to second, third order and even higher harmonics. The reradiation from the oscillating dipoles differs in amplitude with respect to the incident sinusoidal electric field. As a consequence, the distorted reradiated waves contain different frequencies from that of the incident wave.

When the electric field associated with the radiation is small, the induced polarization is given by

$$\vec{P} = \varepsilon_0 \chi^{(1)} \vec{E}, \tag{1}$$

where $\vec{P}$ is the polarization vector, $\vec{E}$ is the electric field vector, $\chi^{(1)}$ is the linear susceptibility, and ε_0 is the permittivity of free space.

When the optical electric field strength is very high and comparable to the intra-atomic electric field, the induced polarization is given by

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

where $\chi^{(2)}$, $\chi^{(3)}$…. are the nonlinear susceptibilities of the medium.

The nonlinear susceptibilities have decreasing magnitudes as their order increases at $\chi^{(1)}$: $\chi^{(2)}$: $\chi^{(3)} \approx$ 1:10^{-8}: 10^{-16}. The first order susceptibility which is the linear term, $\chi^{(1)}$, gives rise to refractive index, absorption, dispersion and birefringence of the medium. The second order, $\chi^{(2)}$, gives rise to Second Harmonic Generation (SHG), frequency mixing and parametric generation, while the third order nonlinear susceptibility, $\chi^{(3)}$,gives rise to third harmonic generation, stimulated Raman scattering, optical bistability and conjugation. Let us study the interaction of two travelling waves

$$\vec{E}_1(z,t) = \vec{E}_1 \cos(\omega_1 t + k_1 z), \tag{3}$$

$$\vec{E}_2(z,t) = \vec{E}_2 \cos(\omega_2 t + k_2 z), \tag{4}$$

Considering the second order nonlinearity in polarization alone

$$\vec{P} = \chi^{(2)} \vec{E}^2, \tag{5}$$

$$\vec{P} = \chi^{(2)} \Big[\vec{E}_1^2 \cos^2(\omega_1 t + k_1 z) + \vec{E}_2^2 \cos^2(\omega_2 t + k_2 z) + 2\vec{E}_1 \vec{E}_2 \cos^2(\omega_1 t + k_1 z) \cos^2(\omega_2 t + k_2 z) \Big]. \tag{6}$$

It can be found that the polarization consists of a number of components with different frequencies viz.,

$$\vec{P}_1 \omega_1 = \chi^{(2)} \vec{E}_1^2 \cos[2(\omega_1 t + k_1 z)], \tag{7}$$

$$\vec{P}_{2\omega_2} = \chi^{(2)}\vec{E}_2^2 \cos[2(\omega_2 t + k_2 z)], \quad (8)$$

$$\vec{P}\omega_1 + \vec{P}\omega_2 = \chi^{(2)}\vec{E}_1\vec{E}_2 \times \cos[(\omega_1 + \omega_2)t + (k_1 + k_2)z], \quad (9)$$

$$\vec{P}\omega_1 - \vec{P}\omega_2 = \chi^{(2)}\vec{E}_1\vec{E}_2 \times \cos[(\omega_1 - \omega_2)t + (k_1 - k_2)z], \quad (10)$$

and a steady term

$$\vec{P}_{direct} = \left(\frac{\chi^{(2)}}{2}\right)\left(\vec{E}_1^2 + \vec{E}_2^2\right). \quad (11)$$

The different components of nonlinear polarization generate electromagnetic waves having frequencies different from those of the incident waves. Fraction of the incident energy used to create nonlinear polarization can be reradiated at one or more number of different frequencies.

By employing proper phase matching conditions it is possible to generate any one of these components of the polarization wave with high efficiency.

$$k_1 + k_2 = k_3 \quad (\text{Or}) \quad \frac{n_1\omega_1}{c} + \frac{n_2\omega_2}{c} = \frac{n_3\omega_3}{c}. \quad (12)$$

Franken et al. (1961) observed the frequency doubling for the first time, by irradiating a quartz crystal with a ruby laser beam that operated at 694.2 nm. A very small amount of the light striking the crystal was converted into a light with a wavelength of 347.1 nm. This wavelength lies in the ultraviolet region of the spectrum and is exactly half the wavelength and twice the frequency of the incident laser light.

For efficient energy transfer, the two waves should remain in phase i.e., n_1=n_2. Due to normal dispersion occurring in the materials 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

$$\Delta k = \left(4\pi/\lambda\right). \quad (13)$$

For improving the efficiency of the doubled frequency, the crystal has to be phase matched .The dispersion in the materials can be offset by using the natural birefringence. There exists two indices of refraction for a given direction of propagation, corresponding to the two allocated orthogonally polarized modes. By an appropriate choice of polarization and direction of propagation, it is often possible to obtain phase matching or index matching, where $\Delta k = 0$. To realize the nonlinear effect, a suitable medium is required. A noncentrosymmetric crystal, which exhibits the following properties, is required for nonlinear device fabrications.

(i) High effective nonlinear optical coefficient
(ii) Good optical quality
(iii) Wide transparency region
(iv) Good mechanical and chemical stability
(v) Large birefringence
(vi) Low absorption
(vii) Easy device fabrication

The conversion efficiency, η_{SHG} defined as the ratio of the emerging second harmonic power $P_{2\omega}$ to the incident power P_ω is one of the most useful measures of the performance of a nonlinear crystal. It is represented by

$$\eta = \frac{P_{2\omega}}{P_\omega} = 2\left[\frac{\mu_0}{\varepsilon_0}\right]^{3/2} \frac{\omega^2 d^2 l^2 \sin^2\left[\frac{\Delta k l}{2}\right]}{n^3\left[\frac{\Delta k l}{2}\right]^2}\frac{P_\omega}{A}, \quad (14)$$

where

$$\Delta k = k_{2\omega} - 2k_\omega,$$

$$k = \frac{2\pi}{\lambda},$$

ε_0 = permittivity of free space, μ_0 = permeability of free space, n = index of refraction, ω = angular frequency of incident light, l = length of the crystal, and A= beam area.

The factor Δk represents the amount of phase mismatch between the second harmonic wavefronts generated at different points in the crystal. If k is zero (proper phase matching) then the interference term,

$$\frac{\sin^2\left[\frac{\Delta k l}{2}\right]}{\left[\frac{\Delta k l}{2}\right]^2} = 1 \quad (15)$$

reaches a maximum value that in-turn maximizes the efficiency of the SHG process. The efficiency of second harmonic generation is directly proportional to the intensity $I(\omega) = P_\omega/A$ of the incident fundamental radiation.

In general higher power density, longer crystal, larger nonlinear coefficients and smaller phase-mismatching will result in higher conversion efficiency. In turn, the input power density has to be lower than the damage threshold of the crystal. Table 1 lists

Table 1. Parameters for selecting a NLO crystal.

Sl. No.	Laser parameters	Crystal parameters
1	NLO process	Type of phase-matching
2	Power, Repetition rate	Damage threshold
3	Divergence	Acceptance angle
4	Bandwidth	Spectral acceptance
5	Beam size	Crystal size, walk-off angle
6	Pulse width	Group velocity mismatching
7	Environment	Moisture, Temperature acceptance

the laser and crystal parameters for selecting a NLO crystal for a particular application.

5. CRITERIA FOR SELECTING USEFUL NONLINEAR OPTICAL MATERIALS

The "ideal" nonlinear crystal does not exist. The applicability of a particular crystal depends on the nonlinear process used, the desired device characteristics and the pump laser. Special material properties that are important in one application may not be significant in another. For instance, efficient doubling of very high power lasers having poor beam quality requires a material with large angular bandwidth.

A crystal, which has a smaller nonlinearity but allows noncritical phase matching, will perform better than one, which is more nonlinear, but is critically phase matched. On the other hand, for the doubling of femtosecond optical pulses, the preferred material will be one with a large nonlinearity so that a very thin crystal can be used to avoid dispersive broadening of the second harmonic output pulses.

For a material that has favourable features such as large nonlinearity, high damage threshold, favourable crystal growth habits etc. The efficiency of the material will be appreciable. From a material point of view, only general criteria can be established to gauge the usefulness of a nonlinear crystal. For specialized applications where device performance requirements are well established, quantitative criteria for the selection of suitable nonlinear crystals can be obtained which are often invaluable in aiding system design.

Nonlinear frequency converters are most commonly used with an efficient nontunable laser source. Obviously, the nonlinear crystal should have good transparency at the pump laser wavelength. Specific applications of nonlinear crystals of current interest can be divided into the following efficient harmonic generation and up-conversion, optical parametric oscillator, frequency conversion of ultrashort pulses, frequency conversion of high average power sources, frequency conversion of low average power sources, and laser fusion.

Kurtz and Perry powder SHG method was introduced at the end of 1960s'. In this method, a powdered sample is irradiated with laser and scattered light is collected and analyzed for its harmonic content with the use of suitable filters. For the first time, rapid and qualitative screening for second order NLO effect was possible. The stage was set for a rapid introduction of new materials, both inorganic and organic.

6. NLO MATERIALS OF RECENT INTEREST

The emergence of new materials with superior quality is often responsible for major advances in new technologies. The high speed, high degree of parallelism of optics will lead gradually to optoelectronic systems where an increasing number of functions will be implemented optically. However, the development of photonic technology relies largely on the progress achieved in fabricating new optical materials with better performance. In that respect, materials with a nonlinear optical (NLO) response are expected to play a major role in enabling optoelectronic and photonic technologies. Many NLO single crystals have been identified as potential candidates in optical and electro-optical devices. Nonlinear optical materials have acquired new significance with the advent of a large number of devices utilizing solid-state laser sources.

NLO materials are essential for the fabrication of electro-optic modulators, which convert an electric signal into an optical one for transmission on a fiber optic cable. Currently, such devices are made with inorganic NLO materials. The exchange and processing of information is growing rapidly and more powerful data-systems including larger networks,

faster processors and mass storage devices are under intensive research and development.

6.1. Inorganic materials

The search for novel crystals with non-linear optical (NLO) property is still a challenge for scientists to fulfill "molecular engineering" application and the non-linear optical crystals should possess high absorption edge, large birefringence and molecular hyper polarizabilities. The essential parameters for an NLO crystal are non-linear optical coefficients χ_{ijk}, optical homogeneity, physico-chemical stability and mechanical property. Second order non-linear optical materials are used in optical switching (modulation), frequency conversion, (SHG, wave mixing) and electro optical applications and the material frequently used for these commercial purposes are inorganic [11]. Sparingly insoluble inorganic substance can be easily grown by gel method [12-14]. SHG generation in $HIO_3NH_4H_2PO_4$ (ADP), and $K_2La(NO_3)5.2H_2O$ [KLN] has been quantitatively studied, and the results proved that the presence of hydrogen bonds contributes to the total non-linearity [15]. Microcrystalline compound beryllium pyrophosphate is a hexagonal system and contains BO_3 anionic group as its basic structural unit, which should play an important role for the SHG coefficients [16]. The most widely used inorganic crystals such as β–BaB_2O_4 (BBO) is effective for SHG [17-18] because of limited UV transparency – range in the former and birefringence problem in the latter. A new inorganic crystal – $KBe_2BO_3F_2$ (KBBF) was later developed and this material overcame the difficulties faced by BBO and LBG, but it could not be grown to a large size [19]. The material $Sr_2Be_2Be_2O_7$ (SBBO) shows all the favorable NLO properties of KBBF and this material could be grown to a bulk size [20].

6.2. Organic materials

Organic single crystals possess unique opto-electronic properties because organic molecules have delocalized electrons, namely, conjugated electron systems which exhibit various photo-responses such as photoconductive, photovoltaic, photocatalytic behavior and so on. The organic materials with intramolecular charge transfer compounds having large second order nonlinear optical effects, Fig. 1.

The organic compounds with electron rich (donor) and deficient (acceptor) substituent provide the asymmetric charge distribution in the p electron system and show large nonlinear optical responses. Nonlinear optical crystals should meet several requirements, such as large phase-matchable non-linear optical coefficient, a wide optical window around the visible region, mechanical and chemical stability and a high damage threshold. Some of these requirements based on molecular properties can be satisfied with the assistance of molecular design. It is possible to control the absorption edges of intramolecular charge transfer compounds by selecting the combination of donor and acceptor. Many of organic crystals have absorption in the blue light region and some of them have a cut-off wavelength more than 450 nm. This indicates the possibility of reduced conversion efficiency of SHG due to self-absorption of materials while using a semiconductor laser with 800 nm bands. Organic materials are perceived as being structurally more diverse and therefore are believed to have more long-term promise than inorganic. A wide variety of organic materials are being investigated for frequency doubling. The scope of this review deals with the growth of organic and semi-organic crystals for nonlinear applications, using low temperature solution growth technique. The low temperature solution growth is a versatile technique to provide proper supersaturation to grow NLO single crystals with less number of defects.

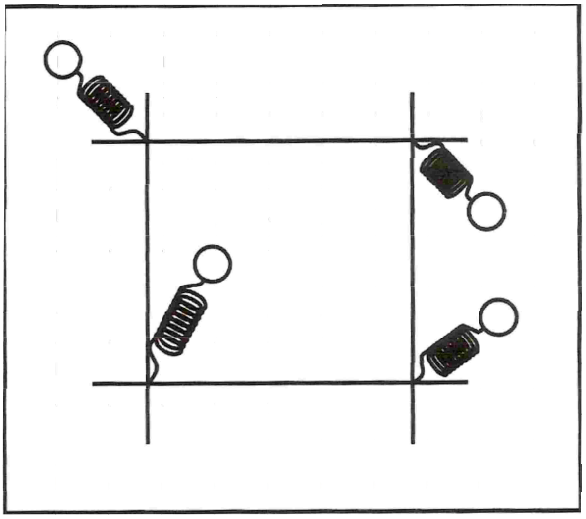

Fig. 1. Electrons in nonlinear crystal are bound in potential well, holding the electrons to lattice points in crystal.

Some of the advantages of these organic materials are their high flexibility in terms of molecular structure, their high optical damage threshold, low cost and their short response time to optical excitation [21,22]. EDMP is an organic material exhibit-

ing quadratic non-linear optical (NLO) property, in the ultra violet region [23]. Attempts have been made to synthesize organic compounds with non-localized π-electron systems to realize non-linear susceptibilities better than their inorganic counterparts [23,24]. The SHG efficiency of Benzoyl glycine is much higher than that of KDP [25]. The range of optical transparencies of hippuric acid is much larger than other organic NLO crystals like POM, NPP, and Vannillin [26].

Different strategies have been proposed to introduce non-centrosymmetric crystal structure of organic materials such as by using chirality's criteria [27,28], hydrogen bonding [29,30], organometallic complex [31-34], reduced ground – state dipole interaction [35], the chemical and physical approach listed above have been proved useful for obtaining non-centro symmetry structures. The powder SHG effect of several salts of organic chromophores of the form $(CH_3)_2NC_6H_4CH=CHC_5H_4\ N–\ (CH_3)^+\ X^–$ first reported by Meredith [36], ($X = CH_3OSO_3$) had SHG efficiency about 220 times that of urea. The transparency of urea extends to 200 nm in the short wavelength limit and it is one of the most promising materials for NLO applications, with SHG 2.5 times that of ADP [37]. Recently, an extremely large number of organic compounds with non-localized $p^–$ electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the inorganic optical materials [38].

The shortcoming of aromatic crystals, such as poor physico – chemical stability and low hardness and cleavage tendency obstruct their device applications. In order to retain high NLO efficiency of organic materials and overcome its shortcoming, some new classes of NLO crystals such as metal organic or semiorganic complex crystals have been developed. The relatively strong ligand bond permits the complex crystals to combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high non-linear and molecular engineering features.

6.3. Semiorganic materials

Organic materials show prominent properties, due to their fast and large non-linear response over a broad frequency range, inherent synthetic flexibility, and large optical damage threshold. However, organic materials may suffer from problems, such as volatility, low thermal stability, mechanical weakness etc., and inorganic materials possess excellent mechanical and chemical property, but most of them show low nonlinear efficiency. The need for materials that combine large nonlinear optical characteristic with resistance to physical and chemical attack has led to the investigation of semiorganic crystals [39]. Semiorganic crystals have large non-linearity, high resistance, low angular sensitivity and good mechanical hardness [40,41]. In semiorganic material, the organic ligand is ironically bonded with inorganic host, and hence the new semi-organic crystals have higher mechanical strength and chemical stability [42]. L-Histidine tetra fluoroborate [43], L-Histidine hydrochloride [44], L-Histidine bromide [45] and L-Histidinehydrofluoridedihydrate [46] are some of the semi-organic NLO materials reported.

Amino acids and strong inorganic acids are good raw materials to produce semiorganic crystals because amino acid crystals possess good optical properties as they contain a proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them [47]. L-arginine and L-arginine phosphate have shown promising results as efficient second harmonic generators and are applied in devices such as optical parametric amplifiers [48]. Growth and characterization of L-PCCM single crystals by slow evaporation and slow cooling technique have been reported [49]. Both ATCC [AllylThiourea Cadmium Chloride] and ATMC [AllylThiourea Manganese Chloride] belong to the trigonal system [50]. TetrakisThiourea Potassium Iodide (TTPI) is an organometallic nonlinear optical (NLO) crystal and this material has positive temperature co-efficient [51]. New types of hybrid NLO materials have been explored from organic inorganic complex with stronger ionic bond such as L-arginine phosphate monohydrate [52].

7. CONCLUSION

This paper presents the theory of nonlinear optics and an areal survey of inorganic, organic and semiorganic NLO materials and advantages and disadvantages of these materials. Kurtz and Perry powder SHG method can be used for analyzing SHG in the case of noncentrosymmetric nature of materials. But, in the case of centrosymmetric crystals, ($\chi^{(2)} = 0$) and there is no possibility for the generation of Second Harmonics. However, they are capable of generating third order NLO properties. By using Z-scan technique, the non-linear optical parameters such as nonlinear refractive index, nonlinear susceptibility (both real and imaginary parts) can be calculated to analyze third order NLO propertie.

REFERENCES

[1] T.F. Krauss and T. Baba // *IEEE J. Quantum Electron*.**38** (2002) 724.

[2] R.M. Delarue // *QuantumElectron.* **34 (**2002) 1.

[3] M. Scalora, J.P. Dowling, C.M.Bowden and M.J. Bloemer // *Phys. Rev. Lett.* **73** (1994) 1368.

[4] S. John and T. Quang // *Phys. Rev.**A*** **54** (1996) 4479.

[5] P. Tran // *Opt. Lett.* **21** (1994) 1138.

[6] A. Forchel // *NatureMat.* **2** (2003) 13.

[7] M. Soljacic, M. Ibanescu, S.G. Johnson, Y. Fink and J.D. Joannopoulos // *Phys. Rev.* **66** (2002) 055601.

[8] A. Huttunen and P. Torma // *J. Appl. Phys*. **91** (2002) 3988.

[9] D.A. Mazurenko, A.V. Akimov, A.B. Pevtsov, D.A. Kurdyukov, V.G. Golubev and J.I. Dijkhuis // *Physica E* **17** (2003) 410.

[10] P. A. Franken, A. Hill, C.W. Peters and G. Weinrich // *Phys. Rev. Lett.* **7** (1961) 118.

[11] P.N. Prasad and D.J, Williams, *Introduction to nonlinear effects in molecules and polymers* (Wiley, New York, 1991).

[12] K. T. Wilke, *Kristallzüchtu* (Verlag Harri Deutsch, Frankfurt / Main, 1988).

[13] K. Mayerand and D. Woermann // *Journal of Crystal Growth* **169** (1996) 317.

[14] D.S. Bhavsar and K.B. Saraf // *Cryst. Res. Technol.* **37** (2002) 51.

[15] Dongfeng Xue and Siyuan Zhang// *Chemical Physics Letters.* **301** (1999) 449.

[16] Zhangzhen He and Hiroshi Moriyama // *Material Research Society*.

[17] Chuangtian Chen, Yicheng Wu, Aidong Jiang, Bochang Wu, Guiming You, Rukang Li andShujie Lin // *J. opt. Soc. Am*. **B6** (1989) 616.

[18] K. Kato // *IEEEJ. Quant. Electron*. **22** (1986) 1013.

[19] C.T. Chen, In: *Laser Science and Technology Vol. 15*, ed. by V.S. Letoknov, C.V. Shank, Y.R Shen and H. Walther (Harwood Acadamic, Langhorne, PA, 1993).

[20] Chuangtian Chen, Yebin Wang, Baichang Wu, Keche Wu, Wenlun Zeng and Linhua Yu // *Nature* **373** (1995) 322.

[21] I. Ledoux, J. Badan, J. Zyss, A. Migus, D. Hulin, J. Etchepare, G. Grillon, A. Antonetti and B. Josa // *J. Opt. Soc. Am. B* **4** (1987) 987.

[22] S. Boomadevi, H.P. Mittal and R. Dhansekaran // *Journal of Crystal Growth* **261** (2004) 55.

[23] S. Manivannana, S.K. Tiwarib and S. Dhanuskodia // *Solid State Communications* **132** (2004) 123.

[24] H.S. Nagaraja, V. Upadhyaya, P. Mohan Rao, P. Sreeramana Aithaland and A.P. Bhat // *Journal of Crystal Growth.* **193** (1998) 674.

[25] D. Xu, X.Q. Wang, W.T. Yu, S.X. Xu and G.H. Zhang // *Journal of Crystal Growth.* **253** (2003) 481.

[26] A.V. Alex and J. Philip Pramana // *J. Phys.* **62** (2004) 87.

[27] H.S. Nagaraja, R. Neumann and P. Mohan Rao // *Nuclear Instruments and Methods in Physics Research Section B*.**185** (2001) 66.

[28] J.L. Ouder and R. Hierle // *J. Appl. Phys*. **48** (1977) 2699.

[29] S.R. Marder // *ACS Symposium Series* **455** (1991) 331.

[30] C. Margaret // *Acc. Chem. Res.* **23** (1990) 120.

[31] C. E. Margaret and M. F. Gayle // *Chem. Mater.***1** (1989) 10.

[32] S.X. Dou, M.H. Jiang, Z.S. Shao and X.T. Tao // *Appl. Phys. Lett.* **54** (1989) 1101.

[33] Hari Singh Nalwa // A*pplied Organometallic Chemistry* **5** (1991) 349.

[34] J. L. Nicholas // *Angewandte Chemie* **34** (1995) 21.

[35] J. Zyss, D.S. Chemia and J.F. Nicoud // *J. Chem. Phys*. **74** (1981) 4800.

[36] D.J. Williams, In: *ACS Symposium Series, American Chemical Society* (Washington, DC., 1983), p. 233.

[37] W.R. Donaldson and C.L. Tang // *Appl. Phys. Lett*. **44** (1984) 25.

[38] J. Zyss and D. S. Chemla, In: *Nonlinear Optical Properties of Organic Molecules and Crystals*, vol. 1, ed. by D.S.Chemla and J.Zyss (Academic Press, NY, 1987), chap. 11-1.

[39] U. Ramabadran, D.E. Zelmon and G.C. Kennedy // *Appl. Phys. Lett.* **60** (1992) 2589.

[40] S. Versko, *Laser Program Annual Report, Lawrence UCRC-JC 105000* (Lawrence Livermore National Laboratory, Livermore, CA, 1990).

[41] C.A. Covina and L. F. Warren // *Proceedings of the Fourth International Sample Electronics Society for the Advancement of*

Materials and Process Engineering. **4** (1990) 388.
[42] D. Xu, M. Jiang and Z. Tan // *Acta Chem. Sin*. **41** (1983) 570.
[43] K.V. Rajendran, D. Jayaraman, R. Jayavel, R. Mohan Kumar and P. Ramasamy // *J. Cryst. Growth.* **224** (2001) 122.
[44] V. Kannan, R.B. Ganesh and P. Ramasamy // *Cryst. Growth Des***. 6** (2006) 1876.
[45] K.V. Rajendran, D. Jayaraman, R. Jayavel and P. Ramasamy // *Journal of Crystal Growth* **255** (2003) 361.
[46] J. Madhavan, S. Aruna, K. Prabha, J. Packium Julius, P.J. Ginson, S. Selvakumar and P. Sagayaraj //*Journal of Crystal Growth* **293** (2006) 409.
[47] C. Razzetti, M. Ardoino, L. Zanotti, M. Zha and C. Paorici // *Cryst. Res. Technol.* **37** (2002) 456.
[48] S.B. Monaco, L.E. Davis, S.P.Velsko, F.T. Wang, D. Eimerl and A. Zalkin // *Journal of Crystal Growth*. **85** (1987) 252.
[49] A. Kandasamy, R. Siddeswaran, P. Murugakoothan, S.P. Kumar and R. Mohan // *Cryst. Growth Des***. 7** (2007) 183.
[50] Xue-Ning Jiang, Dong Xu, Duorong Yuan, Mengkai Lu, Shiyi Guo, Guanghui Zhang, Xinqiang Wang and Qi Fang // *Journal of Crystal Growth* **222** (2001) 755.
[51] R. Perumal and S. Moorthy Babu // *Cryst. Res. Technol.* **42** (2007) 838.
[52] J. Thomas Joseph Prakash, N. Vijayan and S. Kumararaman // *Cryst. Res. Technol.* **43** (2008) 423.
[53] M.D. Aggarwal, W.S. Wang, K. Bhat, B.G. Penn and D.O. Frazier // *Nonlinear Optical Materials* **9** (2001) 193.