CHAPTER 5

LINEAR AND NONLINEAR OPTICAL PROPERTIES OF THE NLO MATERIALS

5.1 INTRODUCTION

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. In the last decade, however, this effort has also brought its fruits in applied aspects of nonlinear optics. This can be essentially traced to the improvement of the performances of the NLO materials. There has been a growing interest in crystal growth process, particularly, in view of the increasing demand for materials for technological applications (Laudise et al 1975, Brice 1986, Nalwa and Miyata 1996). The wide range of applicability of single crystals is evident in the fields of semiconductors, polarizers, infrared detectors, solid state lasers, nonlinear optic, piezoelectric, acousto-optic, photosensitive materials and crystalline thin films for microelectronics and computer industries. The growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their significance in both academic research and applied research.

Nonlinear optical (NLO) materials have a nonlinear response to the electric field associated with the light of a laser beam, leading to a variety of optical phenomena such as the generation of new light frequencies or the alteration of the material’s optical properties. Belt (1985) and Ding (2000) investigated second-harmonic generation (SHG) in short-period periodically
poled bulk and waveguide potassium titanyl phosphate (KTP) crystals to generate blue light using subpicosecond laser pulses in the forward configuration. The highest conversion efficiency is about 32%. They have also generated blue light due to completely quasi-phase matched cascaded SHG and sum-frequency generation (SFG) in periodically-poled waveguides. This phenomenon, with the demonstration of harmonic generation in quartz (Franken et al 1961) is useful in optical communications and signal processing in integrated optics, enriching the development of new nonlinear optical materials of inorganic, organic and semiorganic types. Thus the optical nonlinearities of conjugated system have been widely studied in view of their potential applications in photonic and electro-optic devices (Marder et al 1991, Denning et al 2001).

Organic nonlinear optical materials have been investigated due to their potentially high nonlinearities and rapid response in electro-optic effect compared to inorganic NLO materials. These molecular organic compounds with one or more aromatic systems in conjugated positions, leading to charge transfer systems have been intensely studied for the past two decades (Goto et al 1991). Considerable theoretical and experimental investigations have been done in order to understand the microscopic origin of nonlinear behavior of organic NLO materials Kerkoc et al 1990 and Dimitriev et al 1991. The conjugated $\pi$ electron system provides a pathway for the entire length of conjugation under the perturbation of an external electric field. Fictionalization of both ends of the $\pi$ conjugated system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both the ground and excited states, thus leading to an increased optical non-linearity (Prasad and Williams 1991). When acceptor and donor moieties are placed at terminal position of conjugated backbone, both linear and nonlinear optical properties have increased significantly which involves correlated and high delocalized $\pi$ electron states. The magnitudes of
molecular polarisability and hyperpolarisability coefficients are found to increase superlinearly with an increase in conjugation length between the donor and the acceptor. The strength of donor and acceptor groups and order of their stacking along the backbone plays important roles in determining the magnitude of nonlinear optical (NLO) efficiency (Blanchard-Desce et al 1995).

In case of organic crystals, two requirements are satisfied: (i) they are made of highly polarizable molecules, the so-called conjugated molecules, where highly delocalized p-electrons can easily move between electron donor and electron acceptor groups on opposite sides of the molecule, inducing a molecular charge transfer, (ii) the molecules are adequately packed to build up a noncentrosymmetrical crystal structure that provides non vanishing second-order nonlinear coefficients (Chemla et al 1987 and Bosshard et al 1995).

The linear optical properties showed that L-alanine family crystals have lower cut-off wavelength in the UV-region. One of the L-alanine derivatives, L-alanine acetate (L-A1Ac) possesses high transmittance of 80%. Aravindan et al (2007) already showed that the relative SHG efficiency of LAAN is 7.01 times higher than that of KDP and 1.3 times lesser than that of Urea and 12.89 times greater than its parent material (L-alanine).

LAAN crystal grown by us shows 85 % transmittance level with good optical quality. The powder SHG test confirmed that the nonlinear optical property of the grown crystals of L-alanine derivatives is comparable with other semiorganic crystals. Dhanuskodi and Vasantha (2004) have reported the structural, thermal and optical characterization of L-alaninium oxalate (LAO). LAO has its transparency window from 230 nm onwards, suggesting the suitability of LAO for SHG of the 1064 nm radiation and for other applications in the blue violet region. Ramesh Kumar et al (2004)
reported L-threonic and threonine acetate single crystals grown by slow evaporation and temperature lowering methods from aqueous solution. Also \(\gamma\)-glycine crystals is found to possess good NLO efficiency reported by Narayana Moolya and Dharmaprakash (2002).

A vast majority of organic NLO crystals have their absorption in the blue light region and some of them have their cut-off wavelength exceeding 450 nm. This indicates the possibility of reduced conversion efficiency of second order harmonic generation due to self-absorption of materials while using a semiconductor laser with 800 nm band (Lavine et al 1979, Kerkoc et al 1989).

5.2 DIELECTRIC STUDIES

The dielectric characteristics of the material are important to study the lattice dynamics in the crystal. Hence, the grown L-alanine and L-alanine alaninium nitrate single crystals were subjected to dielectric studies using HP 4275 Multi frequency LCR meter and HIOCKI 3532-50 LCR HITESTER instrument. The cut and polished single crystals of LA and LAAN were used for dielectric studies. The surface of the sample was electroded with silver paste for electrical contact. The experiment was carried out for the frequencies from 50 Hz to 5 MHz with the temperatures 30 °C, 55 °C, 75 °C, respectively. In organic crystal, the dielectric response is good in the lower frequency region, hence, the experiments were carried out in the lower frequency region only. The dielectric constant \(\varepsilon_r\) was calculated using the relation which \(C\) is the capacitance, \(d\) is the thickness of the crystal, \(\varepsilon_o\) is the vacuum dielectric constant and \(A\) is the area of the crystal. The dielectric loss was calculated using the relation \(\varepsilon'' = \varepsilon \cdot D\) where \(D\) is the dissipation factor.

\(\varepsilon_r\) is observed to vary from 40 to 170 and from 40 to 162 for LA and LAAN at room temperature in the frequency range 100 Hz to 5 MHz for
LAAN as shown in Figure 5.1(a) and Figure 5.2(a). The dielectric constant has a higher value at lower-frequency region and then decreases with increase in frequency and remains practically constant. At a little high temperature i.e 348 K the value of $\varepsilon_r$ decreases from a maximum value of 210 and 170 at 100 Hz to a value of 50 and 40 at 100 kHz for LA and LAAN and remains almost constant beyond this frequency implies that both LA and LAAN crystal exhibits normal dielectric behaviour. The very high values of $\varepsilon_r$ at low frequencies may be due to the presence of all the four polarizations, namely, space charge, orientational, ionic and electronic polarizations and its low value at high frequencies may be due to the loss of significance of these polarizations gradually. The increase in the dielectric constant at low frequency is attributed to the space charge polarization (Boomadevi and Dhanasekaran 2004). In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG (Von Hundelshausen 1971).

The dielectric loss is also studied as a function of frequency at room temperature and at higher temperatures for both LA and LAAN crystals, as shown in Figure 5.1(b) and Figure 5.2(b). These curves suggest that the dielectric loss strongly depends on the frequency of the applied field similar to what commonly happens with the dielectric constant in the ionic system (Rao and Smakula 1965, Rao and Smakula 1966). The dielectric loss decreases from 2.5 to 0.125 and 3.5 to 0.5 for LA and LAAN at the lowest temperature considered here, i.e room temperature (308 K) whereas it decreases from 2.75 to almost zero and 10 to 0.9 for LA and LAAN at high temperature i.e. 348 K as the frequency of the applied ac field is increased from 100 Hz to 5 MHz; the fall of loss with respect to frequency being lesser as the temperature increases. The dielectric loss decreases with increase in frequency at almost all temperatures but appears to achieve saturation in the higher frequency range of 1 MHz and above at all the temperatures ranging from 308 K to 348 K. The characteristic of low dielectric loss with high frequency for a
given sample suggests that the sample possess good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application (Balarew and Duhlew 1984).

Figure 5.1(a) Variation of dielectric constant with frequency of the applied electric field of LA crystal

Figure 5.1(b) Variation of dielectric loss with frequency of the applied electric field LA crystal
Figure 5.2(a) Variation of dielectric constant with frequency of the applied electric field of LAAN crystal

Figure 5.2(b) Variation of dielectric loss with frequency of the applied electric field of LAAN crystal
5.3 LINEAR OPTICAL STUDIES
5.3.1 Optical absorption studies

The UV-VIS-NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electron in $\sigma$ and $\pi$ orbitals from the ground state to higher energy states. To find the transmission range of the as grown crystals, optical transmission spectrum was recorded in the range 200 to 1200 nm. Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has a wide transparency window (Periyasamy et al 2007). The good transmission property of the crystal in the entire visible region ensures its suitability for second harmonic generation applications (Roshan et al 2001 and Venkataramanan et al 1997).

The optical transmission range, transparency cutoff and the absorbance band are the most important optical parameters for laser frequency conversion applications. A good transmittance in the entire UV region and lower cut off wavelength at 245 nm and at 320 nm for LA and LAAN (Figure 5.3 and Figure 5.4), is sufficient for SHG laser radiation of 1064 nm or other applications in the blue region. It is assigned to electronic excitation in the COO$^-$ group of L-alanine.

Also in the case of UV visible spectrum of LPN single crystal which was recorded with a 2-mm-thick sample (Figure 5.5). The sample possesses a wide transparency from 295 to 1100 nm. There is no appreciable absorption of light in the entire visible range, as in the case for all amino acids (Rodrigues et al 2003). Also the absence of any overtones and absorbance due to electronic transitions above 300 nm is an essential parameter for frequency doubling process using diode and solid-state lasers (Dmitriev et al 1999).
Optical transmission spectra measured on the as-grown DBLPZ compound (Figure 5.6) shows lower cut off wavelength at 240 nm and there is no remarkable absorption in the entire region of the spectra. The crystal possesses good optical transparency for the second harmonic generation of Nd$^{3+}$:YAG laser.

**Figure 5.3 UV- VIS spectrum of L-alanine**
Figure 5.4 UV- VIS spectrum of LAAN

Figure 5.5 UV- VIS spectrum of LPN
5.4 NONLINEAR OPTICAL STUDIES

5.4.1 SHG Measurement

The NLO property of the crystal was confirmed by the Kurtz and Perry technique (Kurtz and Perry 1968) to identify the materials with noncentrosymmetric crystal structures. The fundamental beam of 1064 nm from Q switched Nd:YAG laser is used to test the Second Harmonic Generation (SHG) property of the L-alanine crystals. Pulse energy of $3.0 \pm 0.2 \text{ mJ/pulse}$ and pulse width of 8 ns and repetition rate of 10 Hz is used. $90^\circ$ geometry was employed. The output-doubled frequency SHG signal was separated from fundamental ones by an IR filter. A photomultiplier tube (Hamasu R2059) was used as detector. KDP sample was used as the reference material and the powder SHG efficiency of L-alanine single crystal was found to be 0.33 times that of KDP.
The fundamental beam of 1064 nm from Q switched Nd:YAG laser of pulse energy 6 mJ/s with pulse width of 8 ns and repetition rate of 10 Hz was used to test the second harmonic generation (SHG) of LAAN and LPN crystal. The emission of green light from the sample confirms the second harmonic generation in the crystal. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. The result obtained for LPN shows a powder SHG efficiency of about 0.26 times that of KDP crystal.

DBLPZ showed SHG efficiencies 0.5 times of KDP at a given pulse energy of 2.4 mJ/s. The SHG efficiency will vary with the particle size of the powder sample. The SHG efficiency will vary with the particle size of the powder sample (Porter et al, 2001). Metal complex of L-proline single crystal showed a better SHG efficiency than the other grown NLO amino acid family crystals.

The presence of chromophores, namely amino group and carboxyl groups in the crystals belonging to amino acid structures, makes them transparent in the UV–Vis region. The useful transmission extends from 200 to 1100 nm which makes it valuable for those applications requiring blue/green light. It is an important requirement for NLO materials having nonlinear optical applications (Vijayan et al 2004).

5.4.2 Laser Damage Threshold (LDT) Studies

One of the decisive criteria for a NLO crystal to perform as a device is its resistance to laser damage, since high optical intensities are involved in nonlinear processes.

In the present study, an actively Q-switched diode array side pumped Nd:YAG laser was used for the Laser Damage Threshold (LDT)
studies on the LA and LAAN crystals. The beam energy of 6.4 mJ/s with pulse width 8 ns and the repetition rate 10 Hz respectively, at 1064 nm radiation was employed to study the LDT of LA and LAAN. For this measurement 8 mm diameter beam was focused onto the sample with 42 cm focal length lens. The beam spot size on the sample was 8 mm. The energy density was calculated using the formula, viz.,

\[ \text{Energy density} = \frac{E}{A} \text{ (MW/cm}^2) \]

where E is the input energy measured in milli-joules and A, the area of the circular spot.

The laser damage threshold was found to be 21.1 MW/cm\(^2\) and 17.6 MW/cm\(^2\) for LA and LAAN which is lesser than that of KDP (0.2 GW/cm\(^2\)), Urea (1.5 GW/cm\(^2\)), BBO (5 GW/cm\(^2\)), BGHC (9.8 GW/cm\(^2\)), BTCC (32 GW/cm\(^2\)) and LAP (10 GW/cm\(^2\)).

### 5.5 CONCLUSION

Significant wider optical transparency and lower cut-off value down to 240 nm and 320 nm for LA and LAAN makes them promising material for NLO applications involving frequency doubling process. The dielectric studies also reveal the low dielectric constant and dielectric loss at high frequency region for these materials. The values of dielectric loss generally decrease exponentially with frequency. Low values of dielectric loss indicate that the LA and LAAN single crystals have very low defects. This supports for the applicability of the crystals of high optical quality with lesser defects for NLO applications. NLO property for all the crystals were confirmed by Kurtz SHG powder technique. The second harmonics signal, generated in the crystals were confirmed from the emission of green radiation.
by the crystals. The result obtained for LPN shows a powder SHG efficiency of about 0.26 times that of KDP crystal. Powdered SHG measurements using 1064 nm radiation revealed that DBLPZ showed SHG efficiencies 0.5 times of KDP at a given pulse energy of 2.4 mJ/s. The damage threshold was found to be 21.1 MW/cm² and 17.4 MW/cm² for LA and LAAN. With these promising optical properties every material chosen for our study could be a potential material for frequency conversion application.