

ABSTRACT

The present investigation is focused on to identified the linear and non linear optical qualities of the well known nlo crystal l-Histidinium 2-nitrobenzoate. The optical quantities such as reflection, refractive index and optical band gap have been evaluated using UV- Visible absorption spectrum. The birefringence nature of the crystal was examined. Photo luminous studies were carried out to find the optical emission of the crystal. Optical limiting method was involved and the linear absorption co efficient was calculated. Z-scan measurements reveal the third order non linear optical property of the crystal.

KEYWORDS: Optical Limiting, birefringence, reflectance, extinction coefficient.

I. INTRODUCTION

Crystals crystallizing in centrosymmetric space groups have been investigated by Nemours researchers because of their several desirable physical and chemical properties including non linear optical property. In the developing research area of NLO materials, number of papers has been published in the resent past [1-3].The third order NLO crystals with highly transparent in the visible and ultra violet range is required for various applications in the field of optoelectronics and photonics [4]. In most of these investigation is on amino acids are used as a reagents for synthesis of new nlo materials. Amino acids family crystals possess high NLO efficiency because of their chiral carbon atom [5].

Crystalline compounds of amino acids are the suitable materials for searching new NLO materials in which much attracted were salts of l-alanine, l-histidine, and l-arginine. l- Histidine compounds have been investigated by many scientist because a number of non-linear l-Histidine optical crystals have higher SHG efficiencies compare to that of KDP. L-Histidine salts possess the high nonlinearity and fast optical response characteristics with better physico-chemical stability. A number of L-Histidine compounds namely l-histidine acetate [6], l-histidine tetrafluoroborate [7] and l-histidinium nitrate [8] exhibiting the NLO behaviors were reported earlier. Crystal structure of L- Histidinium 2-nitrobenzoate was reported [9] and various physical properties like thermal, mechanical, dielectric were reported by Zamara et al [10]. In the present study we are focusing the various optical properties of the L- Histidine 2-nitrobenzoate single crystals.

II. CRYSTAL GROWTH AND STRUCTURE DETERMINATION**Materials and methods**

The title compound of l-histidinium 2-nitrobenzoate [LH2NB(I)] crystals were grown from aqueous solution by employing slow evaporation technique. L- Histidine and 2- nitrobenzoic acid were taken in the equimolar ratio and dissolved in double distilled water. The resultant solution was stirred continuously upto 5 hours to obtain a homogenous solution. The filtered solution was kept undisturbed for crystallization. Good quality single crystals of LH2NB(I) were obtained after about 2 weeks of time. The photograph of the as grown crystal is shown in figure 1.

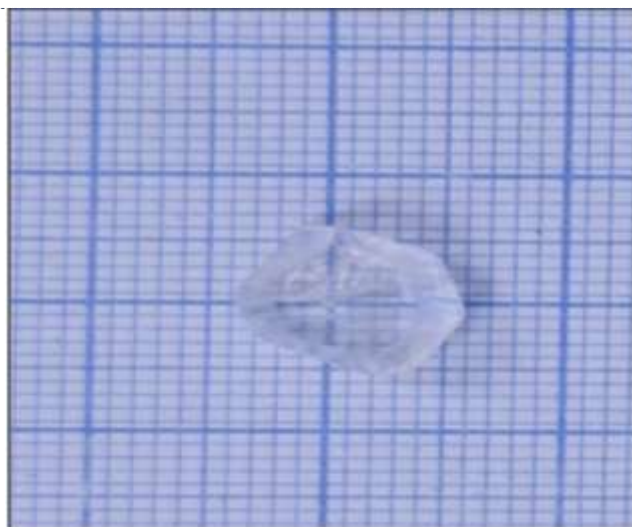


Figure 1. Photograph of LH2NB(I) crystal

Single crystal X-ray study

Lattice parameters and crystal structure of the crystal of LH2NB (I) were determined by single crystal X-ray diffraction analysis. The crystal is crystallizing in monoclinic crystal structure with the centrosymmetric space group $P2_1$. The lattice parameter values of the grown crystal are in good agreement with the reported values [9] and are shown in table 1.

Table 1: Crystal data and structure parameters

| Cell parameters | By Single XRD | Reported values[9] |
|-------------------------|---------------|--------------------|
| a (Å) | 5.089 | 5.1027 |
| b (Å) | 7.064 | 7.089 |
| c (Å) | 18.689 | 18.78 |
| α | 90 | 90 |
| β | 93.55 | 93.68 |
| γ | 90 | 90 |
| Volume (Å) ³ | 670.6 | 674.81 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1$ | $P2_1$ |

III. LINEAR OPTICAL PROPERTIES

Optical Constants

UV-Vis Spectrum of LH2NB(I) was carried out by using a Varian Carry 5E dual beam spectrophotometer in the wavelength region 190-800 nm. It was found from the spectrum that the lower cut off wavelength is 232 nm [10]. The optical band gap was determined from the transmittance value and it is found to be 2.78 eV. The optical absorption coefficient (α) of the crystal was calculated using the formula

$$\alpha = \frac{1}{t} \log 1/T$$

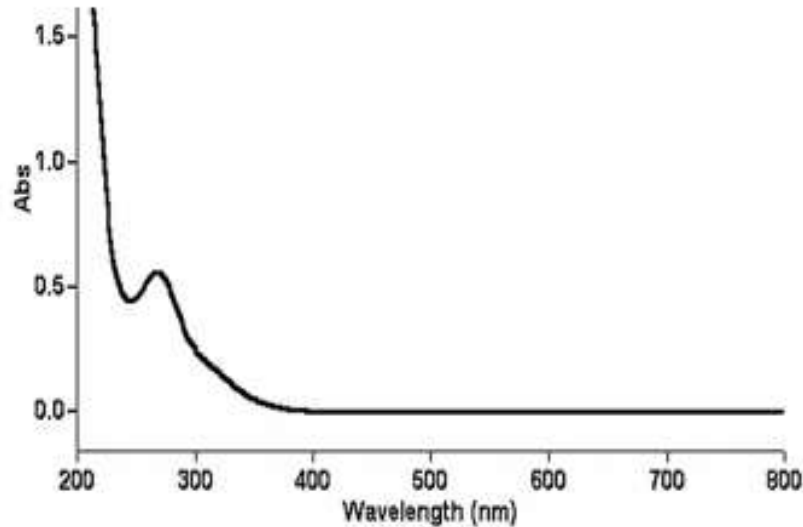


Figure 2. UV-Vis Spectrum of LH2NB(I)

Where, t is the thickness of the crystal and T is the transmittance of the crystal. The extinction coefficient (K) of the grown crystal is calculating using the formula:

$$K = \frac{\lambda \alpha}{4\pi}$$

Where, λ is the wavelength in nm. The reflectance (R) in terms of absorption coefficient can be written as,

$$R = 1 \pm \frac{\sqrt{1 - \exp(-\alpha t) + \exp(\alpha t)}}{1 + \exp(-\alpha t)}$$

The refractive index (n) of the crystal can be calculated from the reflectance value and the equation

$$n = \frac{-(R + 1) \pm \sqrt{-3R^2 + 10R - 3}}{2(R - 1)}$$

The refractive index of the LH2NB(I) crystal is calculated as 1.41 corresponding to a wavelength of 232 nm.

Photoluminescence studies

Photoluminescence (PL) emission measurement is a prominent tool for determining the crystalline quality of a system as well as its excitation fine structure [11]. The PL spectra was recorded using a Perkin Elmer (LS 45) PL unit at room temperature with slit width 8 nm in the wavelength range of 250-600 nm. The recorded emission spectrum of the LH2NB(I) crystal is shown in Fig.3. With the excitation wavelength of $\lambda_{ex} = 318$ nm was calculated at 2 eV. On the title compound's amorphous nature [12, 13] single high intense emission band and only one excitation state has been observed due to intermolecular interactions of lattice vibrations in the LH2NB(I) crystal.

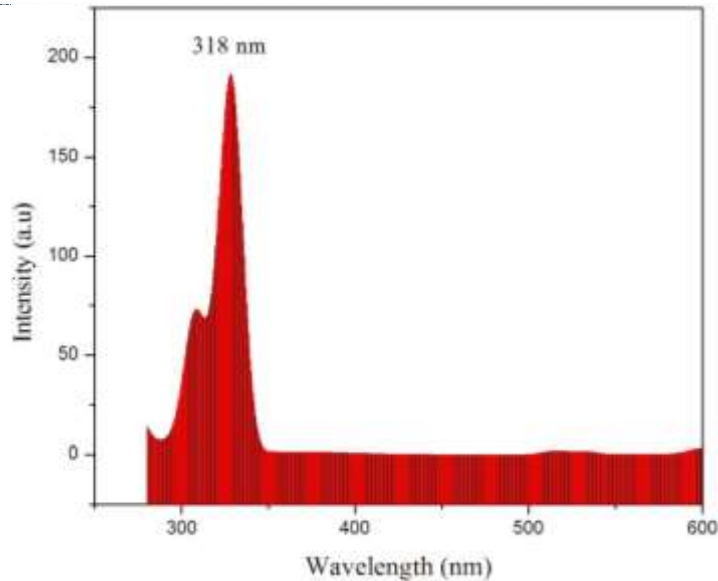


Figure 3. PL Emission spectrum

Optical limiting

Optical limiting method is used to find out the usefulness of Low intense laser in industrial and medical application. Lesser intensity laser devices are commonly used in various practical applications, such as optical switches and modulators [14]. The linear optical absorption coefficient of the LH2NB(I) was examined at room temperature by the Optical Limiting method. The less intense laser power from the source was given to the sample using a modulator and the output power was measured using a power meter detector. This process was continued for several input values and the corresponding output values obtained from the power meter were recorded. A similar procedure was followed to record the output of the laser without the incident of any material [15]. The linear absorption (α) can be measured by using the following relation:

$$\alpha = \frac{1}{L} \ln \frac{P}{P_0}$$

where, P is the output power of the laser receiving from the sample, P₀ is the output power for the direct laser source, L is the focal length. The linear absorption of the 4-MIP crystal was found to be 3.21 J cm⁻¹.

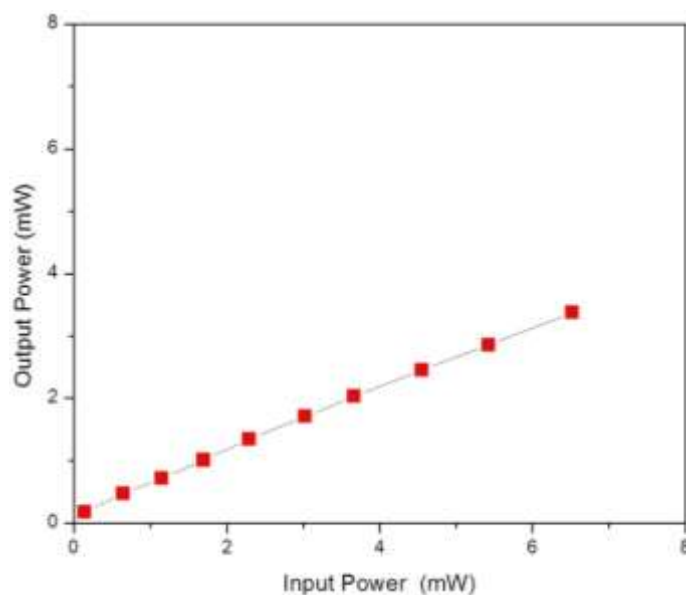


Figure 4. Optical limiting plot of LH2NB(I)

Birefringence Property

Good quality crystals with better Birefringent property play a key role in many optical applications varies from linear optics to frequency conversion in nonlinear optics. The principle of birefringence interferometry is explained by Verma and Shlichta [16]. The LH2NB(I) crystals of thickness 0.72 mm was cut and polished to get the plates. The ell polished crystal plates were placed in a birefringence interferometer for measuring the birefringence value of the crystal. The birefringence values have been calculated by finding the absolute fringe orders using the relation

$$\Delta n = \frac{K\lambda}{t}$$

The birefringence plot of the LH2NB(I) crystal against wavelength is shown in Figure 5. The value of birefringence is lies in between 0.033 to 0.058 in the wavelength range 320 nm to 605 nm. A slight dispersion in the plot from the linear shows in birefringence can highly be helpful in frequency conversion process such as second and third harmonic generations (17)

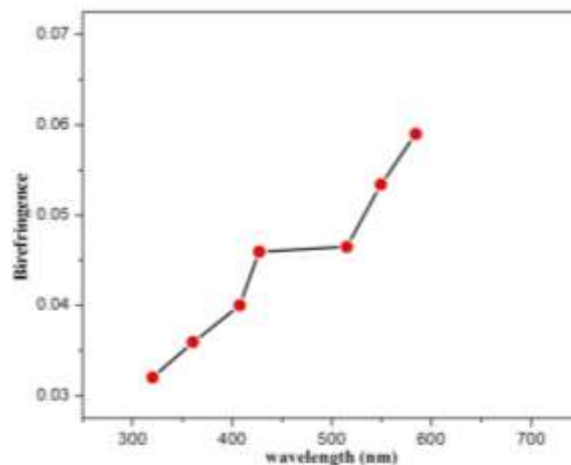


Figure 5. Birefringence plot of LH2NB(I) crystal.

IV. THIRD ORDER NON LINEAR OPTICAL PROPERTY

The third-order non linear optical properties of L-Histidinium 2-nitrobenzoate crystal was tested by Z-scan method. The open and closed aperture Z-scan measurement plots are shown in Fig. 6. Third order optical parameters are calculated using the z-scan measurement results, the calculated values are shown in table 2.

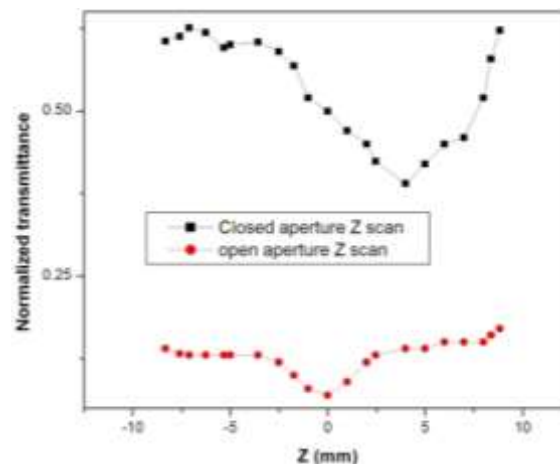


Figure 6. Z-Scan plots of LH2NB(I)

Table2. Third order optical parameters and values

| S.No | Third order optical parameters | Z scan values |
|------|--|------------------------|
| 1 | Non linear refractive index (n_2) | 4.120×10^{-9} |
| 2 | Non linear absorption coefficient (β) | 1.023×10^{-6} |
| 3 | Real part of the third order Susceptibility ($R_e(\chi^3)$) | 3.72 |
| 4 | Imaginary part of the third order Susceptibility ($I_m(\chi^3)$) | 1.883 |
| 5 | Third order non linear optical Susceptibility (χ^3) | 3.007 |

V. CONCLUSION

Single Non linear optical crystal of L-Histidinium 2-nitrobenzoate was grown by slow evaporation method. The linear optical constants such as refractive index, optical band gap and reflectance have been determined for the absorption spectrum values of the grown crystals. It was found that refractive index of the crystal is 1.41. The optical band gap energy of the grown crystal was found to be 2.78 eV. The optical constants such as extinction coefficient (k) and reflectance (R) indicate the high transparency of the crystal and confirm its suitability for optical device fabrication. The birefringence interferogram measurement shows good refractive index homogeneity of the grown crystal. The crystal possesses better OL responses at higher pulse energies to be promising candidates for broadband optical limiters. Third order nonlinear property of the LH2NB(I) was investigated by the Z-scan technique. The nonlinear refractive index and non linear absorption coefficient values were obtained as $4.120 \times 10^{-9} \text{ cm}^2/\text{W}$ and $1.023 \times 10^{-6} \text{ cm}^2/\text{W}$ respectively. All these linear and non linear optical studies confirm that the LH2NB (I) crystal is considered as the potential material for the fabrication of optoelectronic devices.

VI. REFERENCES

- [1] L. Misoguti, A.T. Varela, F.D. Nunes, V.S. Bagnato, F.E.A. Mela, J. Mendes Filho, S.C. Zilio, Optical properties of l-alanine organic crystals, *Opt. Mater.* 6 (1996) 147–152.
- [2] A.B. Ahmed, H. Feki, Y. Abid, H. Boughzal, C. Minot, Crystal studies, vibrational spectra and nonlinear optical properties of l-histidine chloride monohydrate, *Spectrochim. Acta Part A* 75 (1) (2010) 293–298.
- [3] S. Natarajan, S.A. Martin Britto, E. Ramachandran, Growth, thermal, spectroscopic and optical studies of l-alanine maleate, a new organic nonlinear optical material, *Cryst. Growth Des.* 6 (1) (2006) 137–140.
- [4] R.S. Calark, Getting the laser word to subs. *Photonics Spectra*, 22, 135–136 (1988)
- [5] M. Kitazawa, R. Higuchi, and M. Takahashi, “Ultraviolet generation at 266 nm in a novel organic nonlinear optical crystal: l-pyrrolidone-2-carboxylic acid,” *Applied Physics Letters*, vol. 64, no. 19, p. 2477, 1994.
- [6] J. Madhavan, S. Aruna, A. Anuradha, et al., Growth and characterization of a new nonlinear optical l-histidine acetate single crystal, *Opt. Mater.* 29 (9) (2007) 1211–1216.
- [7] M.D. Aggarwal, J. Choi, W.S. Wang, et al., Solution growth of a novel nonlinear optical material l-histidine tetrafluoroborate, *J. Cryst. Growth* 204 (1–2) (1999) 179–182.
- [8] S.A. Martin Britto Das, S. Natarajan, Growth and characterization of two new NLO materials from the amino acid family: l-histidine nitrate and l-cysteine tartrate monohydrate, *Opt. Commun.* 281 (3) (2008) 457–462.
- [9] S. Natarajan, K. Moovendran, J. Kalyana Sundar, K. Ravikumar, Crystal structure of l-histidinium 2-nitrobenzoate, *J. Aminoacids* 2012 (2012), Article ID 463183.
- [10] A. Zamara, K. Rajesh, A. Thirugnanam, P. Praveen Kumar, Growth and characterization of l-histidinium 2-nitrobenzoate [LH2NB(I)]—A promising non linear optical single crystal, *Optik* 125 (2014) 6082–6086
- [11] L. Kumari, W.Z. Li, synthesis, structure and optical properties of zinc oxide hexagonal micro prisms, *Cryst. Res. Tech.* 45 (2010) 311.
- [12] L. Yu, Adv. Amorphous pharmaceutical solids: preparation, characterization and stabilization, *Drug deliver. Rev.* (2001), 27-42.



- [13] P.Di Martino, Molecular Mobility of the Paracetamol Amorphous, Chem. Pharm. Bull. (2000), 48(8), 1105-1108.
- [14] Dehghani, Z., Nadafan, M., Saievar Iranizad, E., The effect of external applied fields on the third order nonlinear susceptibility of ferronematics, Journal of Molecular Liquids ,204 (2015) 70–75.
- [15] K Rajesh, A Arun, A Mani and P Praveen Kumar, Crystal growth, perfection, linear and nonlinear optical, photoconductivity, dielectric, thermal and laser damage threshold properties of 4-methylimidazolium picrate: an interesting organic crystal for photonic and optoelectronic devices, Mater. Res. Express 3 (2016) 106203.
- [16] S. Verma, P.J. Shlichta, Prog. Cryst. Growth Charact. Mater 54 (2008) 1–120.
- [17] Yariv A and Yeh P, 1984, Optical Waves in Crystals (New York: Wiley)

CITE AN ARTICLE

Rajesh, K., and P. Praveen Kumar. "LINEAR AND NON LINEAR OPTICAL QUALITIES OF L-HISTIDINIUM 2-NITROBENZOATE NLO CRYSTAL." *INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY* 6.7 (2017): 710-16. Web. 25 July 2017.