CHINESE JOURNAL OF PHYSICS VOL. 52, NO. 2 April 2014

Optical and Photoconductivity Studies on L-Arginine Benzohydrazide Non-Linear Optical Single Crystal

B. Anitha,[1] S. Rathakrishnan,[2] P. Sagayaraj,[3] and A. Joseph Arul Pragasam[4]

[1]*Department of Physics, SRR Engineering College, Chennai, India*
[2]*Department of Chemistry, SRR Engineering College, Chennai, India*
[3]*Department of Physics, Loyola College, Chennai, India*
[4]*Department of Physics,Sathyabama University, Chennai, India*
(Received July 19, 2013)

An organic nonlinear optical single crystal of L-Arginine Benzohydrazide (abbreviated as LABH) grown by the slow solvent evaporation method is reported. The properties of the grown crystal are determined by single crystal XRD, Fourier transform infrared spectroscopy (FTIR), UV-VIS spectroscopy, Kurtz and Perry technique, and photoconductivity studies. LABH belongs to the orthorhombic system with a P_{21} space group with lattice parameters $a = 8.7740$ Å, $b = 10.4434$ Å, $c = 13.0843$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1198.92$ Å^3. The FTIR spectrum is taken to confirm the functional group present in the grown crystal. A UV-VIS spectrum is also taken for the sample, and it is found that it has very low absorption in the UV and visible region. It also has a wide transparency range. The powder technique is used to confirm the non-linear optical (NLO) property of the grown crystal and it is found that the NLO efficiency of LABH is 1.9 times that of potassium dihydrogen phosphate (KDP). Photo conductivity measurements are carried out in order to reveal the positive photoconductivity of the grown crystal.

DOI: 10.6122/CJP.52.793 PACS numbers: 81.10.Dn, 61.05.Cp, 61.80.Ba, 42.65-Ky, 85.60.Bt

I. INTRODUCTION

Non-linear optical materials have made countless impressions on many fields which includes engineering and technology applications. Nonlinear optical (NLO) materials show a foremost role in nonlinear optics, and predominantly they have a great impact on material technology and engineering applications. Owing to their large pliability of molecular design and superior nonlinear optical efficiency, research on organic and semi-organic NLO materials has been growing. Also, NLO materials have wide applications in optical devices, electronic devices and in many optoelectronic devices [1–3]. So many research scholars show interest in growing new NLO materials having high efficiency which can find applications in various fields. The importance of amino acids for NLO applications lies in the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in a noncentrosymmetric space group. Among all the amino acids, L-Arginine crystal has excellent NLO properties. Also many L-Arginine crystals are promising nonlinear optical materials [4]. The amino acid L-Arginine contains an α-amino group and a terminal guanidyl group. Since L-Arginine is basic in nature, most crystals were grown by using acids, such as phosphoric acid [5–7], acetic acid [8], etc. In such cases, L-Arginine salts (crystals) were grown which depend on the reactivity of the acid (COOH) group. But in our present study, we used an amide which reacts with the amino group. In discovering new NLO materials, it is found that LABH is a promising NLO material. In this present work, crystal structure and properties of LABH is reported. It exhibits excellent optical, electrical and other improved properties.

II. EXPERIMENT

L-Arginine and Benzohydrazide (AR grade) were used as preparatory ingredients for growing L-Arginine Benzohydrazide single crystals. L-Arginine and Benzohydrazide were dissolved individually in deionized water using a 1:1 ratio and are mixed together to prepare a supersaturated solution. This solution is filtered twice to ascertain the growth of pure crystals. The crystal growth process is carried out in an aqueous medium. After a month the solvent is evaporated and small brown colored crystals were obtained. To obtain pure crystals, repeated recrystallization was done using ethanol as a solvent. Finally, small LABH crystals are obtained as shown in Fig. 1.

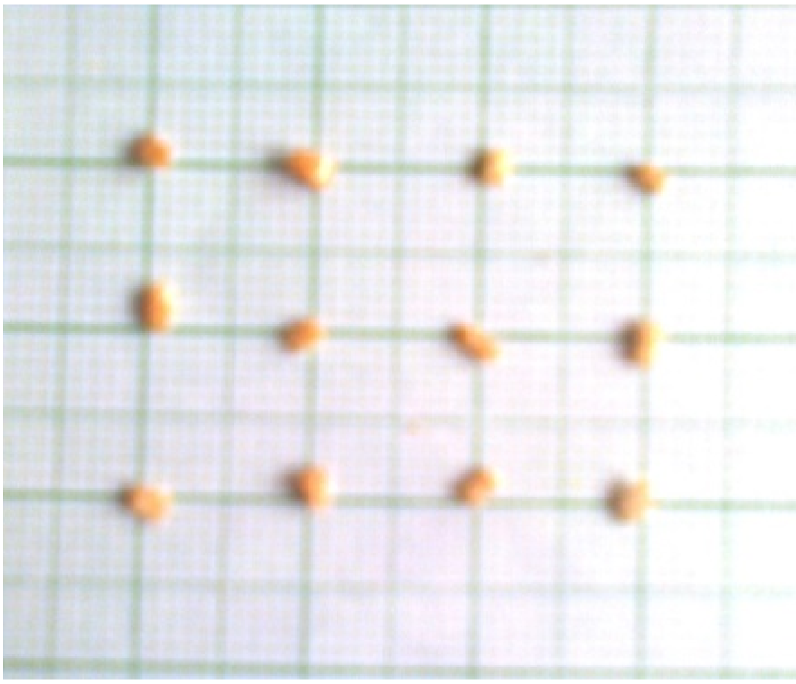

FIG. 1: LABH crystal.

The grown crystal LABH is given for characterizations such as XRD, FTIR, UV-VIS and photoconductivity studies. The NLO properties of the grown crystal is confirmed using the Kurtz and Perry method.

III. SINGLE CRYSTAL XRD STUDIES

Single crystal X-ray diffraction study of LABH show that the crystal belongs to the P_{21} space group with the data given in Table I.

TABLE I:

Crystal system	Orthorhombic
Space group	P_{21}
a (Å)	8.7740 Å
b (Å)	10.4434 Å
c (Å)	13.0843Å
α (°)	90
β	90
γ	90
Z	4
Volume (Å^3)	1198.92
Density mg/m3	1.242mg/m3

IV. FTIR ANALYSIS

The spectrum for the LABH sample was recorded in the frequency range from 4000 cm^{-1} to 400 cm^{-1} and is shown in Fig. 2. The C-H stretch of -CH_2- groups produces the characteristic peak at 3028 cm^{-1}. The COO^- stretch of COOH seems to have an intense sharp peak at 1644 cm^{-1}. Hence the broad band at 1644 cm^{-1} can be assigned to C=O of benzohydrazide. The sharp peak at 1446 cm^{-1} is assigned to COO^- symmetric stretching of L-Arginine. The broad band at 3181 cm^{-1}, is attributed to O-H (-COOH) vibration. The involvement of NH_3^+ in hydrogen bonding is evident by the fine structure of the band in the lower-energy region. The peaks at 1600 cm^{-1} are due to asymmetrical NH_3^+ bending modes. The well-resolved sharp peak at 1554 cm^{-1} is due to symmetrical NH_3^+ bending. The CH_2 bending modes are observed at 1362 cm^{-1}. Since the stretching vibrations of the O–H bonds in the COOH group fall into the same region as the stretching vibrations of the OH bonds in water molecules and the deformation vibrations of the water molecules fall into the region of the deformation vibrations of NH_2^+ and NH_3^+ groups, it is difficult to determine with certainty the presence or absence of water molecules on the basis of the IR spectrum alone.

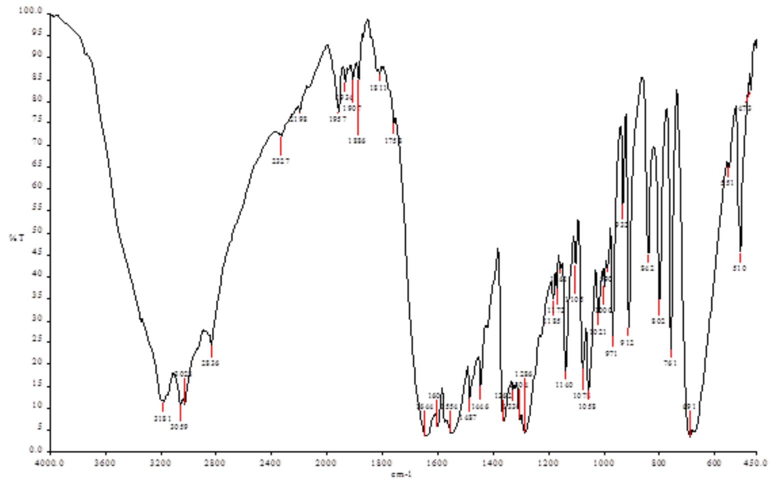

FIG. 2: FTIR spectrum of LABH crystal.

V. UV-VIS SPECTRUM

Wide optical window decides the properties of an NLO material therefore absorption spectrum is taken for the sample LABH using a spectrophotometer in the range of 200–1200 nm. The crystal is well polished so that it becomes totally transparent and the thickness of the crystal is 1 mm.

In all amino acids, the absorption of light in the visible region is absent [9, 10]. The recorded absorption spectrum of the sample is shown in Fig. 3. From the absorption spectrum, it is observed that the optical absorption in the grown crystal is almost negligible in the UV and visible spectral regions with the lower cut off wavelength at around 300 nm. A minimum amount of optical absorption suggests that the LABH crystal is highly transparent in the UV–visible spectral region and is useful for nonlinear optical devices.

VI. KURTZ AND PERRY POWDER SHG TEST

The Kurtz powder technique is a commonly used technique to confirm SHG/NLO properties of the grown crystal [11, 12]. The powdered sample of LABH is illuminated by a laser with the wavelength 1064 nm. The emitted green radiation by the sample LABH shows the confirmation of second harmonic generation. The output is compared with KDP and it is found that the crystal LABH is 1.9 times the KDP.

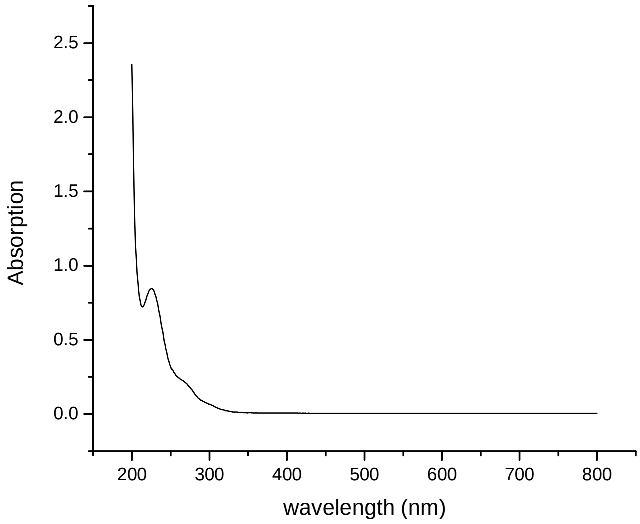

FIG. 3: UV-VIS spectrum of LABH crystal.

VII. PHOTOCONDUCTIVITY STUDIES

The variation of the dark current and photocurrent against electrical fields is measured. From Fig. 4, it is noted that both dark and photo currents increase linearly with increases in the electric field. But the photocurrent is found to be more than the dark current. Hence it can be said that the material exhibits positive photo conductivity. This is caused by the generation of mobile charge carriers caused by the absorption of photons. This is because of an increase in the number of charge carriers or their life time in the presence of radiation [13]. The increase in mobile charge carriers during positive photoconductivity can be explained using the stockman model [14].

VIII. CONCLUSION

An organic NLO crystal of L-Arginine Benzhydrazide (LABH) is grown by the slow evaporation method . Single crystal XRD results show that it belongs to the orthorhombic system having P_{21} space group. Also it has a wide range of transparency in the UV-Vis region and it is a promising NLO material. It is interesting to note that the NLO efficiency of LABH crystals is superior to KDP. The photoconductivity study ascertains the positive photoconductivity nature of the grown crystal. In view of the good optical properties and better SHG efficiency, LABH crystal can be used for nonlinear optical device applications.

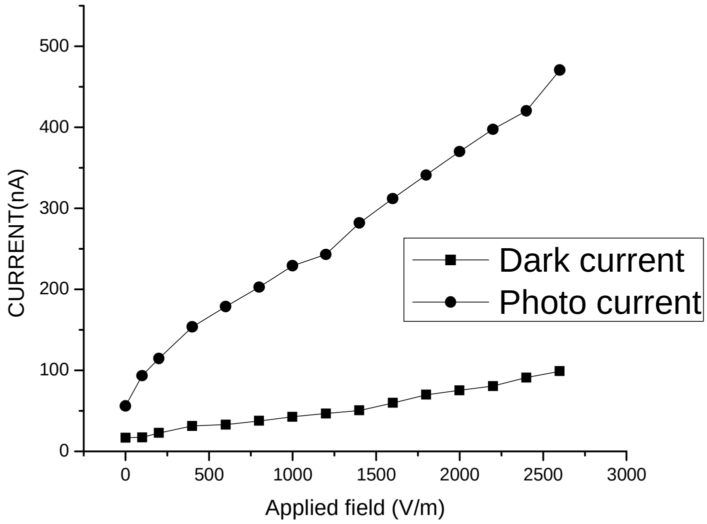

FIG. 4: Photoconductivity study of LABH crystal.

References

[1] W. J. Liu, C. Ferrari, M. Zha, L. zanotti, and S. S. Jiang, Cryst. Res. Technol. **35**, 1215 (2000). doi: 10.1002/1521-4079(200010)35:10<1215::AID-CRAT1215>3.0.CO;2-4

[2] W. Shenglai *et al.*, J. Cryst. Growth **223**, 415 (2001). doi: 10.1016/S0022-0248(00)01030-7

[3] A. Li, C. Xu, A. Li, and N. Ming, J. Cryst. Growth **200**, 291 (2000). doi: 10.1016/S0022-0248(00)00007-5

[4] D. Xu, M. H. Jiang, and Z. K. Tan, Acta Chim. Sin. **41**, 570 (1983).

[5] Y. L. Geng *et al.*, J. Cryst. Growth **273**, 624 (2005).

[6] G. Dhanraj, T. Shripathi, and H. L. Bhat, J. Cryst. Growth **113**, 456 (1991). doi: 10.1016/0022-0248(91)90080-O

[7] G. Ravi, K. Srinivasan, S. Anbukumar, and P. Ramasamy, J. Cryst. Growth. **137**, 598 (1994). doi: 10.1016/0022-0248(94)91004-9

[8] R. Muralidharan, R. Mohan kumar, R. Jayavel, and P. Ramasamy, J. Cryst. Growth **259**, 321 (2009).

[9] T. umadevi, N. Lawrence, R. Tamesh Babu, and K. Ramamurthi, J. Cryst. Growth **310**, 116 (2008).

[10] J. J. Rodrigues JR., L. Misoguti, F. D. Nunes, C. R. Mendonca, and S. C. Zilio, Opt. Mater. **22**, 235 (2003).

[11] S. K. Kurtz and T. T. Perry, J. Appl. Phys. **39**, 3798 (1968). doi: 10.1063/1.1656857

[12] K. Vasantha and S. Dhanuskodi, J. Cryst. Growth **269**, 333 (2004). doi: 10.1016/j.jcrysgro.2004.04.113

[13] R. H. Bube, *Photoconductivity of solids*, (Wiley Interscience, New York, 1981).

[14] N. V. Joshi, *Photoconductivity* (Marcel Dekker, New York, 1990).