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Spectral, optical, etching, second harmonic generation (SHG) and laser damage threshold studies of nonlinear optical crystals of L-Histidine bromide

M. Krishna Mohan*, S. Ponnusamy, C. Muthamizhchelvan

Centre for Materials Science and Nanodevices, Department of Physics and Nanotechnology, SRM University, Kattankulathur, Kancheepuram, 603 203, India

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ABSTRACT

Nonlinear optical (NLO) materials find broad applications in optical data storage, lasers, optical signal processing, second harmonic generation, etc. Though a large number of nonlinear optical materials are available, their applications are limited due to physical and chemical properties.Since the nonlinear optical crystals of amino acids contain a proton donor carboxyl acid (COOH) group and the proton acceptor amino (NH2) group, they are considered as the apt materials for NLO applications. In the present work, good quality crystals of L-Histidine bromide were grown by using slow evaporation technique. The FTIR spectral analysis reveals the presence of different vibrational bands of L-Histidine Bromide.The optical characteristics were assessed by UV–vis analysis, which shows that the crystals have a transmission in the visible range.The etching studies were performed on the crystals, which shows that the crystal does not undergo considerable deformation under the action of solvents. The refractive index of the L-Histidine Bromide crystal was found by Brewster's angle method as 1.516. The Second harmonic generation studies and laser damage threshold studies reveal that crystals have comparable SHG conversion efficiency and high laser damage threshold value to that of the standard KDP crystal, thus making the crystals suitable for applications.

1. Introduction

In the present advancements in science and technology, nonlinear optical (NLO) crystals find applications in the thrust areas of lasers, signal processing, second harmonic generation and data storage. Though there are a large number of nonlinear optical crystals available, their use in technological applications is hindered due to lack of certain physical and chemical properties [1]. Since they contain a proton donor carboxyl acid (COOH) group and the proton acceptor amino (NH_2) group in them, amino acids are considered suitable materials for NLO applications. Amino acids are utilized, as they contain zwitter ionic nature favoring the crystal hardness [2] and chiral carbon atoms. A large number of semi organic nonlinear optical crystals have been grown by slow solvent evaporation technique, and these crystals are gaining more attention due to their applications in device fabrication. Moreover, the high nonlinear optical properties of the organic crystals are combined with the excellent physical properties of the inorganic compounds to enhance the properties. .Histidine (α-amino-β-imidazolepropionicacid) is identified among the amino group as it contains imidazole ring. Histidine exists in both orthorhombic and monoclinic forms [3]. The semi organic nonlinear optical (NLO) materials like L-Histidine diphosphate (LHDP) have become prominent owing to their large nonlinear co-efficient, high laser damage threshold and good mechanical properties. Histidine occurs at the active sites of enzymes and also coordinates ions in larger protein structures [4]. L-Histidine bromide monohydrate (LHB) is a semi-organic nonlinear optical single crystal. Its molecular formula is $C_6H_{12}N_3O_3Br$ [5]. LHB crystallizes in the orthorhombic system, with cell parameters as a = 7.0530 Å, b = 9.0409 Å, c = 15.2758 Å [6]. The LHB crystal is found to be isostructural with L-Histidine Hydrochloride. Reports of basic characterization of L-Histidine Bromide crystals were done by Reena et al., Vijayan et al., [5–7] and Joema et al., [8]. In the present work, efforts were made to grow good quality crystals of L-Histidine Bromide. Many crystals of amino acid are grown by uniaxial growth techniques like Sankaranarayanan Ramasamy (SR) method. The crystals of L-Histidine Bromide have been so far grown only by slow evaporation technique and there are no reports of this crystal grown by other methods. The crystals The grown crystals underwent X-ray diffraction, spectral studies,

* Corresponding author.
E-mail address: krishnamohan.m@ktr.srmuniv.ac.in (M.K. Mohan).

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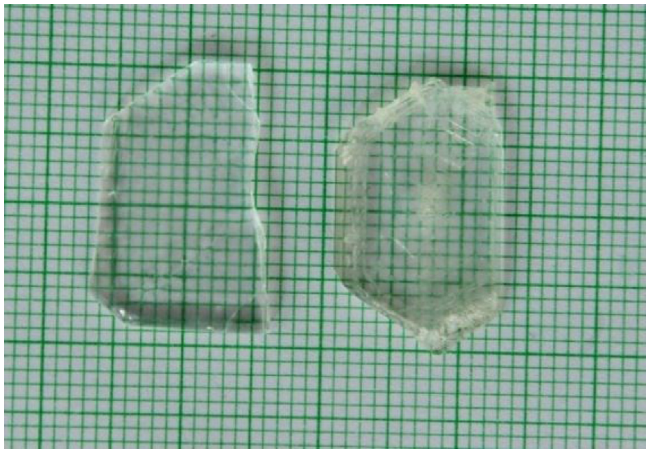

Fig. 1. Photograph of as grown crystal of LHB.

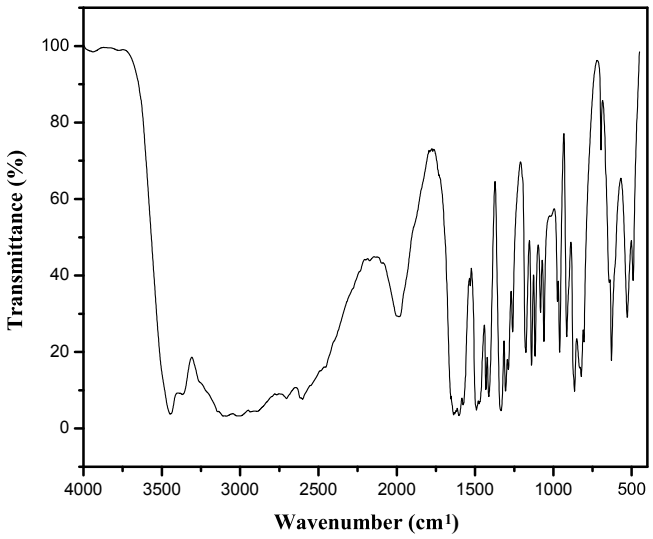

Fig. 2. FTIR spectrum of LHB crystal.

UV–vis studies, refractive index measurements and second harmonic generation studies. The stability of the grown NLO crystals when exposed to laser radiation and the chemical stability are two important parameters in understanding the utility of the crystals. In the present investigation, the laser damage threshold studies and etching studies are performed. The laser damage threshold values and the etch patterns are analysed, as the surface analysis of the crystals largely determines the suitability of crystals for applications [9].

2. Growth of L-Histidine bromide single crystals

L-Histidine and Hydrobromic acid of AR grade were obtained from Loba Chemicals and were used as such without further purification. Reena et al., [5] performed the solubility studies. It was found that the L-Histidine Bromide crystals solubility increases linearly with temperature. The influence of water, acetone and ethanol in the solubility were reported by Rajendran et al., [10]. From these studies, it was found that the solubility is higher in water when compared to other solvents due to the effect of polar molecules in water, which yields good quality crystals.

Water was used as the solvent in the present investigation. 3.9 g of L-Histidine was taken, and it was dissolved in 25 ml of water. The resulting solution is continuously stirred. 1.4 ml of HBr was taken in 25 ml of water and was also stirred continuously. The solutions were mixed and stirred with a magnetic stirrer.

Inorder to obtain a homogenous mixture, the solution was stirred for 5 h. The solution was then filtered using a filter paper. The solution was left as such and by slow evaporation, seeds were obtained. The seed crystal was kept for 15 days in the mother solution. Large crystals of dimensions 20 mm × 15 mm × 5 mm were reported, as shown in Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The lattice parameters of the grown crystals of L-Histidine Bromide crystals were identified using Single crystal X-ray diffraction studies. It was found that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. Least-squares refinement method with setting angles of 25 reflections was used to determine the lattice parameters. The determined lattice parameters are a = 7.052 Å, b = 9.049 Å, c = 15.256 Å. The cell volume is 973.6 Å^3. These values are consistent with the literature [5,10].

3.2. FTIR spectral analyses

FTIR analysis is used to determine the chemical bonds and functional groups present in the material. Fig. 2 represents the FTIR spectrum of the L-Histidine Bromide crystals. The hydrogen bonding interaction between NH_3^+ and COO^- is due to the protonation of COOH and NH_2. This indicates that imidazole and amino are protonated to balance the negative charge of bromide and carboxylate [8]. There is a broad envelope, which is the effect of superimposed OH and NH_3^+ stretching vibrations in the region from 3240 cm $^{-1}$ and 2000 cm $^{-1}$. This is observed in the given spectra at 3448 cm^{-1}. This absorption extends up to 2000 cm^{-1} and is due to multiple fine structures in the lower wave number region. The strong band near 2000 cm^{-1} in the overtone region, is due to the combination of torsional oscillations of NH_3^+ group and asymmetrical NH_3^+ bending vibration. This appears at a wave number of 1986 cm^{-1} in the present work. The asymmetric and symmetric bending vibrations of NH_3^+ respectively occur at the peaks of 1602 cm^{-1} and 1491 cm^{-1}.The peaks at 1576 cm^{-1} and 1412 cm^{-1} are due to the asymmetric and symmetric stretching modes of the carboxylate group.

The peak at 1637 cm^{-1} corresponds to C=O stretching mode. The CH_2 stretching vibrations appears as a very strong peak at 2703 cm^{-1}. The C—C stretching vibrations appear as a strong peak at 1333 cm^{-1} [11]. The NH bending appears as absorption bands at 1287 cm^{-1}, 1175 cm^{-1}, and 1081 cm^{-1}. The CH bending appears as bands in the region 600 cm^{-1} to 1000 cm^{-1}. The CH deformation appears as a strong peak at 1139 cm^{-1}. Table 1 represents the detailed band assignments.

3.3. Optical studies

The UV–vis spectrum was recorded for the grown crystal of LHB in the wavelength range 200 – 800 nm and the obtained spectrum is given in Fig. 3. It is seen from the absorption spectrum that the crystal is transparent in the visible region which is a necessary criterion for NLO crystals, as it does not contain any absorption peak. The UV cut-off of LHB is found as 240 nm. It is also determined that between 250 – 800 nm, the crystal has appreciable transparency, which is consistent with the literature [5,10]. It is a known fact that the non existence of absorption peak in the visible region is an important property of all the amino acids.

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