Growth and birefringence studies of semi organic non-linear optical LHB single crystal

V Jayaramakrishnan¹, T Prasanyaa², M Haris² and G Bhoopathi¹

¹Department of Physics, PSG College of Arts and Science, Coimbatore - 641 014, Tamilnadu, India
²Department of Physics, Karunya University, Coimbatore - 641 114, Tamilnadu, India

E-mail: jayaram.si@gmail.com

Abstract. In the last few decades nonlinear optical materials are getting attention in the field of optical data storage, telecommunication, second harmonic generation (SHG) and optical signal processing, etc. In the present work we are reporting the single crystal growth of L-Histidine with hydro-bromic acid. The L-Histidine bromide (LHB) single crystals have been harvested from the solution in a span of 34 days by adopting slow cooling solution growth technique. The grown crystals have been subjected to powder X-ray diffraction studies to identify the cell parameters and structure. The crystalline perfection has been defined by rocking curve (HRXRD) analysis. Optical transmission spectra reveal the optical properties of the grown crystals. The Modified channel spectrum (MCS) method has been adopted for the study of spectral dependence of linear birefringence over the wavelength range 480–620 nm. The second harmonic generation efficiency was tested by using Kurtz and Perry method, keeping KDP as reference.

1. Introduction
The investigations on materials with potential for large second-order NLO applications are very much emphasized in view of the key-role played by them in the frequency conversion process required for the production of new laser output covering ultraviolet and blue-green region. Recently extensive research is going on materials with the capable of efficient frequency conversion of IR radiation to visible and UV wavelengths. Especially, those materials, which can generate highly efficient second harmonic blue light using laser diodes, are of great interest for applications including optical computing, optical information processing, optical disk data storage, medical diagnostics, etc [1]. Organic amino acids are interesting materials formed by weak van der Waal hydrogen bonds; they contain a proton donor carboxyl acid (–COO) group and the proton acceptor amino (–NH₂) group. Due to this dipolar nature, amino acids have physical properties that make them ideal candidates for NLO applications[2]. Amino acids are widely utilized because they not only contain chiral carbon atoms directing to the crystallization process with the non-centrosymmetric space group, but also possess zwitter ionic nature, which is favouring for crystal hardness [3]. In specific, semi organic combinations render many entertaining structures and bonding patterns for the molecular engineering of novel materials [4].

L-histidine bromide (LHB) is one such semi organic NLO single crystal with molecular formula of C₆H₁₂N₃O₃Br was reported by Reena and Sagayaraj [5]. Structural, vibrational and theoretical studies of LHB single crystals have explained by Ahamad et al [6]. From the structural
point of view, LHB crystallizes in the non-centrosymmetric space group (P2\_1\_2\_1\_2\_1) of the orthorhombic system, whose unit cell parameters are a = 7.0530 Å, b = 9.0409 Å and c = 15.2758 Å [7]. The structure of LHB crystal is found to be isostructural with that of L-histidine hydrochloride. Reena et al., Ahamad et al., and other researchers [5-10] have reported on the studies of L-histidine bromide crystals. Ramajothi and Dhanuskodi [11] have reported on the growth of LHB and reported about SHG conversion efficiency and laser damage threshold were measured using a Nd:YAG laser (1064 nm). Joema et al., [12] have studied the effect of doping urea and ammonium sulphate into LHB crystals. In the present work, the LHB single crystals was successfully synthesized, growth, structural and optical properties were studied, which are mandatory in view of NLO applications and the results obtained are reported here discussed in detail.

2. Experimental details

2.1. Synthesis and crystal growth

The starting material are obtained from Sigma-Aldrich (L-histidine) and Merck (Hydrobromic acid), India. For the entire synthesis and growth processes Millipore water resistivity of 18.2 MΩ.cm was used. The LHB has been synthesized by dissolving L-histidine (NH\_2C\_6H\_7N\_2O\_2) and hydrobromic acid (HBr) in the stoichiometry ratio of 1:1 respectively. After the synthesis of raw material, the saturated solution was prepared (60 rpm) at 30 °C, which was kept in jacketed vessel under controlled temperature water bath for slow cooling technique. The temperature of the saturated solution was raised by 5 °C in order to achieve a homogeneous mixture of solute in solvent. The growth solution of LHB was maintained at the saturation temperature (30 °C) for 2 days and then temperature reduction has done in the solution in order to employ slow cooling technique. The solution was initially cooled at a rate of 0.1 °C /day and subsequently 0.2 °C /day as the growth progresses. The crystals shown in figure 1 were harvested when they attained an optimal size and shape in the growth vessels. Optically transparent and well defined single crystal of dimension 9 × 10 × 7 mm\textsuperscript{3} was harvested from the solution in a span of 34 days.

![Figure 1](image)

**Figure 1.** (a) Photograph of grown LHB single crystal (b) morphology of LHB single crystal and (c) micro crystallization image of LHB in the solution.

2.2. Characterizations

Well defined single crystals of good transparency were collected and crushed properly into the powder for powder x-ray diffraction analysis, which was measured by an advanced D8 powder X-ray diffractometer. The rocking curves of the crystals for the (200) diffraction planes were recorded in symmetrical Bragg geometry using the (121) natural facets by performing a x scan with triple-axis geometry. The monochromated X-ray beam incident on the specimen was obtained using a hybrid two-bounce Ge(220) monochromator with a parabolic multilayer mirror assembly. The diffracted beam from the specimen was detected using a scintillation detector with a triple-axis three bounce Ge(220) analyzer [13]. A Perkin Elmer spectrum 1 Fourier transform infrared spectrometer was
employed to determine the infrared spectrum at room temperature in the range of 4000–450 cm\(^{-1}\). The sample was prepared by pressing the crystal powder with KBr to a pellet form. The UV-Vis transmittance spectrum was recorded with a PerkinElmer Lambda 35 spectrometer in the range 200-800 nm. SHG test for the grown crystals was performed by powder technique of Kurtz and Perry. The modified channel spectrum method (MCS) has been employed for dispersion of birefringence behavior of the grown specimen.

3. Results and Discussion

3.1. XRD analysis

The structure and lattice dimensions of the grown LHB crystal have been found from the powder X-ray diffraction analysis and the recorded spectrum is shown in Figure 2. (a). The well defined prominent Bragg’s peaks were indexed by using TREOR programme. The calculated lattice parameters are \(a = 7.0162 \text{ Å}, b = 9.0213 \text{ Å}, c = 15.2747 \text{ Å}, V = 972.42 \text{ Å}^3\) and the results are in close agreement with those reported by previous researchers [7, 10]. The narrow, sharp and high intensity peaks reveal that the grown crystals were of high degree of crystallinity and the pattern exhibits the single phase of parent orthorhombic phase. However, the microscopic defect cannot be reflected in the XRD analysis.

![Figure 2. (a) Powder X-ray diffraction Indexed spectrum and (b) HRXRD curve of LHB crystal](image)

3.2. HRXRD analysis

The crystalline perfection of the grown single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer. Figure 2. (b) shows the high-resolution DC recorded for a slow cooling grown LHB single crystal using (121) diffracting planes in symmetrical Bragg geometry by employing the multi crystal X-ray diffractometer with MoK\(\alpha_1\) radiation. As seen in the Figure 2. (b) the DC is very sharp without any satellite peaks which may otherwise be observed either due to internal structural grain boundaries [14] or due to epitaxial layer which may sometimes be formed in the crystals grown from solution [15]. The full width at half maximum (FWHM) of the diffraction curves is 7 arc sec, which is close to that expected from the plane wave theory of dynamical X-ray diffraction [16]. The single sharp diffraction curve with low FWHM indicates that the crystalline perfection is extremely good. The slow cooling grown LHB specimen is a nearly perfect single crystal without any internal structural grain boundaries. High quality and crystalline perfection contributes to attractiveness of LHB crystals in future device fabrications.
3.3 FTIR spectral analysis
Functional groups present in the grown LHB crystal were analyzed by FTIR analysis and the spectrum is portrayed in the Figure 3. The protonation of COOH and NH₂ occurs, which gives rise to hydrogen bonding interaction between NH₃⁺ and COO⁻. This confirms that the amino and imidazole are protonated to counter balance the negative charge of carboxylate and bromide ions [12]. There is a broad envelope in the wave number region from 3500 cm⁻¹ to 2000 cm⁻¹ which is due to superimposed O-H stretch of COOH and N-H stretch of NH₃⁺ vibrations. This occurs in the given spectra at 3444 cm⁻¹. This absorption is due to the multiple fine structures in the low wave number regions and it extends up to 2000 cm⁻¹.

Generally in the overtone region, there is a strong band near 1700 cm⁻¹, which is due to the combination of asymmetrical NH₃⁺ bending vibration and the torsional oscillations of NH₃⁺ group. In the present work, this corresponds to a wave number of 1984 cm⁻¹. The peaks at 1602 cm⁻¹ and 1492 cm⁻¹ are due to asymmetric and symmetric bending vibrations of NH₃⁺ respectively. The asymmetric and symmetric stretching modes of carboxylate group are observed at 1573 cm⁻¹ and 1411 cm⁻¹ respectively. The strong peak at 1637 cm⁻¹ is due to the C=O stretching modes of vibration. The shift of –C = O stretch to near 1000 cm⁻¹ supports unprotonation of the carboxyl group, thus confirming the stoichiometry of the LHB crystal, Histidine : HBr, 1:1.

The CH₂ vibrations, which generally lie just below 3002cm⁻¹ is clearly resolved in the given spectrum [9]. The strong peak at 1334 cm⁻¹ is attributed to C-C stretching vibrations. There are absorption bands at 1286 cm⁻¹, 1175 cm⁻¹ and 1082 cm⁻¹ which corresponds to NH bending. The bands from 600 cm⁻¹ to 1000 cm⁻¹ are assigned to CH bending. The torsional oscillation of NH₃⁺ occurs nearly at 526 cm⁻¹. There is a very strong peak at 1139 cm⁻¹ which corresponds to CH deformation. The peak at 809 cm⁻¹ clearly indicates bromide ion bonding with carbon atom. From the spectral analysis it is confirmed that the amino and imidazole group are protonated and counter balance the negative charge of the carboxylate and bromide ions functionality. In the FTIR spectrum all the peaks are not only sharp, but also and highly intense, which indicates grown LHB crystals are lesser defects.

3.4 Linear and nonlinear optical analysis
UV-Visible transmission spectrum for LHB crystal of 6.14×10⁻³ m thickness was taken. It was observed that the crystal has good transmission in the entire visible region. Optical transmission spectrum is (Figure 4. (a)) indicates that the LHB crystal have shorter cut off wavelength of 231 nm and it is close agreement with already reported work[11]. The spectrum suggests that the single transition at near UV region in the grown LHB single crystal. The appearance of higher transmittance...
about 83% of grown LHB crystal (t=6.14×10^{-3} m) shows not only very low defect concentration but also higher transmission in the entire visible region. The large transmission window in UV and entire visible region facilitates, it to be a potential material for second and third harmonic generation of Nd:YAG laser fundamental and for the generation of the higher harmonics of the GaAlAs laser diode emitting the fundamental in the vicinity of 800 nm for the achievement of blue lasers. No appreciable absorption was detected in the visible region of the spectrum and thereby confirming the advantages of the crystal grown in low and homogeneous stirring rate. This is an intrinsic property of all the amino acids, which illustrates that the crystals have good optical obtain properties.

The grown single crystal of LHB was properly powdered and the samples were sieved out for a uniform particle size of 150 μm and used for the SHG Kurtz-Perry experiment. The acquired value from the plot is (Figure 4. (b)) clearly indicates that in the grown LHB sample SHG output is higher in efficiency (1.8 times) when compared to that of the standard KDP. Generally, SHG is always lower for the defective sectors compared to the more perfect sectors. In the grown LHB crystal SHG conversion efficiency is higher than the earlier works [9,11]. This higher efficiency of LHB may be due to better crystalline perfection was achieved by stirring rate (60 rpm), which increases the bond energy and exhibit higher SHG output during present experiment.

![Figure 4](image)

**Figure 4.** (a) UV-Vis transmission spectrum (b) SHG output of the grown LHB and (c) dispersion of birefringence versus wavelength of LHB crystal

### 3.5 Birefringence spectrometry analysis

Birefringence measurement is a precise technique to investigate the optical homogeneity in NLO crystals and the value of birefringence is an important parameter to calculate phase matching angles [17]. The semi organic LHB crystal grown from slow cooling technique was subjected to MCS method in order to obtain accurate birefringence values. The carefully cut and polished LHB crystal with high transparency and without cracks was subjected for this study at room temperature. The effect of crystal, it produce two linearly polarized component rays whose planes of vibration are polarized perpendicular to each other and will encounter two waves, which have amplitudes of 1/√2 equal to that of the incoming wave (neglecting surface reflections). When light passes through the LHB, the extraordinary and ordinary waves have a wavelength of λ/n_e and λ/n_o, respectively. The light wave exit from the flat surface of the SUT has 180° phase difference between two polarized components. The values of the birefringence have been calculated by finding the absolute fringe order for particular wavelength and computed using the relation: Δn = kλ/t, where λ is the wavelength in nm, t, the thickness of the crystal in mm and k, the fringe order [18]. The graph showing the variation of birefringence (Δn) against wavelength (λ) is presented in Figure 4. (c). The crystal possesses low birefringence values and it lies between 4.1310 × 10^{-2} and 3.3640 × 10^{-2} for a thickness of 8.6 × 10^{-5} m and the values are in good agreement with the already published article [8]. The experimental result shows that the birefringence decreases with increasing wavelength of entire
visible region, and so the grown LHB single crystal is classified as optically positive at room temperature.

4. Conclusion
The research presented in this paper was intended to grow good quality single crystal of LHB by the slow cooling technique with homogeniuous stirring of 60 rpm. The grown LHB single crystal possesses not only bulky prismatic morphology but also highly transparent and non hygroscopic. The orthorhombic crystal structure and cell parameters of the LHB were confirmed by powder X-ray diffraction analysis. HRXRD analysis experiment suggested that the LHB crystal is nearly perfect single crystal without any grain boundaries. The UV–Vis spectrum showed good transparency in the UV and Visible region with a lower cut off wavelength of 231 nm and there is no appreciable absorption was detected in the visible region of the spectrum. The SHG relative efficiency of LHB crystal was found to be 1.8 times higher than that of KDP. The crystals showed very low variation in the value of birefringence over a wide wavelength range. The highly perfect LHB crystals obtained from homogeneous stirring rate can be utilized in potential blue laser and NLO related device fabrications.

Acknowledgement
One of the authors (V.J) is grateful to Department of Collegiate Education (DCE), Government of Tamilnadu and University Grants Commision (UGC) for granting the financial support for this work through the Ph.D Scholarship Scheme (2009-2012) and Major Research Project (File No: 38-167/2009-SR; dt. 24-12-2009).

References
[1] Jiang M H and Fang Q 1999 Adv. Mater. 11 1147
[2] Prasanyaa T, Haris M, Jayaramakrishnan V, Amgalan M and Mathivanan V 2013 Phys. Scr. 88 045403
[3] Bhat M N and Dharmaprakash S M 2002 J. Crystal Growth 236 376
[4] Prasanyaa T, Jayaramakrishnan V and Haris M 2013 Spectrochim. Acta A 104 110
[5] Reena I and Sagayaraj P 2003 J. Crystal Growth 249 557
[6] Ahmed A B, Feki H, Abid Y, Boughzala H and Mlayah A 2008 J. Mol. Str. 888 180.
[7] Reena I, Preema T C, Anand D P, Palanichamy M and Sagayaraj P 2005 Mat. Chem. Phy. 93 272.
[8] Vijayan N, Bhagavannarayana G, Nagarajan K and Upadhyaya V 2009 Mat. Chem. Phy. 115 656.
[9] Anandan P, Parthipan G, Saravanan T, MohanKumar R, Bhagavannarayana G, Jayavel R 2010 Physica B 405 4951.
[10] Rajendran K V, Jayaraman D, Jayavel R and Ramasamy P 2003 J. Crystal Growth 254 461.
[11] Ramajothi J and Dhanuskodi S 2007 Spectro. Acta Part A 68 1213.
[12] Joema S E, Perumal S, Ramalingam S and Selvarajan P 2011 J. Res. Scie. Tech. 3 63.
[13] Krishnan P, Gayathri K, Bhagavannarayana G, Jayaramakrishnan V, Gunasekaran S and Anbalagan G 2013 Spectrochim. Acta A 112 152.
[14] Lal K and Bhagavannarayana G 1989 J. Appl. Cryst. 22 209
[15] Bhagavannarayana G, Ananthamurthy R V, Budakoti G C, Kumar B and Bartwal K S 2005 J. Appl. Cryst. 38 768
[16] Betterman B W and Cole H 1964 Rev. Mod. Phys. 36 681
[17] Moovendaran K, Jayaramakrishnan V and Natarajan S 2013 Phot. and Optoele. 3 9
[18] Bhoopathi G, Jayaramakrishnan V, Ravikumar K, Prasanyaa T and Karthikeyan S 2013 Mater. Sci. Poland 31 1