

# Influence of Urea in the Structural, Thermal and Dielectric Studies of L- Histidine Bromide (LHB) Single Crystals

S.E.Joema

**Abstract**— Single crystals of pure and urea doped L-histidine bromide (LHB) were grown by isothermal slow evaporation technique. The zwitterionic nature of L-histidine leads to the formation of many crystals when organic and inorganic additives are added. Even though pure and urea doped LHB crystallize in non-centro symmetric from, it exhibits SHG efficiency and chemical stability. Single crystal X-ray diffraction studies were carried out to confirm the grown crystals and found that grown crystals crystallize in orthorhombic structure. Fourier Transform Infrared (FTIR) spectral analysis was performed to confirm the group ligands on the sample. Thermal stability has been analyzed using TG/DTA studies. The dielectric constant and dielectric loss of the crystal studied as a function of frequencies and also at room temperature and the results of there experiments are discussed.

**Index Terms**— Dielectric Constant, Thermal Analysis, Solution Growth, Structural Studies.

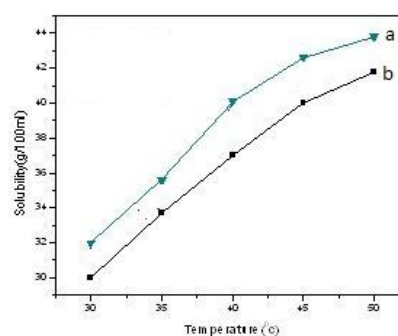
## I. INTRODUCTION

In the last few decades, organic materials have been of particular interest because the nonlinear optical responses in this broad class of material is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility design and produce novel materials [1]-[2]. Nonlinear optical (NLO) organic materials have received much importance for optical second harmonic generation (SHG) owing to their practical applications in the domain of optoelectronics and photonics [3]-[4]. Also, organic nonlinear optical materials are receiving a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power compared with inorganic materials [5]. Recent studies indicate that L-histidine favourably forms several salts with organic/inorganic acids [6]. L-histidine bromide (LHB) is one such member of the L-histidine family, exhibiting NLO properties. It has been reported that doping NLO crystals with organic impurities can alter various physical and chemical properties and doped NLO crystals may also find applications in optoelectronic devices like pure NLO crystals [7]-[8]. The structural, optical, mechanical studies of this material have already been reported by our group [9]. In the present work, a systematic investigation has been carried out on the growth of pure and urea doped L-histidine bromide (LHB) crystals and the grown crystals

have been subjected to single crystal XRD, FTIR, TG/DTA and dielectric studies.

## II. EXPERIMENTAL PROCEDURE

Commercially purchased Analar Reagent (AR) grade L-histidine, urea and concentrated hydro bromic acid (HBr) were used for synthesis and growth. Pure and urea doped LHB are synthesized in our laboratory according to the procedure described earlier [9]. The purity of the synthesized salt was increased by successive recrystallization process. The solubility for pure and urea doped LHB has been determined for five different temperatures 30°C, 35°C, 40°C, 45°C, and 50°C. The solubility was determined by dissolving the solute in water in an air tight container maintained at a constant temperature with continuous stirring. After attaining the saturation of the solute was analyzed gravimetrically and the solubility curves were drawn. From the solubility curve, it is observed that the solubility increases with temperature for the samples and it is found to be more for doped LHB sample compared to the pure sample. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility [14]. Variation of solubility with temperature for pure and doped LHB salts is presented in the Fig.1.



**Fig.1** Solubility curves of (a) pure LHB and (b) urea doped LHB Crystals

The pure and doped LHB crystals were grown by isothermal slow evaporation technique, the crystals are found to be transparent and free from defects. The same procedure is applied to grow the doped crystals by adding 1 mole% of urea to the LHB solution. Fig.2 shows the photograph of as grown pure and doped crystals in a period of 30 days.

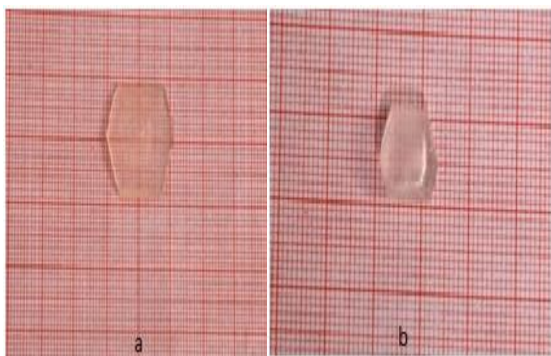


Fig.2 Photograph of as grown (a) pure LHB and (b) Urea doped LHB crystals.

### III. RESULTS AND DISCUSSION

#### A. Single Crystal X-ray Diffraction

The grown crystals were subjected to single crystal to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonius MACH3/CAD4 single X- ray diffractometer. From single crystal X-ray diffraction data, it is observed that the LHB crystal is orthorhombic in structure with space group p212121. The unit cell parameters of pure and urea doped LHB crystals were shown in Table 1. The diffraction data show a very good match with data reported in the literature [10] and slight changes of lattice parameters have been noticed for the urea doped sample compared to pure LHB crystal. The presence of dopants in crystal may produce lattice strain which leads to change of unit cell parameters in the urea doped sample.

Table 1: Single crystal XRD data of pure and urea doped LHB crystals.

Crystal Sample	Parameters (A°)			Unit cell Volume A° <sup>3</sup>	$\alpha^\circ$	$\beta^\circ$	$\gamma^\circ$
	A	b	c				
Pure LHB	7.053	9.037	15.272	974.1	90	90	90
Urea doped LHB	6.998	9.130	15.222	971.494	90	90	90

#### B. FTIR Analysis

The Fourier Transform Infrared (FTIR) spectra of grown crystals were recorded in the region 4000 - 400 cm<sup>-1</sup> using FTIR SHIMADZU 8400S by KBr pellet technique. The observed spectrum is shown in Fig.3. The L-histidine molecule is more basic and therefore the presence of NH<sub>2</sub> group is revealed in the FTIR spectrum that shows an intense band with strong absorption around 3445 cm<sup>-1</sup> and protonated by the carboxyl group (COOH), giving hydrogen bonding interaction between NH<sub>3</sub><sup>+</sup> and COO<sup>-</sup>. It is again confirmed that the amino and imidazole group are protonated and counter balance the negative charge of the carboxylate and bromide ions functionality. The presence of NH<sub>3</sub><sup>+</sup> is corresponding to the asymmetric stretching mode of NH<sub>3</sub><sup>+</sup> and OH stretch of water molecule [11]-[12]. The peak at 1635 cm<sup>-1</sup> gives rise to C=O stretching mode of vibration [13]-[14].

Based on the above discussions, it is concluded that L-histidine is protonated at the heterocyclic ring leaving the carboxyl group unprotonated. The selective protonation of the heterocyclic ring nitrogen is due to its more basic property than the carboxylate ion. Comparing the bands/peaks, it can be seen that FTIR spectra of pure and doped LHB crystal are identical with some changes. So FTIR spectra qualitatively establish the presence of dopants in the lattice of doped LHB crystals. The absorption peaks/bands and their assignments are presented in the Table 2

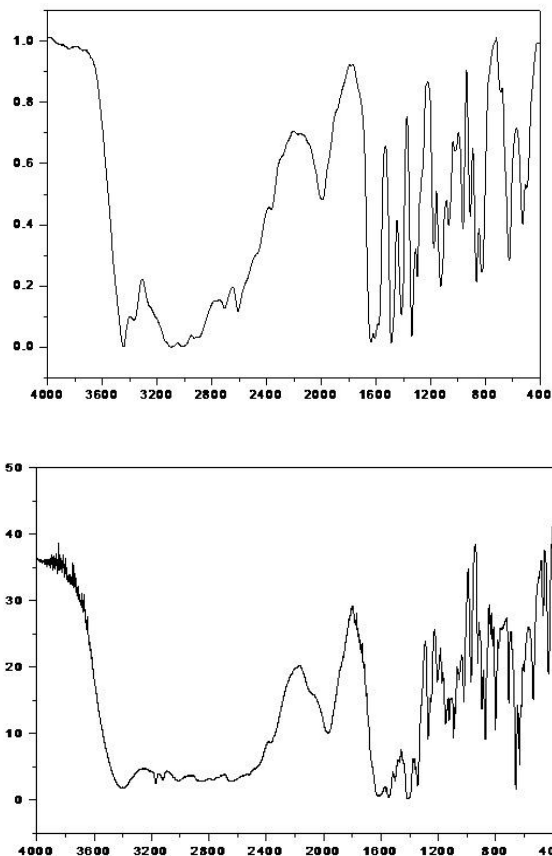


Fig.3 FTIR spectrum of (a) pure LHB and (b) urea doped LHB crystal

Table 2: FTIR data and wavenumber assignment of pure and urea doped LHB crystals.

Pure LHB		Urea doped LHB		Assignment
Wave number cm <sup>-1</sup>	Intensity	Wave number cm <sup>-1</sup>	Intensity	
3445	VS	3413	VS	NH <sub>3</sub> <sup>+</sup> asym. Stretching, OH stretch of water
3170	S	3170	S	NH sym. stretching
		3121	S	NH sym. stretching
3099	S	3011	S	C-H stretching
2707	S	2848	S	CH <sub>2</sub> asym. stretching

2609	S	2629	S	CH <sub>2</sub> asym. stretching
1996	M	1963	M	Combination of NH <sub>3</sub> asym. bending and the torsional oscillation of the NH <sub>3</sub> <sup>+</sup>
1635	VS	1624	VS	C = O stretching
1487	VS	1500	V	C - H deformation
1416	S	1412	VS	COO <sup>-</sup> stretching
1337	VS	1344	S	C - C stretching
		1271	S	N - H bending
1297	S	1206	M	N - H bending
1175	M	1148	S	CH inplane bending
1127	S			C - H bending
1069	M	1092	S	C - H inplane bending
965	M	971	M	C - H bending
910	S	924	M	C - H bending
865	S	895	S	C - N deformation
828	S	801	S	Ring deformation
627	S	658	VS	C - H bending
528	M	537	S	Torsional NH oscillation of NH <sub>3</sub> <sup>+</sup>
430	M	431	S	OH inplane bending
910	S	924	M	C - H bending

C. Thermogravimetric /Differential (TG/DTA) Analysis

The TG/DTA analysis were carried out to investigate the thermal stability of the crystal using an SDT Q600 V8.3 thermal analyser in the temperature range 30- 1100° at a heating rate of 20°C /min in the nitrogen atmosphere and the thermograms are shown in Fig.4.

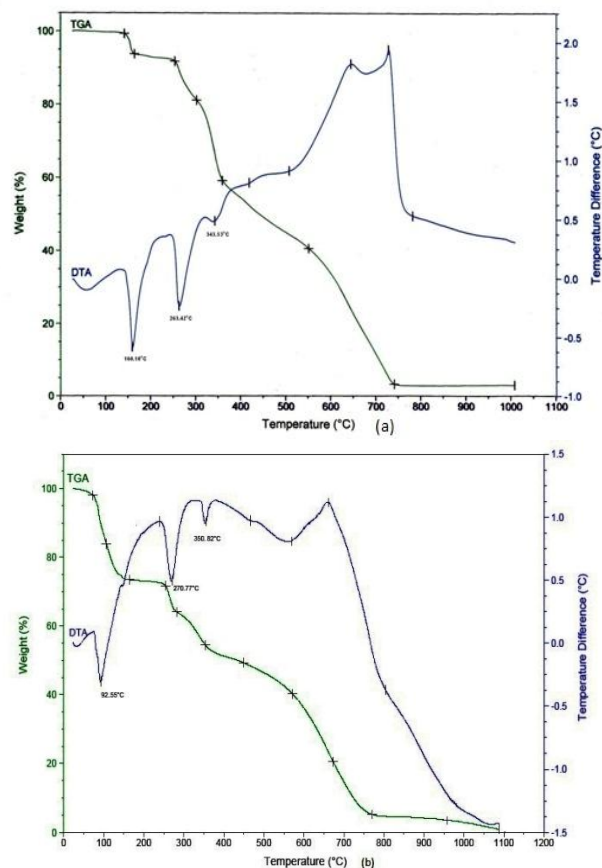


Fig.4 TG|DTA trace of (a) pure LHB and (b) urea doped LHB crystal

For pure LHB crystals, the TG curve indicates there is a gradual removal of water from the lattice in three steps starts from 30-165.26°C, 254-40°C and 302.91-360.45°C respectively. These dehydration steps are again confirmed through the DTA thermal plots with respective endothermic peaks found at 160°C, 263°C and 343°C. However it is decomposed in the temperature interval 552-741°C and forms a residue. This loss is attributed to the liberation of volatile substances probably ammonia and /or carbon dioxide. Above 783°C, the product is stable without any prominent weight loss. For urea doped LHB crystals, the TG curves, it is observed that there is a loss of lattice water in three steps of dehydration starts from 30-165.26°C, 254.40-302.91°C and 302.91-360.45°C. These dehydration steps are again confirmed through the DTA thermal plots with respective endothermic peaks at 92.55°C, 270.77°C, and 350.82°C. However it decomposes further in the temperature interval 650 - 760°C and from a residue. This is confirmed from the exothermic peak centered at 720°C and 661.77°C. Above 850°C, the product is stable without any prominent loss. The TG/DTA analyzes revealed that the grown crystals are hydrated nature and doped crystals are found to be more stable than pure crystals.

D. Dielectric Studies

Dielectric constant is related to the symmetry and structure of crystals, the co-ordination number and the polarizabilities. Various polarization mechanism in solids such as atomic polarization of the lattice, orientational polarization of dipoles and space charge polarization can be understood very

easily by studying the dielectric properties as a function of frequency and temperature for crystalline solids [15]-[16]. For the dielectric measurements, the grown crystal was taken and was polished. The capacitance and dielectric loss factor ( $\tan \delta$ ) measurements were carried out using precision LCR meter (Agilent 4284 A) with frequency range of 102- 106 Hz at different temperature range 30-100°C [17]-[18].

Fig.5 shows the plot of dielectric constant ( $\epsilon_r$ ) Verses log frequency. The dielectric constant has high values in the lower frequency region and then it decreases with the applied frequency. The very high value of at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The variation of dielectric loss with frequency is shown in Fig.6. The characteristic of low dielectric loss with frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [19].

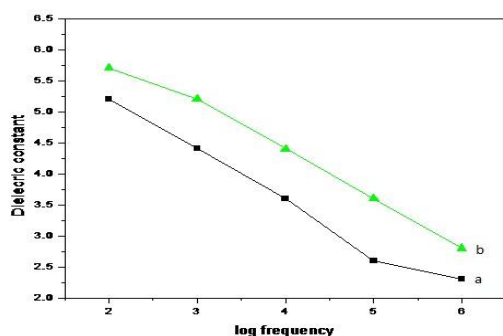


Fig.5 Variation of dielectric constant with frequency of (a) pure LHB and (b) urea doped LHB crystals at 30°C.

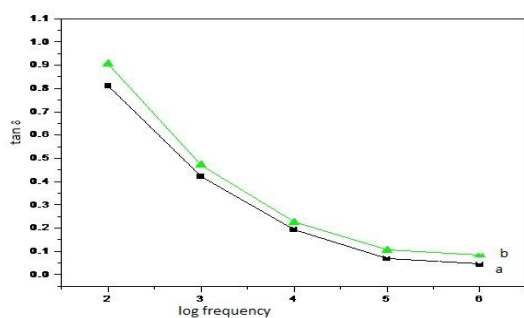


Fig.6 Variation of dielectric loss with frequency of (a) pure LHB and (b) urea doped LHB crystals at 30°C.

Thermal analysis revealed the hydrated nature of the crystals and the doped crystals are found to be thermally stable than pure crystals. It is observed from dielectric studies that both dielectric constant and loss of the sample decrease with increase in frequency. Based on these observations we can say that LHB can be a promising nonlinear material, which can be possibly used for fabrication of photonic devices.

#### IV CONCLUSION

Single crystals of pure and urea doped LHB have been successfully grown by slow evaporation technique in a period of 30 days. X-ray diffraction studies confirmed that the pure

and urea doped crystals crystallize in orthorhombic system with space group p212121. FTIR spectral analysis confirmed the presence of functional groups in the crystals.

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