STUDIES ON STRUCTURAL, OPTICAL, MECHANICAL AND THERMAL PROPERTIES OF UNDOPED AND UREA-DOPED L-HISTIDINE BROMIDE(LHB) SINGLE CRYSTALS

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Abstract

Undoped and urea-doped L-Histidine Bromide (LHB) salt has been synthesized by solution method and solubility studies have been carried out. Single crystals of synthesized salts were grown by isothermal slow evaporation technique. The effect of the dopant(urea) on the growth and morphology has been investigated. Grown crystals were characterized with the aid of single crystal X-ray diffractometry (XRD) to confirm the crystal structure. Fourier Transform Infrared (FTIR) spectral analysis was performed to confirm the group ligands on the sample. UV visible transmittance studies show that the grown crystals have wide optical transparency in the entire visible region. The NLO activity of the grown crystal has been checked by second harmonic generation (SHG) test. The thermal stability has been analyzed using TG/DTA studies. Mechanical strength of the grown crystals was tested by measuring microhardness.

Keywords: L- histidine complex; Growth from solutions; Solubility; Single crystal; XRD; Nonlinear optical; SHG; microhardness

Introduction

Over the past few decades, non-linear optical phenomenon has been focused on inorganic semiconductors, organic molecules, conjugated polymers and organo- metallic compounds[1]. Semi-organic materials possess large optical linearity, high resistance to laser induced damage, inherent ultra fast response times, low angular sensitivity and good mechanical stability[2-4]. The amino acid viz. L-histidine serves as a proton donor, proton acceptor and as a nucleophilic reagent. L-Histidine frequently occurs at the active sites of enzymes and co-ordinates ions on large protein structures[5]. There has been a great interest in synthesizing novel nonlinear optical(NLO) samples by combining L-histidine with organic and inorganic acids and salts. Usually, L-histidine complexes belong to non-centrosymmetric space groups and it is an essential criterion for nonlinear optical (NLO) application. L-Histidine Bromide (LHB) is an NLO material and thorough scan on literature reveals that only a limited work on various properties of this complex has been reported[6-8]. 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 [9-12]. It is believed that if the dopant(urea) is added to LHB, interesting properties may be obtained. Hence the aim of this paper is to report the studies on solubility, growth, XRD studies, SHG studies, optical transmittance studies, microhardness studies and thermal studies of grown undoped and urea-doped LHB crystals.
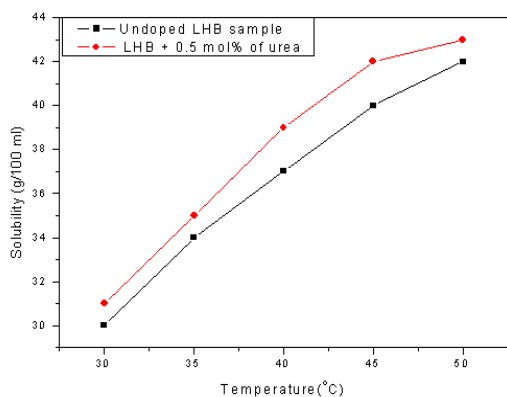
Synthesis, solubility and Growth

Since pure and urea-doped L-histidine Bromide (LHB) crystals are not commercially available, these compounds were synthesized by dissolving L-histidine (Kemphasol 98%) and hydrobromic acid (AR grade) in the equimolar ratio 1:1 in aqueous solution. The solution was stirred well at a constant rate to get homogeneity. Prepared solution was then filtered twice using Whatmann filter paper and the solution was transferred to a petri dish and it was allowed to evaporate isothermally at 40°C in a constant temperature water bath for few days to get the undoped LHB salt. To obtain the urea-doped LHB salt, 0.5 mol% of urea was added to the solution of LHB and similar procedure was followed as the synthesis of undoped LHB salt. After synthesizing the salts, solubility studies of the samples were carried out. Solubility study was carried out using a hot-plate magnetic stirrer and a digital thermometer. Initially, the temperature of solvent was maintained at 30 °C.

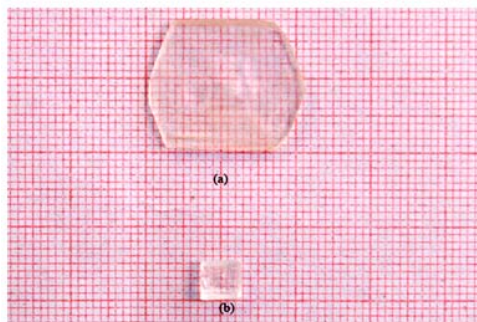* Corresponding Author, *Email*: pselvarajanphy@yahoo.co.in

The synthesized salt of LHB was added step by step to 50 ml of de-ionized water in an air-tight container kept on the hot-plate magnetic stirrer and stirring was continued till a small precipitate was formed. This gave confirmation of supersaturated condition of the solution. Then, 25 ml of the solution was pipetted out and taken in a petri dish and it was warmed up at 40 °C till the solvent was evaporated out and solubility was determined by gravimetrical method[13]. The same procedure was followed to find solubility of pure and urea-doped LHB samples at other temperatures. Variation of solubility with temperature for undoped and urea-added LHB salts is presented in the figure 1. It is observed from the results that the solubility increases with temperature for both the samples and it is found to be more for urea-doped LHB sample compared to the undoped sample. Since solubility increases with temperature, the samples of this work have positive temperature coefficient of solubility.

Fig. 1: Solubility curves for undoped and urea-doped LHB samples

Using the solubility data, the saturated solution of the LHB sample was prepared and the solution was stirred using a magnetic stirrer at a constant rate at 30 C for about 2 hours to get homogeneity and the solution was filtered twice using Whatman filter paper and filtered solution was kept in a borosil beaker covered with a porous paper. Colorless and transparent crystals were harvested after a period of about 30 days. To grow the urea-doped single crystals, saturated solution was prepared using the urea-doped sample and de-ionized water and same procedure was adopted to grow the urea-doped crystals. The grown crystals were found to be highly transparent, free from visible inclusions and non-hygroscopic in nature. Fig.1 shows the photograph of the undoped and urea-doped LHB crystals .

Fig. 2: Photograph showing (a) undoped LHB and (b) urea-doped LHB crystals

Instrumentation

Grown crystals were subjected to single crystal X-ray diffraction (XRD) studies by employing a Nonius CAD4/MACH single crystal X-ray diffractometer. The Fourier Transform Infrared(FTIR) spectra of the grown crystals were obtained using an FTIR spectrometer (Model: SHIMADZU FTIR 8400S) by KBr pellet technique in the region 4000-400 cm^{-1}. The UV-vis spectra were recorded in the wavelength range 190-1100 nm using Perkin Elmer spectrum lambda35 spectrophotometer. The nonlinear optical(NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique[14]. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out to investigate the thermal stability of the crystals using an SDT Q600 V8.3 thermal analyser in the temperature range 30-1100°C. Microhardness study of the grown crystals was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Indentations were made for various loads from 25 g to 100 g. Several trials of indentations were carried out and the average diagonal lengths were measured for an indentation time of 10 seconds. The Vickers microhardness number was calculated using the relation $H_v = 1.8544 \, P / d^2$ kg/mm^2 where P is the applied load and d is the diagonal length of the indentation impression[15, 16]. The measurement of microhardness gives idea of mechanical strength of crystals.

Results and Discussion
Single crystal X-ray diffraction analysis

The grown crystals were subjected to single crystal XRD to confirm the crystal structure. Pure(undoped) and urea-doped LHB crystals crystallize in orthorhombic structure with space group $P2_12_12_1$. 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[17] and slight changes of lattice parameters have been noticed for the urea-doped sample compared to pure LHB crystal. The

changes in the lattice parameters are due to incorporation of urea in the lattice of 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 (Å)			Unit cell Volume Å^3	α^o	β^o	γ^o
	a	b	c				
Pure LHB	7.053	9.037	15.272	974.1	90	90	90
Urea- doped LHB	7.068	9.044	15.247	973.3	90	90	90

FTIR analysis

The FTIR spectra of pure and urea-doped LHB are shown in figures 3 and 4 respectively. The L-histidine molecule is more basic and therefore the presence of NH_2 group is revealed in the FTIR spectrum that shows an intense band with strong absorption around 3445 cm^{-1} and protonated by the carboxyl group (COOH), giving hydrogen bonding interaction between NH_3^+ and COO$^-$. 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 broad envelope band around 3000 to 2000 cm^{-1} is due to superimposed O-H and NH_3^+ stretching vibrations. Absorption in this region is characterized by multiple fine structure in the low wave number region and it extends up to 2000 cm^{-1}. In the overtone region there is a prominent band near 2000 cm^{-1}, due to combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ groups. The presence of NH_3^+ is identified corresponding to the asymmetric stretching mode of NH_3^+ and OH stretch of water molecule[18,19]. The C-H stretching frequency in IR around 3010 cm^{-1} is due to the polarization of the vibrating group. The peaks at 1416 cm^{-1} are assigned to COO$^-$ stretching vibrations.

The peak at 1635 cm^{-1} gives rise to C= O stretching mode of vibrations[20,21]. The absorption peaks/bands and their assignments are presented in the table 2. Thus the molecular structure of synthesized compounds was confirmed by the FTIR spectral analysis.
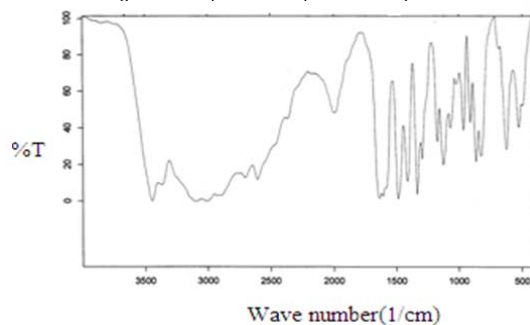

Fig.3: FTIR spectrum of pure LHB crystal

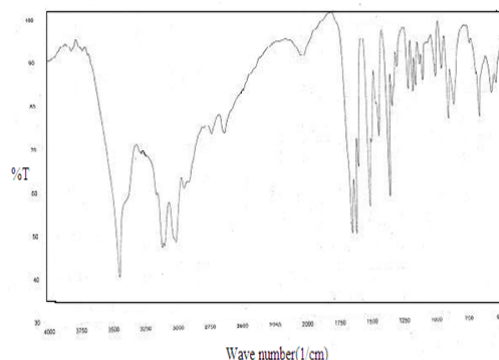Fig. 4: FTIR spectrum of urea-doped LHB crystal

Table 2: Wave number assignments for pure and urea-doped LHB crystals

Wave number (cm^{-1})		Assignment
Pure LHB	Urea-doped LHB	
3445	3443	NH_3^+ asym. stretch, OH stretch of water
3099	3003	C – H stretching
2707	2704	CH_2 asym. Stretching
1635	1635	C = O stretching
1487	1492	C – H deformation
1416	1410	COO^- stretching
1337	1344	C – C stretching
1297	1259	N-H bending
1175	1176	C – H deformation
1127	1112	N – H bending
1069	1058	C – H in plane bending
965	960	C – H bending
910	912	C – H bending
865	868	C – N deformation
828	823	Ring deformation
627	626	C – H bending
528	528	C – C deformation

Optical transmission spectral analysis

UV-visible transmittance spectra of undoped(pure) and urea-doped LHB crystals are depicted the figures 5 and 6. Optical transmission data were taken for the samples of thickness of about 2 mm. The material has a good optical transmittance in the entire visible region and the lower cut off wavelength (λ_{cut}) is observed to be at 218 nm and 208 nm for pure and urea-doped LHB crystals respectively and this is due to π - π^* transition in the compounds. The band gap energy ($E_g = \frac{hc}{\lambda}$) was found to be 5.698 and 5.972 eV for pure and urea-doped LHB crystals respectively and thus ascertain the fact that the crystals are insulators and can be used for laser applications. The useful transmission range of pure and urea-doped LHB crystals extends from 218 to 928 nm and from 208 to 1087 nm respectively ,which makes it valuable for those applications requiring blue green light[22]. The large transmission in the entire visible region and short cut off wavelength enables it to be a potential material for second and third harmonic generation[23].

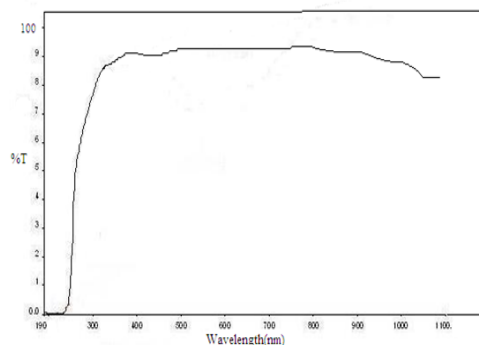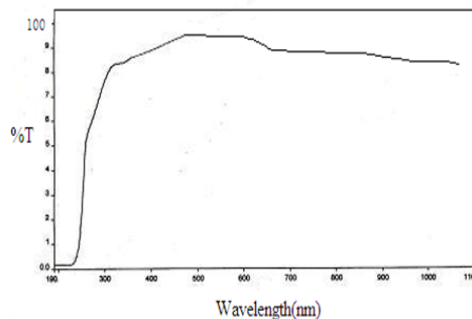Fig.5: UV-visible transmittance spectrum of LHB crystal

Fig.6: UV-visible transmittance spectrum of urea-doped LHB crystal

Second Harmonic Generation (SHG) test

The grown crystals were powdered and they were illuminated using Nd:YAG laser with first harmonics output of 1064 nm, width 8 ns and repetition rate 10 Hz. The second harmonic signal generated in the samples was confirmed from the emission of green radiation. The SHG efficiencies of pure and urea-doped samples are found to be 0.91 and 1.1 times that of KDP. Due to the presence of urea in the crystal lattice, there is an increase in polarizability of the molecule, which tends to increase the SHG efficiency.

Thermogravimetric/Differential thermal (TG/DTA) analysis

The TG/ DTA analysis of pure and urea-doped LHB crystals have been carried out in the nitrogen atmosphere with a heating rate of 20 °C/min in the temperature range 30-1100 °C and the thermograms are shown in the figures 7 and 8. For pure LHB crystals, the TG curve indicates there is a gradual removal of water from the lattice in three steps. The first step of hydration starts from room temperature and ends at 165 °C. Then the residue remains idle up to 254 °C and then the second dehydration continues. This stage is also a dehydration that begins at 254°C and terminates at 302°C. The co-ordinated molecule of water during the third stage in the temperature region 302 – 360 °C leads to the formation of anhydrous LHB. The total loss of water suggesting that the grown crystals were initially hydrated. These dehydration steps are again confirmed through the DTA thermal plots with respective endothermic peaks found at 160 °C, 263 °C and 343 °C. Further, it can be seen from the thermal plot, the dehydrated LHB subjected to continuous heating, does not remain stable for a long temperature change. 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 curve it is observed that there is a loss of lattice water in three steps . The respective three steps of dehydration starts from 30-100 °C, 124-140 °C and 140-240 °C. These dehydration steps are again confirmed through the DTA thermal plots with respective endothermic peaks at 100 °C, 125 °C and 241 °C. However, it decomposes further in the temperature interval 650-760°C, and form a residue. This is confirmed from the exothermic peak centered at 720 °C and 780 °C. Above 890 °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 thermally more stable than pure crystals.
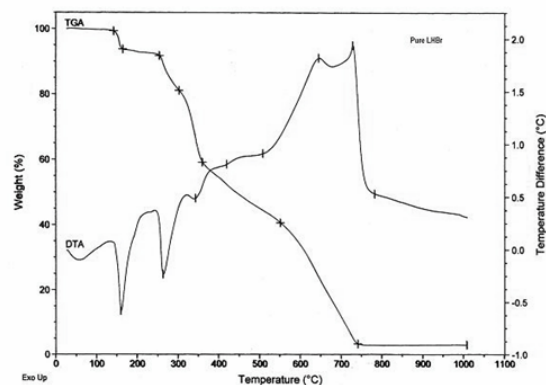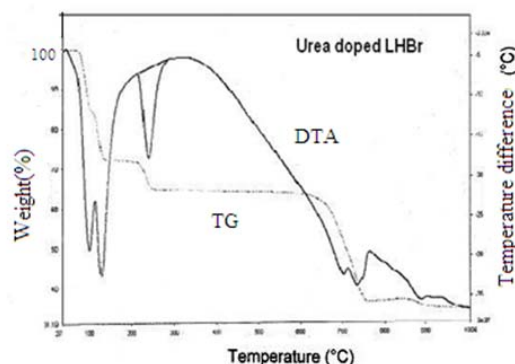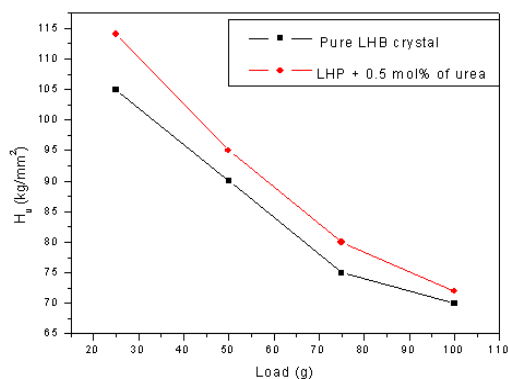

Fig.7: TG/DTA trace of pure LHB crystal

Fig.8: TG/DTA trace of urea-doped LHB crystal

Microhardness studies

The hardness of a material is a measure of its resistance to plastic deformation. The permanent deformation can be achieved by indentation, bending, scratching or cutting. In an ideal crystal, the hardness value should be independent of applied load. But in a real crystal, the load dependence is observed. This is due to normal indentation size effect(ISE)[24]. The variation of microhardness number(H_v) with applied load for grown samples are provided in the figure 9 and it is noticed that Vickers hardness number (H_v) decreases with the applied load satisfying the indentation size effect. From the results, it is observed that the hardness of pure-doped LHB crystal increases when it is doped with urea. This increase in the hardness value of doped sample can be attributed to the incorporation of impurity(urea) in the lattice of LHB crystal. The addition of urea to LHB sample most probably enhances the strength of bonding with the host material and hence hardness number increases[25].

Fig.9: Variation of microhardness number(Hv) with load for the grown crystals

Conclusion

Single crystals of pure and urea-doped LHB have been grown by slow evaporation technique. Both the crystals are optically transparent with well defined morphologies. X-ray diffraction studies confirmed that the pure and urea-doped crystals crystallize in orthorhombic system with space group $P2_12_12_1$. FTIR spectral analysis confirmed the presence of functional groups in the crystals. The grown crystals belong to family of optoelectronic material with second harmonic generation. From optical transmittance studies, the values of band gap were determined to be 5.698 and 5.972 eV for pure and urea-doped LHB crystals respectively. 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 microhardness studies that the mechanical strength of urea-doped LHB crystal is more than that of undoped LHB crystal.

Acknowledgement

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