Chapter - IV

Growth and Optical Studies on Semiorganic NLO Crystals - L-HFB, L-HDP and L-HB
4.1 Introduction and Review of Earlier Work

Recent research on NLO materials reveal that there has been a considerable interest in the design and synthesis of semiorganic nonlinear optical materials for the development of coherent blue-green laser generation. Much work demonstrated that organic materials can have a very high nonlinear susceptibilities compared with inorganics, but the use is impeded by their low optical transparencies, poor mechanical and thermal properties, low laser damage threshold and inability to produce large size single crystals. Inorganic NLO materials typically have excellent thermal and mechanical properties but possess relatively modest optical nonlinearities because of the lack of extended $\pi$-electron delocalization [1,2]. In semiorganics, polarizable organic molecules are stoichiometrically bound within an inorganic host [3], e.g. an organic ion / inorganic counter ion salt such as L-arginine phosphate [4] or an organic ligand / metal ion complex such as tris(thiourea) zinc sulphate [5,6]. In this class of materials, the organic
ligand is ionically bonded to a suitable metal ion or an inorganic host, thereby imparting improved mechanical and thermal properties, which were the major drawbacks of organic materials. For example the second order SHG efficiency of zinc cadmium thiocyanate is 51.6 times as high as that of the reference material urea and the UV transparency cutoff occurs at 290 nm [7,8]. Among the organic materials giving rise to acentric structures, essential for the SHG activity and other second order nonlinear optical effects, the combinations from the amino acids like L-histidine, L-arginine and L-alanine are very remarkable. L-histidine \([(\text{C}_3\text{N}_2\text{H}_3)\text{CH}_2\text{CH(NH}_3^+\text{)}(\text{CO}_2^-)]\) is a strong mono carboxylic amino acid. The investigations on the compounds formed by the reaction of L-histidine with other organic and inorganic acids have shown striking features of great interest in the context of second order nonlinear optical (SONLO) activity. All the compounds in this class contain an optically active carbon atom and therefore lead to the formation of acentric structures, which is an essential requirement for the realization of second order nonlinearity.

The growth of single crystals of L-histidine tetrafluoroborate (L-HFB) up to the size of \(20 \times 20 \times 10 \text{ mm}^3\) from aqueous solution by the solvent evaporation method has been reported by Aggarwal et al. [9]. Marcy et al. have investigated the three dimensional crystal structure solution of L-HFB [10]. Rajendran et al. have studied the
crystal growth and optical properties of L-HFB [11]. Ittyachan et al. have solved the crystal structure and basic characterization of L-histidine diphosphate (L-HDP) and L-histidine bromide (L-HB) [12].

4.2 Present Investigations

The semiorganic NLO materials, L-HFB, L-HDP and L-HB, have been synthesized and characterized. The results of the investigations of these promising solution grown crystals for NLO applications are reported in this chapter. The synthesis and crystal growth by slow evaporation technique and other characterizations of interest like X-ray diffraction (powder and single crystal), FT-IR, microhardness, thermal (TG/DT and DSC) analyses and optical (birefringence, powder SHG and laser damage threshold) studies have been presented. The results of these investigations have already been published by the author [13,14].

4.3 Crystal Growth and Characterization

4.3.1 Material Synthesis and Solubility

L-HFB (C₆H₁₀N₃O₂BF₄) was synthesized from L-histidine (Acros, AR grade) and tetrafluoroboric acid (Loba, AR grade) as per the reaction scheme

\[ C₆H₉N₃O₂ + HBF₄ \rightarrow (C₃N₂H₄)^+CH₂CH(NH₃)^+(COO^-) \cdot BF₄^- \]
The equimolar ratio of L-histidine and tetrafluoroboric acid was thoroughly dissolved in double distilled water at 30°C using a magnetic stirrer. The mixture was then evaporated to dryness by heating carefully below 60°C in a temperature controlled waterbath to avoid any possible decomposition. A white crystalline salt of L-HFB was obtained with the yield of 95%.

Following the above procedure, the material L-HDP \((C_6H_{15}N_3O_{10}P_2)\) was synthesized by taking L-histidine and orthophosphoric acid in the ratio of 1:2 as per the reaction given below.

\[
C_6H_9N_3O_2 + 2H_3PO_4 \rightarrow (C_3N_2H_4)^+(H_2PO_4^-) \text{CH}_2\text{CH}(\text{NH}_3)^+(H_2PO_4^-)(\text{COOH})
\]

Similarly, the material L-HB \((C_6H_{10}N_3O_2Br)\) was synthesized in the equimolar ratio of L-histidine and hydrobromic acid

\[
C_6H_9N_3O_2 + HBr \rightarrow (C_3N_2H_4)^+\text{CH}_2\text{CH}(\text{NH}_3)^+(\text{COO}^-) \cdot \text{Br}^-
\]

The solubility test gives a key to select the best solvent and temperature to grow good quality single crystals. The L-HFB solution was prepared in water and maintained at 25°C with continuous stirring to ensure homogeneity of temperature and concentration over the entire volume of the solution. On reaching saturation the content of the solution was analyzed gravimetrically and this process was repeated for
every 5°C for water, methanol and water mixture of methanol (1:1) from 25° - 50°C and the solubility curve is shown in Fig.4.1.

The solubility of L-HDP (Fig.4.2) and L-HB (Fig.4.3) was determined by the same procedure in water and ethanol in the temperature range 30°-50°C. It is observed that L-HFB, L-HDP, and L-HB have a positive temperature gradient and the solubility of these materials is high at the room temperature in water and hence water can be used as the solvent for crystal growth at 30°C.

![Solubility curves of L-HFB.](image)

**Fig.4.1 Solubility curves of L-HFB.**
Fig. 4.2 Solubility curves of L-HDP.

Fig. 4.3 Solubility curves of L-HB.
4.3.2 Crystal Growth

To grow single crystals of L-HFB, the synthesized salt was thoroughly dissolved in double distillé water using a magnetic stirrer. The solution was saturated at 26°C with pH 3.74. The solution was filtered twice to remove the suspended impurities and allowed for slow evaporation at the same temperature. The single crystals with rectangular shape and size $15 \times 12 \times 3 \text{ mm}^3$ were grown within 30 days with an approximate growth rate of 0.45 mm/day along the a-axis (Fig.4.4a). Also the L-HFB solution was prepared with pH 2.74 and allowed for slow evaporation at 30°C. Good quality single crystals with triangular shape and size $12 \times 10 \times 4 \text{ mm}^3$ were grown within 30 days (Fig.4.5a). The growth kinetics and quality of the crystals grown from solution are considerably influenced by the pH of the solution. Further the morphology of the crystals is considerably different an account of the influence of the pH on the growth rate. It is observed that in the lower pH (2.74), crystal grows faster along the b-direction than in other directions.

Single crystals of L-HDP were grown in aqueous solution by the slow evaporation technique. The saturated solution was prepared at pH 3.4 and then the solution was kept at 30°C for slow evaporation. Good quality single crystals with size $14 \times 7 \times 3 \text{ mm}^3$ were harvested from the
mother solution within 30 days with an approximate growth rate of 0.41 mm/day (Fig. 4.6a).

Fig. 4.4 (a) As grown single crystals of L-HFB
(b) Morphology of L-HFB (T=26°C pH 3.74).

Fig. 4.5 (a) As grown single crystals of L-HFB
(b) Morphology of L-HFB (T = 30°C pH 2.74).
Fig. 4.6(a) As grown single crystal of L-HDP.

Fig.4.6(b) The morphology of L-HDP.

Fig.4.7 As grown single crystals of L-HB.
Single crystals of L-HB were grown by the slow evaporation technique at 30°C with pH 3.2. Transparent crystals with size $9 \times 4 \times 3$ mm$^3$ were harvested from the mother solution within four weeks with an approximate growth rate of 0.32 mm/day. The crystal quality was improved by the repeated recrystallization procedure in water. The harvested crystals were found to be stable, nonhygroscopic and unaffected by the environment (Fig.4.7).

4.3.3 X-ray Diffraction Study

4.3.3.1 X-ray Powder Diffraction

A finely powdered sample of the pure single crystals of L-HFB, L-HDP and L-HB were subjected to X-ray powder diffraction technique using a Rich Seifert X-ray powder diffractometer with CuKα - radiation ($\lambda = 1.540\text{Å}$). The 2θ range was analyzed from 10° to 70°, employing reflection mode for scanning. The detector used was a scintillation counter. Figs.4.8, 4.9 and 4.10 represent the powder diffractogram of L-HFB, L-HDP and L-HB respectively. The prominent planes have been indexed.
Fig. 4.8 X-ray powder diffraction pattern of L-HFB.

Fig. 4.9 X-ray powder diffraction pattern of L-HDP.
4.3.3.2 X-ray Single Crystal Diffraction

The grown crystals were subjected to single crystal X-ray diffraction using an Enraf Nonious CAD4 X-ray diffractometer with MoKα radiation (λ = 0.7107 Å) to find out the unit cell dimensions and morphology. Reflections from a few planes were collected and the morphology of the grown crystals are shown along with the respective crystals (Figs.4.4b, 4.5b & 4.6b). The unit cell parameters are presented in the table 4.1. Both L-HFB and L-HDP belong to monoclinic system with space group P2₁, and L-HB belongs to orthorhombic system with space group P2₁2₁2₁ [12].
Table 4.1  Unit cell dimensions of L-HFB, L-HDP and L-HB.

<table>
<thead>
<tr>
<th>Cell dimensions</th>
<th>L-histidine tetrafluoroborate</th>
<th>L-histidine diphosphate</th>
<th>L-histidine hydrobromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.032(2)</td>
<td>8.815(1)</td>
<td>7.063(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.129(4)</td>
<td>8.922(5)</td>
<td>9.009(3)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>10.254(3)</td>
<td>9.161(2)</td>
<td>15.275(1)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>93.39</td>
<td>111.33</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>470.33(3)</td>
<td>671.180(4)</td>
<td>974.069(6)</td>
</tr>
</tbody>
</table>

4.3.4 FT-IR Spectral Analysis

The FT-IR spectrum of L-HFB, L-HDP and L-HB were recorded using a Jasco 460 Plus FT-IR spectrometer by KBr pellet technique in the region 400-4000 cm⁻¹. In the FT-IR spectrum of L-HFB (Fig.4.11), the N-H stretching is shifted to 3150 cm⁻¹ due to the protonation of nitrogen in the imidazole ring whereas in L-histidine it appears at 3120 cm⁻¹. Similarly, the N-H stretching is shifted to 3185 cm⁻¹ and 3090 cm⁻¹ due to protonation of nitrogen in the imidazole ring in L-HDP (Fig.4.12) and L-FB (Fig.4.13) respectively and deprotonated with orthophosphoric acid and hydrobromic acids [15-17]. The strong bands at 1016, 984 and 529 cm⁻¹ are due to presence of BF₄⁻ stretching in L-HFB compound. From this FT-IR spectral analysis, it is confirmed
In the FT-IR spectrum, the vibrational band at 2000 cm\(^{-1}\) was assigned to C-H stretching in L-HFB and L-HB.

that the imidazole and amino groups are protonated and thus counter balance the negative charges of the acid functionality [18,19].

**Fig. 4.11** FT-IR spectrum of L-HFB.

**Fig. 4.12** FT-IR spectrum of L-HDP.
**Table 4.2 FT-IR spectral assignments.**

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignments [16-20]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>L-histidine</strong></td>
<td></td>
</tr>
<tr>
<td>3120</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>1633</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>1588</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1413</td>
<td>C-H stretching</td>
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<tr>
<td>1248</td>
<td>N-H bending</td>
</tr>
<tr>
<td>1016</td>
<td>BF₄ stretching</td>
</tr>
<tr>
<td>984</td>
<td>BF₄ stretching</td>
</tr>
<tr>
<td>1140</td>
<td>PO₄ sym. stretching</td>
</tr>
<tr>
<td>955</td>
<td>PO₄ asym. stretching</td>
</tr>
<tr>
<td>732</td>
<td>CH₂ stretching</td>
</tr>
<tr>
<td>624</td>
<td>C-H bending</td>
</tr>
<tr>
<td>529</td>
<td>BF₄ stretching</td>
</tr>
</tbody>
</table>

Fig. 4.13 FT-IR spectrum of L-HB.
4.3.5 Thermal Analyses

(i) Thermogravimetric and Differential Thermal (TG/DT) Analyses

TGA and DTA are important techniques used to analyze the thermal stability of the materials. TG and DT analyses were carried out using a Seiko thermal analyzer at a heating rate of 20°C/minute in air atmosphere to determine the thermal stability of the grown crystals. In Fig. 4.14, the DTA curve shows that L-HFB melts at 235°C and undergoes an endothermic transition due to decomposition at 278°C. Another important observation is that there is no phase transition till the material melts and this enhances the temperature range for the utility of the crystal for NLO applications.

The TGA curve shows that there is a weight loss of about 20 % at 334°C due to the liberation of volatile substances probably ammonia and carbon dioxide. There is no endothermic or exothermic peak beyond 500°C in the DTA curve, whereas TGA shows a gradual weight loss and the residual weight obtained at 800°C is only 38 %. These ensure the suitability of the material for possible applications in lasers, where the crystals need to withstand the high temperature.
Fig. 4.14 TG/DTA curves of L-HFB.

Fig. 4.15 TG/DTA curves of L-HDP.
In the TG/DTA curves of L-HDP (Fig.4.15), the endothermic peak in the DTA curve at 185°C represents the melting point of the crystal. The TGA curve shows that there is a weight loss about 13% at 329°C due to liberation of volatile substances in the compound. There is no remarkable endothermic or exothermic peak between 200°-700°C in the DTA curve whereas the TGA shows almost a complete weight loss and the residual weight obtained at 700°C is only 53%. In the TG/DTA curves of L-HB (Fig.4.16), the endothermic peak at 162°C in DTA curve represents the melting point of the material. The TGA curve shows that there is a weight loss of about 4.35% after the melting point. There is a strong endothermic peak at 270°C in DTA, which indicates the decomposition of the compound whereas TGA shows almost a complete weight loss and the residual weight obtained at 700°C is only 30%.

Fig.4.16 DG/DTA curves of L-HB.
(ii) Differential Scanning Calorimetry (DSC) Analyses

The DSC and specific heat measurements were performed for the grown single crystals using a TA instruments (2920 Modulated DSC) in the temperature range 0-200°C at a heating rate of 2°C/min in nitrogen atmosphere (Fig.4.17). A small piece (2 × 2 × 1 mm³) of the grown L-HFB crystal was provided with a special care, which was encased in the aluminum pan for this measurement. The specific heat of the material was found to increase with temperature. The specific heat of the L-HFB is 4.516 mJ/°C at 39.78°C. The DSC curve shows that there is no phase transition in this compound upto 250°C. The DSC and specific heat curves of L-HDP and L-HB are shown in Fig.4.18 and Fig.4.19 respectively. The figures show that there is an increase in specific heat with temperature and there is no phase transition in these compounds below the melting point.

Fig.4.17 DSC and specific heat curves of L-HFB.
Fig. 4.18 DSC and specific heat curves of L-HDP.

Fig. 4.19 DSC and specific heat curves of L-HB.
4.3.6 Microhardness Measurement

The Vicker's microhardness was determined for the grown L-HFB crystal with the size $15 \times 12 \times 3 \text{ mm}^3$ on the smooth and dominant (001) plane. Indentations were carried out using Vicker's indentator for varying loads (5–50 g). For each load, several indentations were made and the average value of the diagonal length was used to calculate the microhardness. Vickers microhardness was determined from the formula

$$H_v = \frac{1.8544P}{d^2} \quad (4.1)$$

where $P$ and $d$ are the load and diagonal length of indentation respectively [20]. The hardness was found to increase with load (Fig.4.20). The work hardening coefficient ($n$) of the material is related to the load ($P$) by the relation

$$P = a d^n \quad (4.2)$$

where 'a' is an arbitrary constant. The plot of log $P$ vs log $d$ is a straight line (Fig.4.21). The work hardening coefficient 'n' was found to be 4.4 for L-HFB. Another well known semiorganic NLO material, L-arginine phosphate (LAP), has a work hardening coefficient 2.0 [21]. The relatively high value of work hardening coefficient for L-HFB proves the high mechanical strength of the grown L-HFB crystals.
Fig. 4.20 Vicker’s hardness of L-HFB.

Fig. 4.21 Plot of log P vs log d.
The microhardness of L-HDP was measured by adopting the foregoing procedure. Transparent crystal plate of 3 mm thickness and surface area of $14 \times 7 \text{ mm}^2$ free from cracks was selected for microhardness study. Microhardness measurements were done on the (100) plane for the applied load varying from 5-25 gm using a Vicker’s microhardness tester. The hardness was found to increase with the load (Fig.4.22).

The work hardening coefficient ‘n’ was found to be 3.25, which shows that the material has a good mechanical stability (Fig.4.23).

![Variations of Vicker's hardness with load.](image-url)
Further comparisons are drawn from the reported values and are presented in the table 4.3 [21, 22].

**Table 4.3. Microhardness – Work hardening coefficient.**

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Materials</th>
<th>Work hardening coefficient</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L-histidine tetrafluoroborate</td>
<td>4.4</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>L-histidine diphosphate</td>
<td>3.25</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>L-histidinium tetrafluorophthalate</td>
<td>4.3</td>
<td>#</td>
</tr>
<tr>
<td>4</td>
<td>L-arginine phosphate</td>
<td>2.0</td>
<td>[21]</td>
</tr>
<tr>
<td>5</td>
<td>Methyl p-hydroxy benzoate</td>
<td>1.94</td>
<td>[22]</td>
</tr>
<tr>
<td>6</td>
<td>Tris (thiourea) zinc sulphate</td>
<td>5.3</td>
<td>**</td>
</tr>
</tbody>
</table>

* Present work; # Chapter - III; ** Chapter - VI.
4.3.7 UV-Vis Transmittance Study

The optical transmittance plays a vital role in identifying the potential of an NLO material because a given material can be of utility in the UV region only if it has a wide transparency window, without absorption at the fundamental and second harmonic wavelengths and lower cutoff wavelength below 400 nm.

The UV-Vis transmittance spectrum of L-HFB, L-HDP and L-HB were recorded using a Varian Cary 5E UV-Vis spectrometer in the range 200-800 nm. Fig.4.24 represents the UV-Vis transmittance spectrum L-HFB. The figure shows that it has a wide optical transmittance in the entire visible region with the lower cutoff wavelength at 220 nm. Figs.4.25 and 4.26 represent the UV-Vis transmittance spectrum of L-HDB and L-HB respectively. The figures show that the materials have a wide optical transmittance and the lower cutoff wavelength ($\lambda_{cutoff}$) down to 230 and 220 nm respectively due to $\pi$-$\pi^*$ transition in these compounds while the parent compound L-histidine has a lower cutoff at 270 nm (Fig.4.25). From the UV-Vis spectral analysis, it is noted that there is no significant absorption in the UV and visible region thereby confirming the advantages of the crystals for optical applications. The large transmittance in the entire visible region and lower cutoff wavelength enables them to be the potential
materials for second and third harmonic generation of an 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.

![Fig.4.24 UV-Vis transmittance spectrum of L-HFB.](image)

![Fig.4.25 UV-Vis transmittance spectrum of L-HDP.](image)
4.3.8 Measurement of Refractive Index

Refractive index of the crystal bears a definite relation to the crystallographic symmetry of biaxial crystals and magnitudes of the index of refraction is intimately related to its structure. The refractive index of the grown crystals was determined by Brewster angle technique using a He-Ne laser ($\lambda = 632.8$ nm). The refractive index of L-HFB, L-HDP and L-HB is 1.54, 1.45 and 1.51 respectively.

4.3.9 Birefringence – Interference Technique

Birefringence is defined as the double refraction of a light in a transparent molecularly ordered material, which is manifested by the
existence of orientation dependent differences in the refractive index. The birefringence of L-HFB was measured by interference method [23-25] with a halogen lamp (500 W) as a source. The polarizer and the analyzer were placed in crossed positions and the crystal was placed with its optical axis perpendicular to the incident ray. When the crystal was introduced between the polarizer and the analyzer, the transmitted light from the analyzer undergoes interference and the pattern was observed through a spectrometer. To measure the birefringence as a function of temperature, an electric furnace (400°C) with an accuracy of ±1°C (Chapter-II) was used. The birefringence was determined in the temperature range 30°C-150°C for every 40°C. The birefringence (Δn) was calculated from these interference fringes using the formula

\[ \Delta n = \frac{\lambda_2 \lambda_1}{(\lambda_2 - \lambda_1)t} \]  

(4.3)

where \( \lambda_1 \) and \( \lambda_2 \) are the successive wavelengths of the fringes and \( t \) is the thickness of the crystal.

Data analysis was performed using Microcal origin 6.0. Figs. 4.27, 4.28 and 4.29 show the birefringence as a function of temperature for L-HFB, L-HDP and L-HB respectively.
Fig. 4.27 Birefringence of L-HFB in the temperature range 30°-150°C.

Fig. 4.28 Birefringence of L-HDP in the temperature range 30°-150°C.
4.3.10 Powder SHG Efficiency – Kurtz and Perry Technique

The powder SHG conversion efficiency of L-HFB was determined by Kurtz and Perry technique [26] using an Nd:YAG laser (1064 nm, 8 ns, 10 Hz). The SHG intensity from the material was measured as a function of particle size. The continuous increase in SHG intensity with increase in particle size and remaining essentially constant at particle size greater than the average coherence length ($l_c$), confirms the phase matching behaviour of the material. The sample was ground and sieved into different particle size ranges (<106, 106-125, 125-150, >150 μm). The powder sample was filled in a microcapillary tube of uniform bore of about 1.5 mm diameter. The SHG at 532 nm (green light) was collected.
by the photomultiplier tube. The optical signal incident on the PMT was converted into a voltage output in the CRO. The reference sample urea was also powdered to the same particle size as the experimental sample. The powder SHG conversion efficiency of L-HF3 was found to be 0.23 times that of urea. Following the same procedure, the powder SHG efficiency of L-HDP and L-HB were found to be 0.21 and 0.20 times that of urea respectively. The SHG efficiency for various particle sizes shows the increase in SHG intensities with increasing particle sizes, and gives the phase matching property of L-HFB, L-HDP and L-HB (Figs.4.30, 4.31 & 4.32).

![Fig.4.30 Phase matching curve of L-HFB.](image)

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**Fig.4.30 Phase matching curve of L-HFB.**
Fig. 4.31 Phase matching curve of L-HDP.

![Phase matching curve of L-HDP](image)

Fig. 4.32 Phase matching curve of L-HB.

![Phase matching curve of L-HB](image)
4.3.11 Measurement of Laser Damage Threshold

The measurement of laser damage threshold was carried out using a Quanta Ray Q-switched Nd:YAG laser (1064 nm, 10 Hz, 10 ns). The grown crystal with size 12 × 6 × 3 mm³ was used to measure the laser damage threshold. The laser beam was focused by a lens on to the (100) plane of the grown crystal (L-HFB). The damage was observed and the energy of the laser beam was measured by Scientech power meter (Model No.ACX5004). The laser damage threshold value was calculated from the laser energy divided by the focused beam area. The above procedure was followed to find out the laser damage threshold of L-HDP and L-HB (Table 4.4). The laser damage threshold of L-FHB and L-HDP are slightly greater than LiNbO₃ [27].

Table 4.4. Comparison of Laser damage threshold with similar materials.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Sample</th>
<th>Laser damage threshold (MW/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L-histidine tetrafluoroborate</td>
<td>116.72</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>L-histidine diphosphate</td>
<td>113.17</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>L-histidine bromide</td>
<td>96.73</td>
<td>*</td>
</tr>
<tr>
<td>4</td>
<td>Lithium niobate</td>
<td>100.00</td>
<td>[27]</td>
</tr>
<tr>
<td>5</td>
<td>L-arginine acetate</td>
<td>162.42</td>
<td>#</td>
</tr>
<tr>
<td>6</td>
<td>L-arginine trifluoroacetate</td>
<td>177.34</td>
<td>#</td>
</tr>
</tbody>
</table>

* Present work; # Chapter – V.
4.4 Conclusions

The semiorganic NLO materials L-HFB, L-HDP and L-HB were synthesized and the solubility test reveals that they have higher solubility in water. Good quality single crystals were grown by the slow evaporation technique at 30°C. The effect of pH on the morphology of the grown crystal has been studied for L-HFB and it shows that the crystal grows faster along a and b-directions than c-direction. The thermal and mechanical studies reveal that the grown crystals have a good thermal and mechanical stability. The materials have a wide optical transmittance in the entire visible region with short lower cutoff wavelengths. The optical birefringence was measured by interference technique as a function of temperature. The powder SHG efficiency of these materials was found to be comparable to KDP and it is phase matchable. The laser damage threshold of these materials is slightly greater than LiNbO₃.
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