

## Crystal growth, thermal and optical studies of L-histidine tetrafluoroborate: A semiorganic NLO material

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L-histidine tetrafluoroborate (L-HFB), a semiorganic nonlinear optical (NLO) material has been synthesized and characterized by elemental analysis and FT-NMR spectroscopic studies. Solubility of L-HFB has been determined in water and ethanol. The single crystals with dimensions  $15 \times 12 \times 3 \text{ mm}^3$  were grown by slow evaporation technique under two different pH conditions. The effect of pH on the morphology of the crystals have been studied. The grown crystals of both pH values has been subjected to single crystal X – ray diffraction to determine the unit cell dimensions and morphology. The thermal stability has been analyzed by TGA and DTA. The microhardness test was carried out in (001) plane and the hardness coefficient was calculated. The birefringence values ( $\Delta_n$ ) were determined in the wavelength region 5540 - 6460 Å.

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### 1 Introduction

Materials that possess optical nonlinearities have been studied extensively for their possible applications in various fields like telecommunication, optical computing, optical data storage and optical information processing. The generation of coherent blue light through second harmonic generation (SHG) from near infrared (NIR) laser sources is an important technological problem that has attracted much attention in the last few years. Potential applications lie in the fields of high-density optical data storage, high-resolution printing and spectroscopy [1-2]. Organic crystals have large nonlinear susceptibilities compared to inorganic crystals. However these crystals have inherent limitations such as increased optical absorption, narrow transparency window, and poor mechanical and thermal stability. Inorganic crystals have excellent mechanical and thermal properties but possess relatively modest optical nonlinearities because of the lack of  $\pi$  - electron delocalization. Combining the high optical nonlinearity and chemical flexibility of organics with temporal and thermal stability and excellent transmittance of inorganics, semiorganic materials have been proposed and are attracting a great deal of attention in the nonlinear optical field [3-4].

L-HFB is a semiorganic NLO material with molecular formula  $\text{C}_6\text{H}_{10}\text{N}_3\text{O}_2\text{BF}_4$ . It has SHG efficiency five times greater than KDP [5]. The FT-IR, FT-Raman and optical studies of this material have already been reported by our group [6]. In the present investigations the growth aspects of LHFBB in two different pH (3.14 & 2.74) values have been studied. The crystals were grown by slow evaporation technique and characterized by single crystal X-ray diffraction, TGA and DTA, UV-Vis and microhardness studies. Further the birefringence of L-HFB has been measured in the visible region.

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## 2 Experimental procedure

### 2.1 Synthesis and solubility

The L-HFB was synthesized at 50°C by dissolving equimolar ratio of L-histidine and tetrafluoroboric acid in double distilled water. In L-histidine the imidazole and amino groups are protonated and thus counterbalance the negative charges of the carboxylate (COO<sup>-</sup>) functionality and tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) ion. The synthesized compound was purified by successive recrystallization process.

Large size good optical quality single crystals are essential to evaluate their physical properties, especially the optical properties. To grow good quality crystals, the selection of a suitable solvent, temperature, and pH of the solution are important parameters. To optimize the growth conditions the solubility of L-HFB in different solvents were measured. The L-HFB solution was prepared in water and maintained at 25°C with continuous stirring to ensure homogeneous 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. The experiment was repeated for ethanol and an ethanol - water mixture (1:1) from 25-50°C and the solubility curve is shown in Figure 1. It is to be noted that the solubility is maximum in water and hence aqueous solutions could be used for the growth of good crystals.

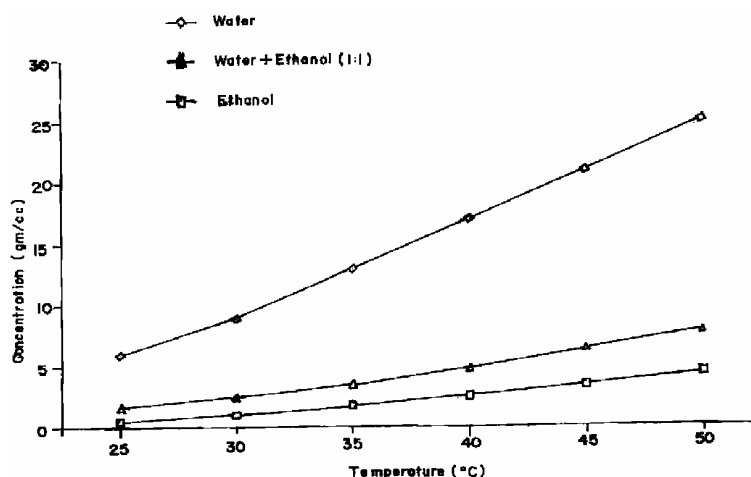


Fig. 1 Solubility curve of L-HFB.

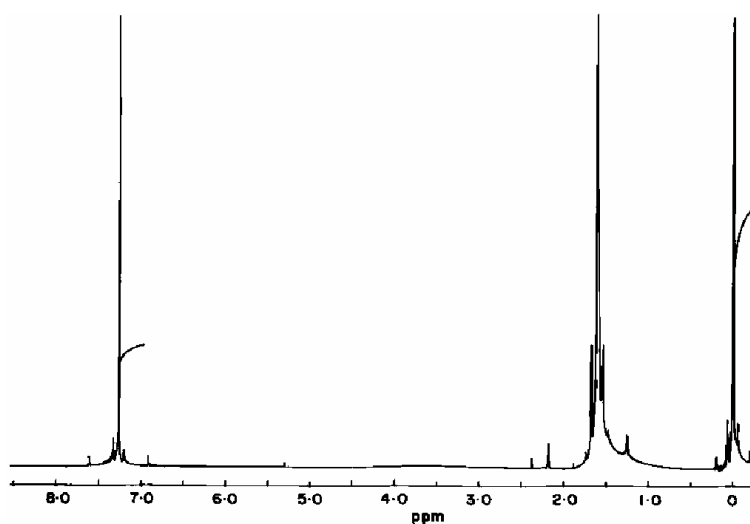


Fig. 2 <sup>1</sup>H – NMR spectrum of L-HFB.

## 2.2 Crystal growth

The aqueous solution of L-HFB was prepared in the pH = 3.74 and kept at 26°C for slow evaporation. Good quality single crystals with regular shape (polyhedron) and size of 15 x 12 x 3 mm<sup>3</sup> were harvested within four weeks with approximate growth rate of 0.4 mm/day. The crystals have two prominent faces (001) and (010). The plane (001) is perpendicular to (010) plane. Again the L-HFB solution was prepared in the pH = 2.74. The solution was kept at 30°C for slow evaporation. Good quality triangle shaped crystals with size of 12 x 10 x 2 mm<sup>3</sup> were grown within four weeks. 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 on account of the influence of pH on the growth rate. It is observed that at the lower pH value (2.74) the crystal grows at a faster rate along the b- direction than the a- direction. As the pH value increases (3.74) the growth is more along the a- than the b- direction. In both pH values, growth rate along c-direction is the least and is not much affected.

## 3 Characterization

### 3.1 Elemental analysis

The percentage composition of the synthesized compound can be established by carbon, hydrogen and nitrogen (CHN) analysis. The result of CHN analysis carried out for the synthesized L-HFB shows that the compound contains the following percentage of carbon, hydrogen and nitrogen: C=30.43 (29.66) %, H= 4.24 (4.14) %, N = 17.02 (17.29) %. The calculated values are given in the bracket.

### 3.2 FT-NMR spectral study

Nuclear magnetic resonance spectroscopy is widely used to confirm the molecular structure. A Bruker-300 MHz FT-NMR spectrometer was used to record the <sup>1</sup>H-NMR spectrum of LHFBB using CDCl<sub>3</sub> as the solvent (Figure 2). In this spectrum, the signal due to C-H of the imidazole ring is observed at 1.367 ppm. Further the signal due to C-H of the amino group appears upfield at 0.141 ppm due to the heavily shielded proton of this group. The signal at 1.474 ppm could be attributed to the CH<sub>2</sub> group. The proton of the N-H groups account for a signal in the range of 7.4 ppm [7-8]. Thus the NMR spectrum is accounted for by the molecular structure.

### 3.3 Single crystal X-ray diffraction study

The single crystal X-ray diffraction of L-HFB crystal (pH=3.14) was carried out using an ENRAF NONIUS CAD4 X- ray single crystal diffractometer. Reflections from a few planes were collected and indexed. The unit cell parameters are a = 5.032 (2) Å, b = 9.129 (1) Å, c = 10.254 (2) Å, β = 93.39 (8)° and it belongs to the monoclinic system. The observed values agree well with the reported values [1]. The (001) plane is highly developed than the other prominent planes. In the triangle shaped crystals (pH=2.74), the planes (001) and (110) are comparatively well developed than the other planes and the planes ( $\bar{1}$  3 0), ( $\bar{1}$   $\bar{1}$  0), (011) have newly emerged.

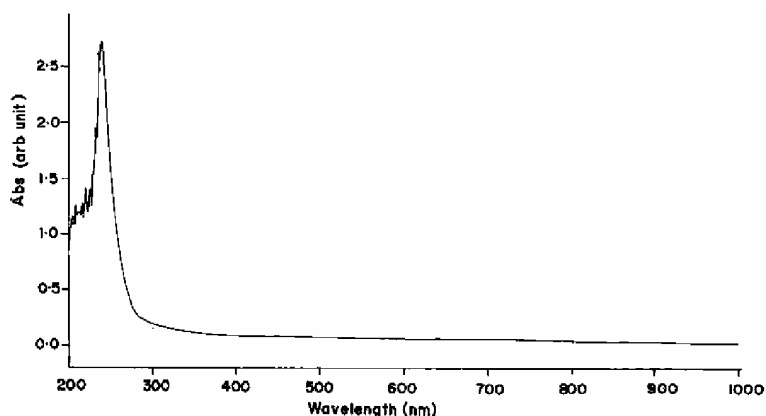
### 3.4 Measurement of melting point and density

The melting point of the synthesized L-HFB was measured using a melting point apparatus (Model Tempo 120 V) and found to be 235 ± 1 °C. The density of the grown L-HFB single crystal was measured as 1.72 gcm<sup>-3</sup> by the floatation method using a mixture of bromoform and glacial acetic acid. This agrees well with the theoretical value (ρ = 1.713) obtained from the crystallographic data.

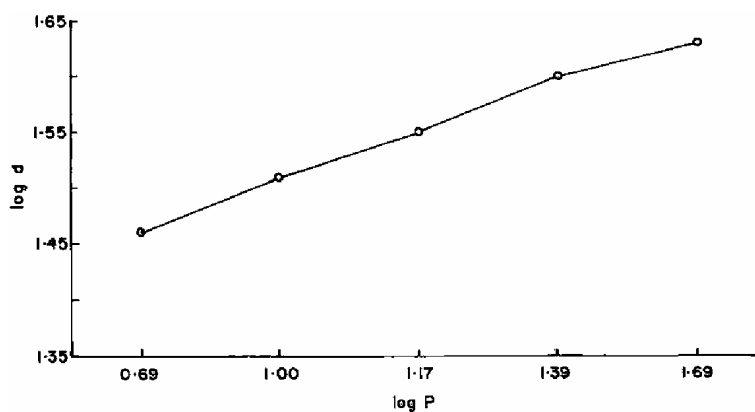
### 3.5 UV-Vis spectral studies

Single crystals are mainly used in optical applications where the optical transmission range and lower cutoff wavelength are very important. The UV-Vis absorption spectra were recorded using Hitachi UV-Vis Spectrophotometer in the spectral range 200–1000 nm (Figure 3). The L-HFB has a lower cutoff wavelength of 270 nm and the high transmittance in the entire visible region enables it to be a potential candidate for optoelectronic applications.

**Fig. 3** UV-Vis absorption spectrum of L-HFB.



**Fig. 4** Plot of Log P vs Log d.



### 3.6 Measurement of microhardness and work hardening coefficient

Hardness is the resistance offered by a material to localized plastic deformation caused by scratching or by indentations. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation [9-10]. The Vicker's microhardness was evaluated for the grown crystal with the size 15 x 12 x 3 mm<sup>3</sup> for the smooth and dominant face (001). Indentations were carried out using Vicker's indenter for varying loads (5–50 g). For each load, several indentations were made and the average value of diagonal length was used to calculate the microhardness. Vickers microhardness in Pascals was determined from the formula  $H_v = 1.8544 P/d^2$ , where P and d are the load (in Kgf) and diagonal length of indentation (in mm) [10]. The hardness is found to increase with the load. The work hardening coefficient (n) of the material is related to the load (P) by the relation  $P = a d^n$  where a is an arbitrary constant. The plot of log P vs log d is a straight line (Figure 4). The work hardening coefficient 'n' is 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 [11]. The relatively high value of work hardening coefficient for L-HFB proves the high mechanical strength of the grown L-HFB crystal.

### 3.7 Thermal analysis

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a Seiko thermal analyzer at a heating rate of 20°C/min in air to determine the thermal stability of the compound. The DTA curve (Figure 5) shows that L-HFB melts at 235°C and it undergoes an endothermic transition due to decomposition at 278°C followed by another endothermic peak at 360°C. The TGA curve shows that there is a weight loss of about 20 % at 334°C due to the volatile substances in the compound 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 %.

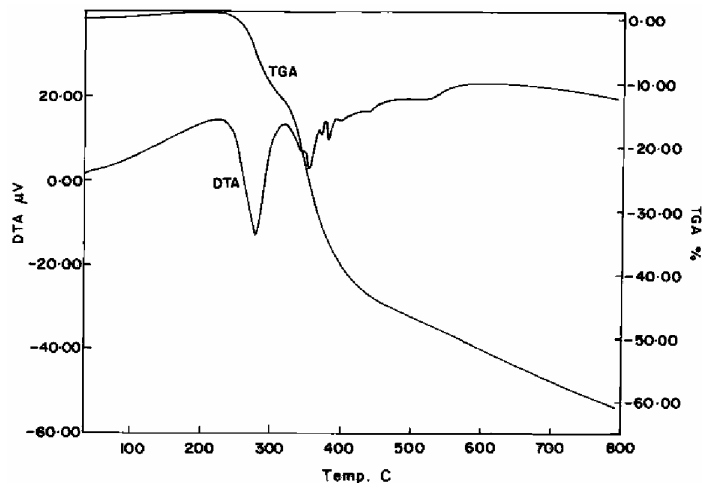


Fig. 5 TGA and DTA curve of L-HFB.

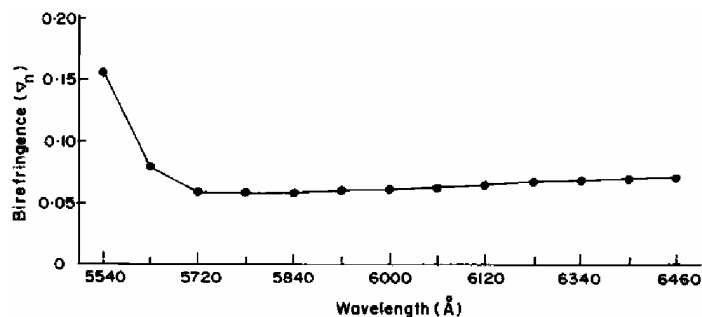


Fig. 6 Birefringence curve of L-HFB.

### 3.8 Measurement of birefringence

Birefringence is one of the important properties for optical materials. Birefringent materials are used as circulators, beam displacers and Glan polarisers [12-14]. The birefringence of L-HFB was measured using channel spectrum method with a high power halogen lamp (500W) as a source. The polarizer and analyzer were placed in crossed positions and the crystal was placed with its optics 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 high-resolution spectrometer. The minimum deviation angle corresponding to each band was measured. Then the wavelength of the corresponding dark bands was obtained from the calibration graph of standard wavelength (Hg) spectrum. The birefringence was calculated by the equation

$$\nabla n = [\lambda_2 / (\lambda_1 - \lambda_2)] (\lambda_1 / t)$$

where  $t$  is the thickness of the crystal and  $\nabla n$  is the birefringence for the pair of wavelengths  $\lambda_1$  and  $\lambda_2$  [15].

The birefringence values have been calculated for different pairs of wavelengths in the range. The birefringence does not vary much and is moderate over the operating wavelengths. The graph connecting wavelength and birefringence is represented in Figure 6.

#### 4 Conclusion

L-histidine tetrafluoroborate was synthesized and water was found to be a suitable solvent for the crystal growth. The effects of pH on the morphology of the crystals have been studied. The UV cutoff wavelength was found to be 270 nm and thus the material is a potential candidate for generating blue – violet light using a diode laser. The mechanical hardness studies reveal that L-HFB has a relatively high value for its work hardening coefficient. The thermal analyses establish the very good thermal stability of the material. The optical birefringence has been calculated for different pairs of wavelengths.

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