

Optical and microhardness studies of semiorganic nonlinear optical material: L- histidine tetrafluoroborate

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L-histidine tetrafluoroborate (L-HFB) a semiorganic nonlinear optical material has been synthesized in aqueous solution at 50°C and characterized by FT-IR and FT-Raman spectroscopy studies. The solubility was determined in different solvents such as water, methanol and water mixture of methanol. The single crystals with dimensions 15x12x3 mm³ were grown by slow evaporation method within four weeks with approximate growth rate of 0.25 mm/day. The grown crystals have been subjected to single crystal X-ray diffraction studies to determine the unit cell dimensions and morphology. The Kurtz powder second harmonic generation test shows that the compound is a potential candidate for frequency conversion. The refractive index has been measured using He-Ne laser. The microhardness test was carried out and the load dependence hardness was observed. The material has a wide transparency in the entire visible region.

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1 Introduction

In recent years there has been considerable interest in the synthesis of semiorganic nonlinear optical materials with excellent second – order optical nonlinearities because of their potential application including telecommunication, optical computing, optical data storage and optical information processing [1]. Much attention has been paid to the search of novel high quality nonlinear optical materials that can generate high second harmonic blue-violet light by using GaAlAs laser diodes. Coherent blue and green light is important for many applications such as display, high-resolution printing, and signal processing [2]. Most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. Also it is difficult to grow large size optical quality crystals of these materials for device applications.

Semiorganic NLO crystals have good thermal and mechanical properties and large nonlinear coefficients [3,4]. L-histidine tetrafluoroborate is a semiorganic nonlinear optical material with molecular formula C₆H₁₀O₂N₃BF₄. L-HFB belongs to monoclinic system with point group 2 and the space group P2₁. Its single crystal SHG efficiency is five times that of KDP [5]. In the present investigation, the synthesis, growth, mechanical and optical characterization of L-HFB have been studied.

2 Experimental

2.1 Synthesis and Solubility

The L-HFB compound was synthesized at 50°C by dissolving equimolar ratio of L-histidine and tetrafluoroboric acid in water [5,6]. The synthesized L-histidine tetrafluoroborate salt was purified by successive recrystallization process. The melting point of the compound was found to be 235 ± 1°C.

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The solubility test gives a key to select the best solvent and temperature to grow good quality crystals. 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 for water, methanol and water mixture of methanol (1: 1) from 25°C to 55°C and the solubility curve is shown in Figure 1.

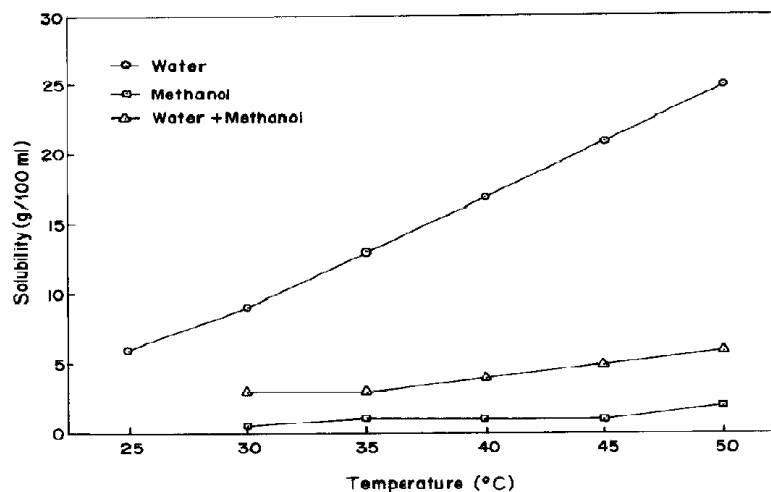


Fig. 1 Solubility curve of L-HFB.

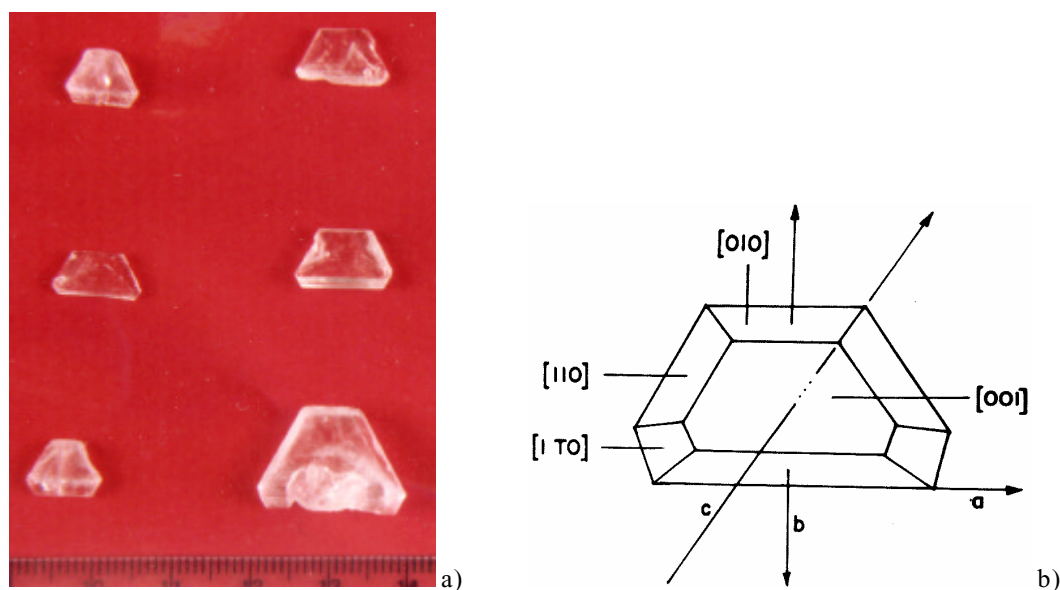


Fig. 2 a) As grown single crystals of L-histidine Tetrafluoroborate, b) Morphology of L-HFB crystal.

2.2 Crystal Growth

According to the solubility test L-HFB is more soluble in water. A saturated aqueous solution of L-HFB was prepared and the pH was adjusted to 3.74. The saturated solution was kept at 26°C for slow evaporation. Good quality crystals with regular shape and size of 15 x 12 x 3 mm³ were obtained within four weeks with approximate growth rate of 0.25mm/day and the growth along (001) plane is large. The grown crystals are shown in the Figure 2a.

3 Characterization

3.1 Single Crystal X-ray Diffraction

The crystals have been subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD4 single crystal X-ray Diffractometer to determine the unit cell dimensions and morphology. The unit cell parameters are $a = 5.032 \text{ \AA}$, $b = 9.129 \text{ \AA}$, $c = 10.254 \text{ \AA}$ and $\beta = 93.39^\circ$ and volume $V = 470.33 \text{ \AA}^3$. The observed values agree well with the reported values [5]. Reflections from a few planes were collected and the morphology of the grown crystals is shown in Figure 2b.

3.2 Kurtz Powder SHG Test

Second harmonic generation from the powder L-HFB has been studied following Kurtz powder technique (7). In this method the powder sample with average particle size $100 \mu\text{m} - 150 \mu\text{m}$ were illuminated using a Q – Switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm with a pulse width of 8 ns . The second harmonic generation was confirmed by emission of green radiation ($\lambda = 532 \text{ nm}$). The amplitude of SHG output voltage was measured using a 1 KV photomultiplier and digital oscilloscope assembly. The measured efficiency values of L-HFB are 0.23 times that of urea.

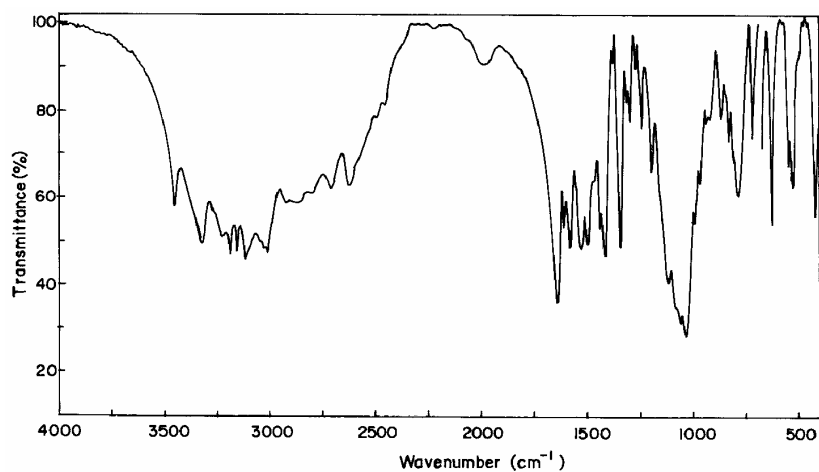


Fig. 3 FT-IR spectra of L-HFB.

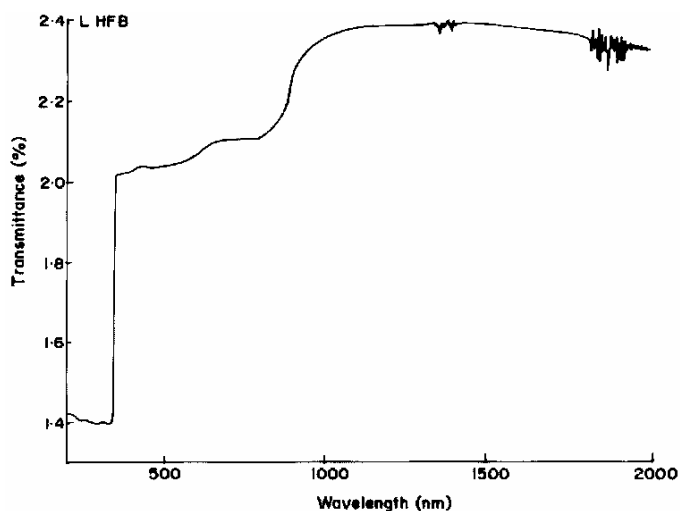


Fig. 4 UV –Vis NIR spectra of L-HFB.

Table 1 FT-IR and FT-Raman Assignment of characteristic vibrational Frequencies in L-HFB.

Wavenumber cm ⁻¹		Assignment	References
FT-IR	FT-Raman		
529		$\nu_{as}(\text{BF}_4)$	[9]
622		$\delta(\text{C-H})$	[8, 9, 10]
712		$\nu(\text{CH}_2)$	[8, 9, 10]
	857	$\delta(\text{C-N})$	[10]
984		$\nu_{as}(\text{BF}_4)$	[9]
	1184	$\nu(\text{C-H})$	[10]
1016		$\nu(\text{BF}_4)$	[9]
1337	1342	$\nu(\text{C-N})$	[8, 9, 10]
	1479	$\nu(\text{C-C})$	[10]
1602		$\nu_{as}(\text{NH}_3)$	[9]
1630		$\nu(\text{C=O})$	[8, 9, 10]
	2953	$\nu_{as}(\text{CH}_2)$	[10]
3150		$\nu_s(\text{N-H})$	[9, 10, 11]
3316		$\nu(\text{NH}_3)$	[8, 9]

ν - stretching δ -bending s-symmetric as – antisymmetric

3.3 FT-IR and FT- Raman Spectral Studies

Infrared and Raman spectroscopies are effectively used to determine the molecular structure and the identification of the functional groups in the synthesized compound. In order to analyze qualitatively the presence of functional groups in the crystal, FT-IR spectra were recorded using Bruker IFS 66V FT-IR spectrometer by KBr pellet technique in the region 400–4000 cm⁻¹ and are shown in Figure 3. The FT-Raman spectra were also recorded in the same range using Bruker RFS 100/S spectrometer. In the FT-IR spectra peaks around 1635 and 1411 cm⁻¹ indicate the presence of the COO⁻ (carboxylate ion) in L-HFB [8, 9]. A sharp peak at 3150 cm⁻¹ is assigned to N-H symmetric stretching and a peak at 3109 cm⁻¹ is assigned to C-H symmetric stretching in the compound [10]. The stretching frequency at 529 cm⁻¹ and 984 cm⁻¹ are assigned to the BF₄⁻ [9 - 11]. It is concluded that the imidazole and amino (NH₃)⁺ groups are protonated and thus counterbalance the negative charges of the carboxylate (CO₂)⁻ functionality and the tetrafluoroborate (BF₄)⁻ ion [6]. Other prominent vibrational frequencies of FT-IR and FT-Raman spectra have been assigned with corresponding functional groups present in the synthesized compound (Table 1).

3.4 UV-Vis NIR Spectral Studies

The UV-Vis spectral studies were carried out using Varian Cary 5E UV-Vis spectrometer in the range 200 – 2000 nm (Figure 4). The L-HFB crystal has a good transmission in the entire visible region and the lower cut off wavelength is 220 nm. The large transmission in the visible region enables it to be a potential candidate for optoelectronic applications [12].

3.5 Microhardness Measurement

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically hardness is the resistance offered by a material to localized plastic deformation (moment of dislocations) caused by scratching or by indentation. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads (~ 100 Kg). But for materials which have low hardness and which are available as small-sized sample, it is convenient to make measurements at low loads of < 200g. The low load hardness is called microhardness. In ideal circumstances, measured hardness values should be independent of the applied

load. But in practice, a load dependence is observed [13]. The grown crystal $15 \times 12 \times 3 \text{ mm}^3$ with smooth and dominant face (001) was selected for microhardness studies. Indentations were carried out using Vickers 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 number was determined using $H_v = 1.8544 P/d^2 \text{ Kg/mm}^2$. The hardness number was found to increase with the load. The plot drawn between the corresponding loads and hardness values of the L-HFB is shown in Figure 5.

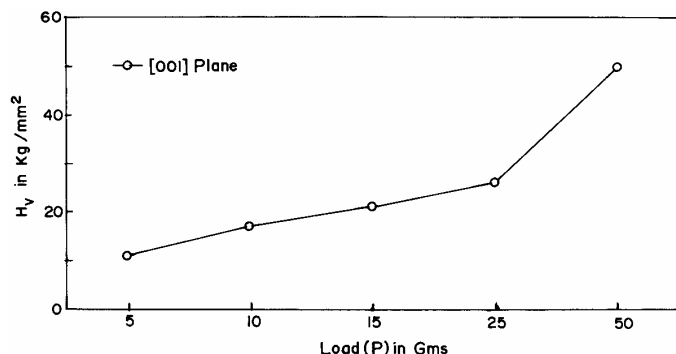


Fig. 5 Variation of load with Vickers Hardness.

3.6 Measurement of Refractive Index

Refractive index bears a definite relation to the crystallographic symmetry of biaxial crystals and magnitudes of the index of refraction which are intimately related to its structure [14]. The L-HFB crystals with the size of $15 \times 12 \times 3 \text{ mm}^3$ were used to measure the refractive index. The refractive index was determined (He-Ne laser $\lambda = 653 \text{ nm}$) by Brewster angle measurement technique and found to be $\mu = 1.54$.

4 Conclusion

L-histidine tetrafluoroborate was synthesized and its solubility was analyzed in the temperature range $25 - 55^\circ \text{ C}$. The solubility test indicates that the L-HFB has the highest solubility in water. Single crystals with dimensions $15 \times 12 \times 3 \text{ mm}^3$ have been grown in an aqueous solution at 26° C . FT-IR, FT-Raman spectra were recorded to analyze qualitatively the presence of functional groups in the crystals. The unit cell parameters have been evaluated by single crystal X-ray diffraction technique. The morphology of the grown crystal shows that the crystal grows faster along a and b directions than along the c direction. The material has good thermal and mechanical stabilities. The powder SHG efficiency of L-HFB is found to be 0.23 times that of urea. The grown crystal has a good optical transmittance in the entire visible region.

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