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Synthesis, Growth and characterization of NLO single crystal: L-Histidine tetrafluroborate

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ABSTRACT

Single crystals of L-histidine tetrafluroborate have been grown by low temperature solution growth technique by using water as a solvent. The grown crystals have been subjected to single crystal x-ray diffraction studies to identify the cell parameters and morphology. The presence of functional groups were identified by fourier transform infrared spectroscopy. Optical transmission spectrum reveals the optical property of the grown crystal. The NLO property of the crystal was confirmed by Kurtz SHG test and compared with NLO of KDP crystals. Thermal studies were carried out to check the thermal stability of the crystal. The encouraging results show that the LHFB crystals have potential application in optical devices.

KEY WORDS: Solution growth technique, FTIR, UV-Vis-NIR, TGA/DTA, Kurtz SHG test.

1. INTRODUCTION

Nonlinear optical materials are used in optical computing, optical communication, harmonic generators, medical diagnostics, frequency mixing, and optical switching. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible, ultraviolet ranges are required for various devices in the field of optoelectronics and photonics. Studies have been made on semiorganic non-linear optical materials because of their potential applications in the field of telecommunications, image processing and data storage devices. Now a days , efforts have been made on the aminoacid mixed organic, inorganic complex, inorder to improve the chemical stability, laser damage threshold, and linear and nonlinear optical properties. A series of semi-organic compound such as L-Arginine phosphate, L-Arginine hydrochloride, L-Histidine di-hydrogen phosphate, L-Arginine tetrafluroborate have been reported. As L-HFB is an organic and inorganic complex, it has good thermal and mechanical properties. L-Histidine tetrafluroborate is a semiorganic NLO material with molecular formula $C_6H_{10}O_2N_3BF_4$. It belongs to the monoclinic system with point group 2 and space group $P2_1$ which was identified as potentially useful non-linear optical material. In the present investigation, the growth aspects of L-HFB have been studied and bulk crystals have been grown by low temperature solution growth technique. The cell parameters and the presence of functional groups were confirmed by single crystal X-ray diffraction (SXRD) and Fourier-transform infrared (FTIR) spectroscopy, respectively. The ultraviolet-visible-near-infrared (UV-vis-NIR) spectrum also recorded to estimate the UV cut-off wavelength. Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were carried out to determine the thermal stability. The NLO property have also been studied and reported.

2. EXPERIMENTAL

2.1. Synthesis and crystal growth: The compound L-Histidine tetrafluroborate was synthesized by dissolving equimolar quantities of L-Histidine (sigma-Aldrich 99% purity) and cadmium tetrafluroboric acid in millipore water. Using the following reaction

$$C_6H_{10}O_2N_3 + Cd(BF_4)_2 \rightarrow C_6H_{10}O_2N_3BF_4$$

After the completion of the reaction anadduct was formed due to the amino group of L-Histidine (NH_3^+) and the tetrafluroborate (BF_4^-) ion of fluroboric acid. Purity of the synthesized salt was improved, from the intermediate compound formed, by successive recrystallization process using water as a solvent. The prepared solution was left standby for several days, thereby colourless L-HFB crystals were obtained after a growth period of 45 days.

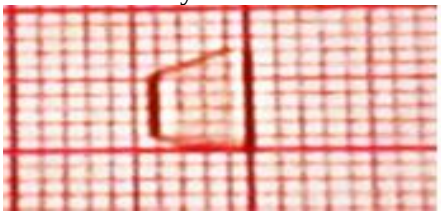

Fig.1.Grown Crystal of LHFB

3. RESULTS AND DISCUSSION

3.1. Single Crystal X-ray analysis: The X-ray data were collected using an automated ENRAF NONIUS CAD4 diffractometer. The structure of LHFB was solved by the direct method and refined by the full matrix least square technique employing the SHELXL program. The title compound crystallize in monoclinic system with point group 2 and space group $p2_1$. The cell dimensions are a=5.022(2) Å, b=9.090(1) Å, c=10.216(2) Å, α=γ=90° and β=93.484(8)°. Volume v=467 $Å^3$. This value are in good agreement with the reported work.

Table.1.Crystal data of LHFB crystal

Empirical formula	$C_6H_{10}O_2N_3BF_4$	**c(Å)**	10.216(2)
Crystal system	Monoclinic	**α(Å)**	90
Space group	$p2_1$	**β(Å)**	93.484(8)
Point group	2	**γ(Å)**	90
a(Å)	5.022(2)	**v(Å^3)**	467
b(Å)	9.090(1)		

3.2. Crystal surface and Elemental Analysis: The SEM studies gives information about surface morphology and also can be used to check the presence of imperfections in the grown crystals. The surface features of the crystal was observed by a scanning electron microscopy in figure 2 shows the obtained micrograph, it is observed that the growth surface shows the spherical shaped atoms. This exhibits the effectiveness of the impurity in changing the surface morphology of L-HFB crystal.

Elemental analysis was carried out for LHFB by the energy dispersive X-ray analysis to confirm the composition of these elements. Incorporation of dopants into the crystalline matrix was observed by EDAX and shown in Fig.3. The presence of carbon, boron, nitrogen, cadmium, radicals in the crystal as obtained. This illustrates the EDAX spectrum of LHFB crystal.

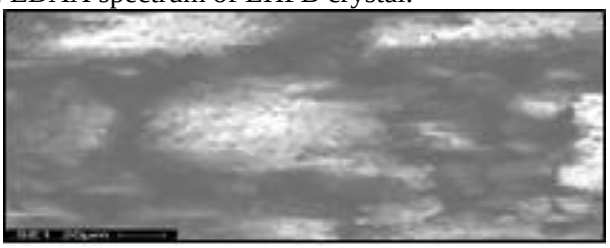

Fig.2.SEM image of L-HFB single crystal

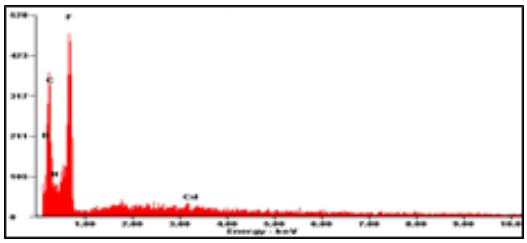

Fig.3.EDAX spectrum of L-HFB single crystal

3.3. FTIR Analysis: In order to analyse the presence of functional groups in the crystals, FTIR spectrum has been recorded. The spectrum was recorded for the wavelength range 4000-400 cm^{-1}. This is shown in Fig.4. In the higher wave number region the pure N-H stretch of histidine appears as a sharp peak at 3317.3 cm^{-1}. The 3016.5 and 3105.2 cm^{-1} peaks may be assigned to the N-H stretches of the same group and also protonated NH_2 group, which are varyingly bonded to the environment. The -CH_2- group of histidine produces peaks at 2800.4 and 2862.2 cm^{-1} due to its symmetric and asymmetric stretching modes. The anionic nature of the carboxylate group in the crystal is clearly evident by the C=O stretch at 1637.5 cm^{-1}, which is a very low value. The peaks at 1579.6 and 1523.7 cm^{-1} may be attributed to the skeletal vibrations of the ring in histidine. The peaks at 1415.7 and 1338.5 cm^{-1} are assigned to –CH_2- bends. The intense broad signal at 1033.8 cm^{-1} is assigned to B-F stretch and its shoulder at 1100 cm^{-1} is assigned to C=O stretch of the carboxylate anion. The cluster of sharp peaks between 3000 and 3442.7 cm^{-1} is the convincing evidence for the protonated form of the histidine ring nitrogen and NH_2 group, which actually stands as the evidence for the bonding interaction between HBF_4 and histidine in the crystal lattice.

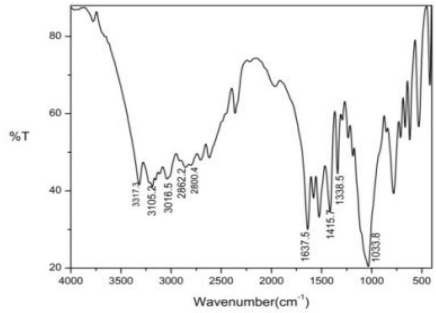

Fig.4.FTIR analysis of LHFB single crystal

Table.2.Tentative assignment of LHFB

Wave number (cm^{-1})	**Assignments**
3317.3,3016.5,3105.2	NH-stretching vibration
1637.5	C=O stretching vibration
2800.4, 2862.2	Symmetric and asymmetric stretching vibration
1415.7,1338.5	-CH_2- bending vibration
1033.8	B-F stretching vibration

The proton necessary to protonate the basic nitrogen in order to have bonding interaction is to be derived exclusively from HBF_4. The vibrational frequencies of various functional groups of LHFB and the tentative assignments are presented in the table. 2.

3.4. Thermal analysis: Thermogravimetric and differential thermal analyses (TG/DTA) and Differential scanning calorimetric (DSC) studies give ideas about phase transition temperature, the melting point and the chemical decomposition of the grown crystals. The TG/DTA thermogram of LHFB crystals are presented in the Fig.5. From the results, it is found that in DSC, the measurement indicates that the material exhibits single stage weight loss starting at 28ºC, which may be due to the decomposition of LHFB and below this temperature no significant weight loss of 98.84% between 242ºC and 365ºC, due to the decomposition of a carboxylic group and amino group. Finally the remaining 33.0668 is observed as residue. The TGA measurement of LHFB was also performed between 0ºC to 1000ºC in the nitrogen atmosphere. In TGA, there is a sharp endothermic peak at 281C, which is assigned to the melting point of the specimen. An endothermic peak observed at around 280ºC may be attributed to the melting point of the material and was also confirmed by the capillary method using melting point apparatus. The value determined by this method was 281ºC which agrees well with that observed in the TGA trace. This is in good agreement with the reported DSC values. Below this endotherm, no exothermic or endothermic peak is observed. The sharp endothermic peak in TGA trace nearly coincides with decomposition in the DSC trace. The sharpness of the endothermic peak observed in TGA shows good degree of crystallinity of the specimen. The electrostatic force due to the perfect proton transfer between tetrafluroboric acid and histidine is the dominating one for the stability of the material.

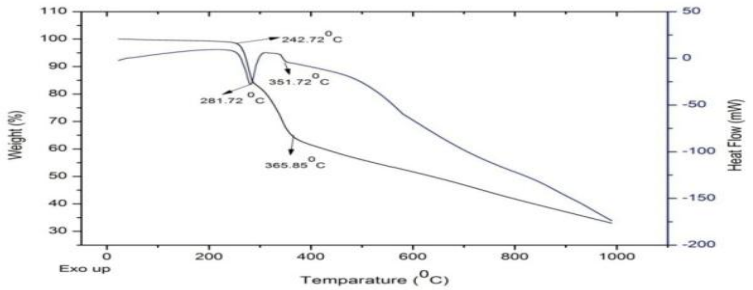

Fig.5.The thermogram curves of LHFB

3.5. UV-Visible NIR spectral analysis: Optical transmittance and absorption spectrum is very important for any NLO material because a nonlinear optical material can be of practical use if it has wide transparency window. The optical absorption and transmission spectrum of LHFB was recorder using Perkin elmer lamda 35 model spectrometer. The spectrum was recorded in the range of 190-1100 nm is shown in Fig.6.The transmittance spectrum shows that LHFB has 50% of transmittance. The crystals are transparent in the entire UV-Visible region with a lower cut-off wavelength 320 nm. The direct band gap energy of L-HFB is found to be 4.79 eV. This transparent nature in the uv-visible region is a desire property for the material used for NLO applications.

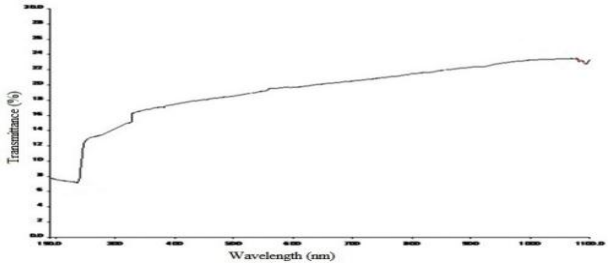

Fig.6.Optical transmission spectrum of LHFB crystal

3.6. Second Harmonic Generation: The conversion efficiency for the second harmonic generation of the grown crystal was carried out by Kurtz-Perry technique. The relative second harmonic generation efficiency was determined using Q switched mode locked Nd:YAG laser emitting 1064 nm radiation. The crystal was grounded into homogeneous powder of particles and then packed in a capillary of uniform bore and exposed to the laser radiation. KDP is used as the reference material. The second harmonic generation was confirmed by the emission of green light of wavelength 532 nm. The experiment confirms that the non-linear optical efficiency of as grown crystal LHFB. The observed relative SHG efficiency is 0.48864 times that of KDP. Hence it proves that the material is applicable for non-linear optical devices.

4. CONCLUSION

Single crystals of LHFB have been grown by low temperature solution growth technique. The harvested crystals of size (0.8*0.4*1.16 mm^3) were obtained after a period of 45 days. The L-HFB has the highest solubility in water. Bi-pyramidal morphology with well-defined appearance. Single crystal XRD analysis confirms the structure of grown crystals to be monoclinic with the space group $P2_1$. The FTIR analysis confirms the bonding interaction between HBF_4 and histidine in crystal lattice. The relative SHG efficiency shows that the non-linear optical property of the material. The crystal is optically transparent with a lower-cutoff at wavelength 320 nm. Thermal analysis

proved a high thermal stability of the material. Thus LHFB with many attracting linear and non-linear properties is suitable for optoelectronic applications.

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