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PHYSICS

STRUCTURAL, MECHANICAL, FTIR, SHG AND THERMAL STUDIES OF L-HTFA SINGLE CRYSTALS GROWN BY SOLUTION METHOD

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Abstract

Single crystals of L-histidine trifluroacetate(L-HTFA) have been grown successfully by solution growth method from its aqueous solution. Single crystals of L-HTFA having dimensions 20 x 5 x 3 mm^3 have been grown by slow evaporation method at room temperature in a growth period of 3 weeks. The grown crystals have been subjected to X-ray diffraction(XRD) studies to identify the morphology and structure. The Differential Scanning Calorimetry(DSC) and TG/ DTA studies confirm the thermal stability of the grown crystal. The FTIR study reveals bonding interaction of trifluroacetate and histidine in the crystal lattice. The NLO property of the crystals has been confirmed by Kurtz powder test. Mechanical property of the grown crystal was carried out by measuring microhardness number.

Keywords: NLO crystal; single crystal; solution method; XRD; crystal structure; FTIR;TG/DTA; DSC;SHG

Introduction

The organic non-linear optical (NLO) crystals with aromatic rings have attracted much attention because of their wide transparency range, fast response and high damage threshold for device applications. However, the shortcomings of aromatic crystals, such as poor physicochemical stability, low hardness and cleavage tendency hinder their device applications [1-3]. Inorganic NLO materials have excellent mechanical and thermal properties but possess low laser damage threshold and low optical nonlinearities[4, 5]. Semi-organic NLO materials are synthesized in such a way that they take the advantages of both organic and inorganic materials. A typical semi-organic NLO material is formed by combining an organic ion and an inorganic counter ion to have a favourable high optical nonlinearity, low damage threshold, excellent mechanical and thermal properties. The research on the synthesis of semi-organic complexes have increased enormously in the last few years specifically, amino acids and strong inorganic acids are good raw materials to produce semi-organic crystals[6-8]. The interesting amino acid-family of semi-organic crystals such as L-arginine hydrochloride, L-histidine tetrafluoro borate, L-arginine phosphate, L-histidine bromide, L-histidine dihydrogen phosphate, L-alanine tetrafluoro borate etc have been already grown and reported[9-12]. Motivated by the earlier reports on amino acid-family of semi-organic crystals, we synthesize and grow a new semiorganic NLO crystal viz. L-Histidine trifluoro acetate (LHFA) crystal in this work. L-histinine is one of the optically active amino acids and when it is combined with a suitable inorganic material, it easily forms an accentric crystal having a point group lacking a centre symmetry. L-histidine trifluroacetate (L-HTFA) is a novel non-linear optical crystal material with molecular formula $C_8H_{10}N_3O_4F_3$ and it is a semi-organic crystal. This crystal derived from organic-inorganic complex combines the high optical non-linearity of a purely organic compound with favourable thermal properties. The aim of this paper is to report the synthesis, growth of L-HTFA crystals and to report the results of various studies of the grown crystals.

Experiental Procedure

Synthesis and solubility

Commercially available L-histidine and trifluro acetic acid were purchased from Merck India Company and were used for synthesis of L-HTFA. L-histidine trifluro acetate (L-HTFA) was synthesized by dissolving one equivalent of L-histidine in de-ionized millipore water containing one equivalent of trifluro acetic acid. The solution was stirred well for 1 hour and it was heated at 50 ^oC to get the synthesized L-HTFA salt. The solubility of L-HTFA was measured in water, acetone and methanol by gravimetrical method[13]. The solubility curves for L-HTFA in water, acetone and ethanol are shown in the figure 1. From the figure, it is noticed that the solubility of L-HTFA is very low in acetone and ethanol. It is less then 4 g in 100 ml of acetone and 3.0 g in 100 ml of ethanol. The solubility of L-HTFB is 15 g in 100 ml of water at 40ºC. Hence water is found to be a better solvent for crystal

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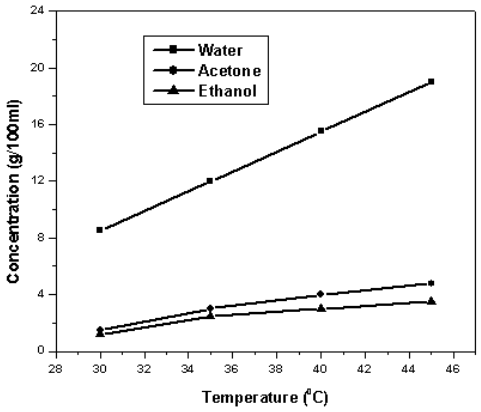
Figure 1: Solubility curves for L-HTFA in different solvents



Growth of single crystals of L-HTFA

In accordance with the solubility data, the saturated solution of the re-crystallized salt of LHFA in de-ionized water was prepared at room temperature (30 °C) and it was left for 1 h under stirring condition to ensure the homogeneity. Then it was filtered using 4 micro Whatman filter paper and it was kept in a borosil beaker covered with a porous paper and kept in a dust-free atmosphere. The grown crystals are found to be stable, non-hygroscopic at ambient temperature, colourless and transparent. The grown crystals are observed to be possessing bi-pyramidal morphology with well-defined appearance. By slow evaporation of solvent, L-HTFA crystal of size 20 x5 x 4 mm^3 was grown in a period of 3 weeks.

Instrumentation for characterization of crystals

X-ray Diffraction (XRD) provides an efficient and practical method for the structural characterization of crystals. This method helps in determining the arrangement and the spacing of atoms in a crystalline material. The grown single crystals were subjected to single crystal X-ray diffraction(XRD) studies using an ENRAF NONIUS CAD4 diffractometer with MoK_α radiation (λ=0.71073 Å) to identify the crystal structure, to find lattice parameters, space group and number of molecules per unit cell(Z). Mechanical property was studied by measuring microhardness of the grown crystals and it was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study. Indentations were made for various loads from 10 g to 65 g. The Vickers micro hardness 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 [14].

Second Harmonic Generation (SHG) test for the grown sample was performed by the powder technique of Kurtz and Perry[15] using a pulsed Nd:YAG laser(Model: YG501C, =1064 nm). Pulse energy of 4 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were used. The grown crystals were ground to powder of grain size 1100-1300 µm and the input laser beam was passed through IR reflector and directed on the powdered sample packed in a sample cell. Microcrystalline material of Potassium Dihydrogen Phosphate(KDP) was used as reference in this experiment. Second Harmonic Generation (SHG) from the samples was detected using a photomultiplier tube(PMT). The FTIR spectra of the sample was recorded using a Perkin Elmer FTIR spectrometer by the KBr pellet technique in the range 400-4000 cm^{-1}. The infrared spectroscopy is effectively used to identify the functional groups of the grown crystals. The thermal stability of the crystal was carried out by DSC and TG/DTA studies. The L-HTFA sample weighing 24.9 mg was placed in the aluminum pan. The pan was encapsulated with a dome lid, which was crimped in position. The normal lid crimping procedure gave a tight seal over the pan. The DSC thermal curve was obtained by using DSC 200PC calorimeter and it was scanned at the rate of 10ºC/min in nitrogen atmosphere. Simultaneous thermogravimetric analysis and differential thermal analysis (TG/DTA) were carried out for L-HTFA sample using a SDT Q600 V8.3 thermal analyser in nitrogen for the temperature range 30-1000°C at a heating rate of 20ºC/min.

Results and discussion

Structure analysis

Single crystal XRD data for the grown L-HTFA crystal were obtained using ENRAF NONIUS CAD4 diffractometer from M.K.University, Madurai. The structure was solved by single crystal XRD analysis by direct method and refined by the full matrix-least-square technique using SHELXL program. The obtained data from single crystal XRD studies are presented in the table 1. From the data, it is observed that the grown crystal crystallizes in monoclinic system with the space group $P2_1$, which is recognized as non-centrosymmetric thus satisfying one of the essential material requirements for the SHG activity of the crystal. From the literature , it is noticed that the space group $P2_1$ is one of the most popular space groups and it allows maximal contribution of the molecular nonlinearity to the macroscopic crystal nonlinearity[16] . The number of molecules per unit cell and volume of the unit cell of L-HTFA crystal were found to be 2 and 476.661 $Å^3$ respectively. It is to be mentioned here that the unit cell parameters of the title compound are reported for the first time in this work.

Table 1: Single crystal XRD data for L-HTFA

Identification code	LHFA
Empirical Formula	$C_8H_{10}O_4N_3F_3$
Formula weight	269.03
Temperature	293(2) K
Wavelength	0.7107 Å
Crystal system	Monoclinic
Space group	$P2_1$
Lattice parameters	a = 5.0321(1) Å b = 9.1590 (1) Å c = 10.3496 (3) Å β = 92.272 (2)°
Volume (Å)^3	476.661(2)
Z	2
density	1.862 g/cc

FTIR studies

In order to analyze the presence of functional groups in the crystals, FTIR spectrum has been recorded. The spectrum was recorded for the wavelength range 500-4000 cm^{-1}. This is shown in the figure 2. The pure N-H stretch of L.histidine appears at the peak at 3450 cm^{-1}. The broad peaks at 3144 cm^{-1} and 3106 cm^{-1} may be assigned to N-H symmetric stretches of the same group and also protonated NH_2 which are varyingly H-bonded to the environment. The peak at 2946 cm^{-1} is due to the symmetric stretching modes of CH_2 group of histidine. The peak at 1963 cm^{-1} confirms the linear chain C = C – C stretching vibration. The anionic nature of carboxylate group in crystal is clearly evident from the C = O stretch at 1680 cm^{-1}. The peak at 1525 cm^{-1} may be due to the skeletal vibrations of the imidazole ring in L-histidine . The peak at 1410 cm^{-1} is due to the CH asymmetric stretch in the imidazole ring. The band at 1336 cm^{-1} and 1050 cm^{-1} is assigned to the C-F asymmetric stretch and its shoulder at 1145 cm^{-1} is assigned to COO^- stretch of the carboxylate anion in the ring of histidine. The sharp peak at 3450 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 trifloraccetate and histidine in the crystal lattice [17]. The other bands which support our interpretation are also given in the table 1.

Fig.2.FTIR spectrum of L-HTFA crystal

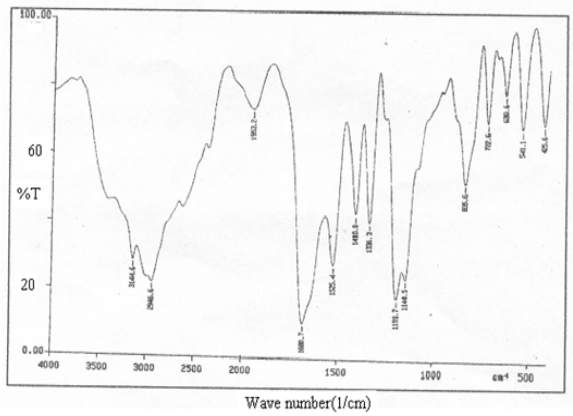


Table 2: FTIR Spectral assignments for L-HTFA

Wavenumber (cm^{-1})	Assignments
3450	N - H stretch
3145	NH_2 symmetric stretch
3016	N - H stretch
2947	C - H asymmetric stretch
2625	N – H stretch
2300	N – H stretch
1963	C = C – C linear chain stretch
1680	C = O stretch in carbonyl group
1525	imidazole ring
1410	C – H asymmetric stretch
1336	CF_3 asymmetric stretch
1210	C – N Stretch
1192	C – C bending
1145	COO^- Stretching
1050	C – F stretch
836	NH_2 Wagging
722	CH_2 rocking
650	O – C bending
630	C – O – H bending
541	COO^- Rocking
425	C – N – C bending

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 thermograms of L-HTFA crystals are presented in the figure 3 . From the results , it is found that the sample is stable up to 220 ^{o}C. From TG curve, it is noticed that there is a maximum weight loss observed in the temperature range 115°C – 255 ^{o}C and correspondingly, there is an endothermic peak at 220.8 ^{o}C observed in the DTA curve and it corresponds to the melting point/decomposition of the sample. Since there is no weight loss below 100 ^{o}C, the crystal is moisture free and it is thermally stable up to 213 ºC. A weight loss of 51.4% between 215 ºC to 315 ºC indicates loss of CO_2 molecules. A weight loss of 7.53% between 315 ºC to 500 ºC indicates the loss of NH_3 , CO and CH_4 molecules.

In order to examine the physicochemical changes, the DSC analysis was performed between 250ºC to 450 ºC. The DSC trace was shown in the figure 4 . Since there is no exo or endothermic transition below 220 ºC, the material confirms the stability suggested by TG/DTA studies . The electrostatic force due to the perfect proton transfer between trifluroacetic acid and hisidine is the dominating one for the stability of the material.

Fig.3: TG/DTA thermograms for L-HTFA crystal

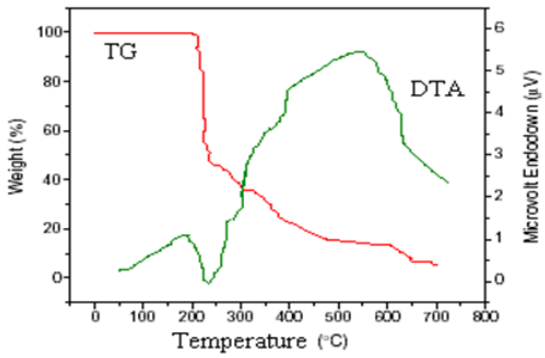
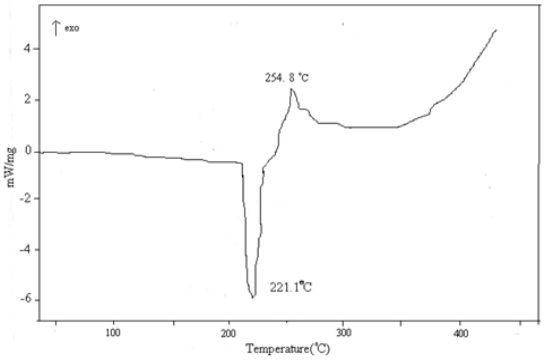


Fig.4: DSC thermal curve for L-HTFA crystal



NLO studies

Kurtz-Perry Second Harmonic Generation(SHG) test was performed to find the non linear optical property of L-HTFA Crystal. The experiment was performed with Nd:YAG laser using the first harmonics output of 1064 nm with a pulse width of 8 ns and pulse energy of 4.6mJ/p. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the crystal.

Microhardness measurement

Microhardness studies for the grown LHFA crystal were performed at room temperature(30 ^{o}C) to determine microhardness number and hence the work hardening coefficient and this study plays an important role in the device fabrication. The hardness of a material is a measure of its resistance to plastic deformation. 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) [18,19]. Smooth, flat surface was selected and subjected to microhardness study of L-HTFA crystal. Indentations were made for various loads from 5 g to 25 g. Several trials of indentation were carried out and the average diagonal lengths were measured for an indentation time of 10 seconds. The variation of microhardness number with load applied to the prominent plane(001) of the sample is displayed in the figure 5 and it is noticed that Vickers hardness number(H_v) decreases with the applied load satisfying the indentation size effect. It is observed that the hardness value is high and this high value of hardness may be attributed to the strong crystal bonding forces within the crystal as a result of protonation of the heterocyclic ring and the carboxylic group of L-HTFA. The relationship between load(P) and diagonal length(d) of indentation is given by $P=a\ d^{n}$ which is known as Mayer's law[20]. Here a and n are constants for a particular material. From straight line graph of log d versus log P (Fig.6), the reciprocal of slope can be obtained and it is equal to the constant n which is known as Mayer's index number or work hardening coefficient. The value of n obtained from the graph is 1.664 for L-HTFA crystal. According to Onitsch's theory, if n is greater than 1.6, the materials are said to be soft materials[21]. Hence the grown crystals of this work belong to the category of soft materials.

Fig.5: Plot of microhardness number versus load for L-HTFA crystal

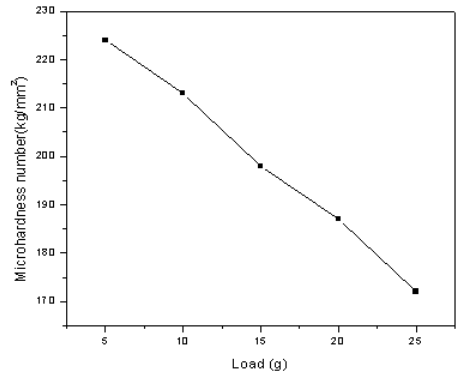
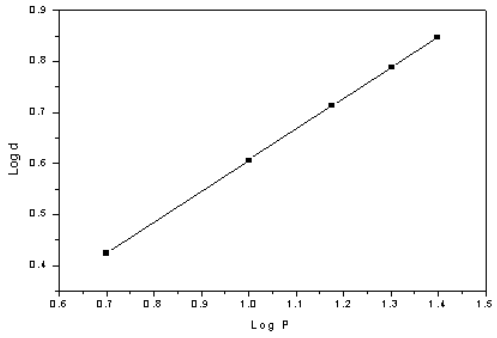


Fig.6: Plot of log d versus log P for L-HTFA crystal



Conclusions

A novel semi-organic crystal viz. L-histidine trifluro acetate (L-HTFA) has been successfully grown by solution method with slow evaporation technique. XRD measurement reveals the structure of the grown crystal and the structure is observed to be monoclinic. The FTIR analysis confirms the presence of various functional groups in the grown L-HTFA crystal. It has been observed that the material is NLO active by Kurtz powder SHG test. The thermal stability is confirmed by the thermal analysis. The mechanical studies for the grown crystal were performed by carrying out measurement of microhardness and the work hardening coefficient for the crystal was found to be 1.664.

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