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Optical, thermal and mechanical studies on a novel nonlinear optical material: TLH crystals

S. Nalini Jayanthi[a], A. R. Prabhakaran[b], D. Subashini[c], T. Panchanathan[d] and K. Thamizharasan[e]

[a]Department of Physics, AIHT, Kazhipattur, Chennai, India
[b]Department of Physics, Pachaiyappa's College, Chennai, India
[c]Department of Physics, Dr. Ambedkar Govt. Arts College,Chennai, India
[d]Bharathiyar University, Coimbatore, India
[e]Department of Physics, Sir Theagaraya College, Chennai, India

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ABSTRACT

Single crystals of Thiourea added L-Histidine (TLH) have been grown by slow evaporation solution growth technique from its aqueous solution. To identify the morphology and structure, the as grown crystals were subjected to single crystal x-ray diffraction analysis. The different modes of vibration present in the crystal was identified with FT-IR. The optical transmission spectrum and Second Harmonic Generation (SHG) have been studied to find its linear and Non-linear properties. The thermal stability of the grown crystal was found by differential scanning calorimetry (DSC). To check the mechanical strength Vicker's microhardness test was carried out and various parameters such as fracture toughness (K_c), elastic stiffness constant (C_{11}) and yield strength (σ_v) were calculated.

Keywords: Solution Growth, Characterization, Organic Crystal, Non Linear Optical material**.**

INTRODUCTION

Organic compounds like amino acids have large optical susceptibility, fast response and high optical threshold for laser radiation. All amino acids except glycine have chiral carbon atoms and are crystallized with noncentro symmetric space group. They possess Zwitter ions in their structure and show good mechanical property. L-Histidine is an optical isomer and also α-amino acid. They have both amino group and carboxylic group in the same carbon atom and also have imiadazole side chain with pK_a value 6.0. L-Histidine always show good SHG efficiency [1]. L-Histidine can form salts with $L\text{-}His^+$ and $L\text{-}His^-$ cations [2]. Large number of L-Histidine compounds show excellent NLO property, namely L-Histidine-4-nitrophenolate 4-nitrophenol [3], L-Histidine hydrofluoride dihydrate [4], L-Histidine trifluoroacetata [5], L-Histidine bromide [6], L-Histidine di phosphate [7] L-Histidine tetrafluoro borate [8] and L-Histidine nitrate [9]. Thiourea crystals exhibit pyroelectric effect. It can be used in Infrared imaging devices. Thiourea itself is a good NLO material. So in this paper Thiourea was selected along with L-Histidine crystal to study the effect of addition of it in the lattice of L-Histidine crystal.

In this paper, slow evaporation solution grown bulk TLH crystals were characterized by single crystal, FT-IR, UV-Vis-NIR, NLO, DSC and Vicker's Microhardness. However, to the author's best knowledge, there is no existing report about mechanical parameters of TLH crystals. Therefore, for the first time in this paper various mechanical parameters like fracture toughness (K_c), elastic stiffness constant (C_{11}) and yield strength (σ_v) were calculated and fully reported.

MATERIALS AND METHODS

TLH crystals were synthesized by dissolving Thiourea and L-Histidine in double distilled water. To get fully reacted solution, the reactants were allowed to dissolve completely in the double distilled water and stirred well in a temperature controlled magnetic stirrer for about 4 hours. Fully reacted homogeneous solution was filtered with micro Wattmann filter paper and kept at room temperature for slow evaporation. By doing repeated recrystallization process good quality seed crystals were obtained and that seeds are used to prepare bulk TLH single crystals. Within a growth period of seven days crystals with dimensions 34x5x8 mm^3 were obtained.[Fig.1].

Fig.1 Photograph of as grown TLH Crystal

Instrumentation for characterization of crystals

The crystalline perfection and lattice parameters of the as grown TLH crystals were examined using ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoKα (λ=0.71073 Å) radiation. The Fourier Transform Infrared spectrum was carried out in KBr phase using the instrument Perkin Elmer Spectrum-1 with frequency range 450 cm^{-1} and 4000 cm^{-1}. The UV-VIS-NIR spectrum was recorded in the wavelength range 200 to 1100nm using VARIAN CARY 5E UV-VIS-NIR Spectrophotometer. The NLO efficiency of the crystal was examined by Kurtz and Perry Powder Technique using Quanta ray series Nd: YAG laser emitting first harmonics output of 1064 nm with a pulse width of 8ns. Differential scanning calorimetric analysis of TLH crystals were carried out between 25 °C to 320 °C at a heating rate of 10 °C/min. The experiment has been performed in nitrogen atmosphere using Netzsch DSC 204. Microhardness studies have been carried out using Leitz Wetzlar Vickers microhardness tester.

RESULTS AND DISCUSSION

Structure analysis

The X ray crystallographic data shows that TLH crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$ and the number of molecules per unit cell is 4 (Z=4). The lattice parameters were found to be a=5.14 Å, b=7.33 Å, c=18.61Å, α = β = ν = 90° with cell volume as 701 Å. The obtained cell parameter values of TLH crystals were compared with already reported lattice parameter values of pure L-Histidine [10]. It was observed that the lattice parameters and cell volume of the as grown TLH crystals were deviated from pure L-Histidine crystals. This was due to the inclusion of Thiourea in the lattice of L-Histidine crystal.

FT-IR spectral analysis

Fig.2 shows the FTIR spectrum of TLH crystal. The recorded spectrum was compared with standard spectra of functional groups [11]. In the spectrum, the sharp peak at 3451cm^{-1} [4] is due to O-H stretch of water. C-H asymmetric stretching occurs at 2933 cm^{-1}. Symmetric bending vibrations of NH_3^+ are seen at 1490 cm^{-1} [3]. It also identifies the symmetric stretching of nitro group [12]. Antisymmetric stretching vibration in five membered imiadazole ring $(C_3H_4N_2)^+$ occurred at 1064 cm^{-1} . The C-C-O stretching and in-plane bend gives a peak at 860 cm^{-1} [5]. Peak at 706 cm^{-1} is due to the stretching mode of C=S which corresponds to the absorption of thiourea [13-15, 12]. The ring in-plane deformation can see at 598 cm^{-1} [16].

Linear and Nonlinear optical property studies

The UV-Vis-NIR spectrum of TLH crystal is shown in Fig.3. It is observed that for an entire visible region transmittance is greater than 80% and the as grown crystal is transparent in the UV-Vis-NIR regions of the spectrum. This is a constructive nature of a NLO material [17]. The lower cutoff wavelength was around 310nm and there was no absorption from 350nm to 1100nm which clearly shows that the crystal possess good optical transparency for the second harmonic generation of Nd:YAG laser radiation at 1064nm[18]. The optical band gap of the crystal is calculated using the formula E_g =1240/λ (nm) and is found to be 4eV.

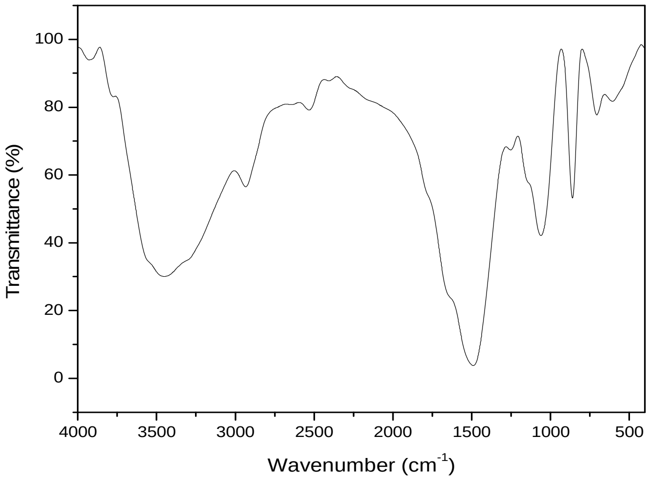

Fig.2 FTIR Spectrum of TLH crystal

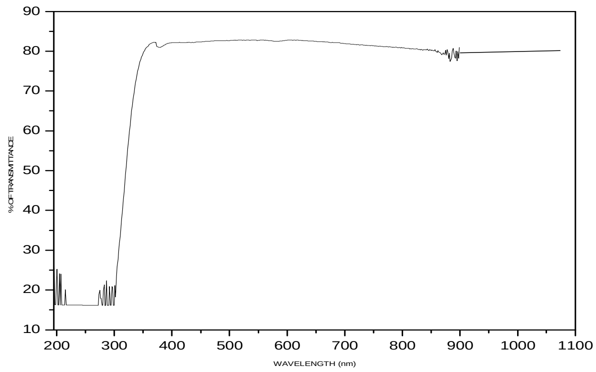

Fig.3. UV-Vis-Transmittance spectrum of TLH crystal

Nonlinear Optical Property (NLO) of TLH crystal was performed using Kurtz SHG test [19]. The microcrystalline TLH crystal powder was introduced in the light path. The SHG efficiency of the crystal was found to be 4.1 times of standard KDP crystal. SHG efficiency of TLH crystal was compared with SHG efficiency of Pure L-Histidine crystals [20] and found that TLH crystals had high SHG efficiency.

Thermal analysis

Differential Scanning Calorimetry analysis was used to identify the purity and melting point (T_m) of the as grown crystal. DSC thermo gram of TLH crystal is as shown in Fig.4. In the thermo gram only one endothermic stage was found. The initial temperature of the endothermic peck was 250.25 °C and equilibrium temperature was 313.36 °C. At 250.25° C initiation of phase change started and completed at 285.678°C. Area under the curve was 161.104mJ and heat of transition was 497.9 J/g. This thermo gram indicated that TLH crystal melted (T_m) completely at 285.678°C and the thermo gram was smooth up to 250.25°C indicating the purity of the crystal.

Micro Hardness Measurement

In the view of device fabrication, calculation of localized plastic deformation is very important. This can be done with the help of Vicker's Microhardness studies. In this present investigation smooth surface of the crystal was chosen and the diamond indenter was allowed to indent on the surface for 10 seconds. The applied load was varied from 25-200gm. The indentation was done on different places of the crystal surface. Hardness value was calculated from the relation

$$H_v = 1.8544\ P/d^2\ \mathrm{Kg/mm^2} \qquad (1)$$

where P is the applied load in Kg and d is the diagonal length of the indentation in millimeter. The variation of H_v with applied load is shown in Fig.5. The plot indicates that Vickers microhardness number increases with increase in load. Fig.6 shows the variation of log d with log P. The relation between log P and log d is given by Meyer's law and it is the simplest way to explain the ISE (Indentation Size Effect).

$$P = A.d^{n} \quad (2)$$

where A is a constant, P is the applied load and d is the diagonal length and the exponent 'n' is called Meyer number (or) Meyer index. Meyer index can be calculated by doing least square fit in the graph of log P versus log d. According to Meyer's law, for normal ISE behavior n < 2, for reverse ISE behavior n > 2 and when n = 2 the hardness is independent of the test load [21]. In the present investigation the value of n is found to be 3.12684 and shows reverse ISE. According to Onitsch, if n > 1.6 then those materials are soft materials [22]. Hence it is concluded that TLH crystal is a soft material.

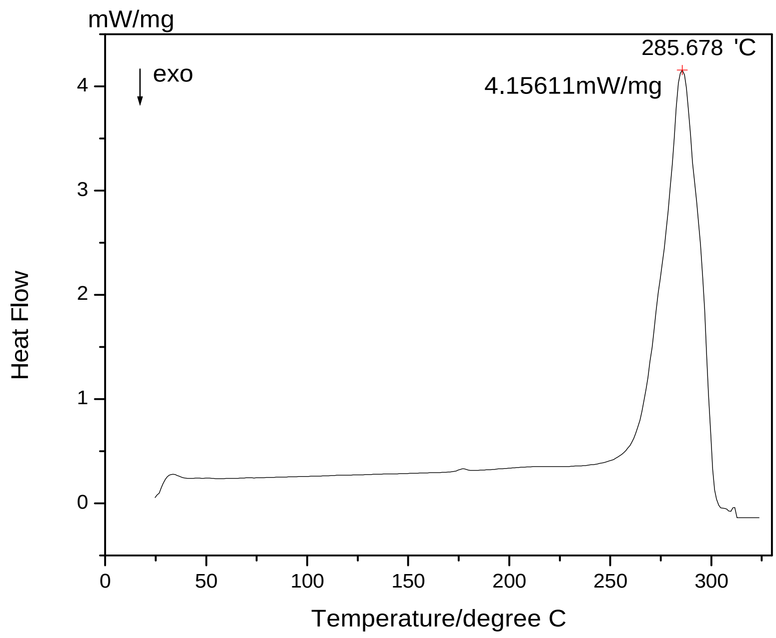

Fig.4. DSC trace of TLH crystal

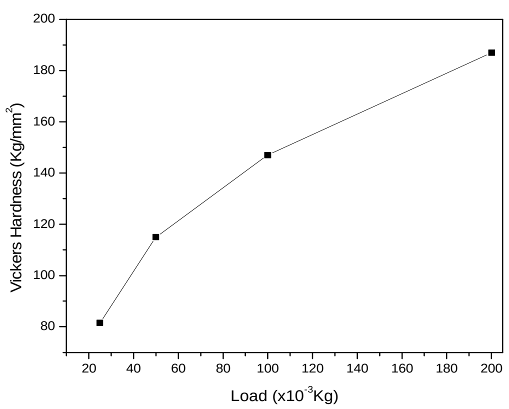

Fig.5 Variation of H_v with P of TLH crystal

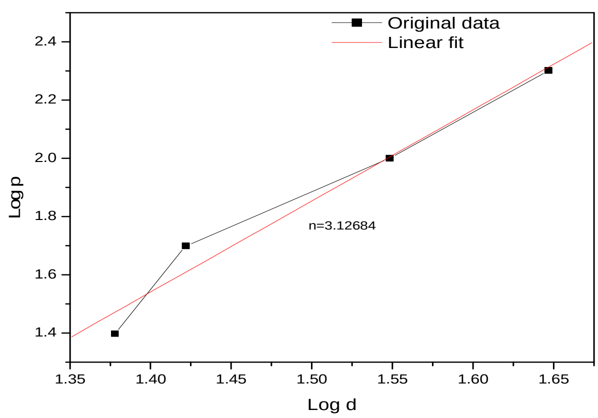

Fig.6 Plot of log P vs. Log d of TLH crystal

According to Meyer's relation

$$P = K_1.d^{n} \quad (3)$$

where K_1 is the standard hardness value. After every indentation the material takes some time to revert to elastic mode. So a correction x is applied to the d value.

According to Kick's law

$$P = K_2 (d + X)^2 \quad (4)$$

From equations (3) and (4)

$$d^{n/2} = (K_2/K_1)^{1/2} d + (K_2/K_1) X \quad (5)$$

The variation of $d^{n/2}$ with d gives K_2/K_1 and the intercept is the measure of X. Using the relations (2), (3), (4) and (5) the hardness parameters such as n, K_1, K_2 and X were calculated and presented in the Table 1.

Table 1: Hardness parameters of TLH crystal

Parameters	Values
n	3.12684
K_1($x10^{12}$ Kg/m^2)	2.75
K_2($x10^6$ Kg/m^2)	12.875
X (μm)	20.18

The yield strength (σ_V) of the material[23]can be calculated using the relation

$$\sigma_V = [H_v/2.9][1-(n-2)]\{[12.5(n-2)]/[1-(n-2)]\}^{(n-2)} \quad (6)$$

The elastic stiffness constant (C_{11}) can be calculation using Wooster's relation [24]

$$C_{11}= H_v^{\,7/4} \quad (7)$$

The fracture toughness K_C [25]is given by

$$K_c = P/[\beta C]^{3/2} \quad (8)$$

where C is the crack length, P is the applied load and β is a constant whose value is 7 for Vicker's indenter. Using the relations (6), (7) and (8) various mechanical properties were calculated and presented in Table 2.

Table 2: Mechanical properties of TLH crystal

Load P (g)	σ_V (MPa)	C_{11}	K_c(Kg/mm$^{3/2}$)
25	69.46	$22x10^2$	2.7382
50	99.15	$41x10^2$	4.2436
100	127.29	$63.54x10^2$	6.07942
200	161.153	$96.34x10^2$	8.6524

CONCLUSION

A Non Linear Optical single crystal, TLH was grown successfully by slow evaporation solution growth method. Single crystal X-ray diffraction study shows the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. The FT-IR spectrum confirms the presence of functional groups. UV-Vis-NIR study reveals that the lower cutoff wavelength is 310nm and energy band gap is 4eV.The crystal shows 80% transparency in entire UV-Vis region. NLO property of the crystal is confirmed by Kurtz Powder method and SHG efficiency is found to be 4.1 times of KDP. DSC thermo gram confirms that the crystal is stable up to 285.68° C. Vickers microhardness measurement reveals the soft nature of the crystal and shows reverse ISE. Various mechanical parameters like fracture toughness (K_c), elastic stiffness constant (C_{11}) and yield strength (σ_v) were calculated and tabulated.

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