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SYNTHESIS, GROWTH AND CHARACTERIZATION STUDIES OF L-HISTIDINE TRICHLOROACETATE SINGLE CRYSTAL

- H. Jude Leonard Hilary [a*]
- G. Vijayakumar[b]

Abstract

Amino acids are naturally occurring chiral species, crystalline in non centrosymmetric space groups, which is an essential criterion for non linear optical application. Especially Trichloroacetic acid and L-Histidine derivates are serving as potential second harmonic generators. L-Histidine has been extensively studied because of its ability of imidazole moiety to act as a proton donor, a proton acceptor and a nucleophilic reagent. Hence L-Histidinium Trichloroacetate (LHTCA) is chosen for study.

The LHTCA salt was synthesized using high purity L-Histidine and Trichloroacetic acid in the appropriate stiochiometric 1:1 ratio. This solution was heated and kept for slow evaporation to dryness at room temperature. LHTCA salt was synthesized according to the reaction.

$$C_2HCl_3 + C_6H_9N_3O_2 \text{--} \rightarrow [(C_3N_2H_4)CH_2CH(NH_3)(CO_2)]^+ CCl_3COO^-$$

Colourless crystals of L-Histidiniumtrichloroacetate (LHTCA) crystal was harvested after 25 days at room temperature. The crystal was subjected to spectral, optical, mechanical, electrical and thermal studies. Vibrational Spectral Frequencies, Transparency, Refractive Index, Reflectance, Work Hardening Co-efficient, Elastic constants, Thermal Gravimetric and Differential Analysis are observed and calculated.

Keywords: Centrosymmetric, Nucleophilic reagent, Stiochiometric ratio, Vibrational Spectral Frequencies, Crystal growth; L-Histidiniumtrichloroacetate

INTRODUCTION

Amino acids are naturally occurring chiral speices; crystallize in non-centrosymmetric space groups, which is an essential criterion for non linear optical application. Especially L-argininie and L-Histidine derivatives are serving as potential second harmonic generators. L-hisditine has been extensively studied because of its ability of imidazole moiety to act as a proton donor, a proton acceptor and a nucleophilic reagent. Hence, there has been a great interest in counterparting the organic / inorganic materials such as fluoride, tartaric acid, phosphoric acid and orthoarsenic acid crystal, etc, with histidine. In the present investigation, we have reported L-Histidinium Trichloroacetate (LHTCA) single crystal and characterization studies such as PXRD, FT-IR, UV- Visible, Mechanical and Thermal studies were carried out.

[a]Department of Physics, St. Joseph College of Arts and Science, Cuddalore, Tamil Nadu, India.
[b]Department of Physics, PSG College of Arts and Science, Coimbatore, Tamil Nadu, India.
[*]Corresponding author E-mail address: judeleonard141@gmail.com, Tel: +91 9994870144.

EXPERIMENTAL

The LHTCA salt was synthesized using high-purity L-Histidine and Trichloroacetic acid in the appropriate stiochiometric 1:1 ratio. The calculated amount of the sample were dissolved in double – distilled water at room temperature. This solution was heated and kept for slow evaporation to dryness at room temperature. LHTCA salt was synthesized according to the reaction

$$C_2HCl_3O_2 + C_6H_9N_3O_2 \rightarrow [(C_3N_2H_4)CH_2CH(NH_3)(CO_2)]^+ CCl_3COO^-$$

The resultant material was purified by recrystallization to obtain high purity raw material for bulk growth. Colourless crystals of L-Histidinium Trichloroacetate (LHTCA) crystal was harvested for 25 days of solvent evaporation at room temperature are shown in Figure 1.

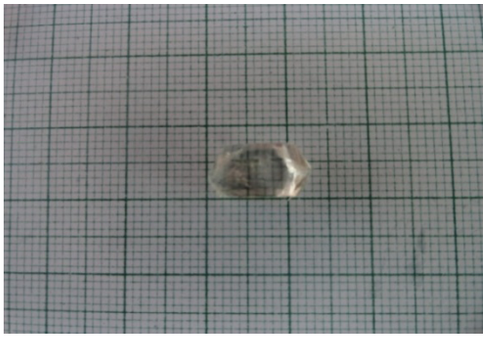

Figure. 1: Photograph of LHTCA Crystal

RESULTS AND DISCUSSION

The grown crystals of LHTCA were confirmed by powder x-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The FT-IR spectra of LHTCA crystal was recorded in the ranges 400-4000cm^{-1} employing KBr pellet method to study the metal complex coordination. In crystalline material the region of transparency to electromagnetic radiation defines the intrinsic loss mechanism and also theoretical transmittance achievable within the region. The observed IR vibrational spectral as shown in Fig.2. UV-Visible spectrum of LHTCA was recorded in the range of 190 nm and 1100 nm. The mechanical strength of a material is primarily studied from its microhardness . The Vickers microhardness, H_v was calculated using the relation $H_v = 1.8544\ (p/d^2)\ kg/mm^{-2}$ Where P is the applied load in kg and d is the average diagonal length of the Vicker's impression in mm after unloading.

The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using NETZSCH STA 409C thermal analyzer at a heating rate of 20^{0}C/min in the nitrogen atmosphere to determine the thermal stability of the compound between the room temperature and 1000 ^{0}C.

The frequencies were compared with the standard values and their assignments for LHTCA crystal was listed in the Table 1.

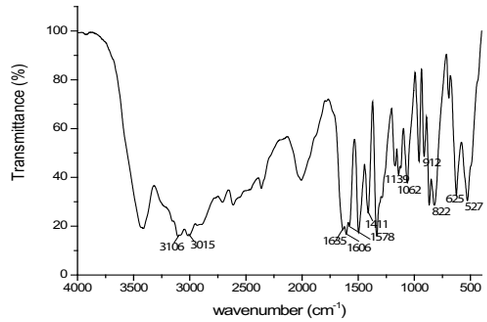

Figure .2: FT-IR Spectrum of LHTCA Crystal

The higher percentage of transmission spectra of L-His-CCl_3COOH crystal was given in Fig.3. The visible region clearly depicts the intrinsic property of amino acids and the crystal is free from any defects. From the graph, the lower cut off frequency was 329nm and has greater transparency over the entire visible region which is the desirable one for optical applications.

Table.1: Mode Assignment for LHTCA Crystal

Wave number (cm^{-1})	Assignment of vibrations for LHTCA crystal
3106 3015	N-H stretching
1635	C-N stretching
1139	N-H wagging
1062	NH_3^+ rocking
1606	Symmetric and antisymmetric of COO^-
1411	Stretching of COO^-
527	Wagging of COO^-, CCN bending mode
822	C-C stretch
912	C-H stretch
625	C-Cl stretch
1578	Asymmetric stretching of COO^-

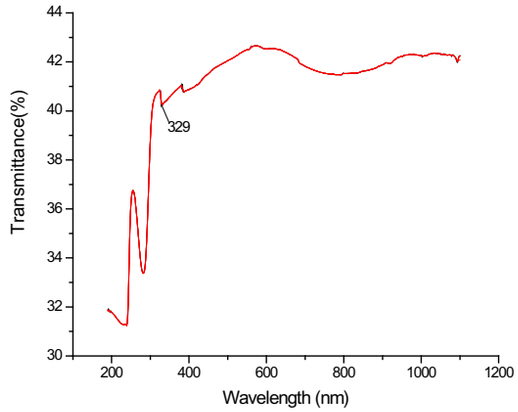

Figure.3: UV – Vis Spectrum of LHTCA Crystal

Figure.4.the band gap for LHTCA was found to be 3.64 eV. As a consequence of wide band gap, this crystal can be a suitable material for the optoelectronic devices like LED and Laser diodes. Hence by tailoring the absorption coefficient and tuning the band gap of material we can achieve the desired material suitable for fabricating various layers of optoelectronic devices.

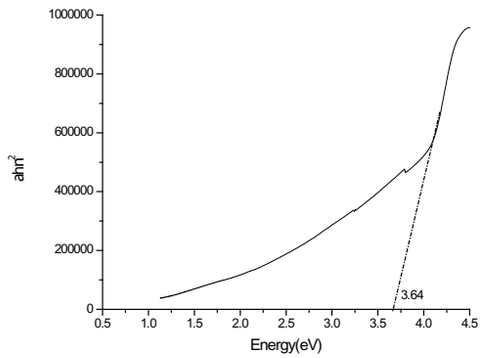

Figure.4: Bandgap Curve of LHTCA Crystals

A profile on the above calculated optical constants as a function of wavelength is graphically illustrated in Fig.5. From the graph it is clear that the extinction coefficient (k), reflectance(R) and refractive index (n) vary with wavelength and hence depend on the photon energy. The internal efficiency also depends on the photon energy. Hence by tailoring the photon energy, one can achieve the desired material for the device fabrication.

A graph is drawn between hardness and the load, shown in Fig.6. From the graph it is evident that the hardness number increases when the load increases. The value of work hardening coefficient n was estimated from the plot of log P versus log d. A linear graph was observed with slope of 5.33 which also conforms the low mechanical strength of the crystal given in Fig.7. The elastic stiffness constant (C_{11}) gives an idea about tightness of bonding between neighboring atoms.

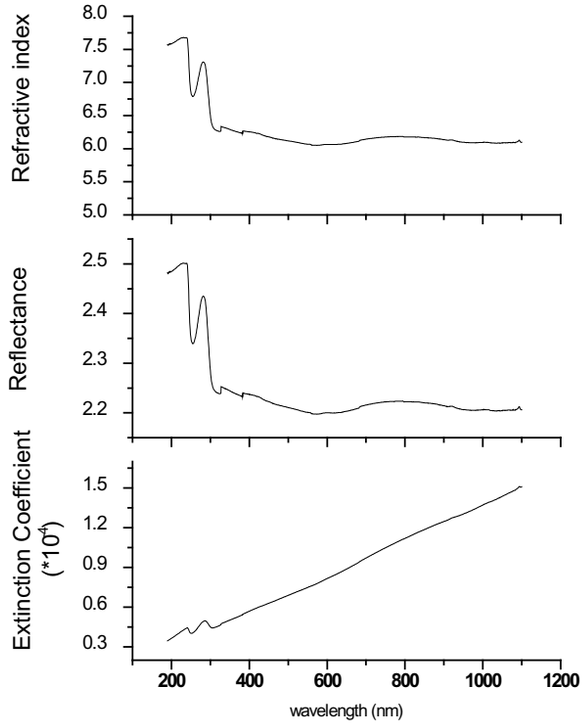

Figure. 5: Profile of Optical Constants as a Function of Wavelength

The toughness of the material is the resistance to fracture. The fracture toughness K_c of the material is dependent on the micro structural features and is generally insensitive to the chemical species in the surrounding environment. The expression for crack propagation under loading condition, determined by the analysis of the deformation fracture mechanics of the indentation process can be represented on the equilibrium conditions.

$$P / l^{3/2} = \beta_0 K_c \qquad for \qquad l \geq d/2$$

where P is the applied load, l is the crack length measured from the centre of the indentation impression to the crack end, d is the diagonal length of the indentation impression and β_0 is the indenter constant, equal to 7 for a Vicker's diamond indenter.

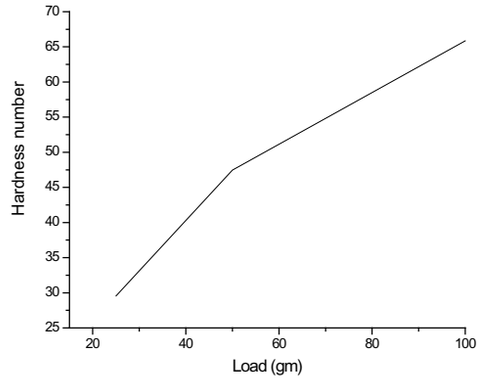

Figure.6: Variation of Hardness Number Versus Load

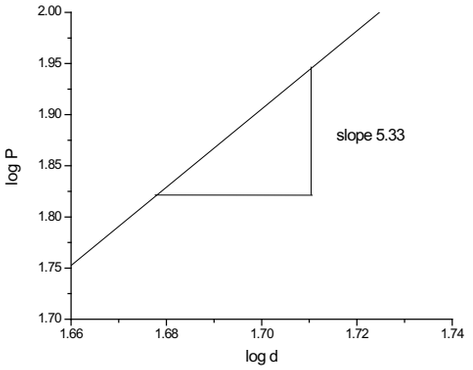

Figure.7: Work Hardening Coefficient Curve for LHTCA Crystal

Brittleness is a property which affects the mechanical behavior of a material. Brittleness indices have been calculated from the ratio between the hardness, H_v and the fracture toughness K_c. The fracture toughness, the brittleness index and stiffness constants for various loads are shown in Fig. 8.

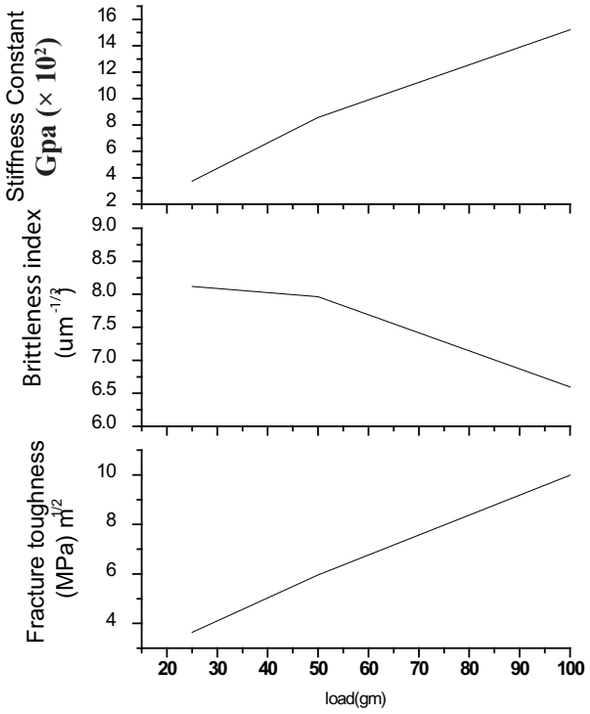

Figure.8: Mechanical Related Constant Curves of LHTCA Crystal

The resulting TGA/DTA trace is shown in Fig.9. From the DTA curve, it is observed that LHTCA undergoes an irreversible endothermic transistion at about 152° C where the decomposition starts. The material is fully decomposed at 173°C which corresponds to the melting point of the material. A second dissociation occurs at261°C. The TG curve indicates that, a sudden decrease of slope upto 173°C with the weight loss of 36% is observed. This may be due to the dissociation of the amine groups present in the material. The decomposition of the main carbon chain occurs at 339°C and continues until the compound becomes volatile (complete weight loss).

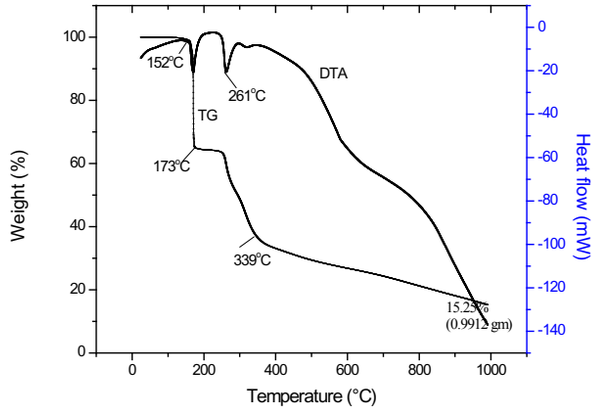

Figure.9: TG/DTA Curve of LHTCA Crystals

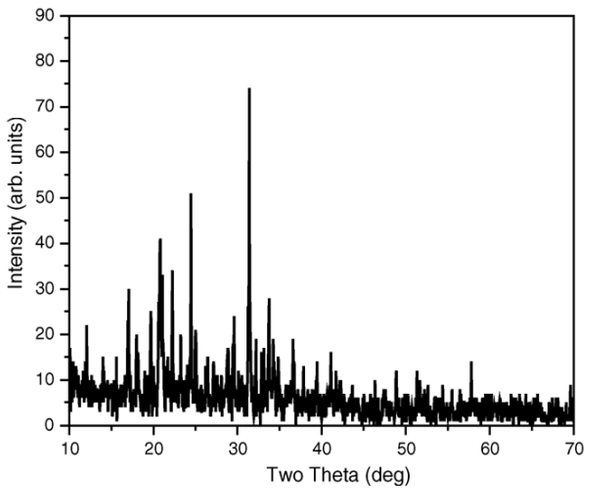

Figure.10 . Powder X-ray diffraction pattern of LHTCA crystal

Table.2 Bragg's peaks of LHTCA crystal

Table 1
Miller's indices, *d* spacing, 2θ, area of the peaks, FWHM of the Bragg's peaks of LHTCA crystals estimated from powder XRD analysis

h k l	*d* (Å)	2θ (deg)	Area	FWHM
0 1 0	8.4775	10.426	101	0.043
−1 0 2	4.2412	20.927	1220	0.005
0 0 3	4.0477	21.940	13	0.052
0 2 1	3.8429	23.125	13	0.139
0 −2 2	3.7617	23.631	4	0.063
−1 −1 2	3.6772	24.182	7	0.094
1 −1 2	3.5773	24.868	7	0.085
−1 0 3	3.4925	25.482	15	0.175
0 −2 3	3.1750	28.080	5	0.084

CONCLUSION

The good quality crystal of L-Histidinium Trichloroacetate (LHTCA) single crystals were grown by slow evaporation method. The spectral, structural, optical, mechanical and thermal properties of the grown crystals were analyzed and calculated.The FT-IR spectrum confirms the presence of functional groups of the parent compounds in the grown crystals.

The lattice parameters were found by powder crystal diffraction technique. The crystal system belongs to monoclinic system.The Bragg's peak for the powder XRD pattern of LHTCA crystal was indexed for the monoclinic system. The cell parameters calculated from the powder XRD pattern were found to be $a = 5.450$ Å, $b = 25.769$ Å, $c = 9.210$ Å and $\beta = 99.98$. Miller indices (h k l), *d*-spacing, diffraction angle (2θ), area of the peaks and full width half maximum (FWHM) of the Bragg's peak are summarized in Table 2.

The UV-Visible spectral analysis shows that the LHTCA single crystals have a wide transparency in the entire visible region with lower cutoff 329 nm. Hence this crystal is used for optical applications. The micro hardness study revealed the mechanical stability of the grown crystal and work hardening coefficient was determined to be 5.33. The elastic stiffness constant, fracture toughness, brittleness index of the grown crystals were calculated. TGA and DTA results show the thermal stability of the grown crystal was found to be 173^{o} C, which indicates the melting point of the crystal.

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