Short Communication

Optical and Dielectric Properties of L-Histidinium Trifluoroacetate NLO Single Crystal

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Abstract

Single crystals of L-Histidinium Trifluoroacetate were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to triclinic crystal system. The optical transmission studies show that the crystal is transparent in the entire visible region with a cut off wave length has been found to be 230 nm. The optical band gap is found to be 4.25eV.The transmittance of L-Histidinium Trifluoroacetate crystal has been used to calculate the refractive index (n), extinction coefficient (K), electric susceptibility (χ_c) and both the real ε_r and imaginary ε_i components of the dielectric constant as functions of wavelength. The dielectric constant and dielectric loss was also studied as a function of frequency at room temperature.
Key words: Solution growth, single crystal XRD, optical transmission, dielectric studies.

Introduction

The search and design of highly efficient nonlinear optical (NLO) crystals for visible and ultraviolet (UV) region are extremely important for laser processing. High quality organic NLO crystals must possess large NLO coefficient, transparency in UV region, high laser damage threshold power and ease of growth with improved dimension[1]. Organic materials draw more interest because of their superior performances involving fairly high NLO coefficient and ultrafast nonlinear response than their inorganic counterparts. In general, most of the organic molecules designed for nonlinear optical (NLO) applications are known to be the derivatives of an aromatic system substituted with a donor and an acceptor. One of the attractive strategies followed by the researchers for developing new NLO materials with better mechanical properties is the employment of small organic molecules possessing large dipole moment with a chiral structure. Especially, the combination of two simple organic molecules, one with a large dipole moment and the other one, a chiral molecule with an acentrosymmetric crystal structure is proved to be a successful one. These molecules are usually linked through the hydrogen bond[2]. Large numbers of organic compound with delocalized π-electron systems and a large polar dipole moment have been synthesized to realize the nonlinear susceptibilities larger than that of inorganic optical materials[3]. These organic materials play an important role in second harmonic generation (SHG), frequency mixing, electro-optical modulation, optical parametric oscillation, optical bistability etc.[4]. The materials in this class are widely used in the ultraviolet (UV) region; because the distance between energy levels in conjugated π-bonds get smaller due to the strong conjugation effect[5]. These enhanced properties

of amino acids are due to the presence of a proton donor carboxyl acid (-COO) group and the proton acceptor amino (-NH₂) groups. In the solid state, these exist as dipolar ions in which carboxyl group is present as carboxylate ion. Due to this dipolar nature, amino acids have physical properties which make them ideal candidates for NLO applications[4]. In the present investigation, we report bulk growth, optical and dielectric properties of L-Histidinium Trifluoroacetate single crystal.

Material and Methods

Crystal growth: L-Histidinium Trifluoroacetate was synthesized with high purity L-Histidine and trifluoroacetic acid (AR grade) in the ratio 1: 1. The stoichiometric amounts of the reactants were dissolved in the deionised water-ethanol mixture and stirred well for about 10 hrs. This was then filtered and allowed to crystallize by slow evaporation technique. Tiny seed crystals with good transparency were obtained due to the spontaneous nucleation. Among them, defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at a temperature of 30°C in a constant temperature bath of ± 0.01K accuracy. Optically good bulk crystals with perfect external morphology are harvested within a period of 15 days and are shown in figure 1.

Results and Discussion

Single-crystal X-ray diffraction: The single crystal X-ray diffraction (XRD) analysis for the grown crystals has been carried out to identify the lattice parameters. The calculated lattice parameters are a = 5.17 Å, b = 8.84Å, c = 12.48Å, α = 96.19°, β= 100.02° and γ =102.01°and the crystal belongs to triclinic structure with space group P1. The XRD results are in good agreement with the reported values[5].
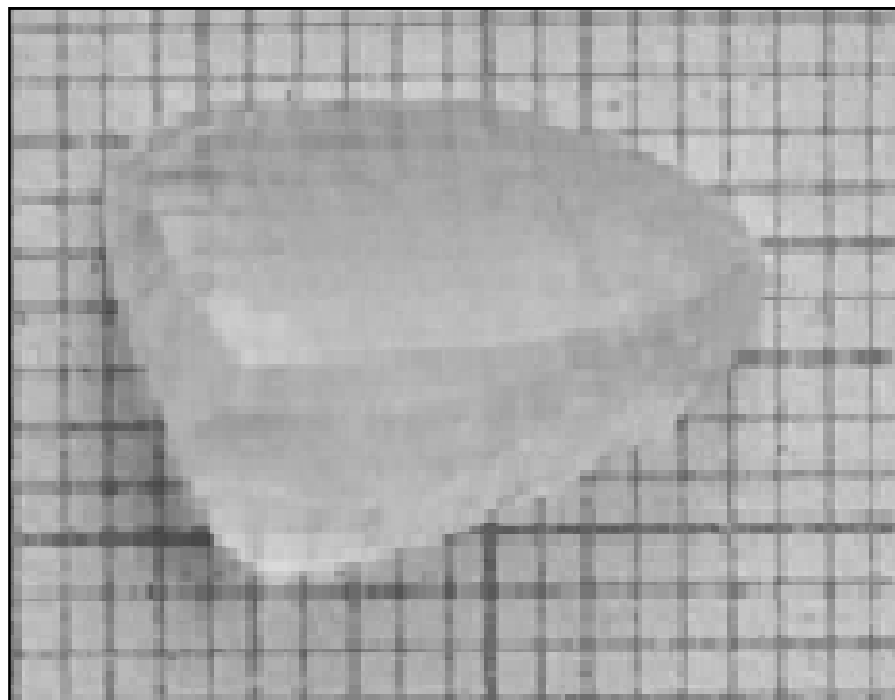
Figure-1
Grown crystal of L-Histidinium Trifluoroacetate

Density measurements: The density of L-Histidinium Trifluoroacetate crystal was calculated by the equation shown below[6]

$$\rho = \frac{MZ}{N_A \times Volume} \qquad (1)$$

where *M* is molecular weight of L-Histidinium Trifluoroacetate; molecular unit cell *Z* = 2; N_A is Avogadro's number and *a*, *b* and *c* are the lattice parameters of L-Histidinium Trifluoroacetate crystal. The theoretical density is found to be 1.643 *g/cm³*. The density of L-Histidinium Trifluoroacetate crystal was measured experimentally by the floatation method at room temperature (32ºC), and the measured density can be obtained by the following equation

$$\rho = M \rho_{solvent} / m - m' \qquad (2)$$

where m is the mass of meta-Nitroaniline crystal sample in the air, m′ is the mass when the L-Histidinium Trifluoroacetate crystal sample was immersed in CCl_4 and $\rho_{solvent}$ is the density of solvent (CCl_4) used at measured temperature. The density was measured by floatation technique. From this measurement, the density of the crystal is found to be 1.641 *g/cm³*. The experimentally measured density is in good agreement with the theoretically found value.

Optical transmission studies: The optical transmission spectrum of L-Histidinium Trifluoroacetate (shown in figure 1) was recorded in the range 200–1200 nm with a crystal of thickness 2 mm. For optical fabrications, the crystal should be highly transparent in the considerable region of wavelength[7-8]. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices[9-10]. The UV absorption edge for the grown crystal was observed to be around 230 nm. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons[11]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation

$$\alpha = \frac{2.3026 \; \log\left(\frac{1}{T}\right)}{t} \qquad (3)$$

where *t* is the thickness of the sample. Optical band gap (E_g) was evaluated from the transmission spectrum and optical absorption coefficient (*α*) near the absorption edge is given by[12]

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \qquad (4)$$

where *A* is a constant, E_g the optical band gap, *h* the Planck constant and n the frequency of the incident photons. The band gap of L-Histidinium Trifluoroacetate crystal was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Figure.2. From the figure, the value of band gap was found to be 4.25 eV. Extinction coefficient (*K*) can be obtained from the following equation:

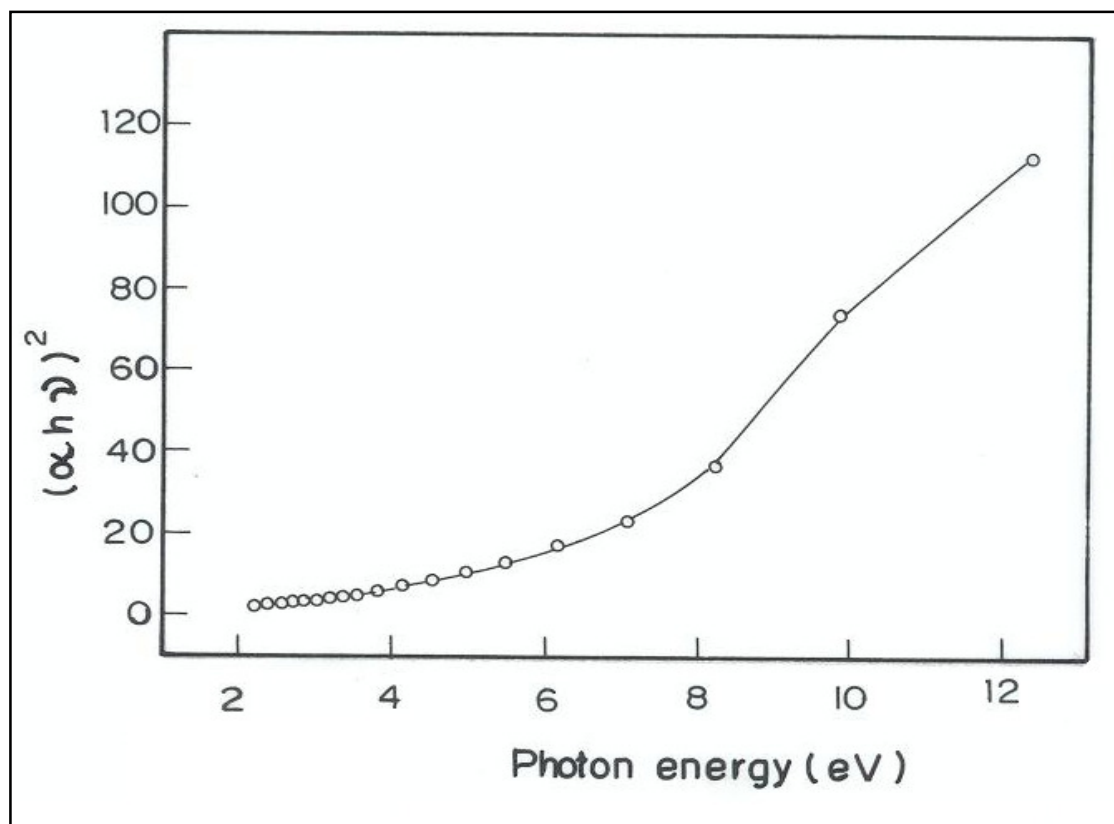$$K = \frac{\lambda \alpha}{4\pi} \qquad (5)$$

Figure-2
Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$)

The transmittance (*T*) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \qquad (6)$$

Reflectance (*R*) in terms of absorption coefficient can be obtained from the above equation.
Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \qquad (7)$$

Refractive index (*n*) can be determined from reflectance data using the following equation;

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \qquad (8)$$

The refractive index (*n*) is 1.521 at λ =1100 nm. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [13]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \qquad (9)$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \qquad (10)$$

The value of electric susceptibility χ_c is 0.113 at λ =1100

nm. The real part dielectric constant ε_r and imaginary part

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dielectric constant ε_i can be calculated from the following relations [14]

$$\varepsilon_r = n^2 - k^2 \;\&\; \varepsilon_i = 2nk \qquad (11)$$

The value of real ε_r and ε_i imaginary dielectric constants at λ =1100 nm are 1.252 and 6.623 x 10$^{-5,}$ respectively.

Dielectric measurements: For dielectric measurements carefully cut and polished samples of grown crystals were carried out using HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5 MHz. A sample of crystal having silver coating on the opposite faces was placed between the two copper electrodes to form a parallel plate capacitor. Figure 3 shows the plot of dielectric constant (ἐ) versus applied frequency. It is observed from the plot (figure 3) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. The dielectric loss is studied as a function of frequency at room temperature is shown in the figure 4. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant.
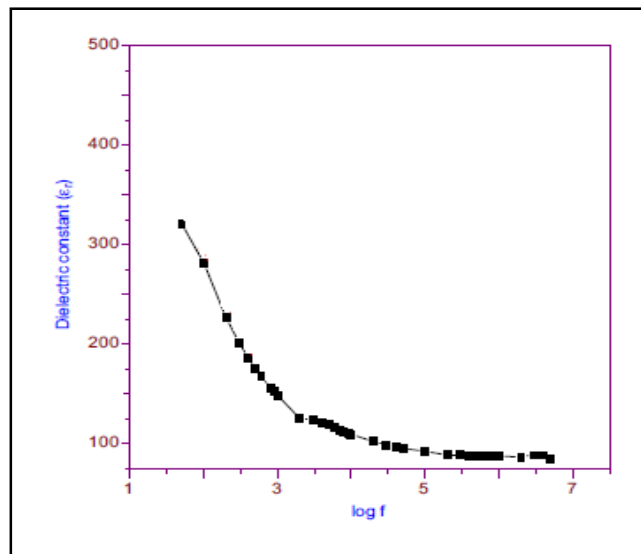
Figure-3
Variation of dielectric constant with log f
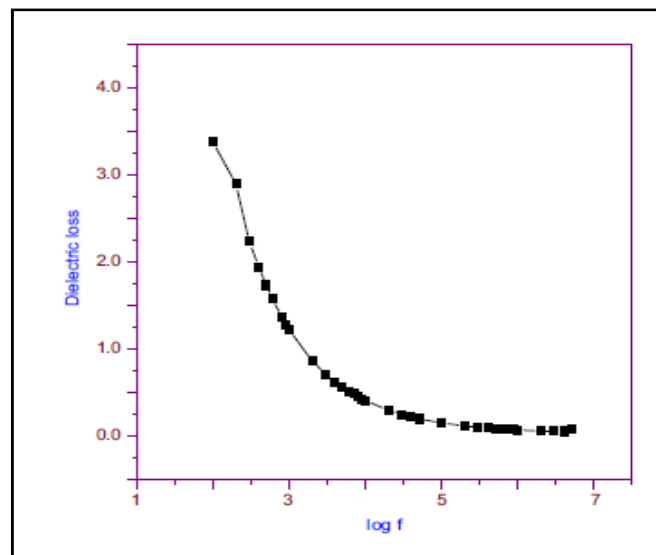
Figure-4
Variation of dielectric loss with log f

Conclusion

Single crystals of L-Histidinium Trifluoroacetate were synthesized and subjected to single crystal XRD, optical and dielectric studies. From the X-ray diffraction, it was confirmed that the crystal belongs to triclinic structure with space group P1. The optical transmittance of the crystal confirms the transparency of the crystal. The band gap energy value (4.25eV) predicted from UV studies confirms the dielectric behaviour of the material. Hence, the material is confirmed as a dielectric material to induce polarization for second harmonic generation when a powerful laser beam is incident on the material. The dielectric studies prove that the sample has low dielectric constant and dielectric loss values at high frequency.

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