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Growth of glycine ethyl ester hydrochloride and its characterizations

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ABSTRACT

Single crystal of glycine ethyl ester hydrochloride by slow evaporation method is reported. The grown crystal characterized by single crystal X-ray diffraction, FT-IR, UV–Vis–NIR and fluorescence spectroscopy. It is established that the crystal falls under the monoclinic system and space group $P21/c$ with the cell parameters as: $a=8.565$ Å, $b=12.943$ Å, $c=6.272$ Å, $\alpha=\gamma=90°$, $\beta=103.630°$. UV–Vis–NIR spectrum shows indirect allowed transition with a band gap of 5.21 eV and other optical properties are measured. The crystal is also shown to have a high transmittance in the visible region. The third order nonlinear property and optical limiting have been investigated using Z-Scan technique. Complex impedance spectrum measured at the dc conductivity. Dependence of dielectric constant, dielectric loss and ac conductivity on frequency at different temperature of applied ac field is analyzed. The mechanical behavior has been assessed by Vickers microhardness indenter. The thermal behavior of glycine ethyl ester hydrochloride was analyzed using TG/DTA thermal curves. From the thermal study, the material was found to possess thermal stability up to 174 °C. The predicted NLO properties, UV–Vis transmittance and Z-scan studies indicate that is an attractive material for photonics optical limiting applications.

1. Introduction

Proteins, the most abundant intracellular macromolecules that occupy the central position in the architecture and functioning of the living matter are built by polypeptide chains of amino acid [1]. Glycine is the simplest among the amino acid, which is found in proteins and the special interest as a model of experimental studies [2]. Unlike other amino acids glycine lacks of the centre of chirality and optical is inactive. Glycine can exist as a natural molecule in the gas phase, and can exist as zwitter ions in solution and in solid state. The complex and the carboxylic acid are expected to throw light on the geometrical feature of bio-molecular interactions. The glycine molecule exists in the cationic form with a positively charged amino group and an unchanged carboxylic acid group [3]. Recently literature reports shows that glycine combines with H_2SO_4[4], $AgNO_3$[5], $CaCl_2$[6], $CaNO_3$[7], $BaCl_2$[8]. The reaction of the glycine ethyl ester and hydrochloride yields glycine ethyl ester hydrochloride (GEC).

In this present work, we report the growth and the result of characterization studies of glycine ethyl ester hydrochloride (GEC) by slow evaporation method. The grown crystals were characterized by various methods such as optical, XRD, Z-scan, dielectric method, mechanical and thermal methods and the results are analyzed and discussed for the first time.

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2. Experimental methodology

2.1. Single crystal Growth

Glycine ethyl ester hydrochloride from the starting materials, namely glycine ethyl ester (Purity 99%) and hydrochloric acid (35%). The expected chemical reaction is as follows:

$$C_4H_9NO_2 + HCl + H_2O \rightarrow C_4H_{10}NO_2Cl + H_2O \text{ (in solution)}$$

Glycine ethyl ester and hydrochloric acid were dissolved in double distilled water in equimolar ratio. The solution prepared was continuously stirred for homogenization for a period of 3 h at room temperature and then filtered to remove the suspended impurities. The beaker filled solution then covered with perforated plastic sheet. The crystal was grown by slow evaporation method at room temperature. The grown crystal was obtained over the period of 18 days. The product was purified by further recrystallization and good quality crystal has been grown a period of 55 days. The photograph of as grown single crystal is shown in the Fig. 1.

2.2. Characterization details

In order to obtain the crystal data of GEC crystal, single crystal X-ray diffraction study was carried out using Bruker Kappa Apex II X-ray diffractometer with M_oK_a radiation. The functional groups were identified with Perkin Elmer RX I spectrometer with KBr pellet technique used to recorded in the range of 400–4000 cm^{-1}.

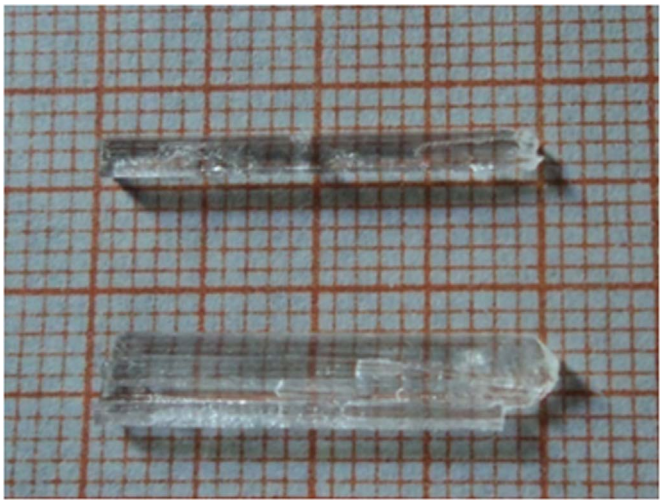

Fig. 1. Photograph of as grown crystal of GEC.

UV–Vis–NIR spectrum was recorded in the range of 190–1100 nm using Perkin Elmer – Lambda 35 spectrophotometer. The third order nonlinearity of GEC crystal was determined by Z-scan method using Nd: YAG laser at 532 nm as the source. Perkin Elmer spectrofluorometer was used for recording luminescence spectrum. Impedance analysis was recorded using model-Zenher LCRZ meter. Dielectric properties of GEC sample were carried out in the frequency range of 100 Hz – 5KHz using LCR meter with parallel plate capacitance. Hardness is a popular solid state property, hardness is commonly carried out to determine the mechanical strength of materials by HMV SHIMADZU microhardness tester fitted with diamond pyramidal indenter. The TG and DTA studies of the grown crystal were carried out of room temperature to 750 °C at a heating rate of 20 °C/min using Perkin Elmer thermal analyzer in nitrogen atmosphere.

3. Result and discussion

3.1. Single crystal X-ray diffraction

In order to reveal that the crystal structure and for the conforming the grown crystal, X-ray diffraction studies were carried out and data collected. The unit cell parameters obtained are $a=8.565$ (6) Å, $b=12.943$ (3) Å, $c=6.272$ (8) Å, $\alpha=\gamma=90^{o}$, $\beta=103.630^{o}$ (3) and Volume (V)=672.6 Å^3. It exhibits monoclinic crystal system with space group of $P21/c$. When they are compared, the result is in good agreed with reported value [9].

3.2. Fourier Transform Infrared Spectrum

Fourier Transform Infrared Spectroscopy has been recorded to analysis the functional group of synthesized GEC compound and it is shown in the Fig. 2. In the spectrum obtain between 3400 cm^{-1} and 1599 cm^{-1} is due to the NH_3^+ stretching and NH_3^+ bending respectively [10]. A ester group of strong C=O stretching occur at 1742 cm^{-1} and the carboxylic ion group of COO^- bending absorb medium at 934 cm^{-1}. The medium rocking of chlorine atom in the molecules at 766 cm^{-1} and 710 cm^{-1} [11]. The absorption peaks characterizing different functional groups are shown in Table 1.

3.3. UV–Vis–NIR Spectrum

To determine the transparency range of GEC single crystal, UV–Vis transmittance and absorption spectrum was recorded and is shown in the Fig. 3 and Fig. 4. Optically clear single crystal of

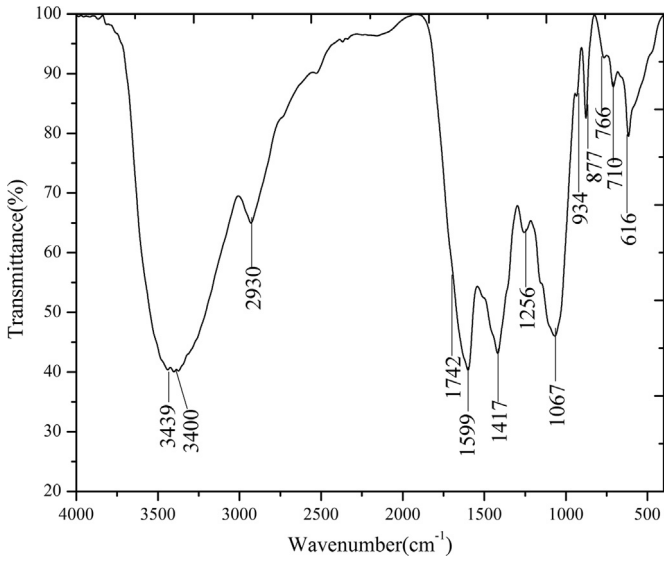

Fig. 2. FT-IR spectrum of GEC crystal.

Table 1
FT-IR Assignments of GEC crystal.

Wavenumber (cm^{-1})	Assignments
3439	O–H stretching
3400	NH_3^+ stretching
2930	C–H stretching
1742	C=O stretching
1599	NH_3^+ bending
1417	C-C stretching
1256	C–N stretching
1067	C–O stretching
934	COO^- bending
877	NH_3^+ wag
766, 710	C–Cl rock
616	C–H bending

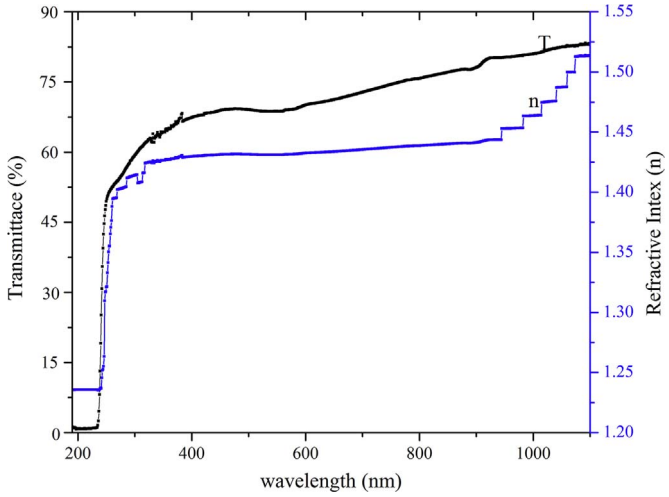

Fig. 3. Transmittance spectrum and refractive index of GEC crystal.

thickness 1.4 mm was used in this study without polishing. If is observed that UV cut-off wavelength is at 238 nm. The crystal has high transmittance around 75% in the visible region. The estimated band gap was calculated 5.21 eV. A peak occurred at 238 nm in the spectrum may be due to the π–π^* transition. A feature that promotes possible optical application in device operating at the visible-NIR wavelength range [12,13].