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Studies of Crystal Growth, Structural and Optical Properties of Glycinium-3-Carboxy-4-Hydroxybenzenesulfonate Single Crystal

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ABSTRACT. Glycinium-3-carboxy-4-hydroxybenzenesulfonate (GCHBS), a new organic compound was synthesized and optical quality single crystal was grown by slow evaporation technique. The structure of grown crystal was elucidated by using single crystal X-ray Diffraction studies. The degree of sharpness and crystallinity was found from the Bragg peaks diffraction pattern. The presence of functional groups was confirmed from the FT-IR spectral analysis. UV-Vis transmission studies show that the grown crystal has optical transparency around 70%. The emission spectrum indicates that the GCHBS exhibits blue lighting emission sharply at 445 nm and it will be useful for fabricating blue light emitting diodes. The thermal stability of grown crystal was studied from thermogravimetric and differential thermal analyses and found that the crystal is stable up to 235°C. The nonlinear absorption coefficient (β), nonlinear optical susceptibility ($\chi^{(3)}$) and nonlinear refractive index (n_2) of GCHBS crystal were estimated by Z-scan technique.

Introduction. Nonlinear optical (NLO) materials are found to have great interest in the recent years, because of their potential numerous optoelectronic applications. In the present modern technology, much more effort has been made to find the new second and third order nonlinear optical materials for several nonlinear optical applications such as third harmonic generation (THG), frequency mixing, electro-optic modulation and optical parametric oscillation. This technology is continuing to grow and refinement in the development of lasers crystals and higher nonlinear optical materials resulted in a variety of commercially available nonlinear optical devices. Many investigations are being carried out to synthesize new materials with large third-order optical nonlinearities in order to satisfy day-to-day technological demands [1]. The presence of benzenesulfonate and hydroxyl functional groups play a vital role in nonlinearity of the GCHBS crystal and glycine is the simplest amino acid, it forms several new compounds with other organic as well as inorganic materials. Adequately, several complexes of glycine have been reported, viz., glycine picrate [2], diglycine picrate [3], glycine glutaric acid [4], etc. However, there is no report available so far on compounds of glycine with 3-carboxy-4-hydroxybenzenesulfonic acid. Hence, in the present work, the synthesis, crystal growth, structure, optical and thermal properties of the new organic material of Glycinium-3-carboxy-4-hydroxybenzenesulfonate have been reported for the first time.

Materials and methods. GCHBS compound was synthesized due to the chemical reaction between the commercially available glycine and 3-carboxy-4-hydroxybenzenesulfonic acid taken in the stoichiometric ratio 1:1. The calculated amount of salts was dissolved in double distilled water. The reaction scheme and photograph of the grown single crystal of GCHBS are shown in Fig. 1. The quality of single crystal depends on the purity of the used materials. Hence, the synthesized

compound was recrystallized several times to obtain highly purified material. The saturated solution was prepared at room temperature (32°C), and it was stirred for more than 10 h to attain homogeneity of solution. Then, the prepared solution was filtered by using Whatman filter paper and covered with a good quality perforated polythene cover to restrict the fast evaporation of the solvent. The defect-free, optically clear, and perfectly shaped tiny crystal was chosen as seed for the growth experiment. After a span of 25 days, a bulk size (13mm×6mm×6mm) GCHBS crystal was harvested by slow evaporation method.

Experimental. The grown GCHBS crystal was subjected to various characterization studies. A Bruker Kappa Apex II single crystal X-ray diffractometer with $\text{MoK}\alpha$ ($\lambda=0.71013 \text{ \AA}$) radiation was used to measure cell parameters of GCHBS crystal with typical cell dimension of $0.36 \times 0.32 \times 0.30 \text{ mm}^3$. Powder X-ray diffraction pattern of the grown crystal was recorded by using BRUKER AXS CAD 4 with $\text{CuK}\alpha$ radiation (1.5406 \AA). The crystal data were obtained over a 2θ range $10\text{--}70^\circ$ using step scan of 0.04° . The vibrational spectrum was performed for GCHBS compound by using FTIR–4100 type spectrometer at a resolution of 4cm^{-1} in the range $400\text{--}4000 \text{ cm}^{-1}$. UV-Vis transmission spectrum of GCHBS crystal was recorded in the range $190\text{--}1100\text{nm}$ by using LABINDIA T90+ UV-Vis spectrophotometer. TG-DTA experiments were carried out using a NETZSCH STA 409 instrument with a heating rate of $10^\circ\text{C}/\text{min}$ starting from 30 to 500°C . The Z-scan technique was employed to determine third-order nonlinearity of grown crystal by using 632.8 nm He-Ne laser source.

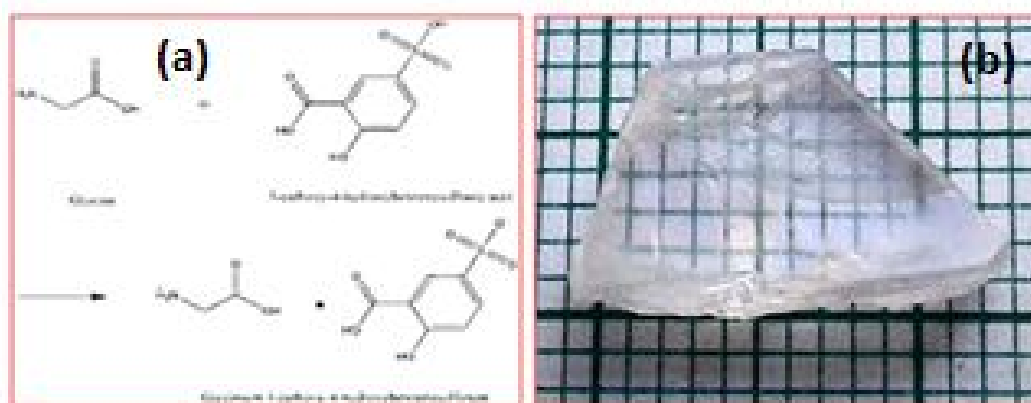


Fig. 1. (a) Synthesis scheme and (b) Photograph of GCHBS crystal.

Results and Discussions

X-ray diffraction studies. The crystalline parameters of GCHBS single crystal was studied from single crystal X-ray diffraction analysis. The XRD data shows that the GCHBS crystal belongs to the monoclinic system with space group $P2_1/c$. The calculated lattice parameter values are $a = 5.3651(3) \text{ \AA}$, $b = 24.72079(15) \text{ \AA}$, $c = 8.6840(5) \text{ \AA}$, $\beta = 90.170(2)^\circ$, volume $V = 1151.75(12) \text{ \AA}^3$ and $Z = 4$ [5]. In the title salt, $\text{C}_2\text{H}_6\text{NO}_2^+ \cdot \text{C}_7\text{H}_5\text{O}_6\text{S}^-$, the dihedral angle between the carboxylic acid group and the benzene ring is $5.02(12)^\circ$. In the crystal, the anions are linked into inversion dimers through pairs of $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds between the carboxylic acid groups and sulfonate O atoms. A pair of $\text{C} \cdots \text{H} \cdots \text{O}$ interactions is also observed within each dimer. The anion dimers and the cations are linked into a three dimensional network by $\text{N} \cdots \text{H} \cdots \text{O}$, $\text{O} \cdots \text{H} \cdots \text{O}$ and $\text{C} \cdots \text{H} \cdots \text{O}$ hydrogen bonds. The crystal structure is exhibited with weak intermolecular π - π interactions and packing of the molecules in the unit cell, viewed down the a-axis. Powder X-ray diffraction studies were carried out to demonstrate the crystalline nature of the grown crystal. X-ray powder pattern of GCHBS is shown in Fig. 2. The sharpness of defined Bragg peaks in the powder X-ray diffraction pattern confirmed its crystallinity. The prominent Bragg peaks in the powder

X-ray diffraction pattern were indexed and the peak corresponding to (102) plane has maximum counts at 2θ value of 26.29.

FT-IR spectral analysis. Infrared spectrum is an exclusive physical tool for finding functional groups of the molecular structure. FTIR spectrum of GCHBS was recorded at room temperature and shown in Fig. 3. Two important features of IR spectrum of carboxylic acids are, strong H-bonding between the carboxylic acid molecules and stretching of carbonyl groups of carboxylic acids. In the present study, the above absorptions observed in the region $3500\text{--}3000\text{ cm}^{-1}$. The band observed at 3255 cm^{-1} is due to the O-H stretching vibration, it showed the presence of amino acid substituted 3-carboxy-4-hydroxybenzenesulfonic acid. A broad strong NH_3^+ stretching band observed in the region between 3164 and 2564 cm^{-1} is due to amino group of GCHBS. The bands observed at 1588 and 1435 cm^{-1} correspond to asymmetric and symmetric stretchings of amino group. The band observed at 1682 cm^{-1} is assigned to the carboxylate (COO^-) symmetric stretching. The peak observed at 1747 cm^{-1} correspond to the $\text{C}=\text{O}$ stretching of the carbonyl group. The band examined at 1164 cm^{-1} indicates the presence of sulfonate group (SO_3). Based on FT-IR results, the formation of Glycinium-3-carboxy-4-hydroxybenzenesulfonate has been confirmed.

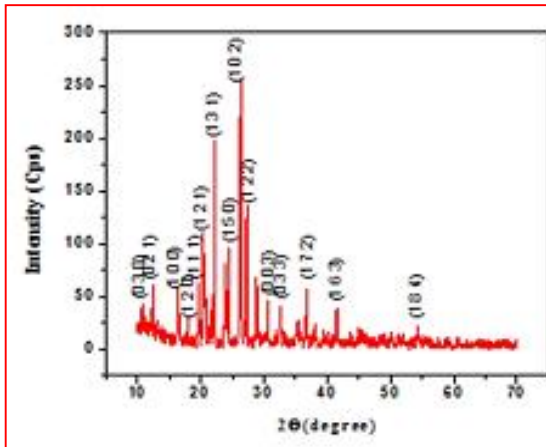


Fig. 2. Powder XRD pattern of GCHBS crystal

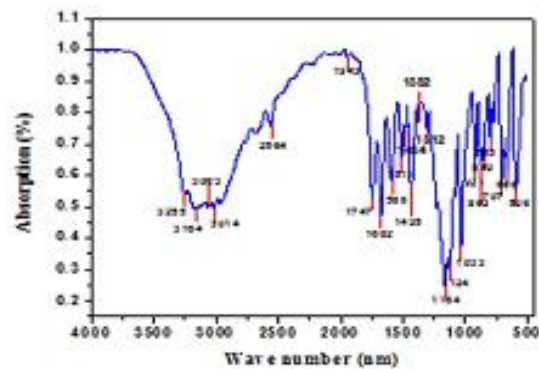


Fig. 3 FT-IR spectrum of GCHBS.

UV-Vis Spectral Studies. The characteristic absorption was observed at 335 nm leading to electronic excitation, and there was no absorption band observed between 350 to 900 nm . The UV-Vis-NIR transmission spectrum of GCHBS is shown in Fig. 4. From the transmittance UV spectrum analysis, it is clear that the grown crystal exhibit good transparency of about 70% in the visible region with lower cut-off wavelength of 335 nm . The optical band gap (E_g) was evaluated from the transmission spectrum and the optical absorption coefficient (α) near the absorption edge was estimated by using the relation,

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

where A is a constant, E_g is the optical band gap.

The Tauc's graph [6] plotted between the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^2$ with the photon energy $(h\nu)$ shows a linear behavior that can be considered as evidence for the direct transition (Fig. 5). The band gap value has been obtained by extrapolating the linear portion of the plot to intercept the photon energy axis and found to be 3.67 eV . The wide optical energy band gap of the grown crystal confirms that the GCHBS crystal possess large transmittance in the visible region. The refractive index of an optical material can be calculated by using transmission

spectrum and the reflectance of the crystal may be described in terms of absorption coefficient (α) obtained from the relation,

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

The refractive index n of GCHBS crystal was found to be 2.50. This behavior is well suitable for optical device applications.

Thermal analysis. The differential thermogravimetric trace of GCHBS crystal is shown in Fig.6. TGA curve shows that, no weight loss observed up to 235°C. This indicates that there is no inclusion of water in the crystal lattice, which is used as the solvent for crystallization. The major weight loss started at 235°C and it continued up to 290°C due to the decomposition of functional groups of molecules which were evaporated before melting point. The residual mass of 1.72% which was left out in the crucible may be carbon mass present after the decomposition process. The nature of weight loss indicated the decomposition stage of the material. However, no weight loss has been observed before this temperature. In the DTA, there is a strong endothermic peak observed at 225°C. This sharp peak at 225°C confirmed the melting of the compound.

Photoluminescence studies. Fluorescence studies inferred the broad applications in biochemical, medical and chemical research fields for analyzing organic compounds. It generally occurs in compounds containing aromatic functional groups with low energy $n-\pi^*$ transition levels. The GCHBS crystal sample was excited at the wavelength of 335 nm chosen from UV-Visible study and it was used to record the PL spectrum of the crystal in the range 300–650 nm (Fig.7). The emission spectrum indicated the blue band emission at 445 nm and its wide optical range observed from 387 to 530nm. The broadening of emission band is due to the intermolecular interactions of GCHBS crystal.

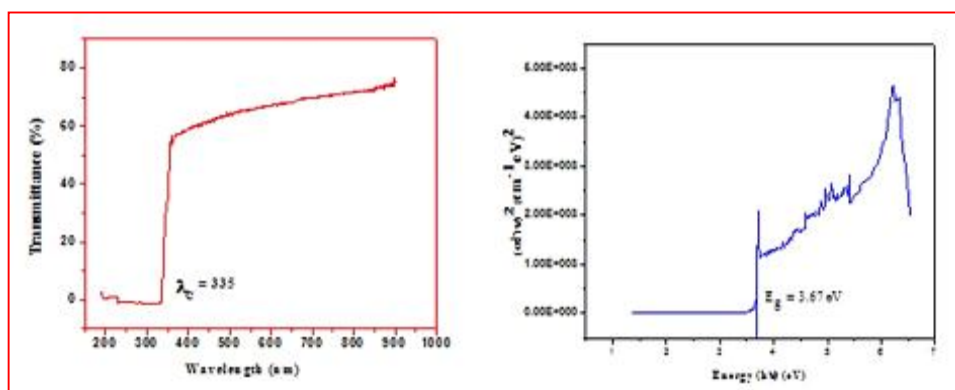


Fig. 4. UV-Visible transmission spectrum of GCHBS

Fig. 5. Plot of $(ahv)^2$ vs. photon energy (hv) .

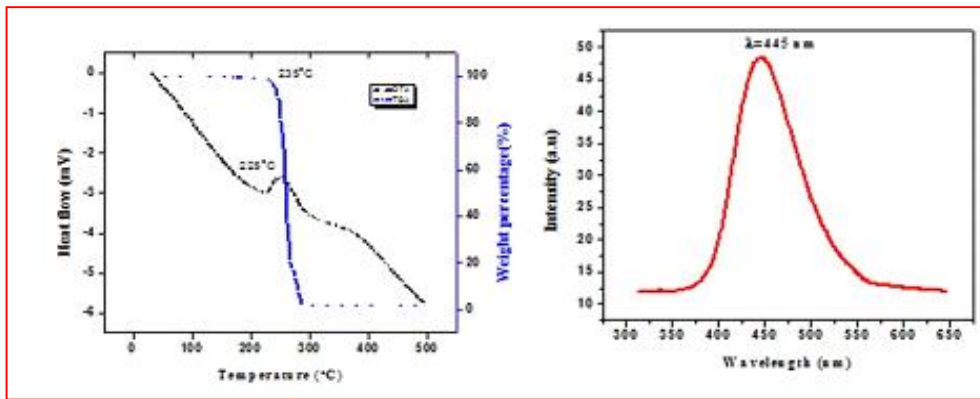


Fig. 6. TG/DTA thermograms of GCHBS.

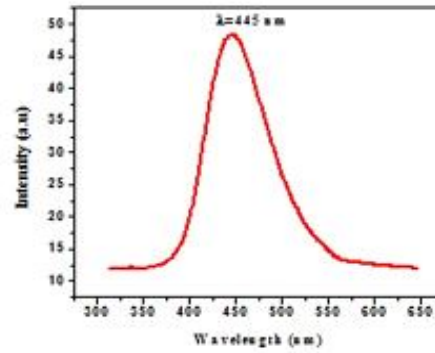


Fig. 7. PL spectrum of GCHBS.

Z-Scan Measurement. The Z-scan study is used to examine the nonlinear optical properties and nonlinear absorption coefficient (β) and nonlinear refractive index (n_2) of the grown crystal have been estimated. The Z-scan curves traced in open and closed aperture modes are shown in Fig.8. From the Z-scan data, the difference between the valley and peak transmittances (ΔT_{v-p}) was evaluated in terms of on-axis phase shift at the focus.

$$\Delta T_{v-p} = 0.406(1-S)^{0.25} |\Delta\Phi_o| \quad (3)$$

where S is the linear transmittance aperture.

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \quad (4)$$

where ‘ r_a ’ is the radius of aperture and ‘ ω_a ’ is the beam radius at the aperture. The nonlinear refractive index (n_2) was calculated using closed aperture Z-scan data [7,8].

$$n_2 = \frac{\Delta\Phi_o}{KI_oL_{eff}} \quad (5)$$

The nonlinear absorption coefficient (β) was estimated from the open aperture Z-scan data.

$$\beta = \frac{2\sqrt{2}\Delta T}{I_oL_{eff}} \quad (6)$$

The third order nonlinear optical susceptibility was calculated using the relation [9],

$$\chi^{(3)} = \sqrt{(\text{Re}\chi^{(3)})^2 + (\text{Im}\chi^{(3)})^2} \quad (7)$$

Table 1. Optical parameters of GCHBS measured in Z-scan experiment.

Effective thickness (L_{eff})	0.9974 mm
Nonlinear refractive index (n_2)	$0.548 \times 10^{-10} \text{ cm}^2/\text{W}$
Nonlinear absorption coefficient (β)	$1.6849 \times 10^{-3} \text{ cm/W}$
Third-order nonlinear optical susceptibility ($\chi^{(3)}$)	$1.3454 \times 10^{-10} \text{ esu}$

The measured third order nonlinear optical parameters are given in Table 1. The third-order nonlinear optical susceptibility of GCHBS crystal formed by anions linked into inversion dimers through the pairs of O—H...O hydrogen bonds between the carboxylic acid groups and sulfonate O-atoms to modify the second order as well as third order nonlinear optical properties. The Z-scan method confirms that the GCHBS crystal can be a promising NLO material for optical device applications such as optical modulators, optical limiters.

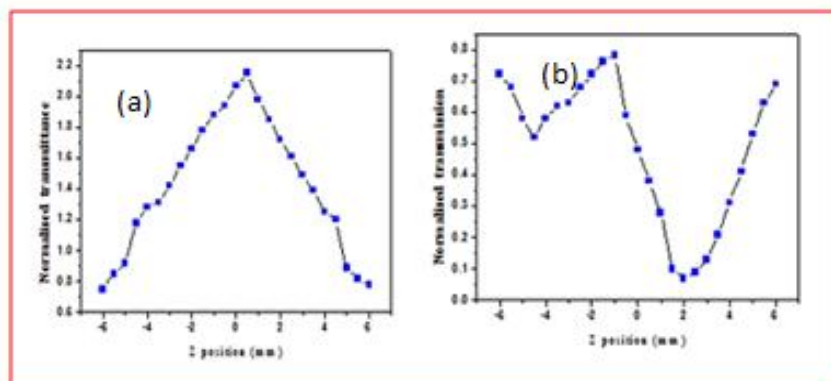


Fig. 8. Z-scan traces observed in (a) Open aperture and (b) closed aperture modes for GCHBS crystal.

Summary. Third-order nonlinear optical GCHBS organic single crystal with 13x 6x6 mm³ dimension was grown by slow evaporation technique. From the single crystal X-ray diffraction study, it was observed that GCHBS crystal belongs to monoclinic system with P2₁/c space group. The quality of the grown crystal was ascertained by using single and powder XRD analyses and found fairly good crystalline perfection. Infrared spectral study was used to confirm the functional groups present in GCHBS compound. TG-DTA thermal study reveals that grown crystal is thermally stable up to 235°C. UV–visible study showed the good transmission region (350–900 nm) in the grown crystal. The cut-off wavelength and band gap energy were found to be 335 nm and 3.67 eV respectively. The nonlinear optical refractive index, nonlinear absorption coefficient and third-order nonlinear optical susceptibility were evaluated by using Z-scan studies.

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