

Growth and Characterization of L-Glycine Formate Single Crystal

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Single crystal of L-glycine formate is a nonlinear optical crystal. It was grown from aqueous solution by slow evaporation method. The unit cell parameters of the grown crystal were estimated by single crystal X-ray diffraction analysis. The presence of functional groups was identified from FTIR spectrum. Thermal analysis was performed to study the thermal stability of the grown crystal. The UV transmission spectra of this crystal show that the lower cut off wavelength lies at 300 nm.

Key Words: FTIR, Thermal studies, L-Glycine formate, Single crystal.

INTRODUCTION

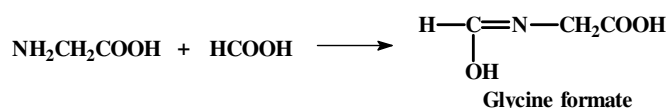
In recent years, organic non linear optical (NLO) crystals are more attractive and more versatile than their inorganic counterparts due to their large electro-optic coefficient with low frequency dispersion and high non-linearity¹. Hence there has been a search for newer organic NLO materials with blue light transmittance^{2,3}. Amino acids are interesting materials for NLO application. The importance of amino acids has chiral symmetry and crystallizes in noncentro-symmetric space groups⁴. Glycine is the simplest amino acid. It has no centre of chirality and is optically inactive. While glycine can exist as a neutral molecule in the gas phase, it exists as zwitter ions in solution and in the solid state. Glycine in solid state crystallizes in three forms (α , β and γ) which have been studied by X-ray⁵⁻⁷ and neutron diffraction^{8,9}. While α -glycine is commonly available, γ -glycine crystallizes in non-centrosymmetric space group P_{31} making it a potential candidate for piezoelectric and nonlinear (NLO) applications. The carboxylic acid group present in the γ -glycine donates its proton to the amino group to form the structure $\text{NH}_3^+\text{CH}_2\text{COO}^-$. Thus in solid state, γ -glycine exists as a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. Due to this dipolar nature, glycine has a high melting point. Another added advantage of glycine is the presence of chromophores namely amino group and carboxyl group which makes it transparent in the UV-vis region. In this paper, the growth of L-glycine formate by slow evaporation technique is reported for the first time along with characterization of L-glycine formate by XRD, FTIR, UV-vis-NIR, TGA/DTA techniques.

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EXPERIMENTAL

Single crystal of L-glycine formate was grown by slow cooling technique of an equimolar solution of glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) (AR grade) and formic acid [HCOOH] (AR grade). The salt was synthesized by dissolving it in de-ionized millipore water which was used as a solvent. The reaction took place with the formation of the following compound.



The calculated amounts of the reactants were thoroughly dissolved in deionized water and stirred well for about 3 h using a magnetic stirrer to ensure homogeneous temperature and concentration over entire volume of the solution. The solution was filtered and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation under room temperature. Good quality seed crystals harvested in 15 days by slow evaporation. Good quality crystals are obtained by repeated re-crystallization. The bulk crystals of dimension $1 \text{ cm}^3 \times 1.4 \text{ cm}^3 \times 0.5 \text{ cm}^3$ are obtained as shown in the photograph (Fig. 1).

RESULTS AND DISCUSSION

Single crystal X-ray diffraction study: To estimate the crystal data, single crystal X-ray diffraction studies were carried out using Enraf nonius CAD4 single crystal X-ray diffractometer with $\text{MoK}\alpha$ ($\gamma = 0.7170 \text{ \AA}$) radiation L-glycine formate single crystal. The L-glycine formate crystal retained its monoclinic structure with lattice parameters $a = 5.09 \text{ \AA}$, $b = 11.95 \text{ \AA}$, $c = 5.45 \text{ \AA}$, $V = 947 \text{ \AA}^3$, $\beta = 111.64^\circ$.

FTIR analysis: The grown crystals were subjected to FTIR analysis with sample prepared with KBr in the palletized form. The FTIR spectrum for L-glycine formate was recorded in the region $4000\text{--}400 \text{ cm}^{-1}$ employing BRUKER IFS 66V spectrometer. The FTIR spectrum of L-glycine formate is shown in Fig. 2. The broad envelope in the higher energy region between 3100 and 2600 cm^{-1} is due to NH_3^+ stretching vibrations. The region of absorption bands extends to about 2169 cm^{-1} due to multiple combination and overtone bands. The prominent band near $2228\text{--}2169 \text{ cm}^{-1}$ may be assigned to a combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ group¹⁰. The NH_3^+ stretching region shows broad bands characteristic of hydrogen bonding. The frequencies of the vibrational mode of the crystal and their assignments are given in Table-1. The absorption peaks characterizing the various functional groups are in very good agreement with those reported in literature^{11,12}.

Thermal analysis: The TGA and DTA response curves for the powder sample L-glycine formate is shown in Fig. 3. In the TGA trace, there is a major weight loss of 52.20 % starting at about 274.2°C and ending at 310°C . It is due to the decom-

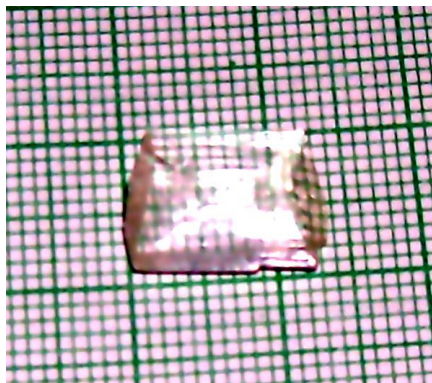


Fig. 1. L-Glycine formate

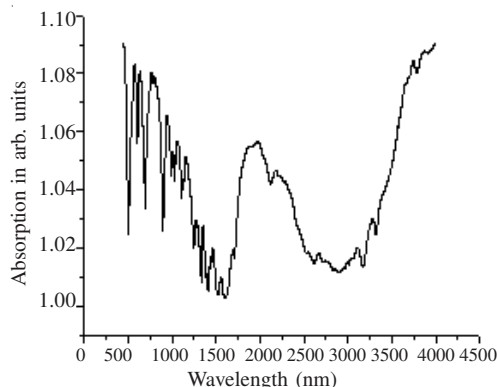


Fig. 2. FTIR spectra of L-glycine formate

TABLE-1
FREQUENCIES OF THE FUNDAMENTAL VIBRATIONS OF L-GLYCINE FORMATE

Frequency in wave number (cm ⁻¹)	Assignment of vibrations
3400	NH ₃ ⁺
3200	OH ⁻
2900	CH ₂
2614	NH ₃ ⁺
1612	COO ⁻ asymmetric stretch
1463	NH ₃ ⁺
1437	CH ₂ bend
1390	COO ⁻ symmetric stretch
1335	CH ₂ wag
1322	CH ₂ twist
1164	NH ₃ ⁺ rock
1112	NH ₃ ⁺ rock
1033	CCN asymmetric stretch
944	CH ₂ rock
893	CCN symmetric stretch
698	-COO ⁻ bend
571	NH ₃ ⁺ torsion
521	-COO ⁻ rock

position and volatilization of the compound. The next weight loss of about 14.43 % occurs between 310 and 530 °C shows that that the decomposition is almost complete. There is one more weight loss between 530 and 999.8 °C is due to the decomposition of the residue that is left over after the major weight loss, which corresponds to 34.58 %. However, in the DTA trace an endothermic peak which is not much sharp at 258 °C, may be assigned to melting of the sample. The other endotherms or exotherms observed coincides exactly with the decomposition observed in TGA trace. It is concluded that the L-glycine formate crystal is suitable for NLO applications up to 258 °C. Fig. 3 shows the TG/DTA of L-glycine formate.

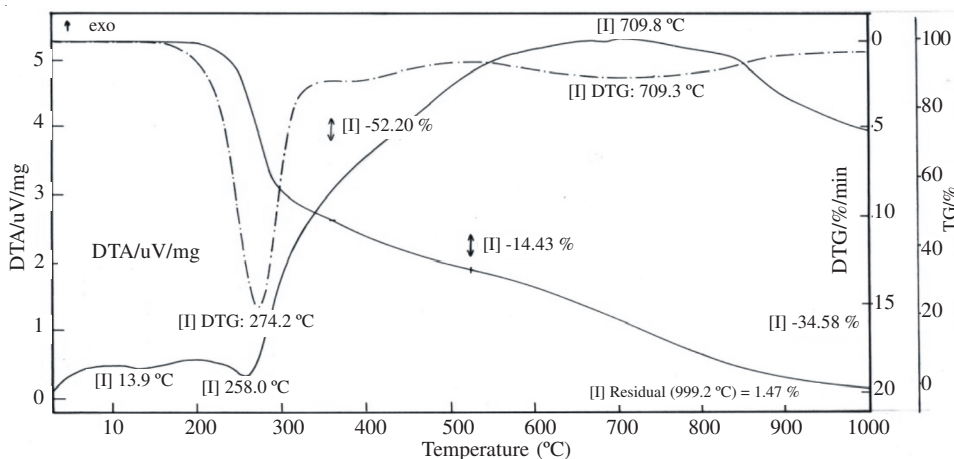


Fig. 3. TG/DTA of L-glycine formate

Optical studies: The UV-vis-NIR transmittance and absorption spectra (Fig. 4) was recorded using Varian Cary 5E UV spectrophotometer in the range 200-500 nm. Optically clear single crystal of thickness 3 mm was used for this study and the crystal is transparent and there is no absorption in the entire region. The lower cut off wavelength is 300 nm. As there is no absorption in the visible and near infrared region it can be used as a potential material for frequency doubling.

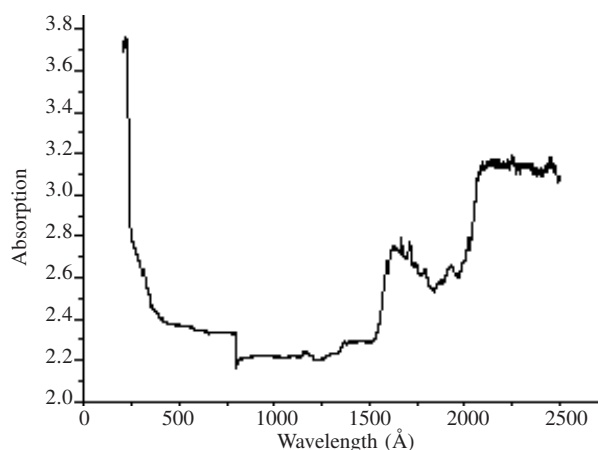


Fig. 4. UV absorption spectra of L-glycine formate

Non-linear optical studies: The NLO property of the crystal was confirmed by Kurtz powder technique. The determination of SHG intensity of the crystals using powder technique was developed by Kurtz and Perry¹³. The crystals are ground to powder and packed between two transparent glass slides. The first harmonic output of 1064 nm from a Nd:YAG laser was made to fall normally on the prepared sample with a pulse width of 8 ns. The second harmonic signal generated in the

crystal was confirmed from the emission of green radiation by the sample. It is found that the SHG efficiency of the crystal is one and a half times higher than that in the case of KDP, which is in agreement with literature^{14,15}.

Conclusion

Colourless and transparent crystals of L-glycine formate has been grown successfully in deionized water by slow evaporation method. Single crystal X-ray diffraction analysis confirms the lattice parameters of LPN crystals which are in accordance with the literature values. The FT-IR spectrum reveals the mode of vibrations of different molecular groups present in L-glycine formate. Optical transmission studies showed that L-glycine formate was optically transparent in the entire visible region with a lower cut-off below 330 nm. Thermal studies reveal that L-glycine formate does not decompose before melting and its suitability for NLO applications up to 258 °C. Its SHG efficiency tested by high intensity Nd:YAG laser as a source is about 0.2 times than that of KDP. Owing to all these properties L-glycine formate crystals could be a promising material for the nonlinear optical applications involving frequency-doubling process.

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