ORIGINAL ARTICLE

Spectroscopic and thermal studies of γ-glycine crystal grown from potassium bromide for optoelectronic applications

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Abstract Single crystals of an organic nonlinear optical material γ-glycine have been synthesized by slow evaporation technique from aqueous solutions of α-glycine and potassium bromide at room temperature. Single crystal X-ray diffraction analysis confirmed the growth of γ phase of glycine. The powder X-ray diffraction of the grown crystal was recorded and indexed. Functional groups present in the sample were identified by FTIR spectral analysis. The optical absorption studies show that the UV cut-off wavelength of γ-glycine is at 238 nm and has a wide transparency window. The thermal characteristics of the grown crystal were determined by thermogravimetric and differential thermal analysis (TG/DTA), which show the thermal stability of the grown crystals. The powder second harmonic generation (SHG) efficiency of γ-glycine crystals was measured by Kurtz and Perry powder technique using Nd:YAG laser and it was found to be 2.56 times that of potassium dihydrogen phosphate (KDP) crystals.

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1. Introduction

Over the past few decades, the synthesis and characterization of NLO materials for second harmonic generation (SHG) have received consistent attention due to their wide spread applications in optoelectronics and photonics (Chemla, 1987; Bosshard et al., 2000). The family of amino acid crystals has over the years been subjected to extensive investigation by several researchers for their NLO properties (Suresh Kumar et al., 2006; Sankar et al., 2007; Shivasankar et al., 2008; Deva et al., 2008; Ali Ahamed et al., 2010). Glycine (NH_2CH_2COOH:

amino acetic acid), the simplest amino acid, has no centre of chirality and is optically inactive. It has three distinct polymorphic forms: α-, β- and γ-forms at ambient environment (Litika, 1961). Very recently, three additional polymorphic forms: δ-, ε- and β^1-forms have been discovered under high pressure conditions (Dawson et al., 2005; Boldyreva, 2007). The two polymorphic forms α- and β-crystallizes in centrosymmetric space group $P2_1/c$ while the γ-glycine crystallizes in noncentrosymmetric space group $P3_1$, making it a potential candidate for piezoelectric and NLO applications (Srinivasan and Arumugam, 2007; Moolya et al., 2005).

The presence of carboxylic acid groups in the γ-glycine donates its proton to the amino group to form the structure $CH_3CH–COO^- NH^{3+}$. Thus in the solid state, γ-glycine exists as a dipolar ion in which the carboxyl group is present as a carboxylate ion and the amino group is present as an ammonium ion. Due to this dipolar nature, glycine has a high melting point. Moreover, the presence of chromophores namely amino group and carboxylic group makes the γ-glycine crystal transparent in the UV–vis region. The study on the growth of γ-glycine crystals from aqueous solutions of glycine with (i) sodium chloride, (ii) sodium hydroxide, (iii) sodium fluoride, (iv) sodium nitrate, (v) sodium acetate, (vi) lithium acetate followed by analyzing the effect of these solvents on the various physical characteristics has been reported (Bhat and Dharmaprakash, 2002; Dhanaraj and Rajesh, 2009). In the present study, we report the growth and characterization studies of γ-glycine crystals grown from aqueous solution of α-glycine in the presence of potassium bromide for the first time, since some of the physical properties of the reported γ-glycine crystals are enhanced by this solvent.

2. Experimental procedure

For growing the crystal, analytical grade chemicals of α-glycine and potassium bromide supplied by Merck (India) were mixed in the stoichiometric ratio 1:1 in double deionized water of resistivity 18.2 MΩ cm^{-1}. The super saturated solution was filtered by Whatman filter paper of pore size 11 μm and allowed to evaporate slowly at room temperature over a period of month, which yielded optically good quality crystals up to several millimeters in size. The grown single crystal is shown in Fig. 1.
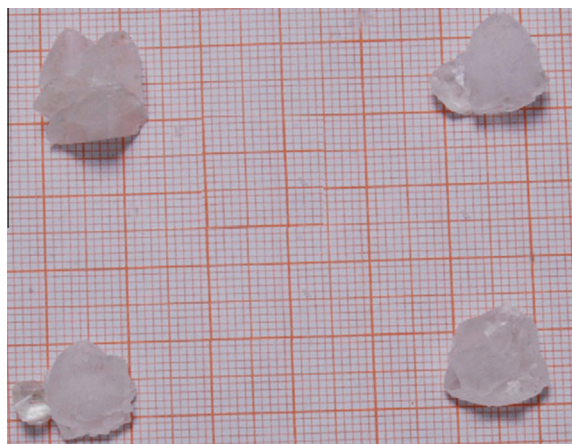

Figure 1   The grown γ-glycine crystal from potassium bromide.

Table 1   Single crystal XRD data of the γ-glycine.

Unit cell dimensions	$a = b = 7.0397$ Å
	$c = 5.4922$ Å
	$α = β = 90°$
	$γ = 120°$
Volume	235.71 Å^3
Crystal structure	Hexagonal
Space group	$P3_1$
Crystal size	$0.42 \times 0.32 \times 0.28$ mm^3
Wavelength	0.71073 Å
Refinement method	Full matrix least square on F^2
Z	3
Density	1.587 mg/m^3

3. Characterization studies

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction data recorded using ENRAF-NONIUS MACH3 X-ray diffractometer with Mo Kα radiation ($λ = 0.71073$ Å) to reveal the crystal structure of the grown crystal. The structure was solved by direct method and refined by the full matrix least square technique using SHELXL program. The determined unit cell parameters are tabulated in Table 1 and these values are in good agreement with the reported values (Anbuchezhiyan et al., 2010).

3.2. Powder X-ray diffraction analysis

A sample in powdered form was subjected to XRD analysis using SIEFERT 3003 TT powder X-ray diffractometer with a characteristic Cu Kα ($λ = 1.540598$ Å) radiation from 10° to 60° at a scan rate of 2°/min. Powder XRD pattern for the grown crystal is shown in Fig. 2. Appearance of sharp and strong peaks confirms the good crystallinity of the grown sample. The observed values are in good agreement with the data available in JCPDS Card No: 06-0230. Slight shift in the sharp peak position at 25.3° in lower angle side may be due to doping of KBr in the γ-glycine crystal, which is also confirmed by the
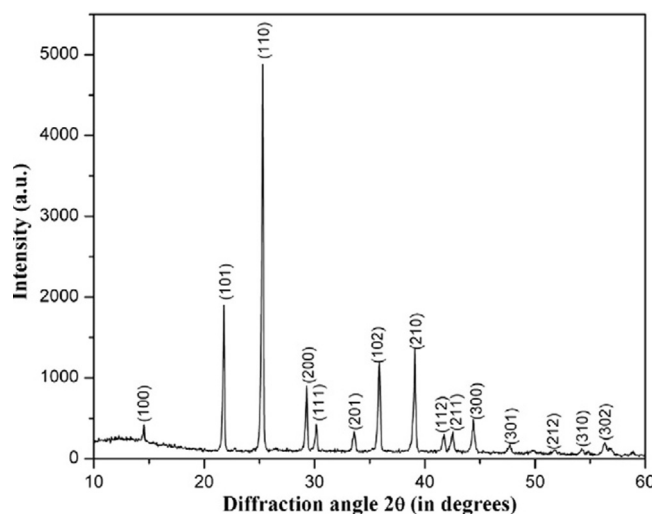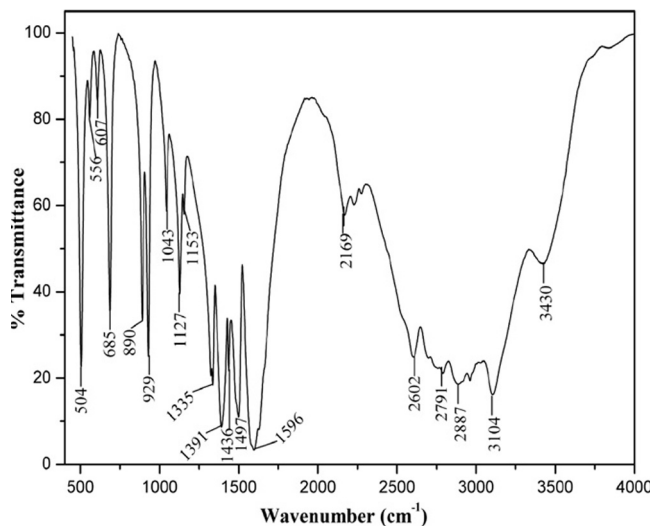

Figure 2   Powder XRD pattern of γ-glycine crystal.

Table 2 Lattice parameters of γ-glycine grown with various solvents.

Sample	Lattice parameters		References
	$a = b$ (Å)	c (Å)	
γ-Glycine	7.024	5.472	JCPDS No. 06-0230
γ-Glycine with H₃PO₃	7.028	5.447	Parimaladevi and Sekar (2010)
γ-Glycine with KBr	7.039	5.492	Present work

Table 3 FTIR spectrum of γ-glycine.

Frequency in wavenumber (cm^{-1})

α-Glycine	γ-Glycine	Assignment of vibrations
504	504	$-COO^-$ rock
607	607	$-COO^-$ wag
694	685	$-COO^-$ bend
893	890	CCN symmetric stretch
910	929	CH_2 rock
1033	1043	CCN asymmetric stretch
1133	1127	NH_3^+ rock
1333	1335	CH_2 twist
1413	1391	COO^- symmetric stretch
1445	1436	CH_2 bend
1507	1497	NH_3^+
1605	1596	Strong asymmetric CO_2 stretching
2122	2169	Combinational bond
2614	2602	NH_3^+ stretching
3175	3104	NH_3^+ stretching

Figure 3 FTIR spectrum of γ-glycine crystal.

Figure 4 Absorption spectrum of γ-glycine crystal.

slight variation observed in lattice parameters of the grown crystal. Table 2 represents the lattice parameters of γ-glycine with various solvents.
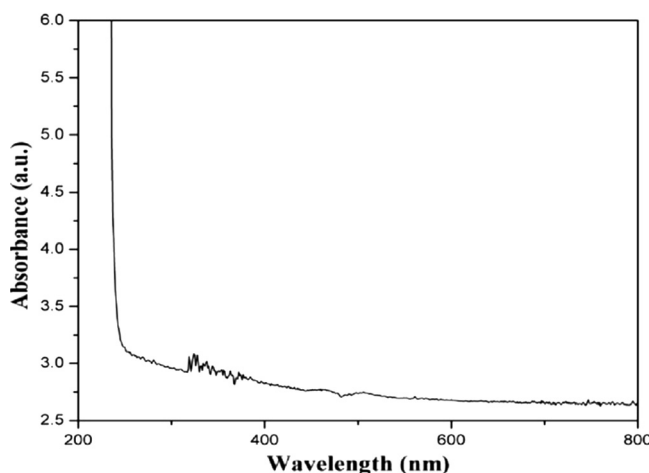
3.3. Vibrational analysis

The FTIR spectrum of γ-glycine was recorded in the range of 4000–450 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique. The resulting spectrum is shown in Fig. 3. The observed frequencies and their assignment of the γ-glycine crystals are given in Table 3.

The transition peaks due to the carboxylate group (COO$^-$) of free glycine is normally observed at 607, 1414 and 1605 cm^{-1}, where as in the case of γ-glycine these peaks were shifted to 607, 1391 and 1596 cm^{-1}. Similarly, the transmission peaks due to the ammonium group (NH$_3^+$) of free glycine were observed in the region 1133, 1507 and 2614 cm^{-1}, but in the present case these are shifted to 1127, 1497 and 2602 cm^{-1}, respectively. This observation is strongly evident that the glycine molecule in crystalline state exists in zwitterionic form in which the carboxylic acid group is present as a carboxylate ion and the amino group is present as ammonium group. The peaks observed at 890 and 1436 cm^{-1} are attributed to CCN and CH$_2$ stretching groups, respectively. The presence of various functional groups of the grown crystal is in very good agreement with those reported in the literature (Dhas and Natarajan, 2007).

3.4. UV–vis–NIR spectral analysis

The optical absorption spectrum of good quality γ-glycine crystal was recorded in the wavelength range of 200–800 nm using Perkin Elmer Lamda 935 UV–vis–NIR spectrometer. The obtained absorption spectrum is shown in Fig. 4 in which the lower cut off region is obtained at 238 nm. The UV spectra shows the presence of a wide transparency window lying between 238 and 800 nm with λ_{max} = 238 nm. From the relation $E_g = 1.243 \times 10^3 / \lambda_{max}$ the forbidden energy gap was estimated and is found to be 5.23 eV, which is the typical value of dielectric materials (Khandpekar and Pati, 2010). Hence, from the analysis of absorption spectrum, it is evident that the grown crystal is transparent in the entire visible region without any absorption peak, which is the key requirement for any nonlinear optical crystal having applications in second harmonic generation, parametric oscillations, etc.

3.5. Thermal analysis

Thermo gravimetric and differential thermal analysis of the grown γ-glycine was carried out from 20 to 800 °C in the nitro-
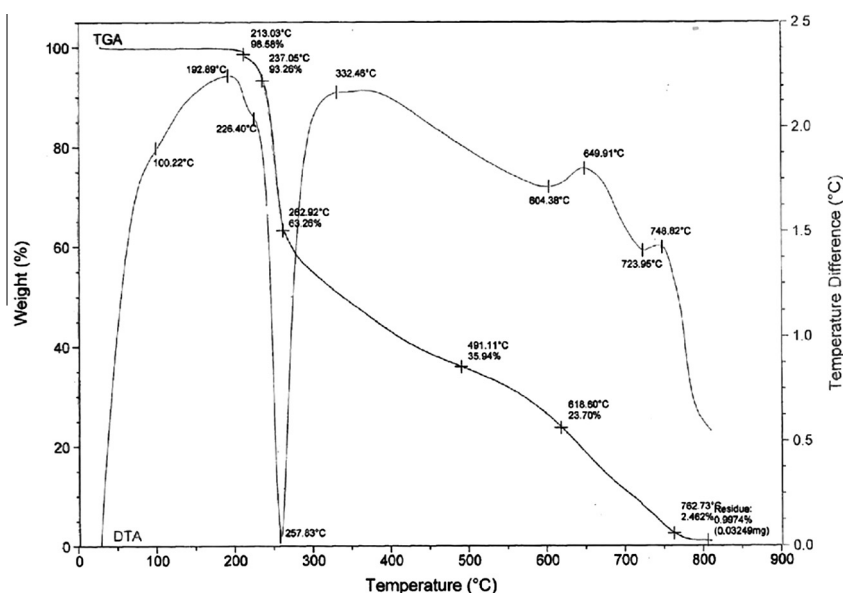
Figure 5   TG/DTA profile.

Table 4   Comparison of SHG efficiency of γ-glycine.

Solvent	SHG efficiency with relative to KDP	Reference
Water and strontium chloride	1.06	Anbuchezhiyan et al. (2010)
Phosphoric acid	1.30	Parimaladevi and Sekar (2010)
Water and NaNO$_3$	1.60	Bhat and Dharmaprakash (2002)
Water and KBr	2.56	Present work

gen atmosphere at a heating rate of 20 °C/min using SDT Q600 thermal analyzer. Crystal weighing about 3.157 mg was used for this study. The obtained profile is shown in Fig. 5. The TGA curve shows no change in weight up to 213.03 °C, which eliminates the possibility of hydrate or solvent formation of the crystal. The major weight loss of 35.32% in TGA curve occurring between 213.03 and 262.92 °C suggests that the sample could be sublimation and decomposition of γ-glycine. From the DTA thermogram, it is observed that an endothermic event begins at 192.89 °C and then a sharp peak appears at 259.65 °C which corresponds to decomposition point of the sample. Thus, in the present work, γ-glycine crystal grown from a mixture of glycine and potassium bromide is structurally stable up to 213.03 °C. Hence, it can be useful for making the NLO devices below its decomposition temperature (Selvaraju et al., 2006; Parimaladevi and Sekar, 2010).

3.6. Nonlinear optical studies

The second harmonic generation efficiency of the powdered material was tested using the Kurtz and Perry method (Kurtz and Perry, 1968). A Q-switched Nd:YAG laser beam of wavelength 1064 nm and 10 ns pulse width with an input rate of 10 Hz was used to test the NLO property of the sample. The grown γ-glycine SHG signal of 64 mV was obtained while the KDP gave an SHG signal of 25 mV for the input beam

energy of 7 mJ/Pulse. Hence, the SHG efficiency of γ-glycine crystal grown in the medium of potassium bromide is 2.56 times higher than that of the KDP crystal. The SHG conversion efficiency of the crystals grown from different solvents is given in Table 4 for comparison. Hence, it is used for applications in nonlinear optical devices.

4. Conclusions

- Transparent single crystals of γ-glycine were successfully synthesized by slow evaporation method from a mixture of aqueous solution of glycine and potassium bromide at ambient temperature.
- The lattice parameters were found by single crystal and powder XRD analysis and they agree well with reported values.
- The presence of various functional groups of γ-glycine was confirmed by vibrational analysis.
- The UV–vis–NIR absorption spectrum shows a wide transparency window between 238 and 800 nm with the energy gap of 5.23 eV, making it a potential candidate for NLO applications.
- The thermal studies revealed that the transition temperature corresponding to phase transition from γ- to α-glycine has improved due to the presence of KBr.

- The relative SHG conversion efficiency of the grown γ-glycine crystals is about 2.56 times higher than that of KDP sample, which indicates the suitability of γ-glycine crystals for application in nonlinear optical devices and optoelectronic devices.

Acknowledgments

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