Crystal growth and characterization of γ-glycine grown from potassium fluoride for photonic applications

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ARTICLE INFO

ABSTRACT

Single crystals of γ-glycine, an organic nonlinear optical material have been synthesized in the presence of potassium fluoride (KF) by slow evaporation technique at ambient temperature. The size of the grown crystal is up to the dimension of 12 mm × 10 mm × 8 mm. The γ-phase was confirmed by single crystal X-ray diffraction, powder XRD and the FTIR analysis. Optical absorption spectrum reveals that the grown crystal has good optical transparency in the entire visible region with an energy band gap of 5.09 eV, which is an essential requirement for a nonlinear optical crystal. Thermal stability of the grown γ-glycine crystal was determined using the thermo gravimetric and differential thermal analyses. The NLO activity of γ-glycine was confirmed by the Kurtz powder technique using Nd:YAG laser and the grown crystal exhibits high relative conversion efficiency when compared to potassium dihydrogen phosphate (KDP).

1. Introduction

Nonlinear optics (NLO) is at the vanguard of current research, because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing and optical interconnections [1,2]. Organic crystals have been shown to have potential applications in nonlinear optics. The second order nonlinear optical materials, a lot of organic compounds with polarized π conjugation systems have been found to have potential to exceed inorganic compounds. The organic nonlinear optical materials have good nonlinear optical susceptibilities but low laser damage threshold value in comparison with inorganic counterparts. Therefore, in order to satisfy the day to day technological requirements, new nonlinear optical materials are mandatory [3,4].

A variety of amino acids like glycine, alanine, arginine, and histidine have been employed to grow crystals with fairly large SHG coefficient [5–8]. Glycine is the basic of all amino acids and it is found to exist in three polymeric crystalline forms namely α-, β- and γ-forms at ambient environment. Recently, three additional polymorphic forms of δ-, ε- and β[1]-forms, have been reported under high pressure conditions [9–11]. The α-form of glycine crystallizes in the monoclinic system with centrosymmetric space group $P2_1/m$, hence it does not exhibit second harmonic generation, whereas β-form crystallizes in noncentrosymmetric crystal structure but it is unstable and the γ-form crystallizes in the trigonal–hexagonal system with non-centrosymmetric space group of $P3_1$ structure. This makes γ-glycine a suitable candidate for piezoelectric, electro optic and non-linear optical applications [12–14]. The zwitterionic form of glycine molecule is capable of forming compounds with anionic, cationic and neutral chemical compounds. Thus, the investigation in the suitable environment in which glycine crystallizes into γ-form gains importance. In this paper, a report is presented for the effect of potassium fluoride on the growth of γ-glycine for the first time, since some of the physical properties of the reported γ-glycine crystals are enhanced by this solvent. The characterization studies such as single crystal XRD, powder X-ray diffraction, Fourier transform infrared (FTIR), UV–vis–NIR spectroscopic analysis, thermogravimetric and differential thermal analysis (TG/DTA) have been carried out.

2. Crystal growth

Single crystals of γ-glycine were grown from a saturated aqueous solution containing AR grade α-glycine (Merck) and potassium

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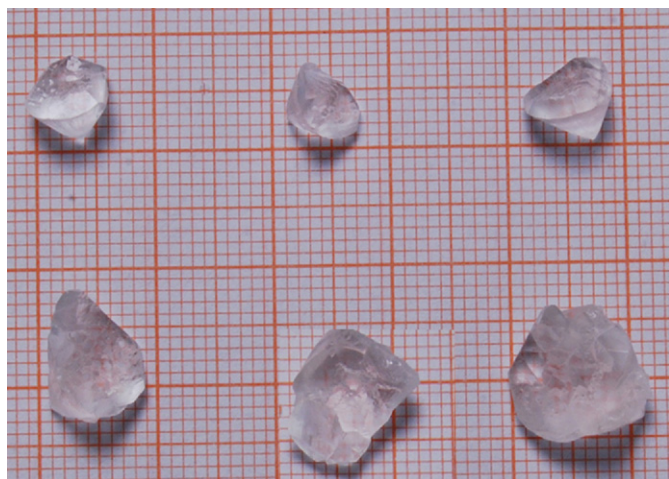E-mail address: drdevaprasadraju@gmail.com (B.D.P. Raju).

Fig. 1. The grown γ-glycine crystal.

fluoride (Merck) in 5:1 ratio respectively. The calculated amount of these materials was dissolved in doubly deionised water of resistivity $18.2\,M\Omega\,cm^{-1}$ at room temperature. The super saturated solution was filtered by Whatman filter paper of pore size $11\,\mu m$ and allowed to evaporate slowly at ambient temperature. Transparent good optical single crystals of γ-glycine were harvested in a growth period of 35 days. The grown single crystals of γ-glycine are shown in Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction study was carried out to reveal the crystal structure and for confirming the grown crystal as a single crystal using ENRAF-NONIUS MACH3 diffractometer with Mo Kα radiation in the wavelength 0.71073 Å. The structure was solved by direct method and refined by the full matrix least square technique using SHELXL-97 program and is given in Table 1. The atom numbering scheme for the grown crystal is shown in Fig. 2. The crystal structure data confirms that the glycine molecule exists in the zwitterions form. Selected bond lengths and angles for titled compound are listed in Table 2. The various hydrogen bond
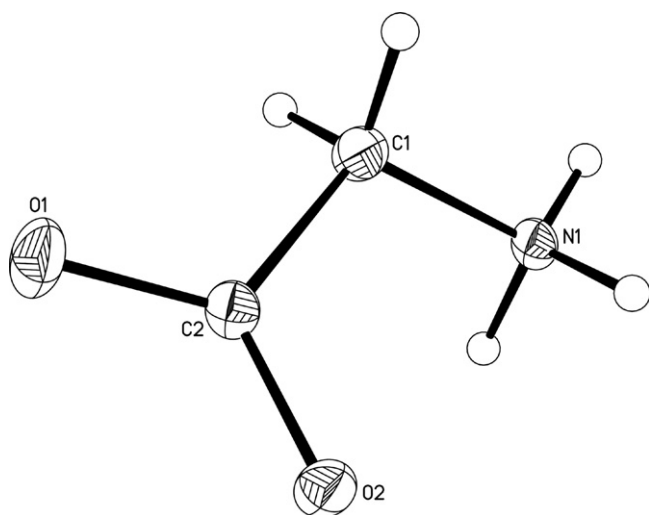
Table 1
Crystal data and structure refinement for the γ-glycine crystal grown from KF.

Empirical formula	$C_2H_5NO_2$	
Formula weight	75.07	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	$P3_1$	
Unit cell dimensions	$a = 7.0397(5)$ Å	$\alpha = 90°$
	$b = 7.0397(5)$ Å	$\beta = 90°$
	$c = 5.4922(4)$ Å	$\gamma = 120°$
Volume	235.71(3) Å^3	
Z	3	
Density (calculated)	1.587 mg/m^3	
Absorption coefficient	0.141 mm^{-1}	
F(0 0 0)	120	
Crystal size	0.42 mm × 0.32 mm × 0.28 mm	
Theta range for data collection	3.34–26.31°	
Index ranges	$-4 \leq h \leq 8, -8 \leq k \leq 7, -6 \leq l \leq 3$	
Reflections collected	523	
Independent reflections	411 [R(int) = 0.0117]	
Completeness to theta = 26.31°	99.7%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9616 and 0.9432	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	411/1/59	
Goodness-of-fit on F^2	1.068	
Final R indices [$I > 2\text{sigma}(I)$]	R1 = 0.0300, wR2 = 0.0766	
R indices (all data)	R1 = 0.0307, wR2 = 0.0780	
Absolute structure parameter	−1(2)	
Extinction coefficient	1.20(9)	
Largest diff. peak and hole	0.150 and −0.164 e Å^{-3}	

parameters are summarized in Table 3. It is confirmed from this study that γ-glycine crystallizes in hexagonal structure with space group $P3_1$. The determined unit cell parameters are in good agreement with the reported values [15,16]. Further, it is evident that the potassium fluoride is not incorporated into the lattice of the grown crystal, but its presence in the aqueous solution yielded the γ-glycine [17].

3.2. Powder X-ray diffraction analysis

The purified samples of the grown crystals have been crushed to a uniform fine powder and subjected to SEIFERT 3003 TT pow-

Fig. 2. Atom numbering scheme for the γ-glycine crystal grown from KF.

Table 2
Bond lengths [Å] and angles [°] for the γ-glycine crystal grown from KF.

C(1)–N(1)	1.471(3)
C(1)–C(2)	1.526(3)
C(1)–H(1D)	0.9700
C(1)–H(1E)	0.9700
C(2)–O(1)	1.244(3)
C(2)–O(2)	1.258(2)
N(1)–H(1A)	1.00(3)
N(1)–H(1B)	0.90(4)
N(1)–H(1C)	0.92(3)
N(1)–C(1)–C(2)	111.83(19)
N(1)–C(1)–H(1D)	109.2
C(2)–C(1)–H(1D)	109.2
N(1)–C(1)–H(1E)	109.2
C(2)–C(1)–H(1E)	109.2
H(1D)–C(1)–H(1E)	107.9
O(1)–C(2)–O(2)	125.7(2)
O(1)–C(2)–C(1)	116.84(17)
O(2)–C(2)–C(1)	117.46(18)
C(1)–N(1)–H(1A)	106.0(15)
C(1)–N(1)–H(1B)	109.5(15)
H(1A)–N(1)–H(1B)	109(2)
C(1)–N(1)–H(1C)	113.6(19)
H(1A)–N(1)–H(1C)	109(2)
H(1B)–N(1)–H(1C)	110(3)

Symmetry transformations used to generate equivalent atoms.

Table 3
Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for the γ-glycine crystal grown from KF.

	x	y	z	U(eq)
H(1D)	9264	4731	3262	32
H(1E)	11 726	5334	3451	32
H(1A)	8150(50)	1080(40)	3050(50)	32(7)
H(1B)	9770(50)	2380(40)	960(70)	29(7)
H(1C)	10 590(50)	1610(50)	3030(60)	41(9)
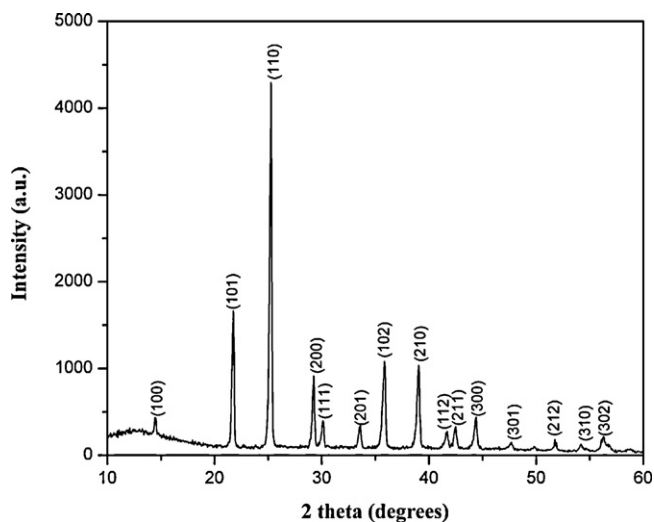
Fig. 3. Powder XRD pattern.

der X-ray diffractometer with Cu Kα ($\lambda = 1.540598\,\text{Å}$) radiation for structural analysis of the crystal. The sample was scanned over the range 10–60° at the rate of 2°/min. The indexed diffraction pattern is shown in Fig. 3. The observed peaks were found to be in good agreement with the data available in JCPDS file no: 06-0230.

3.3. FTIR analysis

The grown crystals were subjected to FTIR analysis to analyze the presence of functional groups quantitatively. The spectrum was recorded in the range 450–4000 cm^{-1} employing Perking–Elmer spectrometer by KBr Pellet method, resulting spectrum is shown in Fig. 4. The observed frequencies and their assignment of the γ-glycine crystals are given in Table 4. The peaks observed at 504, 608 and 686 cm^{-1} are attributed to carboxylic groups while the
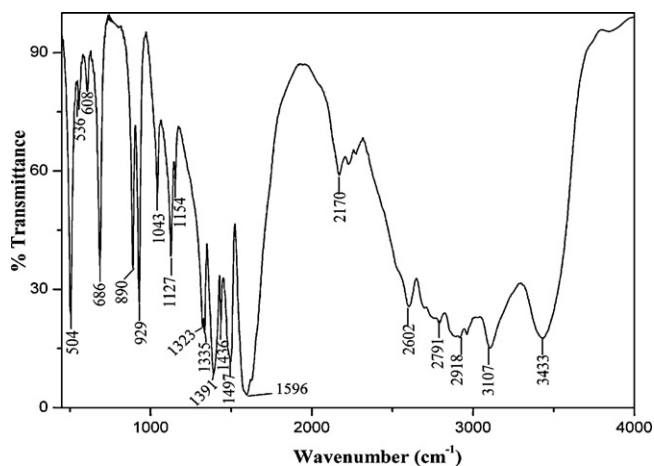
Fig. 4. FTIR spectrum.

Table 4
Frequencies of the fundamental vibrations of the γ-glycine crystal.

Frequency in wavenumber (cm^{-1})		
α-Glycine	γ-Glycine	Assignment of vibrations
504	504	–COO$^-$ rock
607	608	–COO$^-$ wag
694	686	–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	2170	Combinational bond
2614	2602	NH$_3^+$ stretching
3175	3107	NH$_3^+$ stretching
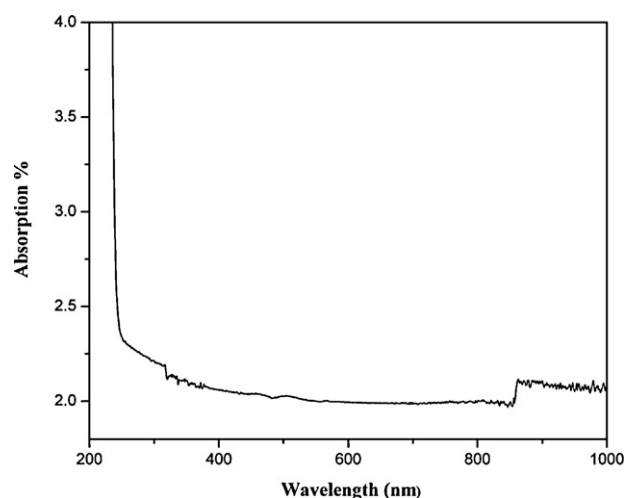
Fig. 5. Optical absorption spectrum.

peak observed at 1497 cm^{-1} correspond to NH$_3^+$ group. Frequencies observed at 1043 and 890 cm^{-1} are attributed as C–N stretching and C–C stretching. The absorption peaks observed at 1596 and 1391 cm^{-1} respond to asymmetric and symmetric stretch modes respectively for the COO$^-$ group. The NH$_3^+$ stretching vibration reveals at 2602 and 2170 cm^{-1}. The other peaks around 1335 and 1043 cm^{-1} have been attributed to CH$_2$ wagging and CN$^+$ stretching. The band appears at 3105 cm^{-1} attributed to N–H stretching for γ-glycine, while the N–H stretching for α-glycine is at 3164 cm^{-1} and for β-glycine is at 3191 cm^{-1} has been reported in literature [18,19]. In the present investigation, the N–H stretching is observed

Table 5
Comparison of SHG efficiency of the γ-glycine crystal.

Solvent	SHG efficiency with relative to KDP
Phosphoric acid[a]	1.3
Water and NH$_4$NO$_3$[b]	1.5
Water and NaCl/KCl[c]	1.5
Water and NaF[d]	1.3
Water and KF[e]	3.0

[a] Ref. [17].
[b] Ref. [23].
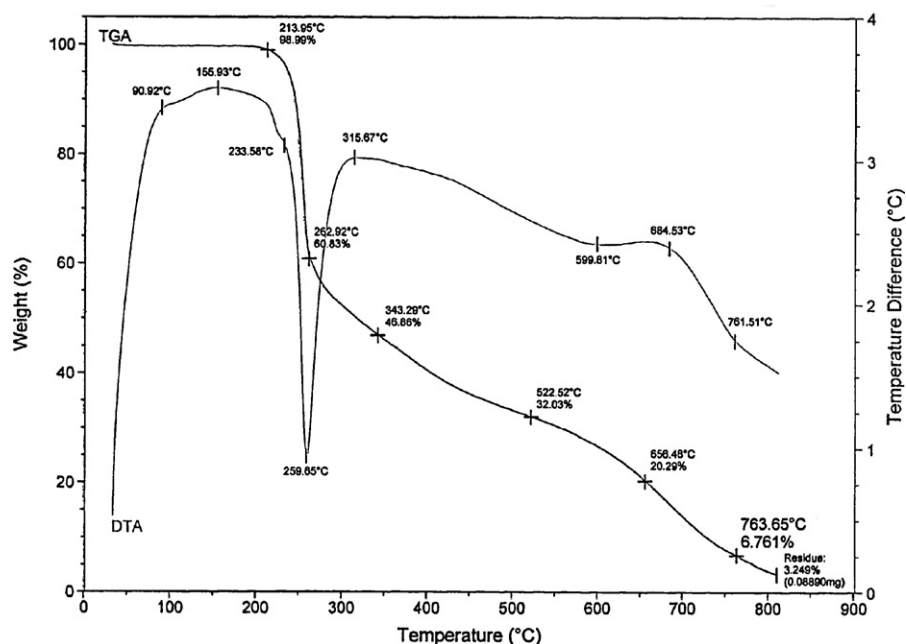[c] Ref. [24].
[d] Ref. [25].
[e] Present work.

Fig. 6. TG/DTA profile of the γ-glycine crystal.

at 3107 cm^{-1} which confirms the γ-phase of glycine. It shows that, the glycine molecule in crystalline state exists as a dipolar ion in which the carboxylic group is present as a carboxylate ion and amino group is present as an ammonium group.

3.4. Optical absorption spectrum

For studying optical transparency of the grown γ-glycine single crystals in the UV–vis–NIR, an optical absorption spectrum was recorded in the wavelength range 200–1000 nm using Perkin–Elmer Lamda 935 UV–vis–NIR spectrometer. The obtained absorption spectrum is shown in Fig. 5. The UV spectra show the presence of a wide transparency window lying between 244 nm and 1000 nm with λ_{max} = 244 nm. The forbidden energy gap was estimated from the relation $E_g = 1.243 \times 10^3/\lambda_{max}$ and is found to be 5.09 eV, which is typical of dielectric materials [20]. Hence, from the analysis of absorption spectrum the crystal is transparent in the entire visible region without any absorption peak, which is the key requirement for the materials having NLO properties. Therefore, the title compound can be used as a good nonlinear optical material.

3.5. Thermal analysis

The grown γ-glycine crystals were subjected to TG and DTA analysis in the temperature range 20–800 °C at a heating rate of 20 °C/min in the nitrogen atmosphere using SDT Q600 thermal analyzer. Crystal weighing about 3.15 mg was used for this study. The obtained trace is shown in Fig. 6. Thermogravimetric analysis shows that γ-glycine is stable up to 213.95 °C and the weight loss starts above this temperature. It is observed from the DTA thermogram that an endothermic event begins at 155.93 °C and then a sharp peak appears at 259.65 °C corresponding to decomposition point of the sample.

The weight percentage of about 98.99% observed at 213.95 °C may attribute to the loss of lattice water. The resulting residue gives a weight loss for a wide range of temperature between 213.95 °C and 763.65 °C. The weight loss corresponds to 3.422% and 0.088 mg

of residue remains. Hence, it can be useful for making the NLO devices below its decomposition temperature [21].

3.6. Nonlinear optical studies

The second harmonic generation behaviour of the grown crystal was determined by Kurtz powder technique [22]. The sample was grounded into the fine powder and tightly packed in a micro capillary tube. It was mounted in the path of Nd:YAG (λ = 1064 nm) laser beam of energy 7 mJ/pulse with a pulse width of 10 ns. The emission of green radiation confirmed the second harmonic efficiency of the grown crystal. It was observed that, the output voltage was 75 mV of the γ-glycine crystal, but in the case of standard inorganic potassium dihydrogen phosphate crystal was 25 mV. Hence, the SHG efficiency of γ-glycine crystal grown in the medium of potassium fluoride is 3 times higher than that of the KDP crystal. The SHG conversion efficiency of the crystals grown from different solvents is given in Table 5 for comparison. The good second harmonic generation efficiency indicates that the γ-glycine crystals can be used for applications in nonlinear optical devices.

4. Conclusions

Optically transparent γ-glycine single crystals have been grown by slow solvent evaporation method. The growth experiments suggest that, the presence of potassium fluoride in the solution during the growth does not affect cell parameters of the grown crystal. The lattice parameters are found by single crystal and powder XRD analysis, they agree well with reported values. The presence of functional groups of the γ-glycine has been confirmed by vibrational analysis. The UV–vis–NIR absorption spectrum shows that the cut-off wavelength lying at 244 nm with energy gap of 5.09 eV and a wide transparency window between 244 and 1000 nm, making it a suitable candidate for NLO applications. The thermal studies reveal that γ-glycine is stable up to 213 °C without decomposition. The SHG efficiency of the grown γ-glycine crystals is about 3 times than that of standard inorganic KDP sample. Owing to its

wide transparency range, high thermal stability with relatively high SHG efficiency, γ-glycine grown in the presence of KF, becomes a potential material for laser application and fabrication of electro optic devices.

Acknowledgement

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