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Enhancement of Optical and Thermal Properties of γ - Glycine Single Crystal: in the Presence of 2-Aminopyridine Potassium Chloride

R. Srineevasan^{1,a}, D. Sivavishnu¹, K. Arunadevi¹, R. Tamilselvi¹, J. Johnson¹, S. M. Ravi Kumar¹

1 – P. G & Research Department of Physics, Government Arts College, Tiruvannamalai, 606603, India

a – rsrinee61@gmail.com



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ABSTRACT. In this research paper, an overview of polymorph γ -form glycine single crystal crystallization in the presence of 2-aminopyridine potassium chloride as an additive at an ambient temperature by slow evaporation solution growth technique (SEST) has been presented. FTIR and NMR studies confirm the presence of functional groups in the grown crystal. In the UV–Visible NIR optical absorption spectral studies from 200 nm to 900 nm, the observed 0% absorption with lower cutoff wave length at 240 nm and high band gap (5.5 eV) enabled enhanced linear optical properties. Powder XRD study confirms crystalline nature of the grown γ -glycine crystal. The single crystal XRD study shows that the grown crystal possesses hexagonal structure and belongs to space group $P3_1$ with the cell parameters $a=7.09 \text{ \AA}$; $b=7.09$; $c=5.52 \text{ \AA}$; $\alpha = \beta = 90^\circ$; and $\gamma = 120^\circ$. Thermal studies have been carried out to identify the elevated thermal stability and decomposition temperature of the grown sample. Dielectric studies of as grown γ -glycine crystal exhibit low dielectric constant at higher frequencies, which is most essential parameters for nonlinear optical applications. Enhanced SHG efficiency of the grown crystal was confirmed by the Kurtz powder technique using Nd:YAG laser and found 1.6 times greater than that of inorganic standard potassium dihydrogen phosphate.

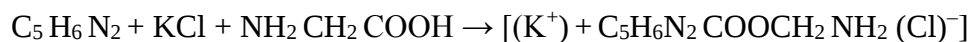
1. Introduction. Highly polarizable conjugated system of organic molecule possesses non-centro symmetry structure and the inorganic molecule (anion), linking through hydrogen bond with organic molecule (cation) yields strong mechanical and high thermal stability [1, 2]. Molecular charge transfer induced in semiorganic complex by delocalized π electron, such that moving between electron donor and electron acceptor which are in opposite sides of the molecules [3, 4]. In the base acid interaction of organic and inorganic molecules, there is a high polarizable cation derived from aromatic nitro systems, linked to the polarizable anion of inorganic molecules through hydrogen bond network yields a noncentrosymmetric structural systems and this hydrogen bonding energy between organic and inorganic molecules made the dipole moment in parallel fashion ensures the increase of second harmonic generation activity [5]. The structures of 2-aminopyridine complexes have already been studied by Chao and his co-workers [6]. In recent years metal organic complexes have been played reasonable attention in advancement of technology [2,7]. Growth of 2-aminopyridine complex crystals is widely used in the rapid advancement in technology, such as ultra-fast phenomena, optical communication and optical storage devices, frequency doublers and optical modulators [8]. Optical properties of 2-aminopyridine complexes and their suitability for optoelectronic devices have been reported [9-14]. Metal organic nonlinear optical crystals possess good second harmonic generation efficiency, hence rich demand in optical storage devices, color display units and optical communication systems [7]. Recent research focus is on designing of new materials capable of attaining SHG processes by strong interaction with an oscillating field of light. Amino acids with ionic salt complex crystals have been investigated and recognized as materials having good nonlinear optical properties [1,3,15-17]. In this present work, synthesis and crystallization of glycine into γ -form glycine in the presence of aqueous solution 2-aminopyridine potassium chloride and their suitability for device fabrication with various enhanced optical and thermal properties are reported.

2. Experimental Procedure

2. 1 Material synthesis

The title compound was synthesized by taking analytical grade glycine, 2-aminopyridine and potassium chloride in the stoichiometric ratio (1:1:1) with Millipore water of resistivity 18. 2 mega-ohm. cm⁻¹ as a solvent.

In this synthesis, protonation of nitrogen in pyridine ring facilitates hydrogen bonding interaction between potassium chloride and glycine such that 2-aminopyridine is linked to the metal K⁺ ion through pyridine ring nitrogen, rather than amino group nitrogen leaving (Cl)⁻ ion [18].



Amino group hydrogen in 2-aminopyridine coordinates through hydrogen bond with carboxylic groups of monoprotonated glycinium ion. Stacking of γ - glycine crystal one over the other is shown in figure 1.

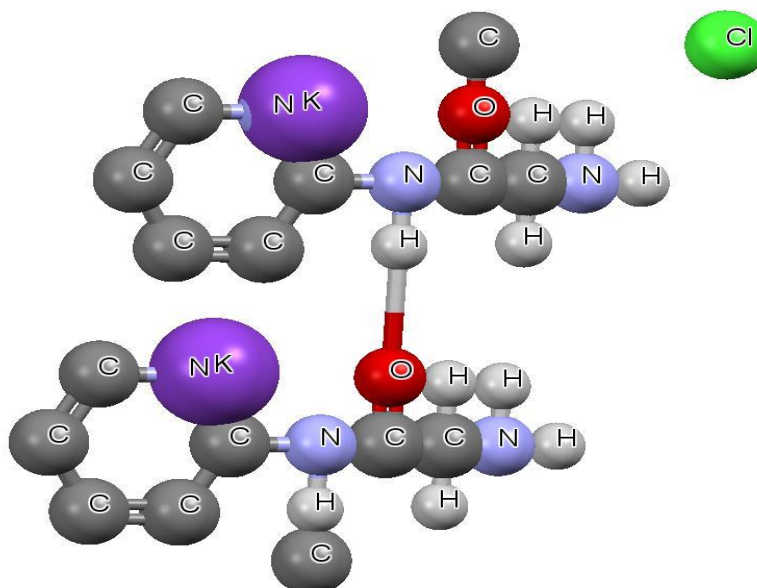


Fig. 1. Scheme of as grown γ -glycine crystal.

2. 2 Solubility study of γ -glycine in the presence of 2-aminopyridine potassium chloride

Solubility is an important parameter, which dictates the crystal growth process. The solubilities of the title compound in aqueous medium were estimated in the temperature range between 25 and 50°C. Neither a flat nor a steep solubility curve and less viscous solution enabling the faster transfer of the growth units by diffusion of the title compound, enables the growth of bulk crystals from solution. Variations in solubility at different temperatures is plotted in figure 2. The moderate variations in solubility indicate the reasonable growth rate of title compound along all crystallographic directions.

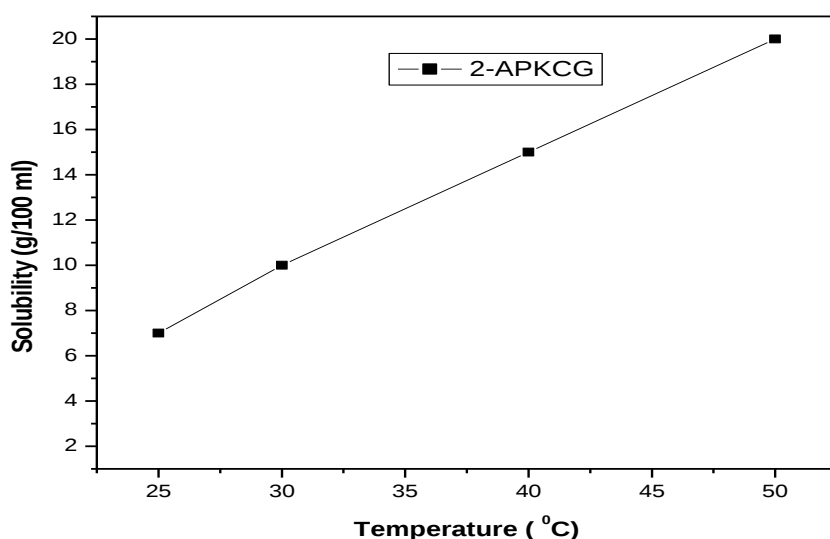


Fig. 2. Solubility curve of title compound at different temperatures.

2.3 Crystal Growth

The prepared mother solution was stirred vigorously for 4h using magnetic stirrer. High degree of purification of synthesized salt was achieved by successive recrystallization process. Synthesized saturated solution was filtered using filter paper of micron pore size. The filtered solution was poured in different petri dishes and covered with porous paper for slow evaporation. After a time span of 15 days, quality crystals of average size 13mm x 12mm x 3mm were harvested. The as grown crystal is shown in figure 3.



Fig. 3. As- grown γ -glycine crystal.

3. Results and discussion

The as grown γ -glycine crystal was subjected to FTIR analysis using PERKIN ELMER SPECTRUM RX1 Fourier Transform infrared spectrometer. ^1H NMR and ^{13}C NMR spectroscopic studies were done by a Bruker Advance III 500MHz FTNMR spectrometer using D_2O as solvent to identify the functional groups. The transmission behavior was studied by using LAMBDA-35 UV-VIS Spectrophotometer. Single crystal and powder XRD analysis were carried out on a PHILIPS X PERT MPD system. TGA and DTA analysis were carried out using NETZSCA STA 409 instrument at a heating rate of $20^\circ\text{C min}^{-1}$ from ambient to 500°C . Dielectric studies were carried out by using HIOKI 3532 HiTESTER LCR meter. The NLO efficiency of the grown crystal was tested by KURTZ powder technique using Nd: YAG laser of wavelength 1064 nm.

3.1 Fourier Transform Infrared (FTIR) analysis

The as grown γ -glycine crystal was subjected to FTIR analysis by KBr pellet technique in the wavelength between 4000 and 400 cm^{-1} . The recorded absorption spectrum of title compound confirms the presence of various functional groups and their frequency assignments are shown in figure 4. The doublet frequency 928.06 and 888.46 cm^{-1} clearly shows the γ - glycine formation [19]. The vibrational frequencies are assigned with structure as shown in Table 1.

Table 1. Frequency of the vibrations and their assignment of as grown γ -glycine crystal.

Frequency in wave number (cm^{-1})	Assignment of vibration
3105.77	NH_3^+ Stretching
2887, 2604	Aliphatic CH_2 Stretching
2171.48	NH_3^+ Stretching
1586.84	NH_2^+ Bending
1492.95	COO^- Symmetric Stretching
1327.82	CH_2 Twisting
1126.21	NH_2^+ Rocking
1041.67	C-N Stretching
928.06	CH_2 Rocking
888.46	C-C-N Symmetric Stretching
683.10	COO^- Bending
502.87	COO^- Rocking

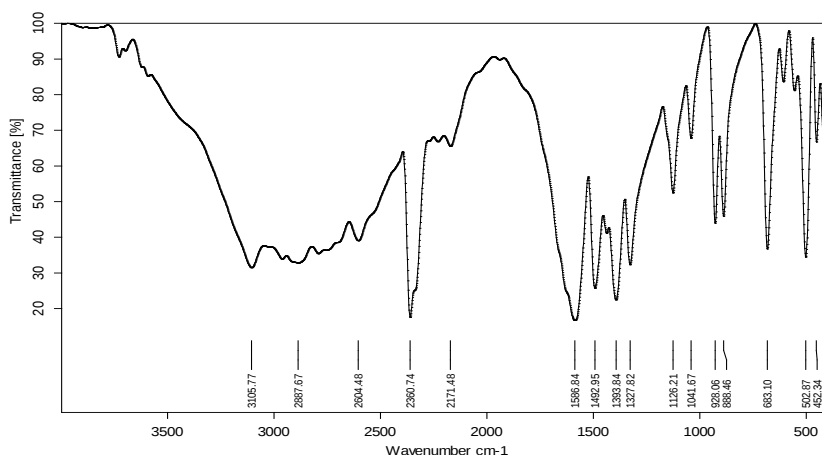


Fig. 4. FTIR spectrum of the grown γ -glycine crystal.

3.2 NMR spectrum

^1H NMR and ^{13}C NMR analysis of the as-grown γ -glycine crystal were shown in figure 5 & 6. ^1H NMR spectrum of as-grown γ -glycine crystal showed multiple peak signals at δ 3.461 to 3.445 ppm (quartet or triplet) corresponds to protons of methylene group (CH_2) and peak at δ 4.678 ppm due to amino group protons (NH_2). ^{13}C NMR spectrum of as-grown γ -glycine crystal showed peaks at δ 41.

429 ppm and δ 172.41 ppm corresponding to methylene carbons and carbonyl carbon respectively. All the above results support the true chemical reactions in the formation of the γ -glycine crystal.

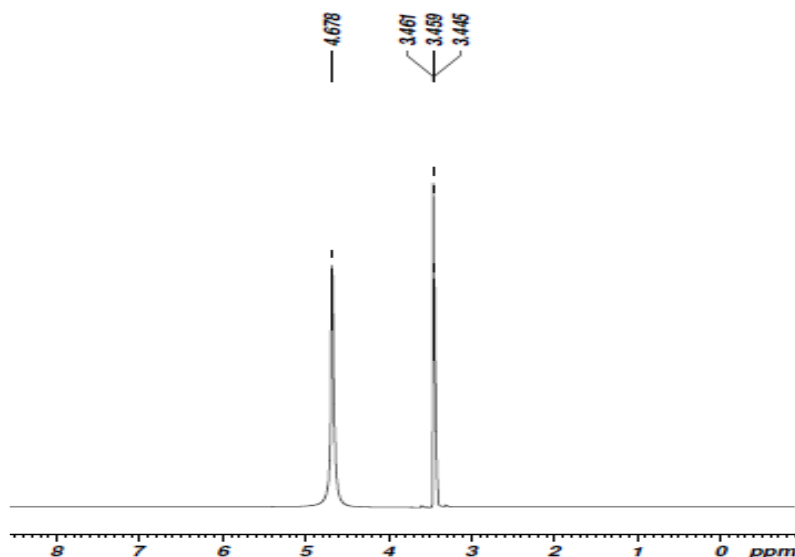


Fig. 5. ^1H NMR of γ -glycine crystal.

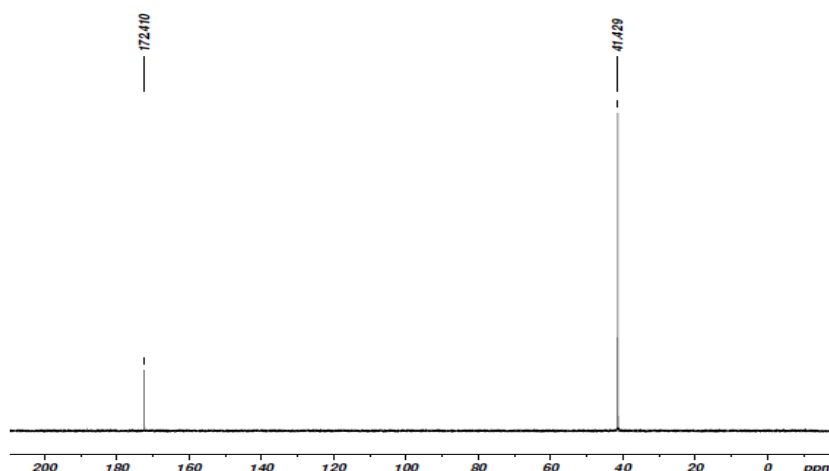


Fig. 6. ^{13}C NMR of γ -glycine crystal.

3.3 UV- Visible spectral analysis

The optical properties of the crystals are mainly depends on the interaction between crystal and components of electric and magnetic fields of the electromagnetic wave. UV-Visible absorption spectrum of the grown crystal recorded in the wave length range 200-900 nm was shown in figure 7. The grown crystal has good transmission (100%) in UV, Visible and IR region. This highest transmission percentage (100%) clearly shows the intrinsic property of amino acid and their defect less nature of the grown γ -glycine crystal [20]. The absorption spectrum shows that the grown crystal has lower cut off wavelength at 240 nm and this characteristic is most favorable for nonlinear optical materials. Lower cut off wavelength value of the γ -glycine crystal (240nm) is compared with Glycine potassium chloride (GPC), Serine sodium chloride (SSC), Bis glycine Maleate, Pure Glycine, Glycine potassium sulphate (GPS), and Glycine picrate as shown in Table 2. This observed decreasing lower cutoff wavelength value of the as grown crystal is due to the addition of 2-aminopyridinium potassium chloride. Hence the lower cut off wave length of as grown crystal can be suitably used for optoelectronic application in the UV, Visible and IR range.

Table 2. Comparison of cutoff wave length.

Crystals Name	Cutoff wave length(nm)
GPC	295
SSC	300
Bis glycine Maleate	330
Pure Glycine	346
GPS	384
Glycine picrate	450
γ- glycine crystal*	240

***present work**

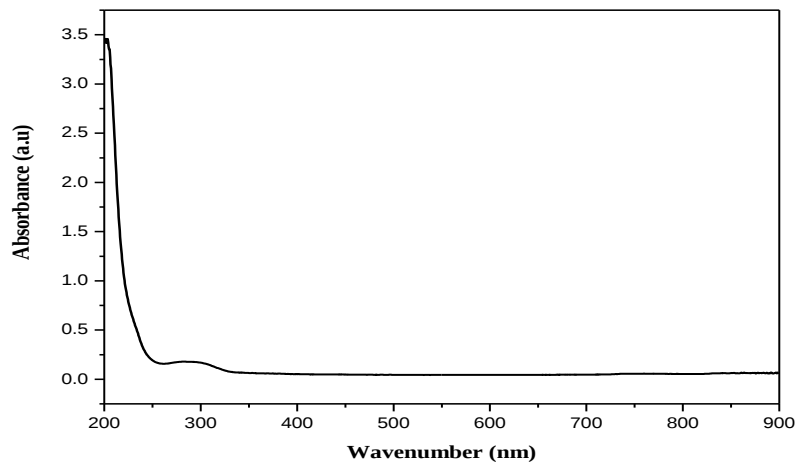


Fig. 7. UV-Visible absorption spectrum of grown crystal of γ -glycine.

Since optical properties of the crystals are governed by the interaction between the crystal and the electric and magnetic fields of the electromagnetic wave, transmittance (T) was used to calculate the absorption coefficient (α) using the formula:

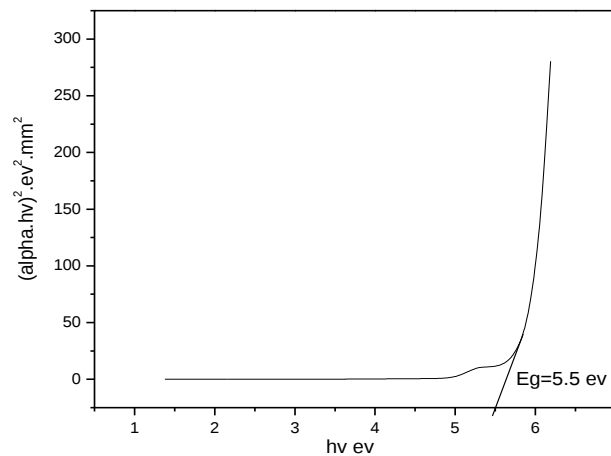


Fig. 8. Plot of $h\nu$ versus $(\alpha h\nu)^2$ of as grown γ -glycine crystal.

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t}$$

Where t is the thickness of the sample. The optical band gap (E_g) was evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by [21].

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

where A – constant,

E_g – the optical band gap, h – the Plank's constant

ν – the frequency of the incident photons.

The graph drawn between $h\nu$ ($E=h\nu$) and $(\alpha h\nu)^2$ is used to estimate the direct band gap value of the grown crystal as shown in figure 3. 5. The band gap of γ -glycine single crystal was estimated by extrapolating the linear portion near the onset of absorption edge to the $E=h\nu$ axis. From the figure 8, the optical band gap value is calculated to be 5.5 eV. The wide band gap of the as grown γ -glycine crystal confirms the 100% transmittance in the UV-vis-NIR region and less defect concentration of the grown crystal [22]. The observed lower cutoff wavelength 240 nm of the as grown γ -glycine due to the addition of 2-aminopyridinium potassium chloride leads to an increase in the band gap of the grown γ -glycine crystal 5.5 eV.

Intrication of electromagnetic wave with high band gap materials (> 1 eV known as Wide-bandgap) create a bound electron-hole pair, which can permit devices to operate at much higher voltage, temperature and frequency applications. Also this high band gap material brings the electronic transition in the range of the energy of visible light as light-emitting diodes even blue LEDs or even produce ultraviolet LEDs with wavelengths down to 200–250 nm and lasers.

3. 4 Powder XRD studies

The grown γ -glycine crystal crushed to a uniform powder and subjected to powder x-ray diffractometer with $\text{CuK}\alpha$ ($\lambda=1.540598 \text{ \AA}$) radiations for structural analysis study. The powder form sample was scanned over the range $10\text{--}45^\circ$ at the rate of $2^\circ/\text{min}$. The indexed powder XRD pattern of grown crystal is shown in figure 9. Peaks in the XRD without any broadening confirm that the grown sample is higher order of crystalline nature.

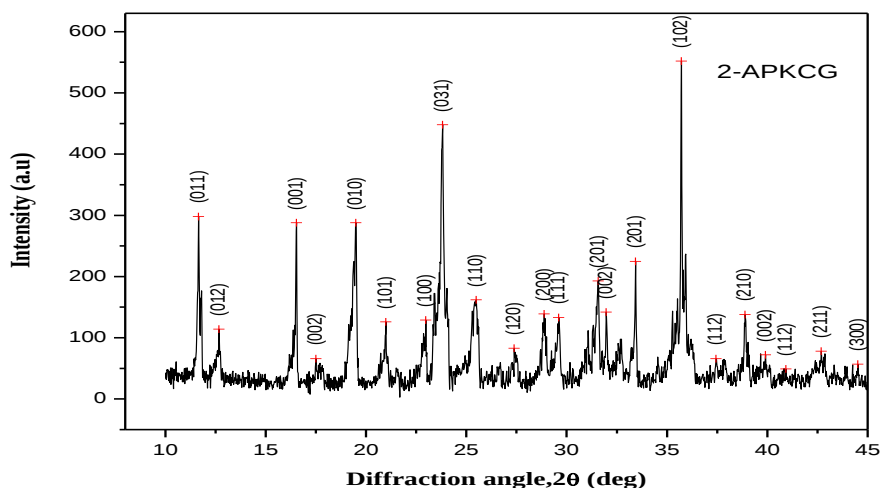


Fig. 9. Powder XRD pattern of as grown crystal γ -glycine.

3. 5 Single crystal XRD analysis

Single crystal X-ray diffraction analysis confirms the hexagonal structure of the γ -glycine crystal with space group $P3_1$. The unit cell parameters of the grown γ -glycine are $a = 7.09\text{\AA}$; $b = 7.09\text{\AA}$; $c = 5.52\text{\AA}$; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$ and volume of the unit cell was found to be $278\text{\AA}^3$. These values are in-line with the literature values [23-25]. Further, it is evident that the presence of 2-aminopyridine potassium chloride in the aqueous solution, without enter into the grown crystal lattice, yields the polymorph form γ -glycine, as a physical change.

3. 6 Thermal analysis

Thermo gravimetric (TG) and Differential thermal analysis (DTA) gives information regarding phase transition, water of crystallization and different stages of decomposition of the crystal. Samples of γ -glycine crystals were weighed in an Al_2O_3 crucible with a microprocessor driven temperature control. TGA and DTA curves of grown crystals were recorded in nitrogen atmosphere between ambient temperature to 500°C shown in figure 10. There is no weight loss up to 216.6°C indicating that there is no inclusion of solvent (water) in the crystal lattice. The thermogram reveals that the major weight loss (42.4%) starts at 216.6°C and continues up to 484.4°C with 1.255mg (57.6%) as residue. The nature of weight loss indicates the decomposition of the material. Below 484.4°C no weight loss was observed.

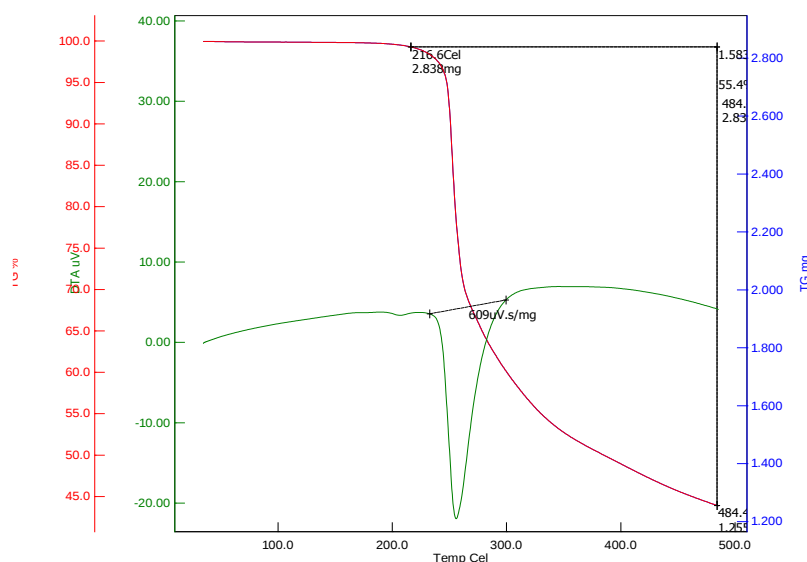


Fig. 10. TGA& DTA graph of as grown γ -glycine crystal.

DTA curve shows that the decomposition point of as grown γ -glycine crystal is 270°C . This decomposition point was compared with the decomposition point of pure γ -glycine crystal (246°C) and γ -glycine synthesizes in the presence of different additives are shown in Table 3.

Table 3. comparison of decomposition point.

γ-glycine crystal	Decomposition point
In the presence of CoCl	116. 86 °C [26]
In the presence of CaCl ₂	265 °C [27]
In the presence of AgNO ₃	208 °C [28]
In the presence of Li NO ₃	195 °C [29]
In the presence of LiBr	200 °C [30]
In the presence of NH ₃	145. 7 °C [31]
In the presence of NaNO ₃	256 °C [32]
In the presence of MgCl ₂	213 °C [33]
In the presence of KCl	170 °C [34]
In the presence of KF	259 °C [25]
In the presence of HF	240 °C [35]
In the presence of H ₃ PO ₃ & In the presence of H ₃ PO ₃ + Urea	51 °C [36] 155 °C [36]
In the presence of C₅H₆N₂+KCl (present work)	270 °C

3. 7 Dielectric studies

Cut and polished samples were used as a dielectric material, which is placed between two copper electrodes of parallel plate capacitor. To ensure the good electrical conductivity to electrodes graphite was coated on opposite side of the sample.

The capacitance of the grown crystal was measured in the frequencies range between 500Hz to 5MHz for different temperatures. The formula used to calculate dielectric constant is,

$$\epsilon_r = Ct/\epsilon_0 A$$

Where C – is the capacitance; t-thickness of the sample;

ϵ_0 – the permittivity of the free space and A-the area of cross section.

The graph shown in fig 8, shows the variation of ϵ_r Vs frequency for the grown γ -glycine crystal at different temperature. The dielectric constant value increases at low frequency region and then dielectric constant value decrease with the increasing frequency. The ϵ_r value reached the least value of about 250 at the applied frequency of 2 KHz and the value remains constant for further frequency. A similar trend was observed for all the recorded temperatures and is compared with previous research report which is shown in table 4. Among the all four polarizations, electronic and space charge polarizations are predominant in the low- frequency region. The characteristic of low dielectric constant at higher frequency evident that the γ -glycine possesses an improved optical quality with lesser defects and this dielectric property is most important for nonlinear optical materials and their applications.

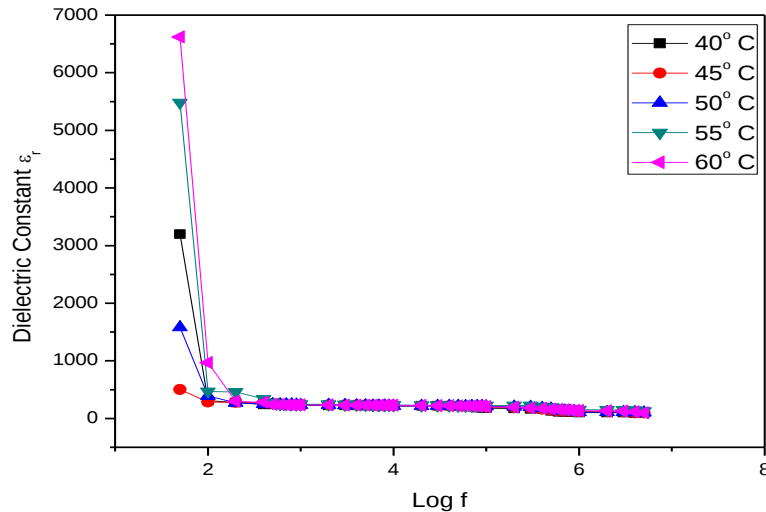


Fig. 11. Dielectric behavior of γ -glycine crystal.

Table 4. Comparison of dielectric constant.

Crystal	Dielectric constant
2APTZS	2.5[37]
2APKSNG	3.5[38]

3. 8 NLO studies

In order to confirm the NLO property, powdered sample of grown crystal was subjected to KURTZ and PERRY powder technique, which is a powerful tool for initial screening of the materials for second harmonic generation (SHG) [39]. The beam of wave length $\lambda = 1064$ nm from Q-switched Nd:YAG laser was made to fall normally on the prepared powdered sample of grown γ -glycine crystal, which was packed between two transparent glass slides. Suitable solution (CuSO_4) was used to absorb the transmitted beam and the optical second harmonic signal was detected by a photomultiplier and displayed on CRO. Here powder form of KDP crystal of identical size to grown γ -glycine crystal powder particles were used as standard in the SHG measurement. The SHG behavior was confirmed from the emission of bright green radiation (532nm) by the sample. The measured amplitude of second harmonic green light for as grown γ -glycine crystal was 14.9mJ as against 8.8mJ of KDP and 8.9mJ of UREA.

The enhanced powder SHG efficiency of as grown γ -glycine crystal is about 1.65 times that of KDP and 1.63 times of UREA. This value is relatively high when compared to the SHG values reported for γ -glycine crystals grown with other additives and comparison is given in Table 5. This enhanced lasing performance of as grown γ -glycine crystal is due to the additive influence of 2-aminopyridinium potassium chloride. The good second harmonic generation efficiency of as grown γ -glycine crystal in the presence of 2-aminopyridine potassium chloride attests, that the grown crystal is a potential candidate for nonlinear optical applications.

Table 5. Comparison of SHG efficiency of γ -glycine crystals.

γ -glycine crystal	# SHG efficiency
In the presence of NaF	1. 3[40]
In the presence of NaOH	1. 4[40]
In the presence of NaCl/KCl	1. 5[41]
In the presence of NaCH ₂ COOH	1. 2[41]
*In the presence of C₅H₆N₂+KCl	1. 65

***Present work, # With reference to KDP**

Summary. We have successfully grown polymorph γ -form of glycine single crystals by slow evaporation solution growth technique at ambient temperature. FTIR & NMR spectral studies confirm that 2-aminopyridine potassium chloride not entered into the crystal structure, but they inhibit the growth of polymorph form γ -glycine. UV –Visible spectral studies show that it has the wide range of transmission from 240nm to 900nm with cut off wave length 240 nm and the observed high transmittance percentage (100%) from 240 nm clearly indicates that the grown crystal possessing good optical transparency for second harmonic generation of Nd:YAG laser and attests the enhancement of optical properties. Powder and single crystal XRD studies reveal that the grown γ -glycine crystal is having higher order of crystallinity. Thermal studies show the sample is thermally stable up to 270°C (elevated temperature) and this makes the grown crystal's suitability for possible application in laser, where the material is required to with stand high temperatures. Dielectric studies of grown crystal confirm the improved optical quality. NLO studies of the grown sample show that the enhanced SHG efficiency is greater than KDP (1. 65 times) and Urea (1. 63 times) crystals. The grown title compound was possessing various enhanced properties such as wide transparency range with 100% transmission, low dielectric constant value at higher frequency and hence improved optical quality with lesser defects and elevated decomposition temperature (270°C) with greater SHG efficiency as that of KDP suggest that the grown γ -glycine crystals in the presence of 2-aminopyridine potassium chloride is a promising materials for optoelectronic applications.

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