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Growth, Structural and Spectral Studies On Acid Mixed Glycine-Nitrate (GPCN) Crystal

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Abstract:

Semi-organic acid mixed glycine nitrate crystal (GPCN) for photonics applications has been synthesized and grown in bulk from an aqueous solution with pH 4.8 at room temperature. Transparent crystals measuring 8 x 6 x 4 mm³ were obtained over a period of 2-3 weeks. The solubility of GPCN in water was determined, and the chemical composition of the crystals was confirmed through CHN and EDAX analysis. The crystals were characterized using powder XRD, FTIR, and UV spectroscopy. The GPCN crystals belong to the orthorhombic system, with cell parameters a = 14.827 Å, b = 13.287 Å, c = 9.954 Å, and a unit cell volume of 1961.30 Å³. The presence of fundamental functional groups was verified and UV studies revealed a wide transparency window with a cutoff wavelength at 216 nm, making it suitable for optoelectronic applications. The second harmonic generation (SHG) efficiency of GPCN was found to be 0.66 times that of KDP when using a 1064 nm Nd:YAG laser, as per the Kurtz and Perry method have been carried out.

Keywords: Crystal growth, XRD, NMR, FTIR, RAMAN, SHG.

1. INTRODUCTION

The field of photonics is driven by the development of new materials that exhibit strong interactions with light beams. Recently, semi-organic compounds have emerged as promising candidates for second harmonic generation (SHG). Amino acid complexes with various ionic salts have been identified as suitable nonlinear optical materials [1,2]. Among these, the basic amino acid alpha glycine has been utilized to synthesize numerous organic and semi-organic materials that demonstrate dielectric, ferroelectric, nonlinear optical, photonic switching, and light sensing properties [3,4]. However, the molecular arrangement in these materials, characterized by large inter-atomic distances, often results in poor thermal and mechanical properties. The incorporation of inorganic elements into the organic matrix has been shown to enhance the mechanical strength of the material, making it more suitable for practical applications.

These hybrid materials are promising for future photonic technologies, including information processing, image processing, frequency conversion, and optical switching. The large NLO coefficients of organic molecules are effectively combined with the mechanical robustness provided by the inorganic component. Various amino acids, such as glycine, L-arginine, and L-histidine, have been employed [5,6]. Glycine, in particular, exists in three polymeric crystalline forms: α, β, and γ, with the alpha form being the simplest. Alpha-glycine has been combined with NaNO3[7], AgNO3[8] and CaNO3[9], to produce intriguing nonlinear optical compounds. In glycine sodium nitrate, the zwitterion form of glycine is retained, and the sodium atom exhibits eight-fold coordination, forming a distorted hexagonal bipyramid. Additionally, glycine molecules link through head-to-tail hydrogen bonds, creating layers of molecules sandwiched between these bonds [10].

In this study, we report on the growth and characterization of amino-potassium-calcium nitrate (GPCN) crystals from solution. The grown crystals have been thoroughly characterized using CHN, EDAX, X-ray diffraction (XRD), FTIR, Raman spectroscopy, UV-Vis spectroscopy and SHG measurements.

2. CRYSTAL GROWTH

GPCN crystals were grown using the slow evaporation technique from an aqueous solution. The crystals were prepared in double-distilled water using AR grade α-glycine, potassium nitrate (KNO_3), and calcium nitrate [$Ca(NO_3)_2$] in a molar ratio of 3:0.5:0.5, along with 0.5% concentrated HCl, starting with a pH of 4.8. Transparent crystals measuring 8 x 6 x 4 mm³ were obtained over three to four weeks at room temperature (Fig. 1). The size of the crystals was found to depend on the amount of material available in the solution, which is determined by the solubility of the material in the solvent. The solubility of the synthesized GPCN was measured in distilled water at four different temperatures using a constant temperature bath (Fig. 2). Solubility was observed to increase with temperature from 300 to 350 K. The density of GPCN crystals, determined using the flotation method, was 1.632 g/cc. The melting point was recorded at 221°C, and the sample decomposed at 232°C [16,17].

$$[NH_2CH_2COOH]_3+[KNO_3]_{1/2} + [\ Ca(NO_3)2]_{1/2} + 0.5\%\ HCl \longrightarrow [K(NO_3)_2]_{1/2}\cdot[NH_2CH_2COOH]_3.\ [CaNO_3]_{1/2}HcCl$$

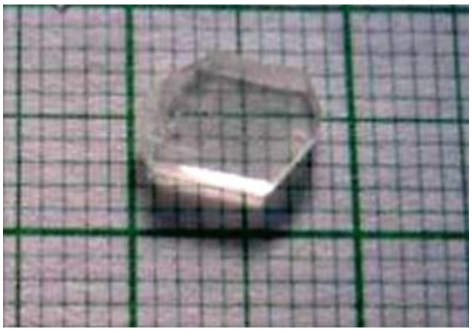

Figure.1 As grown GPCN crystal.

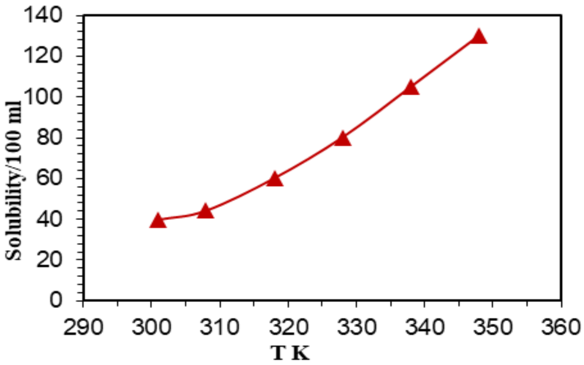

Figure.2 Solubility curve for GPCN crystal

3. CHARACTERIZATION

3.1 CHN and EDAX analysis

The chemical content of the grown GPCN crystals was verified using a THERMO FINIGAN–CHN analyzer (FLASH 1112 SERIES) and an EDAX analyzer attached to a scanning electron microscope (JSM-840). The CHNS analysis confirmed the chemical compositions and units, as shown in Figure 3. The experimental and computed percentages of carbon, hydrogen, nitrogen, and oxygen were found to match well, as detailed in Table 1. The oxygen percentage was determined by considering the total composition to be 100%. Additionally, the presence of potassium and chlorine in the GPCN crystals was confirmed through EDAX analysis. This combination of analytical techniques provided a comprehensive verification of the chemical content and elemental composition of the grown crystals, ensuring the accuracy and consistency of the synthesized material.

Table 1 Elemental analysis of GPCN crystal.

Sample-GPCN	%N	%C	%H	%O	%EDAX Element	Chemical Unit
Peak No.	1	2	3	45.285	K, Ca, Cl	$(KNO_3)_{1/2}\cdot(NH_2CH_2COOH)_3\cdot(Ca(NO_3)_2)_{1/2}\ HCl$
Retention time	0.81	1.23	3.8			
Elements (%)	17.858	30.530	6.328			

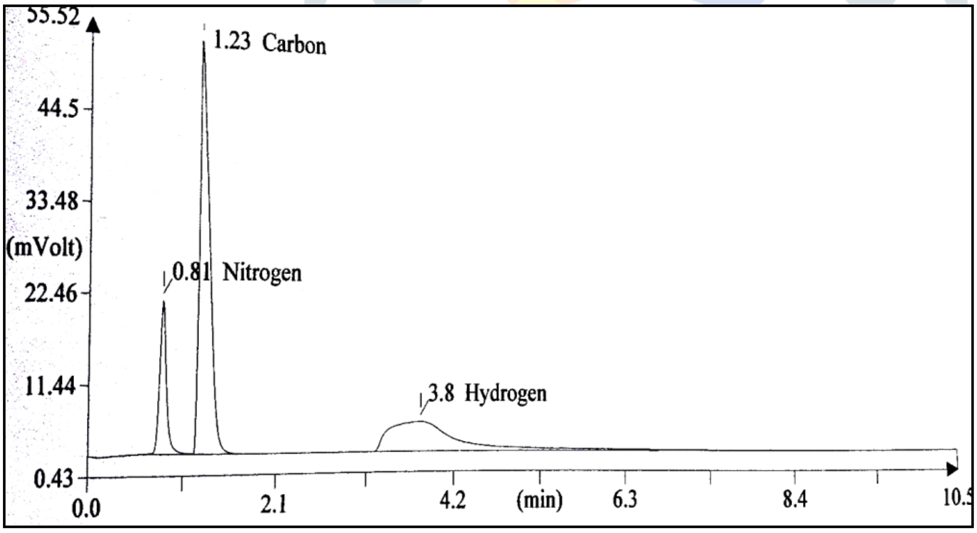

Figure. 3 CHN spectrum for GPCN crystal.

3.2 X-Ray Diffraction

The grown GPCN crystals were subjected to X-ray powder diffraction using the JEOL X-Ray diffractometer system (JDX-8030 Series) with characteristic Cu-Kα radiation (λ = 1.541 Å). The sample was scanned in the range from 10° to 80° at a rate of 5° per minute. The new GPCN crystal was characterized by powder X-ray diffraction to confirm its phase [17]. Analysis of the observed spectra was carried out using POWD-Interactive powder diffraction data interpretation and indexing software program (Version 2.2, Australia). The XRD peaks were indexed, revealing that the grown crystal possesses orthorhombic symmetry. The cell parameters were determined to be a = 14.827 Å, b = 13.287 Å, c = 9.954 Å, with a unit cell volume of 1961.30 Å³. Intense peaks were recorded between 20° and 30°, with the maximum intensity of 12208 observed on the (4 0 2) plane, as depicted in the spectrum (Fig. 4). This detailed analysis confirms the crystalline structure and phase purity of the GPCN crystals, supporting their potential application in photonic technologies.

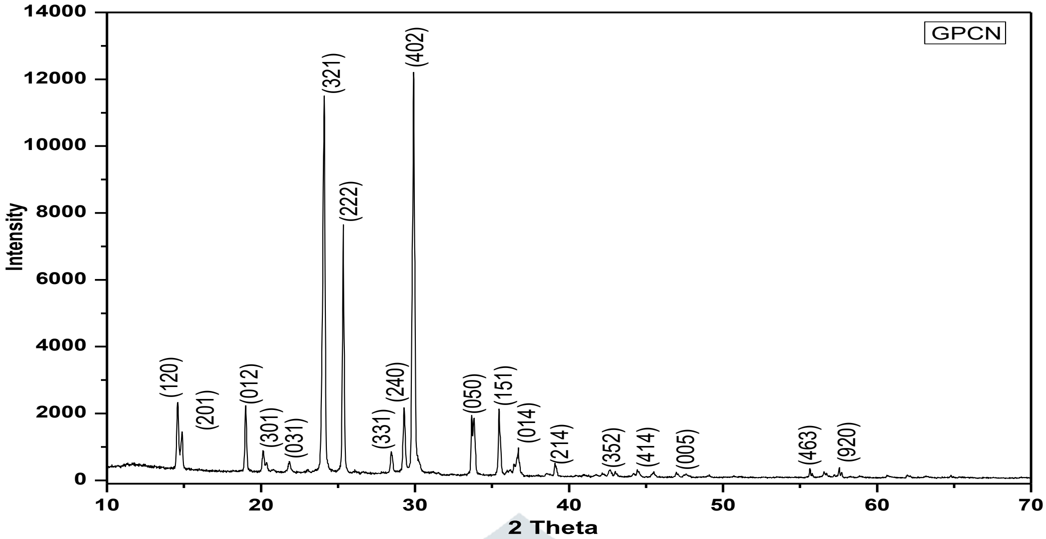

Figure. 4 XRD Spectrum of as grown GPCN Crystal

3.3 NMR studies

The presence of proton and carbon-containing groups in the grown GPCN crystals was confirmed through 1H NMR and 13C NMR analysis. The 1H NMR spectra were recorded using a Mercury Plus Varian instrument operating at a frequency of 300 MHz. The 13C NMR spectra were recorded using a Bruker (AV-500) spectrometer at a frequency of 500 MHz. The comparative assignments of the NMR spectra, which detail the chemical environments of the protons and carbons within the GPCN crystals, are presented in Table 2. This analysis verifies the molecular structure of the grown crystals, confirming the successful incorporation of glycine, potassium nitrate, and calcium nitrate in the GPCN compound. [18]. This NMR analysis confirms the molecular structure of the grown GPCN crystals, validating the successful incorporation of glycine, potassium nitrate, and calcium nitrate into the GPCN compound.

Table 2 ^{1}H NMR and ^{13}C NMR Chemical Shifts for GPCN sample

^{1}H-nmr		^{13}C-nmr	
$\delta(NH_2)$ ppm	$\delta(CH_2)$ ppm	$\delta(COO^-)$ ppm	$\delta(CH_2)$ ppm
4.679	3.470/3.468	172.429	41.397

3.4 FTIR and Raman analysis

The FTIR spectra of sample were recorded in KBr phase in the frequency range from 400 cm^{-1} to 4000 cm^{-1} using the Perkin Elmer infrared spectrometer (1600 series) with a resolution of 4 cm^{-1}and a scanning speed of 2 mm/s [13,14]. Laser Raman Spectra were recorded in solid form using Jobin Yvon Raman spectrometer (HG-2S) with Ar^{+} laser source (λ=5145 A.U) in range 200 cm^{-1}–3500 cm^{-1}. Fig. 5 shows FTIR spectrum of the grown GPCN crystal. The characteristic absorption peaks have been observed in the range 400 cm^{-1}to 3200 cm^{-1}. The active IR peaks were found to lie in the region from 400 cm^{-1} to 1800 cm^{-1}. A broad characterization peak appears between 1600 cm^{-1}and 3100 cm^{-1}. The absorptions due to carboxylate group of free glycine (zwitterion) are observed between 503 cm^{-1}and 686 cm^{-1}.

In the IR spectrum, CH2 stretching is found to occur at 2962.4 cm−1. The amino acid combination band is found at 2170.3 cm^{-1}.The strong NH_3^+ deformation occurs between 1497.2 cm^{-1} and 1577.5 cm^{-1} and NH_3^+ stretching occurs between 2791.4 cm^{-1}and 2887.5 cm^{-1}. The CH_2 stretching is found to be weak in FTIR at 2996.4 cm^{-1}, which have been noted in Raman spectra. The NO_3^- symmetric stretch appears at 1043.2 cm^{-1} and NO_3^- asymmetric stretching frequency is found to lie at 1386.1 cm^{-1}. The Raman profile for the GPCN crystals is shown in Fig. 6. The messing IR peaks have been trace out by Raman spectrum and rocking/wagging/bending, CCN symmetric stretching, CH_2 wagging/ twisting, CH_2 scissor, NH_3^+ deformation, amino acid combination bond, NH_3^+ deformation, CH_2 stretching and NO_3^- symmetric/asymmetric stretching are examining by IR and Raman spectrums with prominent peaks.

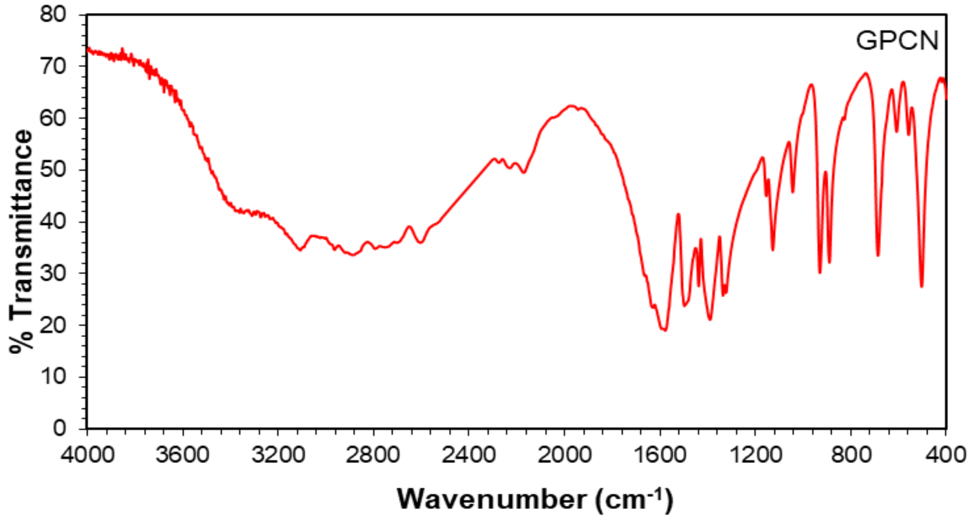

Figure. 5. FTIR spectrum of GPCN crystal.

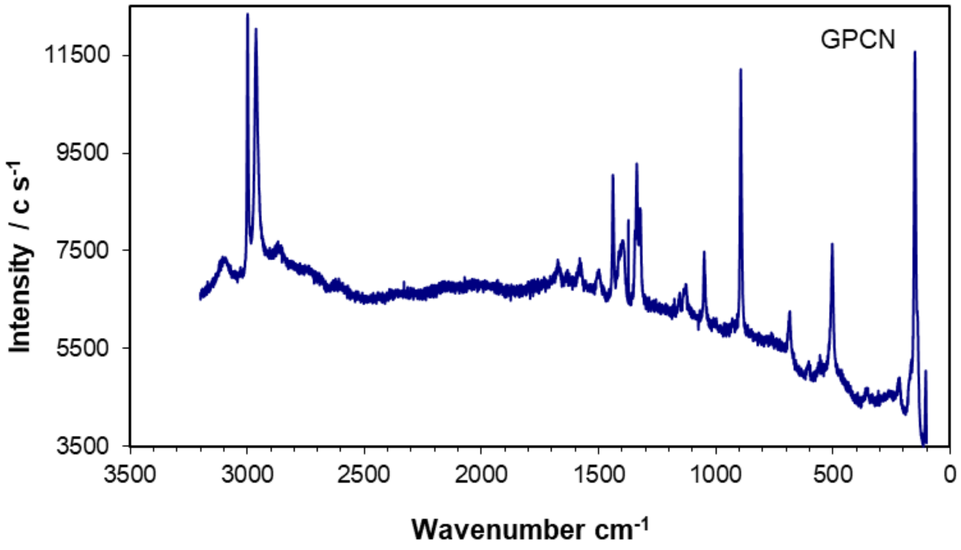

Figure. 6. Raman spectrum of GPCN crystal.

3.5 UV studies

The UV–vis absorption spectrum was recorded using Hitachi system (U-2900) in range 100 nm – 1200 nm covering the entire ultraviolet and near visible region [17]. The UV absorption spectrum for GPCN crystal was recorded in the UV–vis region (Fig.7). The peak at 205-212 nm is due to n–π* transition [19]. The cut off wavelength λ_{max} lies at 216 nm with corresponding energy gap of 5.75 eV. A wide transparent window is present between 250 nm and 1200 nm suggesting its use in optoelectronics devices [5].

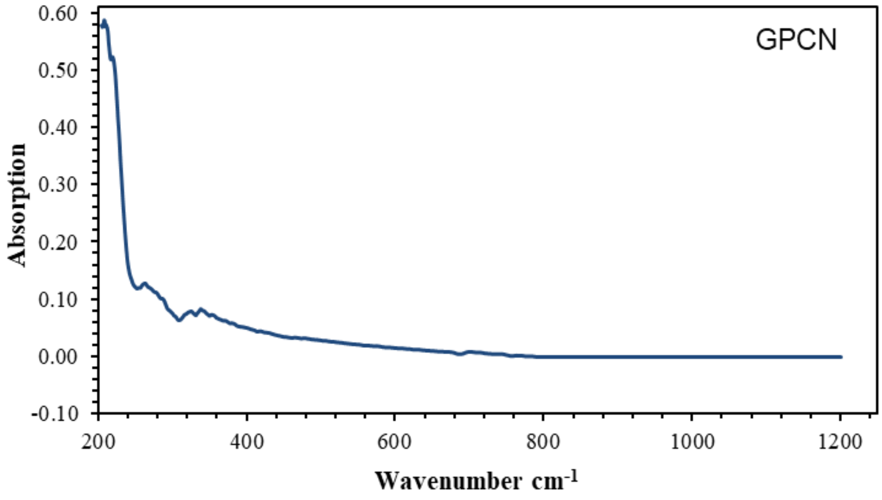

Figure.7. UV–vis-NIR spectrum of GPCN crystal.

3.6 Powder SHG measurement

The nonlinear optical conversion efficiency was tested using a modified Kurtz and Perry setup [20]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm with an input power 2.69 mJ/pulse was used for SHG measurements. The pulse width was maintained at 8 ns at a repetition rate of 100 Hz/pulse. The crystals of GPCN were ground to a uniform particle size of about 125–150 μm and then packed in a capillary of uniform bore and exposed to laser radiation. The second harmonic signal generated in crystalline sample was confirmed from the emission of green radiation (532 nm) from the crystal. The intensity of green light was measured using photo multiplier tube and CRO. The grown GPCN crystals were subjected to second harmonic generation test for NLO property. The crystal were initially ground into fine powder with particle size is about 125–150 μm and densely packed into two transparent slide which was then illuminated by pulsed, Q-switched (Nd:YAG) laser source operating at a wavelength of 1064 nm. The SHG signal generated in the crystalline sample was collected and displayed as green light radiation (λ=532 nm) on a cathode ray oscilloscope. A SHG signal of 123 mV was obtained as compared to 185 mV of that of standard KDP crystal for the identical input energy of 2.69 mJ/pulse. The SHG efficiency however depends upon the method, the conditions during growth, composition used as well as on the size of crystallites exposed during measurements.

4. CONCLUSION

Transparent glycine-potassium-calcium nitrate (GPCN) crystals of size 8 x 6 x 4 mm³, were successfully grown using the slow evaporation method from an aqueous solution with a pH of 4.8 at room temperature. The solubility of GPCN crystals varied linearly within the temperature range of 300K to 350K. Chemical composition analysis through CHN and EDAX confirmed the presence of carbon, hydrogen, nitrogen, oxygen, potassium, calcium and chlorine in the crystals. X-ray diffraction (XRD) analysis determined that the crystals belong to the orthorhombic system, with cell parameters a = 14.827 A. U, b = 13.287 A. U, c = 9.954 A. U, and a unit cell volume of 1961.30 (A.U) ³.

To further investigate the molecular environment and chemical groups, ^{1}H and ^{13}C NMR studies were conducted, revealing two prominent peaks corresponding to NH_2 and CH_2 groups. Comparative FTIR and Raman spectroscopic analyses verified the presence of fundamental groups, with a close match between IR and Raman peaks indicating a molecule lacking a center of symmetry.

Optical studies demonstrated that GPCN crystals possess a wide transparent window in the 350 nm to 1200 nm range, making them suitable for optoelectronic applications. The optical second harmonic generation (SHG) efficiency of GPCN was found to be 0.66 times that of standard potassium dihydrogen phosphate (KDP), as measured by the Kurtz and Perry technique. This leads to grow new material with interesting characteristics in optoelectronic industries.

Overall, the successful growth and comprehensive characterization of GPCN crystals indicate their potential as novel materials with promising properties for the optoelectronic. The combination of good optical transparency and acceptable SHG efficiency, makes GPCN crystal useful for a candidate application in advanced optoelectronic and photonic devices.

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