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Crystal growth, structural, optical, thermal and SHG studies of γ-glycine single crystal grown from ammonium formate

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ABSTRACT

Single crystals of the organic nonlinear optical material γ-glycine have been grown in the presence of ammonium formate by slow evaporation method. The crystal structure is confirmed by X-ray powder diffraction method. CHN analysis shows the non-inclusion of ammonium formate species in the grown γ-glycine single crystals. The UV spectrum shows existence of wide transparency window suitable for optoelectronic applications with bandgap energy of about 5.90 eV. Spectroscopic and DSC studies have been carried out for analyzing the presence of functional groups, thermal stability and phase transition of the grown crystal. Second harmonic generation (SHG) conversion efficiency has been estimated as 150 mV and the output power by the crystal is more than that of potassium dihydrogen phosphate (KDP) crystal.

1. Introduction

Organic nonlinear optical (NLO) crystals have attracted much interest due to their superior properties over inorganic NLO materials, such as good optical response time, non-resonant susceptibility, higher susceptibility, high phase-conjugate reflectivity and the capacity of designing components at the molecular level [1]. Organic nonlinear optical (NLO) materials formed from aminoacids have potential application in second harmonic generation (SHG), optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplifiers, optical image processing, optical bistable devices, optical modulators, optical switches etc. [2]. Glycine, the simplest aminoacid, has three polymeric crystalline forms: α, β and γ. Both α and β forms crystallize in centrosymmetric space group $P2_1/c$, γ-glycine crystallizes in non-centrosymmetric space group $P3_1$ making it a candidate for piezo-electric and NLO applications [3]. The metastable α-glycine grown from aqueous solution transforms in to γ-form spontaneously. The least stable β-form is always obtained from water–alcohol mixed solvent. The β-form transforms rapidly to α- and γ-forms in presence of moisture at room temperature. The more stable γ-glycine crystals are grown from aqueous solution or in the presence of additives or gel method. The single crystals of γ-glycine in the presence of small amount of sodium nitrate [4], lithium nitrate [5], strontium chloride [6], potassium fluoride [7], potassium chloride [8], potassium bromide [9], phosphoric acid [10], ammonium acetate [11], ammonium nitrate [12], sodium acetate [13], hydrofluoric acid [14], ammonium chloride [21] and lithium acetate [15] are reported as good NLO material. In this manuscript, we are reporting the effect of growing γ-glycine single crystals from aqueous solution in the presence of a small amount of ammonium formate for the first time.

2. Experimental

2.1. Chemicals used

Glycine (aminoacetic acid) SD-fine, AR (99.5%), ammonium formate SD-fine, AR (99.5%) and double distilled water were used in the experiment.

2.2. Crystal growth

Gamma glycine was prepared at ambient temperature by dissolving 1 mol of glycine and 1 mol of ammonium formate in 100 ml double distilled water. The reaction mixture was stirred at ambient temperature for 5 h, and then filtered using a high quality Whatman 41 filter paper. The prepared solution was covered with perforated cover and kept in dust free environment. The nucleation period τ for γ-glycine is 5 days. The nucleated crystals were allowed for further growth to get an affordable size. The photograph of the harvested γ-glycine crystal is presented in Fig. 1. The ammonium formate salt is very irritant with odour and it is taken utmost care to use this salt as additive to yield γ-glycine crystal.

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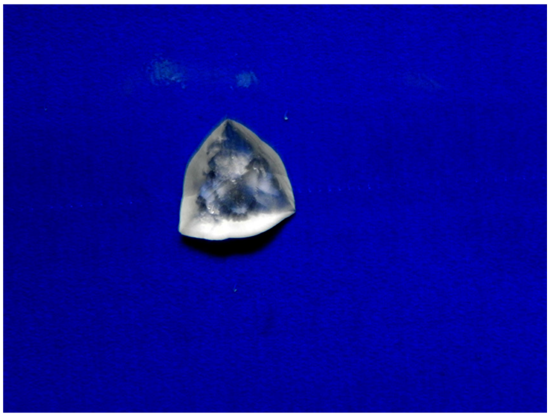

Fig. 1. γ-Glycine single crystal grown from ammonium formate.

Table 1
CHN analysis of γ-glycine crystal.

Element	Composition (%)	
	Experimental	Theoretical
Carbon	31.945	32.000
Hydrogen	6.673	6.714
Nitrogen	18.632	18.659

3. Results and discussion

3.1. Elemental analysis

CHN analysis of the grown γ-glycine crystals were carried out using Elemental Vario EL III Carbon, Hydrogen and Nitrogen analyzer and the results are shown in Table 1. The results of CHN analysis confirm the molecular formula of the grown crystal.

3.2. Powder X-ray diffraction analysis

The γ-glycine crystallizes in hexagonal structure with space group of $P3_1$. A sample in powdered form was subjected to XRD analysis using Bruker D8 advance powder X-ray diffractometer with a characteristic Cu K_α (λ = 1.5406 Å) radiation from 5° to 70° at a scan rate of 1° per minute. Powder X-ray diffraction patterns of the grown crystals are shown in Fig. 2. Appearance of sharp and strong peaks confirmed the good crystallinity of the grown crystals. The lattice parameters have been calculated using UNIT CELL software package. The observed lattice parameter values are in good agreement with the data available in JCPDS Card No.: 06-0230 [16]. The characteristic peak at 25.5° (2θ) corresponds to γ-glycine. Slight shift in the sharp peak position at 25.5° in higher angle side may be due to doping of ammonium formate in the γ-glycine crystal, which is also confirmed by the slight variation observed in lattice parameters of the grown crystal. The prominent faces of γ-glycine crystals are (1 0 0), (1 0 1), (1 1 0), (2 0 0), (1 1 1), (2 1 0), (2 1 1), (3 0 2). The calculated lattice parameters of γ-glycine single crystal grown from ammonium formate additive and lattice parameters of γ-glycine single crystal grown from various solvents were compared and it is given in Table 2.

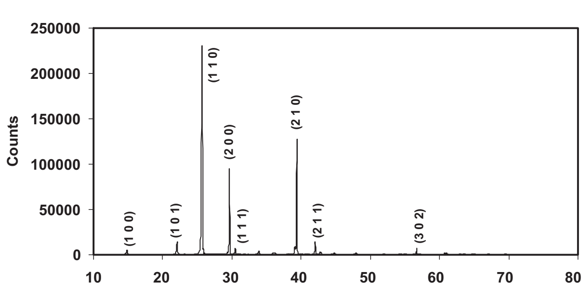

Fig. 2. Powder XRD pattern of γ-glycine.

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

Sample	Lattice parameters (Å)		References
	a = b	c	
γ-Glycine with potassium fluoride	7.039	5.492	[7]
γ-Glycine with phosphoric acid	7.028	5.447	[10]
γ-Glycine with ammonium formate	7.009	5.437	Present work

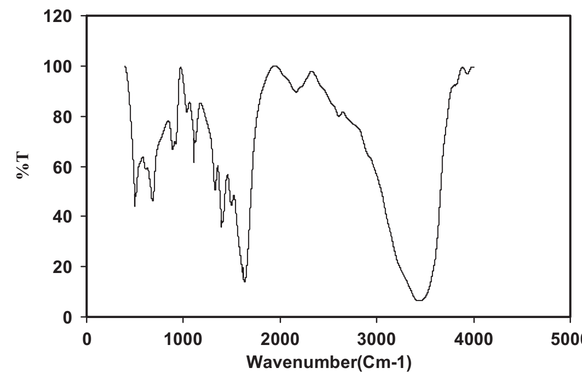

Fig. 3. FTIR spectrum of γ-glycine.

3.3. Vibrational analysis

The FTIR spectrum of gamma glycine was recorded in the range 400–4000 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique. The resulting spectrum is presented in Fig. 3. The observed frequencies and their assignment of the gamma glycine crystals are given in Table 3. The absorption peaks observed at 500, and 678 cm^{-1} are assigned to carboxylate groups, while the peaks observed at 2600, 1490 and 1120 cm^{-1} are attributed to NH_3^+ group. Thus, the carboxyl group is present as carboxylate ion and amino group exists as ammonium ion in γ-glycine. The C—C—N asymmetric and C—C—N symmetric stretching vibration are observed at 1034 and 883 cm^{-1}. The absorption at 1324 cm^{-1} is due to CH_2 twisting mode. The COO^- symmetric stretching and COO^- asymmetric stretching vibration are observed at 1388 cm^{-1} and 1625 cm^{-1}. The absorption peak at 3424.99 cm^{-1} is due to N—H asymmetric stretching vibration. The prominent band near

Table 3

FTIR wave numbers (cm^{-1})	Tentative assignments [18]
500	—COO^- rocking
678	—COO^- bending
883	CCN symmetric stretching
1034	CCN asymmetric stretching
1120	NH_3^+ rocking
1324	CH_2 twisting
1388	—COO^- symmetric stretching
1490	NH_3^+ group
1625	—COO^- asymmetric stretching
2163	Combination band
2600	NH_3^+ group