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Growth and characterization of γ-glycine single crystals from cadmium chloride for optoelectronic applications

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ABSTRACT

Single crystal of γ-glycine, an organic nonlinear optical material has been grown by solvent evaporation technique from the aqueous solutions of glycine and cadmium chloride at ambient temperature for the first time. The γ-phase of glycine is confirmed by single crystal X-ray diffraction. The crystal is in hexagonal system with non-centrosymmetric space group P31. The FTIR spectral analysis shows the functional group vibration of γ-phase glycine. UV–vis–NIR analysis reveals that the crystal has good optical transparency window in the entire visible and IR region. UV cut-off wavelength is at ~350 nm. Thermal analysis shows the thermal stability, phase transition of the grown crystals and its melting point. Second harmonic generation efficiency of the crystal is about 1.7 times that of KDP.

1. Introduction

Nonlinear optical processes provide the key functions of frequency conversion and optical switching [1]. The oriented nonlinear optical fields will be strengthened by the production of new nonlinear optical materials [2,3]. 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 [4,5].

An intense search for new NLO materials has been carried out by many researchers and a wide variety of both organic and inorganic materials have been developed. As far as second order effects are concerned organic materials exhibit higher nonlinear second order coefficients. Organic materials have been of particular interest because of the nonlinear optical responses in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [4].

Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power as compared with inorganic materials [6]. Other advantages of organic compounds apart from the above include amenability for synthesis, multifunctional substitutions, higher resistance to optical damage and maneuverability for device applications, etc. Hence, it will be useful to synthesize organic NLO materials and study their structural, physical and thermal properties.

The family of amino acid crystals has over the years been subjected to extensive investigation by several researchers for their NLO properties [7–11]. Glycine (NH_2CH_2COOH) (an amino acetic acid), the simplest amino acid, has no center of chirality and is optically inactive. It has three distinct polymorphic forms: α, β and γ forms at ambient environment [12]. The γ-glycine is thermodynamically more stable, while α-glycine is metastable, with β-glycine being least stable [13,14]. The α-glycine nucleates and grows fast, whereas stable γ-glycine nucleates very slowly and is hardly produced from a pure aqueous glycine solution [13,15–18]. γ-glycine can only be crystallized in the presence of chemical additives [13,15,16,19] including tailor made additives [20,21]. A new insight into the growth rates of both α and γ-glycines in acidic and basic media was studied by Han et al. [22]. Very recently, three additional polymorphic forms: δ-, ε- and β^1-forms have been discovered under high pressure conditions [23,24]. The two polymorphic forms α- and β-crystallizes in centrosymmetric space group $P2_1/c$ while the γ-glycine crystallizes in non centrosymmetric space group $P3_1$, making it a potential candidate for piezoelectric and NLO applications [25,26].

The large second order optical nonlinearity originates from organic π conjugated molecules having an electron acceptor group at one end and donor group at the opposite end [27–29]. γ-glycine exists as a dipolar ion and 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 NIR region [30].

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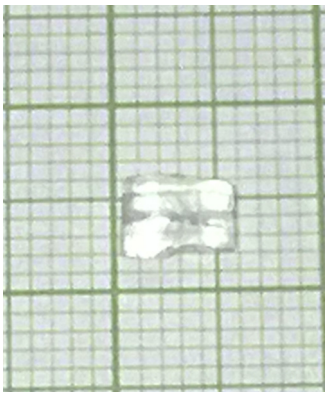

Fig. 1. As grown single crystal of γ-glycine.

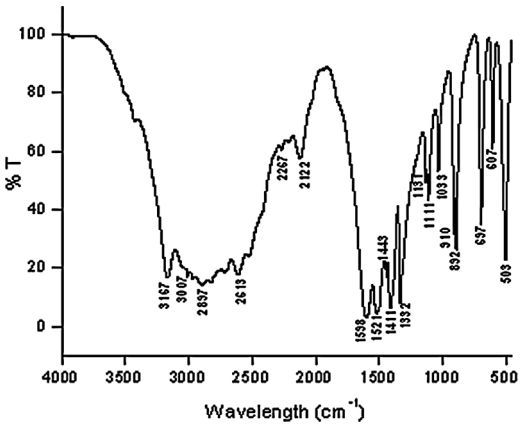

Fig. 2. FTIR spectrum of γ-glycine crystal.

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, and (vi) lithium acetate is reported [31,32]. The single crystal of γ-glycine grown in the presence of small amount of sodium chloride [33], ammonium nitrate [26], strontium chloride [34] and lithium nitrate [35] are reported as good NLO materials.

In this paper, we are reporting the growth of γ-glycine single crystals from aqueous solution of glycine and cadmium chloride for the first time. The grown single crystal of γ-glycine has been subjected to single crystal XRD, FTIR, UV–vis–NIR, SHG and thermal analysis.

2. Experimental procedure

Analytical grade chemicals of glycine and cadmium chloride (Merck, India) were mixed in the stoichiometric ratio 3:1 in double deionized water. The super saturated solution was filtered and allowed to evaporate slowly at room temperature over a period of 30 days, which yielded optically good quality crystals. The as grown single crystal is shown in Fig. 1 (Table 1).

3. Characterization studies

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction data recorded using Bruker Kappa APEXII X-ray diffractometer with Mo *K*α radiation (λ = 0.71073 Å) reveal the crystal structure of the grown crystal. The determined unit cell parameters are tabulated in Table 1 and these parameters are in good agreement with the reported values [12]. It confirms that the grown crystal is in the γ phase and belongs to the hexagonal system. Further it is evident that the cadmium chloride is not incorporated into the grown crystal but its presence in the solution yielded γ-glycine.

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

Unit cell dimensions	$a = b = 7.04$ Å $c = 5.48$ Å $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
Volume	235 Å^3
Crystal structure	Hexagonal
Space group	$P3_1$

3.2. Vibrational analysis

The FTIR spectrum of γ-glycine was recorded in the range of 4000–450 cm^{-1} using Perkin Elmer Spectrum1 FT-IR spectrometer by KBr pellet technique. γ-glycine has particularly interesting features like the splitting of infrared active vibrational modes due to long range electrostatic interactions and variation of the frequency of such modes with the angle between the optic axis and the direction of the phonon propagation in the crystal [30]. The FTIR spectrum is shown in Fig. 2. The broad envelope in the higher energy region between 3160 cm^{-1} and 2600 cm^{-1} is due to NH_3^+ stretching vibrations. The region of absorption bands extends to about 2122 cm^{-1} due to multiple combinations and overtone bands. The prominent band near 2228–2169 cm^{-1} may be assigned to a combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillation of the NH_3^+ group [36,37]. The NH_3^+ stretching region shows broad band characteristic of hydrogen bonding. The torsional oscillation of COO^- occurs at 503 cm^{-1}. The carboxylate ion group COO^- absorbs strongly at 1598 cm^{-1} and more weakly at 1521 cm^{-1}. These bands result respectively, from asymmetrical and symmetrical CO_2 stretching. The peaks at 1350 and 1332 cm^{-1} are due to the COOH group. All these observations demonstrate the existence of γ-glycine. The observed frequencies and their assignment of the γ-glycine crystals are given in Table 2, they are in good agreement with the earlier reported values [30,38,39] (Table 2.)

3.3. UV–vis–NIR spectral analysis

The optical absorption spectrum of good quality γ-glycine crystal was recorded in the wavelength range of 200–2500 nm using

Table 2
FTIR spectrum of γ-glycine.

Frequency in wavenumber (cm^{-1})	Assignment of vibrations
503	—COO^- rocking
607	—COO^- wagging
697	—COO^- bending
892	CCN symmetric stretching
910	CH_2 rocking
1033	CCN asymmetric stretching
1111, 1131	NH_3^+ rocking
1332	CH_2 twisting
1411	COO^- symmetric stretching
1443	CH_2 bending
1521	Weak symmetrical CO_2 stretching
1598	Strong asymmetric CO_2 stretching
2613, 3167	NH_3^+ asymmetric stretching
2897	—OH— stretching
3007	CH_2