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Growth and characterization of nonlinear optical γ-glycine single crystal from lithium acetate as solvent

P.V. Dhanaraj, N.P. Rajesh*

Centre for Crystal Growth, SSN College of Engineering, Kalavakkam 603110, India

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ABSTRACT

Single crystals of organic nonlinear optical material, γ-glycine were grown by slow evaporation technique from aqueous solutions of glycine and lithium acetate. The γ-phase was confirmed by single crystal XRD and powder XRD analysis. Presence of various functional groups was identified by FTIR spectrum analysis. Thermal analysis was performed to study the thermal stability of the grown crystals. The dielectric and microhardness studies of the crystals were determined. The optical analysis shows that UV cut-off of γ-glycine is at 240 nm and it has a wide transparency window. The second harmonic generation relative efficiency of the grown crystals was measured by Kurtz and Perry powder technique using Nd:YAG laser and was observed to be 3.4 times that of potassium dihydrogen orthophosphate.

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1. Introduction

Nonlinear optical (NLO) materials are attracting a great deal of attention because of their use in optical devices such as optical switches, optical modulators, optical bistable devices, electro-optical devices, etc. [1]. Organic materials have been of particular interest because the NLO responses in this broad class of materials are microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [2]. In solid state, amino acid contains the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second order nonlinearity [3–7]. Glycine [NH_2CH_2COOH: amino acetic acid] is the simplest amino acid. Unlike other amino acids, it has no centre of chirality and is optically inactive.

Certain chemical compounds show the ability to crystallize into more than one structural form with different physical properties, known as polymorphs. A series of works are available in the literature on the polymorphs of different compounds and their studies [8–11]. Ivanova et al. [12] reported solid-state linear-dichroic infrared spectroscopic and theoretical analysis of glycine-containing peptides and their hydrochlorides. Under different conditions, glycine crystallizes in three kinds of polymorphs with different relative stabilities, α, β and γ which exhibits different characteristics. Both α and β forms crystallize in centrosymmetric space group $P2_1/c$ ruling out the possibility of optical second harmonic generation [13,14]. But γ-glycine crystallizes in noncentrosymmetric space group $P3_1$ making it a potential candidate for piezoelectric and NLO applications [15].

In the γ-glycine, the presence of carboxylic acid group donates its proton to the amino group to form the structure $NH_3^+CH_2COO^-$. Thus in solid state, γ-glycine exists as a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. Due to this dipolar nature, glycine has high melting point. In addition to this, the presence of chromophores namely amino group and carboxyl group which makes the γ-glycine crystal transparent in the UV–Vis region. Narayan Bhat et al. [16,17] carried out a detailed 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 and (v) sodium acetate and analyzed the effect of these solvents on the various physical characteristics. In this paper we report the growth and characterization studies of γ-glycine crystals grown from aqueous solution of glycine in the presence of lithium acetate for the first time, since some of the physical properties of the reported γ-glycine crystals are enhanced by this solvent.

2. Experimental

2.1. Synthesis

The starting materials glycine (Merck-GR grade) and lithium acetate (Alfa Aesar) were taken in the equimolar ratio. The calculated amount of salts was dissolved in Millipore water of resistivity 18.2 MΩ cm at room temperature. The solution stirred well for about 2 h using a magnetic stirrer to obtain a homogeneous mixture. Then the mixture was evaporated to dryness, by heating below an optimum temperature

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* Corresponding author. Tel.: +91 44 27474844; fax: +91 44 27474844.
E-mail addresses: rajeshnp@ssn.edu.in, rajeshnp@hotmail.com (N.P. Rajesh).

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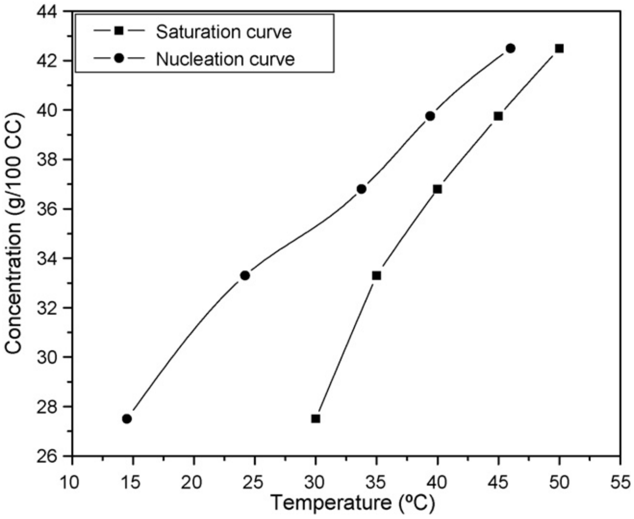

Fig. 1. Solubility curve and metastability limit curve.

of 50 °C to prevent decomposition. The material was repurified from the aqueous solution by recrystallization processes.

2.2. *Solubility and metastable zone width*

The nucleation studies were carried out in a constant temperature water bath with cryostat facility with an accuracy of ±0.01 °C. The solubility at 30 °C was determined by dissolving the recrystallized salt in 100 ml Millipore water taken in an air tight container. The solution was stirred continuously for 6 h to achieve stabilization using an immersible magnetic stirrer. After attaining the saturation the concentration of the solute was estimated gravimetrically. The same procedure is repeated for different temperatures (35, 40, 45 and 50 °C).

The metastable zone width was measured by adopting the conventional polythermal method [18]. The saturated solution (100 ml) at 30 °C was prepared according to the presently determined solubility data. After attaining the saturation, the solution was filtered by the filtration pump and Whatman filter paper of pore size 11 μm. The solution was preheated to 5 °C above the saturated temperature for homogenization and left at the superheated temperature for about 1 h before cooling. Then it was slowly cooled at a desired cooling rate of 4 °C h^{-1}, until the first crystal appeared. The temperature was instantly recorded. The difference between the saturation temperature and nucleation temperature gives the metastable zone width of the system. Then experiment was repeated for different saturation temperatures 35, 40, 45, 50 °C and the corresponding metastable zone widths were measured. The variation of solubility along with the metastable zone width for different temperatures is shown in Fig. 1.

2.3. *Crystal growth*

Slow evaporation method was employed for growing the single crystals of γ-glycine. The recrystallized salt was used for the preparation of saturated solution at room temperature. The solution was filtered by filtration pump and Whatman filter paper of pore size 11 μm and kept undisturbed in a dust free environment. The nonhygroscopic single crystal of γ-glycine grown by slow evaporation method is shown in Fig. 2.

3. Results and discussion

3.1. *Single crystal X-ray diffraction studies*

The grown crystal was subjected to single crystal X-ray diffraction study using NONIUS CAD-4/MACH 3 diffractometer with Mo Kα radiation in the wavelength 0.71073 Å to identify the structure and to estimate the lattice parameter values. At room temperature, the cell parameters are $a = b = 7.029$ (2) Å (7.037 Å), $c = 5.474$ (2) Å (5.483 Å) and the volume of the unit cell is 234.1 (1) $Å^3$ (235.1 $Å^3$). The determined lattice parameter values are in-line with the literature values [15] given in the parentheses which confirm that the grown crystal is in the γ-phase and belongs to the hexagonal system. Further it is evident that lithium acetate is not incorporated into the lattice of grown crystal, but its presence in the aqueous solution yielded γ-glycine.

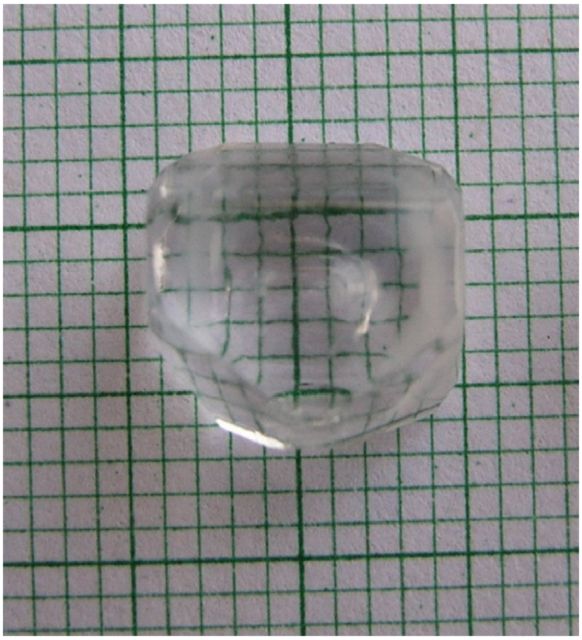

Fig. 2. Photograph of as grown crystal.

3.2. *Powder X-ray diffraction studies*

Powder X-ray diffraction study was carried out by employing SEIFERT, 2002 (DLX model) diffractometer with Cu Kα (λ = 1.5405) radiation using a tube voltage and current of 40 kV and 30 mA respectively. The grown crystals were finely powdered and have been subjected to powder XRD analysis. The sample was scanned over the range 10–70° at the rate of 1° min^{-1}. The indexed powder X-ray diffraction pattern of the grown crystal is given in Fig. 3. The positions of the peaks were found to be in good agreement with the data available in JCPDS files.

3.3. *FTIR spectral analysis*

The FTIR spectrum was recorded using a PerkinElmer FTIR spectrum RXI spectrometer by KBr pellet technique. Fig. 4 shows the

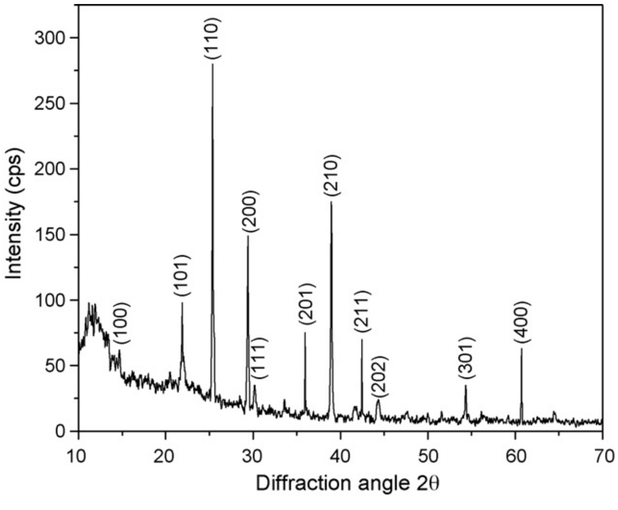

Fig. 3. Indexed powder X-ray diffraction spectrum of γ-glycine.

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