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A study on Fourier transform infrared spectroscopy, thermal, mechanical, NLO and laser damage properties on unidirectional Glycinium Picrate Mono Glycine crystal

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HIGHLIGHTS

- FTIR study shows the vibrations of the molecules which made in studying other characteristics also.
- Large size of GPMG crystals are obtained.
- Hardness is found to be higher.
- Transparency of the crystal is good.

GRAPHICAL ABSTRACT

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ABSTRACT

By directional solidification, single crystal of Glycinium Picrate Mono Glycine (GPMG) was successfully grown by Sankaranarayanan–Ramasamy (SR) method. An optically transparent crystal of GPMG has been grown along ⟨0 1 1⟩ plane by a mixed solvent of acetone and double distilled water. The evaporation rate was controlled and a single crystal of 12 mm diameter and 35 mm length was obtained. Single crystal X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), thermal, mechanical, SHG and laser damage studies were carried out. The results are discussed in detail.

Introduction

In the field of non-linear optics (NLO), the orientation control of molecules creates new functions. Hence, technology for the growth of bulk materials with effective orientation control is required for achieving significant applications in the field of NLO. The uniaxial crystallization method of Sankaranarayanan–Ramasamy (SR) [1] is a versatile method to effectively control the orientation of molecules during the bulk crystal growth from solution at ambient temperature with 100% solute-crystal conversion efficiency.

The present article discusses the unidirectional growth of organic NLO single crystal of Glycinium Picrate Mono Glycine abbreviated as GPMG. This crystal belongs to monoclinic system with space group $P2_1/a$. The cell dimensions of GPMG are $a = 14.88$ Å, $b = 6.69$ Å, $c = 15.08$ Å. SHG is the most commonly

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investigated NLO effect in crystallographic study for non-centro-symmetric crystals, but it is observed that SHG is found in centro-symmetric GPMG [2].

The investigation of the reaction between glycine and picric acid started with the work of Levene more than a hundred years ago [3], who concluded that a compound with 1:1 M ratio is formed, which logically has been named Glycine Picrate. Later it has been pointed out [4] that the crystal obtained in [3] is diglycine picrate (DGP) and a probable reason for the error committed was indicated.

The crystal structure shows that the obtained crystal consists of two glycine molecules and one picric acid molecule thus confirming the previous results [3,4]. As per Ghazaryan et al. [5] the hydrogen atom of the phenolic hydroxyl group in picric acid is formally transferred from picric acid to one glycine molecule. This molecule forms a strong hydrogen bond with the second glycine molecule. This confirms that this class of amino acid salt with dimeric cations should be more aptly called Glycinium Picrate Mono Glycine.

In this paper the gown crystal is characterized by single crystal X-ray diffraction, thermal analysis, mechanical strength, SHG conversion efficiency, High resolution X-ray Diffraction (HRXRD) and laser damage threshold.

Experimental set-up

SR method setup Fig 1 was arranged to grow the GPMG crystals. It consists of ring heaters positioned at the top and bottom of the growth ampoule connected to the temperature controller. The top heater provides the necessary temperature for solvent evaporation. The GPMG solution of optimized saturation was prepared using de-ionized water and it is transferred to growth vessel. Glycine and picric acid used in the present study was commercially bought from M/s Merck, GR grade, India and the de-ionized water got from Millipore water pre-filtration unit. The resistivity of the used de-ionized water is 18.2 MΩ cm.

Growth of GPMG single crystal

Saturated solution of GPMG was prepared and the conventional slow solvent evaporation technique was conducted at room temperature in order to collect the seed crystal. Based on the quality of the grown crystals, a suitable seed crystal having a size of 17 mm × 2 mm × 3 mm was selected for single crystal growth. The seed crystal with (0 1 1) direction was mounted at the bottom of the ampoule without polishing the surface. To control the spurious nucleation, care has been taken while preparing the growth vessel and the solution. The growth vessel was porously sealed and placed in a dust free chamber. The growth was initiated with suitable temperature provided by the ring heater at the top region of the saturated solution under equilibrium condition. The placement of ring heater at the top of the growth solution also controls the spurious nucleation near the surface region of the solution during the entire growth period. Under optimized condition, highly transparent crystal growth was seen. After 15 days, 35 mm long and 12 mm diameter, rod like good quality transparent crystal was harvested. The grown crystal is shown in Fig. 2a. Using the same ingredients, crystal of size 17 mm × 2 mm × 3 mm, grown by conventional method is shown in Fig. 2b.

Fig. 2a. Photograph of crystal grown by SR method.

Results and discussion

X-ray diffraction analysis

From the single crystal X-ray diffraction analysis using ENRAF NONIUS CAD–4 single crystal X-ray diffractometer with Mo Kα radiation, it is observed that the crystal belongs to monoclinic crystal system having centrosymmetry with $P2_1/a$ space group. The calculated lattice parameter values are $a = 14.88$ Å, $b = 6.69$ Å, $c = 15.08$ Å, $\alpha = 90°$, $\beta = 93.71°$, $\gamma = 90°$ which are in very good agreement with the reported values [2].

Fig. 1. Photograph of experimental setup.

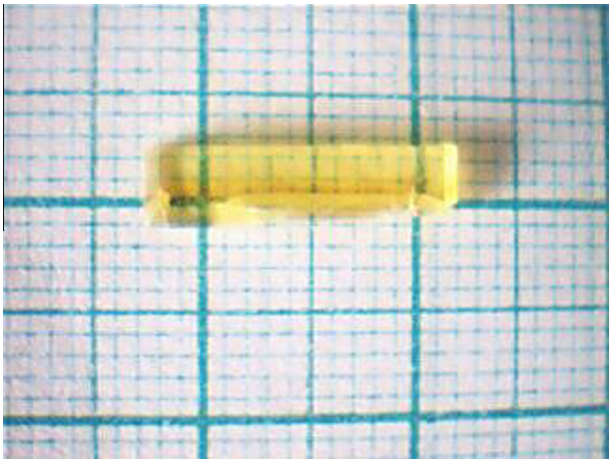

Fig. 2b. Photograph of crystal grown by Conventional method.