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Investigation on the growth, spectral, thermal, laser and optical properties of glycinium 2-carboxy 6-nitrophthalate single crystal

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ABSTRACT

Glycinium 2-carboxy 6-nitrophthalate (G3N) has been grown by slow evaporation method at ambient temperature using water solvent in 1:1 M ratio. Single crystal XRD study confirmed that the G3N crystal having a monoclinic structure with space group $P2_1/c$. The solid-state parameters like Fermi energy, Penn energy, Plasma energy, and polarizability were estimated theoretically. The crystalline quality of grown crystal was scrutinized by High-resolution XRD study. The mode of vibrations and presence of functional groups in the G3N compound was identified from the vibrational analysis. The lower cut-off wavelength of the G3N crystal is endowed to be 377 nm and the calculated band gap energy is 3.09 eV. Photoluminescence (PL) property of G3N crystal was studied. The imaginary (Im $(\chi)^{(3)} = 0.43 \times 10^{-6}$ esu) and real parts (Re $(\chi)^{(3)} = 5.68 \times 10^{-6}$ esu) of the third order susceptibility values were determined from Z-scan studies. The surface laser damage threshold value of G3N crystal was endowed to be 6.22 GW/cm^2 using an Nd: YAG laser. TG-DSC analysis divulges that the crystal was thermally steady up to 184 °C. The dielectric manner of a G3N crystal was evaluated in the frequency between 40 and 70 Hz at various temperatures. The hardness of G3N crystal was accomplished on the (1 0 0) and (−1 0 0) planes to understand the mechanical properties of the crystal.

1. Introduction

In the middle of nonlinear optical (NLO) crystals, organic salts occupy a moderate position between molecular organic compounds with covalent bonds and inorganic compounds with essentially ionic bonds. Many of these organic molecular crystals owe to their NLO properties to the occupation of delocalized π-electron systems joining donor and acceptor groups which increase the necessary asymmetric polarizability [1]. For the last few decades, the occurrence of promising NLO materials are producing blue and green lasers by frequency conversion are of great interest among the researchers. Organic NLO materials are performing a vital role in nonlinear optics as they have quick response, high NLO productivity and high laser damage threshold compared to inorganic nonlinear optical materials [2]. In the area of photonics and lasers, organic molecules are accomplished by influencing photonic signal efficiency in technologies such as optical computing, optical communication, and dynamic image processing. The adaptability of organic materials is owed to their higher-level properties such as higher susceptibility, faster response, and flexibility [3–5]. The optical nonlinearity of organic materials can be improved by the addition of a strong electron donating and withdrawing group can generate charge transfer compound with an asymmetric electron distribution. This is mainly due to asymmetric molecules carry a dipole moment in their ground state, and to decrease the dipole-dipole interaction, which is firm over the van der Walls interaction in the lattice. This arrangement has suggested a crystal for forming in centrosymmetric crystalline structure. All the centrosymmetric materials have third-order NLO properties and third-order nonlinear susceptibilities which are necessary for optical switching, modulating and summing devices [6]. The third-order NLO materials have weak nonlinear absorption, but strong nonlinear refraction and have attracted significant attention due to their potential utilizes in the optical-signal processing devices [7]. Glycine is an amino acid and it has no asymmetric carbon atoms. It consists of three polymeric crystalline forms α, β, and γ and its methylated analogs appearance complexes with mineral acids give physical properties like ferroelectric, ferroelastic or anti-ferroelectric behavior often correlated with transitions to adequate or inadequate phases [8]. The 2-carboxy-6-nitrophthalic acid is imitative of phthalic acid which is an aromatic dicarboxylic acid and they are interesting for crystal engineering owed to their ability of hydrogen bond formation. 2-carboxy 6-nitrophthalic acid is mainly used as responsive materials and pharmaceutical intermediates and it is available for the

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preventative measure of medicines, crop safety agents in organic synthesis materials and dyes [9]. Some of the 2-carboxy-6-nitrophthalic acid based compounds reported in the recent years are quinolinium 2-carboxy 6-nitrophthalate monohydrate [10], Brucinium 2-carboxy-6-nitrophthalate dihydrate [11]. The stiffness, density and electrical conductivity of the crystal are known as structure insensitive and these are not overwhelmed via the defects present in the crystal. There are numerous properties of scientific importance like mechanical strength, ductility, and dielectric strength are called as structure sensitive are affected by the small alters in structure of crystal caused by defects or imperfections. For organic compounds the bonding contains intramolecular and intermolecular contributions and interactions corresponding to dipole moments [12]. The structure of Glycinium 2-carboxy-6-nitrophthalate has been reported by Zong-Sheng Li et al. [13]. We have already reported the crystal growth and characterization of glycinium 3- nitrophthalate nonlinear optical single crystal for AIP conference proceedings [14]. In the current research work solubility, single XRD theoretical data, dielectric behavior and thermal studies of G3N are discussed. In addition to that, the G3N crystal is subjected to spectral, linear and nonlinear optical, surface laser damage threshold studies and mechanical studies.

2. Experimental procedure

2.1. Material synthesis and crystal growth of G3N

The precursor materials glycine (5 g) and 3-nitrophthalic acid (3 g) were taken in 1:1 M ratio to synthesis G3N and the reaction scheme is delineated in Fig. 1. The calculated amount of glycine dissolved in water, then after 1 h, the 3-nitrophthalic acid was slowly added to the dissolved glycine solution with continuous stirring for evolving a homogeneous solution which was filtered off utilizing A1 filter paper and allowed for evaporation. Duration of 15 days was taken for growth of an excellent quality single crystal having dimension $10 \times 9 \times 5\,mm^3$ and as-grown crystal photograph and morphology is portrayed in Fig. 2. The size of a crystal depends on solubility of solute that is dissolved in the solvent and G3N crystal is well soluble in water. For the solubility of a study at the temperature of 30 °C, the powdered G3N salt was dissolved in water and the dissolved solution was stirred well using temperature controlled motorized magnetic stirrer to acquire a homogeneous solution. The same procedure was followed for the temperatures 35, 40, 45 and 50 °C to get the solubility of G3N crystal and the solution could evaporate at room temperature to give the crystalline salt of G3N. From the solubility data (Fig. 3), it is noted that the G3N crystal having positive solubility gradient in water.

2.2. Characterization techniques

G3N crystal was employed to powder X-ray diffraction (PXRD) pattern was recorded to analysis the crystalline nature of the sample in the range 10°–70° by SEIFERT powder X-ray diffractometer equipped Cu $K\alpha_1$ radiation ($\lambda = 1.5418$ Å), Cu filter, 45 kV, 20 mA. The WINXMORPH software was employed to create the morphology of G3N crystal. The quality of the G3N crystal is evaluated by the PANalytical X'Pert PRO MRD high-resolution X-ray diffraction system, with Cu $K\alpha_1$ radiation. FT-IR spectrum was recorded between the ranges 400 to 4000 cm^{-1} using Perkin Elmer spectrum one FTIR spectrometer to substantiate the presence of mode of vibrations in the compound. UV–Vis transmittance spectrum was traced in the range 190–900 nm for the grown crystal by LAB INDIA (Model No-3209) UV–Vis spectrophotometer. Photoluminescence emission spectrum was traced by stimulating sample with an excitation wavelength 360 nm in the wavelength range 300–700 nm using Cary Eclipse Spectrofluorometer. The third-order NLO property of G3N crystal was estimated by Z-scan method. The dielectric study was taken using the instrument HIOKI 3532-50 LCR HITESTER to know the electrical properties of the material. Thermal analysis was taken using the instrument NETZSCH STA 449F3 to verify the melting point of the sample. The LDT (laser damage threshold) study was executed on the G3N crystal using Q - switched High-Energy Nd: YAG Laser (QUANTA RAY Model LAB – 170 - 10). Mechanical study was executed on the G3N crystal using Leitz-Weitzler hardness tester fitted with a diamond indenter.

3. Results and discussion

3.1. Powder XRD studies

Powder XRD analysis is used to study the crystalline nature of G3N crystal. The XRD pattern (Fig. 4) was indexed by powder X software. The G3N crystal belongs to the monoclinic crystal system with the space group $P2_1/c$ and the calculated lattice parameters are, a = 12.97 ± 0.05 Å, b = 10.97 ± 0.01 Å and c = 8.66 ± 0.06 Å and volume = 1173.88 $Å^3$. The calculated lattice parameters are in good agreement with that obtained from single crystal data [13]. The dislocation density of the grown crystal is related to the crystallite size of a relation [15]:

$$\delta = \frac{1}{t^2} \tag{1}$$

The crystallite size 't' is calculated from Scherer's equation as given below,

$$t = \frac{0.95\lambda}{\beta \cos\theta} \tag{2}$$

where 'β' is the width measured in radians of half maximum peak intensity, 'λ' is the X-ray wavelength and 'θ' is the Bragg's angle. The calculated value of dislocation density, 4.566×10^3 cm^{-2} on (−410) diffracting plane indicates the perfection of the crystal.

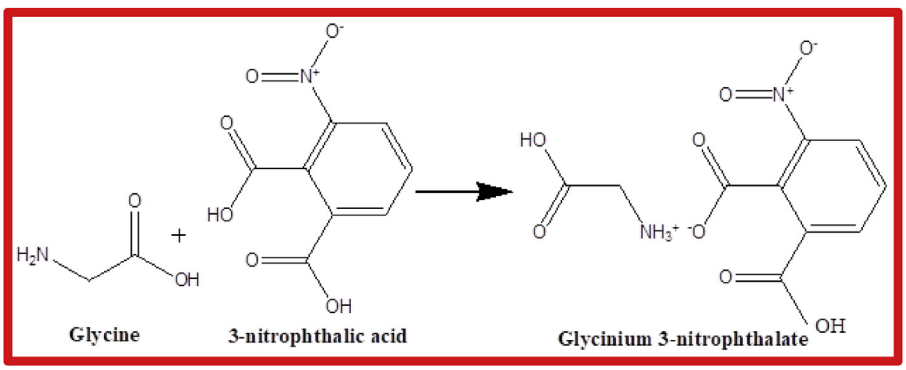

Fig. 1. Reaction scheme of G3N.