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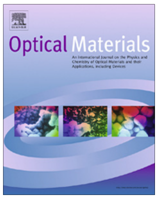

Third order nonlinear optical, luminescence and electrical properties of bis glycine hydrobromide single crystals

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ABSTRACT

Optical quality bis glycine hydrobromide (BGHB) single crystal was grown by slow evaporation technique. The third order nonlinear refractive index and nonlinear absorption coefficient of the grown crystal were measured by Z-scan studies. The third order nonlinear susceptibility was found to be 9.612×10^{-4} esu which is fairly higher than the other glycine compounds. The Photoluminescence spectra reveal the emission bands for BGHB crystals. The band gap energy was calculated to be 3.1 eV. The Photoconductivity studies were employed to determine the dependence of photocurrent on the applied electric field. Negative photoconductivity was exhibited by the sample. The d.c. conductivity of the grown crystal was measured by the complex impedance analysis wherein the obtained plot in the form of semicircle finds application in Debye relaxation for materials having large dc conductivity.

1. Introduction

In recent years, there has been considerable interest on organic materials due to their potential applications such as frequency conversion, optical signal processing, light modulation, optical switching and logic gates. Though organic crystals are highly advantageous due to their structural flexibility and large NLO coefficients, still they possess some intrinsic weaknesses like physico-chemical strength, narrow transparency window, small size and low mechanical strength. To overcome these difficulties, semi-organic crystals have been focused which combine the advantages of both organic and inorganic complexes. The incorporation of inorganic salts or acids in organic compounds forms semi-organic complexes whose mechanical stability and thermal properties get enhanced. Basically, the semi-organic group of crystals involving organic–inorganic salts [1] and metal–organic coordination complexes [2] were extensively researched for the past two decades. Combining the high optical nonlinearity and chemical flexibility of organics with temporal and thermal stability and excellent transmittance of inorganics, semi organic materials have been proposed and are attracting a great deal of attention in the nonlinear optical field [3]. Among the semi organic crystals, the crystal structures of amino acids and their complexes have provided a wealth of interesting information on the patterns of their aggregation and the effect of other molecules and ions on their interactions and molecular properties [4]. Of all the existing amino acid organic crystals, glycine plays a remarkable role.

Glycine is hydrogen bonded simplest amino acid, optically inactive, dipolar exhibiting high melting point. It is the most extensively studied amino acid as it is known to form innumerable complexes with metals, inorganic salts and inorganic acids. It has secured vast attention in the field of crystal growth due to its interesting optical and electrical properties, structural phase transition and easy crystallization. Reports say that using glycine as a dopant, even the second harmonic generation of a semi-organic material was enhanced [5]. When glycine reacts with HBr, either glycine hydrobromide (GHB) or bis glycine hydrobromide (BGHB) may be formed depending on the ratio of the reactants taken and its growth environment. The crystal structures and their bulk crystal growth are already reported in the literature [6–9]. Recently in one of the papers, the BGHB growth process, crystal parameters, FTIR, UV–Vis spectral studies, dielectric, thermal and mechanical properties were thoroughly discussed [10]. However, to the best of author's knowledge, there is no report available on the third order nonlinear properties of the BGHB crystal which is presented here for the first time. This paper brings out photoluminescence, photoconductive, complex impedance analysis of the crystal along with its z-scan studies that reveals the high-speed switching operations which are ideally faster than even the conventional electronics.

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2. Materials processing

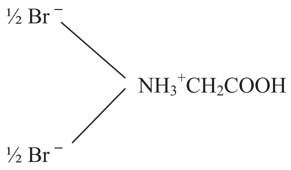
2.1. Synthesis

The BGHB crystals were synthesized and recrystallized as per the method reported in literature [10]. The analytical grade glycine and hydrobromic acid were taken in the ratio of 2:1 and dissolved in the mixed solvent of water: acetone (in the ratio 1:1). The resulting solution was completely stirred for about 6 h to obtain a homogenous mixture after which it was filtered using Whatmann's filter paper and poured into a beaker with perforated lid. To initiate slow evaporation, the beaker along with the contents was suspended in a Constant Temperature Bath at a temperature of 40 °C. After a period of 50–55 days, non-hygroscopic bulk transparent crystals were harvested. The yielded crystal was confirmed to be BGHB by X-ray diffraction studies [8]. It crystallizes in the non-centrosymmetric orthorhombic crystal system having space group P_{212121}. The composition of the synthesized material is established as $C_4H_{11}N_2O_4Br$. From the single crystal structural study, the structural formula of the compound is affirmed as:

$$(NH_3^+CH_2COOHBr^-)\ (NH_3^+CH_2COO^-)$$

(I) (II)

According to this structure, it can be implied that molecule II occurs as a zwitter ion of the type $NH_3^+CH_2COO^-$, while molecule I has the normal glycine configuration. This molecule formally receives an additional H^+ ion from HBr and these H^+ acts as an ionic connection between molecule I and a pair of Br^- ions, thus making the formula structure of the molecule II as given below:



$$\begin{matrix} \tfrac{1}{2}Br^- \searrow & \\ & NH_3^+CH_2COOH \\ \tfrac{1}{2}Br^- \nearrow & \end{matrix}$$

The carboxyl acid group is a proton donor and the amino group is a proton acceptor. In a glycine molecule, the carboxylic acid group donates its proton to the amino group to form molecule II namely ($NH_3^+CH_2COO^-$). This arrangement fulfils the rule of maximum hydrogen bonding, since all six hydrogens belonging to the two glycine molecules are engaged in hydrogen bond formation. The last hydrogen, which is formally part of HBr, connects one molecule with two bromines but not as a hydrogen bond in the usual meaning. The two-carboxyl groups behave quite differently. In molecule I, it exists as a carboxylic acid group, whereas it is present as a carboxylate ion in molecule II.

3. Results and discussions

3.1. Z-scan analysis

The z-scan technique is a versatile standard tool in the study of nonlinear optics which evaluates the third order nonlinearity and determines the changes in nonlinear refractive index and variation in absorption. The third order optical nonlinearity was investigated by the Z-scan technique which enables simultaneous measurement of magnitude and sign of the nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β) of the sample leading to different properties like acoustically induced optical Kerr effect, self-defocusing effect, etc. The study of acoustically induced optical Kerr effect in NLO materials leads to design of variety of acoustically-operated quantum electronic devices [11].

The z-scan is a single beam technique developed by Sheik Bahae to measure the magnitude of nonlinear absorption as well as the sign and magnitude of nonlinear refraction [12]. Basically, the method consists of translating a sample through the focus of a Gaussian beam and monitoring the changes in the far field intensity pattern as shown in Fig 1. When the intensity of the incident laser beam is sufficient to induce nonlinearity in the sample, it either converges (self-focusing) or diverges (self-defocusing) the beam, depending on the nature of that nonlinearity. By moving the sample through the focus, the intensity dependent absorption is measured as a change of transmittance through the sample (open aperture). The nonlinear refraction is determined by the intensity variation at the plane of a finite aperture placed in front of the detector (closed aperture), because the sample itself acts as a thin lens with varying focal length as it moves through the focal plane.

The Z-scan experiments were performed using a 532 nm diode pumped Nd:YAG laser beam (Coherent Compass TM 215M-50), which was focused by 3.5 cm focal length lens as depicted in Fig 1. The distance between the lens and the laser was 13 cm. The BGHB crystal is translated across the focal region along the axial direction that is the direction of the propagation of laser beam. The transmission of the beam through an aperture placed in the far field was measured using photo detector fed to the digital power meter (Field master GS-coherent). For an open aperture Z-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture.

The Z-scan theory is of vital significance in the field of nonlinear optics as it is an optimum tool for separately determining the nonlinear changes in index and absorption. A spatial distribution of the temperature in the crystal surface is produced due to the localized absorption of a tightly focused beam propagating through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam [13]. The difference between the peak and valley transmission (ΔT_{p-v}) is written in terms of the on axis phase shift at the focus as,

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\Phi|, \tag{1}$$

where S is the aperture linear transmittance and is calculated using the relation,

$$S = 1 - \exp(-2r_a^2/\omega_a^2), \tag{2}$$

where r_a is the aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index is given by,

$$n_2 = \Delta\Phi / K I_0 L_{eff}, \tag{3}$$

where $k = 2\pi/\lambda$ (λ is the laser wavelength), I_0 is the intensity of the laser beam at the focus ($Z = 0$), $L_{eff} = [1-\exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the absorption and L is the thickness of the sample.

From the open aperture Z-scan data, the nonlinear absorption coefficient is estimated as,

$$\beta = 2\sqrt{2}\Delta T / I_0 L_{eff}, \tag{4}$$

where ΔT is the one valley value at the open aperture Z-scan curve. The value of β will be negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ are defined as,

$$\mathrm{Re}\,\chi^{(3)}\ (\mathrm{esu}) = 10^{-4}\,(\varepsilon_0 C^2 n_0^2 n_2)/\pi \quad (\mathrm{cm}^2/W), \tag{5}$$