Asian Journal of Chemistry; Vol. 23, No. 1 (2011), 37-40

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Structural, Optical and Photoconductivity Studies on Benzoyl Glycine NLO Single Crystals

S. SURESH[1], A. RAMANAND[1] and R. VASANTHAKUMARI[2,*]

[1]Department of Polymer Technology, B.S.A. Abdur Rahman University, Seethakathi Estate, GST Road, Vandalur, Chennai-600 048, India
[2]Department of Physics, Loyola College, Chennai-600 034, India

*Corresponding author: E-mail: kumarirv@yahoo.co.in

(*Received*: 27 July 2009; *Accepted*: 19 August 2010) AJC-8981

Single crystals of benzoyl glycine (BG) with high degree of transparency were grown by slow evaporation technique. Powder crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic system with the space group $P2_12_12_1$. The physical parameters have been determined for the grown crystal. The optical absorption study reveals the transparency of the crystal in the entire visible region and the cut off wavelength was found to be 240 nm. The optical band gap was found to be 3.75 eV. The dependence of extinction coefficient (k) and refractive index (n) on the wavelength have also been reported. The dielectric constant was also studied as a function of frequency at room temperature. The photo conductivity study proves that benzoyl glycine crystal exhibits negative photoconductivity.

Key Words: Benzoyl glycine, Single crystals, Optical constants, Transport properties.

INTRODUCTION

New molecular organic compounds with one or more aromatic system in conjugated positions leading to highly efficient optical non-linearity have been actively studied for the past two decades[1]. The organic non-linear optical materials play an important role in second harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation and optical bi-stability[2]. Recently, an extremely large number of organic compounds with non-localized π-electron systems and a large dipole moment have been synthesized to realize the non-linear susceptibility compared to the inorganic optical materials[3]. The first observation of second harmonic generation in an organic material was reported in 1964 in benzopyrene by Rentzepis and Pao[4]. Two years later Orlov[5] reported second harmonic generation from benzoyl glycine. Benzoyl glycine also called N-benzoyl glycine is a colourless NLO crystal with chemical formula $C_6H_5CONHCH_2$-COOH[6,7]. It crystallizes in orthorhombic structure with space group $P2_12_12_1$, and with lattice parameters a = 8.874 Å, b = 10.577 Å and c = 9.117 Å[8]. Growth of benzoyl glycine by double diffusion method in silica gel has been reported[9,10]. To enable a material to be potentially useful for NLO applications, the material should be in bulk single crystal form. Hence bulk single crystals of benzoyl glycine were grown by slow evaporation solution growth technique using acetone as a solvent. In this work, growth and some physical parameters have been obtained for the grown benzoyl glycine crystal. The band gap energy for the grown crystals has been calculated using optical absorption spectrum. The photoconductivity studies for BG crystal have been determined by measuring photo current and dark current.

EXPERIMENTAL

The low temperature solution growth technique has been employed to grow benzoyl glycine crystal using acetone as solvent. Analytical grade benzoyl glycine was taken and was dissolved in acetone solvent to prepare the saturated solution. The saturated solution of benzoyl glycine was obtained by dissolving the material with continuous stirring of solution using magnetic stirrer. The resulting solution was filtered using borosil filter paper of porosity 0.1 μm. The filtered solution was taken in a beaker and then allowed to evaporate in a petri dish at ambient temperature. High quality transparent colourless crystals of size 6 mm × 9 mm × 4 mm were obtained in a period of 5 days. Selected seed crystals were used to grow bulk single crystals of benzoyl glycine (Fig. 1) and its some physical parameters are given in Table-1.

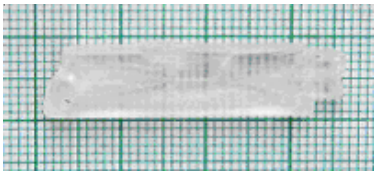

Fig. 1. Benzoyl glycine grown crystal

TABLE-1
THEORETICAL DATA FOR BENZOYL GLYCINE SINGLE CRYSTAL

Parameters	Values
Plasma energy (eV)	17.03
Penn gab (eV)	17.63
Fermi gap (eV)	13.52
Polarizability (cm^3) Penn analysis	10.35×10^{-24}
Density (g/cm^3)	1.385
Unit cell volume ($Å^3$)	850.77
Unit cell mass (Kg)	6.720×10^{-22}

RESULTS AND DISCUSSION

Single crystal X-ray diffraction analysis: The X-ray diffraction data was collected using automatic diffractometer (MESSRS, ENRAF NONIUS CAD 4). The structure was solved by the direct method using SHELXL program. From the analysis the cell parameters were found to be a = 8.874 Å, b = 10.577 Å and c = 9.117 Å. ORTEP diagram and the packing diagram of the grown crystal are shown in Figs. 2 and 3, respectively. Single crystal X-ray diffraction analyses for the grown crystals have been carried out to identify the cell parameter, using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. The calculated lattice parameters are a = 8.8514 Å, b = 9.0842 Å, c = 10.5807 Å and the crystal belongs to orthorhombic system with the space group $P2_12_12_1$ which agrees with the reported values[11]. The crystals obtained are non-hygroscopic in nature and exhibits orthorhombic morphological forms. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (1)$$

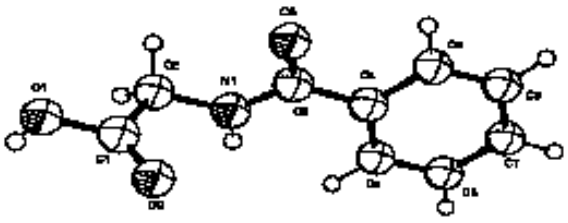

Fig. 2. TEP diagram of the benzoyl glycine crystal

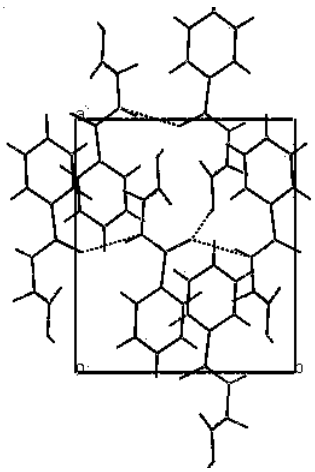

Fig. 3. Packing diagram of the benzoyl glycine crystal

where $Z = [(9 \times Z_C) + (9 \times Z_H) + (1 \times Z_N)] = 48$ is the total number of valence electrons, ρ = density and M = molecular weight of the benzoyl glycine single crystal. Explicitly $\hbar\omega_P$ dependent Penn gap and Fermi energy[12], is given by

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \quad (2)$$

and

$$E_P = 2.2948(\hbar\omega_P)^{4/3} \quad (3)$$

Polarizability, α obtained using the relation[13]

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (4)$$

where S_0 = constant for a particular material which is given by

$$S_0 = 1 - \left[\frac{E_P}{4E_P}\right] + \frac{1}{3}\left[\frac{E_P}{4E_P}\right]^2 \quad (5)$$

Density is one of the basic physical property by which a specimen may be characterized. The density of benzoyl glycine crystal was calculated by using the equation[6]

$$\rho = \frac{MZ}{N_A}abc \quad (6)$$

where M = molecular weight, Z = number of molecules in unit cell, N = Avogadro number and V = volume of the unit cell.

Unit cell volume V of benzoyl glycine crystal was calculated by using the equation. The crystal system for benzoyl glycine orthorhombic so that volume of orthorhombic system is given by

$$V = abc \quad (7)$$

Unit cell mass, M obtained using the relation[14]

$$M = 0.60226V\rho \quad (8)$$

where ρ = density, V = Unit cell volume.

Optical absorption studies: The optical absorption spectrum of benzoyl glycine single crystal was recorded in the wavelength region ranging from 200-1000 nm using VARIAN CARY 5E spectrophotometer and is shown in Fig. 4. For optical fabrications, the crystal should be highly transparent in a considerable region of wavelength[15,16]. The UV cut off wavelength for the grown crystal was found to be 240 nm which makes it a potential material for device fabrication. The optical absorption coefficient was calculated using the following relation.

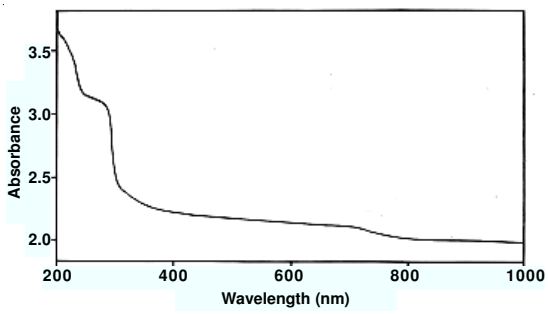

Fig. 4. Optical absorption spectrum of benzoyl glycine crystal

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \quad (9)$$

where T = transmittance and d = thickness of the crystal. As a direct band gap material, the crystal under study has an

absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (10)$$

where E_g in the optical band gap of the crystal and A is a constant. The plot of variation of spectral dependence $(\alpha h\nu)^2$ *versus* photon energy (hν) is shown in Fig. 5 and the band gap is found to be 3.75 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region[17].

Determination of optical constants: The optical constant (n, k) are determined from the transmission (T) and reflection (R) spectrum based on the following relations[18].

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \quad (11)$$

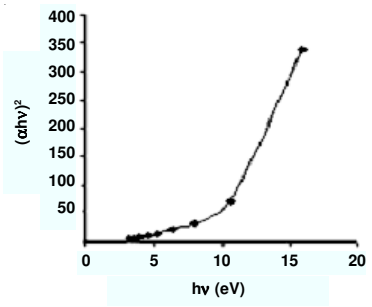

Fig. 5. $(\alpha h\nu)^2$ *versus* hν for benzoyl glycine single crystals

where t = thickness and α is related to extinction coefficient k by

$$K = \frac{\alpha\lambda}{4\pi} \quad (12)$$

The refractive index (n) can be determined from the reflectance (R) data using the relation[19].

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (13)$$

where R the reflectance in terms of absorption coefficient can be written

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \quad (14)$$

From the above equation, the refractive index n can also be derived as

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (15)$$

Fig. 6 shows the plot of extinction coefficient (k) as a function of wavelength. From the graph, it is clear that extinction coefficient (k) value increases with increase in the photon energy. The dependence of refractive index (n) on the wavelength is shown in Fig. 7. It is clear from the graph that refractive index decreases as the photon energy increases. Thus, the extinction coefficient (k) and refractive index (n) depends on the photon energy. Hence by tailoring the photon energy, one can achieve the desired material for device fabrication.

Dielectric constant measurement: Single crystals of benzoyl glycine of thickness 1 mm were subjected to dielectric studies at room temperature for various frequencies ranging from 50 Hz to 5 MHz using HIOKI 3532-50 LCR HITESTER. The dielectric constant is evaluated using the relation

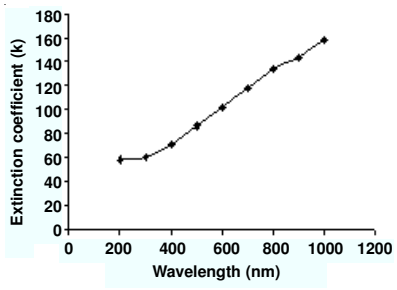

Fig. 6. Extinction coefficient (k) *versus* wavelength

$$\varepsilon' = \frac{Cd}{\varepsilon_0} A \quad (16)$$

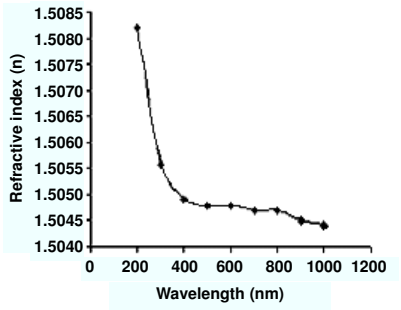

Fig. 7. Refractive index (n) *versus* wavelength (nm)

where d = thickness and A = area of the cross section of the grown crystal. The variation of dielectric constant as a function of frequency at room temperature is shown in Fig. 8. From the graph, the dielectric constant is found to decrease with increase in frequency. The dielectric loss is studied as a function of frequency at room temperature is shown in Fig. 9. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant.

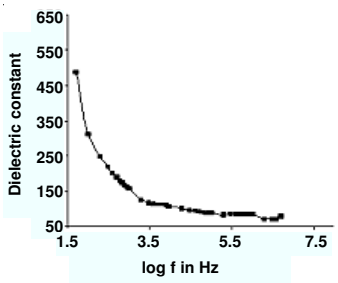

Fig. 8. Variation of dielectric constant *versus* log f

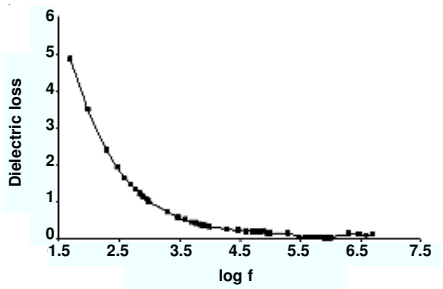

Fig. 9. Variation of dielectric loss *versus* log f

Electrical conductivity studies: Electrical conduction takes place as a result of electron jump from the low valence state of high valence state as the movement of ions. The dc electrical conductivity of the grown crystal at room temperature was determined using the relation.

$$\sigma = \frac{t}{RA} \quad (17)$$

where R = total resistance of the sample, t = thickness of the sample and A = area of the cross section of the grown crystal. The variation with temperature of dc conductivity is shown in Fig. 10. From the graph, the conductivity is seen to decrease with increase in frequency. The low value of electrical conductivity in the crystals is due to the mobility of the charge carriers by ion size, which leads to change in the electronic band structure[20].

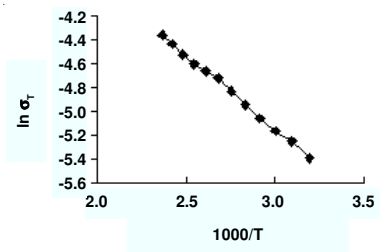

Fig. 10. Variation of ln σT with 1000/T for benzoyl glycine crystal

Photoconductivity studies: Using Keithley 485 picoammeter, photoconductivity studies crystals were carried out on benzoyl glycine single crystal. The dark current was recorded for the sample by not allowing any radiation to fall on the sample and by varying the applied field from 105-1578 V/cm. To measure the photocurrent, the sample was illuminated with a halogen lamp (100 W) containing iodine vapour by focusing a spot of light on the sample with the help of a convex lens[21]. The applied voltage was increased from 105-1578 V/cm and the corresponding photocurrent was recorded. Both photocurrent and dark current are plotted as a function of the applied voltage (Fig. 11). The dark current increases with increase in applied field. The dark current at any instant is found to be greater than that of the photocurrent. Hence the crystal is found to possess negative photo conduction[22]. The negative photoconductivity in the solid is due to the reduction in the number of charge carriers of their life time, in the presence of radiation.

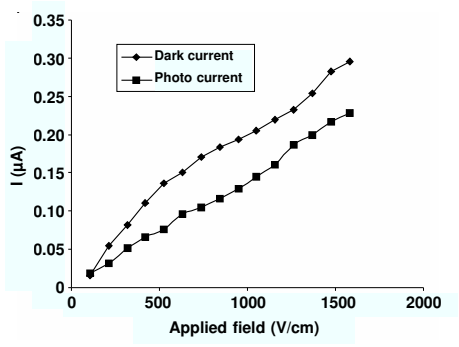

Fig. 11. Field dependent conductivity

According to this model, the forbidden gap in the material contains two energy levels in which one is situated between the Fermi level and conduction band while the other is located close to valence band. The second state has high capture cross section for electrons and holes. As it captures electrons from the conduction band and the holes from the valence band, the number of charge carries in the conduction band gets reduced and the current decrease in the presence of radiation.

Conclusion

Single crystals of benzoyl glycine were grown by slow evaporation solution growth method by using acetone as a solvent. The grown crystals were characterized by single crystal XRD analysis and confirmed that the crystal belong to orthorhombic system with space group $P2_12_12_1$. The physical parameters such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability have been determined for the grown crystal. The band gap energy for the grown crystal is found to be 3.75 eV. The optical investigations such as extinction coefficient (k) and refractive index (n) indicates the high transparency of the crystal and confirms its suitability for optical device fabrication. The dielectric constant was studied as a function of frequency at room temperature and dc electrical conductivity of the grown crystal was determined by using graph. The photoconductivity study reveals that the crystal has negative photoconductivity.

REFERENCES

1. A. Corenco, J. Jerphagon and A. Perigand, *J. Chem. Phys.*, **66**, 3806 (1977).
2. P.M. Rentzepis and Y.H. Pao, *Appl. Phys. Lett*., **6**, 156 (1964).
3. R. Yu. Orlov, *Soviet. Phys*., **11**, 410 (1966).
4. H. Ringertz, *Acta Cryst.*, **27B**, 285 (1971).
5. H.S. Nagaraja, V. Upadhyaya, P.M. Rao, P.S. Aithal and A.P. Bhat, *J. Cryst. Growth*, **193**, 674 (1998).
6. N. Vijayan, R.R. Babu, R. Gopalakrishanan, P. Ramasamy, M. Ichimura and M. Palanichamy, *J. Cryst. Growth*, **273**, 564 (2005).
7. K. Selvaraju, R. Valluvan and S. Kumararaman, *Mat. Lett*., **60**, 1549 (2006).
8. M.N. Bhat and S.M. Dharmaprakash, *J. Cryst. Growth*, **243**, 526 (2002).
9. E. Ramachandran and S. Natarajan, *Cryst. Res. Tech.*, **37**, 1274 (2002).
10. E. Ramachandran and S. Natarajan, *Cryst. Res. Tech.*, **40**, 765 (2005).
11. V.R. Thalladi, M. Nusse and R. Boese, *J. Am. Chem. Soc.*, **122**, 9227 (2000).
12. N.M. Ravindra, R.P. Bharadwaj, K.S. Kumar and V.K. Srivastava, *Infrared Phys.*, **21**, 369 (1981).
13. N.M. Ravindra and V.K. Srivastava, *Infrared Phys*., **21**, 369 (1981).
14. J.P. Dougherty and S.K. Kurtz, *J. Appl. Cryst*., **9**, 145 (1976).
15. V. Krishnakumar and R. Nagalakshmi, *Spectrochim. Acta*, **61A**, 499 (2005).
16. V. Krishnakumar and R.J. Xavier, *Spectrochim. Acta*, **60A**, 709 (2005).
17. D.D.O. Eya, A.J. Ekpunobi and C.E. Okeke, *Acad. Open Internet J*., 17 (2006).
18. R.E. Denton, R.D. Campbell and S.G. Tomlin, *J. Phys.*, **D5**, 852 (1972).
19. A. Ashour, N.E.L. Kadry and S.A. Mahmoud, *Thin Solid Flims*, **269**, 117 (1995).
20. J.H. Lee, S.M. Yoon, B.K. Kim, H.W. Lee and H.S. Song, *J. Mater. Sci.*, **37**, 1165 (2002).
21. F.P. Xavier, A.R. Inigo and G.J. Goldsmith, *J. Porphyr. Phthalocy.*, **3**, 679 (1999).
22. V. Joseph, S. Gunasekaran and V. Santhanam, *Bull. Mater. Sci*., **26**, 383 (2003).