Semnan University

Progress in Physics of Applied Materials

journal homepage: https://ppam.semnan.ac.ir/

Growth and Characterization of 1, 2, 3- Benzotriazole 2-chloro 4-nitrobenzoic Acid (BCNB) Single Crystal for NLO Applications

B. Sahaya Infant Lasalle *, T. Kamalesh, P. Karuppasamy, M. Senthil Pandian, P. Ramasamy

SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai-603110, Tamil Nadu, India.

ARTICLE INFO

Article history:
Received: 7 April 2022
Revised: 9 June 2022
Accepted: 10 June 2022

Keywords:
Nonlinear optics
Single crystal
PXRD
UV-Visible-NIR
Z-scan

ABSTRACT

The organic single crystal of 1,2,3- benzotriazole 2-chloro 4-nitrobenzoic acid (BCNB) was successfully grown by slow evaporation solution method using methanol as a solvent. The single crystal X-ray diffraction was used to analyse the lattice cell parameters of the grown BCNB crystal. The cell and lattice parameters of the BCNB crystal confirms the formation of monoclinic crystal structure with the P21/n space group. The diffraction planes (h,k,l) were determined by the powder X-ray diffraction (PXRD), which is in good agreement with the corresponding CIF file. The BCNB crystal exhibits good optical transmittance in the entire visible region, which is evident from the UV-Visible-NIR analysis. The photoconductivity analysis exposes the negative photoconductive nature of BCNB crystal. The self-defocusing and reverse saturable absorption effects of the BCNB is evident from the Z-scan experiment, which is prescribed in closed and open apertures and these results were used to deduce the 3rd order NLO parameters like n_2, β and ($\chi^{(3)}$).

1. Introduction

In the past few years, researches on crystals have been intensified due to their extensive applications in optical data storage, photonics, optical switching and electro-optical amplitude modulations, etc [1-2]. In particular, the organic NLO materials has gained limelight because of their capability of generating the second and third order harmonic frequency plays. For example: the organic NLO crystals namely DKDP, BBO and KTP are mostly incorporated in devices such as Q-switching or electro-optical amplitude modulators due to their optoelectronic properties [3]. The organic crystals exhibits tremendously large NLO coefficients and structural diversity when compared to other inorganic counterparts. The organic crystal consists of polar and chiral types of aromatic rings and it possesses several benefits such as high optical nonlinearity, high molecular polarizability, large band gap and high laser damage threshold. One of the main advantages of organic materials is that their structure can be modified to get the desired NLO properties. The origin of nonlinearity in organic NLO materials is due to the presence of delocalized π-electron connecting donor and acceptor groups, which can enhance the necessary asymmetric polarizability [4].

A benzotriazole is a triazole derivative that has a benzene ring linked to a trizole molecule. The triazole is having π-π stacking conjugated interactions along with three nitrogen atoms to form hydrogen and coordination bonds easily. The benzotriazole compound is an important nonlinear optical material with strong UV absorption and non-covalent interactions results in their good optical properties and also second harmonic generation (SHG) properties [5]. The acid compound 2-chloro-4-nitrobenzoic acid (CNBA) is a derivative of benzoic acid groups, containing one electrophilic group, which accepts a pair of electrons to form a covalent bond by accepting a pair of e^-s as well as labile group associated with an aromatic ring. In fact, 2c4n is a historically significant polymorphism molecule since this was one of the samples employed by Ebert and Gottlieb in 1952 to illustrate that polymorphs can be recognised or distinguished by the IR spectra. [6]. CNBA and its isomers are well-known active antiviral agent medicinal materials [7].

In the present work, the organic BCNB crystal was grown by the conventional method for the first time. The grown BCNB crystal was characterized by SXRD, PXRD, UV-Visible-NIR, Photoconductivity and Z-scan analysis.

2. Synthesis, Crystal growth and Morphology

BCNB crystal was grown by dissolving the raw materials of 1,2,3-benzotriazole and 2-chloro-4-nitrobenzoic acid (BCNB) in equal molar ratio (1:1) using methanol as a solvent. The prepared solution was continuously stirred for almost 8 hours. The solution was filtered using Whatman filter paper and then poured into a glass dish. A thick polythene covering was placed over the glass dish and small holes was punched in the top portion

* Corresponding author. Tel.: +91 7448617868
E-mail address: sahayainfant@gmail.com

DOI: 10.22075/ppam.2022.26678.1025

for controlled solvent evaporation. After some days, BCNB multi-crystals gets nucleated and starts the formation of crystal inside the glass dish. Further, the BCNB crystals were recrystallized 2 to 3 times for improving the crystal quality. Finally, the transparent BCNB single crystal was obtained after a period of 21 days. The reaction scheme of BCNB compound is shown in Figure 1. The photograph of the grown BCNB crystal is exhibited in Figure 2(a). Fig. 2(b) shows the morphology of BCNB crystal determined using a WinXMorph programme.

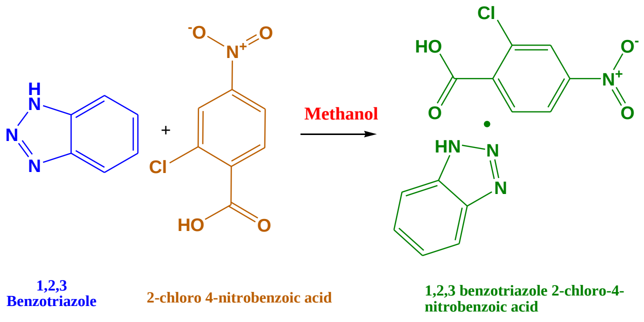

Fig. 1. Reaction scheme of BCNB compound.

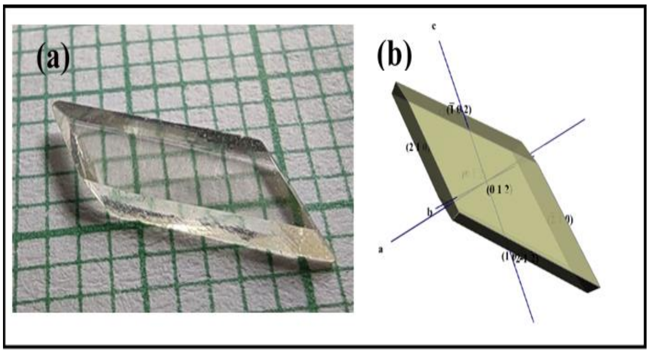

Fig. 2. (a) As grown BCNB single crystal and (b) its Morphology.

3. Characterization techniques

The Single Crystal XRD measurements was carried out using Bruker AXS kappa APEX II CCD Diffractometer, which possesses graphite-monochromated Mo-kα radiation (λ=0.71073Å). The PXRD pattern was obtained using PANalytical empyrean X-ray diffractometer. Shimadzu, UV-2600 spectrometer was operated in the range between 200-1000 nm to find the optical bandgap. The photoconductivity measurements were done using Keithley picoammeter (MODEL M6487). The 3rd order NLO properties were examined using the Z-scan method and it was done using a continuous wave (CW) He-Ne laser (21mW) with a wavelength (λ) = 632.8 nm.

4. Results and discussion

4.1. Single crystal X-ray diffraction

From the SXRD measurements, it is confirmed that the grown BCNB crystal belongs to the monoclinic crystal system and centrosymmetric P21/n space group. The lattice parameters of BCNB crystal are a =7.059Å, b =11.77 Å, c = 16.09 Å, v = 2367 Å3, α=90°, β=93.8° and γ=90°. The acquired results are quite similar to the previously reported values [8].

4.2. Powder X-ray diffraction analysis

The well grained crystalline powder sample of BCNB was subjected to PXRD measurement in the range between 5° to 80° at ambient temperature. The PXRD spectrum of BCNB is illustrated in Figure 3. The respective (hkl) planes were identified by comparing the CIF file (CCDC NO: 198950) data using mercury software. The observed peaks are in the (0 1 2), (1 1 0), (1 0 -2), (1 0 -3), (0 3 1), (2 1 0) and (2 1 -2) planes. The obtained results were in good agreement with the previously reported values [8]. The sharp PXRD peaks indicates the crystallites are properly oriented without imperfections.

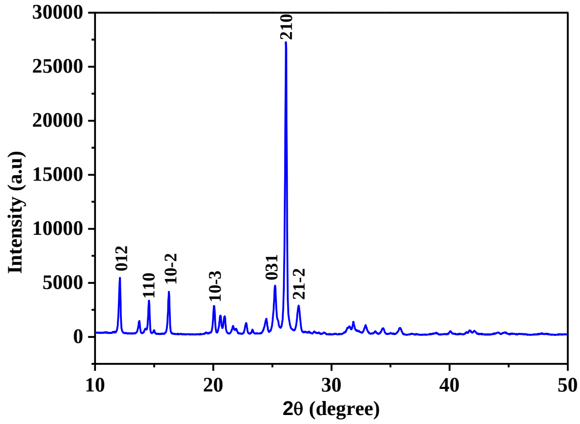

Fig. 3. PXRD pattern of BCNB.

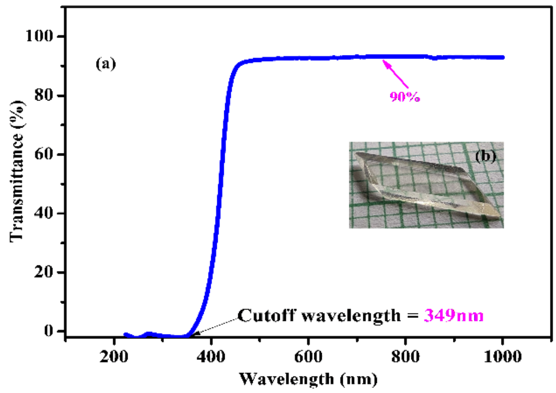

Fig. 4. (a) UV-Visible-NIR transmission spectrum of BCNB and (b) the photograph of BCNB sample (inset).

4.3. Optical transmission analysis

Grown crystal transmittance is one of the most essential parameters of an NLO material for device applications [9]. The transparent BCNB crystal (1mm thickness) was pacified to UV-Visible-NIR analysis in the wavelength (λ) range between 200- 1000 nm. Fig. 4 shows the UV-Visible-NIR spectrum for BCNB crystal. The BCNB crystal exhibits well reduced scattering from crystal point and line imperfections, which may account for the increase in the percentage of transmission. From the UV-Visible-NIR spectrum, it is known that the BCNB has a maximum transmittance of 90% and lower cut-off wavelength of 349 nm. The absorption that exists at 349 nm is associated with the n-π* electronic transitions that takes place in the benzotriazole ring. The wide transmittance window between 380 and 1000 nm creates an advantage for a number of optical applications [10].

4.4. Photoconductivity studies

Photoconductive phenomena plays an important role in photo sensors, guided weapons, radiation measurements and fiber optics communication [11]. When an electric potential is applied to a solid material, it reveals the gain or loss of photoelectrons (charge carriers) in the occurrence of radiation (V). To make interaction between the electrodes and the crystal surface, silver paint was coated on the crystal surface. The dark current (I_d) was dignified by applying a voltage to the electrodes in steps of 1 V/s from 0 to 50 V (DC) without allowing any radiation. The photocurrent (I_p) was measured (50 W halogen lamp) through the same voltages. The I_d and I_p graph have been plotted as a function of applied voltage as shown in Figure 5. The I_p values observed was lower than the I_d values, since the quantity of charge carriers or their duration reduces the occurrence of radiation. Which confirms the negative photoconductive nature of the grown BCNB single crystal. The Stockmann model was used to clarify the phenomenon of negative photoconductivity [12-13]. Based on this, many reports have remarked on the negative photoconductivity nature of single crystals such as P4HBS [14], AMT [15], and LAM [16] and these are all materials mostly used for UV and IR detector applications [17].

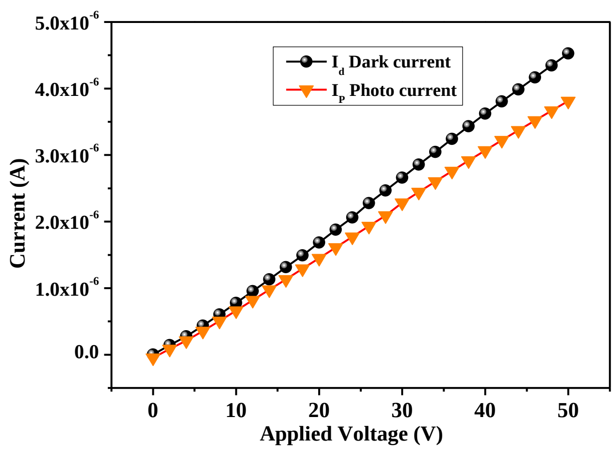

Fig. 5. Photoconductivity of BCNB crystal.

4.5. Z-scan analysis

The crystalline material of BCNB was analysed by the Z-scan method, which is used to determine the 3rd order NLO properties namely the nonlinear refractive index (n_2), absorption co-efficient (β), and third order susceptibility ($\chi^{(3)}$). He-Ne laser (21 mW) source with a λ of 632.8 nm was used as source. The BCNB crystal was mounted vertically on a holder with a thickness (L) of 1 mm, the minimum thickness of the sample by which the laser can be passed through the material smoothly. The programmable stepper motor system controls the movement of the sample holder at the focal point and the corresponding transmittance intensity was inscribed by a photodetector. The recognized open aperture Z-scan system, which was invented by Bahae et al [18]. The technique is more sensitive and experimentally easy way of detecting nonlinear absorption. The open and closed aperture Z-scan curves are illustrated in Figure 6 respectively. The n_2 and β of BCNB crystal were calculated from the open and closed aperture data respectively. The normalised transmittance vs sample location, estimated from the closed and open aperture measurements and their respective n_2 and β calculations were done [18-19]. From the acquired values, the real (Re ($\chi^{(3)}$)) and imaginary Im ($\chi^{(3)}$) susceptibility of the BCNB material is found as 8.14347×10^{-10} and is 2.3804×10^{-8} (esu) respectively. The third order susceptibility of the BCNB was determined by the following equation:

$$\chi^{(3)} = \sqrt{(\mathrm{Re}\,\chi^{(3)})^2 + (\mathrm{Im}\,\chi^{(3)})^2} \quad (1)$$

The $\chi^{(3)}$ value of BCNB was calculated as 2.38179×10^{-8} esu. The obtained susceptibility value is high compared with other NLO materials [20-25]. The self-defocusing nature of any crystal is shown by the negative sign of n_2, which is mainly executive for the impact of the photorefractive negative lens. This might be helpful in devices application like inspecting devices, night vision devices, telescopes, and gun sights [26].

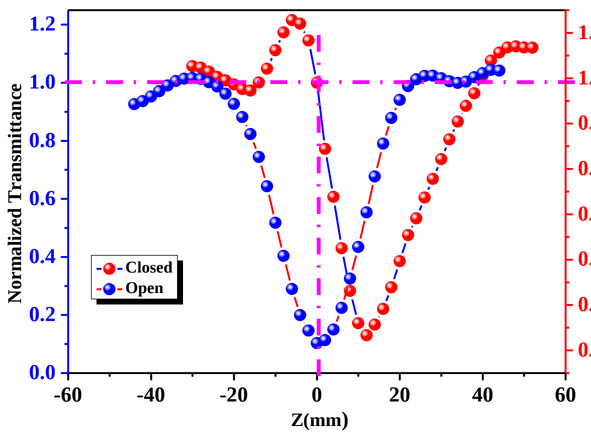

Fig. 6. Open and Closed aperture spectrum of BCNB.

5. Conclusion

Good quality single crystal of BCNB was grown by conventional slow evaporation solution method. The transparent colorless crystal with 7 × 6 × 4 mm³ dimensions. The BCNB crystal belongs to the centrosymmetric space group $P2_1/n$, which was determined by the SXRD. The different (hkl) planes were indexed by PXRD spectrum. From the PXRD analysis crystalline phase, purity of material was identified. The spectrum of UV-Visible-NIR transmittance displays that the BCNB crystal has high transparency and used for optical applications. The negative photoconductivity present in the title material was confirmed by photoconductivity study. The Z-scan techniques n_2, β and $\chi^{(3)}$ indicates the capability of generating third harmonics. The grown BCNB crystal's $\chi^{(3)}$ value is 2.38179×10^{-8} esu. It is concluded that BCNB is a suitable candidate for optoelectronic applications.

Acknowledgements

The present work is supported by SSN Research centre, SSN college of Engineering. The author Sahaya Infant Lasalle B thanks SSN for providing SSN Senior Research Assistant (SRA) fellowship financial support is hereby gratefully acknowledged.

References

[1] A. Senthil, P. Ramasamy, Investigation on the SR method growth, etching, birefringence, laser damage threshold and thermal characterization of strontium bis (hydrogen L-malate) hexahydrate single crystal, J. Cryst. Growth. 401 (2014) 200-204.

[2] B. Babu, J. Chandrasekaran, and S. Balaprabhakaran, Growth, structural, spectral, optical and electrical properties of 2-aminophenol single crystals, Optik. 125 (2014) 3005-3008.

[3] N. Prabavathi, A. Nilufer, & V. Krishnakumar, FT-IR, FT-Raman and DFT quantum chemical study on the molecular conformation, vibrational and electronic transitions of 1-(m-(trifluoromethyl) phenyl) piperazine. Spectrochim. Acta A Mol. Biomol. 121 (2014) 483-493.

[4] P. Vijayakumar, G. A. Babu, & P. Ramasamy, Synthesis, crystal growth and characterization of nonlinear optical organic crystal: p-Toluidinium p-toluenesulphonate. Materials Research Bulletin, 47 (2012) 957-962.

[5] A. Thirunavukkarsu, S. Sudhahar, G. Maheshwaran, T. Sujatha, P. R. Umarani & R. M. Kumar, Synthesis, growth, structural, optical, thermal and mechanical properties of bis-benzotriazole trichloroacetic acid single crystals. Bull. Mater. Sci. 43 (2020) 1-11.

[6] C. B. Aakeröy, A. M. Beatty, B. A. Helfrich, & M. Nieuwenhuyzen, Do polymorphic compounds make good cocrystallizing agents? A structural case study that demonstrates the importance of synthon flexibility. Crystal growth & design, 3 (2003) 159-165.

[7] K. S. Ramesh, M. Saravanabhavan, M., Rajkumar, D. Edison, M. Sekar, S. Muhammad, & A. G. Al-Sehemi, Synthesis, growth, structural, thermal, third order nonlinear and computational studies of organic single crystal: 2-Amino-4-picolinium 2-chloro-4-nitrobenzoate, Opt. Mater. 96 (2019) 109341.

[8] H. Ishida, T. Fukunaga, and S. Kashino. "The 1: 1 complex of 2-chloro-4-nitrobenzoic acid and 1, 2, 3-benzotriazole." Acta Crystallographica Section E: Structure Reports Online, 58 (2002) 1083-1084.

[9] V.G. Dmitriev, G.G. Gurzadyan, D.N. Nikogosyan, Handbook of nonlinear optical crystals, Springer, 2013.

[10] M.K. Kumar, S. Sudhahar, P. Pandi, G. Bhagavannarayana, & R. M. Kumar, Studies of the structural and third-order nonlinear optical properties of solution grown 4-hydroxy-3-methoxy-4′-N′-methylstilbazoliumtosylate monohydrate crystals, Opt. Mater. 36 (2014) 988-995.

[11] B.M. Boaz, R.S. Selvaraj, K. S. Kumar, S.J. Das, Growth, microhardness, dielectric and photoconductivity characterization of a highly polarizable NLO material: Sodium p-nitrophenolate dehydrate (NO 2- C6H4-Ona. 2H2O), Indian J. Phys. 83 (2009) 1647-1657.

[12] F. Stockmann, Negative Photoeffekte in halbleitern, Zeitschrift fur Physik, Bd. 143 (1955) 348-356.

[13] P.R. Crippa, V. Cristofoletti, N. Romeo, A band model for Melanin deduced from optical absorption and photoconductivity experiments, Biochim. Biophys. Acta. 538 (1978) 164-170.

[14] P. Karuppasamy, Muthu Senthil Pandian, and P. Ramasamy "Crystal growth and characterization of third order nonlinear optical piperazinium bis (4-hydroxybenzenesulphonate) (P4HBS) single crystal." Journal of Crystal Growth, 473 (2017) 39-54.

[15] V. Sivasubramani, Muthu Senthil Pandian, and P. Ramasamy. "Comparative investigations of nonlinear optical (NLO) ammonium D, L-tartrate (AMT) single crystals grown by conventional and unidirectional method." AIP Conference Proceedings, 1 (2015) 100017.

[16] A. Gupta, R. Rahman MK, R. O. M. U. Jauhar, V. Sivasubramani, N. Vijayan, G. Vinitha, and Lekha Nair. "Growth of L-asparagine monohydrate and its structural, optical, mechanical, thermal and electrical studies for nonlinear optical applications." Materials Research Express 6, 12 (2020) 125119.

[17] V.N. Joshi, Photoconductivity, Marcel Dekker, New York, 1990.

[18] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, Quant. Electron. 26 (1990) 760–769.

[19] E.W. Van Stryland, M. Sheik-Bahae, Z-scan measurements of optical Nonlinearities Charact. Tech. Tabul. Org. Nonlinear Mater. 60 (1998) 655–692.

[20] K. S. Ramesh, M. Saravanabhavan, M. Rajkumar, D. Edison, M. Sekar, S. Muhammad & A. G. Al-Sehemi, Synthesis, growth, structural, thermal, third order nonlinear and computational studies of organic single crystal: 2-Amino-4-picolinium 2-chloro-4-nitrobenzoate, Opt. Mater. 96 (2019) 109341.

[21] L. Chandra, J. Chandrasekaran, K. Perumal, & B. Babu, Third order nonlinear optical and electrical properties of new 2-aminopyridinium 2-chloro 4-nitrobenzoate single crystals, Optik. 127 (2016) 3206-3210.

[22] A. Thirunavukkarsu, S. Sudhahar, G. Maheshwaran, T. Sujatha, P. R. Umarani, & R. M. Kumar, Synthesis, growth, structural, optical, thermal and mechanical properties of bis-benzotriazole trichloroacetic acid single crystals, Bull. Mater. Sci. 43 (2020) 1-11.

[23] V. Sivasubramani, A. Raja, P. Karuppasamy, K. Ramachandran, Muthu Senthil Pandian, & P. Ramasamy, Crystal growth and characterization of semi-organic 2-amino-5-nitropyridinium bromide (2A5NPBr) single crystals for third-order nonlinear optical (NLO) applications, Appl. Phys. Res. A. 123 (2017) 780.

[24] V. Parol, A. N. Prabhu, M. A. Taher, S. R. G. Naraharisetty, N. K. Lokanath & V. Upadhyaya, A third-order nonlinear optical single crystal of 3, 4-dimethoxy-substituted chalcone derivative with high laser damage threshold value: a potential material for optical power limiting, J. Mater. Sci: Mater. Electron. 31 (2020) 9133-9150.

[25] D. Wang, T. Li, S. Wang, J. Wang, Z. Wang, X. Xu, & F. Zhang, Study on nonlinear refractive properties of KDP and DKDP crystals. RSC Adv. 6 (2016) 14490-14495.

[26] Y.S. Zhou, E.B. Wang, J. Peng, J. Liu, C.W. Hu, R.D. Huang, X. You, Synthesis and the third-order optical nonlinearities of two novel charge-transfer complexes of a heteropoly blue type (C9H7NO=quinolin-8-ol) and (phen) 3 H7PMo12O40. Ch3CN. H2O (Phen=1, 10-phenanthroline). Polyhedron 18 (1999) 1419–1423.