Synthesis and Characterization of Piperazinium Benzoate Crystal: A Third Order Nonlinear Optical Limiting Material

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Abstract. Organic charge transfer molecule of Piperazinium benzoate single crystal was crystallized by slow evaporation technique. The single crystal XRD was carried out to determine the cell parameter values. The FTIR and FT-Raman spectral studies are used to confirm the presence functional groups. The absorption spectrum shows that the crystal possesses minimum absorption between 200 to 800 nm. The third order optical absorption and optical refractive index were calculated by Z scan technique. Optical limiting method is used to find the limiting behavior of PBA crystal.

INTRODUCTION

Organic substances are required for countless nonlinear optical applications such as high information processing, wave guide, fabrication, optical communication and optical storage [1][2]. Organic materials have more efficient nonlinear property, when compared to inorganic counterpart [3]. The presence of delocalized π electrons (donor-π-acceptor) system in organic substances relating donor and acceptor groups enhances the nonlinear optical and electro optic effect [4][5]. The advantage of organic materials over inorganic materials is that it allows the researchers to fine tune the chemical structure and properties for desired NLO applications.

Piperazine is an organic compound which contains N-H bonds in equilateral positions and resides at the crystallographic inversion center. Crystal containing piperazinium cations play an important role in the complex molecule for their hydrogen bond interaction and vibrational investigations [6]. In the present work, the crystal growth, FTIR, FT Raman, third order nonlinear optical studies, UV analysis and limiting response of piperazinium benzoate crystal are reported.

PBA CRYSTAL SYNTHESIS

The starting material Piperazine and Benzoic acid were taken in equimolar ratio and dissolved in 2D water and continuously stirred. The solution was then filtered to remove the impurities and transferred to the beaker and the solution was allowed crystallize by slow evaporation method under room temperature. The growth period of crystals was 25-30 days. The prominent planes (010), (011), (0-1-1), (0-10), (11-1), (123), (-1-11) and (-1-2-3) are identified from morphology of PBA crystal. The photograph and morphology of the PBA crystal is shown in Fig. 1.

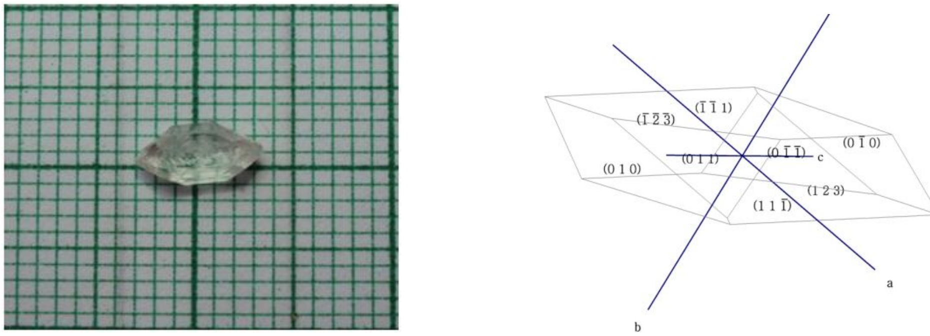


FIGURE 1. Photograph and Morphology of PBA crystal.

RESULTS AND DISCUSSION

Single crystal X- ray diffraction

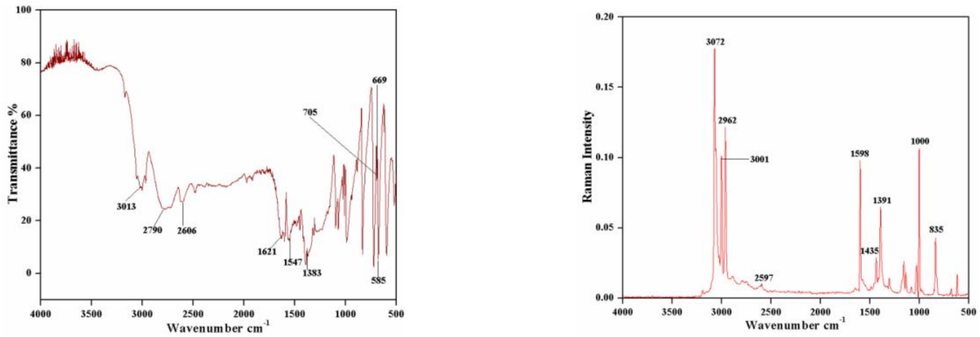
The XRD data of Piperazinium Benzoate indicated that it crystallizes in orthorhombic system with Pbca centrosymmetric space group. The lattice parameters values are presented in Table 1 and the obtained values are in agreement with the reported values

Table 1. *Unit cell parameters of PBA crystal*

Cell parameters	Present work	Reported value
a ( )	8.33	8.34
b ( )	8.33	8.24
c ( )	25.03	24.67
Crystal system	Orthorhombic	Orthorhombic

FTIR and FT Raman Studies

The FTIR spectrum is shown in Fig 2(a) and FT Raman spectra is shown in Fig 2(b). The bands which are noticed in the measured region are due to the internal vibrations of both N-H...O and C-H...O types of hydrogen bond in the lattice. The N-H...O interaction taking place between the molecules in the crystalline network can be observed from the band position of NH stretching vibrations. These bands are strong and broad in infrared band at 3013 cm^{-1} and weak and sharp Raman band at 3001 cm^{-1}. The CH stretching vibration of Piperazine produce medium intensity peak at 2597 cm^{-1} for Raman and infrared counterparts are seen at 2606 cm^{-1}. Bands in Raman spectrum at 1435 cm^{-1} is assigned to CH_2 deformation vibration and the same vibration is occurred at 1383 cm^{-1} for infrared bands. Symmetric vibration of ionized carboxylate groups are observed at 1391 cm^{-1} for Raman and 1383 cm^{-1} for infrared.



(a) (b)

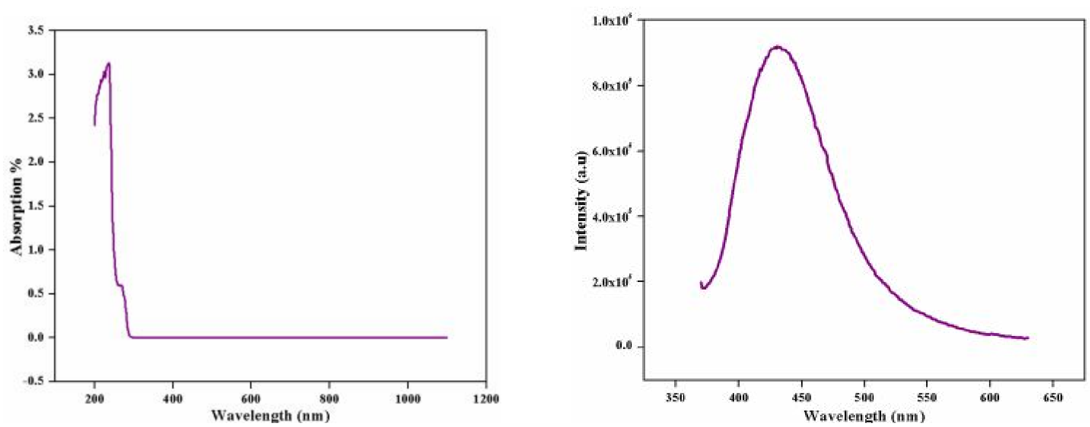
FIGURE 2. (a) FTIR spectrum of PBA crystal, (b) FT Raman spectrum of PBA crystal.

UV Visible analysis & Fluorescence spectral analysis

The absorption spectrum of the grown PBA crystal is shown in Fig 3(a). The spectrum indicates that the crystal is transparent in the visible region and has a lower cut off wavelength at 235 nm. The optical band gap of PBA crystal is 5.2 eV and it is calculated using the relation,

$$E_g = \frac{hc}{\lambda} \text{ (in eV)} \tag{1}$$

where h is the Planck constant, c is the velocity of light and λ is the cut off wavelength. Fluorescence is the continuous emission of light radiation by absorption of photons. Fluorescence spectrum of grown PBA crystal was recorded at room temperature by exciting at 300 nm. The emission peak was observed at 430 nm is shown in Fig 3(b). The broad peak at 430 nm is in visible region (violet emission). The result shows that PBA crystal may have suitable applications in violet emitting diodes.



(a) (b)

FIGURE 3. (a) UV visible spectrum of PBA crystal, (b) Fluorescence spectrum of PBA crystal

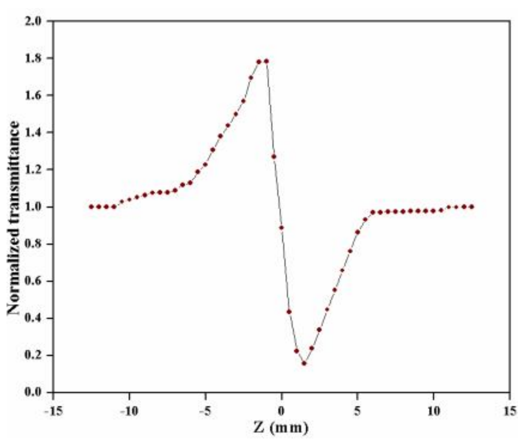
Nonlinear optical studies

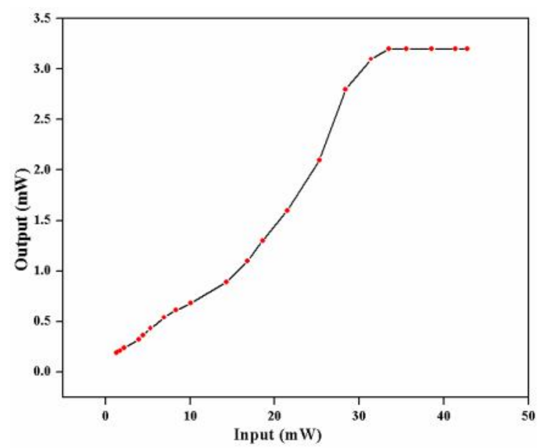
The third-order nonlinear optical properties were investigated by standard Z scan technique [6]. This technique is widely used to evaluate both magnitude and sign of nonlinear refractive index (n_2) and absorption coefficient (β) of the crystal. The absorption coefficient (β) is determined from the open aperture setup and n_2 is obtained from the closed aperture setup, also the ratio of closed to open aperture is taken to get pure nonlinear refraction [7] is shown in Fig 4(a). The peak-to-valley normalized transmission suggest that the crystal has a negative refractive index, which reveals the self defocusing effect [8]. The calculated nonlinear refractive index (n_2), absorption coefficient (β) and third order nonlinear susceptibility (χ^3) are -7.73 x 10^{-8} cm^2/W, 0.08 x 10^{-4} cm/W and 7.53 x 10^{-6} esu respectively.

The third order optical parameters such as refractive index (n_2), absorption coefficient (β) and third order susceptibility (χ^3) of the crystal are calculated. The obtained results imply that the PBA crystal possesses negative refractive index. Thus the PBA crystal is good candidate for optical limiting, optical switching and NLO applications.

Optical limiting studies

Optical limiter is a device used to transmit low intensity light, while blocking laser radiation with high irradiance. Optical limiting behaviour of PBA crystal is shown in Fig 4(b). From the spectrum, transmitted output intensity is varying linearly with low input intensity and at high incident intensities it become nonlinear, by further increasing the input intensity, the output transmittance become constant. The limiting threshold for saturation and output clamping values are found to be 33.5 mW and 3.2 mW respectively. Thus PBA crystal is suitable for nonlinear application such as solid state optical sensors.





(a) (b)

FIGURE 4. (a) Closed/Open aperture spectrum of PBA crystal, (b) Optical limiting spectrum of PBA crystal

CONCLUSION

Single crystal of Piperazinium Benzoate (PBA) was grown by slow evaporation technique and the crystal belongs to orthorhombic system. The functional groups were confirmed by FTIR and FT Raman analyses. Grown PBA crystal is transparent in the entire visible region and the lower cut off wavelength and band gap energy was found to be 235 nm and 5.2 eV. The Z-scan technique was carried out to investigate the third order nonlinear optical property of the grown crystal. The interesting applications of PBA crystal is in optical limiting in low intensity controller for continuous wave (cw) lasers, which could be used to protect optically sensitive components with different damage thresholds. It is concluded that the PBA crystal can be used for device fabrication.

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