RESEARCH ARTICLE

Studies on the Growth, Structural, Optical, Mechanical and Nonlinear Optical Properties of Piperazinium Bis (Salicylate) Single Crystal

B. Valarmathi[1], R. Premanand[2], G. Vinitha[3], R. Mohan Kumar[1,*]

[1]Department of Physics, Presidency College, Chennai 600 005, India
[2]Department of Science and Humanities, Sri Sairam Engineering College, Chennai 600 044, India
[3]Division of Physics, School of Advanced Sciences VIT, Chennai 600 127, India

*Corresponding author: E-mail: mohan66@hotmail.com

Organic materials have outstanding upturn striking high nonlinear optical properties. One such NLO material of good quality single crystal of protonated Piperazinium bis (Salicylate) (PSL) was synthesized by slow solvent evaporation solution growth technique. XRD studies analyzed that the PSL crystallize monoclinic system with space group $P2_1/n$. FTIR spectral analysis ascertained the frequencies of various functional groups present in PSL crystal. The optical transmittance and optical band gap were explored from the optical transmission phenomena of PSL crystal. PL studies revealed that prominent emission at 410 nm, when PSL was excited at 320 nm. The mechanically soft nature of the crystal was divulged by Vickers hardness measurement. The LDT value of PSL crystal was estimated as 2.65 GW/cm². The third order NLO properties of PSL crystal was ascertained by Z-scan studies.

Introduction

Recently, many researchers are greatly fascinated in giving more thoughtfulness to the field of organic nonlinear optical materials. When compared to inorganic material, organic materials are optically more nonlinear due to its hydrogen bonds and weak vander Waal's force and it also possesses higher degree of delocalization of the π electrons [1]. A third order nonlinear optical organic single crystalline material has paying attention because of their potential applications and also variety of designing possibilities [2]. Piperazine ($C_4H_{10}N_2$) is an organic base. The combination of Piperazine and salicylic acid, with carboxyl and hydroxyl groups, might be practically expected to give a good sample to examine the H-bonding interaction. Here, we report the crystal growth of the Piperazinium bis (Salicylate) single crystal (PSL) and subjected to various characterization for NLO application.

Experimental procedure

The title compound prepared from Piperazine and Salicylic acid was taken in 1:2 molar ratio. The raw materials were dissolved in deionized water and ethanol mixed solvent. To obtain the homogeneity, solution was stirred by using a magnetic stirrer. The prepared solution was filtered, covered and maintained at 35°C which was kept in a constant temperature bath. The reaction mechanism was displayed in **Fig. 1 (a)** and PSL crystal with dimension $9 \times 7 \times 4$ mm³ was harvested in 15-20 days. **Fig. 1 (b)** depicted the photograph of as-grown PSL crystal.
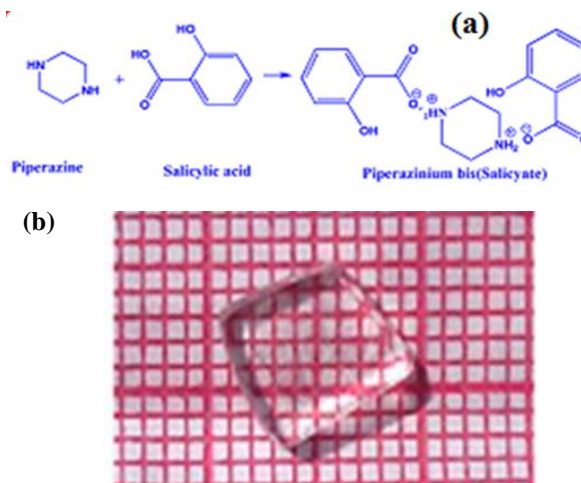

Fig. 1. (a) Reaction mechanism and (b) Photograph of as grown PSL crystal.

Results and discussion

Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction analysis have been performed by using Bruker Kappa APEXII diffractometer with MoKα (λ = 0.71073 Å) radiation for the confirmation of crystallinity and lattice parameters of as-grown PSL crystal. The title crystal of Piperazinium bis (Salicylate) (PSL) belongs to monoclinic system with space group $P2_1/n$, a = 6.27Å, b = 14.73Å, c = 9.35Å, α=γ=90°, β = 92.75° and volume V = 862 Å³. These cell parameters disclose good agreement with earlier report [3].

FTIR studies

The recorded FTIR spectrum with corresponding spectral bands assignment of PSL crystal was depicted in **Fig. 2**. The NH stretching vibration observed at 3058 cm^{-1}. The C-H stretching bands detected at 2977 cm^{-1} and 2856 cm^{-1}. The bands observed at 2691 cm^{-1}, 2591 cm^{-1}, 2340 cm^{-1} are due to NH^{2+}stretching. The C=O stretching assigned to the band appeared at 1618 cm^{-1}. The detected bands appeared at 1117 cm^{-1} and 1097 cm^{-1} are due to C-C asymmetric stretching and C-C symmetric stretching. The band detected at 858 cm^{-1} is due to para substitution [4].
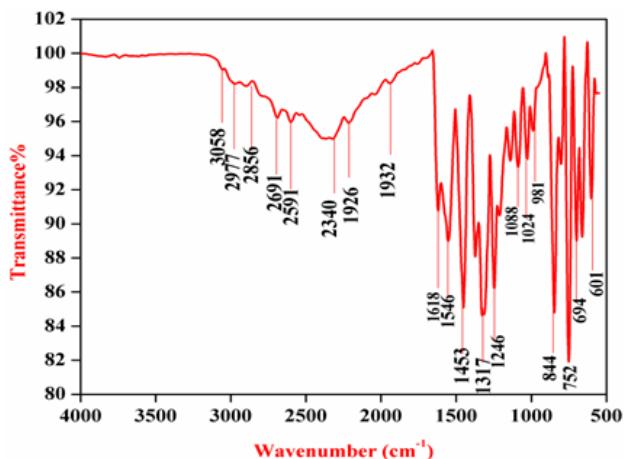

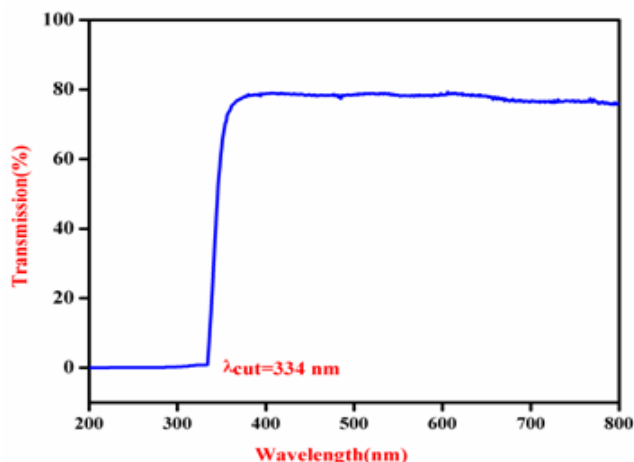**Fig. 2.** FTIR spectrum of PSL crystal.

Fig. 3. UV-Visible spectrum of PSL crystal.

UV-Vis transmission studies

UV-Vis transmission of the PSL single crystal was ascertainedby UV spectrophotometer in the range 200-800 nm as depicted in **Fig. 3**. The lower cut-off wavelength of PSL crystal was found to be 334 nm which is owing to π - π^* transition and transmission percentage was found to be 75%. Absence of absorption employed in the entire visible region is the essential for the NLO materials [5]. The optical absorption coefficient (α) was evaluated using the relation,

$$\alpha = \frac{2.3026 \times log\left(\frac{1}{T}\right)}{t} \qquad (1)$$

where 'T' is the transmittance and 't' is the thickness of the PSL crystal used for this study.

The absorption coefficient (α) obeys the relation for high photon energies (hν).

$$(\alpha h\nu)^2 = A\ (E_g - h\nu) \qquad (2)$$

The band gap energy (E_g) was obtained by Tauc's plot asdepicted in **Fig. 4** and the estimated band gap energy E_g is in the order of 3.71eV [6].
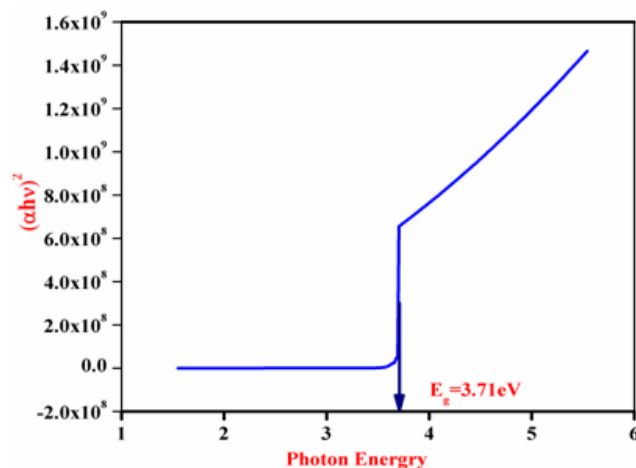

Fig. 4. Tauc's plot of PSL crystal.

Photoluminescence (PL) studies

It is the processes of spontaneous emission by the excitation of photons. **Fig. 5** divulged the (PL) spectrum of PSL crystal. The selected excited wavelength of the crystal was at 320 nm, and a broad spectrum with maximum peak intensity was appeared at 410 nm, which ascertained the violet colour emission of PSL crystal. The peak at 410 nm attributed to the protonation of the nitrogen attached to Piperazine by the carboxylic group present in Salicylic acid [7].
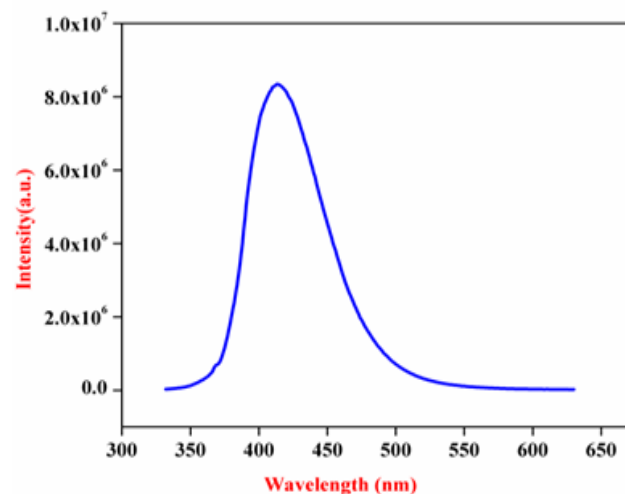

Fig. 5. Photoluminescence spectrum of PSL crystal.

Laser damage threshold

High power laser damage tolerance factor is requirement to select the NLO material that must be able to resist high power laser related device applications [8]. Using Q-switched Nd-YAG laser, the LDT study was ascertained

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for the PSL crystal. The surface damage threshold value of the PSL crystal was evaluated using the expression: $P = (E/\tau\pi r^2)$, where E is the input energy (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). The damage threshold value of PSL crystal was estimated as 2.65 GW/cm^2.

Vickers microhardness studies

The microhardness of the PSL crystal was ascertained by Vicker's microhardness. PSL crystal was subjected hardness measurement to different loads from 10g to 200g at constant indentation time of 10s. Vicker's microhardness number (H_v) of PSL crystal was calculated using the relation,

$$H_v = 1.8544*P/d^2 \text{ (kg/mm}^2) \quad (3)$$

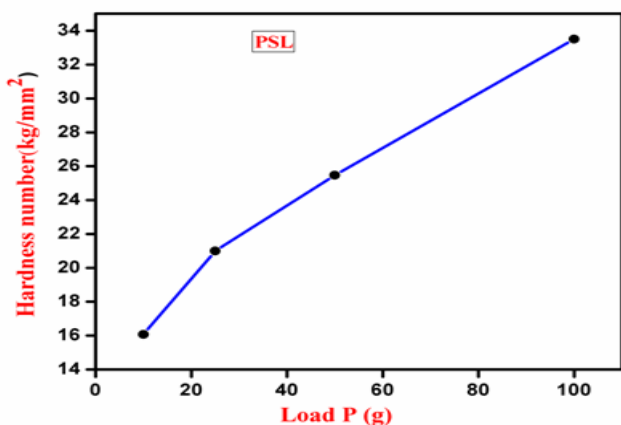where P is the load applied and d is the average diagonal length of indentations in millimeter.

Fig. 6. Plot of H_v with applied load of PSL.

The plot drawn between load P and H_v (**Fig. 6**) revealed that the microhardness increases with the increasing load. This behavior divulged the work hardening of the surface layers and it is known as reverse ISE effect. **Fig. 7** was depicted between log P vs. log d. The obtained value of n for PSL was found to be 3.49. According to Onitsch, for harder materials the work hardening coefficient 'n' should be in the range 1 and 1.6 and for softer materials it is beyond 1.6. From the obtained 'n' value, the PSL crystal categorized as soft material [**9**].
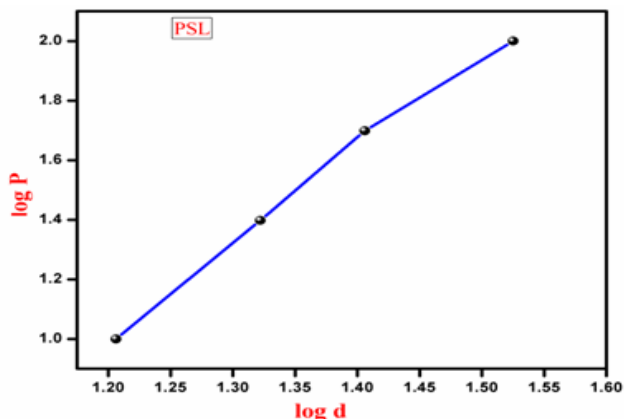
Fig. 7. Plot of log d versus log P of PSL.

Z-scan studies

Z-scan technique is a simple, very sensitive and accurate method for the measurement of nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third order susceptibility ($\chi^{(3)}$). **Fig. 8** and **Fig. 9** depicted the closed and open aperture patterns. From the Z-scan data as revealed in Fig. 8, the measurable quantity $T_{p-v} = T_p - T_v$ was obtained, where T_p and T_v are the normalized peak and valley transmittances.
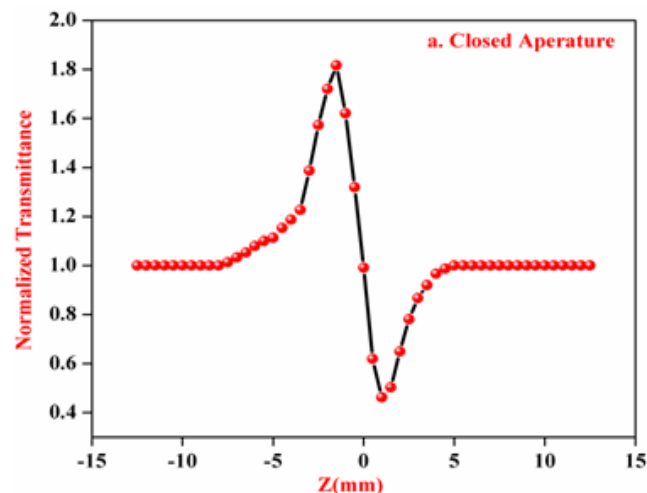
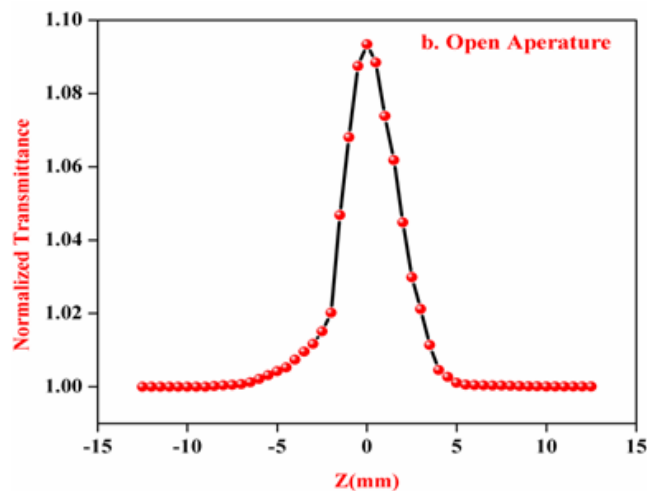**Fig. 8.** Z-scan closed aperture mode.

Fig. 9. Z-scan open aperture mode.

Fig. 8 and **Fig. 9** depicted the closed and open aperture mode traces which are revealed the self-defocusing effect and the saturable absorption respectively. The evaluated values of nonlinear refractive index are (n_2) = 7.150×10^{-8} cm^2/W, nonlinear absorption coefficient (β) = 0.072×10^{-4} cm/W, the real and imaginary part of third order susceptibility values were $R_e\chi^{(3)}$ = 9.002×10^{-6} esu, $I_m\chi^{(3)}$ = $\mathbf{0.448} \times 10^6$ esu. The third order nonlinear susceptibility was expressed as $\chi^{(3)} = \sqrt{(R_e\chi^{(3)})^2 + (I_m\chi^{(3)})^2}$ and the value of third order nonlinear susceptibility was estimated as $\chi^{(3)}$ = 9.014×10^{-6} esu by Z-scan technique [**10**].

Conclusion

Optically, good transparent PSL single crystal was grown successfully. SXRD affirmed the crystallinity and lattice parameters of as grown crystal. The functional groups were identified by FTIR studies. The lower cut-off wavelength of PSL crystal was ascertained as 334 nm and band gap was found to be 3.71eV. Photoluminescence studies divulged the violet colour (410 nm) emission of PSL crystal. The LDT value of as grown PSL crystal as evaluated to be 2.65 GW/cm^2. Z-scan studies analyzed that the PSL crystal shows the saturable absorption with the self-defocusing nature. Based on the investigation, it can be accomplished that the as-grown PSL single crystal is a potential candidate for NLO applications.

Keywords

Organic crystal, solution growth, optical properties, mechanical stability, nonlinear optical properties.

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