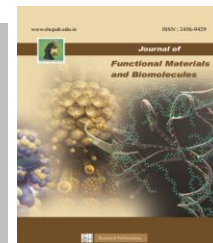




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Growth, Optical, Mechanical, Dielectric and Thermal properties of Piperazinium Succinate Single Crystal for NLO optical applications

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Abstract

An organic nonlinear optical Piperazinium Succinate single crystal was grown by employing controlled solvent evaporation technique. The cell parameter of the grown crystal was identified by single crystal XRD analysis and the functional groups present in the crystal were identified by FTIR spectral studies. The mechanical behavior of the crystal was studied using Vickers hardness tester. The cut off wavelength, energy gap and optical constants of the crystal were calculated from UV-visible analysis and fluorescence analysis. The dielectric constant and dielectric loss of the grown crystal was studied as a function of frequency and temperature. The TGA analysis shows that the crystal is thermally stable up to 156 °C. The NLO property of the crystal was studied using Z scan technique.

Keywords: Organic compound, XRD, FTIR, Microhardness, Fluorescence analysis, dielectric property, third order NLO property.

1 Introduction

Nonlinear optical crystals are more attractive for both academic research and technology because of the practical use in optoelectronic, remote sensing, optical data storage, laser frequency conversion, dynamic image processing, and photonic applications such as signal processing, optical limiting and optical switching respectively [1,2]. Organic nonlinear optical materials play a major role in the field of crystal growth as organic crystals exhibit harmonic generation. Recent research reports that organic materials possess fast response time, lower dielectric constant, enhanced NLO property and better growth characteristics [3]. The nonlinear optical responses of organic molecules emerge from delocalized π -electron and strong donor-acceptor intermolecular reaction [4]. In the hitherto, materials with larger nonlinear coefficient have been identified for the frequency conversion and optical processing applications. In the last ten years, research on third order NLO materials has been largely focused for their applications such as optical limiting, optical switching etc. The third order NLO application is the

emerging field in molecular and crystal growth techniques [5-7].

In this research, for the very first time, the third order NLO properties of Piperazinium Succinate crystal is analysed by z-scan technique using continuous wave He-Ne laser. The growth, optical, mechanical, thermal and fluorescence properties have been studied to try out the appropriateness of the crystal for NLO applications. The material possesses low dielectric loss in the high frequency region which proves that the crystal is optical quality with lesser defects which is one of the criterion for NLO applications.

2 Experimental

2.1 Crystal Growth

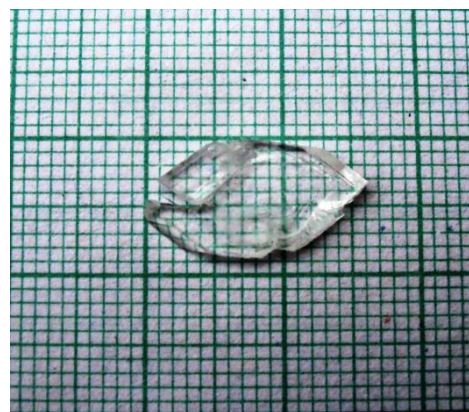


Fig. 1 Photograph of the grown PSU crystal

Pierazinium Succinate (PSU) single crystal was grown from an aqueous solution of Piperazine and Succinic acid in 1:1 molar ratio. The supersaturated and homogenous solution was prepared in the aqueous medium after continuous stirring for 4 hours at 303 K which was then filtered using Whatman filter sheet and allowed to evaporate at ambient temperature in a constant temperature water bath without any mechanical disturbances to ensure the growth of high quality crystal. After the growth period of ten days, well grown good

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quality crystals were harvested. The photograph of the grown crystal is shown in Fig.1.

3 Results and Discussion

3.1 Single Crystal XRD Analysis (SXRD)

Single crystal XRD analysis of the grown crystal was carried out using ENRAF NONIUS CAD4 diffractometer. The lattice parameters of the grown PSU crystal is $a = 5.837 \text{ \AA}$, $b = 6.019 \text{ \AA}$, $c = 6.923 \text{ \AA}$, $\alpha = 95.14^\circ$, $\beta = 99.45^\circ$, $\gamma = 93.63^\circ$ and it belongs to triclinic system with centrosymmetric space group $P\bar{1}$ which are very much in agreement with the data reported earlier [7]. The crystallographic information is presented in Table I.

Table I Single crystal XRD data.

Cell Parameters	PSU crystal	Reported value
a (Å)	5.837	5.8225
b (Å)	6.019	6.0027
c (Å)	6.923	6.8943
α°	95.14	95.06
β°	99.45	99.54
γ°	93.63	93.77
Volume (Å) ³	238.2	235.91

3.2 Polarizability Evaluation

The electronic polarizability of the materials are essential for the desired efficiency of nonlinear effect. The high frequency dielectric constant value of PSU crystal is used to calculate the electronic properties like valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability. From the single XRD data, the molecular weight $M = 204.23 \text{ g/mol}$ and density $\rho = 1.437 \text{ g/cm}^3$. The value of dielectric constant at 1MHz is calculated to be $\epsilon_r = 32$. The total number of valance electron in PSU crystal is $Z = \{(8 \times Z_C) + (16 \times Z_H) + (2 \times Z_O) + (3 \times Z_N)\} = 58$. From this calculated values, the valance electron plasma energy $\hbar\omega_p$ is given by

$$\hbar\omega_p = 28.8 \left(\frac{Z_P}{M} \right)^{\frac{1}{2}}$$

The Fermi energy and Penn gap energy are dependent on $\hbar\omega_p$ which are given by

$$E_p = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{\frac{1}{2}}} \quad \text{and}$$

$$E_f = 0.2948 (\hbar\omega_p)^{\frac{4}{3}}$$

Electronic polarizability (α) was obtained by using a relation

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_o}{(\hbar\omega_p)^2 S_o + 3 E_p^2} \right] \times \frac{M}{\rho} \times 0.39$$

Where S_o is the constant of the material it can be obtained by

$$S_o = 1 - \left[\frac{E_p}{4E_f} \right] + \frac{1}{3} \left[\frac{E_p}{4E_f} \right]^2$$

The obtained value of polarizability agrees well with that of Clausius-Mossotti equation which is given by

$$\alpha = \frac{3M}{4\pi N_a \rho} \left(\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right)$$

where N_a is the Avogadro number. The calculated values are compared with the standard KDP material is shown in Table II. From the table, it is observed that electronic parameters are found to be higher than those of KDP. In particular, the polarizability of PSU crystal is found to be three times higher than that of KDP.

Table II Theoretical parameters of PSU crystal and KDP single crystal.

Parameters	Values of PSU crystal	Values of KDP crystal
Plasma energy (eV)	18.398	17.28
Penn Gap (eV)	3.304	2.37
Fermi energy (eV)	14.318	12.02
Electronic polarizability using penn analysis (cm ³)	5.104 x 10 ⁻²³	2.12 x 10 ⁻²³
Electronic polarizability using Clausius-Mossotti equation (cm ³)	5.04 x 10 ⁻²³	2.12 x 10 ⁻²³
Electronic polarizability using bandgap (cm ³)	2.997 x 10 ⁻²³	2.10 x 10 ⁻²³

3.3 Vibrational Studies

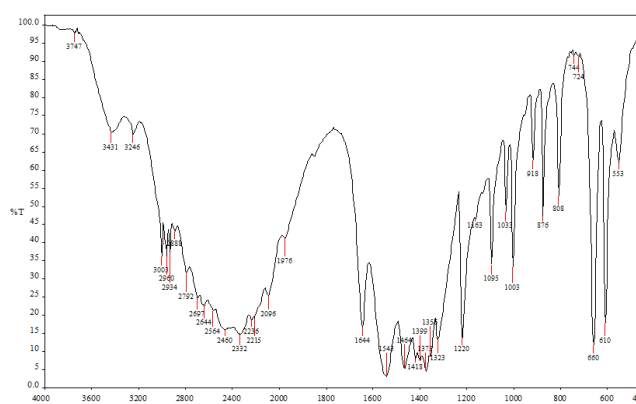


Fig .2 FTIR spectrum of PSU crystal

In order to study the functional groups present in the PSU crystal, fourier transform infrared spectrum has been recorded for the fine particles in the range from 400 cm⁻¹ to 4000 cm⁻¹ at room temperature and the recorded FTIR spectrum is shown Fig.2. The peaks appearing at 3246cm⁻¹, 2729 cm⁻¹ and 2934 cm⁻¹ may be due to O-H stretching which indicates the occurrence of carboxylic acid. The

peak at 2960 cm^{-1} is attributed to C-H stretching vibration. C-N-C deformation peaks were observed at 553 cm^{-1} . The bending and rocking vibration of COO- are observed at 808 cm^{-1} and 610 cm^{-1} respectively. The peak at 2644 cm^{-1} shows the presence of the secondary amine group and the peak at 1644 cm^{-1} and 1543 cm^{-1} is assigned to the NH_2^+ deformations [8].

Table III The observed frequencies and corresponding assignments

Wavenumber (cm^{-1})	Assignment
3246, 2792 and 2934	OH stretching vibration of Carboxylic acid group
2960	C-H stretching vibration
2644	NH_2^+ stretching vibration
1644, 1543	NH_2^+ deformation
808, 610	bending and rocking vibration
553	C-N-C deformation

3.4 UV- Vis Spectral analysis

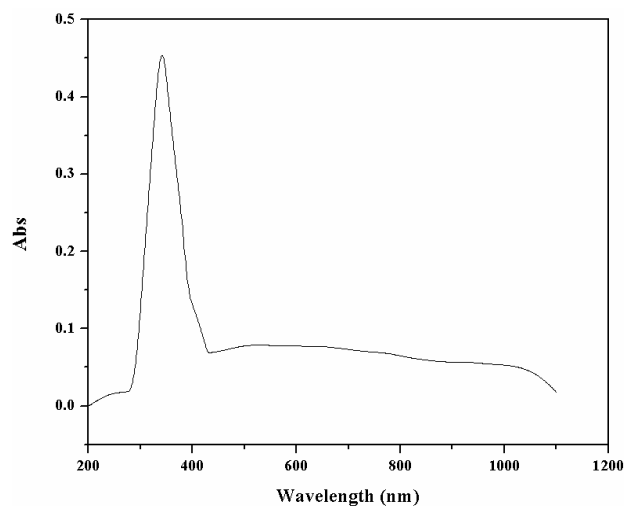


Fig. 3 Optical absorption spectrum of PSU crystal

The absorption spectra of PSU crystal was recorded in the range from 200 to 1100 nm using Shimadzu 1601 UV-Vis spectrometer at 303 K (Fig.3). The UV-Vis spectrum contributes the absorption behaviour of electron from valence band to conduction band in σ and π orbits [9]. The NLO material with wide optical transmission plays a significant role in the practical applications particularly in optics. The lower cut off wavelength for the grown crystal is identified at 341 nm and from the absorption spectrum, it is noticed that there is a broad transmittance in the complete visible and near IR region.

3.4.1 Determination of Optical Constants

Optical parameters such as energy gap and refractive index are the important variables in linear and nonlinear optical applications. Since, based on the atomic and electronic bonds in the crystal the band gap energy will vary [10]. The optical absorption coefficient (α) was calculated using the relation

$$\alpha = \frac{2.303}{t} \log_{10} \left(\frac{100}{T} \right)$$

where T is the transmittance and t is the thickness of the sample. The energy gap of the crystal is calculated from

$$E_g = \frac{hc}{\lambda}$$

Where h, c and λ are the planck's constant, velocity of light and the cut off wavelength respectively. The calculated energy band gap of PSU crystal is 3.6 eV. The other important limiting factors such as refractive index (n) and reflectance (R) of the crystal were studied using the following equations [11-12]. The reflectance in terms of absorption coefficient (α) is obtained from the relation,

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

The refractive index (n) was calculated from,

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

The calculated refractive index of PSU crystal is 1.14, due to the low refractive index, the material can be used in antireflection coating in solar devices.

3.5 Mechanical Studies

Vicker's microhardness test is a technique to understand the mechanical property of the material. Microhardness was tested on the smooth surface of the crystal at 303 K for different loads such as 10, 25, 50 and 100 g using Vicker hardness tester fitted with diamond pyramidal indenter. The indenter is pressed on the surface of the crystal under the influence of the load and size of the indentation is measured. The hardness is measured as the ratio of applied load to indentation on the surface area. The hardness number Hv were calculated from,

$$Hv = (1.8544 p) / d^2$$

where, p is the applied load (kg) and d is the diagonal length (mm) of the indentation. The variation of Hv as the function of applied load is shown in Fig. 4(a), it is clear that the Hv increases with increase in load. The slope from the straight line gives the value 'n', (Fig. 4(b)) where 'n' is Mayer's index. If n lies between 1 and 1.6 the material becomes hard material category, if it is above 1.6 the material belongs to soft material category [13]. The value of 'n' for PSU crystal is 2.31, hence the PSU crystal belongs to soft material category.

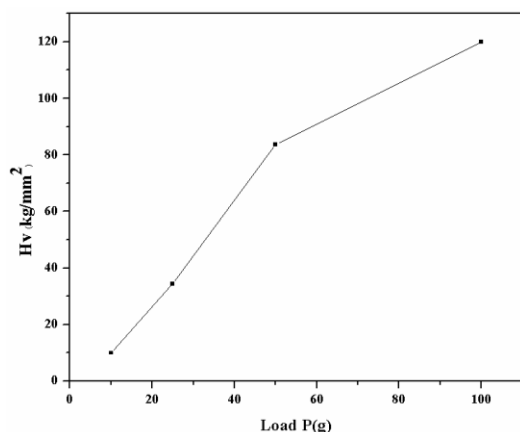


Fig. 4(a) Variation of H_V as the function of applied load

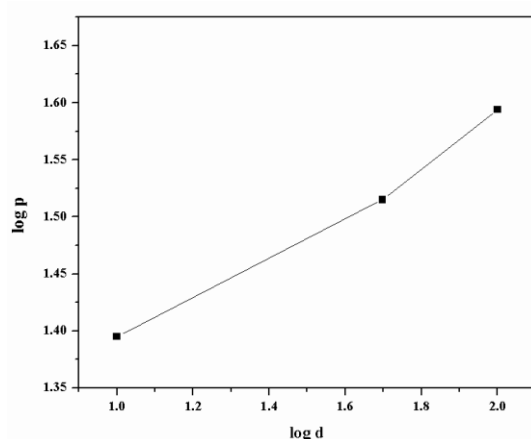


Fig. 4(b) Plot between $\log p$ and $\log d$ of PSU crystal

3.6 Fluorescence Analysis

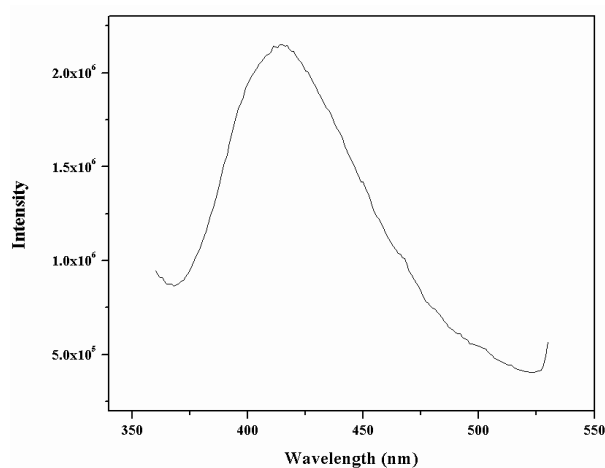


Fig. 5 Fluorescence spectrum of PSU crystal

The fluorescence spectroscopy was used to understand the luminescence properties of the crystals. Fluorescence occurs due to the molecules that are aromatic or molecules that contains multiple conjugate bonds with high degree of resonance stability [14]. The sample was excited at 300 nm and the emission peak was observed at 415 nm is

shown in Fig. 5. The emission spectrum shows a peak characteristics of violet fluorescence emission at $\lambda = 415$ nm [15].

3.7 Dielectric Studies

A study of dielectric response of the crystals is important since it gives valuable information about the electric field distribution within the crystal for different frequencies at a particular temperature. A well polished crystal coated with silver paint on the opposite faces of was placed in between the two copper electrodes to form a parallel plate capacitor and an electric field of 2 Volt is applied across the crystal. The dielectric constant (ϵ_r) is calculated using the formula $\epsilon_r = Cd\epsilon_0/A$, where C is the capacitance, d is the thickness, A is the area and ϵ_0 is the absolute permittivity of the free space. Dielectric behaviour of the grown PSU crystal was examined using HIOKI 3532-50 LCR HITESTER. The change in dielectric constant with respect to frequency is shown in Fig. 6. At low frequency, the dielectric constant is relatively high and as the frequency increases, the dielectric constant decreases for all the temperatures. This is probably due to the presence of space charge polarization, orientation polarization, electronic polarization and ionic polarization. The decrease in dielectric constant at higher frequencies is due to the loss of these four polarizations moderately.

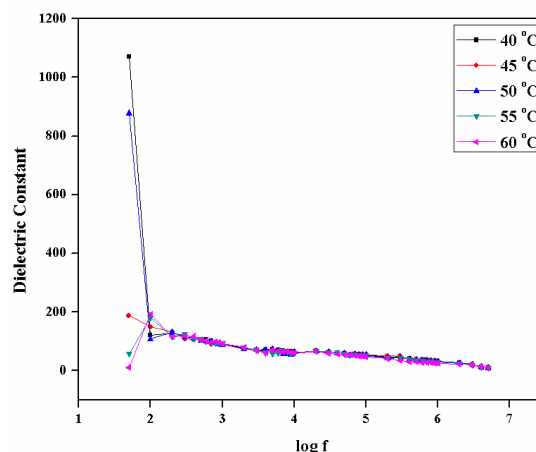


Fig. 6 Plot of dielectric constant and $\log f$ of PSU crystal

The dielectric loss plot reveals the frequency dependant variation with high dielectric loss at lower frequencies, however, as the frequency is increased, the dielectric loss decreased abruptly and when the frequency is very high, the dielectric loss spectrum shows no further change in the dielectric loss with almost frequency independent behavior. This trend of low dielectric loss at high frequency proves that the crystal is optical quality with lesser defects (Fig. 7) which is one of the criterion for NLO applications [16].

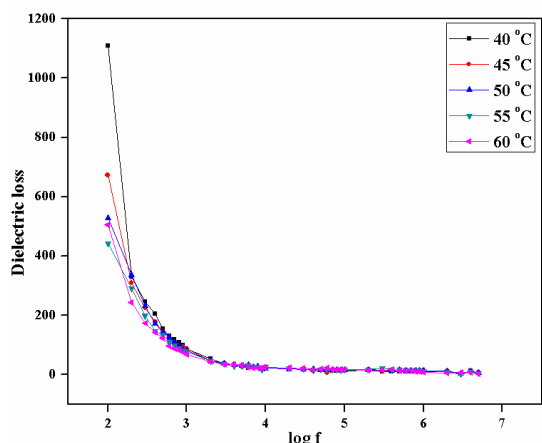


Fig. 7 Plot of dielectric loss and log f of PSU crystal

3.8 Thermal Analysis

The thermal property of the PSU crystal was analyzed using Q 500 HI-RES TGA in nitrogen atmosphere. From the TG-DTA curve (Fig. 8), it is noticed that the sample is stable up to 156 °C and it is decomposed in four stages. Since there is no endothermic peak is absorbed, it is understood that this crystal starts to decompose without melting and after this temperature it started to decompose by evaporation. The first weight loss occurred between 156 °C and 240 °C with the decomposition of 30.09 % of the sample. The second stage starts at 237 °C with the weight loss of 11.77 % of the sample into gaseous products. The third stage comprises of 46.86 % weight loss of the material at 379 °C. The fourth stage has 10.85 % weight loss of the material at 426 °C. The various gaseous products evolved in second, third and fourth stages may be due to the liberation of CO, CO₂ and NO respectively.

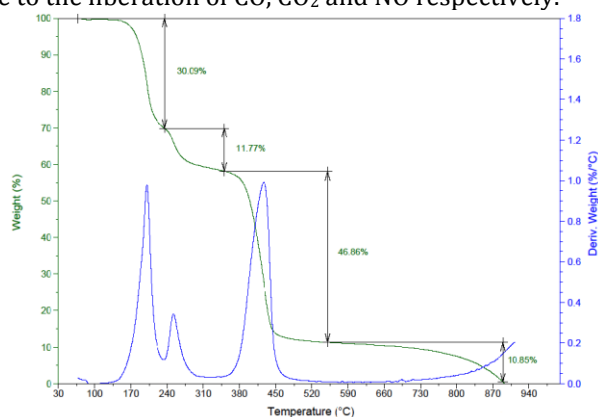


Fig. 8. TGA and DTA Spectrum of PSU crystal

3.9 Z Scan technique

Z scan is a technique used to determine the third order optical nonlinearity of the materials [18, 19]. The open and closed aperture methods of Z scan technique are used for the measurements of nonlinear absorption and nonlinear refractive index. The closed aperture curve shows a peak followed by a valley of normalized transmittance which indicates the self-defocusing effect and it exhibit a negative nonlinear refractive index (Fig. 9) [20]. The maximum

peak at the focus represents the saturable absorption, which is shown in Fig. 10. The peak and valley difference from the closed aperture is calculated from,

$$\Delta T_{p-v} = 0.4606(1 - S)^{0.25} |\Delta\phi|$$

where $\Delta\phi$ the phase difference, S is the linear transmittance of the aperture and it was calculated from,

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right)$$

where r_a is the radius of the aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index (n_2) was calculated using closed aperture curve of Z - scan data and is given by,

$$n_2 = \frac{\Delta\phi}{KI_0 L_{\text{eff}}}$$

where K is the wave number ($K = 2\pi/\lambda$), I_0 is the intensity of the laser beam at focus ($z = 0$) and $L_{\text{eff}} = \{[1 - \exp(-\alpha L)]/\alpha\}$ is the effective thickness of the sample, α is the linear absorption and L is the sample thickness. From the open aperture Z - scan data, the nonlinear absorption coefficient is estimated as

$$\beta = \frac{2\sqrt{2} \Delta T}{I_0 L_{\text{eff}}}$$

where ΔT is the one valley value at open aperture Z scan data. The value of β is negative for saturable absorption and positive for two photon absorption. The real and imaginary parts of third order nonlinear optical susceptibility (χ^3) were calculated using the relations,

$$\text{Re } \chi^3 = \frac{10^{-4} (\epsilon_0 C^2 n_2 n_0^2)}{\pi} \text{ (cm}^2/\text{W)}$$

$$\text{Im } \chi^3 = \frac{10^{-4} (\epsilon_0 C^2 n_2 n_0^2)}{4n^2} \text{ (cm/W)}$$

Where ϵ_0 is the vacuum permittivity, C is velocity of light, n_0 is the linear refractive index of the material. The third order nonlinear optical parameters are calculated and are shown in Table IV and the comparison of χ^3 with some other crystals is shown in Table V. The Z scan measurement on the grown crystal shows a saturable absorption coefficient and the crystal is suitability for third order nonlinear optical applications.

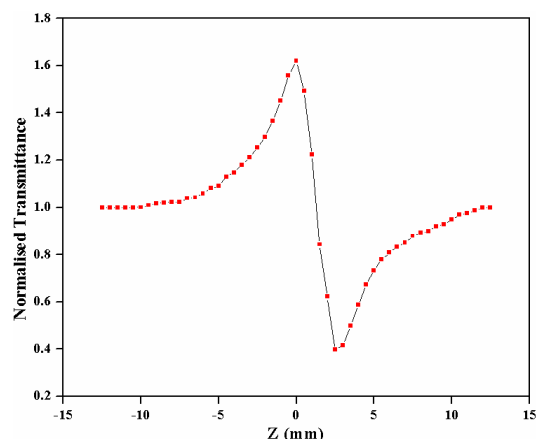


Fig. 9 Closed aperture curve of PSU crystal

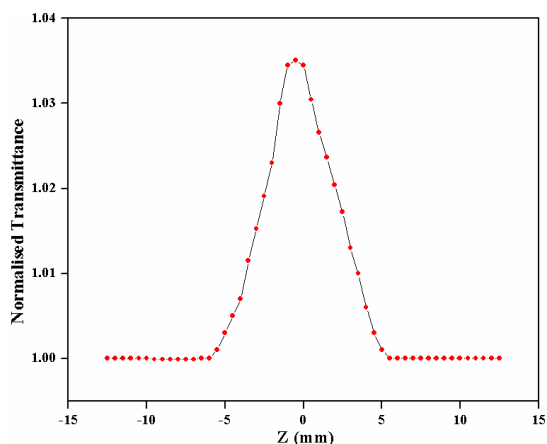


Fig. 10 Open aperture curve of PSU crystal

Table IV. Third order nonlinear optical parameters of crystal using Z scan technique

Nonlinear refractive index (n_2)	$-5.92 \times 10^{-8} \text{ cm}^2/\text{W}$
Nonlinear absorption coefficient (β)	$0.02 \times 10^{-4} \text{ cm/W}$
Third order nonlinear optical susceptibility (χ^3)	$1.95 \times 10^{-6} \text{ esu}$

Table V. Comparison of some third order crystal

Crystal name	Third order susceptibility (χ^3) esu
Sodium phthalate 4-brom-4' hemihydrate ²¹	64.999×10^{-9}
Nitrodenzyliden aniline ²²	5.95×10^{-9}
2 - Furoic acid ²³	2.547×10^{-7}
Piperazinium succinate (Present case)	1.95×10^{-6}

3.10 Optical Limiting

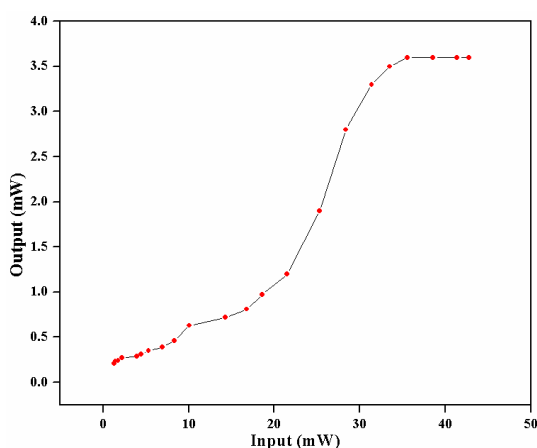


Fig. 11 Optical limiting of PSU crystal

Fig. 11 shows the optical limiting behavior of PSU crystal. From the spectrum it was noted that the intensity of output transmittance varies linearly at low input intensity. By continually increasing the input power, the output transmittance is maintained and after 35.5 mW it is saturated which is obvious for limiting amplitude. The threshold limiting and output clamping were found to be 35.5 mW and 3.5 mW respectively. Thus PSU crystal possess optical limiting property, it can be used in solid state optical sensors.

4 Conclusions

Piperazinium Succinate, an organic crystal was synthesized and single crystal was grown by slow evaporation technique. The single crystal XRD confirms that the crystal belongs to triclinic system. The functional groups present in the grown crystal were confirmed by FT-IR spectral analysis. The mechanical behavior was determined by using Vickers micro hardness tester. The emission peak is observed at 415 nm and it is suitable for violet wavelength emission. The dielectric constant was measured with frequencies as a function of temperatures. The decomposition and weight loss of the material were obtained from TG/DTA analyses. The Z scan measurement showed that a moderately high NLO response of the crystal with $n_2 = -5.92 \times 10^{-8} \text{ cm}^2/\text{W}$, $\beta = 0.02 \times 10^{-4} \text{ cm/W}$, and $\chi^3 = 1.95 \times 10^{-6} \text{ esu}$. Thus, with many attracting linear and nonlinear optical properties Piperazinium Succinate is found to be a suitable candidate for optoelectronic applications.

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