Asian Journal of Chemistry; Vol. 38, No. 4 (2026), 1059-1064
ASIAN JOURNAL OF CHEMISTRY
https://doi.org/10.14233/ajchem.2026.35152

Optical, Thermal and Mechanical Properties of Creatininium 5-Sulphosalicylate Organic Crystal for Optical Limiting Applications

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Received: 28 October 2025 *Accepted*: 11 March 2026 *Published online*: 8 April 2026 AJC-22329

A novel organic nonlinear optical single crystal of creatininium 5-sulphosalicylate (C5SS) was grown by slow evaporation. From FTIR analysis, the presence of various vibrational modes and functional groups in the synthesised material was confirmed. The thermal stability of grown crystal was analysed by TG-DSC analysis. UV-visible transmittance studies showed the transparency region, cut-off wavelength and band gap of the grown crystal. Laser tolerance of the grown crystal was estimated to be 5.23 GW cm^{-2}. Microhardness studies were also performed on C5SS single crystal to reveal its mechanical properties. A Z-scan technique was employed to evaluate the nonlinear absorption coefficient, nonlinear refractive index and nonlinear optical susceptibility. The optical limiting behaviour of C5SS was observed at 28.14 mW input power.

Keywords: Creatininium 5-sulphosalicylate, Slow evaporation, Organic crystal, Optical properties.

INTRODUCTION

Organic nonlinear optical (NLO) materials are possessing huge deal of interest due to their high nonlinearity and quick response in electro-optic modulation, optical computing, optical memory and terahertz generation and frequency mixing, *etc.*, above the inorganic materials [1-3]. Fundamentally, organic compounds have high delocalised π-electrons and additional electron donor and electron acceptor on the opposite sides of the molecules. From these kinds of molecular units, the molecules tend to be highly polarised, which is the root for high nonlinearity in organic compounds [4,5]. Nowadays, the third order nonlinear optical materials have more investigations compared to second order nonlinear optical materials [6].

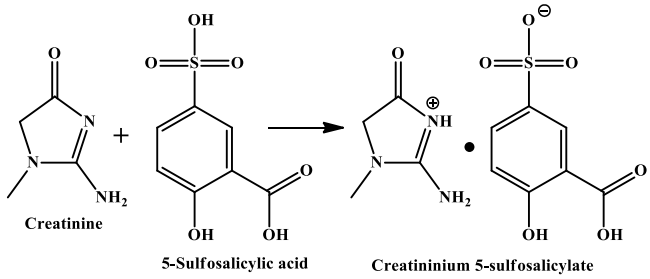
Third-order nonlinear optical materials have attracted considerable attention due to their efficient optical limiting and optical switching properties [7,8]. These characteristics make them highly suitable for applications in photonic technologies and optoelectronic devices. Consequently, significant efforts have been devoted to designing molecules with enhanced third-order nonlinearities, which can be integrated into advanced optical devices for signal processing, optical communication and information storage applications [9,10].

Creatinine, also known as creatine anhydride, is a breakdown product of creatine phosphate. 5-Sulphosalicylic acid contains three potential coordination centers namely -COOH, $–SO_3H$ and –OH, which allow a variety of coordination modes. Such multifunctional groups enhance the possibility of electron transfer in organic salts, particularly in *N*-heterocyclic systems, resulting in tunable optical properties [11]. Recently, several creatinine-based crystals, including creatininium L-tartrate (CTM), creatininium succinate (CS) and creatininium 4-nitrobenzoate (C4NB), have been reported as effective NLO materials [12-14]. The synthesized creatininium 5-sulphosalicylate (C5SS) single crystal possesses a centrosymmetric nature; therefore, it is of considerable interest to investigate its third-order NLO susceptibility. In present exploration, the synthesis and growth of creatininium 5-sulphosalicylate single crystal from aqueous solution using slow evaporation process have been performed based on the solubility measurement. The grown crystal was characterised by single crystal X-ray diffraction, spectral, thermal, UV-Vis, laser damage threshold and mech-

anical studies. The Z-scan technique was used to reveal the third order nonlinear optical parameters of grown crystal.

EXPERIMENTAL

Synthesis and crystal growth: High pure creatinine ($C_4H_7N_3O$) and 5-sulphosalicyclic acid ($C_7H_6O_6S$) in a stoichiometric ratio were taken to synthesise creatininium 5-sulphosalicylate (C5SS) compound. Initially, the calculated amount of 5-sulphosalicyclic acid was dissolved in deionised water and appropriate amount of creatinine was slowly added into the solution. The solution was stirred continuously for obtaining homogeneous state and the solution was allowed for evaporation using a constant temperature bath. The nucleation was occurred in the period of 25 days and C5SS salt was collected (**Scheme-I**). By repeated recrystallisation the purity of the synthesised product was improved. Then, the solution was filtered with high quality filter paper for more purification. The filtered solution was kept in a constant temperature bath at 35 ºC with an accuracy of ± 0.01 ºC. The evaporation rate of the solution was controlled by covering a pin hold laminated sheet. The photograph of grown C5SS single crystal with dimension of 14 mm × 14 mm × 4 mm is shown in Fig. 1.



Scheme-I: Synthetic route of creatininium 5-sulphosalicylate (C5SS) crystal

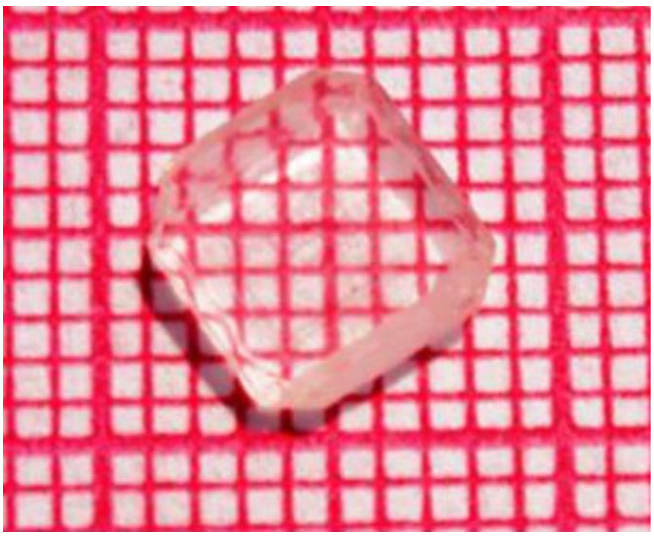


Fig. 1. Photograph of as-grown creatininium 5-sulphosalicylate crystal

Characterization: Single crystal X-ray diffraction analysis of the creatininium 5-sulfosalicylate (C5SS) crystal was carried out using a BRUKER KAPPA AXS II single crystal X-ray diffractometer with graphite monochromated Mo*K*α radiation (λ = 0.71073 Å) at 293 K. The FTIR spectrum of the C5SS crystal was recorded using the KBr pellet technique on a Perkin-Elmer FTIR spectrometer in the range of 4000–400 cm^{-1} to identify the functional groups present in the crystal. Thermal studies of the C5SS compound were performed using an SII TG-DSC 6300 EXSTAR instrument under a nitrogen atmosphere at a heating rate of 2 ºC min^{-1} to evaluate its thermal stability and decomposition behaviour. The optical transmission spectrum of a cut and polished C5SS crystal with a thickness of 1 mm was recorded in the wavelength range of 190-900 nm using Shimadzu UV-2600 UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction: Single crystal XRD study was performed on the creatininium 5-sulfosalicylate crystal. The crystal was found to crystallize in the monoclinic crystal system with the space group $P2_1/c$, which belongs to a centrosymmetric crystal structure. The calculated unit cell parameters of C5SS are in good agreement with the reported data [15].

FTIR spectral studies: FT-IR spectrum of organic crystal C5SS is shown in Fig. 2. The O–H stretching vibration is observed at 3047 cm^{-1}. The N–H stretching band appearing at 2418 cm^{-1} is attributed to the protonation of the amino group, confirming the formation of the C5SS compound. The asymmetric stretching of deprotonated carboxylate ions is observed at 1582 cm^{-1}. The C=N asymmetric stretching vibration appears at 1498 cm^{-1}, while the peaks at 1225 and 1066 cm^{-1} correspond to C–N asymmetric and symmetric stretching vibrations, respectively. The band observed at 916 cm^{-1} is assigned to S–O asymmetric stretching vibration. The C–H out-of-plane bending vibration is observed at 766 cm^{-1}. The peaks appearing at 588 and 530 cm^{-1} are attributed to COOH wagging and COO^- wagging vibrations, respectively. These vibrational assignments confirm the formation of the C5SS salt and indicate the influence of proton transfer and intermolecular hydrogen bonding interactions within the crystal lattice [16].

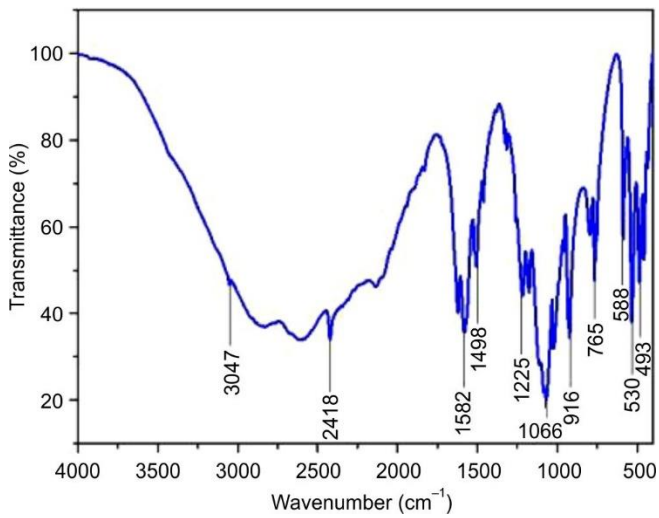


Fig. 2. FTIR spectrum of creatininium 5-sulphosalicylate (C5SS) crystal

Thermal studies: The thermal stability of the grown C5SS crystal was examined using thermogravimetric (TG) and

differential scanning calorimetric (DSC) analyses. Thermal studies of the C5SS compound were carried out using an SII TG-DSC 6300 EXSTAR instrument in a nitrogen atmosphere at a heating rate of 2 ºC min^{-1}. From the TG curve (Fig. 3), the decomposition of the C5SS compound occurs in three stages. The initial weight loss starts at around 121 ºC and continues up to 222 ºC, while the third stage extends up to 319 ºC. The observed weight losses may be attributed to the liberation of volatile species such as CO, CO_2 and hydrocarbons. In the corresponding DSC curve, a sharp endothermic peak is observed at 110 ºC, which corresponds to the melting point of the C5SS material. These results indicate that the C5SS crystal is thermally stable up to about 120 ºC, suggesting its suitability for optical applications.

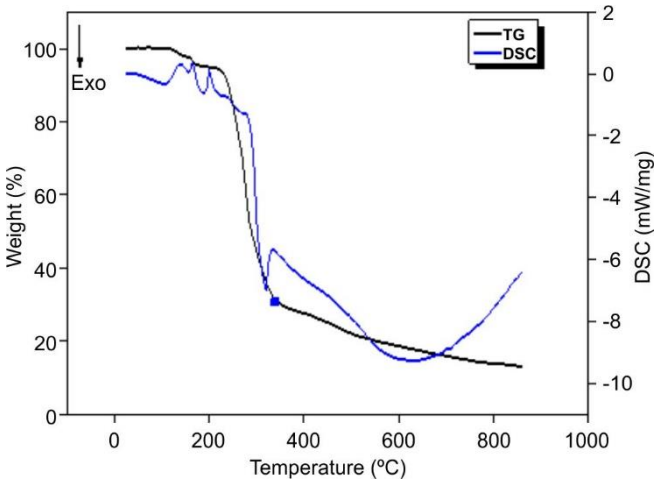


Fig. 3. TG-DSC thermograms of creatininium 5-sulphosalicylate (C5SS)

UV-Vis transmission studies: UV-visible transmission spectrum (Fig. 4a) reveals that C5SS crystal has the optical transmittance about 73% with cut-off wavelength 328 nm (UV region). The optical band gap of the crystal was calculated using the Tauc's relation: $(\alpha h\nu)^n = A(h\nu - E_g)$, where α indicates the absorption coefficient (cm^{-1}), ν is the incident frequency, h is the Planck's constant and E_g is the band gap energy [17]. Tauc's plot drawn between $(\alpha h\nu)^2$ and photon energy ($h\nu$) is shown in Fig. 4b. From the plot, the band gap energy (E_g) was found to be 3.7 eV.

Laser damage threshold studies: The laser damage threshold was measured by using induced high intensity laser light on C5SS crystal surface. A Q-switched Nd:YAG laser source of pulse width 10 ns and repetition rate of 10 Hz was used. The controlled energy of laser beam produced by the variable attenuator was made to fall on the test sample located at the focus of converging lens. The energy density of input laser beam was recorded for which the crystal gets damaged. The LDT value was calculated using the relation:

$$\text{Power density } (P_{(d)}) = \frac{E}{\tau A} \quad (1)$$

where E is the energy (mJ), τ is the pulse width (ns) and A is the area of the circular spot size (cm^2). The calculated laser damage threshold value of C5SS crystal was found to be 5.23 GW/cm^2, which is higher than that of KDP crystal [18]. The high value of LDT depends on the quality of the crystal. The C5SS crystal can able to use the laser damage capability level upto 5.23 GW/cm^2.

Mechanical studies: A well-polished C5SS crystal was placed on the flat surface and indentations were made under different applied loads. The load was gradually increased until cracks were formed due to excess stress, which indicates the hardness limit of the crystal. The Vicker's hardness values (H_v) were determined using the following relation:

$$H_v(\text{kg/mm}^2) = \frac{1.8554P}{d^2} \quad (2)$$

where P is the applied load in kg and d is the average indentation diagonal length in mm. The relation between hardness number (H_v) and load (P) of C5SS is shown in Fig. 5.

The hardness number decreases progressively with the increase in load. Meyer's index 'n' was calculated from the graph (Fig. 6). Plotted against log P *versus* log d, the value of 'n' obtained for C5SS crystal using linear fit is found to be n = 1.5. According to Onitsch, 'n' should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials [19].

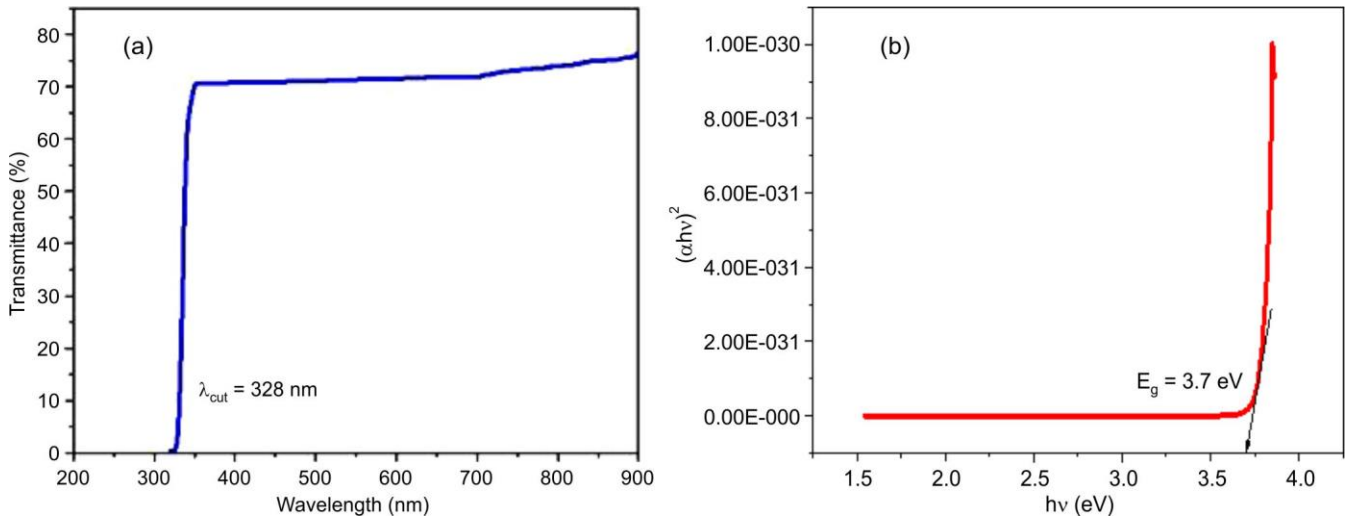


Fig. 4. (a) UV-Visible transmission spectrum and (b) Tauc's plot drawn between $(\alpha h\nu)^2$ and $h\nu$ of creatininium 5-sulphosalicylate (C5SS)

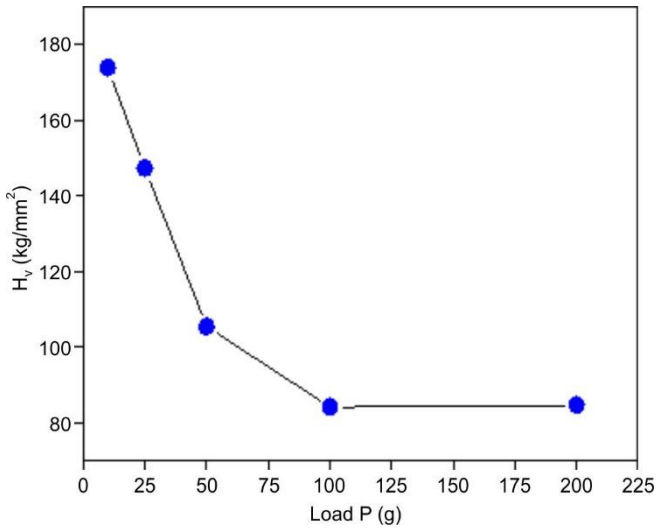


Fig. 5. Plot drawn between Vicker's hardness (H_v) and load (P) of C5SS crystal

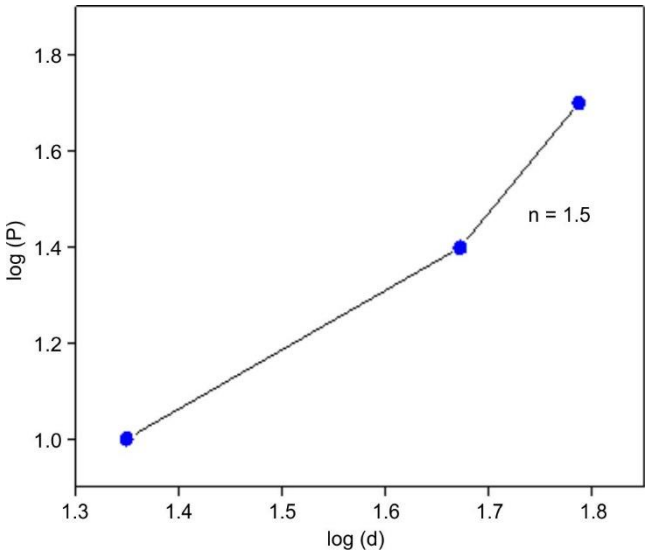


Fig. 6. Plot drawn between log P and log d of C5SS crystal

Hence, C5SS crystal is found to possess hard material category.

Third order nonlinear optical studies: From the single crystal X-ray diffraction studies, it is confirmed that the C5SS belongs to centrosymmetric space group $P2_1/n$. The second order susceptibility ($\chi^{(2)}$) becomes zero because centrosymmetric nature of this crystal have inversion symmetry. Z-scan method is usually used to determine the nonlinear optical parameters, such as the sign and magnitude of the nonlinear refractive index (n_2) and nonlinear absorption coefficient (β). The third order nonlinear optical susceptibility (χ^3) and hyperpolarizability (γ) of C5SS crystal were evaluated using continuous 632.8 nm He-Ne laser. The Z-scan measurement in closed aperture and open aperture modes was used to evaluate the third order nonlinear optical properties. Using a convex lens, the beam was focused and the focal point was taken as Z = 0. The normalised transmission was elucidated by placing the sample in different positions with respect to the focus of beam. Depending on Z-position with respect to the focal plane, the transmission of the sample can increase or decrease. From the normalised transmission of corresponding Z-position, the nonlinear absorption coefficient and nonlinear optical refraction of C5SS crystal sample were calculated. The plane convex lens of 22.5 cm focal length was used to focus the laser beam for this study. A well-polished 1 mm thickness crystal was fixed in the travel range of 12 mm. Using the powermeter, the input energy and energy transmitted through the sample were measured. From the Z-scan data, Fig. 7 shows the self-defocusing and the difference between the peak and valley transmittances (ΔT_{p-v}) was calculated using the relation [20]:

$$\Delta T_{p-v} = 0.406\,(1-S)^{0.25}\,|\,\Delta\Phi_o\,| \quad (3)$$

where $\Delta\Phi_o$ is the axis phase shift at the focus, S is the linear transmittance aperture. It can be calculated using the following relation:

$$S = 1 - \exp\left(\frac{-2r_o^2}{\omega_o^2}\right) \quad (4)$$

where r_a is the radius of aperture and ω_a is the beam radius at the aperture. The nonlinear refractive index (n_2) was calculated using the following relation:

$$n_2 = \frac{\Delta\Phi_o}{KI_oL_{eff}} \quad (5)$$

where k is the wavenumber, I_o is intensity of laser beam at the focus (z = 0) and $L_{eff} = (1-\exp(-\alpha L))/\alpha$ is the effective thickness of the sample, α is the linear absorption and L is thickness of the sample. The nonlinear absorption coefficient (β) was calculated from the open aperture Z-scan plot [21].

$$\beta = \frac{2\sqrt{2}\Delta T}{I_oL_{eff}} \quad (6)$$

where ΔT is the peak value at the measured open aperture from the Z-scan curve (Fig. 8) and it shows the saturable absorption. The real and imaginary parts of the third order nonlinear optical susceptibility (χ^3) were calculated using eqns. 7 and 8:

$$\mathrm{Re}\,\chi^3(\mathrm{esu}) = \frac{10^{-4}(\varepsilon_o C^2 n_o^2 n_2}{\pi}\,(\mathrm{cm}^2/\mathrm{w}) \quad (7)$$

$$\mathrm{Im}\,\chi^3(\mathrm{esu}) = \frac{10^{-2}(\varepsilon_o C^2 n_o^2 \lambda\beta}{4\pi^2}\,(\mathrm{cm}^2/\mathrm{w}) \quad (8)$$

where ε_o is the vacuum permittivity, c is the velocity of light in vacuum, n_o is the linear refractive index of the sample and λ is the wavelength of laser beam. The third order nonlinear optical susceptibility was estimated using eqn. 9:

$$\chi^{(3)} = \sqrt{(R_e\chi^{(3)} + (I_m\chi^{(3)})^2} \quad (9)$$

From the above analysis, the nonlinear refractive index (n_2), absorption coefficient (β) and third order susceptibility (χ^3) of C5SS crystal were calculated and these values are listed in Table-1. The nonlinear absorption can be attributed to the saturable absorption process, while the nonlinear refraction leads to self-defocusing behaviour in the C5SS crystal. The evaluated third-order nonlinear optical parameters confirm the suitability of the material for optical limiting and optical switching applications [22].

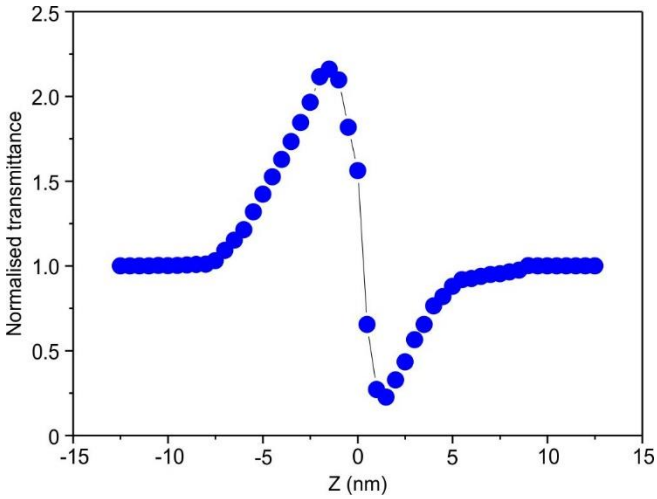


Fig. 7. Z-scan plot traced for C5SS crystal in closed aperture mode

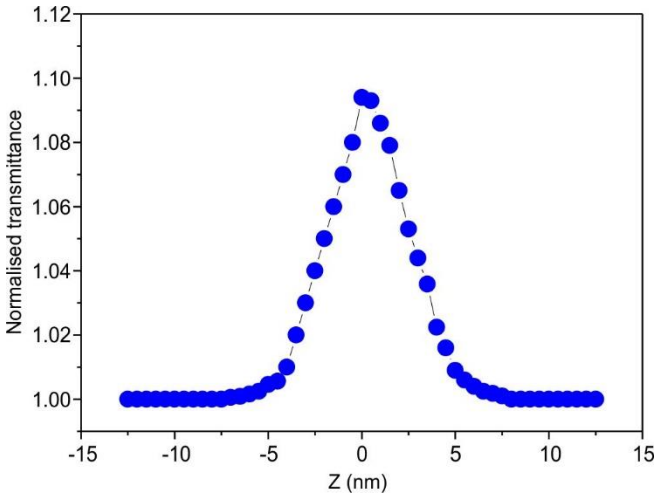


Fig. 8. Z-scan plot traced for C5SS crystal in open aperture mode

TABLE-1
THIRD ORDER NONLINEAR OPTICAL PARAMETERS OF C5SS CRYSTAL MEASURED IN Z-SCAN EXPERIMENT

Parameters	Values
Nonlinear refractive index (n_2)	9.77×10^{-8} cm^2/W
Nonlinear absorption coefficient (β)	0.07×10^{-4} cm/W
Third-order nonlinear optical susceptibility ($\chi^{(3)}$)	11.21×10^{-6} esu

The optical limiting behaviour of C5SS is shown in Fig. 9. This study shows that the transmitted output power increases linearly with the input power up to the irradiance of 28.14 mW. With the further increment of input power, the transmitted power reached a plateau and saturated at a point defined as the limiting amplitude, *i.e.*, the maximum output power showed an obvious limiting property. Thus, the C5SS crystal could be a suitable for optical limiting applications [23].

Conclusion

Creatininium 5-sulphosalicylate (C5SS) nonlinear optical single crystal was grown by slow evaporation solution growth technique. The C5SS crystal crystallised in monoclinic crystal system with the space group of $P2_1/c$. FTIR spectral analysis

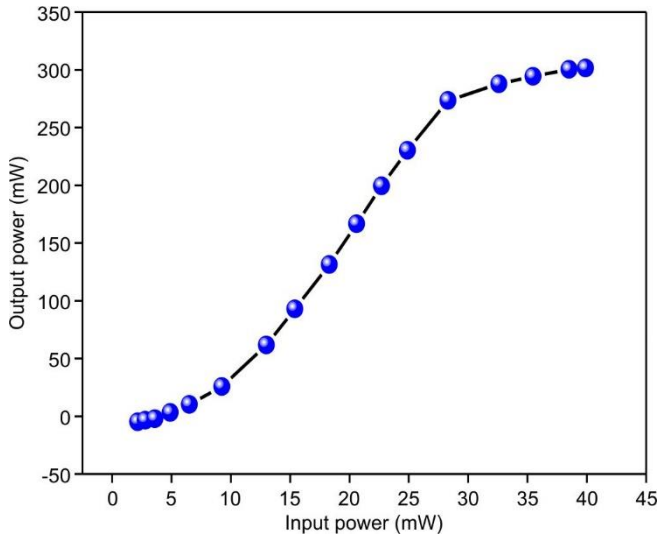


Fig. 9. Optical limiting curve of C5SS crystal

revealed the vibrational behaviour of the synthesised crystal. From the thermal analysis, it is evident that the material is thermally stable up to 120 ºC and the melting point (110 ºC) of grown crystal was observed. From the UV-vis spectral analysis, it is found that the C5SS crystal is transparent in the visible region with the lower cut-off wavelength of 328 nm and band gap energy (3.7 eV) of C5SS crystal. The laser radiation withstand capacity of grown C5SS crystal was found to be 5.23 GW/cm^2. The third order nonlinear optical susceptibility (χ^3), nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) were estimated by the Z-scan technique. From the optical limiting study, it is found that the C5SS crystal is suitable candidate for the optical limiting applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language. The authors reviewed and edited the content and take full responsibility for the published work.

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