Optical non-linearities by Z-scan measurements, thermal characterization of single crystal: 8-hydroxyquinolinium 3-carboxy-4-hydroxy benzene sulfonate monohydrate

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Abstract. Single crystals of 8-hydroxyquinolinium 3-carboxy-4-hydroxy benzene sulfonate monohydrate were grown by slow evaporation technique at room temperature by using ethanol as solvent. Single crystal X-ray diffraction study elucidated that the crystal structure of8-hydroxyquinolinium 3-carboxy-4-hydroxy benzene sulfonate monohydrate belongs to monoclinic crystal system with space group $P2_1/n$. The solid state physical parameters have been also determined for the grown crystal from the single crystal data. The cut-off wavelength and optical band gap energy of grown crystal was found to be 420 nm and 2.67 eV respectively.Thermogravimetric and differential thermal analysis reveals that the 8-hydroxyquinolinium 3-carboxy-4-hydroxy benzene sulfonate monohydrate single crystal is thermally stable up to 144˚C without any weight loss. The mechanical properties of the grown crystal were studied by Vickers microhardness technique and it is found that 8-hydroxyquinolinium 3-carboxy-4-hydroxybenzene sulfonate monohydrate belongs to hard material category. The third order nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and nonlinear optical susceptibility (χ^3) of the grown crystal were also measured by Z-scan studies.
Key words: Solution growth, Optical properties, Mechanical studies, Thermal properties

1. Introduction

The potential applications such as optical electronics, laser technology, bio imaging, telecommunication and data processing are relay upon the organic nonlinear optical crystals, hence the researchers have taken keen interest in these fields [1-4]. Organic nonlinear materials are highly active than inorganic materials due to the presence of weak Van der Waals forces and hydrogen bonds. Hence, it provides a high degree of delocalization for charge transfer [5]. Large optical laser damage threshold, low frequency dispersion and response time of nonlinear optical crystals of second and third order polarizability stimulated the investigation towards the synthesis of novel π-conjugated organic molecules [6-8]. 8-hydroxyquinoline is a versatile compound having extraordinary antifungal and antimicrobial activities where the complexes are formed due to variety of charge transfer chromophores [9-12]. The optical nonlinearities of 8-hydroxyquinoline compounds are improved due to increasing acceptor character of pyridine or by increasing the donor character of benzene ring. So, we can ascertain that 8HQ acts both as acceptor as well as donor [13]. The grown crystals were characterized by single crystal X-ray diffraction, UV–Visible spectroscopy, thermal, mechanical,Z-scanstudies and obtained results were discussed.

2. Experimental Procedure:

2.1. Material Synthesis and Crystal Growth

The 8HQ3C4S compound was synthesized using 8-hydroxyquinoline (Merck) 5-sulfosalicyclic acid (Merck) raw materials in 1:1 molar ratio. The calculated amount of

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5-sulfosalicyclic acid and8-hydroxyquinoline were dissolved in ethanol solvent. The solution continuously stirred using a motorized magnetic stirrer to ensure homogenous solution and concentration throughout the volume of the solution. The chemical synthesis scheme of the reaction is shown in Fig.1.The resultant saturated solution kept in a dust free atmosphere at room temperature, allowed for slow evaporation towards bulk growth. A good quality 8HQ4C3S crystal harvested having dimension of 23 × 4 × 4 mm^3 over the period of 15 days. The photograph of the grown crystal is shown in Fig.2.

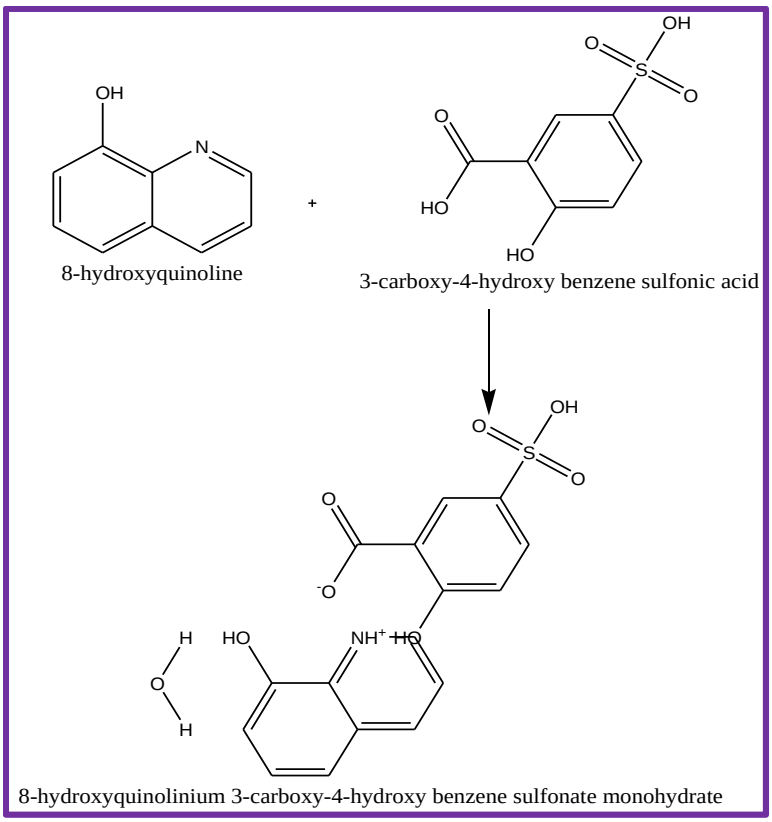

Figure 1. Reaction scheme of 8HQ3C4S crystal

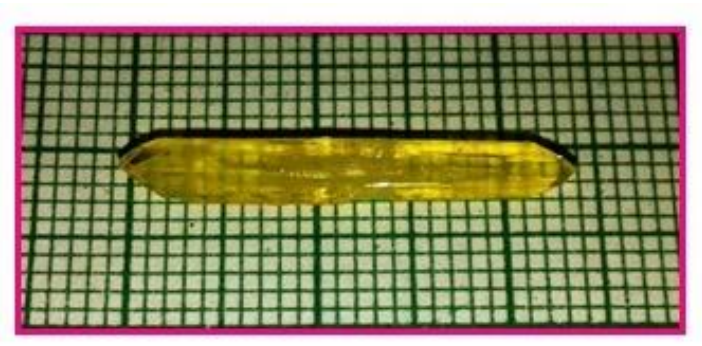

Figure 2. As-grown 8HQ3C4S crystal

3. Results and Discussion

3.1. X-Ray Diffraction Studies

The crystal structure was studied from single-crystal X-ray diffraction analysis using Bruker AXS Kappa Apex II CCD diffractometer with Mo-Kα radiation (λ=0.71073 Å, graphite monochromator). The XRD data reveal that the 8HQ3C4S crystal belongs to the monoclinic system with the space group of $P2_1/n$. The calculated cell parameter values are good agreement with reported values a = 13.24 Å, b = 10.62 Å, c = 13.56 Å, α=γ= 90°, β=119.11° and volume V = 1665 $Å^3$ [14]. The density of grown crystal was found to be ρ = 1.518 mg/m^3 and the dielectric constant at 5 MHz is ε_∞= 46.86. The molecular weight of the 8HQ3C4S crystal is M= 381.35 and the total number of valance electron Z = 198. The valance electron plasma energy, $\hbar\omega_p$ is given by the relation

$$\hbar\omega_{\mathrm{P}} = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \quad (1)$$

where, Z is the total number of valance electrons, ρ is the density and M is the molecular weight of 8HQ3C4S crystal. The fermi energy in terms of plasma energy is given by the relation [15],

$$E_P = \frac{\hbar\omega_P}{\left(\varepsilon_\infty - 1\right)^{1/2}} \quad (2)$$

and

$$E_F = 0.2948\left(\hbar\omega_P\right)^{4/3} \quad (3)$$

Polarizability α is obtained using the relation [16]

$$\alpha = \left[\frac{\left(\hbar\omega_p\right)^2 S_o}{\left(\hbar\omega_p\right)^2 S_o + 3E_P{}^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^{-3} \quad (4)$$

where, S_0 is a constant for a particular material and is given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \quad (5)$$

The value of α so obtained agrees well with that of clausius - Mossotti equation given by,

$$\alpha = \frac{3M}{4\pi \mathrm{N}_A \rho} \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \quad (6)$$

where,N_A is Avogadro number (6.6022 x 10^{-23}) and the calculated fundamental data on the grown crystal of 8HQ3C4S are given in Table.1.

Table.1.Theoretical data for 8HQ3C4S crystal.

Parameters	Values
Plasma energy (eV)	26.07
Penn gap (eV)	1.79
Fermi gap (eV)	22.78
Polarizability (cm^{-3}) using Penn analysis	9.241x 10^{-23}
Polarizability (cm^{-3}) using Clausius-Mossotti equation	9.257x 10^{-23}

3.2. Uv-Visible Spectral Studies

The optical properties of solid provide an important tool for studying energy band structure, impurity levels, lattice vibrations, localized defects, excitons and certain magnetic excitations. The band gap energy and refractive index are the two fundamental physical quantities which characterize the electronic and optical properties of materials. The different arrangement of ions and free charges in a crystal gives raise to the energy band-gap. These lattice arrangements given by the different elements combined (binary, tertiary, etc,) and doping result in different refractive indices, thus light propagates differently in every crystal [17]. The UV-vis transmission spectrum of an 8HQ3C4S crystal was recorded in the range 250-800 nm using a PerkinElmer Lambda 650 instrument spectrophotometer. The crystal has a sufficient transmission in the visible region as shown in Fig.3(a). The lower cut-off wavelength of 8HQ3C4S was found to be 420 nm.

3.2.1. Determination of Optical Band Gap

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the relation,

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (7)$$

The optical band gap (E_g) was evaluated from the transmissions spectrum and the optical absorption coefficient (α) near the absorption edge is given by [18]

$$h\nu\alpha = A\left(h\nu - E_g\right)^{1/2} \quad (8)$$

where $E_g$the optical band gap, A is a constant of the material, h is a Planck's constant and υ the frequency of the incident photons. The optical band gap was calculated from the plot between hυ and $(\alpha h\upsilon)^{1/2}$depicted inFig.3(b) and the band gap energy of the crystal was found to be 2.69 eV.

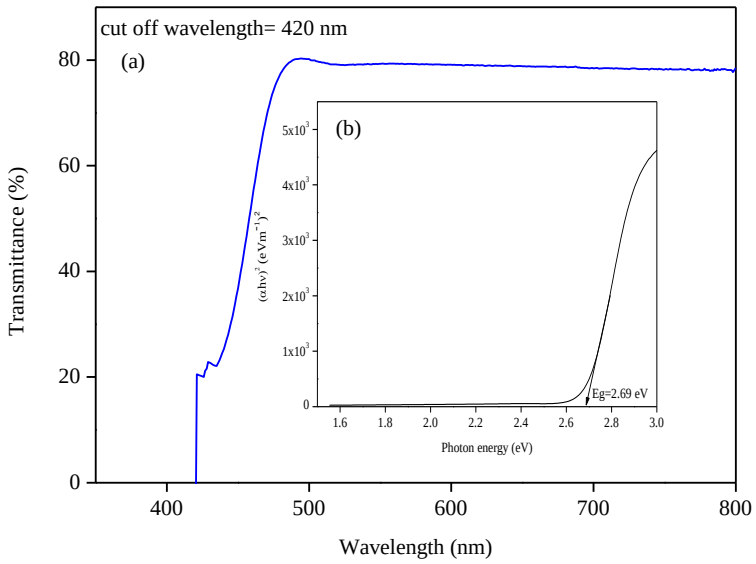

Figure 3(a). UV-vis spectrum (b) Plot of $(\alpha h\upsilon)^2$ vs. photon energy of 8HQS crystal.

3.2.2. Refractive Index

The refractive index of the material can be measured from the reflectance (R) in terms of absorption coefficient can be obtained from the following relation [19]

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t) - \exp(3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad (9)$$

The refractive index (n) can be determined from the reflectance data using

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

The refractive index 1.64 obtained the 8HQ3C4S crystal is used to calculate third order nonlinear successbility.

3.3. Thermal Studies

Thermal stability was analysed for the grown 8HQS crystal by thermogravimetric analysis using the model NETZSCH STA 449F3 in a nitrogen atmosphere at a heating rate 20 K/ min in the range from room temperature to 500^{o}C in the alumina crucible. The thermogravimetric (TG) and differential thermal analysis (DTA) are the important characterization technique to study the thermal stability, melting point, phase transition and different stages of decompositions of the sample. The thermogram TGA and DTA of the compound is shown in Fig.4. From TGA trace, The TG curve shows a three-stage weight loss pattern when the material was heated from 30^{o}C to 500^{o}C. The initial weight loss up to 144^{o}C reveals the presence of 1 mole of water in the lattice. Removal of water is immediately followed by decomposition of 8HQ3C4S and this decomposition extends up to 283^{o}C**.** In DTA curve shows the initial exothermic peak at 128^{o}C is due to desorption of water. The sharp exothermic peak at 223^{o}C is due to the decomposition of the compound. From the thermal analysis the 8HQ3C4S crystal is thermally stable up to 144˚C without any weight loss and can be useful for NLO applications.

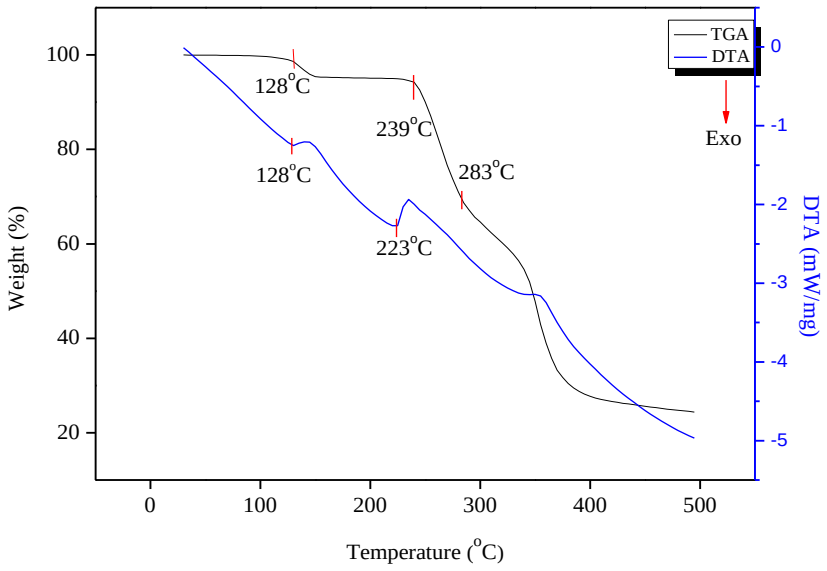

Figure 4. TG-DTA curve of 8HQS compound

3.4. Mechanical Studies

Hardness of a crystal sample takes over enormous information such as the strength, molecular bindings and elastic constant hence it plays a major role in device fabrication [20-22]. Mechanical behaviour of single crystal is related mainly to the molecular structure and composition of crystalline solids. Mechanical strength of 8HQ3C4S crystal is tested using Vicker's microhardness study. It was carried out on a crack free smooth polished surface of the grown crystal. The indentations were taken for different loads ranging from 10g to 100g with a constant indentation time of 10s at room temperature in all of each case. The standard equation for finding out the Vicker's Microhardness number (H_v) is given by,

$$H_v = 1.8544(P/d^2)\ (kg/\ mm^2) \quad (11)$$

The parameters 'H_v' is the hardness number in kg/mm, 'P' is the applied load in gm and 'd' is the mean diagonal length of indentation impression in mm. The variation of hardness number (H_v) with respect to the applied load (P) is represented in the Fig .5. From the figure it is evident that the microhardness of 8HQ3C4S sample gradually increases with increase in applied loads from 10g to 100g, and on further applying load after 100g the smooth crystal surface breaks due to the external stress created by the indentation [23]. The relation connecting the applied load (P) and the mean diagonal length (d) of the indenter is given by the Meyer's Law as shown below:

$$P = K_1 d^n \quad (12)$$

where, 'k' is the material constant and 'n' is the Meyer's index. This relation is used to plot the graph between log (d) and log (P) as drawn in Fig.6.for the 8HQ3C4S crystal. The slope of this straight line gives the Meyer's index number 'n'. According to the concept of Onitsch 'n' should lie between 1 and 1.6 for harder material and above 1.6 for softer materials [24,25]. The Meyer's index number of 8HQ3C4S sample was calculated to be 1.15, thus the grown 8HQ3C4S crystal belongs to harder material category.

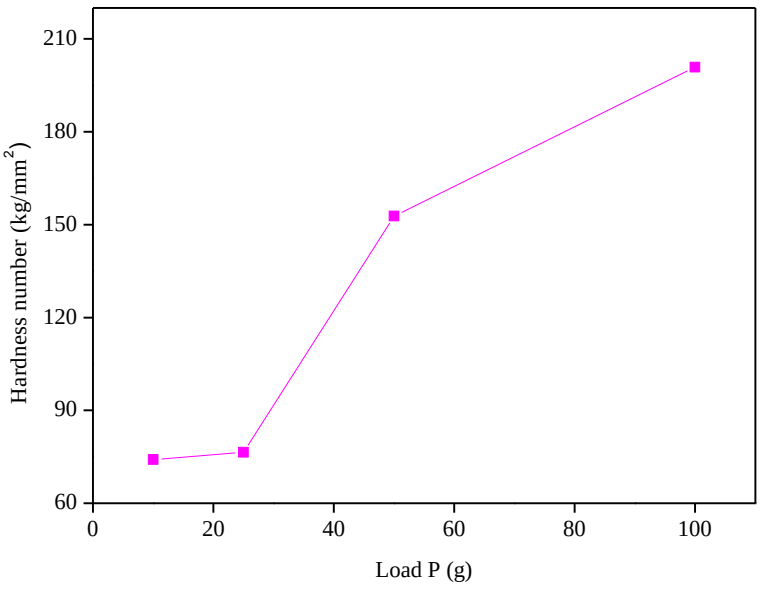

Figure 5. Variation of hardness number (Hv) with respect to the applied load (P).

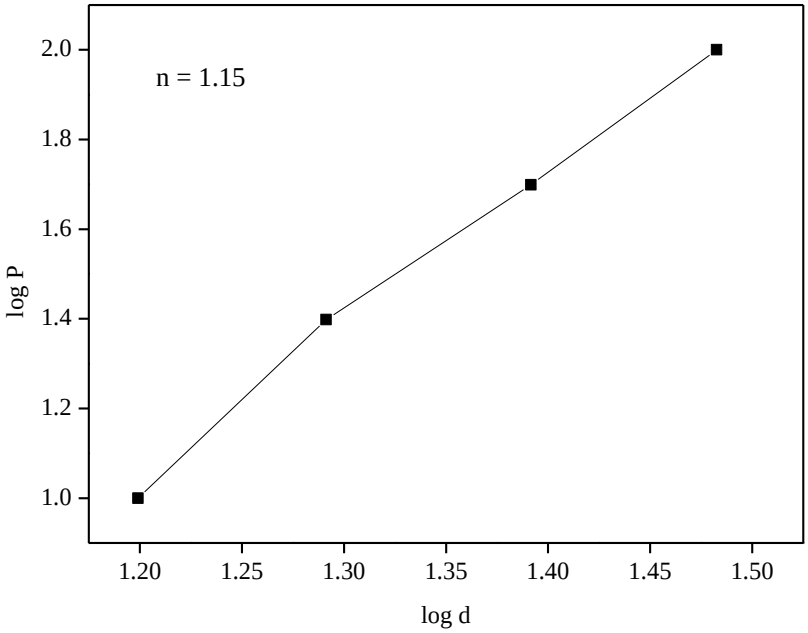

Figure 6. Plot of log P with log d of 8HQS crystal

3.5. Z-Scan Technique

The third order nonlinearities of 8HQS were investigated with Z-scan method by using A CW He-Ne laser of wavelength of 632.8nm. The laser beam was focused to a waist of 45μm with the help of a lens of focal length 12cm to give the intensity of 6.25×10^7 W/m^2 at the focus. The sample is moved along the optic axis (z-direction) through the focus of the lens. The energy transmitted through an aperture is recorded as a function of the sample position. Generally, typical z-scan data with fully open aperture is insensitive to nonlinear refraction [26]. Therefore, the data are expected to be symmetric with respect to focus. For materials with two – photon absorption, there is a minimum transmittance in focus (valley) and for saturable absorber samples there is a maximum transmittance in the focus (peak). The saturation of absorption enhances the peak and suppresses the valley, while saturation produces the opposite effect [27]. It is a successful technique to study the third order NLO properties of the grown crystal, namely, nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and the third order susceptibility($\chi^{(3)}$). In the z-scan measurements, it is assumed that the sample thickness is much less than Rayleigh's range (z_0). It is written as,

$$Zo = \frac{k\omega_o^2}{2} \qquad (13)$$

where,k is the wave vector and ω_0 is the beam waist radius given by

$$\omega_o = \frac{f\lambda}{D} \qquad (14)$$

Here, D is the beam radius at the lens used, $\lambda$is the wavelength of the source and f is the focal length of the lens.Fig.7. shows the normalized transmission is symmetric for the open curvature (OA). The transmission is symmetric with respect to the focus (Z=0), where it has a minimum transmission. The phase shift at focus (Z=0) is calculated using the relation,

$$\Delta\phi = \frac{BI_o L_{eff}}{Z} \qquad (15)$$

where,L_{eff} is the effective thickness of the sample, I_o is the intensity of the beam focused at the focus, Z is the propagation depth of the light and β is the non-linear absorption coefficient. B and L_{eff} can be calculated using the following relation,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_o L_{eff}} \qquad (16)$$

where ΔT is the value at the open curvature Z-scan curve. L is the linear absorption co-efficient at 632.8 nm and d is the thickness of the sample. The imaginary part of the third order nonlinear is given by

$$\chi_I^{(3)} = \frac{10^{-2}\varepsilon_o c^2 n_o^2 \lambda\beta}{4\pi^2} \qquad (17)$$

where n_o is the linear refractive index (n_o= 1.661 at λ = 632.8 nm), ε_o is the permittivity of free space and c is the velocity of light. The non-linear refractive index of the solid crystal can be calculated using the relation,

$$n_2 = \frac{\Delta\Phi_o}{KI_o L_{eff}} \qquad (18)$$

The real part of the third order non-linear susceptibility is given by the relation,

$$\chi_R^{(3)} = \frac{10^{-4}\left(\varepsilon_o c^2 n_o^2 n_2\right)}{\pi} \qquad (19)$$

The normalized transmittance for closed aperture is shown in Fig.8. The importance of this curve is to understand the sign of the nonlinear refractive index and to calculate the nonlinear susceptibilities. In Fig.8, the peak is followed by valley. This suggests that the nonlinear refractive index and nonlinear susceptibilities are positive exhibiting defocusing effect. The third order nonlinear coefficientis -1.380 ×10^{-6}esu. Theabsolute value of $\chi^{(3)}$ is given as,

$$\chi^{(3)} = \sqrt{\left(\chi_I^{(3)}\right)^2 + \left(\chi_R^{(3)}\right)^2} \qquad (20)$$

The negative sign of the nonlinear absorption coefficient is attributed to the saturation absorption process in 8HQ3C4S material [28]. The third-order nonlinearity of a material is dominated by nonlinear absorption and nonlinear refraction, which lead to the strong optical limiting of the laser. The Z-scan measurements indicate that 8HQ3C4S exhibits negative nonlinear optical properties. It is worth noting that the value of nonlinear susceptibility ($\chi^{(3)}$) for 8HQ3C4S is larger than those of some representative third-order nonlinear optical materials [29-31].

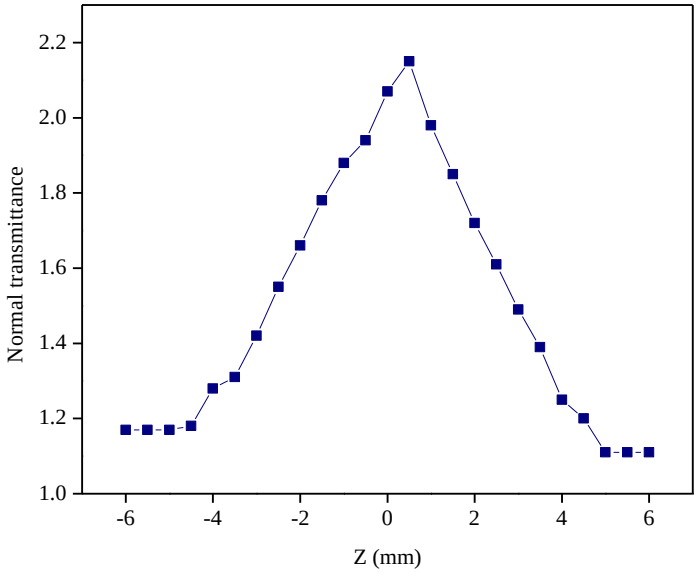

Figure 7. Normalized Transmission for Open aperture (OA)

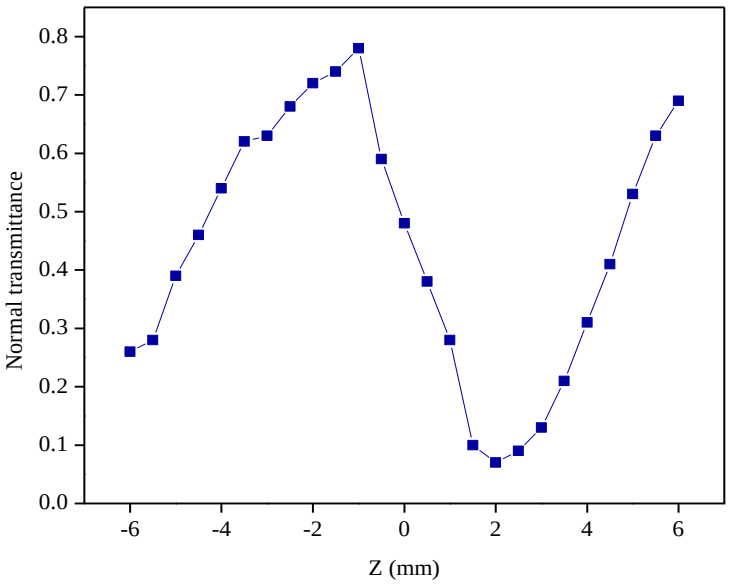

Figure 8. Normalized Transmission for Closed aperture (CA)

4. Conclusion

Good quality organic NLO crystals of 8HQ3C4S have been successfully grown by slow evaporation technique. The cell parameter was measured by single crystal XRD method and confirms the crystal system as monoclinic. The absence of absorption in the entire visible region in UV–Vis spectrum of 8HQ3C4S makes the crystal in to a suitable material for optoelectronic applications. The melting point of the compound was found to be 223^{o}C from the thermal study. The Vickers microhardness numbers H_v for the crystals were calculated and it increases with increasing load.The third order nonlinear coefficients were estimated using z-scan technique and these coefficients are found to exhibit self-defocusing effect. Hence 8HQ3C4S is an excellent third order NLO material which can find applications in optoelectronic, photonics and holographic applications.

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