CHAPTER III

GROWTH, STRUCTURAL, ELECTRICAL, MECHANICAL AND NONLINEAR OPTICAL STUDIES OF 2-PHENYLETHYLAMINIUM 5-SULFOSALICYLATE CRYSTAL

3.1 INTRODUCTION

In the last few decades, the third order nonlinear optical materials have invited much interest because of their potential applications in optoelectronic telecommunications. The different types of NLO materials along with organic materials have triggered a vast deal of studies on their high nonlinearities and electro optic coefficients, ultra fast response, high laser damage threshold, comfort of fabrication into devices (Zhang et al 2011; Takahashi et al 2006). Organic nonlinear optical materials are the most technologically important materials owing to their broad range of applications in different attractive and capable technologies counting nonlinear optics (NLO), electro-optic modulation, optical communication and terahertz (THz) wave generation (Brahadeeswaran et al 2006). Expansion of benzene derivative has allowed to increase the number of π-electrons as well as their delocalization length, and it leads to phenomenal development in hyperpolarizability (Srinivasan et al 2007).

Smith et al (2004), reported the crystal structure of 5-sulfosalicylate derivative crystals such as Bis(guanidinium) 5-sulfosalicylate monohydrate and Dhavamurthy et al (2015), reported the growth of bis(guanidinium) 5-sulfosalicylate (BG5SS) by slow evaporation method. It was observed that BG5SS compound is thermally stable up to 65°C. BG5SS crystal possessed high hardness value which belongs to hard material.

Yang-Yang et al (2015) reported the structure and growth of Ammonium 5-sulfosalicylic acid monohydrate ($NH_4 \cdot C_7H_5O_6S \cdot H_2O$, ASSA). The crystal belongs to monoclinic system with $P2_1/c$ space group. The ASSA crystal showed optical transmission range upto 80%.

Sivakumar et al (2013) reported the crystal refinement of 4-nitroanilinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate. The single crystal of 4-nitroanilinium 5-sulfosalicylic acid monohydrate (4NASA) was investigated by Sivakumar et al (2015), the crystal structure and growth aspects were discussed. 4NASA was grown by the slow evaporation technique, which belongs to the orthorhombic crystal system with space group Pbca. Z-scan method was used to measure the third-order nonlinear optical properties.

Storp et al (2012) investigated the single crystal X-ray diffraction, crystal structure, quantum chemical calculation and thermal properties of 5-sulfosalicylate organic crystal. The crystal refinement and hydrogen

bonding in the proton-transfer salt of nicotine with 5-sulfosalicylic acid have been reported by Smith et al (2014).

The result of hydroxyl group in 5-sulfosalicylic acid, as an extra proton-donor substituent, on the structure of 2-phenylethylammine have been studied. The crystal structures of some 2-phenylethylammonium salts have also been reported (Hlel et al 1999; Huh et al 2006; Rademeyer et al 2006). Experimental studies on the correlation of the structure and spectroscopic properties of 2-phenylethylammonium derivatives are fairly rare.

The growth of 2-phenylethylaminium 4-nitrophenolate monohydrate single crystal and crystal structure refinement were reported by Swarna Sowmya et al (2014). The crystal structure of 2-phenylethanaminium 3-carboxyprop-2-enoate single crystal was reported by Swarna Sowmya et al (2015).

Sudhahar et al (2014) investigated the crystal structure and growth aspects of 2-Phenylethylammonium p-hydroxybenzoate (2PPHB). The 2PPHB crystal was grown by slow evaporation solution growth method. Single crystal X-ray diffraction studies reveal that 2PPHB crystallizes in orthorhombic crystal system with Pna21 space group. 2PPHB crystal was thermally stable up to 155^{o}C and the nonlinear property of SHG efficiency was found to be 3.17 times than that of KDP.

The newly synthesized 2-phenylethylaminium 5-sulfosalicylate (2PE5S) possesses centrosymmetric nature, due to this reason it can be motivated to investigate the third order nonlinear susceptibility (χ^3). In the present investigation, the synthesis and bulk growth of 2-phenylethylaminium 5-sulfosalicylate single crystal from aqueous solution were performed based on the solubility measurement. The grown crystal was characterized by single crystal X-ray diffraction, spectral, thermal, UV-Vis, Photoluminescence, laser damage threshold, dielectric, mechanical and Z-scan measurements.

3.2 EXPERIMENTAL

3.2.1 Material Synthesis

An equimolar ratio of high pure 2-phenylethylamine ($C_8H_{11}N$) and 5-sulfosalicyclic acid ($C_7\ H_6\ O_6\ S$) were dissolved in deionized water for the synthesis of 2-phenylethylaminium 5-sulfosalicylate (2PE5S) and the synthesis scheme is shown in Fig.3.1. The solution was continuously stirred for about 6 hr using a magnetic stirrer to achieve the supersaturated state at 60°C and then the solution was cooled to room temperature using cryostat system. The white crystalline precipitate was obtained at the base of crystallizer while decreasing the temperature. The purity of 2PE5S salt was increased by using the recrystallization process. Then, the solution was fully covered with pin hold laminated sheet and kept in a CT bath maintained at 35°C with an accuracy ± 0.01°C.

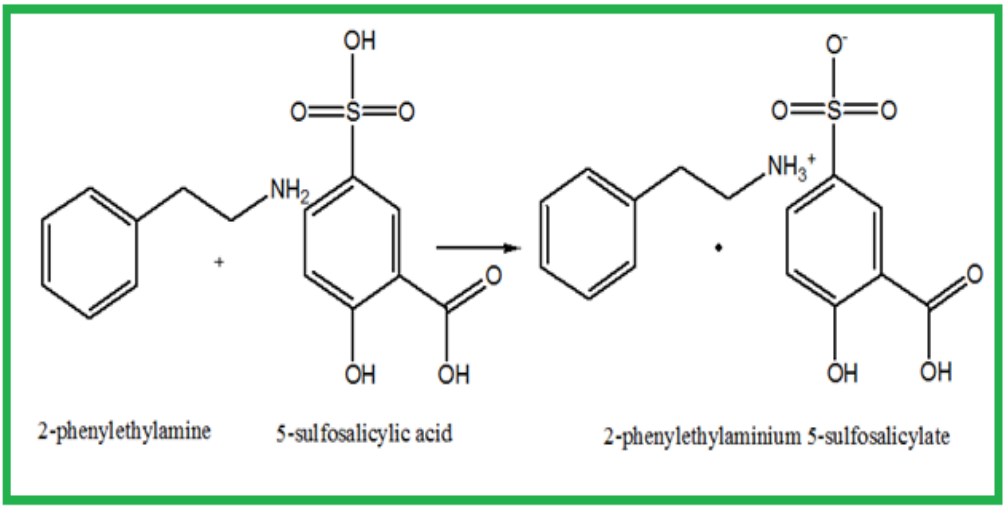

Fig.3.1 Material synthesis scheme for 2PE5S compound

3.2.2 Solubility Studies

The solubility is a significant parameter to achieve the well growth condition of 2PE5S crystal. The solubility measurement was carried out by adding 2PE5S salt in water solvent. The solubility was determined by gravimetric analysis for different temperatures ranging from 30°C to 50°C with an interval of 5°C. To attain homogeneous concentration, the solution was stirred continuously by using a magnetic stirrer. The solubility of 2PE5S compound was calculated gravimetrically, once accomplished the saturation state. From the solubility data of 2PE5S (Fig.3.2), it was observed that the 2PE5S is highly soluble in water (34 g/100 ml at 30°C) which confirms the positive solubility gradient.

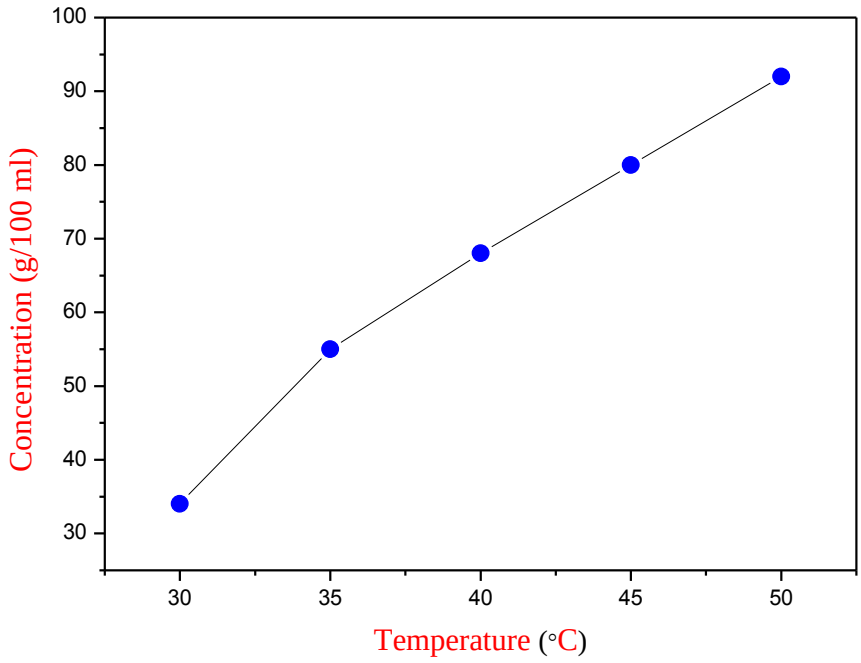

Fig.3.2 Solubility of 2PE5S in water

3.2.3 Crystal Growth and Morphology

Single crystal of 2-phenylethylaminium 5-sulfosalicylate (2PE5S) was grown by dissolving the purified salt in the deionized water solvent. The growth solution was stirred continuously for about 6 hr to achieve the homogeneous saturated solution at 35°C. Then, the growth solution was filtered using Whatman filter papers. The beaker containing the solution was closed with a perforated polythene sheet and kept in a CT bath (35°C) with an accuracy of ±0.01°C. After three week growth period, a well developed 2PE5S crystal with dimension upto 18 x 6 x 4 mm^3 was harvested as shown in Fig.3.3(a).

X-ray goniometry was used to identify the crystal planes and morphology of the crystal sample was drawn by using WinX morph software. The well developed as grown crystal of 2PE5S was subjected to morphology studies (Fig.3.3(b)), which revealed the following prominent hkl growth planes (1 2 3), (-1 -1 -1), (0 -1 -1) and (0 1 0).

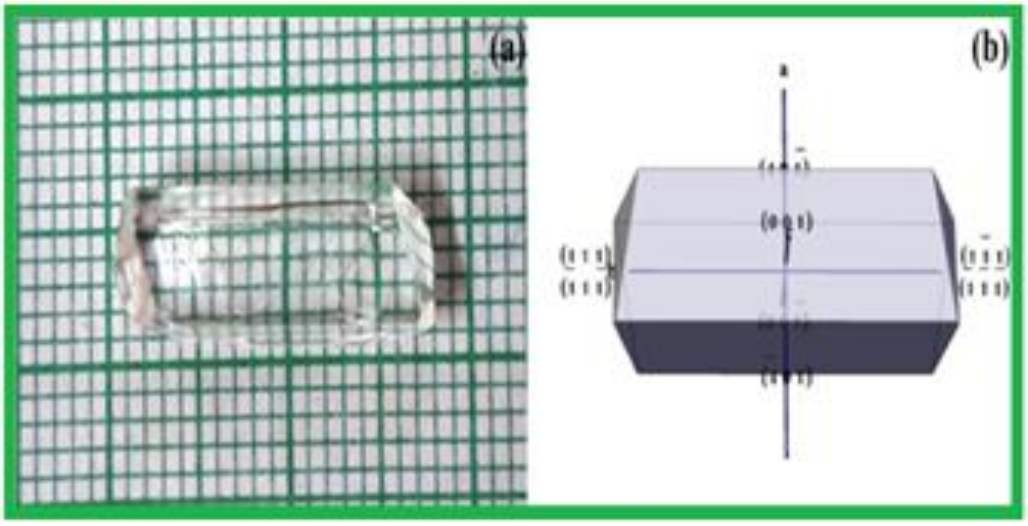

Fig.3.3 (a) Photograph of as-grown 2PE5S crystal and (b) Morphology of 2PE5S crystal

3.3 RESULTS AND DISCUSSION

3.3.1 Single Crystal and Powder X-Ray Diffraction Studies

Single crystal X-ray diffraction is a non-destructive analytical method which gives brief information about the interior lattice crystalline, dimension of unit cell, bond lengths and bond angles. Bruker Kappa APEX II single crystal X-ray diffractometer with MoK_{α} radiation (λ = 0.71073 Å) was

used to measure the cell parameters of 2PE5S crystal. From the single-crystal X-ray diffraction data, the structure was solved by the direct method and refined by the full matrix least-squares technique on F^2 employing the SHELXL 97 program package (Sheldrick et al 2008). The crystallographic data of title compound for structure analysis is listed in Table 3.2. The chemical composition of crystal is C_8 H_{10} N, C_7 H_4 O_6 S. The 2PE5S crystallizes in monoclinic crystal system with space group C_2/c which is a centrosymmetric. The estimated cell parameters are a = 29.5715(16) Å, b = 5.1829(2) Å, c = 22.1834(10) Å, α = γ = 90°, β =111.601(2)° and volume V = 3161.2(3) $Å^3$.

In the 2PE5S crystal, the cations and anions are connected via N-H…O and C-H…O hydrogen bonds, forming a two-dimensional network (Fig.3.4). The asymmetric unit of the title compound comprises of two crystallographically independent phenylethylaminium cation and sulfosalicylate anion (Fig.3.5). Figure 5 shows two pairs of phenylethylaminium cation and sulfosalicylate anion in one asymmetric unit. 2-phenylethylaminium cation and 5-sulfosalicylate anion are essentially planar, with a maximum deviation of 0.154 (2) Å for atom C4 and 0.003 (1) Å for atom C9, respectively. The diheral angle between these two planes is 43.76 (2)°. The anion is stabilized by an intramolecular O1–H1A···O2 hydrogen bond between phenolic OH and the carboxyl group, which forms an S(6) ring motif (Bernstein et al 1995). This motif is also

observed in the crystal structure of 2-aminopyridinium salicylate (Gellert et al 1988). In the solid state, the sulfonate group of 5-sulfosalicylate anion interacts with 2-phenylethylaminium cation *via* intermolecular N–H0···O4 hydrogen bonds, forming a hydrogen bonded ring motif with graph-set notation R_2^2 (10) ring motifs (Etter et al 1990). The neighbouring supramolecular chain is further interlinked *via* C-H···O hydrogen bond (C13) of 5-sulfosalicylate anion and carboxylate oxygen atom (O13) (symmetry code: -x, y, 3/2-z) of anion, forming a hydrogen bonded ring motif with graph-set notation R_2^2 (10) ring motifs as shown in Table 3.1. The identification of such supramolecular pattern will help to design and construct preferred hydrogen bonding patterns on molecules.

Powder X-ray diffraction is dominant tool for the study of crystalline materials. Each crystalline material shows a distinct X-ray diffraction pattern due to differences in lattice parameters, atom types and arrangements of molecules. The powder X-ray diffraction pattern of 2PE5S crystal was recorded in the 2θ range from 10° to 50° using CuK_α radiation of wavelength 1.5406 Å as shown in Fig.3.6. The presence of prominent Bragg peaks at specific 2θ angles confirmed the perfect crystalline nature.

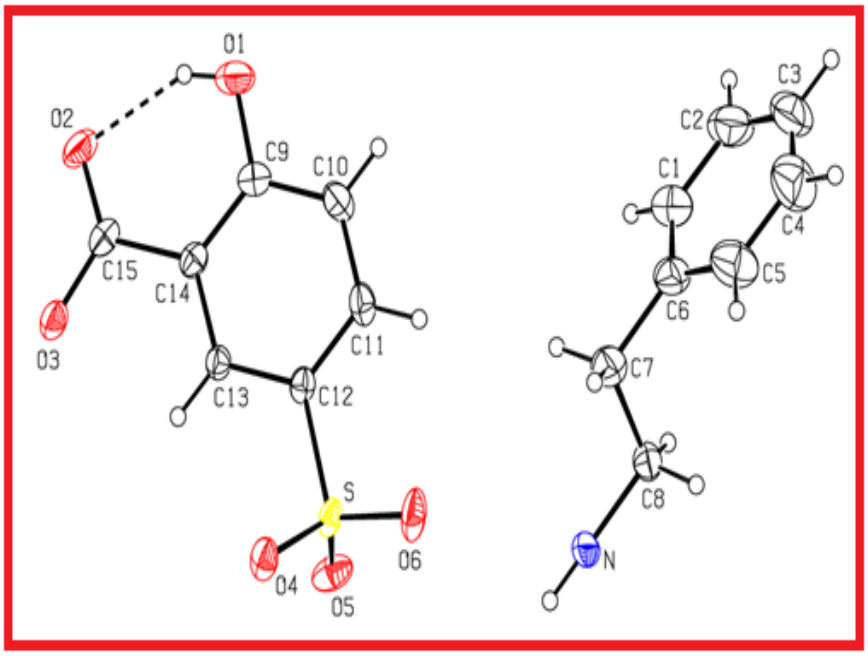

Fig.3.4 Molecular ORTEP diagram of 2PE5S crystal

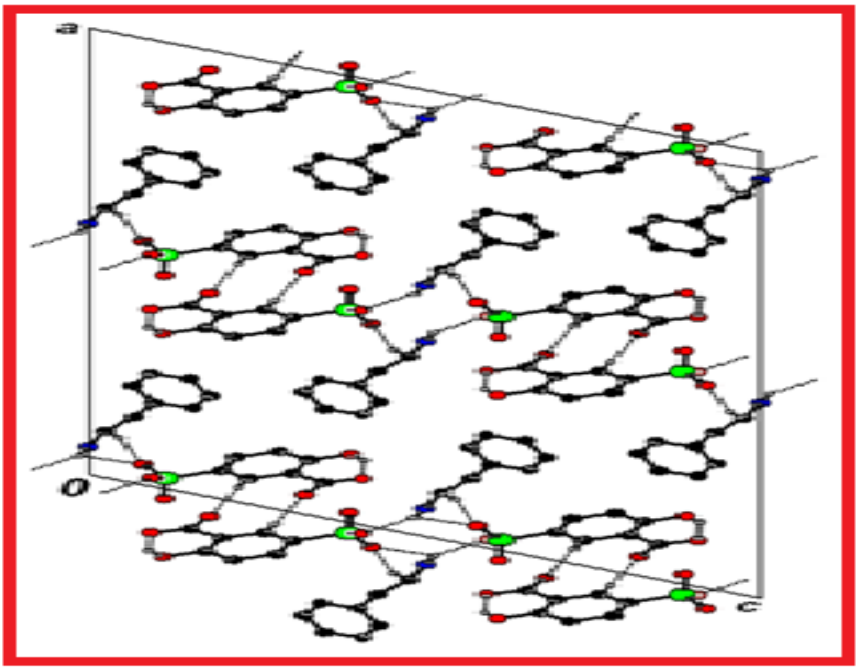

Fig.3.5 Crystal packing diagram of 2PE5S viewed along '*b*' axis

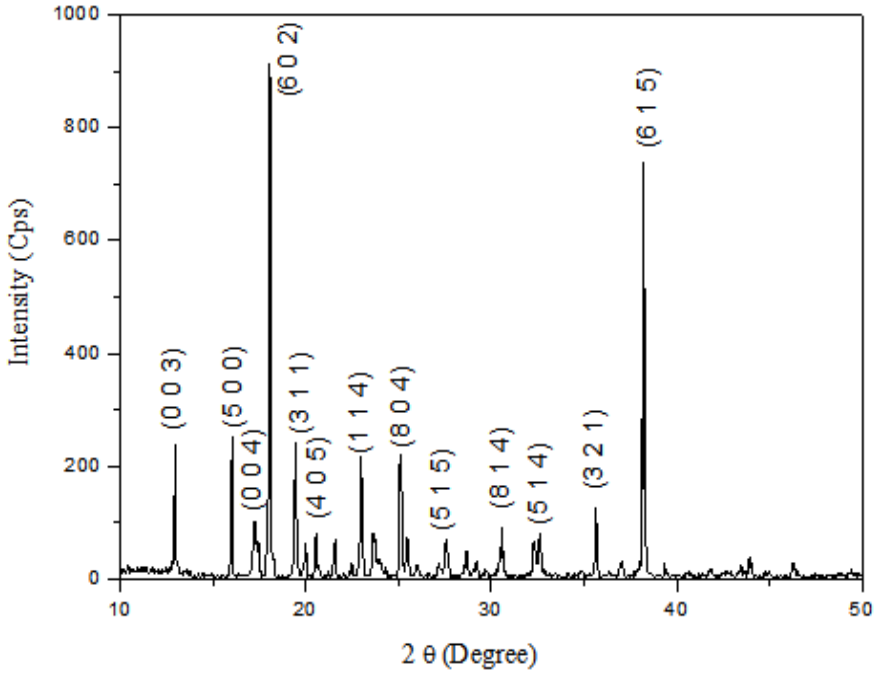

Fig.3.6 Powder X-ray diffraction pattern of 2PE5S crystal

Table 3.1 Hydrogen bonds for 2PE5S [Å and deg]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N-H(0)...O(4)#2	0.86	2.17	2.952(3)	151.0
O(1)-H(1A)...O(2)#1	0.82	1.89	2.609(3)	146.0
C(8)-H(8A)...O(6)#3	0.97	2.43	3.358(3)	160.2
C(13)-H(13)...O(3)#4	0.93	2.43	3.336(3)	164.7

Table 3.2 Crystal data and structure refinement for 2PE5S

Empirical formula	**C_{16} H_{12} N_2 O_4 S_1**
Identification code	2PE5S
Formula weight	319.72
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, C_2/c
Unit cell dimensions	a = 29.5715(16) Å α = 90° b = 5.1829(2) Å β = 111.601(2)° c = 22.1834(10) Å γ = 90°
Volume	3161.2(3) A^3
Z, Calculated density	8, 1.344 Mg/m^3
Absorption coefficient	0.260 mm^{-1}
F (000)	1320
Crystal size	25 mm X 10 mm X 5 mm
Theta range for data collection	1.48 to 26.37°
Limiting indices	-36<=h<=33, -6<=k<=6, -27<=l<=27
Reflections collected / unique	16955 / 3243 [R (int) = 0.0258]
Completeness to theta = 25.00°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3243 / 54 / 208
Goodness-of-fit on F^2	1.086
Final R indices [I>2sigma(I)]	R1 = 0.0447, wR2 = 0.1301
R indices (all data)	R1 = 0.0628, wR2 = 0.1556
Largest diff. peak and hole	0.480 and -0.886 $e.A^{-3}$

3.3.2 HRXRD Studies

The crystalline perfection of the grown 2PE5S single crystal was analysed by HRXRD studies. Figure 3.7 shows the high resolution (DC) diffraction curve recorded for 2PE5S crystal using a multicrystal X-ray diffractometer with MoKα1 radiation. From this figure, it is clear that the diffraction curve contains a single peak without any satellite peaks, which may be observed owing to internal grain boundaries in crystals (Bhagavannarayanna et al 2005). The FWHM of the DC was found to be 8 arc sec, which is slightly higher to that expected from the plane wave theory of dynamical X-ray diffraction (Betterman et al 1964). The single crystal diffraction curve with very low FWHM indicated the crystalline quality of 2PE5S crystal.

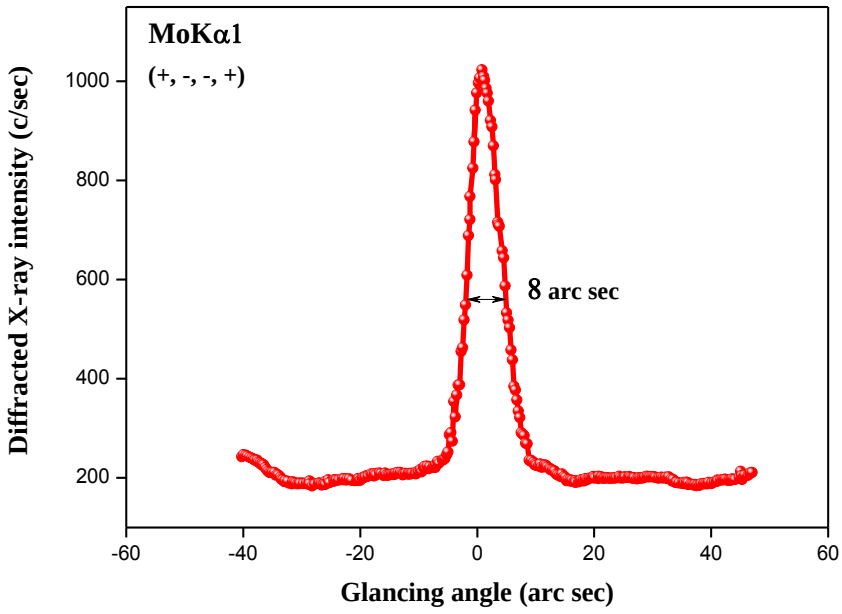

Fig.3.7 HRXRD curve of 2PE5S crystal

3.3.3 FTIR Spectral Analysis

Using Perkin Elmer FTIR spectrometer in the range 4000-400 cm^{-1}, the FTIR spectrum of 2PE5S crystal was recorded by KBr pellet technique (Fig.3.8). The presence of various functional groups in 2PE5S was identified using FTIR spectral analysis. The N-H bend primary amines assigned at 1650 cm^{-1} is due to the protonation of amino group leading to the formation of 2PE5S compound.

The C-H stretching vibration observed at 3093 cm^{-1}. In general, C-H stretching vibration appears in the region 3200-3000 cm^{-1}. The observed band at 944 cm^{-1} is assigned to C-H in-plane bending. The C-H out-of-plane bending vibration observed at 768 cm^{-1}. The O-H stretching appeared around 3590-2400 cm^{-1}. The peaks observed at 2502 and 2945 cm^{-1} are due to O-H stretching vibrations. C-O stretching vibration appeared as a strong band in the region 1306-1200 cm^{-1}. In the 2PE5S compound, it appeared at 1226 cm^{-1}.

The C=O stretching vibration occurred in the region 1780-1650 cm^{-1}. The peak appeared at 1677 cm^{-1} is due to the C=O stretching vibration. The sulfonate functional group gives IR bands for symmetric and asymmetric stretching vibrations. The asymmetric and symmetric stretching vibrations of sulfonate group in the title compound appeared at 1352 cm^{-1} and 1174 cm^{-1}

respectively (Silverstine et al 2004). Table 3.3 shows the spectral assignments of 2PE5S compound.

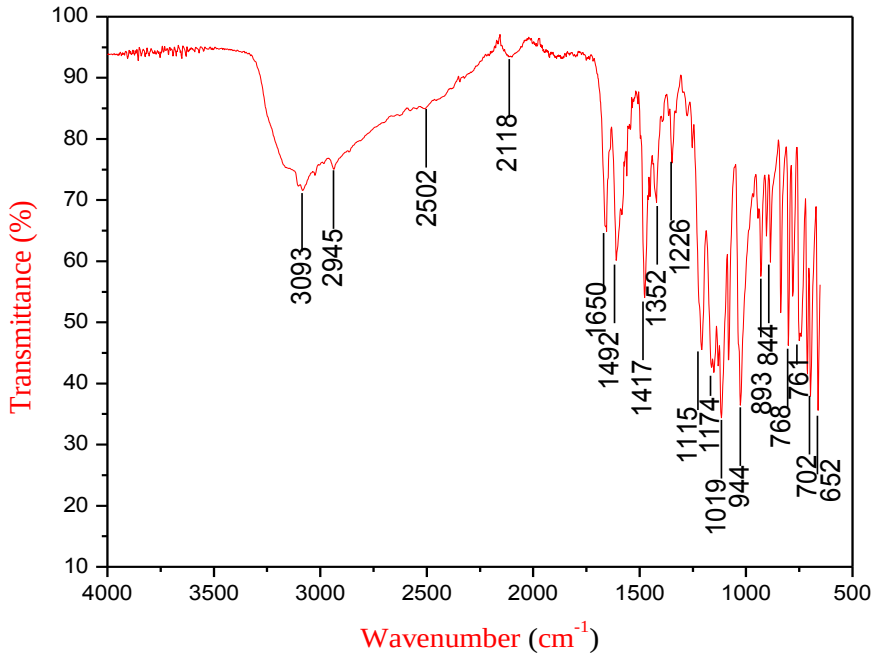

Fig.3.8 FTIR spectrum of 2PE5S crystal

Table 3.3 FTIR molecular vibrational assignments of 2PE5S

Wave number (cm^{-1})	**Assignments**
3093	C-H stretching
2945	O-H stretching
2502	O-H stretching
1650	N-H bending
1677	C=O stretching
1417	O-H plane deformation
1352	asymmetric S=O stretching
1226	C-O stretching
1019	C-O stretching
944	C-H in-plane bending
844	Out-of-plane C-H bending
768	C-H out-of-plane bending

3.3.4 TG/DTA Analysis

Thermal behaviour of 2PE5S crystal was studied by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). TGA trace gives the quantitative measurement of mass change as a function of temperature associated with transition and thermal degradation and DTA trace provides information on chemical reaction, structural change, purity and phase transition. Using NETZSCH STA 409 thermal analyser, TG-DTA curves were recorded in nitrogen atmosphere with a heating rate of 10K/min. From the TG-DTA curve (Fig.3.9) it was observed that, the compound is thermally stable upto 220°C and the decomposition process of the crystal could be divided into two steps. The first weight loss of the compound occurred in the temperature range between 221°C and 413.7°C with successive decomposition about 90.25% of compound which was evaluated into gaseous products. The endothermic peak appeared at 301.16°C in DTA is matched with the corresponding weight loss in TGA curve which is attributed to the energy required for the release of gaseous molecules. The second decomposition stage observed at 414°C and found that it lost almost all the weight of the compound. Thus, the 2PE5S crystal is capable to function upto 220°C in optical applications.

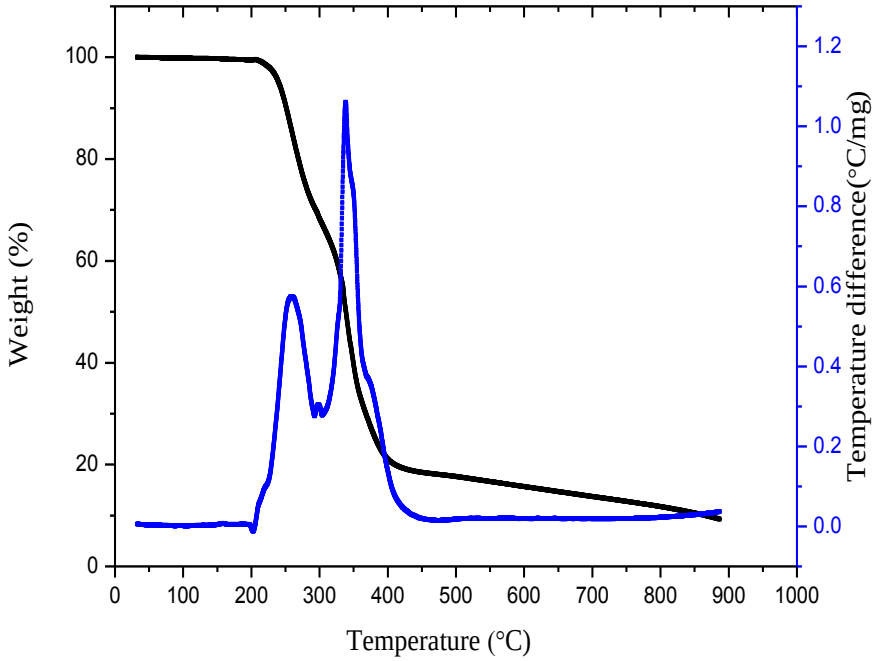

Fig.3.9 TG/DTA thermogram of 2PE5S crystal

3.3.5 UV-Visible Transmission Studies

For linear and nonlinear optical applications, the material should be very transparent in the wavelength region of particular interest. In order to find the transparency window, UV-Vis transmission spectral study of 2PE5S crystal was taken in the wavelength range 190-900 nm using T90+PG instrument spectrometer. 2PE5S crystal sample of 2 mm thickness was used to record the UV-Vis transmission spectrum as shown in Fig.3.10. UV-Vis spectrum of 2PE5S showed transparency about 65% with lower cut-off wavelength around 321 nm.

The exploration of optical coefficient with the photon energy is used to find the band structure and type of transition of the electron. From the

transmission (T), the absorption coefficient (α) has been determined. The energy dependent absorption coefficient explicitly occurred due to direct band gap of the crystal in the high photon energy region. Tauc's plot was drawn between $(\alpha h\upsilon)^2$ and photon energy ($h\upsilon$) (Fig.3.11). From the linear part of the graph, the band gap energy of the crystal was evaluated and found to be 3.8 eV (Tauc et al 1966).

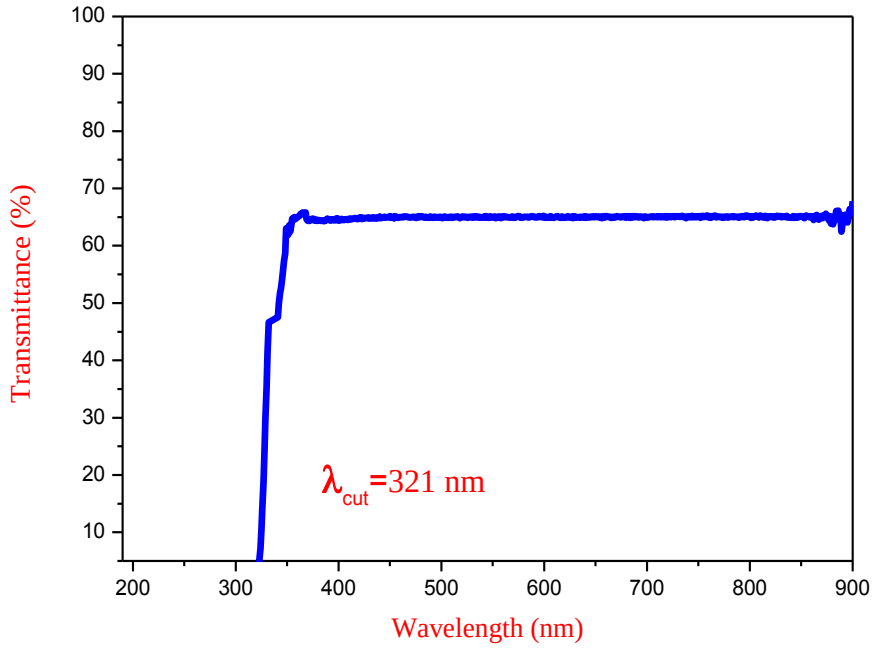

Fig.3.10 UV-Visible transmission spectrum of 2PE5S crystal

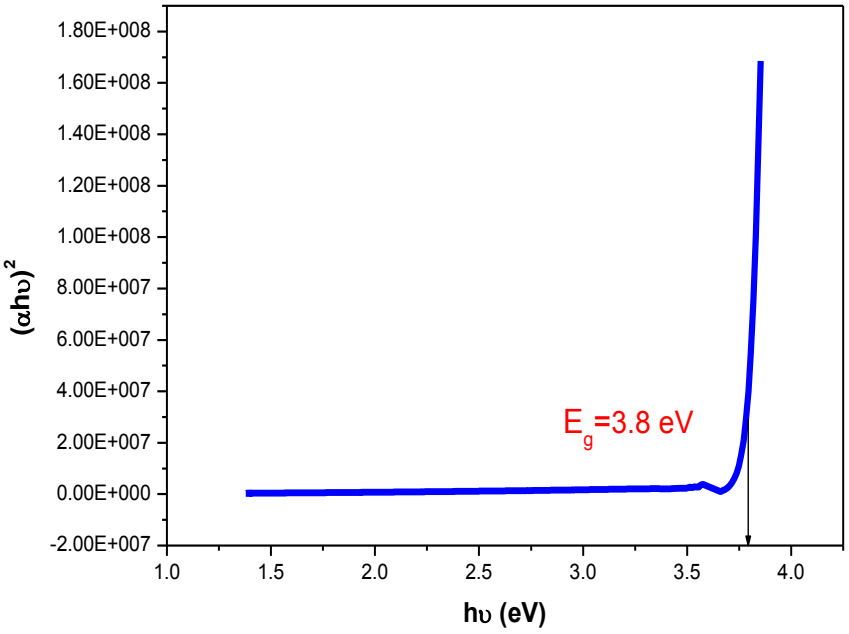

Fig.3.11 Tauc's plot drawn between $(\alpha h\upsilon)^2$ and hυ of 2PE5S crystal

3.3.6 Photoluminescence Studies

Photoluminescence is a dominant and sensitive tool for studying the effect of purification and contamination during the crystal growth process. He–Cd laser was used as the excitation source in this experiment. Photoluminescence spectrum of 2PE5S was recorded at room temperature with an excitation wavelength 280 nm as shown in Fig.3.12. From the PL spectrum, it was observed that 2PE5S compound exhibits a strong UV band peak at 468 nm, which is attributed to high purity and perfect crystallinity. The deep level holes are answerable for the green, yellow, orange and red emissions, while the shallow level holes are answerable for the violet and blue emissions (Krishna Kumar et al 2014). PL emission peak observed at 468 nm

(E_g = 2.6 eV) in the blue emission, is due to the $\pi^* \rightarrow n$ transition. The defect-free good quality 2PE5S crystal could be favoured for optoelectronic applications particularly in the blue emission.

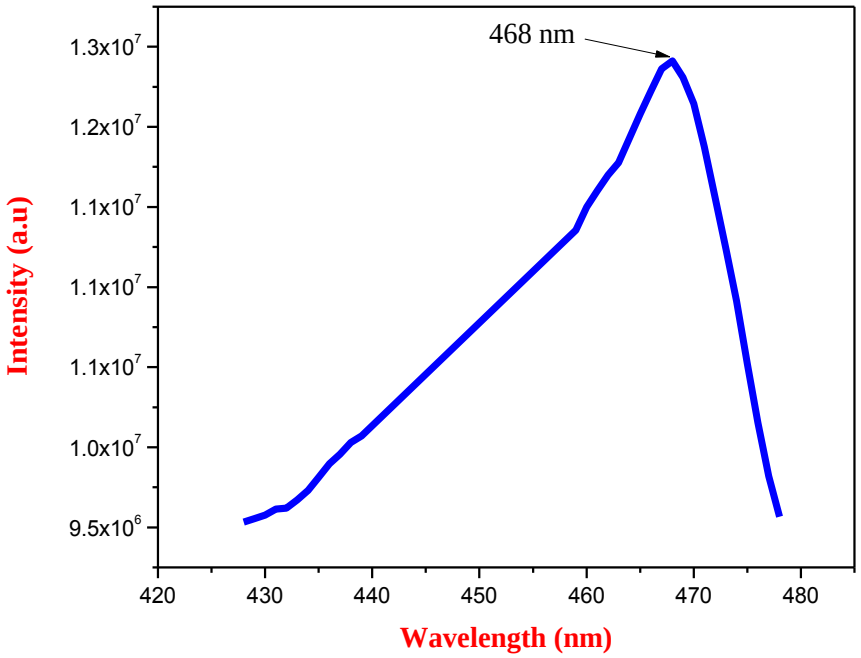

Fig.3.12 Photoluminescence spectrum of 2PE5S crystal

3.3.7 Laser Damage Threshold Studies

The optical damage tolerance is one of the most significant considerations in the preference of material choice for nonlinear optical applications. Large optical intensities are involved in the nonlinear optical applications, so that nonlinear crystals must resist to high power intensities. The laser damage threshold was measured by using induced high intensity laser light on 2PE5S crystal surface. A Q-switched Nd:YAG laser source of pulse width 10 ns and repetition rate of 10Hz was used. The output intensity

of laser beam was controlled with changeable attenuator and delivered on the test sample, which was positioned at the next to focus of the converging lens. The power meter recorded the energy density of the laser beam at which the crystal gets crack and the surface damage threshold was determined using the relation,

$$\text{Power density } P_{(d)} = E/\tau A \tag{3.1}$$

The multiple shot laser damage energy density obtained from the Q-switched Nd:YAG laser was found to be 6.3 GW/cm^2 for 2PE5S crystal which is higher than that of KDP crystal (Vijayan et al 2006) .

3.3.8 Dielectric Studies

To understand the nature of dielectric materials, it is essential to find the mechanism of charge distribution inside the material. Dielectric properties are related with electro-optic property of the crystals: mainly when they are non-conducting materials. Using HIOCKI 3532-50 LCR HITESTER instrument, the dielectric constant (ε_r) and dielectric loss (tan δ) of the grown crystal were determined. The dielectric studies were carried out for 2PE5S crystal in the frequency range from 100 Hz to 6 MHz at room temperature. The dielectric constant ε_r can be calculated using the relation,

$$\varepsilon_r = \frac{Ct}{\epsilon_0 A} \tag{3.2}$$

From the Fig.3.13, the dielectric constant has large value at low frequencies and nearly constant at high frequencies. The value of dielectric constant depends on the degree of polarization and space charges in crystals. It has been reported that the 2PE5S crystal possess low dielectric constant which leads to decrease the power dissipation. Figure 3.14 shows the variation of dielectric loss (tanδ) with applied frequency for 2PE5S crystal. The low dielectric loss with high frequency provides that the crystal acquired good optical quality. Consequently, the low value of dielectric constant and dielectric loss are greatly important for materials used in the photonics and NLO devices (Smyth et al 1955).

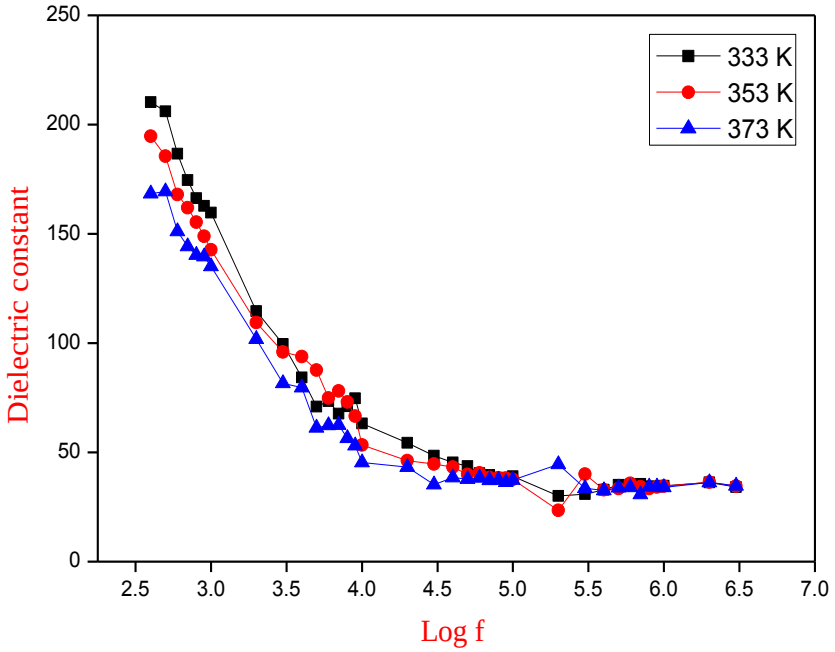

Fig.3.13 Plot drawn between dielectric constant and log frequency of 2PE5S crystal

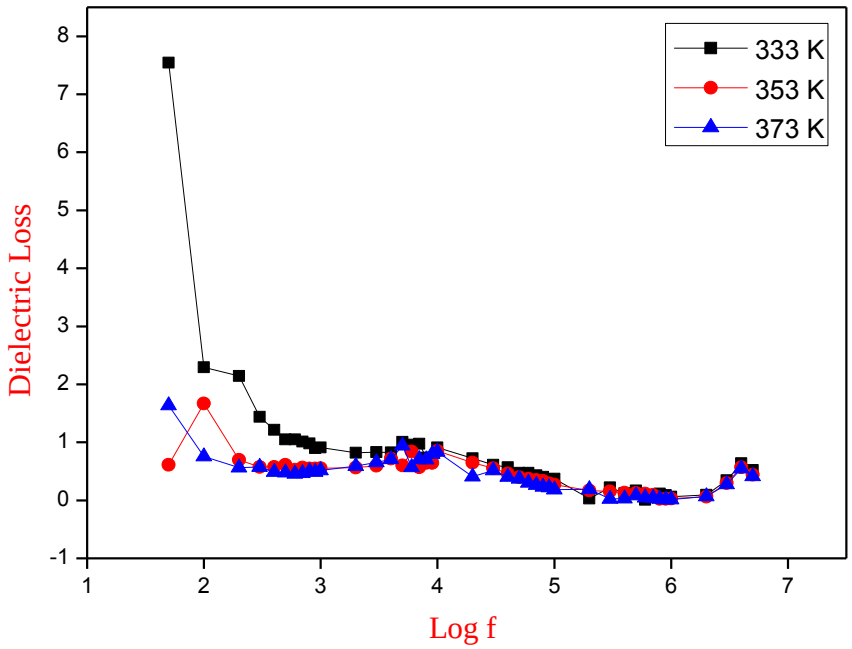

Fig.3.14 Plot of dielectric loss vs log frequency of 2PE5S crystal

3.3.9 Mechanical Studies

Hardness is one of the essential mechanical properties to find the nature and strength of a material. Vicker's microhardness indentations were made on the flat surface of the grown 2PE5S crystal at room temperature with the applied load ranging from 10 g to 100 g using Vicker's microhardness tester. The well polished 2PE5S crystal having the flat surface was used and hardness measurement was made for different loads and it continued up to the cracks formed due to the excess load, which is the indication of hardness limit of the crystal. The Vicker's hardness values were determined using the relation,

$$H_v = \frac{1.8554\ P}{d^2} \quad (kg/mm^2) \qquad (3.3)$$

The variation of hardness number (H_v) with applied load (P) for 2PE5S is depicted in Figure 3.15. The hardness increases progressively with the increase in load. Meyer's index 'n' was calculated from the graph (Figure 3.16) drawn between log P and log d. The value of 'n' obtained for 2PE5S crystal using linear fit is n = 1.6. Hence, 2PE5S crystal is found to possess hard material category (Onitsch et al 1947).

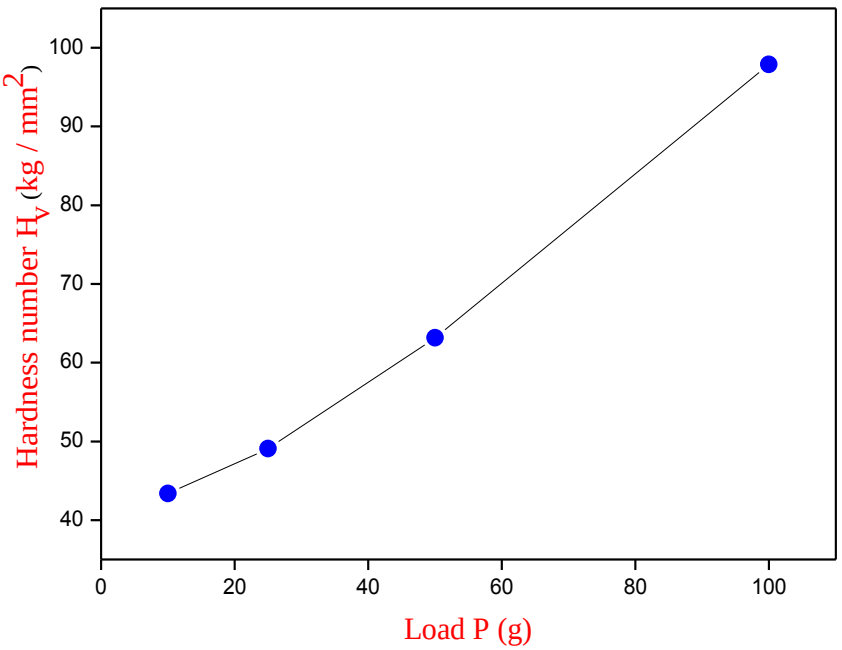

Fig.3.15 Plot drawn between Vicker's hardness (H_v) and load (P) of 2PE5S crystal

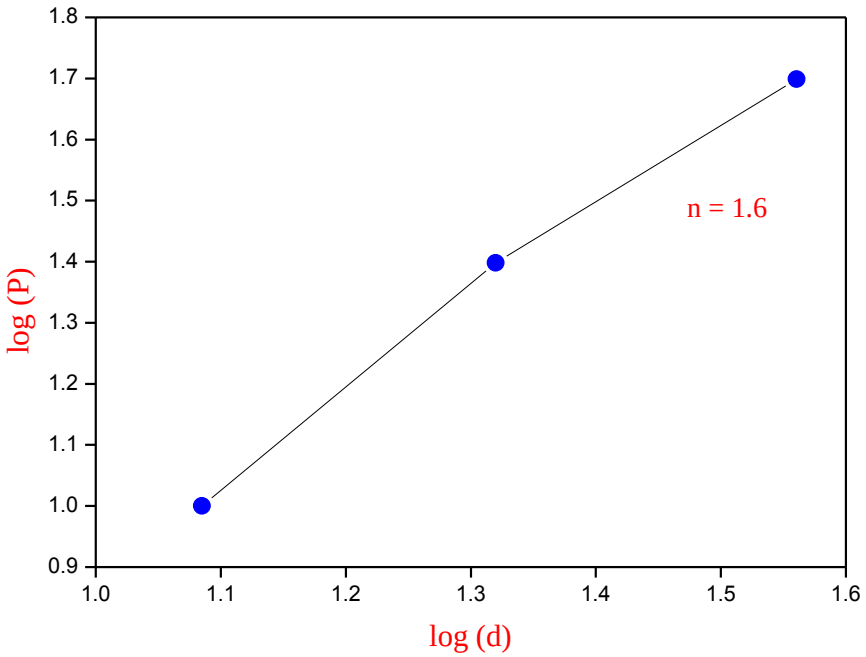

Fig.3.16 Plot drawn between log P and log d of 2PE5S crystal

3.3.10 Nonlinear Optical Studies

Based on the Z-scan measurement data in open and closed aperture modes, the nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and nonlinear optical susceptibility (χ^3) of the grown 2PE5S crystal were estimated. In this experiment, an optically polished crystal sample was used for molecular excitation and its propagation direction has been taken in the Z-axis. The beam was focused by using a convex lens of focal length 22.5 cm and the focal point was taken as Z=0. The normalized transmission from the crystal was measured, by placing the crystal sample in different positions with respect to the focus of the beam. From the normalized transmission of Z-positioned crystal sample, the nonlinear absorption coefficient and

nonlinear optical refraction were measured. The monochromatic laser light (632.8 nm) with output power of 20 mW beam from He-Ne laser source was used. The optically polished 1mm thick crystal sample was fixed in the travel range of 12 mm. Using the powermeter, the input energy and the energy transmitted by the sample were measured.

From the normalized transmittance, it was observed that a peak followed by a valley is the signature for nonlinearity of the material (Subashini et al 2011). The normalized transmittance of closed and open apertures is shown in Figs.3.17&3.18. The difference between the normalized peak and valley transmittances in the quantity (ΔT_{p-v}) was calculated. The real and imaginary parts of the third order nonlinear optical susceptibility (χ^3) were calculated using the relations,

$$\text{Re } \chi^3 \text{ (esu)} = \frac{10^{-4}\,(\varepsilon_o C^2 n_o^2 n_2)}{\pi} \quad (\text{cm}^2/\text{W}) \tag{3.4}$$

$$\text{Im } \chi^3 \text{ (esu)} = \frac{10^{-2}\,(\varepsilon_o C^2 n_o^2\, \lambda\beta)}{4\,\pi^2} \quad (\text{cm/W}) \tag{3.5}$$

where ε_0 is the vacuum permittivity, c is the velocity of light, 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 calculated using the relation,

$$\chi^{(3)} = \sqrt{(R_e\chi^{(3)})^2 + (I_m\chi^{(3)})^2} \tag{3.6}$$

The second order hyperpolarizability (γ_h) can be explained in terms of the nonlinear induced polarization per molecule which is related to the third order bulk susceptibility (Sabari Girisun et al 2011).

$$\gamma_h = \frac{\chi^{(3)}}{L^4 N} \tag{3.7}$$

where N is the density of the molecules and L is the local field factor of Lorentz approximation which is equal to,

$$L = \frac{n_0^2 + 2}{3} \tag{3.8}$$

where n_0 is refractive index of the medium. The calculated third order nonlinear optical susceptibility values are given in Table 3.4. The high value of third order nonlinear susceptibility ($\chi^{(3)}$) and γ_h are owing to the π-electron cloud movement from the donor to acceptor, which can produce the molecules of highly polarized. The cause for large third order NLO properties of 2PE5S crystal is due to the contribution of inter-molecular interaction and partially of phonon subsystem. The measured third-order nonlinear properties of grown crystal confirm its purpose for optical limiting and switching applications (Sudharsana et al 2012).

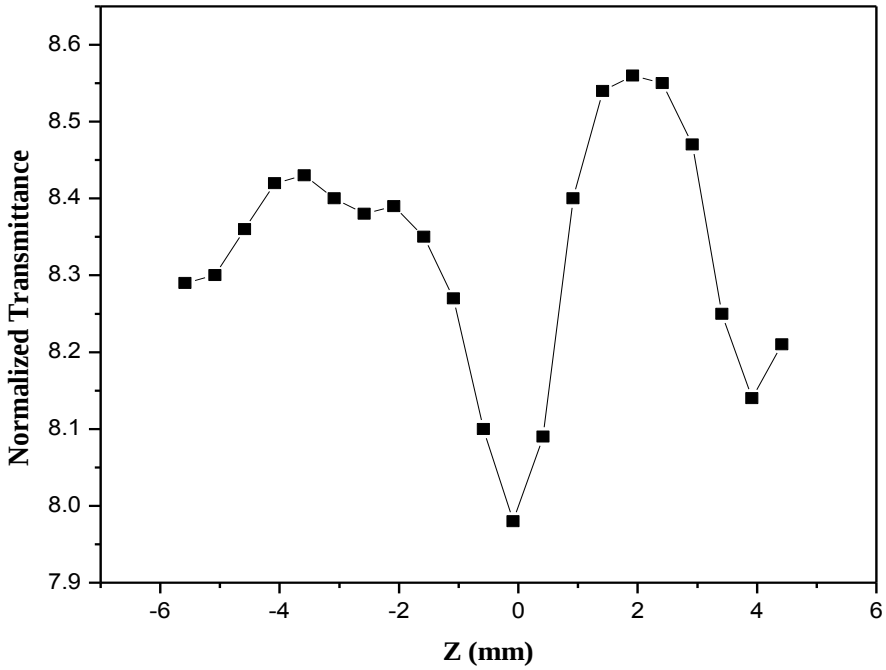

Fig.3.17 Z-scan plot traced for 2PE5S crystal in closed aperture mode

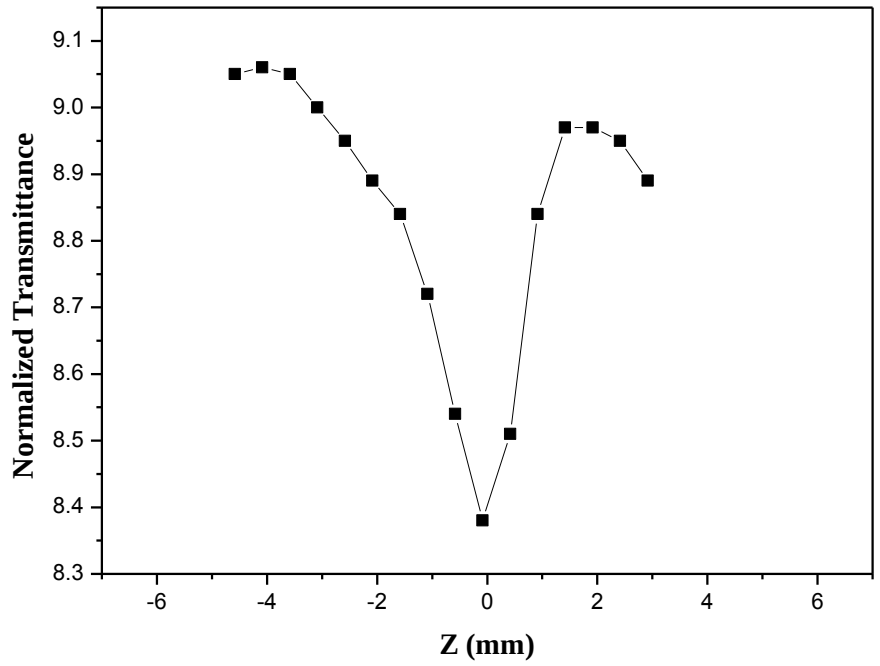

Fig.3.18 Z-scan plot traced for 2PE5S crystal in open aperture mode

Table 3.4 Third order nonlinear optical parameters of 2PE5S crystal measured in Z-scan experiment

Optical Parameters	Values
Nonlinear refractive index (n_2)	1.3024×10^{-11} c m^2/W
Nonlinear absorption coefficient (β)	2.6451×10^{-4} cm/W
Third-order nonlinear optical susceptibility ($\chi^{(3)}$)	1.5107×10^{-7} esu
Second order hyperpolarizability (γ_h)	1.637×10^{-7} esu

3.4 CONCLUSION

2-phenylethylaminium 5-sulfosalicylate (2PE5S) nonlinear optical single crystals were successfully grown by solution growth method. X-ray diffraction analysis reveals that, 2PE5S crystal crystallizes in monoclinic crystal system with space group C_2/c.

From HRXRD studies, the low value of FWHM of the grains proved the perfection of crystal. FTIR spectra revealed the vibrational behaviour of the synthesized compound and confirmed its necessary functional groups.

The thermal analysis revealed the thermal stability of the grown crystal upto 220°C. UV-visible transmission spectrum showed the transmission region and the cut-off wavelength and band gap energy were found to be 321 nm and 3.8 eV respectively.

Photoluminescence spectrum reveals that, the 2PE5S could be used in blue emission region. The laser damage threshold of 2PE5S (6.3 GW/cm^2) was found to be high. The dielectric constant and dielectric loss studies of 2PE5S crystal showed the normal dielectric behaviour.

Vicker's microhardness measurement reveals that 2PE5S crystal belongs to hard category NLO material. From Z-scan technique, the nonlinear refractive index, nonlinear absorption coefficient and third-order nonlinear optical susceptibility were calculated.