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GROWTH AND CHARACTERIZATION OF SEMI ORGANIC SINGLE CRYSTAL: PIPERAZINIUM SULPHATE

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Abstract

Piperazinium sulphate (PPS) is a semi organic single crystal. The PPS single crystals were grown from aqueous solution by slow evaporation technique at room temperature. The crystal system and lattice parameter values of the grown crystal were found from Single crystal XRD. The grown crystals were characterized by FTIR spectroscopy which confirms the presence of functional group and modes of vibration. The cut off wavelength of PPS was found to be 242nm from Uv-Vis spectroscopy. The mechanical properties of the grown crystals were studied by using Vickers hardness tester. The dielectric properties of the crystals were studied with different frequency at different temperature. The surface laser damage threshold for the grown crystals were measured using Nd:YAG laser. Thermal behavior has been studied with TGA/DTA analyses. The excitation and emission spectra of PPS were recorded using spectrofluorometer.

Keywords: Semi organic Single Crystal, Slow Evaporation Technique, X-Ray Diffraction, FT-IR, Microhardness, Laser Damage Threshold.

1. INTRODUCTION:

In Material Science, Crystal growth is a significant field which involves controlled phase transformation. In the current decades, the interest in crystal growth has been growing, particularly in view of the emergence of technological applications [1]. The combination of organic and inorganic materials have attracted in huge consideration. In particular, the existing field of research is to synthesize, grow and characterize semi organic crystals. There are so many attempts has been made to synthesize and grow number of NLO semi organic crystals. The discussion from that shows semi organic crystal possesses both the good qualities of host organic materials and additive-inorganic material [2]. Piperazine is an organic amine compound that consists of a six - membered ring containing two nitrogen atoms at symmetrically opposite positions [3-4]. It is an excellent hydrogen-bond acceptor and due to this nature, it is capable of yielding both second and third order NLO properties. Recently, Piperazinium crystals such as Piperazinium L-tartrate, piperazine (bis) p-toluenesulfonate, Piperazinium perchlorate, 4-hydroxytetramethylpiperazinium picrate and Piperazin-1-ium 4-aminobenzenesulfonate have been reported [5-8].Sulphuric acid is a dibasic acid, because it contains two hydrogen atoms which ionize in aqueous solution to become hydrogen Ions. It has a deprotonated group of SO_4^- and a

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protonated H_2^+ group. This dipolar nature makes them suitable candidate for NLO applications. In this present work growth, structural, optical, thermal, and mechanical, fluorescence and dielectric property of Piperazinium sulphate (PPS) has been reported.

2. EXPERIMENTAL PROCEDURE:

Piperazinium sulphate (PPS) single crystals were grown by dissolving piperazine and Sulphuric acid of equimolar ratio (1:1) in distilled water. The solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. In a span of fifteen days a well-defined hexagonal shape crystals were harvested. The grown crystals were shown in Fig.1.

Fig.1: As grown PPS

3. RESULT AND DISCUSSIONS:

3.1 Single Crystal Xrd:

Piperazinium sulphate (PPS) was subjected to single crystal X-ray diffraction (XRD) using a Bruker AXS Kappa Apex II CCD diffractometer. The compound PPS crystal belongs to monoclinic system and space group P21/n. The unit cell parameter values are a = 6.390(7) Å, b = 11.670 (11) Å and c = 11.696 (10) Å. The volume of the crystal is V = 855(2) $Å^3$. These values are found to be in good agreement with the reported values [9].

3.2 FTIR Spectral Analysis:

The FTIR spectrum of the crystal was recorded in the frequency region from 400cm^{-1} to 4000cm^{-1} with SHIMADZU IR AFFINITY 1S spectrometer using KBr pellet techniques. The Fourier transform infrared spectrum of PPS crystals has been carried out to analysis the presence of functional group in the compound. The observed FTIR spectrum of PPS compound is shown in Fig2.The stretching vibration of C-H is observed at 3238cm^{-1} and 3017cm^{-1}. The peak at 2744cm^{-1} and 2491cm^{-1} is due to stretching vibration of secondary amine (NH_2^+) which confirms the protonation of piperazine. The appearance of NH_2^+ bending vibration occurs at 1604cm^{-1} and 1563cm^{-1}. The band occurs at 1442cm^{-1} is due to C-H bending mode. The C-N stretching appears at 1321cm^{-1}. The symmetric stretching of SO_4^- sharp peak appears at 1120cm^{-1} [10]. The band at 948cm^{-1}, 736cm^{-1} and 584cm^{-1} assigned to C-H out of plane bending vibration [11].

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3.3 Thermal Analysis:

Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) give information regarding different stages of decomposition of the grown crystal and phase transition [12].The sample was heated in a crucible between 20°C to 500 °C heating rate of 20°C ***/*** min in nitrogen atmosphere. There are two stages of decomposition observed in the spectrum of TG-DTA (Fig.3). PPS grown crystal were thermally stable up to 72^{0}C.In DTA, the first stage endothermic peak represents the losses of water molecules from the grown crystal. The maximum weight loss of the grown crystal is from 340^{o}C to 420^{o}C. The sharp endothermic peak also occurs at 380^{o}C which shows a good degree of crystallinity of the sample [13].

Fig.2 FTIR Spectrum of PPS

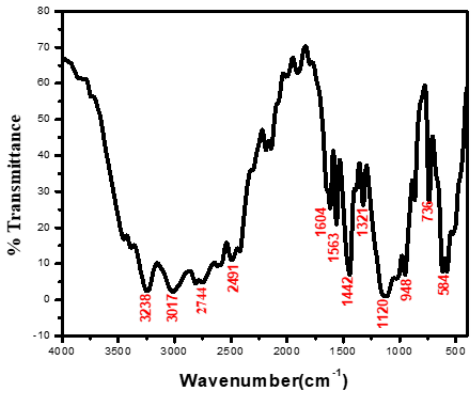
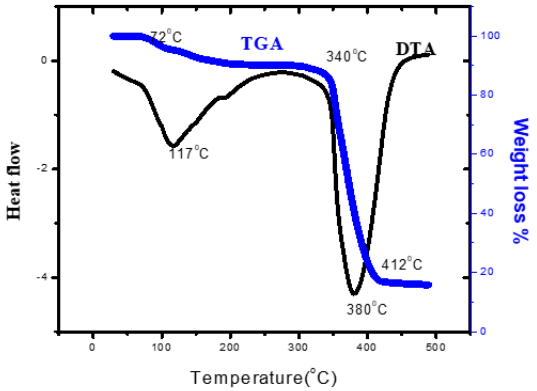


Fig.3: TG-DTA spectrum of PPS



3.4 UV-VIS SPECTRAL ANALYSIS:

The UV-VIS spectrum of grown PPS single crystal has been recorded using SHIMADZU SPECTROMETER UV-1800 in the range of 200nm-1100nm. The UV-Vis spectrum is shown in Fig.4. For NLO applications, the crystal should be highly transparent throughout the visible region. The cut off wavelength of the grown crystal was found to be 242nm. The absorption coefficient (α) was calculated from the spectrum using following relation [14].

$$\alpha = (2.303/t) \log (1/T) \quad (1)$$

where T is transmittance and "t" is the thickness of the crystal. The optical band gap (E_g) was estimated using the following relation [15].

$$\alpha h\upsilon = A (h\upsilon - Eg)^{1/2} \quad (2)$$

The plotted curve between $(\alpha h\upsilon)^2$ and photon energy ($h\upsilon$) shows linear behavior which can be shown in Fig.5. The optical energy band gap (E_g) is estimated by extrapolation of the linear portion of the curve to the point $(\alpha h\upsilon)^2 = 0$. Using this method, the optical band gap of grown crystal was found to be 5.07ev. By theoretical calculation using the relation

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E_g= hc/λ, the optical band gap energy was found to be 5.1eV.This high band gap value indicates that the grown crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material.

Fig.4 UV-Spectrum of PPS

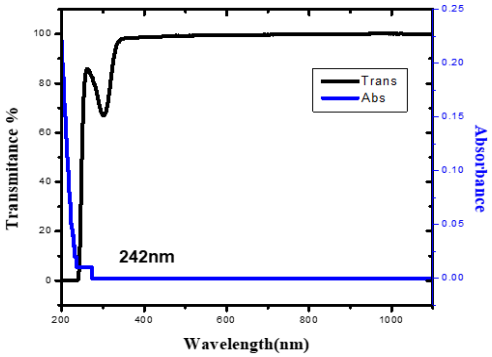
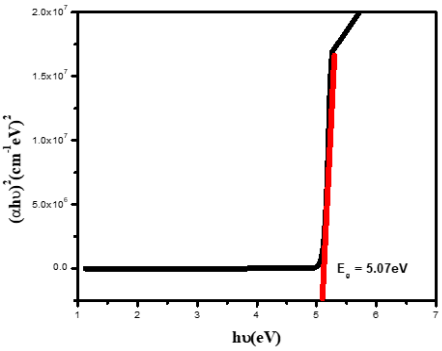


Fig.5. Band gap spectrum of PPS



3.5 Microhardness Studies:

The mechanical properties of the grown crystal are very important for fabrication of electronic and optical devices. The mechanical properties of the crystal were investigated by using Vickers microhardness tester fitted with a diamond pyramidal indenter with the dwell time of 10s. The diagonal length of the indentation impression was measured using micrometer eyepiece. The indentation marks were made on the surface by varying load from 10 to 100gm.The microhardness value was calculated using the formula:

$$H_v = 1.8544(P/d^2)\ Kg/mm^2. \qquad (3)$$

Where P is the applied load in Kg and d is the diagonal length of the impression in mm. Fig. 5 shows that the variation of hardness with applied load. It is evident that the hardness of PPS increases by increasing load, which indicates the reverse indentation size effect (RISE). The size of indentation and the loads are related through Mayer's law

$$P = Kd^n \qquad (4)$$

Where n is the work hardening co-efficient or Mayer index. The work hardening coefficient was found from the slope of the plot between log p versus log d. The slope value was found to be 2.15 for PPS as shown in Fig.6. According to onitisch [16], if n is greater than 1.6, the material belongs to soft material category. Thus, PPS crystal can be used for device fabrication, which can withstand thermal local stresses.

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Fig.6 Plot between Hv Vs Load

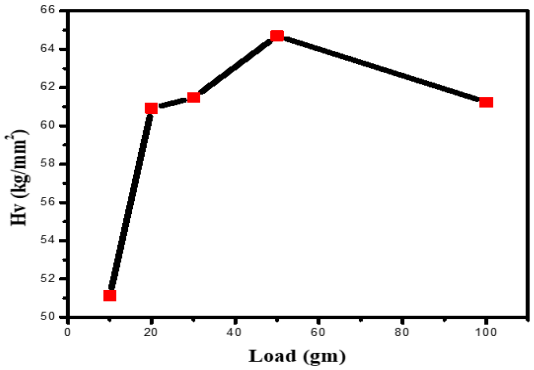
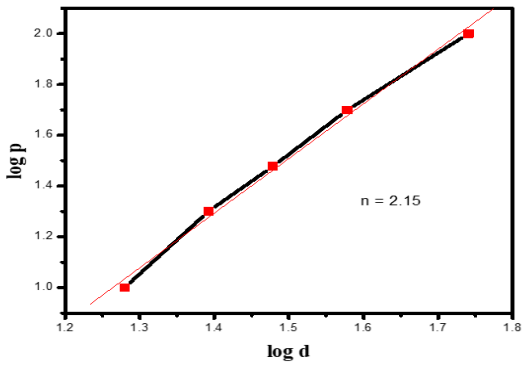


Fig.7 Log p Vs Log d



The elastic stiffness constant is calculated using Wooster's empirical formula, given by

$$C_{11} = H_v^{7/4} \quad (5)$$

which gives an idea about the tightness of bonding between the neighboring atoms. The calculated value of C_{11} indicates that the binding forces between ions are quite strong [17]. From the hardness value, the yield strength $\sigma_v$of a material is calculated using the relation [18].

$$\sigma_v = \frac{Hv}{2.9}\{1\text{-}(n\text{-}2\}\left[\frac{12.5(n-2)}{1-(n-2)}\right]^{n-2} \quad (6)$$

The tensile strength (T) and yield point (y) of the PPS crystal have been calculated using the linear mathematical relation [17]

$$T = 0.2\ H_v + 6 \quad (7)$$

And $Y = 0.23H_v - 13.5.$ (8)

The load dependent hardness parameters n, yield strength (σ_v) and stiffness constant are calculated for PPS crystal are given table 1.Hardness is important factor in selecting the processing (cutting, grinding, polishing) steps of bulk in fabrication devices based on the crystals.

Table 1: Mechanical parameters of PPS

Parameters	Values
Hardening co-efficient n	2.15
YieldStrengthσ_v(GPa)	0.26
StiffnessConstantC_{11}(GPa)	12.68
Tensile Strength T(GPa)	1.76
Yield Point Y(MPa)	26.79

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3.6 Dielectric Studies:

The dielectric studies on PPS single crystals are carried out using LCR meter by a conventional parallel plate capacitor method. Graphene was coated on the opposite faces of the crystal which was then placed between two copper electrodes. The capacitance was measured for various frequency ranges with different temperature. The dielectric constant was calculated using the relation

$$\epsilon_r = ct/\epsilon_0 A \quad (9)$$

where C is capacitance, t is thickness of the sample, ϵ_0 is the free space permittivity and A is the area of the cross section. The variation of ϵ_r with applied frequency is shown in fig.7. The figure shows that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in high frequency region. The large values of dielectric constant at lower frequency are due to the impedance to the motion of charge carriers at the electrodes [19]. At higher frequency, the dielectric constant is low due to the presence of ionic and electronic polarization. According to the miller rules, the lower values of dielectric constant are suitable parameters for the enhancement of optical properties. Fig.8 shows that the variation of dielectric loss versus frequency. It is clear that dielectric loss decreases with increasing frequency similar to dielectric constant. The property of lower dielectric loss at higher frequency suggests that the grown crystal has defect free and good optical quality. This parameter acts the important role for NLO materials in their applications.

Fig.7 Dielectric constant Vs log f

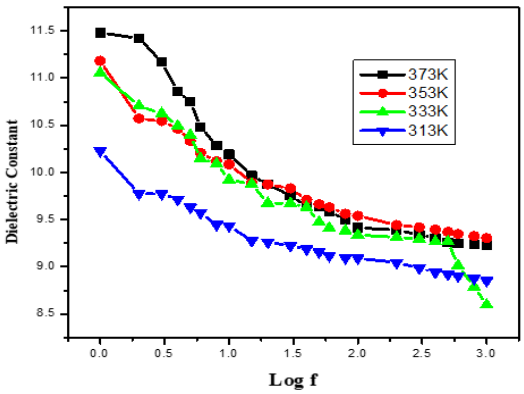
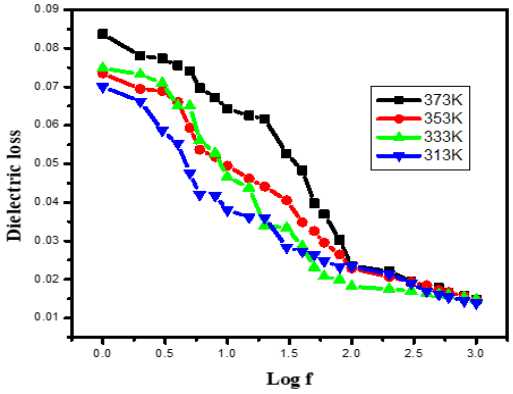


Fig.8 Dielectric loss Vs log f



3.7 Laser Damaged Threshold Studies:

The laser induced damage occurs in the crystals caused by various physical process such as electron avalanche, multi photon absorption and photo ionization for the transparent materials whereas in case of high absorbing materials, the damage threshold is mainly due to the temperature rise, which leads to strain induced fracture [20]. For the present investigation laser damaged threshold value of PPS crystal was determined by

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using Q-Switched Nd: YAG laser operating at 1064nm radiation. The laser was operated at the repetition rate of 10Hz with the pulse duration of 6ns. For the laser damaged threshold measurement, the beam was focused on the sample with the focal length of 15cm. During laser radiation, the power meter records the energy density of the input laser beam for which the crystal gets damaged. The energy density is calculated as

$$P=E/\tau\pi r^2 \quad (9)$$

where E is the energy (mJ), τ- pulse width (ns) and r is the radius of the spot (mm). The measured laser damaged threshold value for PPS is 1.0GW/cm^2. A good value of LDT indicates that the grown crystal contains a low defect.

3.8 Fluorescence Studies:

Fluorescence spectroscopy is a spectroscopy method which is used to analyze the fluorescence properties of a sample. It uses a beam of light that excites the electrons in molecules of certain compounds and causes them to emit light.Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, of lower photon energy, than the absorbed radiation. Jasco FP-6300 spectrofluorometer was used to record the fluorescence spectrum of the PPS crystal at room temperature with 450W high pressure xenon lamp as an excitation source. The excitation spectrum of grown crystal is shown in Fig.10. The excitation wavelength of the grown PPS crystal is 349nm and the emission wavelength is 406nm. The band gap energy was calculated using the formula, $E_g = hc/ke$. Here h, c, and e are constant; k is the wavelength of absorbed fluorescence. The band gap energy calculated is about 5.6 eV for the crystal, which also matches with the band gap obtained from UV visible absorption spectrum[21]. The wavelength of emission and excitation spectra indicates that the PPS crystal is a violet light emitting material.

Fig. 10: Fluorescence excitation spectrum of PPS.

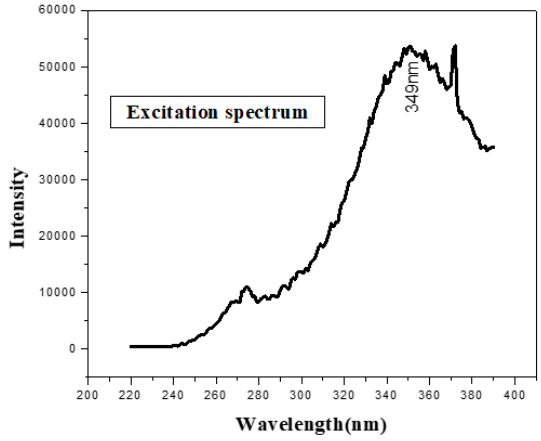
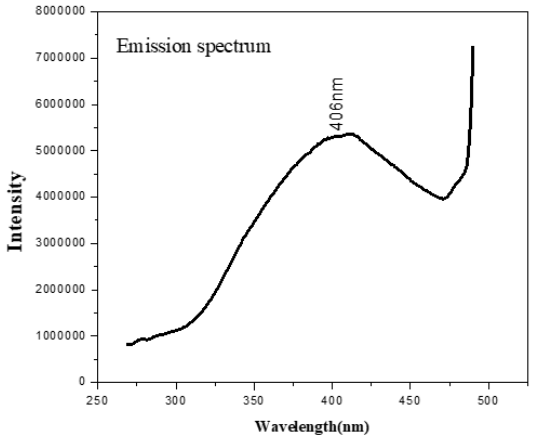


Fig. 11: Fluorescence emission spectrum of PPS



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CONCLUSIONS:

Single crystals of Piperazinium sulphate (PPS) were successfully grown by slow evaporation technique at room temperature. The grown crystals belong to monoclinic system. The presence of functional group was identified by FTIR spectral analysis. The optical UV-spectrum indicates that the crystal is transparent throughout the visible region and it has cut off wavelength of 242nm. The microhardness studies reveal that the PPS crystals belong to soft materials. The dielectric properties of the grown crystals were measured. TG/DTA studies shows that the grown crystal was thermally stable up to 72^0C.The laser damage threshold value was found to be 1.0Gw/cm^2. The fluorescence studies reveal that the grown crystal is a violet light emitting material. Hence the PPS crystal can be used for optical applications.

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