Spectroscopic, NLO and thermal studies of single crystals of picric acid

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ABSTRACT *Organic nonlinear optical (NLO) crystals have been recognized as the materials of the future, due to their molecular nature, added with the versatility of synthetic chemistry helpful in changing and control their molecular structure, leading to the betterment of NLO properties. Picric acid (PA) crystal is an organic NLO material and single crystals of picric acid were grown by slow evaporation technique. XRD analysis reveals that the crystal belongs to orthorhombic in structure. The functional groups are confirmed by FTIR and FT-Raman vibrational analysis. Optical transmission spectra revealed the optical properties of the grown crystal. The range and percentage of optical transmission were ascertained by recording UV–Vis–NIR spectrum. Thermal properties were investigated by TG and DTA analyses. Energy Dispersive X-ray Spectroscopy (EDAX) reveals the presence of elements in the title compound. The emission spectrum is determined by measuring the variation in emission intensity as a function of wavelength for a fixed excitation wavelength at 250 nm. SHG efficiency was measured by Kurtz and Perry powder technique using Nd: YAG laser.*

Keywords: *Spectroscopy, X-ray diffraction, Growth from solution, Organic compound, EDAX, TG/DTA, NLO material*

1. Introduction

Picric acid or 2, 4, 6-trinitrophenol is widely used in industry and it is the starting material for the synthesis of chloropicrin and picramic acid, used in the synthesis of dyes, medicines and other compounds and in studying the structure of metals. Picric acid exhibits relatively strong acidic properties and it is one of the most acidic phenols [1-3]. Picric acid is an organic material with aromatic ring and most of the organic NLO materials are of great interest for second and third-order nonlinear optical applications due to their high nonlinearity, high optical damage threshold and their ultrafast, almost purely electronic response. Picric acid acts as an electron acceptor by electrostatic interactions [4, 5]. By hydrogen bonding it forms molecular charge-transfer complexes with a number of electron-donor compounds such as aromatic hydrocarbons and amines. Picric acid has a tendency to form stable picrate compounds with various organic molecules due to the presence of active electron cloud and ionic bonds [6]. It has been reported that intermolecular hydrogen bonding interactions are absent in most of the picrate salts and picric acid derivatives are interesting candidates, as the presence of phenolic OH and electron withdrawing nitro groups favors the formation of salts with various organic bases [7-13]. From the literature survey it is found that the results of various studies of picric acid crystal are not reported. Hence, different studies of picric acid crystal have been carried out experimentally and the obtained results are reported in this paper.

2. Experimental for crystal growth

Picric acid (PA) is an acidic phenol and its molecular structure is shown in the figure 1. AR grade chemical of picric acid was purchased commercially and its purity was improved by re-crystallization process. The solute was dissolved in the mixture of double distilled water and ethyl alcohol. Here the volume of the mixture of solvents is taken in the ratio of 9:1. Homogeneous solution was prepared by dissolving picric acid salt in the solution by stirring for 3 hours. Then the solution was filtered using Whatmann filter paper and it was kept in an undisturbed place. After 3-4 weeks, single crystals of picric acid was separated out and the harvested crystals are shown in the figure 2. The grown crystals are observed to be yellow in colour, slightly hygroscopic and transparent.

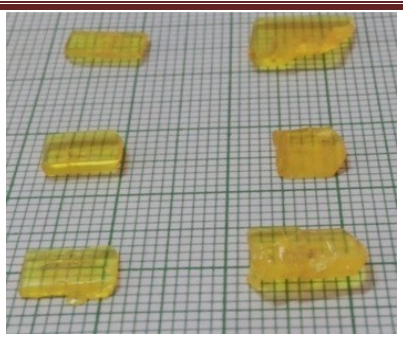

Fig. 2: The grown crystals of Picric acid

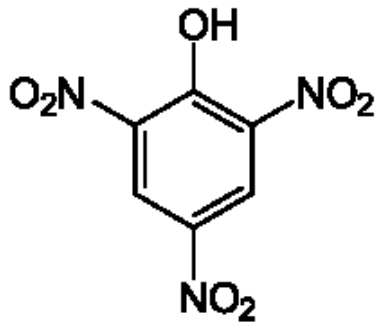

Fig. 1: Molecular structure of the picric Acid crystal

3. Results and discussion

3.1 XRD analysis

Powder XRD pattern of the grown PA crystal was recorded using BRUKER AXS D8 advances diffractometer with Cu K_{α} (=1.5418Å) radiation after crushing the sample into fine powder. The sample was scanned over the range 0-80° at the rate of 2° per minute and the recorded powder XRD pattern is shown in the figure 3. The unit cell parameters were obtained using a single crystal X-ray diffractometer with a Mo K_{α} radiation and the data are given the table 1. The unit cell parameters were used to index the reflecting planes. In the figure 3, we can notice the appearance of sharp peaks in the diffraction pattern which indicates the good crystalline nature of the grown PA crystal. The powder XRD data of picric acid crystal are provided in the table 2.

Table 1: Single crystal XRD data for picric acid crystal

1	Empirical formula	$C_6H_3N_3O_7$. C2HCl3O2
2	Formula weight	229.10 g·mol^{-1}
3	Temperature	293(2) K
4	Wavelength	0.71073 Å
5	Crystal system, space group	Orthorhombic, $Pca2_1$
6	Unit cell dimensions	a= 9.212(3) Å, b= 18.821(5) Å c=9.795(2) Å , α= 90 °, β= 90 ° , γ 90°
7	Volume of unit cell	1698.24(3) Å^3
8	Crystal size	0.30 * 0.20 * 0.20 mm^3
9	Refinement method	Full matrix least square method
10	Z	4
11	Density	1.762 g/cm^3

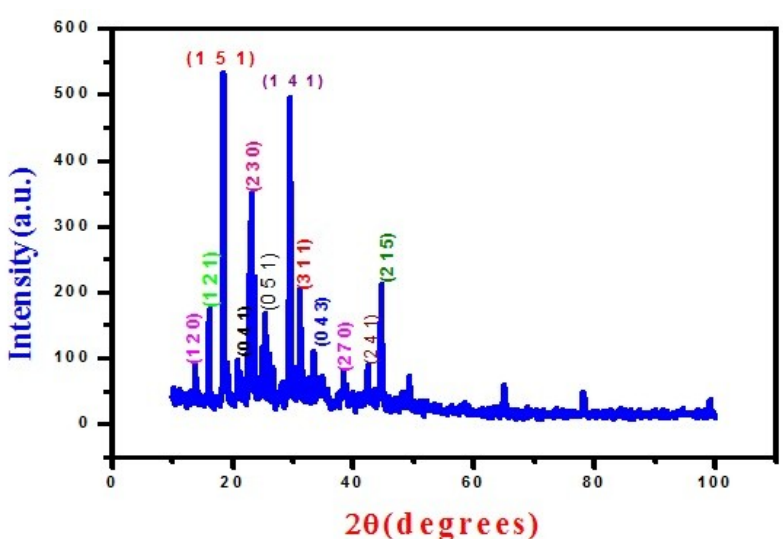

Fig.3: Powder XRD spectrum of picric acid crystal

Table 2: Powder XRD data for picric acid crystal

Peak No.	2θ (degrees)	Relative intensity (%)	hkl	d (Å)
1	13.6583	15	1 2 0	6.5294
2	16.2728	28	1 2 1	5.5022
3	18.4717	100	1 5 1	4.8662
4	20.8907	13.02	0 4 1	4.3236
5	23.7250	63	2 3 0	3.832
6	25.2643	26.5	0 5 1	3.6124
7	29.1981	87	1 41	3.1606
8	30.9574	33.3	3 1 1	2.9972
9	33.3763	15.64	0 4 3	2.8026
10	38.4096	10.55	2 7 0	2.4804
11	44.3225	37	2 1 5	2.2066

3.2 Identification of functional groups by FT-IR and FT-Raman spectral analyses

The infrared spectroscopy is effectively used to identify the functional groups of the sample. When infrared radiation interacts with a sample, a portion of the incident radiation is absorbed at specific wavelengths. The vibrational analysis of the grown crystal was done using FTIR spectrometer. The FTIR spectrum is recorded in the range of 500–4500 cm^{-1} .The recorded spectrum is shown in Fig. 4. In FTIR spectrum, the broad intense peak is observed between 3126 cm^{-1}, which is due to NH_3^+ vibrations. This confirms that the amine group presented in the PA molecule bonded through hydrogen bonding. The broad bands around 1655.26 cm^{-1} and 1597.68 cm^{-1} are due to NH_3^+ bending vibrations. The C=O stretching band observed at 1425.14 cm^{-1} indicates the presence of carboxylic acid group. The CH_3 bending deformation was assigned to the peak at 1460 cm^{-1}. The peak at 1407 cm^{-1} was assigned to symmetrical stretching of the COO^- group. The C-N stretching was assignedto1342.10 cm^{-1} and 1310.81cm^{-1}.The peaks between 1069 and 1055.42 cm^{-1} are assigned to asymmetrical coupled vibrations of PA crystal. In the lower frequency range, the sharp peaks observed at 707.54 and 795.54 cm^{-1} are assigned to NO_2 vibrations. The assignments to the vibrational peaks are given in accordance with the data reported in the literature [14]. The complete FTIR and FT-Raman spectral assignments are given in the table 3.

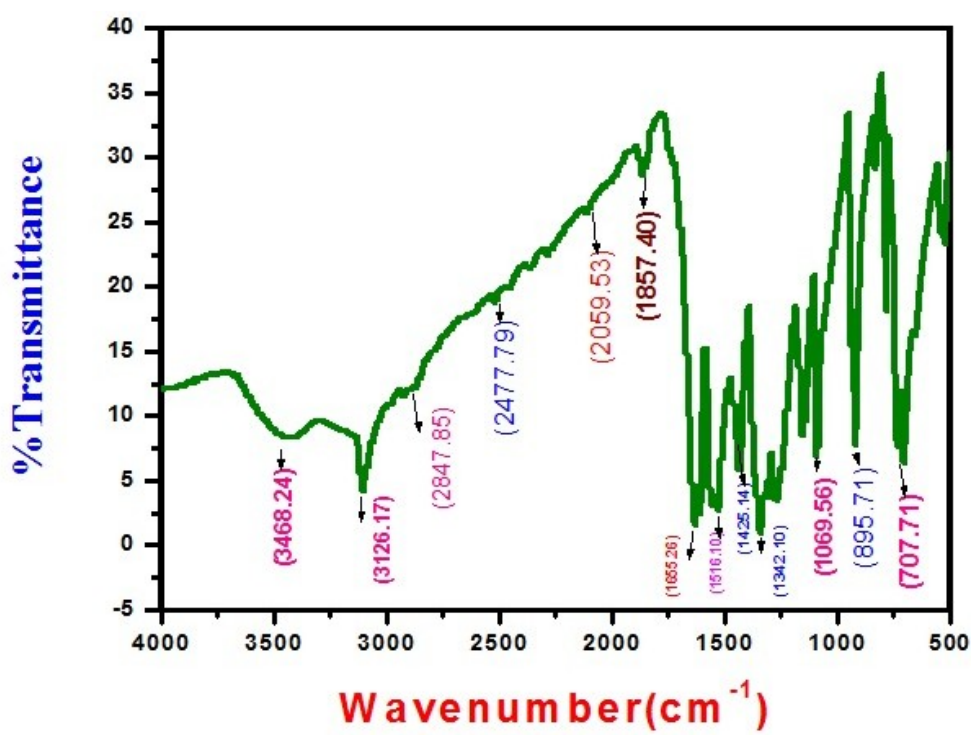

Fig.4: FT-IR spectrum of picric acid crystal

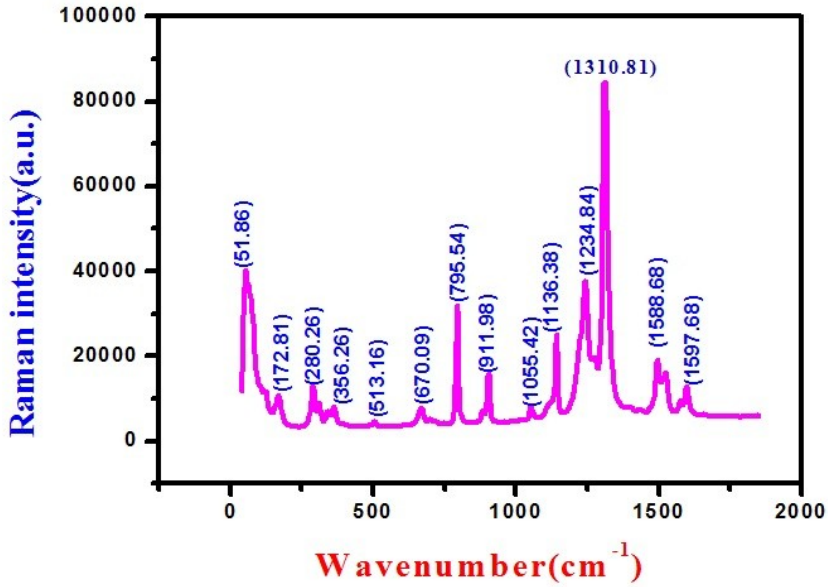

Fig. 5: FT-Raman spectrum of picric acid crystal

Table 3: FT-IR and FT-Raman assignments for picric acid crystal

S.No	FTIR(cm^{-1})	FT-Raman (cm^{-1})	Band Assignments
1	3126.17	-	ν O-H
2	2847.85	-	νs(C-H)
3	1655.26	1597.68	νasy NO_2
4	1516.10	1588.68	NH_3^+ symmetric deformation
5	1425.14	-	COO^- symmetric stretching
6	1342.10	1310.81	νs(C-N)
7	-	1234.84	C-O stretching
8	-	1136.38	$NH3^+$ rocking
9	1069.86	1055.42	C-N stretching
10	-	911.98	CH_2 rocking
11	895.71	-	C-C-N symmetric stretching
12	707.54	795.54	NO_2 deformation
13	-	670.09	C-C-out –of plane ring deformation
14	-	513.16	COO^- rocking

3.3 Optical Properties

Linear optical properties of the crystal were studied using Varion Cary 5E UV–vis–NIR spectrophotometer. Optical transmittance range and transparency cut-off wavelength of single crystals are important factors for optical applications. The UV-visible spectrum of PA single crystal was recorded and it is shown in the figure 6. UV-vis-NIR studies give important structural information because absorption of UV and visible light involves promotion of the electrons in π and σ orbitals from the ground state to higher energy states [15]. Lower cut-of wavelength and low absorption band of a crystal are important parameters for a crystal to use it in laser frequency conversion applications. Picric acid crystal has lower cut-off wavelength at 430 nm, the crystal is found to be transparent n the 508 - 900 nm.

The optical absorption coefficient (α) was calculated using the following equation

$$\alpha = (1/d) \ln (1/T)$$

Where T is the transmittance and d is the thickness of the crystal. The variation of absorption coefficient with wavelength for picric acid crystal is shown in the figure 7. Assuming parabolic trends, the relation between α and hν is given by

$$\alpha = A (h\nu - E_g)^n / h\nu$$

Where E_g is optical band gap of the crystal, n and A are constants. In a crystalline material, either direct or indirect optical transitions are possible depending on the band structure of the material.For a direct transition, n = 1/2 depending on whether the transition is allowed or forbidden in quantum mechanical sense. Hence, the Tauc's plot of $(\alpha h\nu)^2$ versus $h\nu$ is drawn and it is shown in Fig.8. Using this plot, the optical band gap of picric acid crystal is found to be 4.90 eV. The reflectance spectrum of picric acid crystal using the UV-visible spectrophotometer and it is shown in the figure 9. The reflectance spectrum is like a transmittance spectrum of picric acid crystal. Extinction coefficient (K) is the fraction of light lost due to scattering and absorption per unit distance in a participating medium and it can be calculated from the relation

$$K = \frac{\alpha\lambda}{4\pi}$$

Where is the absorption coefficient and is the wavelength of light. The variation of extinction coefficient with wavelength for picric acid crystal is shown in the figure 10. Beyond the cut-off wavelength, the extinction coefficient is observed to be increasing with increase in wavelength. The linear optical constants like transmittance, absorbance, extinction coefficient, absorption coefficient and reflectance are found to vary with wavelength or energy. Using the values of linear optical constants, the desired NLO applications of picric acid crystal can be explored [15-17].

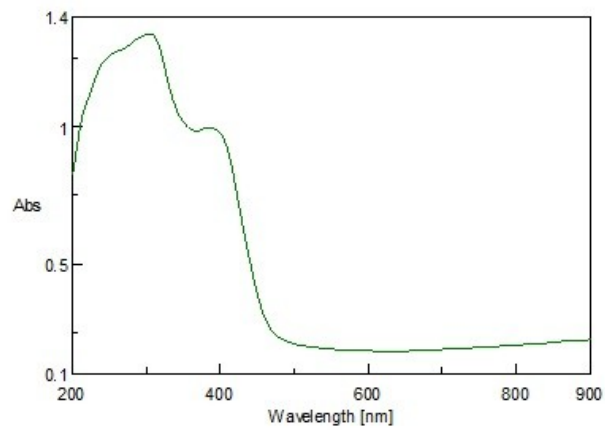

Fig. 6: UV-visible absorbance spectrum of picric acid crystal

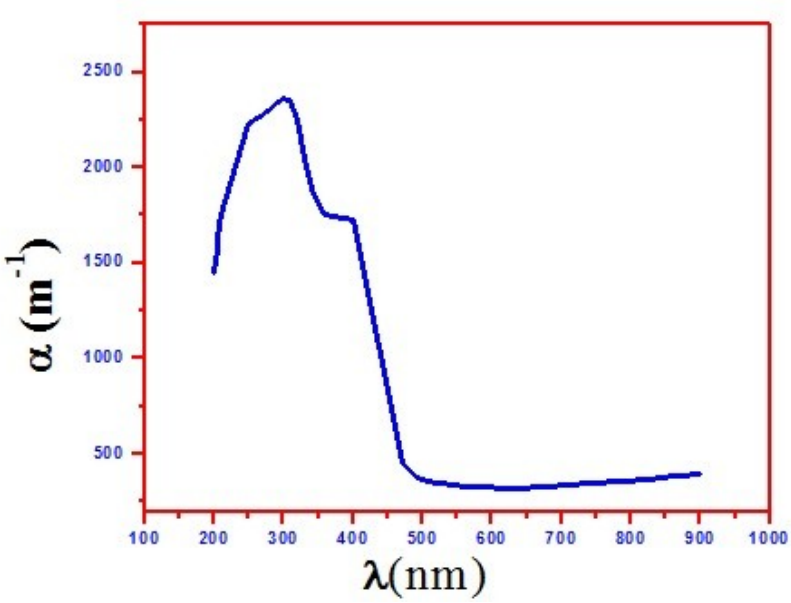

Fig.7: Plot of absorbance coefficient versus wavelength for PA crystal

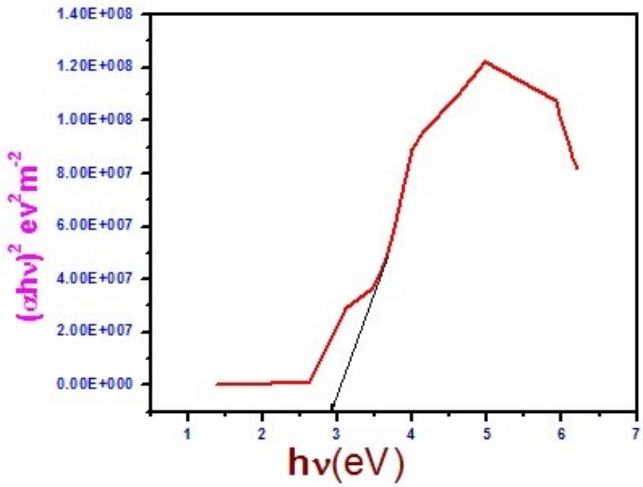

Fig. 8: Tauc's plot of picric acid crystal

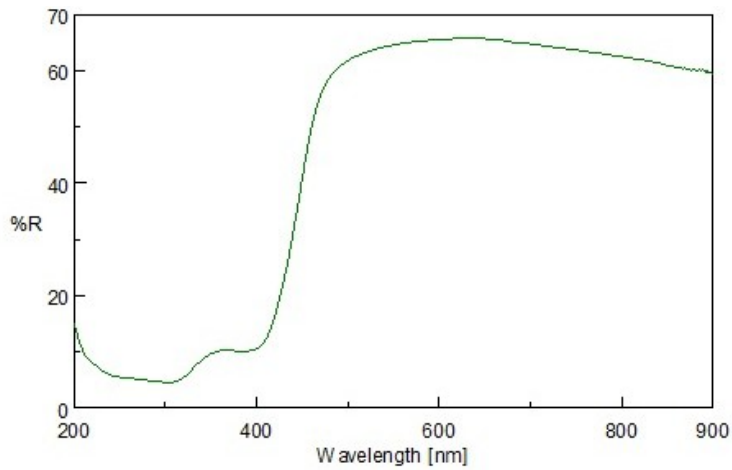

Fig. 9: UV-visible reflectance spectrum of picric acid crystal

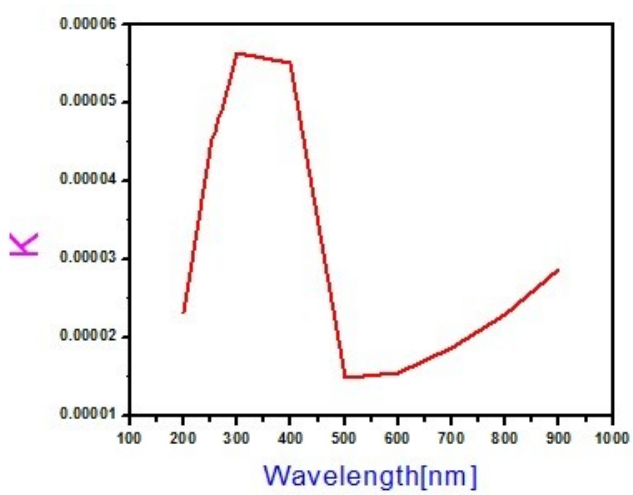

Fig.10: Variation of extinction coefficient with wavelength for picric acid crystal

3.4 Thermal analysis

The thermogravimetric analysis and differential thermal analysis (TG and DTA) curves for PA crystal are obtained using simultaneous TG/DTA analyser (STA) 409C (NETZSCH) at a heating rate of 10 ^{o}C/min in nitrogen atmosphere and are reported in Figure 11. From the thermal curves, it is the clear indication of melting point of PA crystal is at 115 ^{o}C, at which there is no weight loss of the sample. The

endothermic peat at 220 °C is corresponding to the decomposition of the sample because there is a huge weight loss at this temperature. The emission of gaseous particles is noticed in the temperature range 250-700 °C. Hence, there are three thermal processes are taking place in the sample and they are melting, decomposition and emission of gaseous particles from the sample. The sharpness of the endothermic peaks shows good degree of crystallinity of the grown PA crystal.

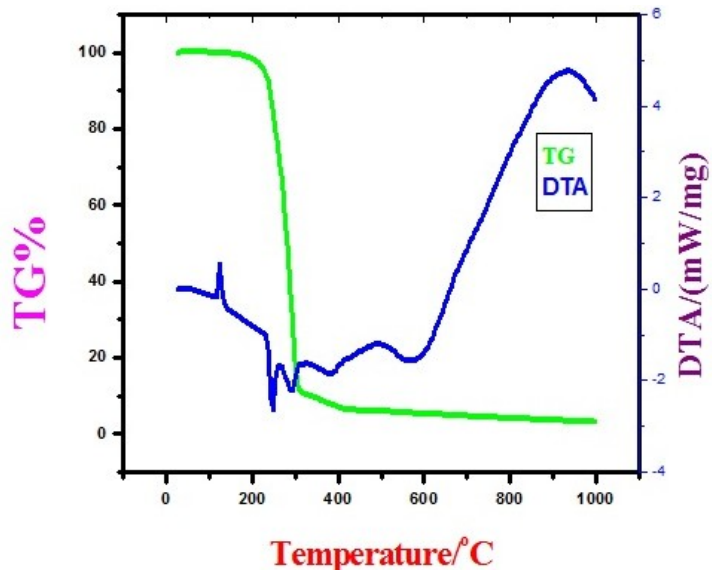

Fig.11: TG/DTA spectrum of picric acid crystal

3.5 Finding the elemental composition

The determination of elemental composition of the picric acid single crystal is carried out using EDAX and CHN analysers. In the present work an energy dispersive spectrometer (OXFORD ISIS-300 system) was used to the record the EDAX spectrum and it is presented in the figure 12. The peak heights or areas in the EDAX spectrum give a measure of the quantity of concerned elements in the specimen [19]. The elements like oxygen, nitrogen and carbon were detected in PA crystal using EDAX and hydrogen was identified using CHN analyser. The experiment shows that no other impurities have entered into PA crystal during the solution growth. The weight percentage of the various elements present in picric acid crystal is given in the table 4.

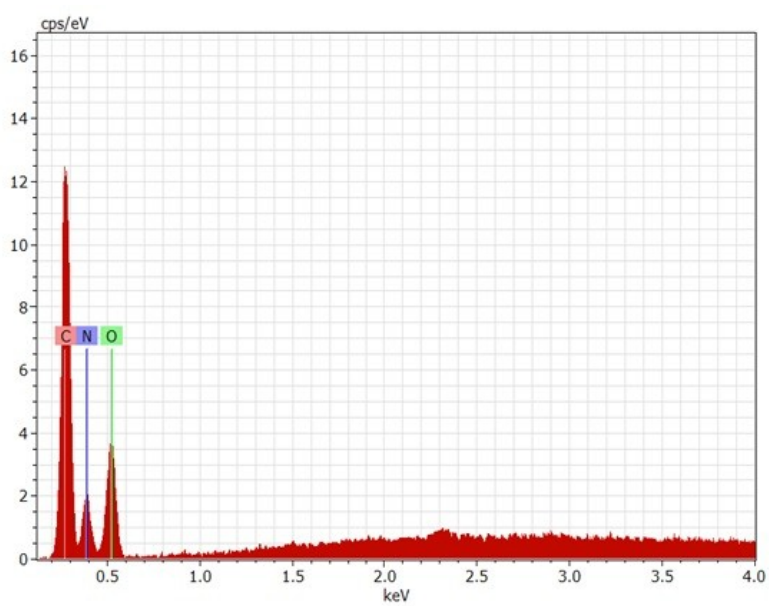

Fig.12: EDAX spectrum of picric acid crystal

Table 4: Weight % of elements present in the picric acid single crystal

S.No.	Elements	W%
1	C	31.45
2	N	18.34
3	O	48.88
4	H	1.319

3.6 Powder SHG analysis

The Second Harmonic Generation (SHG) test for the grown PA sample was performed using Nd: YAG laser with first harmonics output of 1064 nm, width 8 ns and repetition rate 10 Hz. The second harmonic signal generated in the sample was confirmed from the emission of green radiation. In this experiment, potassium dihydrogen phosphate (KDP) was used as the reference. Both the reference material and the sample are taken in powder form. The powder SHG test confirms the NLO property of the sample. Here Kurtz and Perry powder SHG method is used to measure the NLO efficiency of the experimental crystal [20]. The obtained relative SHG efficiency of PA crystal is 0.83. The output from SHG test confirms that PA crystal is a second order NLO material. The relevant data obtained from the SHG experiment are provided in the table 5.

Table 5: The obtained SHG data for Picric acid crystal

S.No.	Sample Code / name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	Picric Acid	7.42	0.70
2	KDP (Reference)	8.91	0.70

3.7 Photoluminescence study

The photoluminescence excitation measurements were carried out for PA crystal using a FP-6500 fluorescence spectrometer. The emission spectrum is recorded by measuring the variation in emission intensity as a function of wavelength for a fixed excitation wavelength at 250 nm [21]. The recorded PL spectrum of picric acid crystal is shown in the figure 13. The emitted light is detected at the green region in a wavelength range of 414- 434 nm. The maximum emission (λ_{max}) occurs at 434 nm obtained for PA crystal. Additionally, it should be mentioned that no further emission peaks were observed, indicating that the energy is fully transferred into the intermolecular carboxylate ions. The luminescence in the solid state indicates the title compound is an excellent candidate for pure fluorescent material.

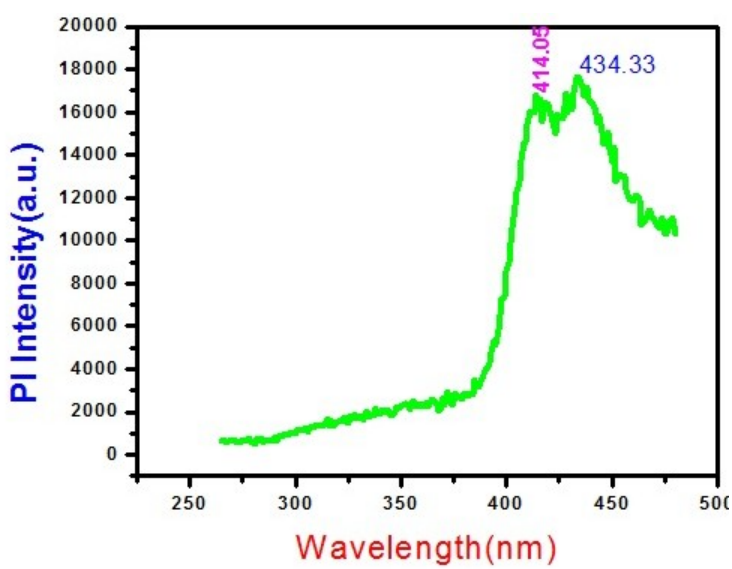

Fig. 14: PL spectrum of picric acid crystal

4. Conclusions

Novel organic nonlinear optical crystals of picric acid have been grown by slow evaporation technique. Optically transparent, yellow coloured PA crystals were harvested after a growth period of 25 days. XRD data reveals that the picric acid belongs to orthorhombic system. The FT-IR and FT-Raman

analyses confirm the presence of various functional groups. The lower cut-off wavelength and low absorbance were noticed for picric acid crystal. The TG/DTA curves recorded for the PA crystal and thermal stability was checked. The photoluminescence emission spectrum indicates that there are two emission peaks at 414 and 434 nm. EDAX spectrum of PA crystal was recorded and different elements in the picric acid sample were detected. The Kurtz and Perry method reveals that the SHG efficiency of picric acid crystal is 0.83 times that of KDP sample.

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