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Research Article

SYNTHESIS AND CHARACTERIZATION STUDIES OF DIPHENYLAMINE PICRATE CYSTAL – A NON-LINEAR OPTICAL MATERIAL

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ABSTRACT

Picric acid with Diphenyl amine resulting the Diphenyl amine picrate crystals exhibit the nonlinear optical properties, which is an important parameter in laser optics.Acetamide-Picrate crystals are synthesized in equi molar proportions of picric acid and Diphenyl amine by slow evaporation technique. The grown crystals are investigated by various spectral techniques like FTIR Spectroscopy, U.V Spectroscopy. It is examined using the XRD Studies powdered pattern. The well-defined peaks at specific 2theta values show high crystallinity of the grown crystals. The values of hkl, relative intensity and 2 theta values for the reflection peaks of the powder XRD pattern are given. The crystals have wide transparency between 200 to 1100nm. The recorded transmission is almost above 95% throughout the region. This is the most desirable property of the crystals used for nonlinear optical application. The Diphenyl amine picrate crystals are studied for its unit cell measurements by taking Single Crystal XRD measurements. SEM-EDAX studies are also carried out to study the morphology of the crystals.

Keywords: Acetamide-picrate, Laser optics, nonlinear optics, FTIR, XRD, SEM.

INTRODUCTION

Picric acid forms crystalline picrates of various organic molecules through ionic, hydrogen bonding and π-π interactions.[1] It is known that picric acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions.[2] Bonding of electron donor/acceptor picric acid molecules strongly depends on the nature of the partners. The linkage could involve not only electrostatic interactions but also the formation of molecular complexes.[3]

Many new organic crystals have been examined based on the predictive molecular engineering approach and have been shown to have potential applications.[4] Other advantages of organic compounds involve amenability for synthesis, multifunctional substitution, higher resistance to optical damage and manoeuvrability for device application etc.[5]Molecular flexibility of organic materials is an added advantage to enhance the nonlinear optical properties in a desired manner.[6] In addition, they have large structural diversity. By adopting molecular engineering methods in chemical synthesis one can easily refine the optical properties of organic molecules.[7] Picric acid forms crystalline picrate salts with various organic molecules by virtue of its acidic nature and forms salts through specific electrostatic or hydrogen bonding interactions.[8] The sub-networks induce non centrosymmetry in the bulk and enhance the thermal and mechanical stabilities through hydrogen bonding interactions.[9,10]

EXPERIMENTAL PROCEDURE

Exactly one molar picric acid and Diphenylamine are weighted. Equi molar solutions are prepared and heated separately for five minutes. They are

mixed thoroughly using the stirrer while in the hot condition. It is filtered which is also maintained in the hot condition. It is kept aside for five minutes. After having attained the room temperature, it is cooled in the ice bath till the precipitate is formed. It is filtered dried and a portion is taken for preparing the saturated solution. Saturated solution is prepared for growing crystals. It is filtered and kept undisturbed. The induction time is noticed. The fine crystals are harvested.

The picric acid-Diphenylamine-crystals are characterized using FT-IR, UV, XRD &SHG studies

RESULT AND DISCUSSION

FT-IR Studies

The two bands of NH^+ stretching frequency of absorption at 2782.80 cm^{-1} and 2594.12 cm^{-1} are noticed. The N-H bending frequency of absorption at 1629.22 cm^{-1} confirms the presence of amines. The band at 1056.50 cm^{-1}C-N stretching frequency further supports the presence of amines. The C-H bending frequency of absorption at 809.86 cm^{-1} and 707.56 cm^{-1} confirm the aromatic compound. Two bands of absorption frequency, 3403.52 cm^{-1} the N-H stretching and 3033.28 cm^{-1} the C-H stretching are also appeared. Band that corresponds to C-C, C-O &C-N observed at a frequency of 911.85 cm^{-1} is also noticed. From the available FTIR Spectral information, it has been established that the compound under investigation is picric acid and Diphenyl amine.

UV VISIBLE SPECTROSCOPIC STUDIES

Figure shows the absorbance zone around 214.83nm (Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infrared wavelengths)[11,12] This means that this material presents a good non-absorbance band in the visible range for expected applications. A little protuberance around the 357.06 nm is observed[13]. This little peak is still outside the visible zone (UV zone) and it could present some absorbance if the crystal were to be excited with 600 nm (red color) trying to obtain a second harmonic of 357.06 nm (UV color). Optical properties of the grown crystals were studied using Arithmetic UV spectrometer. Optical transmittance and absorption were recorded for the crystals of thickness approximately around 2mm.From the spectra [Figure], it is evident that crystals have UV cut off below 300nm (214.83 nm), which is sufficient for SHG Laser validation of 1064 nm or other application in the blue region. There is a shift in the cut off wavelength due to additive effect. The crystals have wide transparency between 200 to 1100 nm. The recorded transmission is almost above 95% throughout the region. This is the most desirable property of the crystals used for nonlinear optical application. The peak around 214.83 nm corresponds to π - π^* conjugation. The depth of the peak varies with the additive present. The increased depth which is favorable for more non-linear effect is observed in this crystal at 357.06 nm.

The dependence of optical absorption coefficient and the photon energy helps to study the band structure and the type of transmission of electrons. As a consequence of wide band gap, the crystals under study have relatively longer in the visible region. The internal efficiency of the device also depends upon the absorption coefficient. Hence by tailoring the absorption coefficient and tuning the band gap of the material, one can achieve devised material, which is suitable for fabricating various layers of the optoelectronic devices as per requirements[14].

XRD Studies

The grown specimen was first lapped and chemically etched in a non preferential etchent of water and acetone mixture in 1:2 volume ratio to remove the non-crystallized solute atoms remained on the surface of the crystals and also to ensure the surface planarity of the specimen. Fig. shows the high-resolution rocking or diffraction curve (DC) recorded for the specimen Picric acid acetamide copper sulphate using (002) diffracting planes in symmetrical Bragg geometry by employing the multicrystal Xray diffractometer (0000000083004288) described above with $MoK\alpha 1$ radiation. The powder XRD studies for the grown crystals were carried out and the collected data are provided in the table.

The powder X-ray diffraction (XRD) pattern Picric acid Diphenyl amine crystal are shown in the figure. The well-defined peaks at specific 2theta values show high crystallinity of the grown crystals. The values of hkl, relative intensity and 2 theta values for the reflection peaks of the powder XRD pattern are given table. The resultant peaks in the diffractogram (Figure) show an intense peak at 23.2247°(intense peak). The peaks appearing in the spectrum that have not been identified can be attributed to the formation of the compound Picric acid Diphenyl amine crystal. As seen in the figure, in addition to the main peak at the centre, this curve contains two more additional peaks. The solid line in these curves

which is well fitted with the experimental points is obtained by the Lorentzian fit.

The additional peaks at 26.7800° and 30.2864° and 31.2051^0 away from the main peak are due to internal structural very low angle (≤ 1 arc min) grain boundaries . The tilt angle i.e. the misorientation angle of the boundary with respect to the main crystalline region for both the observed very low angle boundaries are 26.7800 ° and 31.2050 °. The full width at half maximum (FWHM) values for the main peak and the two low angle boundaries are respectively 0.1338°, 0.1506°and 0.1336 °. Though the specimen contains very low angle boundaries, the relatively low angular spread of around 5 arc min of the diffraction curve and the low FWHM values show that the crystalline perfection is around 700 .The affect of such low angle boundaries may not be very significant in many applications, but for the phase matching applications, it is better to know these minute details regarding crystalline perfection. It may be mentioned here such very low angle boundaries could be resolved only because of the high-resolution of the multicrystal X-ray diffractometer used in the present investigation.

SHG Measurement

The study of nonlinear optical conversion efficiency was carried out using the experimental setup of Kurtz and Perry[15]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, with an input power of 6.1.mj. The grown crystal of Diphenylamine-picrate was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The generation of the second harmonics was confirmed by the emission of green light. A sample of potassium dihydrogenphosphate (KDP), also powdered to the same particle size as the experimental sample, was used as a reference material in the present measurement. The relative SHG conversion efficiency of Diphenyl amine –picrate was found to be greater than that of KDP. This may be attributed to the molecular structure of Diphenyl amine -picrate residue is engaged in a strong hydrogen bond with the picrate anion[16]. Table 3 shows comparison of SHG signal energy output of Diphenyl amine-picrate

CONCLUSION

Transparent crystals of Diphenyl amine -Picrate crystals were grown by slow evaporation technique at low temperature. Evaluation of lattice parameters and density measurements confirm that the Diphenyl amine has gone into the lattice of the crystals.

X- ray diffraction studies are conducted on Diphenyl amine -Picrate crystals using XPERT-PRO – Philips X-diffractometer using the powdered pattern.

The FT-IR study confirms the presence of Diphenyl amine -Picrate crystals The spectra reveal that the functional group additives have sufficient transmission in the entire IR region.

In the U.V absorption studies- characteristic feature in the absorption spectrum is a wide transparency window within the range of 357 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG.The dependence of optical absorption coefficient and the photon energy helps to study the band structure and the type of transmission of electrons. The SHG measurement shows that Diphenyl amine -Picrate crystals is a promising material that has the Non-linear optical properties.

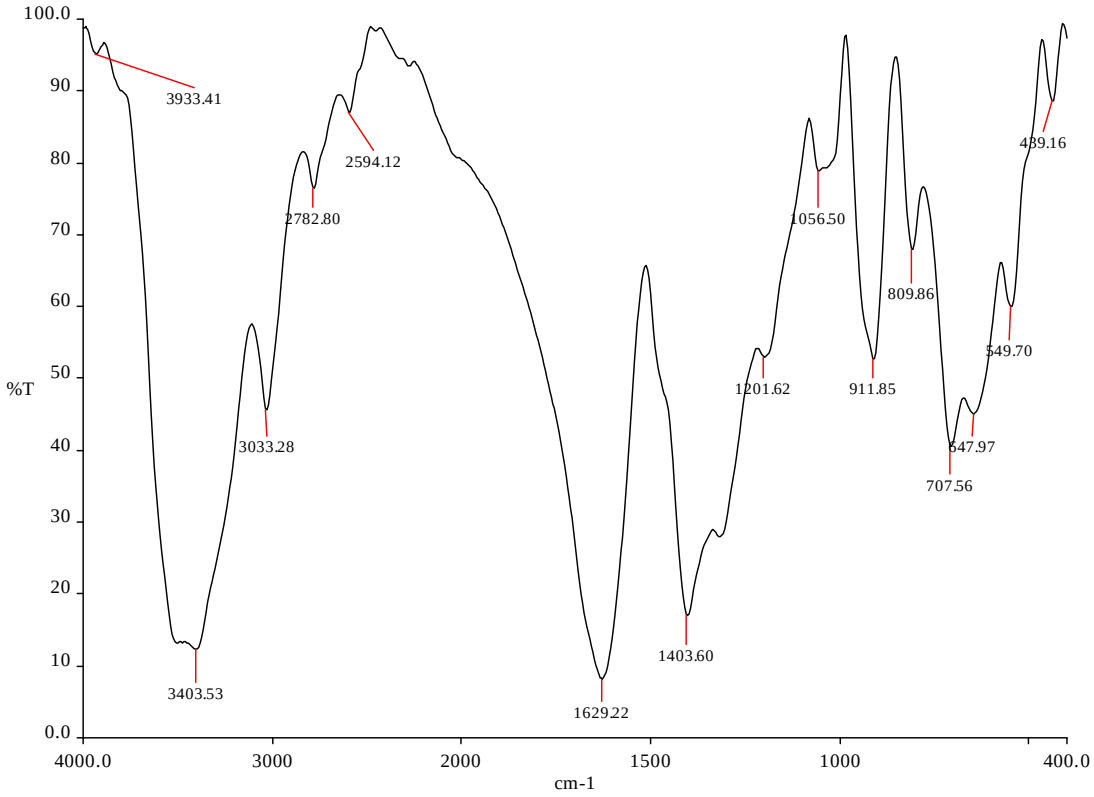
Table 1: FTIR absorption frequencies of picric acid- Diphenyl amine

S.NO	WAVE NUMBER cm^{-1}	MODE	COMMENT
1.	3403.52 cm^{-1}	N-H stretch	Amides -two bands for 2^o one for 1^o
2.	3033.28 cm^{-1}	C-H stretch	Sharp,above 3000 cm^{-1}
3.	2782.80 cm^{-1}	NH^+ stretch	Medium,broa,highly structured
4.	2594.12 cm^{-1}	NH^+ stretch	Major maximum
5.	1629.22 cm^{-1}	N-H bend	Amines
6.	1403.60 cm^{-1}	O-H bend	Carboxylic
7.	1201.62 cm^{-1}	C-O stretch	alcohols
8.	1056.50 cm^{-1}	C-N stretch	Amines
9.	911.85 cm^{-1}	C-C C-N C-O	Single bond
10.	809.86 cm^{-1}	C-H bend para	Aromatics
`11.	707.56 cm^{-1}	C-H bend	Aromatic compound

ACIC
St.Joseph's College (Autonomous)
Trichy-2

FTIR SPECTRUM
Date: 11/8/2011

Spectrum Name: RSGC-11.sp



RSGC-11.pk

RSGC-11.sp 3601 4000.00 400.00 8.21 99.37 4.00 %T 5 1.00

REF 4000 98.74 2000 80.47 600
3933.41 95.09 3403.53 12.36 3033.28 45.66 2782.80 76.42 2594.12 87.06
1629.22 8.21 1403.60 16.96 1201.62 53.00 1056.50 78.83 911.85 52.67
809.86 67.87 707.56 40.63 647.97 45.05 549.70 59.99 439.16 88.56

Fig. 1: FTIR Spectrum of Diphenyl amine-picrate

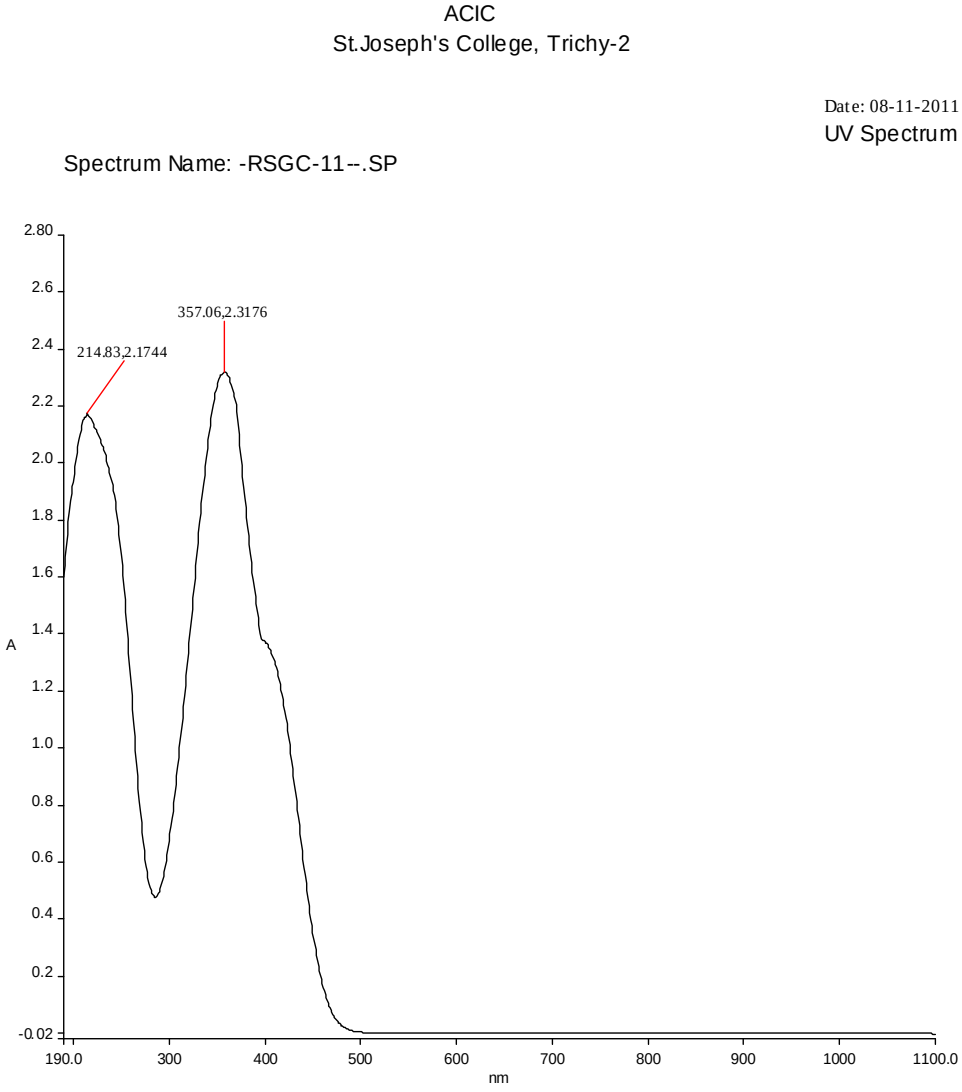


Fig. 2: Absorption spectrum of Diphenylamine picrate

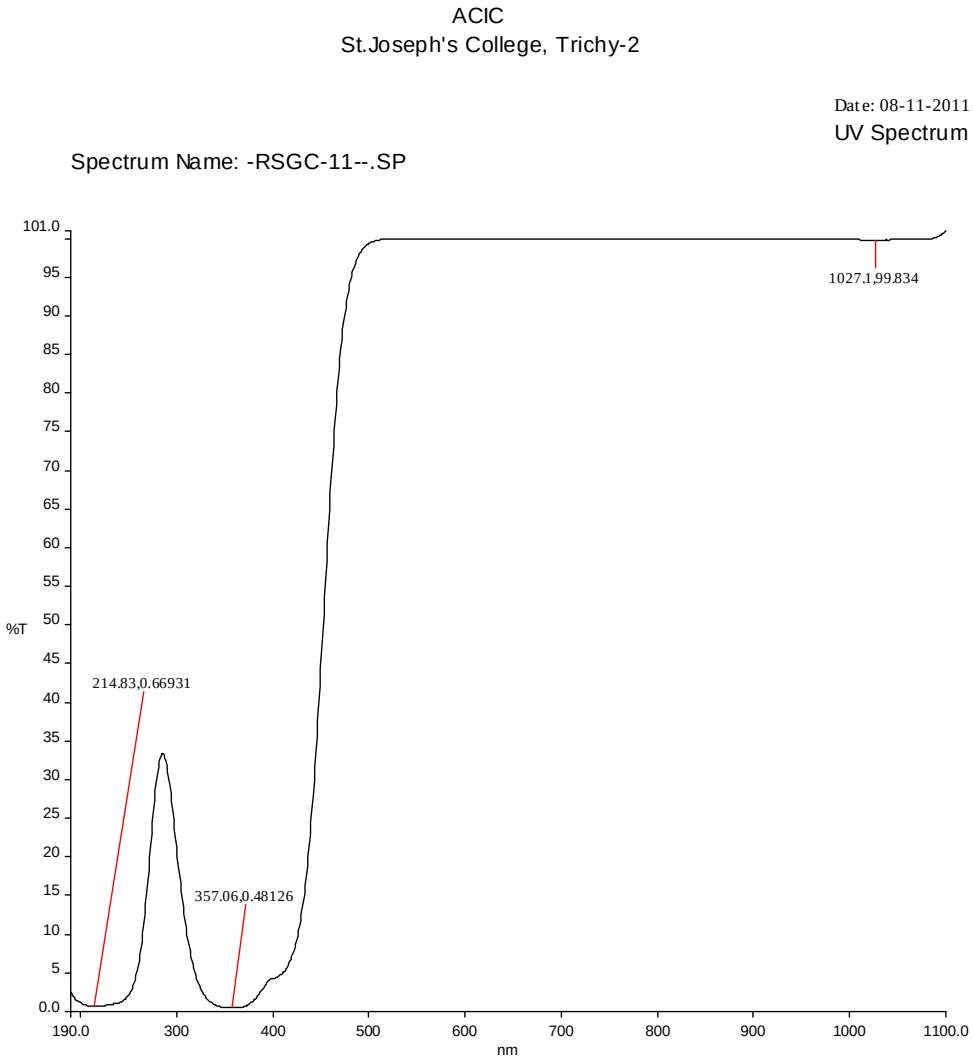


Fig. 3: Emission spectrum of Diphenylamine picrate

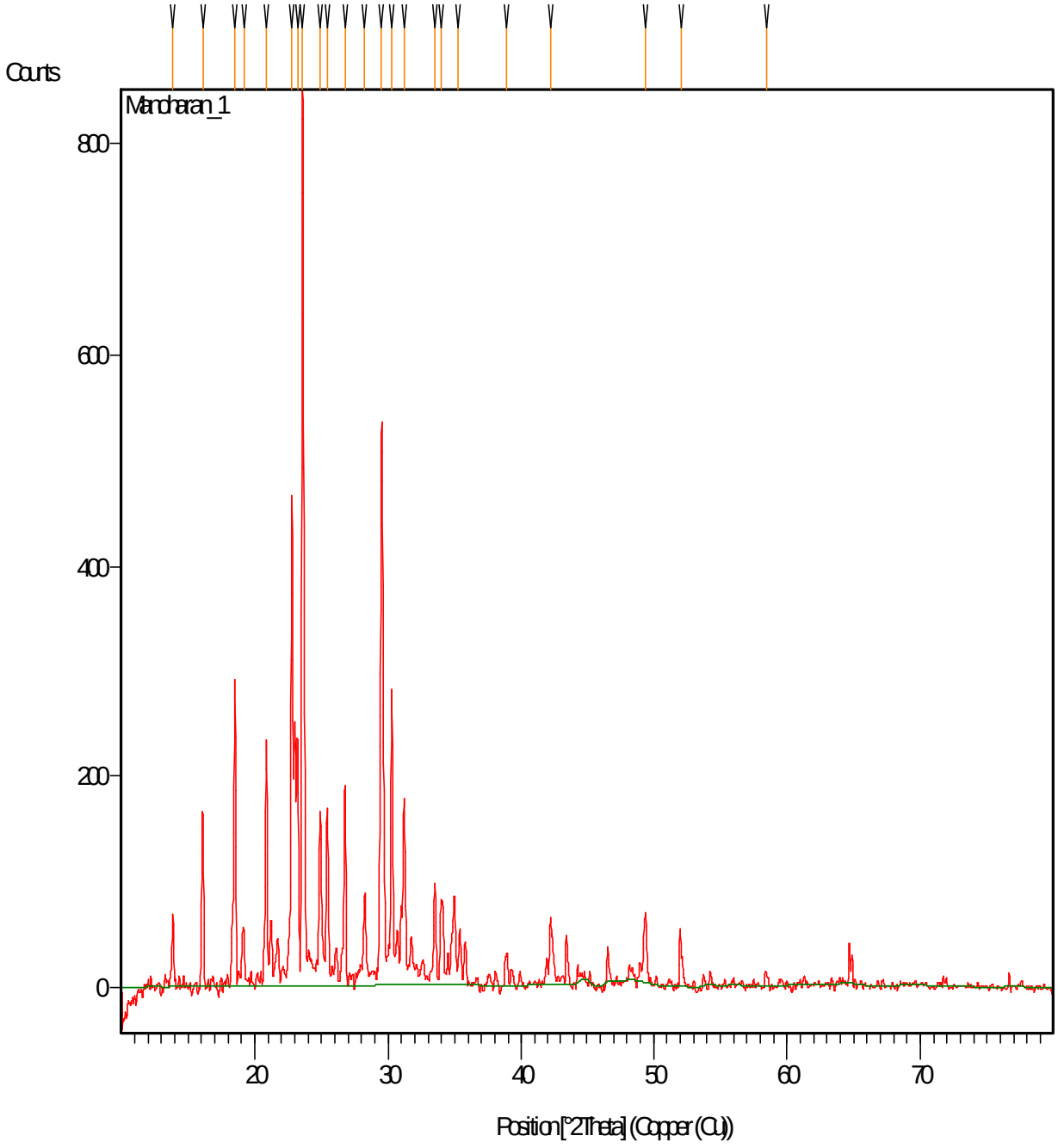


Fig. 4: XRD spectrum of Diphenylamine picrate

Table 2: Details of XRD Studies of Picric Acid-Diphenyl Amine

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
13.8547	62.47	0.2007	6.39195	7.85
16.1074	164.85	0.2175	5.50272	20.73
18.5346	283.11	0.1506	4.78722	35.59
19.1859	54.00	0.2007	4.62615	6.79
20.8613	229.61	0.1506	4.25826	28.87
22.7965	468.08	0.1171	3.90097	58.85
23.2247	225.64	0.1338	3.83000	28.37
23.5666	795.40	0.1840	3.77520	100.00
24.8982	163.61	0.1673	3.57623	20.57
25.4246	161.79	0.1673	3.50337	20.34
26.7800	187.77	0.1338	3.32906	23.61
28.2554	87.28	0.1673	3.15849	10.97
29.5069	523.24	0.1338	3.02732	65.78
30.2864	281.25	0.1506	2.95116	35.36
31.2051	174.80	0.1338	2.86633	21.98
33.5197	94.49	0.1673	2.67352	11.88
33.9539	69.94	0.2676	2.64032	8.79
35.2760	28.28	0.8029	2.54433	3.56
38.8623	30.62	0.2007	2.31740	3.85
42.3145	55.29	0.2676	2.13598	6.95
49.3758	65.36	0.2676	1.84578	8.22
52.0312	41.38	0.2676	1.75766	5.20
58.4584	10.31	0.3264	1.57750	1.30

Table 3: SHG Efficiency of Diphenyl amine -picrate with respect to KDP

INPUT POWER mj /pulse	KDP mv	Diphenyl amine-picrate crystals mv
6.1 m.v	6.8	8.mv

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