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Spectral, optical, thermal and electrochemical characterizations of organic nonlinear optical (NLO) triphenylamine single crystal

S. KOTTESWARAN, M. SENTHIL PANDIAN, P. RAMASAMY*
SSN Research Centre, SSN College of Engineering, Chennai-603 110, Tamilnadu, India

Single crystals of triphenylamine were grown by slow evaporation solution technique (SEST) at room temperature. The crystal structure was identified by single crystal X-ray diffraction (SXRD) analysis and the crystal was found to have monoclinic crystal system. Molecular structure of the grown crystal was investigated by ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) and ^{13}C Nuclear Magnetic Resonance (^{13}C NMR). The various functional groups of the crystal were identified by Fourier transform infrared spectrum (FTIR) analysis. Thermal stability of the grown crystal was studied by thermogravimetric and differential thermal analysis (TG-DTA). The optical absorption of the grown crystal was ascertained by UV–Vis NIR absorption studies. Photoluminescence (PL) spectrum of the triphenylamine crystal shows the emission behavior of the crystal. Second harmonic generation (SHG) efficiency of the crystal was determined by Kurtz and Perry technique and the efficiency was found to be equal to that of standard KDP material. The Cyclic voltammogram of the triphenylamine crystal was analysed using electrochemical workstation. Oxidation and Reduction peaks of the crystal are analysed.

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Keywords: Crystal growth; X-ray diffraction; Optical absorbance; Photoluminescence; Thermal analysis, Cyclic voltammogram

1. Introduction

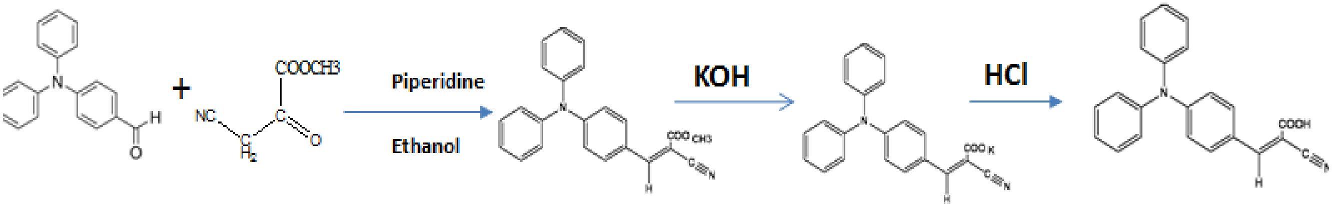
In recent years, an intense effort has been focused worldwide on the design and development of highly efficient organic and semi-organic nonlinear optical (NLO) crystals [1-3]. Organic nonlinear optical crystals are drawing a great deal of attention, due to their efficient nonlinearities and rapid response in electro-optic effect when compared with the inorganic NLO crystals. A number of organic nonlinear optical crystals have been accounted in literature owing to their nonlinear optical and photonic applications [4-5]. Organic NLO crystals are attracting a great deal of attention for possible use in optical devices because of their large optical nonlinearity, low cut-off wavelengths, short response time and high laser damage thresholds [6]. Considerable works have been done in order to understand the microscopic origin of nonlinear behavior of organic crystals [7-10]. The NLO properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades and they have been investigated widely due to their high nonlinear optical properties, rapid response in electro-optic effect and large second or third-order hyperpolarizabilities compared to inorganic NLO crystals [11]. The nonlinear susceptibility of an organic crystal would be larger when it has donor-acceptor conjugated molecular systems. Moreover, the selection of this type of donor, acceptor and conjugated electron system is a key factor in the molecular engineering and design of organic NLO crystals for particular wavelength conversion. Several novel organic NLO crystals with excellent properties have been developed by considering the above factor [12-16].

In this paper we report triphenylamine crystal (chemical formula C_{18} H_{15} N, molecular weight 245.31 g/mol, crystal system Monoclinic and space group Cc) grown from the dye solution for the first time. The structural, optical, thermal and electrochemical behaviors have been analysed using single crystal XRD, UV-Vis NIR, TG-DTA and cyclic voltammogram analysis, respectively. Molecular structure and functional groups have been confirmed by NMR and FTIR analysis, respectively. The NLO property of the grown crystal was analysed by SHG measurement.

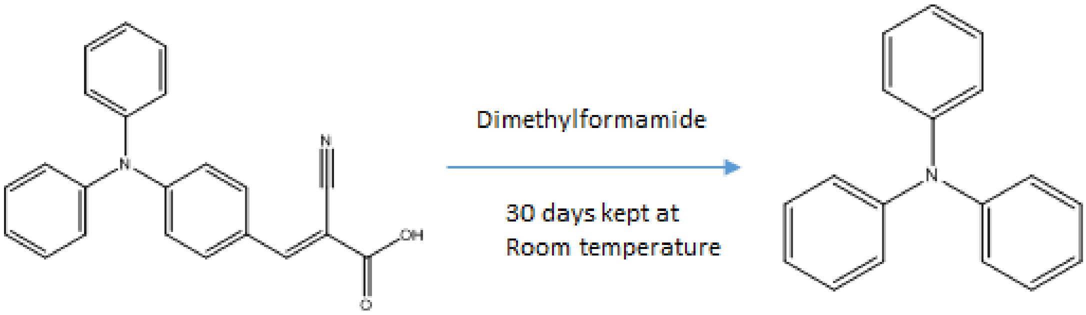
2. Experiments

2.1. Growth of triphenylamine crystal by conventional method

All the chemicals were obtained from Sigma-Aldrich Chemicals, India. Solvents are used without any further purification. 2-cyano 3-(4-diphenylaminophenyl) prop 2-enoic acid dye was synthesized from 4-diphenylaminobenzaldehyde (98% pure), methylcyanoacetate (99% pure), pipyridine (99.8% pure) and ethanol (99.9% pure) which was purified by column chromatography (ethyl acetate/petroleum benzene 95:5). 2-cyano 3-(4-diphenylaminophenyl) prop 2-enoic acid dye with dimethylformamide (99.8% pure) saturated solution was prepared and it was poured into the petri dish. Petri dish was covered with a perforated polyethylene sheet and then placed at room temperature for collecting the seed crystal by conventional method. Finally the transparent triphenylamine crystals were obtained in a period of 30 days. The purity of the synthesized material was further improved by successive recrystallization process. The recrystallized triphenylamine crystal was used to prepare the saturated solution. In this procedure the impurity content of triphenylamine crystal was minimized. The crystal was purified by recrystallization process. The crystal structure was deposited in CCDC. The CCDC Number is **1036084.** The synthesis of 2-cyano 3-(4-diphenylaminophenyl) prop 2-enoic acid dye chemical reaction is following.



From the dye molecule the triphenylamine crystal is formed by following reaction



2.2. Characterization techniques

Single crystal X-ray diffraction study was carried out by using ENRAF NONIUS CAD -4 MV3 single crystal X-ray diffractometer. ^{1}H NMR and ^{13}C NMR spectra of the grown crystal were recorded using DMSO-d_6 on a Bruker AV III 500 MHz FT NMR spectrometer to identify the different types of protons and carbons. The optical property of the crystal was recorded on a Perkin-Elmer Lambda-35 UV-Vis NIR spectrophotometer. The fluorescence spectrum of the compound was recorded using Shemadzhu RF-5301 PC spectroflurometer. Room temperature FTIR spectrum was recorded with KBr technique using Bruker FTIR spectrophotometer in the range of 4500-500 cm^{-1}. Cyclic voltammetry was carried out with an Ametek Instruments Electrochemical Analyzer. TG-DTA analysis was carried out under nitrogen atmosphere and heating rate of 20°C min^{-1} using a Perkin-Elmer Pyres Diamond TG-DTA thermal analyzer.

3. Results and discussions

3.1. Single Crystal X-ray Diffraction (SXRD)

The SXRD study reveals that the crystal belongs to monoclinic system and space group was found to be “Cc” with the lattice parameters a = 15.6086 (3) Å, b = 15.7428 (3) Å, c = 22.1891 (4) Å and Volume = 5451.56 (18) Å^3. The structure of the crystal has been solved by direct method and refined by full-matrix least square techniques using SHELXL – 97 program shown in Table-1. The ORTEP diagram of the triphenylamine crystal is shown in Fig. 1. The generated molecule of the title compound $C_{18}H_{15}N$ possesses an inversion centre situated at the mid-point of the bridging N-C bond. This clearly shows that the crystal structure contains one amino (N) molecule bonded with three phenyl group carbon atoms, other carbon atoms bonded with seven hydrogen atoms. The crystal packing diagram is shown in Fig. 2 in which the hydrogen atoms are denoted in white color, carbon atoms are denoted in gray color and amino (N) atoms are denoted in blue color.

Table 1. Crystal data and structure refinement of triphenylamine crystal

Empirical formula	$C_{18}H_{15}N$
Formula weight	245.31 g/mol
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions	a = 15.6086(3) Å α = 90° b = 15.7428(3) Å β = 90.987° c = 22.1891(4) Å γ = 90°
Volume	5451.56(18) A^3
Z, Calculated density	16, 1.196 Mg/m^3
Absorption coefficient	0.069 mm^{-1}
F(000)	2080
Crystal size	0.35 × 0.30 × 0.30 mm^3
Theta range for data collection	1.84 to 25°
Limiting indices	-18<=h<=18, -18<=k<=18, -26<=l<=26
Reflections collected / unique	36808 / 9605 [R(int) = 0.0412]
Completeness to theta	25.00 100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9814 and 0.9710
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9605 / 2 / 686
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0451, wR2 = 0.1009
R indices (all data)	R1 = 0.0808, wR2 = 0.1193
Absolute structure parameter	0(3)
Extinction coefficient	0.00143(14)
Largest diff. peak and hole	0.202 and -0.166 e.A^{-3}

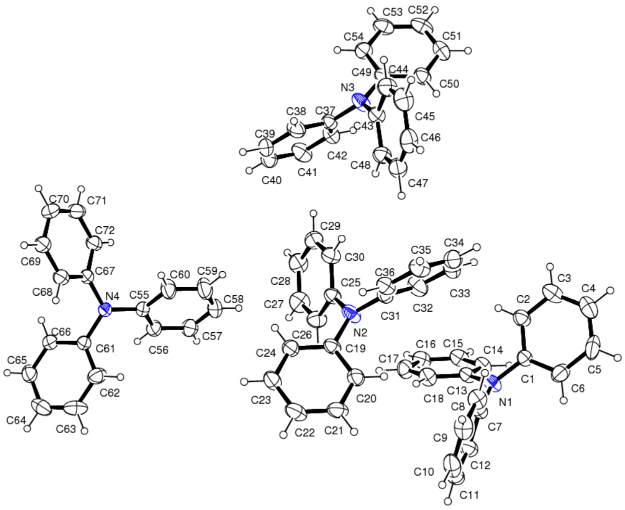


Fig.1. ORTEP diagram of triphenylamine

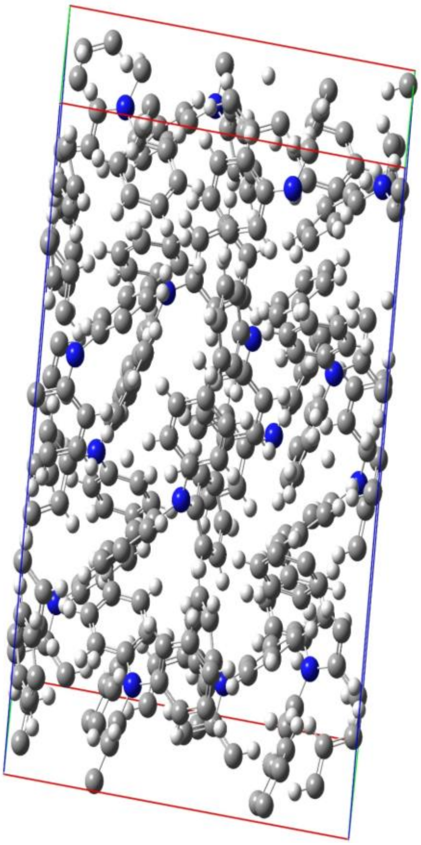


Fig. 2. Crystal packing diagram of triphenylamine

3.2. ^{1}H NMR and ^{13}C NMR spectrum

^{1}H NMR and ^{13}C NMR spectra are the important tools for identifying different environment protons and carbons in the compound. The triphenylamine crystal has been subjected to ^{1}H NMR spectral study by using cadmium chloride solvent and recorded spectrum is shown in Fig. 3. The hydrogen atoms present in the various chemical environment have given their signal at different chemical shift (δ) position. From these signals the different environment hydrogen atoms have been identified and discussed. The triphenylamine contains three types of hydrogen atoms. In this spectrum three signals at different δ positions depend upon the shielding nature of the hydrogen atoms. Hence the para hydrogens appear as triplet because each neighbouring carbon contains one hydrogen and it produces their signal at 6.98 (t, J=14.8 Hz, 3H), the ortho hydrogens appear as doublet because neighbor carbon atom contains one hydrogen only. So it produces signal at 7.07 (d, J=8 Hz, 6H) and the meta hydrogens appear as triplet because each neighbor carbon atom contains one hydrogen and so it gives signal at 7.22 (t, J=14.8, 6H). From ^{13}C NMR spectrum the four different environment carbons are obtained at different chemical shift (δ) position which is shown in Fig. 4. C_1, C_2, C_3, and C_4 chemical shift (δ) positions are 122.70, 124.28, 129.25 and 148.08, respectively [17].

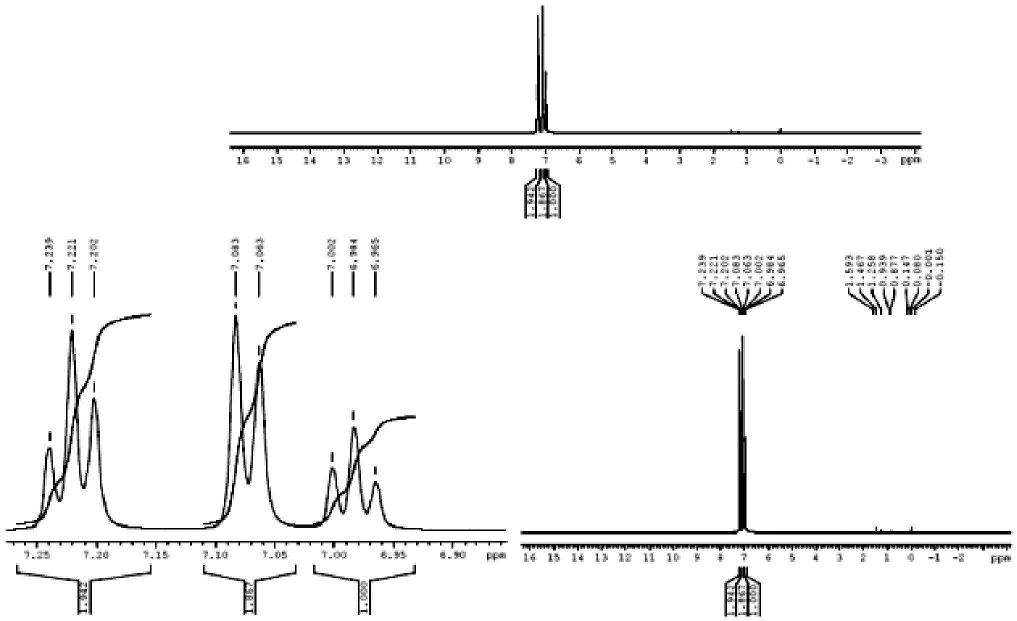


Fig. 3. ^{1}H NMR spectrum of triphenylamine

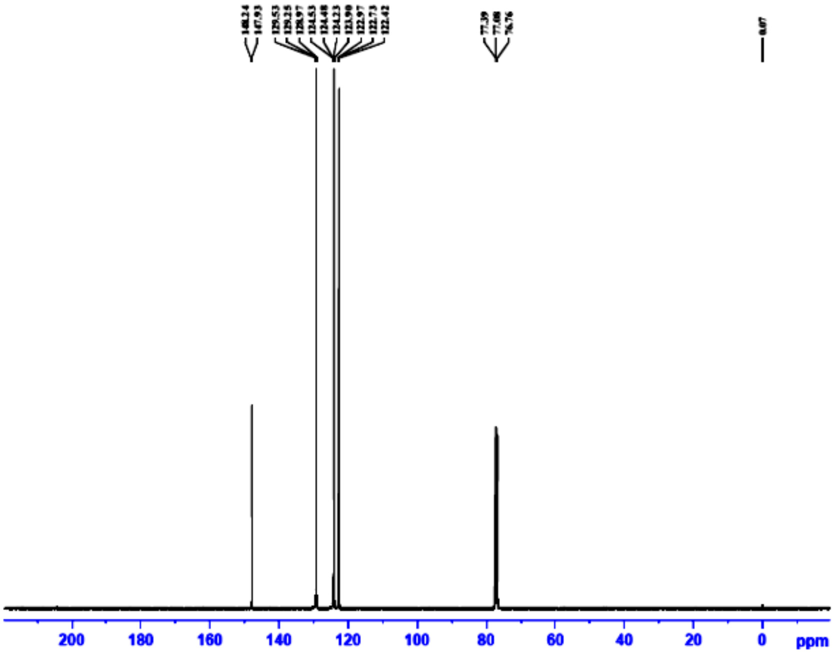


Fig. 4. ^{13}CNMR spectrum of triphenylamine

3.3. FTIR Studies

FTIR spectrum is the most commonly used method to identify the functional groups of the compounds. The functional groups of the triphenylamine were confirmed by the FTIR spectrum. The FTIR spectrum of the triphenylamine was carried out using KBr pellet technique at 450-4000 cm^{-1} and it is shown in Fig. 5. The band around 1580 cm^{-1} is due to the stretching vibrations of the aromatic C=C groups, the band around 1475 cm^{-1} is due to the deformation of C-H bonding and the bands around 1271 cm^{-1} are due to the stretching frequency of the aromatic amine.

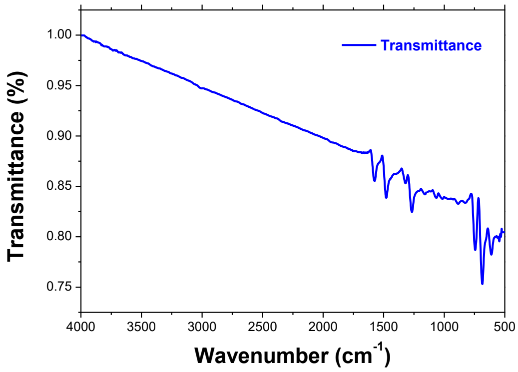


Fig. 5. The FTIR spectrum of triphenylamine

3.4. Photoluminescence studies (PL)

The photoluminescence spectrum of triphenylamine was recorded at 280-650 nm. The excitation peak is obtained around 385 nm and the emission peak is obtained at 430 nm which is shown in Figs. 6 and 7 respectively. The relative intensities of the long wavelength emission and short wavelength emission are dependent on the electronic transitions of the triphenylamine molecule. The first excitation peak is due to the π→π* transition and the second emission peak is due to the n→π* transition. The maximum emission is shifted to longer wavelength at excitation wavelength 430 nm thus exhibiting a positive fluorescent solvatochromism, which indicates that the molecule becomes more polar in the excited state than the ground state.

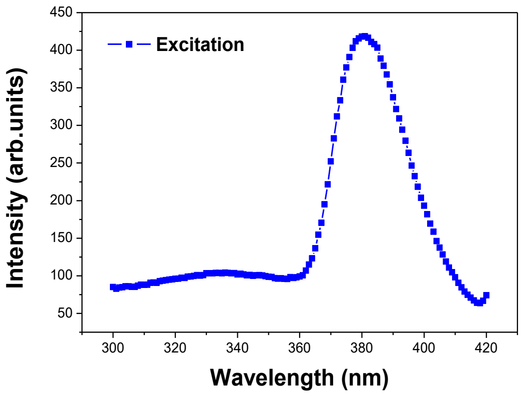


Fig. 6. Excitation spectrum of triphenylamine crystal

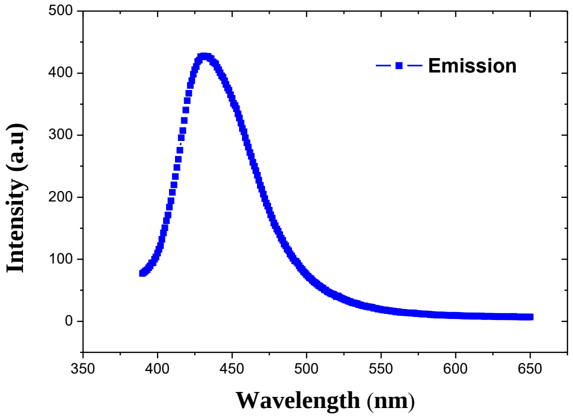


Fig.7. Emission spectrum of triphenylamine crystal at the excitation wavelength of 388 nm

3.5. Cyclic-Voltammetry analysis (CV)

Cyclic Voltammetry is one of the techniques to check the electrochemical behavior of the molecules and characterize the organic materials and estimate the energy band diagram. The electrochemical behavior of the triphenylamine was investigated in three electrode system and the distilled N,N-dimethylformamide (DMF) solution containing 1.0mM (M = $mol.dm^{-3}$) of the triphenylamine and 0.1 M of tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was used as supporting electrolyte. The reduction and oxidation peaks are shown in the Fig. 8. Cyclic voltammetry of triphenylamine was conducted with reference electrode, Ag/AgCl; working electrode Glassy carbon, and counter electrode, Pt; scan rate, 100 mVs^{-1}; temperature 20°C. For organic materials Highest Occupied Molecular Orbital (HOMO) represents the energy required to extract an electron from a molecule, which is an oxidation process and Lowest Unoccupied Molecular Orbital (LUMO) is the energy necessary to inject an electron to a molecule, thus implying a reduction process. The HOMO and LUMO energy levels of molecule can be calculated from the onset oxidation potential (E_{Ox}(onset)) and the onset reduction potential (E_{Red}(onset)).

$$\text{HOMO} = -[4.65\ \text{V}-E_{Ox}\ (\text{onset})]$$
$$\text{LUMO} = -[4.65\ \text{V}-E_{Red}\ (\text{onset})]$$

Triphenylamine produces one oxidation peak and one reduction peak. This is due to one electron involved in the oxidation and reduction process. E_{Ox}(onset) value of the triphenylamine is 1.24 V and E_{Red}(onset) value of the triphenylamine is -0.39 V. The HOMO value is 5.89 eV and LUMO value is -4.26 eV.

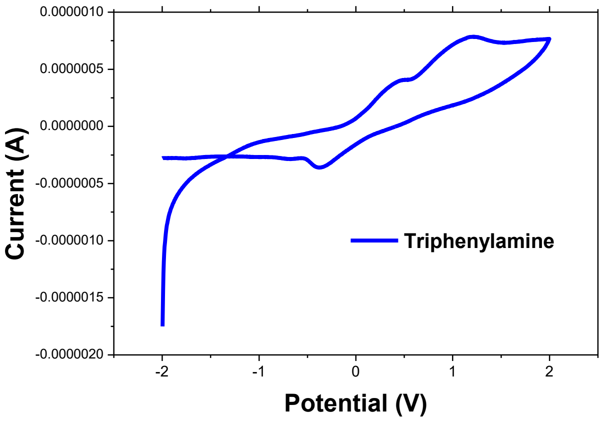


Fig. 8. Cyclic Voltammetry of triphenylamine

3.6. UV-Vis NIR spectral analysis

Absorption in the NLO crystal near the fundamental or second harmonic region will lead to loss of conversion efficiency. It is essential to have good transparency in the visible region for a NLO crystal. The optical absorption spectrum of the grown crystal was recorded in the wavelength range of 200–1100 nm at room temperature. A triphenylamine crystal of 3 mm thickness was used for UV-Vis NIR absorptions studies. The recorded UV-Visible absorption spectrum is shown in Fig. 9. It is observed that the crystal absorbed in UV and visible region.

The lower optical absorption in triphenylamine shows that the defect concentration is low in the grown crystal which in turn reduced scattering centers.

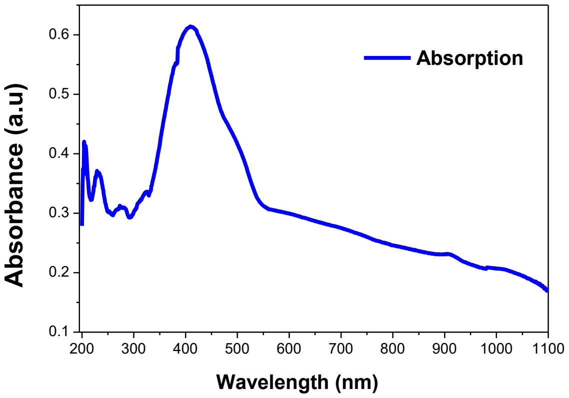


Fig. 9. UV-Vis-NIR spectrum of triphenylamine crystal

3.7. Thermal analysis

TG-DTA of triphenylamine was carried out between 35°C to 300°C in nitrogen atmosphere at a heating rate of 10°C/min using Perkin-Elmer diamond TG-DTA analyzer. There is a sharp melting point at 126°C and the percentage of weight loss observed in TG is negligible which is shown in Fig. 10. The second sharp endothermic peak is observed at 251°C which corresponds to about 100% of the weight loss. This confirms the decomposition of the sample is at 251°C. The comparison of decomposition point of the organic crystals is shown in Table 2. The molecular formula and molecular weight of the present compound is $C_{18}H_{15}N$ and 245.31 g/mol respectively. This 100% of the weight loss is due to the liberation of gaseous molecules. Triphenylamine may liberate one molecule of ammonia (NH_3), four molecules of methane (CH_3) and fourteen carbon molecules (C) when heated to 251°C. In this stage of decomposition the theoretical weight loss is 100% and experimental weight loss is also 100%. On examining the TG/DTA it is apparent that triphenylamine is a good candidate for crystal growth from melt.

Table 2. Comparison of decomposition point of triphenylamine with other organic single crystals.

Serial No	Organic Crystals	Decomposition Point (°C)	Reference
1	p-anisaldehyde	200	[19]
2	urea thiourea mercuric sulphate	221.5	[20]
3	Triphenylamine	251	Present work
4	2-amino-5-nitropyridinium Chloride	150	[21]
5	2-amino-5-nitropyridinium trifluoroacetate	234	[22]

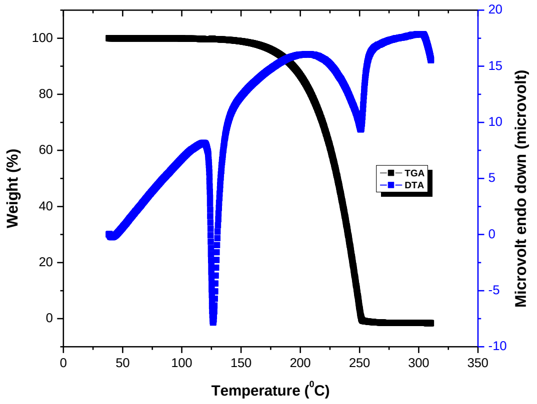


Fig. 10. TG-DTA spectrum of triphenylamine

3.8. Second harmonic generation (SHG) analysis

SHG conversion efficiency was carried out using Kurtz and Perry technique [18]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm with input beam energy of 2.1 mJ/pulse and pulse width 10 ns with a repetition rate of 10 Hz was used. The grown single crystal was powdered with uniform particle size and tightly packed in a micro-capillary of uniform pore and exposed to the laser radiation. The bright green light emission (λ = 532 nm) has been observed which indicates the SHG behavior of the grown crystals. The relative SHG efficiency of the triphenylamine crystal (72) mV is equal to that of KDP.

4. Conclusion

The organic NLO triphenylamine crystals have been grown by slow evaporation solution technique, using dimethylformamide as a solvent. The crystals were harvested after 30 days. Single crystal X-ray diffraction was carried out to find out the unit cell parameters and the crystal structure of the crystal. The structure of the crystal was confirmed by ^{1}H NMR and ^{13}C NMR spectrum. The presence of various functional groups of the grown crystal was confirmed by FTIR. The UV-Vis NIR spectrum reveals that the optical absorptions of triphenylamine. The Oxidation and Reduction values of the triphenylamine were observed from Cyclic Voltammetry. Using the oxidation and reduction value the HOMO-LUMO of the triphenylamine molecules has been calculated. Thermal stability of the grown crystal was studied by TG-DTA analysis and melting point of the material was found to be 127°C and decomposing point of the crystal was 251°C. The SHG relative efficiency of the material was found equal to that of standard KDP material. Thus the characterization confirms the suitability of the grown crystal for NLO applications.

Acknowledgements

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[*] Corresponding author: ramasamyp@ssn.edu.in