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Synthesis, Crystal Growth, Spectroscopic and DFT studies of 2-[(2,5-dimethyl phenyl)imino]methyl)phenol as a nonlinear optical single crystal

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Abstract

2-[(2,5-dimethyl phenyl) imino] methyl) phenol, a second order single crystal with the dimension of (7x9x2 mm^3) has been successfully grown in ethanol solution by slow evaporation method , which crystalizes in orthorhombic system with a non-centrosymetric space group of $P2_12_12_1$. The single crystal cell parameters were determined by single crystal X-ray diffraction method. FTIR spectroscopic study was carried out to confirm the presence of various functional groups in the crystal. The range of optical absorbance, optical transmittance window and lower cut off wavelength were identified by Ultra Violet visible spectral study. The thermal properties of crystals were evaluated from thermogravimetric and differential scanning calorimetry. The crystal was stable up to 261° C. Emission of greenish yellow radiation confirms that the crystals can be used for optical applications. The highest occupied molecular orbit and lowest unoccupied molecular orbital energies are also found by Density Functional Theory method. The second order nonlinear optical property of the crystal was confirmed by Kurtz-Perry powder technique and the efficiency was found to be 0.5 times greater than standard KDP crystal.

Keywords: *Single crystal XRD, UV-Visible, TGA/DSC, Photoluminescence, SHG, DFT.*

1. Introduction

The non linear optical crystals, both organic and inorganic with large second-order optical materials have significant applications in ultraviolet, near and far-infrared wavelength regions [1-3]. The impact of single crystals is clearly visible in industries that deal with semiconductors, laser technology, organic light

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emitting diode (OLED's) and optoelectronics devices etc., The physio-chemical properties such as spectral, thermal, electrical, mechanical and non-linear optical properties are essential to study the ability of organic compound being explored for its stability at ambient conditions [4-6]. Moreover organic compounds with a high degree of delocalization of aromatic π electron cloud exhibit hydrogen bonds and weak Vander Waal's bonds satisfying the necessary prerequisites for NLO material.Large second order NLO response is possible in the molecule with various delocalization π electrons, since there will be a change in the dipole moment from ground state to keyed up state which will have large transition moment and noncentro symmetric response [7–9]. The second order NLO materials are used in optical switching,, frequency conversion and electro-optic applications,, especially in electro-optic modulators.

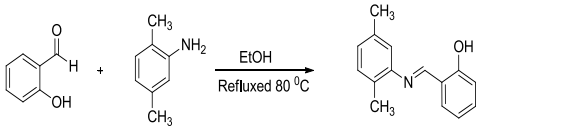
In the present work we report the result of 2-[(2, 5-dimethylphenyl)imino]methyl)phenol (DPMP) single crystals right from the crystal growth by slow-evaporation growth and various characterizations such as XRD, FT-IR, UV-Visible, Thermogravimetric Analysis/differential scanning calorimetry (TGA/DSC), and Photoluminescence. In addition of density functional theory (DFT) and theoretical of optimized geometry, highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbital (LUMO) energy gap NBO analysis of the title compound theory with B3LYP/6-31, and second harmonic generation (SHG) are made.

2. Materials and Methods

2.1 Synthesis

All the reagents were purchased from sigma Aldrich analytical grade. The title compound was grown by slow evaporation method. The calculated amount of salicyaldehyde (1equ) and 2 methyl-5-dimethylaniline (1equ) were taken in 250 ml round bottomed flask and 50ml of ethanol is taken as a solvent. These two are mixed by the help of magnetic stirrer for nearly 8 hours. The reaction mixture was heated to the boiling temperature and refluxed for 7 hours. Then it is cooled to room temperature in overnight and a solid compound was formed which was yellow in colour. The ethanol was removed in using 45mm whattman filter paper and the compound is kept for dryness. The purity of the synthesized compound was further increased by step by step recrystallization. The obtained crystal is 2-[(2,5-dimethyl phenyl)imino]methyl)phenol (DPMP) or Salicyaldehyde 2,5, dimethyl aniline.

Reaction mechanism



2{(2,5-dimethylphenyl)imino]methyl}phenol

2.2 Crystal Growth

The final product was dissolved in hot ethanol in an ambient temperature which was filtered in 100 ml beaker. The filtered solution is covered in polythene sheet and small pin hole are made, then kept undisturbed at room temperature for slow evaporation. Spontaneous nucleation was formed after one week and good quality DPMP single crystals of size 7 mm x 9 mm x 2 mm were harvested. This is shown in Fig 1.

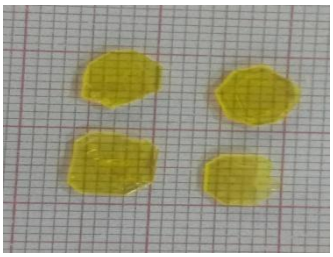


Fig. 1-DPMP Grown Crystal

3. Results and Discussions

3.1 Single crystal X-ray diffraction

The structure of DPMP crystal was examined by single crystal XRD analysis and the lattice parameters values were determined using Enraf-Noius CAD-4diffractometer. It was found that the grown crystals belong to orthorhombic system with non-centrosymmetric space group $P2_12_12_1$ and Z= 4. The number of molecules per unit cell parameter were observed and the lattice parameters were found to be a = 6.84Å, b = 7.74Å, c = 23.22Å and $\alpha = \beta = \gamma = 90°$. The molecular geomentry of the grown crystal was shown in Fig 2.

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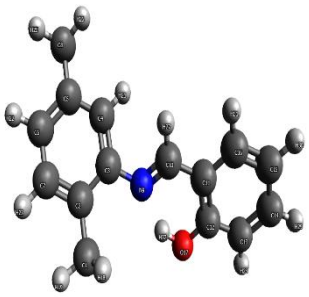

Fig 2. Molecular Geometry

3.2 FTIR spectral analysis

The Fourier transform infrared (FTIR) analysis is an important study to identify the various functional groups and structure of the compound. To determine the presence of functional group in DPMP crystal was recorded in the range from 400 cm^{-1} to 4000 cm^{-1} shown in Fig.3. The spectrum was recorded on PERKIN ELMER spectrometer with using the KBr pellet technique. In this spectrum, the peak at 468.70 gives out the plane bending of C-O vibration the C-H in-plane bending vibration is observed at 1114.86 cm^{-1}. The absorption band at 1564.42 cm^{-1} is due to the formation of imine group (C=N) as a result of the condensation reaction between aldehyde and amine. In this spectrum the peak at 3051.39 cm^{-1} assigned to the aromatic C-H stretching vibration. Absence of characteristic aldehyde bands at 2720 cm^{-1} and 2820 cm^{-1} indicate that there is no aldehyde group in the final product. The FTIR spectrum does not show any signal corresponding to aldehyde and amine group present in the final product.

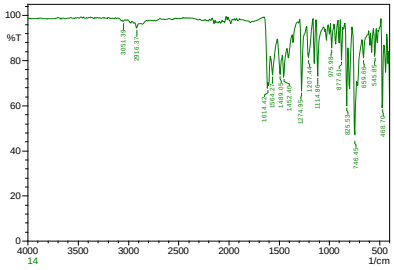

Fig.3- FT-IR Spectrum of DPMP single crystal

3.3 UV-Vis-NIR Spectral analysis

The absorption/ transmission spectrum is an essential parameter for all NLO application, as it gives the useful information about the electronic transition, transparency window, and its optical band gap of the material. In this work very small absorption peaks present in the region of 286 nm, which shows DPMP crystals are a potential candidate for optoelectronic and NLO applications. Below 300 nm the absorbance may be due to the electronic transition π-π* taking place in the benzene ring of the material. The optical constants of the materials play an important role in fabricating optical devices. The dependence of the optical absorption coefficient on the photon energy helps in determining the nature of optical transition of electrons which take place in the materials. Absence of absorbance in the region between 450 and 800 nm is desired property for the NLO materials. The grown DPMP crystal has good transparency (up to 86%) in the visible and near IR region. The uniform transparency indicates that DPMP crystal has high optical homogeneity which significantly confirmed crystallinity of the crystal [10]. The absorption and transmission spectrums are shown in Fig 4 and Fig 5.

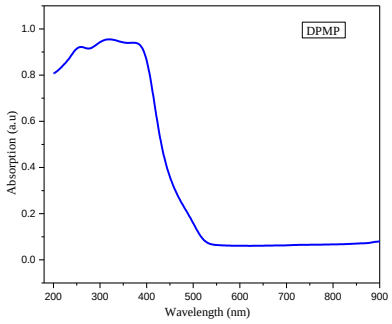

Fig. 4-UV Visible Absorption spectrum

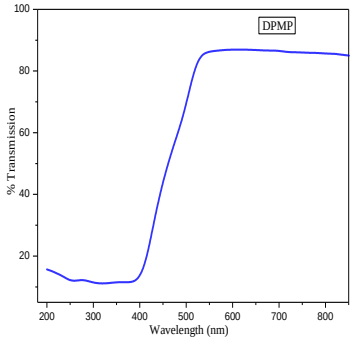

Fig. 5-UV Visible transmission spectrum

To find optical energy band gap

The optical energy band gap of grown crystal its also calculated using the relation

$$\alpha = \frac{2.306 \log(1/T)}{t}$$

The measured transmittance (T) and the sample thickness (t) were used to calculate the absorption coefficient (α) for high photon energy (hυ) and absorption coefficient (α) obeying the following relation

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

Where Eg is the optical band gap of the material, A is a constant value. The graph plotted between variation of $(\alpha h\upsilon)^2$ and photon energy hυ shown in fig 6. The optical energy band gap was found to be 2.88 eV. The large transmittance in the visible region and wide band gap makes the crystal suitable for optical application.

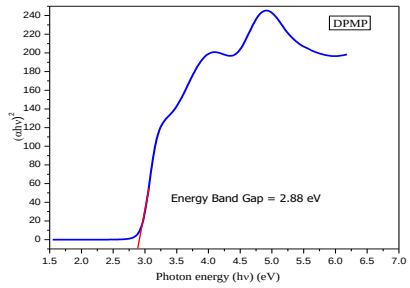

Fig. 6 - Energy Band Spectrum

3.4 Thermal Analysis

The thermal activity of the DPMP crystal was investigated via TGDSC Measurement using TA instrument model Q20 V24.2 Build 107 differential scanning calorimeter. This study provides the qualitative information such as, phase transition, melting point, decomposition point and the stability of the analyzed material as a function of increased temperature. 1.169 mg of DPMP crystalline powder was taken in an inert nitrogen atmosphere at a heating rate of 10 °C/min and alumina (Al2O3) was used as the reference material for the measurement. In DSC thermograph the first endothermic peak at 114.20°C addressed the intermediate melting point of the DPMP crystal. Here, it is worthy to register that, the spiky of the endothermic pinnacle confirmed the good crystallinity and purity of the DPMP. Within this process, the apparent of second endothermic peak at 261.04°C signifies the decomposition point of the material. Above finding clearly endorse that, the NLO applicability of DPMP is limited up to 160°C. Moreover, the melting point of DPMP crystal is quite good compared to reported organic NLO crystals like, 4DMB (76 °C) [11], DMMC (93.98°C) [12], BMP (107 °C) [13]. Fig 7 and 8 gives the DSC and TGA graph of DPMP crystals.

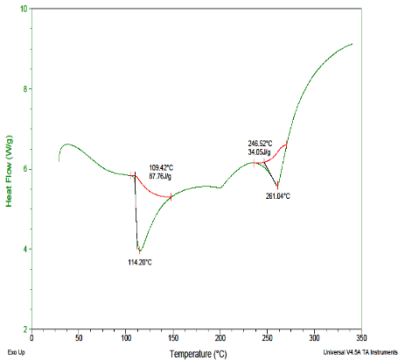

Fig. 7-DSC Graph of DPMP Crystal

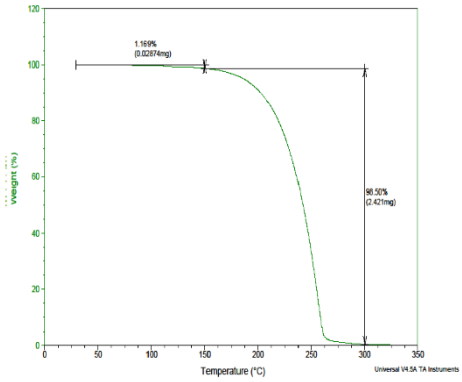

Fig. 8- TGA Graph of DPMP crystal

3.5 Photoluminescence

Photoluminescence spectroscopy is a powerful tool for investigating the levels of structural organization at medium range [14]. The photoluminescence property of the grown crystal was recorded using a JobinYvon - SpexsSpectrofluorometer (Fluor log version-3; model FL3-11) at room temperature with 450W high pressure Xenon lamp source which encloses a photomultiplier tube (PMT) (R 928) at the detector side. The excitation and emission spectra were recorded using a spectral slit width of 2 nm. The high sensitivity of PL technique often highlights the features which UV–Vis absorption measurements rarely define. In particular, PL is a fundamental tool to determine a class of energy levels that are invisible at UV–Vis absorption measurements. The photoluminescence spectrum of the grown DPMP crystal was recorded at room temperature with excitation wavelength at 445 nm and the emission spectrum displays a strong band from 568 nm which is indicate the greenish yellow radiation confirming the possibility of using the materials for optical applications. The maximum intensity was assigned to the electronic transition of the aromatic ring and Vander Waal's force present in the parent molecule. This broadening of strong PL signal indicates the optical quality with the

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existence of defects in the title compound. However, the strong emission peaks may indicate the presence of intrinsic defects in the forbidden band region and highly coherent with large second order NLO activity.

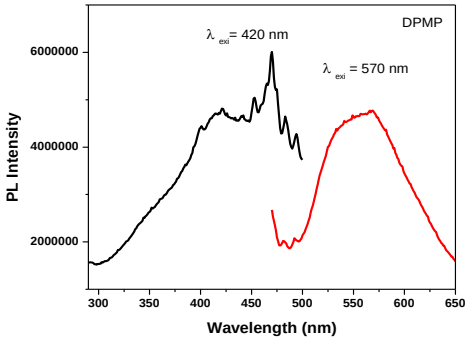

Fig. 9- Photoluminescence graph of DPMP single crystal

3.6 Frontier molecular orbital energies

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are termed as Frontier molecular orbital, used to characterize how the molecule interacts with other species. The HOMO-LUMO energy gap determines the chemical reactivity, kinetic stability, bio-activity and chemical hardness of the molecules [15]. The HOMO orbital will act as an electron donor because it is the outermost orbital containing electrons and the LUMO orbital act as an electron acceptor, since it is the innermost orbital has the ability to accept electrons [16]. The HOMO-LUMO plots of DPGF molecule is shown in Fig. 10. The HOMO–LUMO energy gap value of DPMP compound was found to be 4.1051eV which implies that DPMP possesses higher energy barriers to transfer electrons between the occupied and unoccupied orbitals.

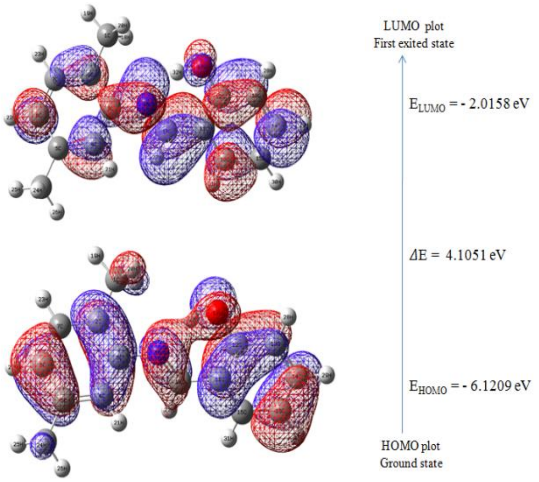

Fig.10 - Frontier molecular orbital energies

Table. 2. HOMO-LUMO energy values calculated by DFT method DPMP single crystal

Parameter	Value
HOMO(eV)	-6.1209
LUMO(eV)	-2.0158
Ionization potential	6.1209
Electron affinity	2.0158
Energy gap(eV)	4.1051
Electronegativity	4.0684
Chemical potential	-4.0684
Chemical hardness	2.0525
Chemical softness	0.2436
Electrophilicity index	4.0320

3.7. First-order hyperpolarizability (β)

The first-order hyperpolarizability is the second-order electric susceptibility per unit volume. The molecule with large hyperpolarizability will have strong NLO properties and could be used for fabricating optical devices [17]. To exhibit a large molecular hyperpolarizability, the system should be asymmetric and should contain polarizable electron donor and acceptor groups [18]. The first-order hyperpolarizability is a third rank tensor, which is described by 3×3×3 matrix. The 27 components of the 3D matrix are reduced to 10 components due to kleinman symmetry [19]. The total first-order hyperpolarizability in terms of x, y, z components are given by the following equation:

$$\beta = (\beta + \beta + \beta)^{1/2} \quad (5)$$

The first-order hyperpolarizability value for DPMP molecule was calculated by the B3LYP/6–311++G (d, p) level and is shown in Table 3.

Parameter	B3LYP/6–311++G(d, p)	Parameter	B3LYP/6–311++G(d, p)
Bxxx	275.613	α xy	-5.791
Bxxy	-249.869	α yy	193.525
Bxyy	61.486	α xz	0.113
Byyy	-131.058	α yz	6.306
Bzxx	-163.855	Azz	117.885
Bxyz	18.493	α (a.u)	211.485
Bzyy	-21.979	α (e.s.u)	3.1342×10^{-23}
Bxzz	22.442	Δ α (a.u)	587.679
Byzz	-48.091	Δ α (e.s.u)	8.7094×10^{-23}
Bzzz	-57.323	μ x	-0.292
βtot (a.u)	610.287	μ y	-0.766
βtot (e.s.u)	5.2725×10^{-30}	μ z	-0.396
α xx	323.044	μ (D)	0.910

Table. 3 - The values of calculated dipole moment μ (D), polarizability (α) and first order hyperpolarizability (β) of title compound.

3.8. Second harmonic generation (SHG)

Kurtz and Perry [20] second harmonic generation (SHG) test was performed to estimate the NLO efficiency of the title sample. The grown single crystal was crushed in uniform particle size and tightly packed in a micro capillary tube. A Q-switched High Energy Nd: YAG laser (Quanta RAY MODEL LAB -170-10) Model HG-4B High efficiency, angle tuned and temperature stabilized second harmonic generator crystal, energy; 850 mJ, beam of initial wavelength 1064 nm with an input power of 5.7 mJ and pulse width of 6 ns with repetition rate of 10 Hz was made to fall on the sample. The SHG efficiency is indicated by the bright green light emission from the material which showed that the good NLO property of the grown crystal. The second harmonic generation efficiency has been found to comparable in phase matched potassium dihydrogen phosphate (KDP) crystal. It is observed that the conversion efficiency of DPMP is 0.5 time greater than that of standard KDP

4. Conclusion

DPMP single crystal with good optical quality was grown using solution growth technique at room temperature. The unit-cell parameters and various planes present in the grown crystal were studied using single crystal diffraction analysis. The various functional groups present in the DPMP crystal was evaluated using FT-IR studies. The optical behavior of grown crystal was assessed using UV-Vis-NIR and PL studies, from which the absorbance, transmittance and band gap of the DPMP crystal was calculated. PL spectrum of the grown crystal shows UV emission. The TG-DTA study shows that the grown crystal has good thermal stability with high purity. The relative SHG efficiency of DPMP is 0.5 times greater than that of standard KDP crystal. The HOMO–LUMO energy gap and first order hyperpolarizability of DPMP crystal was calculated. Thus the grown DPMP singe crystal can be used as a potential material for electro-optics, photonics and SHG device applications.

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