# PREPARATION, GROWTH, SPECTRAL, THERMAL AND BAND GAP STUDIES OF PHENYL HYDRAZONE OF N –PHENYLACETAMIDE (PHPA) CRYSTAL.

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**Abstracct**

Phenylhydrazone of N-phenylacetamide (PHPA) is one of an organic non linear optical material. It has been effectively grown by slow evaporation solution growth technique at room temperature. The crystal got the above technique was subjected to various characterization analysis. Crystalline nature of the sample was affirmed by powder X-ray diffraction method. A functional group present in the crystal was identified by using FT-IR spectral analysis. Transparency and Optical properties of the crystals examined by UV-Visible studies. The thermal stability of the grown crystal was found by differential thermal analysis and differential scanning calorimetry (DTA/DSC). $H^1$ NMR spectra was recorded to illustrate the molecular structure. Band gap determination of crystal support the application oriented properties of the material.

**Keywords : Crystallization, FT-IR, UV-Visible, X-ray diffraction, Thermal analysis, Band gap studies.**

## INTRODUCTION

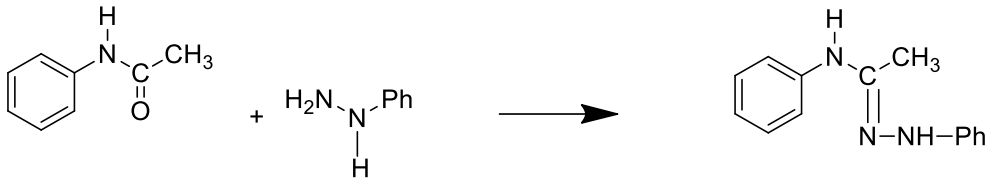
In recent years materials appearing optical nonlinearity have potential applications in signal transmission, information storage , optical trading, and so on(1-7). Due to potential applications in various photonic advances, the NLO properties of organic molecular materials have been the object of exceptional research. Using organic molecules for the nonlinear media has several advantages, such as low cost, low dielectric constant and great diversity of possible organic structures. A number of organic materials showing considerable NLO effects have been identified and synthesized Be that as it may, just a couple of them could be crystallized and investigated for second order NLO applications. The search for new NLO materials has been growing a result of creating enthusiasm for such materials . The organic molecular materials have emerged as a new class of promising nonlinear optical materials because of their superior qualities over inorganic systems. Organic compounds with asymmetric charge distribution π-electron system show large nonlinear optical responses, which have been attributed to the presence of electron rich donor and deficient acceptor substituent in the system. Thermal , spectral and XRD studies are vital devices in the characterization of different materials(8-14) . Here crystals of phenyl hydrazone of N – phenyl acetamide has been grown by slow evaporation solution growth technique and the grown crystals were characterized by FT-IR , UV ,H1 NMR , X-ray diffraction (XRD) and TGA-DSC studies and reported for the first time. The application oriented properties of PHPA was evidenced by Band gap determination.

## EXPERIMENTAL

By adopting the general procedure(15), The semi organic crystal of phenyl hydrazone of N – phenyl acetamide (PHPA) was reported . To a hot solution of phenyl hydrazine in methanol, a solution of N –phenyl acetamide in methanol was added drop wise during 30 minutes. The mixture was stirred and refluxed for 4 hours. At that point it was filtered and the filtrate was concentrated to half the volume. After a slow evaporation of the concentrate at room temperature, crystals were gathered by filtration,

washed with cold ethanol and afterward dried. The grown crystal were purified by repeated-recrystallization. These crystals were grown by slow evaporation solution growth technique using methanol as a growth medium.

## REACTION




N –phenyl acetamide Phenyl hydrazine Phenyl hydrazone of N –phenyl acetamide

## RESULT AND DISCUSSION

## FT-IR SPECTRAL STUDIES

Fourier transform infrared spectra study was done in the range of 400-4000 cm $^{-1}$ utilizing PERKIN ELMER FT-IR spectrometer. The absorption range of the grown crystal of PHPA is clearly evidenced in figure.1. The peak at 3294.27cm $^{-1}$ is corresponding to NH stretching vibration .The signal at 1598.91 cm $^{-1}$ and 1435.50 cm $^{-1}$ is due to the presence of phenyl ring. The presence of peak at 1556.64 cm $^{-1}$ is observed at C=N immine group(16)The peak at 1500 cm $^{-1}$ show N-N stretching vibration.

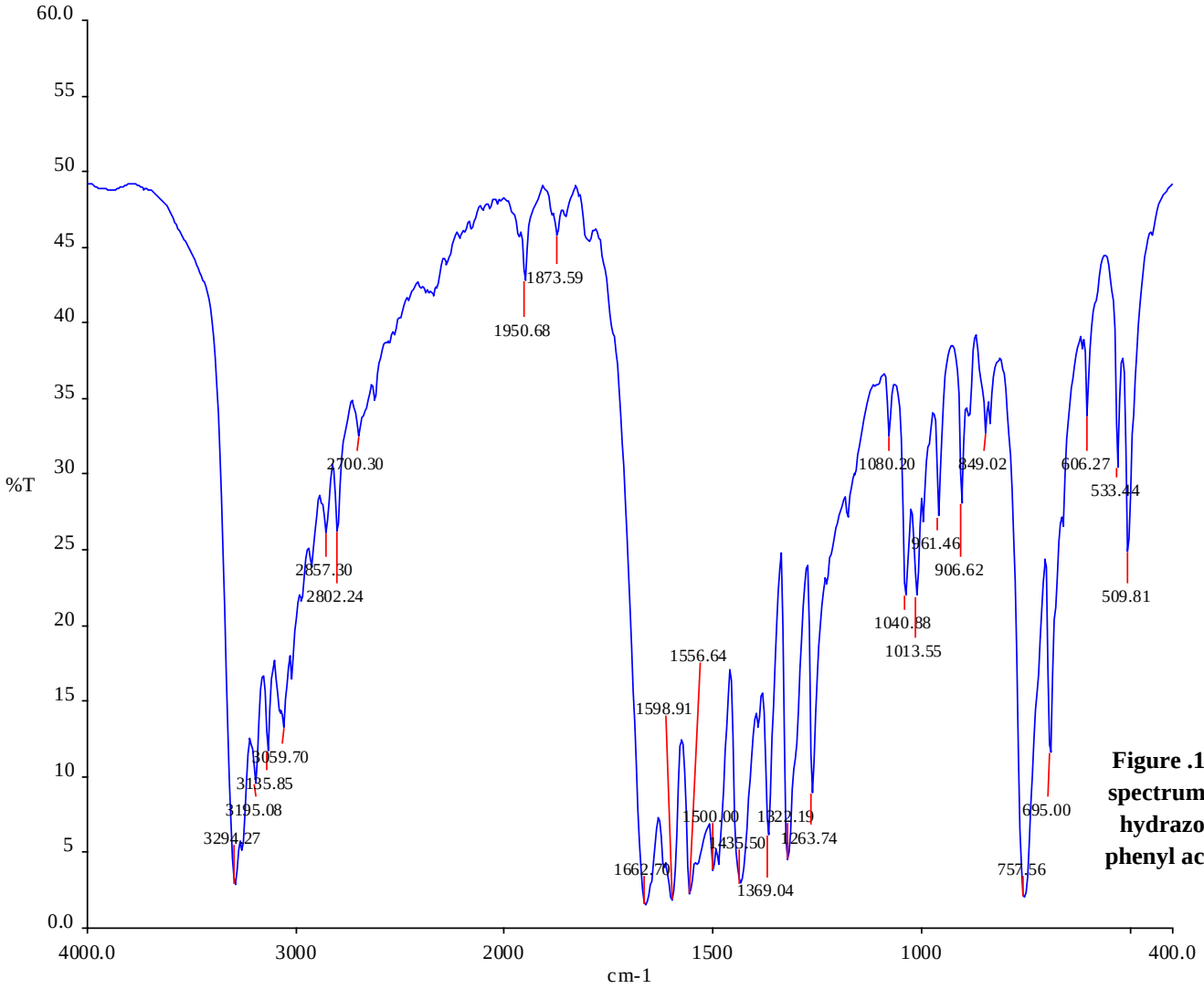



**Figure .1 FT-IR spectrum of phenyl hydrazone of N – phenyl acetamide**

## UV –VISIBLE ANALYSIS

UV-Visible spectral analysis is an important tool to determine the optical property and transparency of the grown crystals. The UV visible spectrum of phenyl hydrazone of N-phenyl acetamide crystal was recorded in LAMBDA 25 spectra meter in the range of 200-900 nm. The recorded UV-Visible spectrum shown in the figure.2.The characteristic absorption of PHPA is found at 200-300 nm. Two sharp peak is seen at 223.76 and 261.99 nm. There is no absorption between 300-900nm. The application oriented properties of harvested crystal is evidenced by the highly transparent nature of crystal .

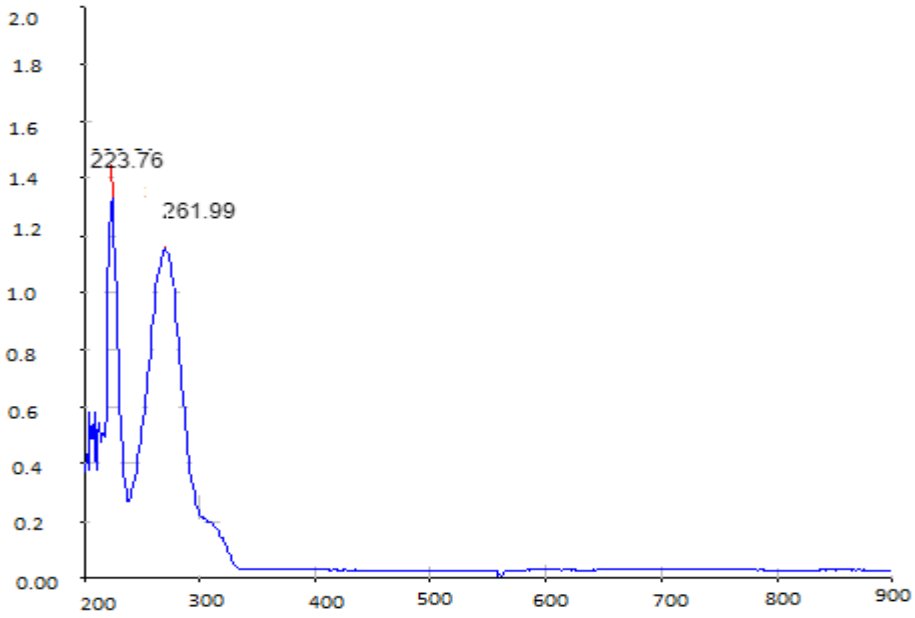



**Figure:2. UV-Visible spectrum of phenyl hydrazone of N –phenyl acetamide**

## BAND GAP ENERGY CALCULATION

The Band gap is the real application to decide the electrical conductivity of solid. The UV-Visible spectrum wavelength of grown crystal of phenyl hydrazone of N –phenyl acetamide was observed to be 223.76 and 261.99 nm. . The band gap energy of PHPA crystal is assessed from the relationship between absorption coefficient and photon energy.

$$(\alpha h\vartheta) = A(h\vartheta - Eg)n$$

Where A is a constant , Eg is the band gap of the absorption coefficient , $h\vartheta$ is an incident photon energy and n is the directly allowed transition. Figure .3. demonstrate the plot among $(\alpha h\vartheta)^2$ and ev of PHPA crystal. The value of band gap energy for prepared crystal is 4.9 ev. It refer to the energy difference between the top of the valence band and bottom of the conducting band in insulator and semi conductor.

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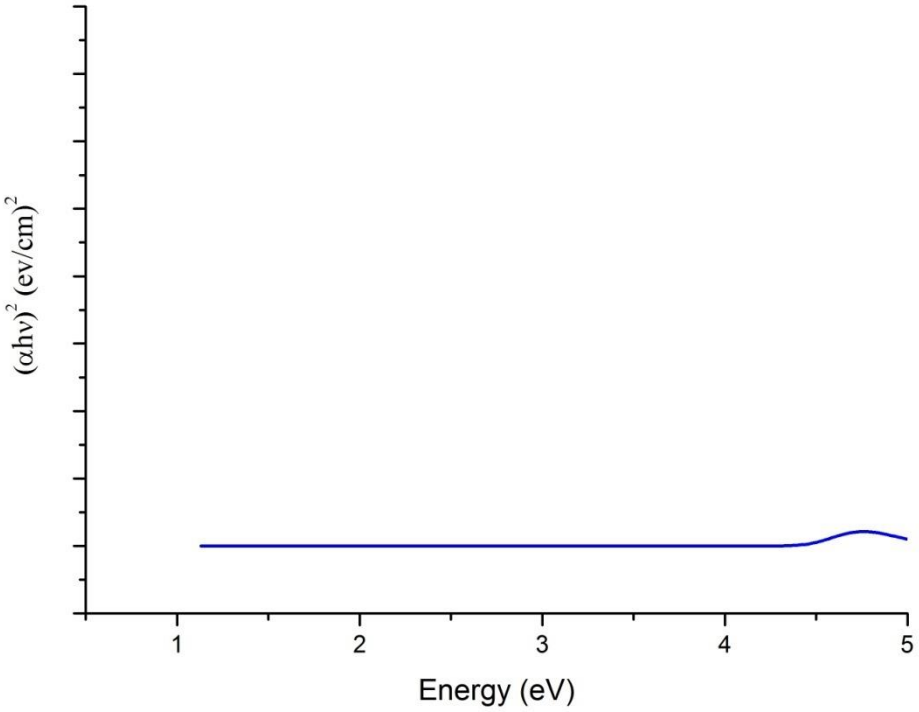


**Figure:3. Band gap energy of phenyl hydrazone** of **N –phenyl acetamide.**

## NMR SPECTRAL ANALYSIS

The $H^1$NMR spectral analysis was carried out on the BRUKER AV300 .The range of PHPA was showed up in figure.4. The peak observed at 2.507-2.512 ppm are due to the presence of C-NH proton. The multiplet at observed between 6.993-7.308ppm affirms the aromatic group(16) . The peak at 7.589ppm is seen at aromatic N-H proton. A singlet at 9.951ppm asserts the presence of $NH_2$ group.

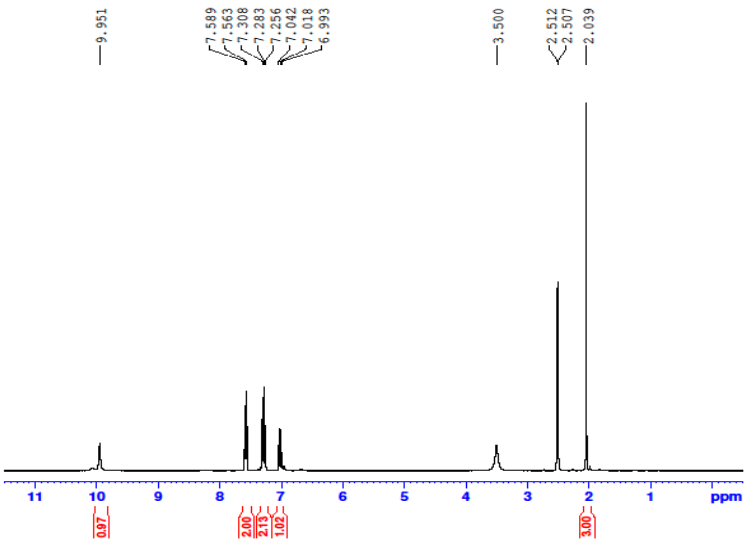


**Figure : 4. $H^1$ NMR Spectrum of phenyl hydrazone of N –phenyl acetamide.**

## X-RAY DIFFRACTION STUDIES

Powder X-Ray diffraction is a well established technique to determine crystalline order in three dimension solid. The XRD pattern of phenyl hydrazone of N –phenyl acetamide was decided by utilizing BRUKER D8 advanced power diffractometer with cu kα radiation(1.5418A$^0$).In the range 20-80 degree examined at a rate of 1$^0$/min .The recorded range for grown crystal is shown in Figure.5.The strong and sharp peak is absorbed(17) .It confirm the good crystalline nature of harvested crystal.

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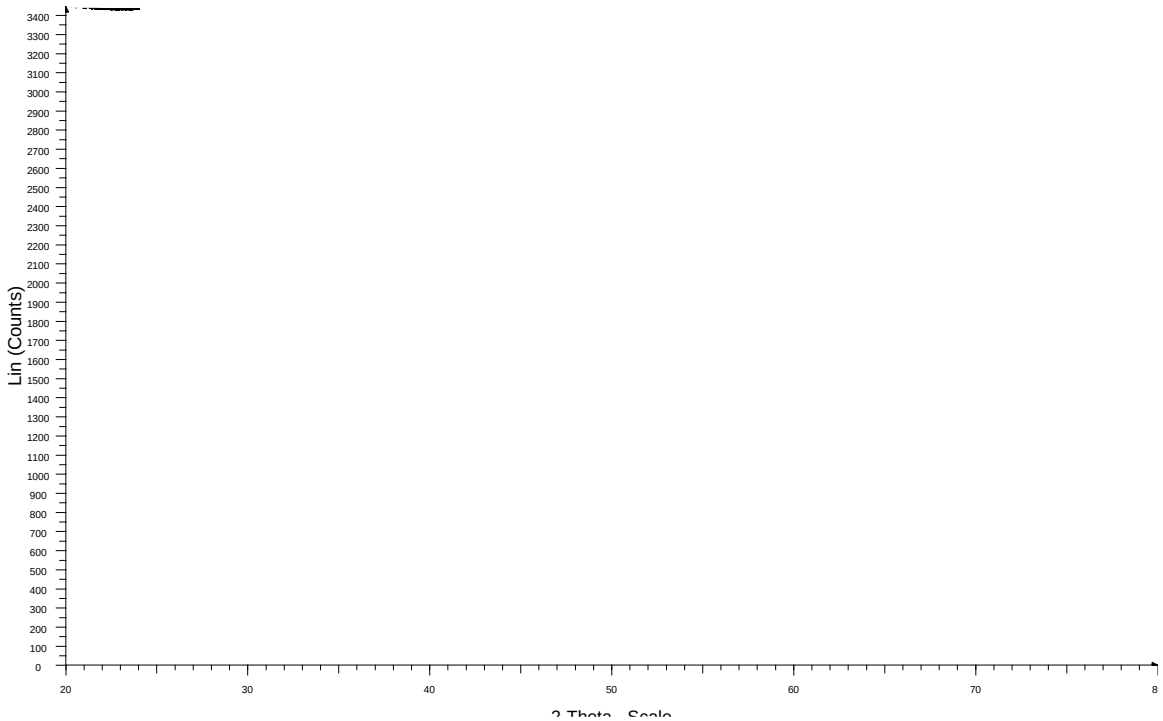


**Figure : 5. X-ray diffraction pattern of phenylhydrazone of N –phenyl acetamid**

## THERMAL ANALYSIS

The thermogram of Phenyl hydrazone of N –phenyl acetamide was recorded by utilizing SDTQ 600V 20.9 BUILD 20 instrument between the temperature 0$^o$C to 350$^o$C at a heating rate of 10$^o$C/minute under nitrogen atmosphere. The thermogram is appeared in figure .6. The sample give the data about the thermal properties of grown crystal. The Phenyl hydrazone of N –phenyl acetamide was weighing 4.5840 mg is taken to the estimation. The DTA curve demonstrates the two sharp endothermic peak at 112.5$^o$C and 230$^o$C(18). The two sharp peak show its melting point. In DGA weight loss started around 233.74$^o$C.Thermal investigation clearly show the crystals having thermal stability and crystalline nature .

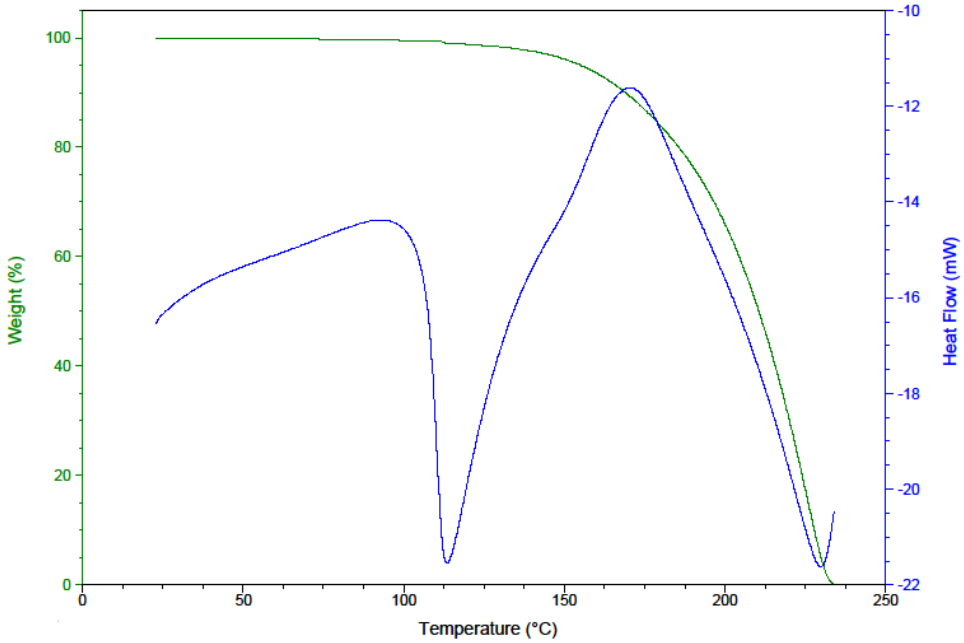


**Figure : 6.Thermogram of phenyl hydrazone of N –Phenyl acetamide**

## CONCLUSION

Good quality crystals of PHPA were grown successfully for the first time by the slow evaporation solution growth method using methanol as a solvent. From the powder X-ray diffraction pattern confirms the purity and cystallinity of the harvested crystal. From the FT-IR and proton NMR spectral assignments, the presence of functional groups in the grown crystal has been confirmed. . The thermal behaviour of the grown crystal was analyzed by TGA and DSC studies and the thermal stability of the material was determined. Optical properties and transparent nature of crystal is revealed the UV-Visible spectral studies. The application oriented properties of grown crystals were evidenced by band gap analysis, high transparent range in the UV-Visible spectrum and TGA and DSC studies.

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