

PREPARATION, GROWTH, SPECTRAL, THERMAL AND BAND GAP STUDIES ON THIOSEMICARBAZONE OF 4-HYDROXY-N – PHENYL ACETAMIDE (TSCHPA) CRYSTAL.

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INTRODUCTION

Crystal growth is a frontier area of science and technology, which plays a major role in technology of photonics. Rare earth complexes have different properties such as optical, electrical and magnetic. These type of materials used in many field such as photoluminescence, electroluminescence and laser etc. The non linear optical (NLO) molecule materials have great impact on information technology and industrial applications.

Organic non linear optical crystals with aromatic rings have high non linearity, fast response and tailor made flexibility, low mobility, higher laser damage threshold when compared to inorganic materials. Thermal, spectral and XRD studies are important tools in the characterization of various materials(1-18). Here crystal of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide (TSCHPA) has been grown by slow evaporation solution growth technique (SESGT) and the grown crystal were characterized by FT-IR, UV, ¹H NMR, X-ray diffraction (XRD) and TGA-DSC studies. Band gap was also determined to ascertain the application oriented properties of TSCHPA.

EXPERIMENTAL

The semi organic crystal of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide (TSCHPA) is prepared by adopting general procedure(19). To a hot solution of thiosemicarbazide in methanol, a solution of 4-hydroxy-N –phenyl acetamide in methanol was added drop wise during 30 minutes. The mixture was stirred and refluxed for 4 hours. Then it was filtered and the filtrate was concentrated to half the volume. After a slow evaporation of the concentrate at room temperature, crystals were collected by filtration, washed with cold ethanol and then dried. The grown crystal were purified by repeated-recrystallization. These crystals were grown by slow evaporation solution growth technique using methanol as a solvent. The harvested crystals are shown in Figure 1.

REACTION

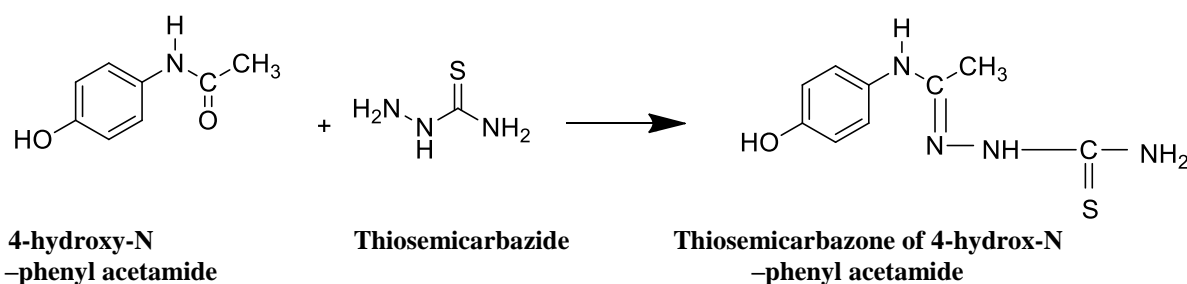




Figure :1. The harvested crystal of thiosemicarbazone of 4-hydroxy-n –phenyl acetamide

RESULT AND DISCUSSION

FT-IR SPECTRAL STUDIES

The infra red spectrum is used to understand the chemical bonding and it provides useful information about the molecular structure of compounds. Fourier transform infra red (FT-IR) spectrum of TSCHPA was recorded using PERKIN ELMER spectrum 1 spectrometer between 400cm^{-1} and 4000cm^{-1} . The spectrum of thiosemicarbazone of 4-hydroxy-N –Phenyl acetamide is shown in figure 2. The peak shows at 1611.35cm^{-1} is corresponding to imine group $\text{C}=\text{N}$. It confirms the bond between ketone and hydrazide(27). The peak at 1107.71cm^{-1} shows $\text{C}=\text{S}$ stretching vibration. The peak at 3325.07cm^{-1} shows Phenyl hydroxide. The peak 1327.16cm^{-1} shows phenyl nitrogen.

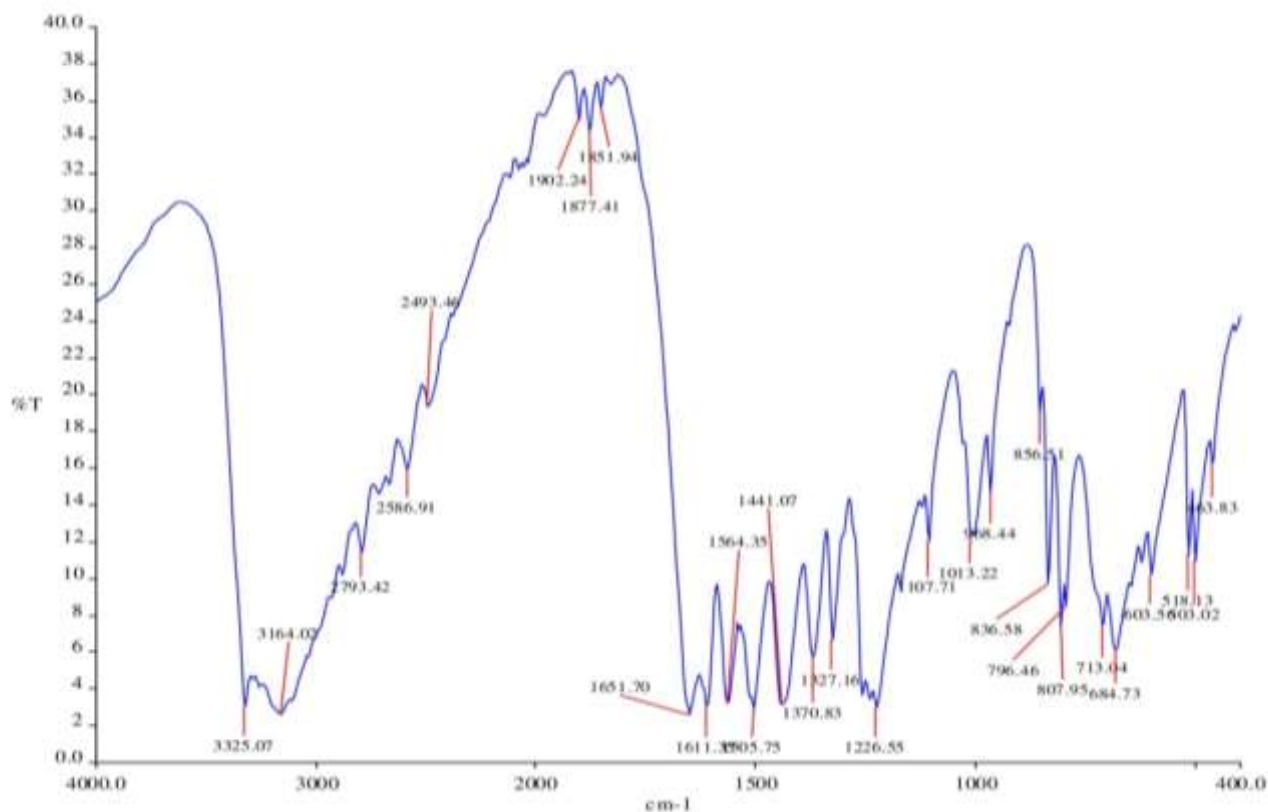


Figure .2 FT-IR spectrum of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide

UV –VISIBLE ANALYSIS

The UV Visible spectrum of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide(TSCHPA) were recorded using Lambda 25 spectrometer . The UV visible spectrum of TSCHPA is shown in figure 3. The characteristic absorption of TSCHPA crystal is found at 200nm to 350nm. The two sharp peak is observed at 269.47nm and 222.81nm(28).The spectrum shows the highly transparent nature of the TSCHPA.

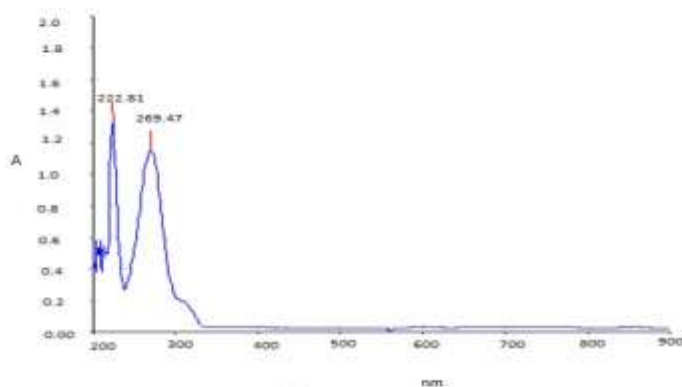


Figure:3. UV-Visible spectrum of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide

BAND GAP ENERGY CALCULATION

For optical device fabrication, the crystal should have high transparency in a considerable range of wavelength. The UV cut-off wavelength of the grown TSCHPA crystal was found to be 269.47nm and 222.81 nm, and it is useful to make them potential material for optical device fabrication. The band gap energy of prepared thiosemicarbazone of 4-hydroxy-N –phenyl acetamide(TSCHPA) crystal is evaluated from the relation between the absorption co-efficient(α) and photon energy ($h\nu$).

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

where $h\nu$ = incident photon energy,

α = absorption coefficient,

E_g = band gap of the material,

A = constant that depends on the electronic transition probability and

n = an exponent that characterizes the type of electronic transition

responsible for the optical absorption process.

For direct allowed transition $n = \frac{1}{2}$, indirect allowed transition $n = 2$.

The figure 4. depicts the extrapolation of linear portion of the curve on $h\nu$ axis gives the direct band gap energy. The value of band gap energy for prepared TSCHPA crystal is 4.5 eV. It refers to the energy difference between the top of the valence band and the bottom of the conduction band in insulators and semiconductors.

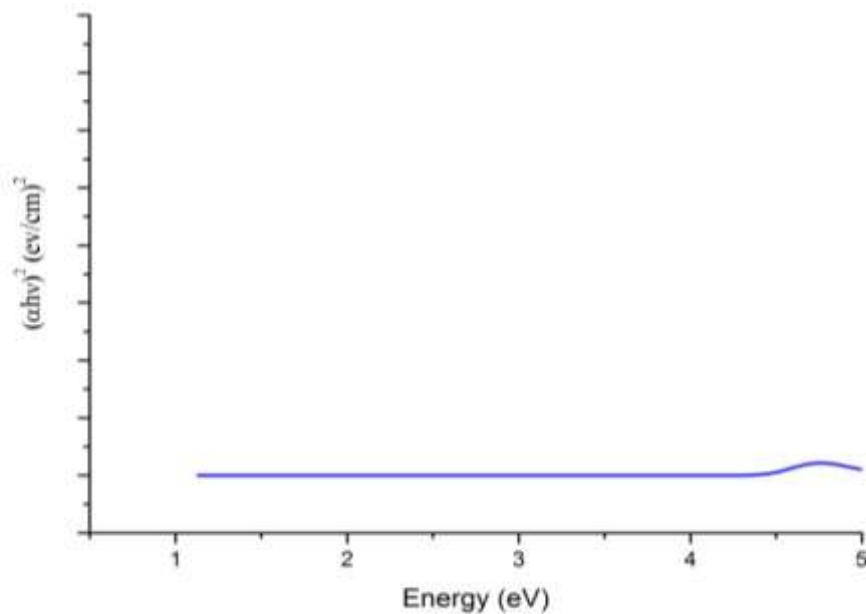


Figure:4. Band gap energy of thiosemicarbazone of 4-hydroxy-N-phenyl acetamide.

NMR SPECTRAL ANALYSIS

H^1 NMR spectral analysis was carried out on the thiosemicarbazone of 4-hydroxy-N-phenyl acetamide (TSCHPA) crystal in BRUKER-AV 300. The proton NMR spectrum of TSCHPA was shown in figure 5. The peak observed at 1.977 ppm confirm the presence of methyl group(28). 7.350-7.321 ppm peak was observed by aromatic group. The multiplet at 6.685 -6.656 ppm confirms the phenyl hydroxide (29). The peak observed at 3.367 ppm indicate the presence of hetero sulphur atom (N-C=S). The peak observed at 9.657 ppm shows the presence of NH_2 group. The peak 9.144 ppm confirms the aromatic NH proton. The peak observed at 2.510-2.506 ppm shows the presence of C-NH proton.

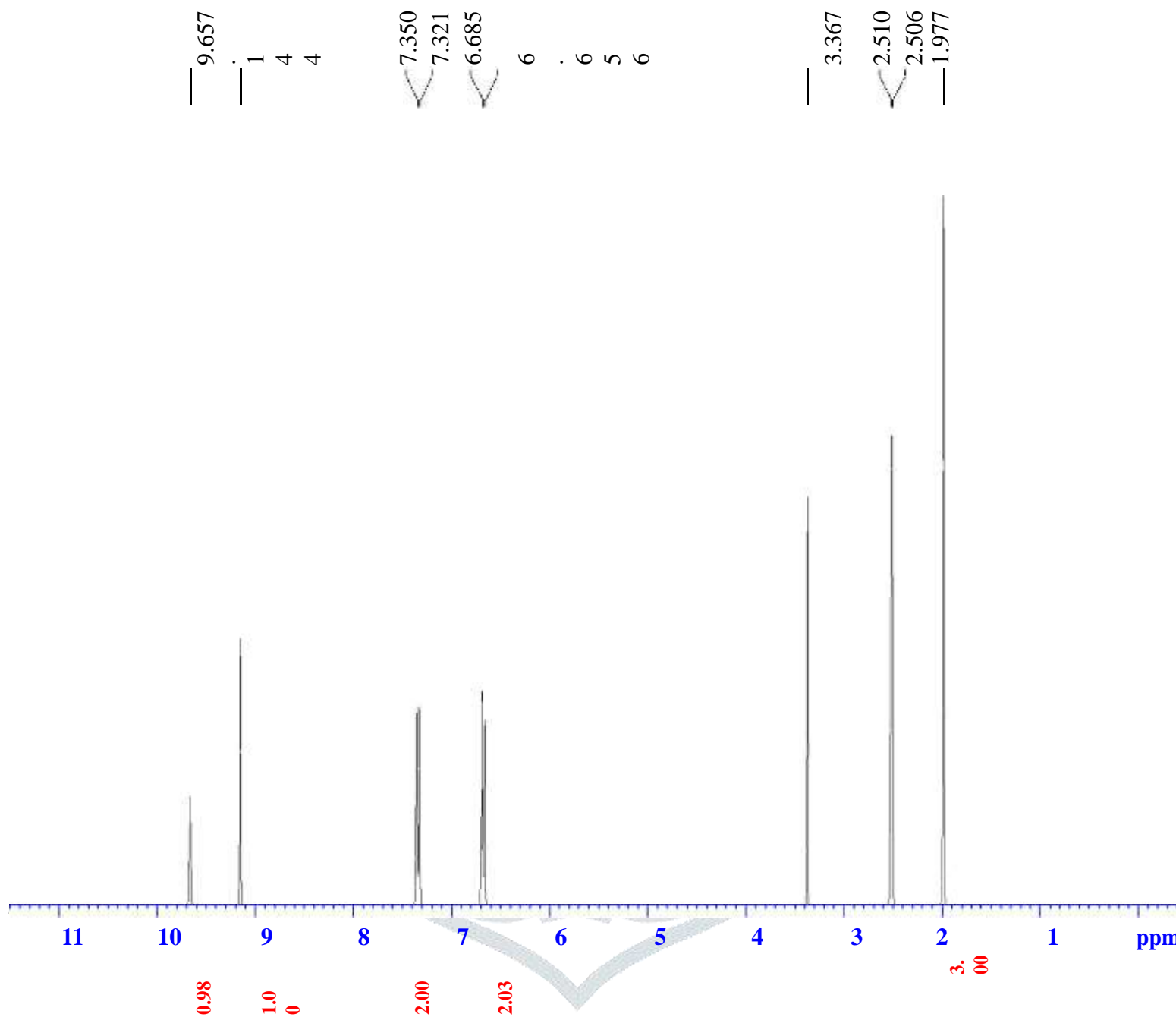


Figure : ¹H NMR Spectrum of thiosemicarbazone of 4-hydroxy-N-phenyl acetamide.

X-RAY DIFFRACTION STUDIES

The X-Ray diffraction studies of the harvested crystal of thiosemicarbazone of 4-hydroxy-N-Phenyl acetamide (TSCHPA) was carried out using BRUKER D8 Advance powder diffractometer with Cu α radiation ($\lambda=1.5418\text{\AA}$). The crystal was scanned at a rate of $1^\circ/\text{min}$ in the range $20-80^\circ$. The diffraction pattern shown the Figure 6. The sharp peaks observed in the XRD pattern confirms the crystalline nature of the harvested crystal which shows the application oriented properties of thiosemicarbazone of 4-hydroxy-N-phenyl acetamide (TSCHPA).

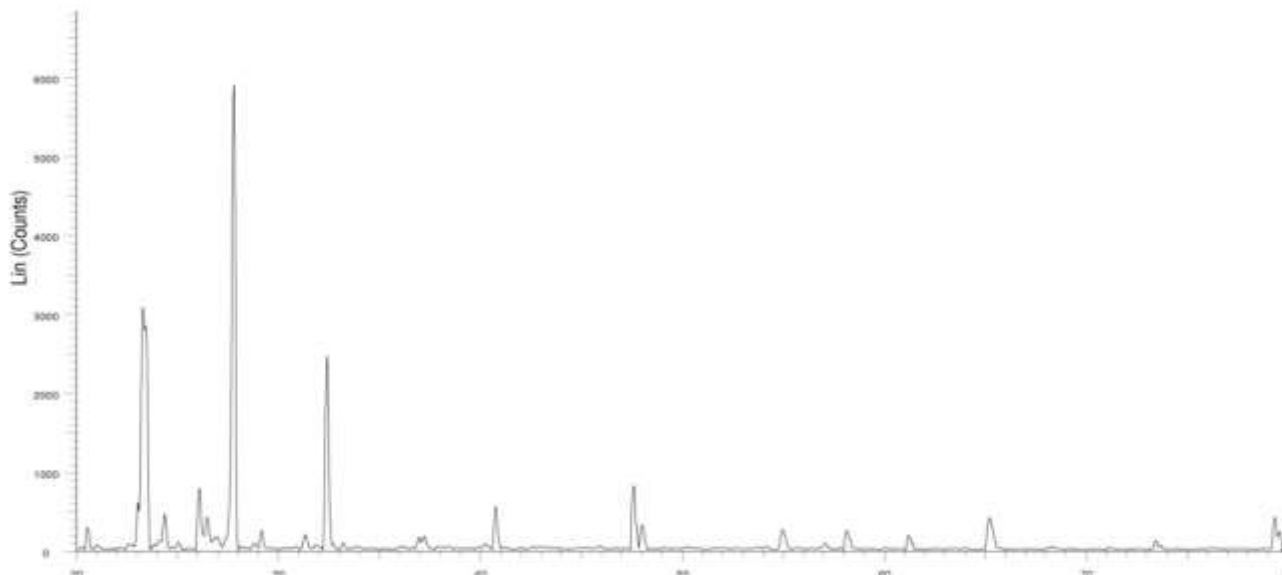


Figure : 6. X-ray diffraction pattern of thiosemicarbazone of 4-hydroxy-N –phenyl acetamide

THERMAL ANALYSIS

Thiosemicarbazone of 4-hydroxy-N –phenyl acetamide(TSCHPA) was analysed using SDTQ 600V 209 BUILD 20 instrument between the temperature 0°C to 500°C at a heating rate of 10°C/min under nitrogen atmosphere. The thermogram is shown in figure 7. It provides information about thermal properties of the material. The TSCPHA sample weighing 4.6810 mg is taken for measurement . The endothermic peak at 175°C show its melting point .The thermogram shows the thermal stability and crystalline nature of the grown crystal(30). The sharpness of the endothermic peak confirm the good degree of crystallinity and purity of the crystal.

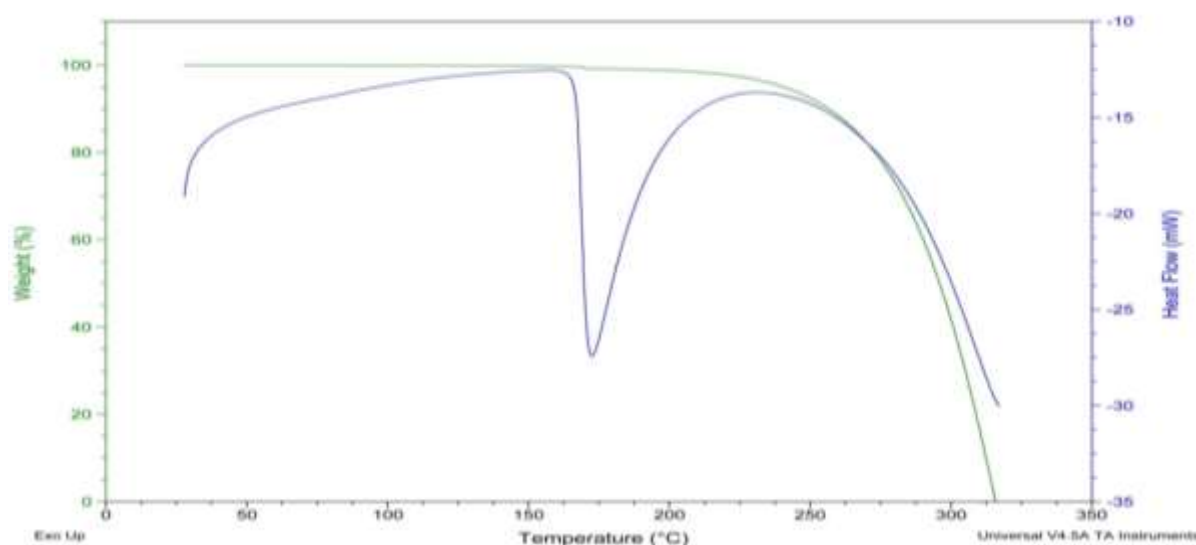


Figure : 7. Thermogram of thiosemicarbazone of 4-hydroxy-N –Phenyl acetamide

CONCLUSION

The semi organic crystal of Thiosemicarbazone of 4-hydroxy-N –phenyl acetamide(TSCHPA) was prepared from 4-hydroxy-N –phenyl acetamide and thiosemicarbazide in methanol solution . The prepared crystal was grown by slow evaporation solution growth technique. The UV-Visible spectrum analysis give evidences that the crystal may found application in optical device fabrication. Band gap energy 4.5 ev predicts the semiconducting properties of the TSCHPA. The FT-IR and NMR spectral studies supports the presence of functional groups and purity. The sharp peaks observed in the XRD and DSC-TGA analysis further confirms the purity , crystalline nature and high thermal stability of the grown crystal. The structure as well as vide transparency in UV-Visible spectrum provide evidences that the grown crystal should have good NLO property and so have application oriented properties.

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REFERENCE

- 1) Sankaranarayanan K, Ramasamy P. 2006. Unidirectional crySTALLIZATION of large diameter benzophenone single crystal from solution at ambient temperature. *J crystgrowth*, (292)405 – 43.
- 2) Arulchakkaravarthi. A, Jayavel. P, santhanaragavan.P, Ramasamy. P. 2002 Growth of organic molecular single crystal tran-stilbence by selective self-seeding from vertical Bridgman technique: *J Cryst Growth* (234) 159 -5.
- 3) Yun – zhang, Yonggangwang, Yunxiache, Jiminezheng. 2007 Growth and properties of two new organic nonlinear optical crystals; Hydroxyethylammonium – l-tartrate monohydrate and Hydroxyethylammonium –o-tartratemonohydrate; *J crystal growth* (299) 120 – 5.
- 4) Vasudevan. G, Anbusrinivasan. P, Madhurambal. G, Mojumdar.S. 2009. Thermal analysis effect of dopants Spectral characterization and growth aspect of KAP crystals. *J Therm Anal Calorim* (96) 99 – 102.
- 5) Anbusrinivasan.P, Madhurambal. G, Mojumdar.SC. 2012. Thermal and spectral properties and induction period, Intrafacia energy and nucleation parameters of solution grown Anthracene: *J Therm Anal Calorim* (108)939-46
- 6) Ramalingam.S, Anbusrinivasan.P, Periandy. S. 2011. FT-IR and FT-Raman Spectrual Investigation, Computed IR – Intensity and Raman activity analysis and frequency estimation analysis on 4-chloro-2-bromoacetophenone was – HF and DFT calculations; *Spectrochimica Acta part A* (78) 826 – 34.
- 7) Mojumdar.SC, Raki.L2006.Preparation, Thermal, spectral and microscopic studies of calcium silicate hydrate poly(acrylic acid) nanocomposite materials; *J. Therm Anal calorim* (85) 99-105.
- 8) Ezhilvizhi. R, Kalainathan. S, Bhavannarayana.G. 2008 . Structural and icro hardness studies of urea and thiourea doped glycine phosphate single crystal; *Cryst Rev Technol* (43) 778 -82.
- 9) Mojumdar. SC. 2001. Processing moisture resistance and thermal analysis of MDF material; *J Therm Anal calorim*. (64) 1133 -9.
- 10) Madhurambal. G, Ramasamy. P, Anbusrinivasan.P, Vasudevan.G, Kavitha.S, Mojumdar.SC. 2008. Growth and characterization studies of 2 – bromo-4@ - Chloro-acetophenone (BCAP) crystals. *J Therm Anal calorim* (94)59-62

- 11) Mojumdar.SC. 2005 . Thermal properties, environmental deterioration and application of macro-defect-free cements; *Res J chem environ* (9) 23-7.
- 12) Madhurambal. G, Mojumdar.SC, Hariharan.S, Ramasamy.P. 2004. TG,DTC,FT_IR and Raman spectral analysis of Zn/Mg, Ammoniumsulphate mixed crystals; *J. Therm Anal Calorim* (78) 125 – 33.
- 13) Selvaraju.K, Valluvan.R, Kumararaman.S.2006 .A new metal organic potassium thiourea chloride single crystal; *Mat Lett* (440) 574 -81.
- 14) Sawant.SY, Verenkar. VMS, Mojumdar.SC 2007.Preparation, Thermal,XRD, chemical and FT-IR spectral analysis of NiMn₂O₄ nanoparticles and respective precursor; *J Therm Anal Calorim* (90) 669 – 72.
- 15) Prob. R.A, Khan.SZ, Mojumdar.SC, Verenkar VMS. 2006. Synthesis, TG,SDC and infra-red spectral study of NiMn₂(C₂H₄O₄)₃·6N₂H₄-A precursor for NiMn₂O₄ nanoparticles; *J Therm Anal Calorim* (86)605 -8.
- 16) Mojumdar.SC, Varshney.KG, Agarwal.A. 2006 . Hybrid Fibrous ion exchange materials past-preparation and failure; *Res J Chem Environ.* (10) 89-103.
- 17) Doval.M, Palou.M, Mojumdar.SC. Pyridine based cerium (IV) phosphate hybrid fibrous ion exchanger synthesis characterization and thermal behavior; *J. Therm Anal Calorim*
- 18) Varshney.G, Agarwal.A, Mojumdar.SC. 2007.Pyridine based cerium (IV) Phosphate hybrid fibrous ion exchanger synthesis characterization and thermal behaviour: *J Therm Anal Calorim* (90)731-4
- 19) Santhakumari .R,Ramamoorthy.K. 2011.Structural thermal optical characterization of an NLO material-Benzaldehyde thiosemicarbazone of monohydrate single crystals 3part A:(78)653-659.
- 20) Mojumdar .SC., Sain.M, Prasad RC, Sun.L. Venart.JES. 2007 . Selected thermoanalytical methods and their application from medicine to construction. *J Therm Anal Calorim* (60) 653 – 62.
- 21) Mojumdar .SC, Simon.P, Krutosikova.A, 2009 [1] Benzofural3,2-cjpyridine synthesis and coordination reactions; *J Therm Anal Calorim.* (96) 103 – 9.
- 22) Mojundar.SC, Miklovic.J, Krutosikova.A, Valigura.D, Stewart.J.M. 2005. Europyridine- Ni(II) complexes – Synthesis, Thermal and spectral characterization. *J Therm Anal Calorim.* (81) 211 – 5.
- 23) Mojundar.SC. 2001 Thermoanalytical and IR spectroscopy investigation of Mg (II) complexes with heterocyclic ligands. *J Therm Anal Calorim.* (64) 629 – 36.
- 24) Narayanamoolaya.B. Dharmaprakash.S.M 2006.Synthesis , growth and characterization of nonlinear optical crystal L –tyrosine hydro bromide. *Crystal growth* (290) 498 – 503.
- 25) Jayalakshmi.D, Kumar.J .2006.Growth and characterization of bithiourea Zinc acetate ;*Cryst Res Technol*,(41)37-40.
- 26) Mojundar.SC, Mazanec.K ,Drabik.M. 2006. Macro Defect Free(MDF) Cements ; synthesis , thermal chemical, SEM and Magnetometric study and moisture resistance ; . *J Therm Anal Calorim* (83) 135-9.
- 27) William Kemp, 1991.Organic spectroscopy –Third edition .
- 28) Kalsi.P, 1987.Spectroscopy of organic compounds , New Delhi, Wiley Eastern.
- 29) Rao CNR. 1975. Ultraviolet and visible Spectroscopy, Chemical applications,New York Plenum Press.
- 30) Dyer JR. 1987.Application of absorption spectroscopy of organic compounds.New Delhi Prentice-hall of India.