

PREPARATION, GROWTH, SPECTRAL, THERMAL AND BAND GAP STUDIES ON SEMICARBAZONE OF N –PHENYL ACETAMIDE (SCPA) CRYSTAL.

¹ S.Sasikala, ² P.Anbusrinivasan

¹ Department of Chemistry,

¹ Vivekananda College of Arts and Science for women, Sirkali, Tamil Nadu, India.

Abstract

Semicarbazone of –N-phenyl acetamide has been prepared and grown successfully by slow evaporation solution growth technique. The crystal was collected and subjected to various analysis. The functional group were identified using FT-IR spectroscopy. The optical transparency of grown crystal was recorded by UV-visible spectroscopy. The SCPA crystals were subjected to thermo gravimetric and differential scanning calorimetry analysis. The crystallinity of the sample was ascertained by the powder XRD method. The arrangement of protons and nature of protons were identified by NMR spectral analysis. Band gap was determined by the application oriented properties of grown crystal.

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

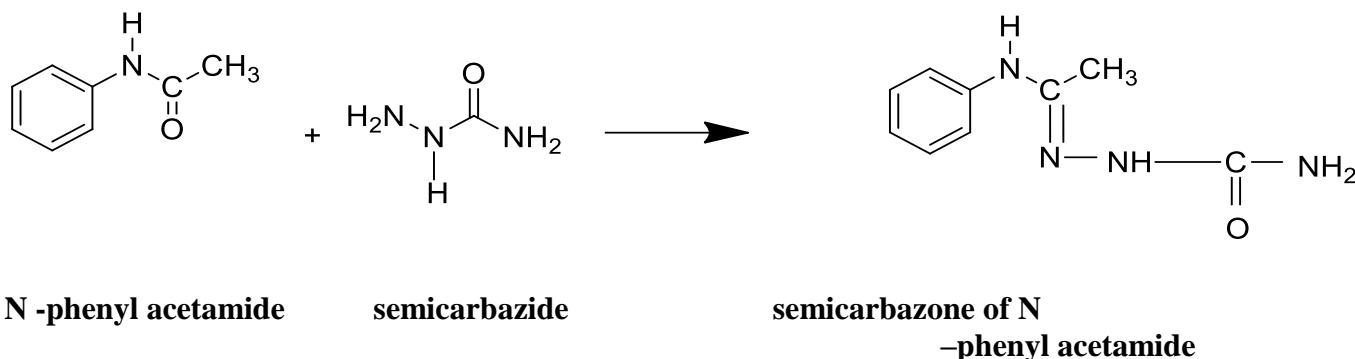
INTRODUCTION

Crystal growth is a major and fundamental part of material science and engineering. Organic non linear optical material have attracted much attention due to their potential applications in telecommunication and optoelectronic materials. Non linear optical properties of several inorganic crystals have been widely investigated. Generally non linear optical crystals possess shorter wave length, optical quality, sufficiently larger non linear coefficient, structural, thermal, spectral and optical studies are essential tools in the characterization of various material. Here crystal of semicarbazone of –N-phenyl acetamide have been synthesis and grown by slow evaporation solution growth technique (SESGT). The harvested crystal was subjected to characterization like 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 SCPA.

EXPERIMENTAL

The semi organic crystal of Semicarbazone of N –phenyl acetamide (SCPA) is prepared by adopting general procedure(). To a hot solution of Semicarbazide 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. 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.

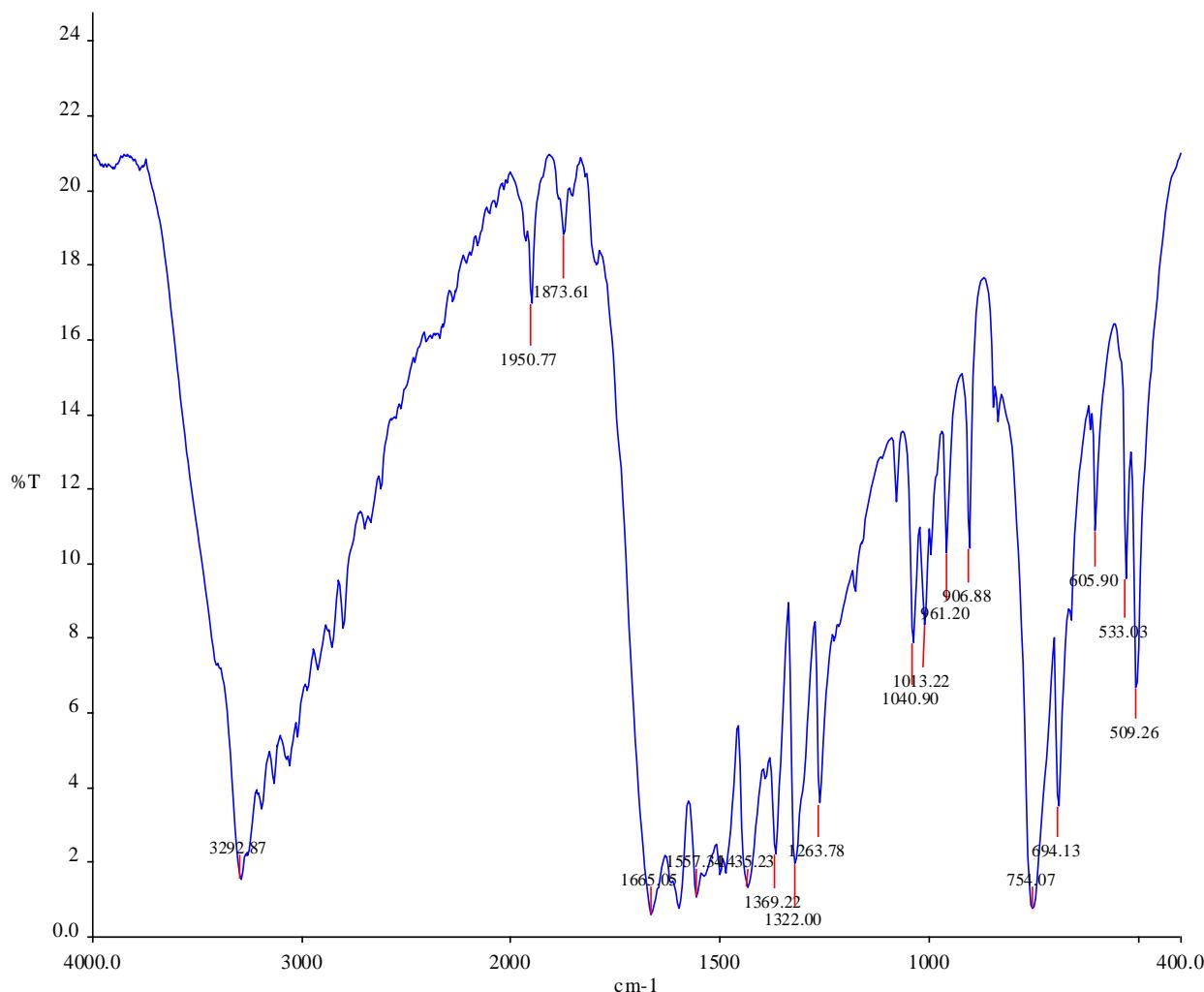
REACTION



RESULT AND DISCUSSION

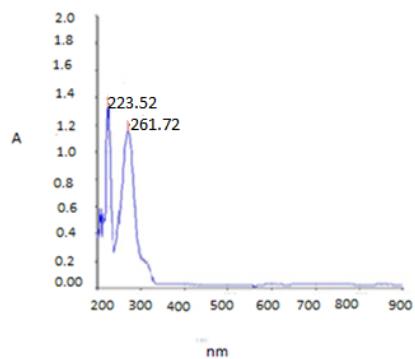
FT-IR SPECTRAL STUDIES

The spectrum of Semicarbazone of N -phenyl acetamide was recorded in the range of 400-4000 cm^{-1} at room temperature using the PERKIN ELMER spectrum one FT-IR spectroscopy. The presence of functional groups of semicarbazone of N -phenyl acetamide crystal were identified from the spectrum shown in figure.2. The absorption peak shows at 3292.87 cm^{-1} is due to N-H stretching vibration. The peak at 1665.05 cm^{-1} corresponding to C=O stretching vibration of carbonyl group. The peak at 1557.34 cm^{-1} is confirm the C=N immine group. The presence of phenyl ring is affirmed by the peak at 1435.23 cm^{-1} .



UV –VISIBLE ANALYSIS

The UV-Visible spectrum of SCPA crystal were recorded in the range of 200-900 nm using LAMBDA 25 spectra meter. UV-Visible spectrum of Semicarbazone of N –phenyl acetamide is shown in figure.3. The maximum wavelength lying within the region , the wide transparency window indicates material of NLO properties and find the application in electronic appliances. The two sharp absorption peak is observed at 261.72 nm and 223.52 nm (). The grown crystal of SCPA spectrum is support the transparent nature of materials.

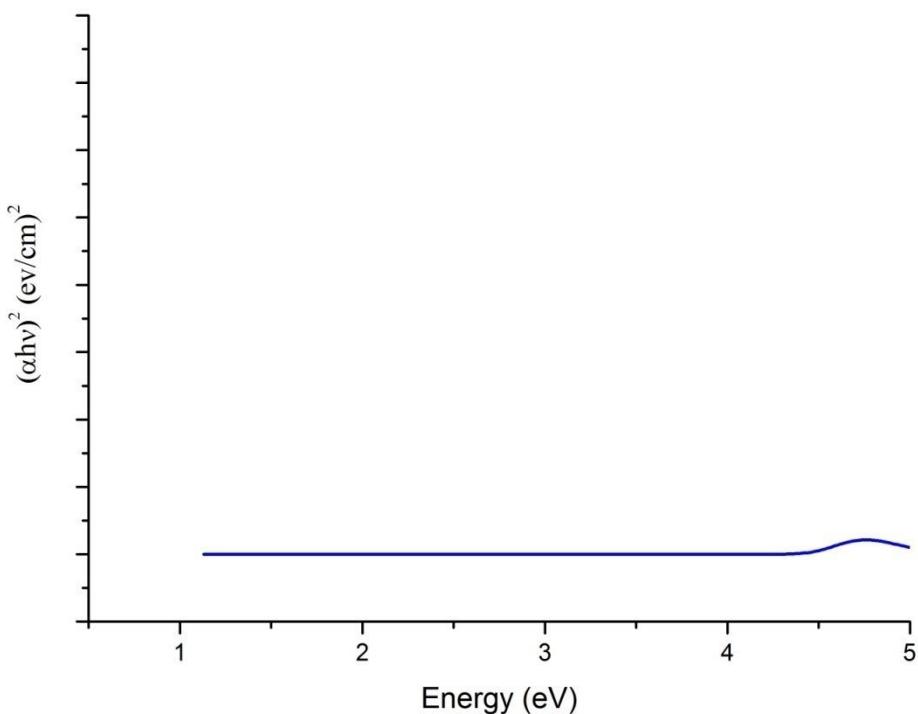


BAND GAP ENERGY CALCULATION

The Band gap is the major application to determine the electrical conductivity of solid. The UV-Visible spectrum wavelength of grown crystal of Semicarbazone of N –phenyl acetamide was found to be 261.75 and 223.35 nm . The band gap energy of SCPA crystal is evaluated from the relationship between absorption coefficient and photon energy.

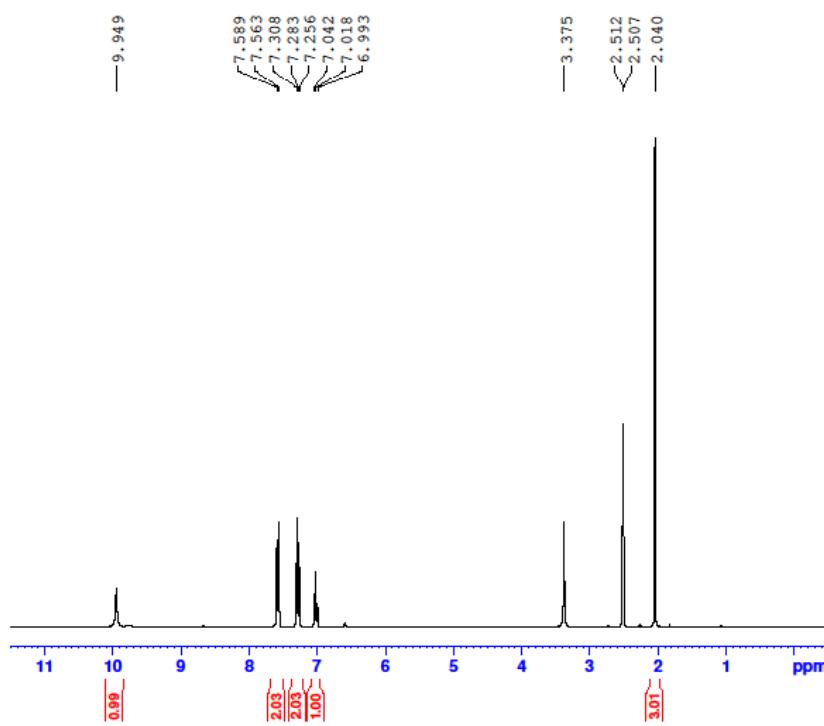
$$(\alpha h\nu) = A(h\nu - E_g)n$$

Where A is a constant , Eg is the band gap of the absorption coefficient , $h\nu$ is an incident photon energy and n is the directly allowed transition. Figure .4. show the plot between $(\alpha h\nu)^2$ and ev of SCPA 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.



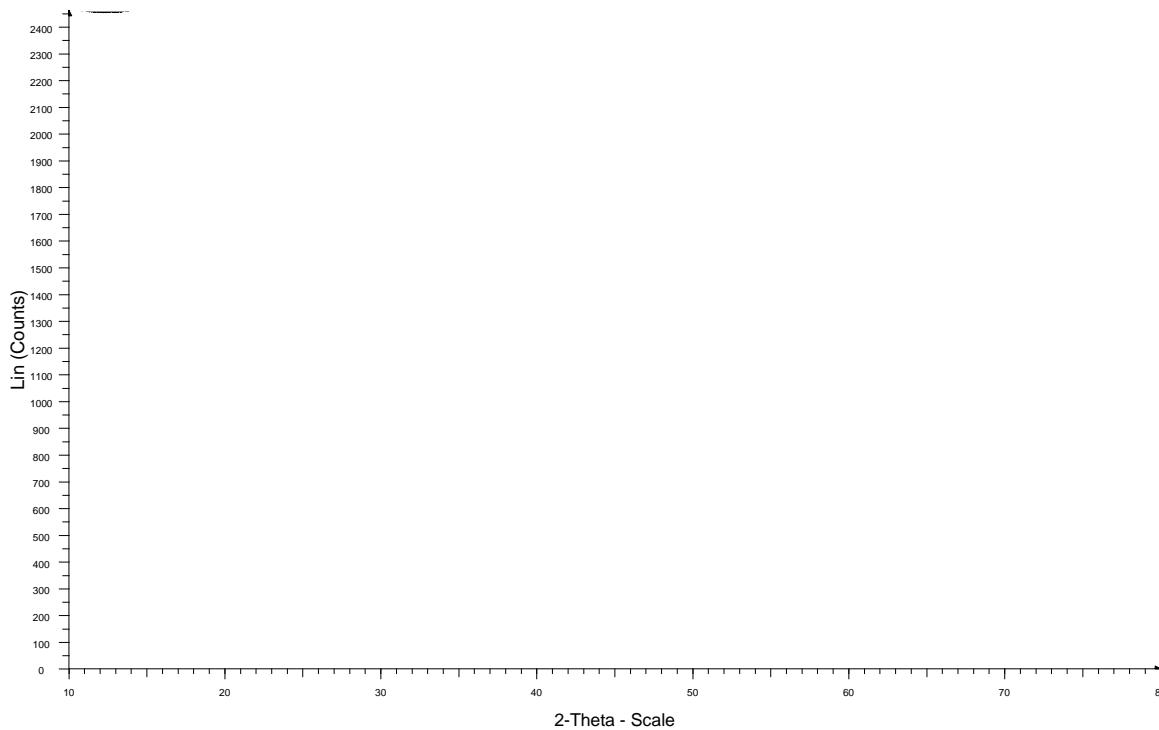
NMR SPECTRAL ANALYSIS

The NMR spectral analysis is the very useful method to determine the molecular structure and chemical environment of the crystal .H ¹ NMR spectral analysis of SCPA was carried out in BRUKER AV 300. The H ¹ NMR range of Semicarbazone of N –phenyl acetamide was appeared in figure.5. The peak observed 2.040ppm is confirm the presence of methyl group. The signal at 2.507-2.512 ppm due to the presence of C-NH proton. The multiplet at 6.993ppm revealed an aromatic group. The peak at 9.948 ppm confirm the aromatic NH proton.



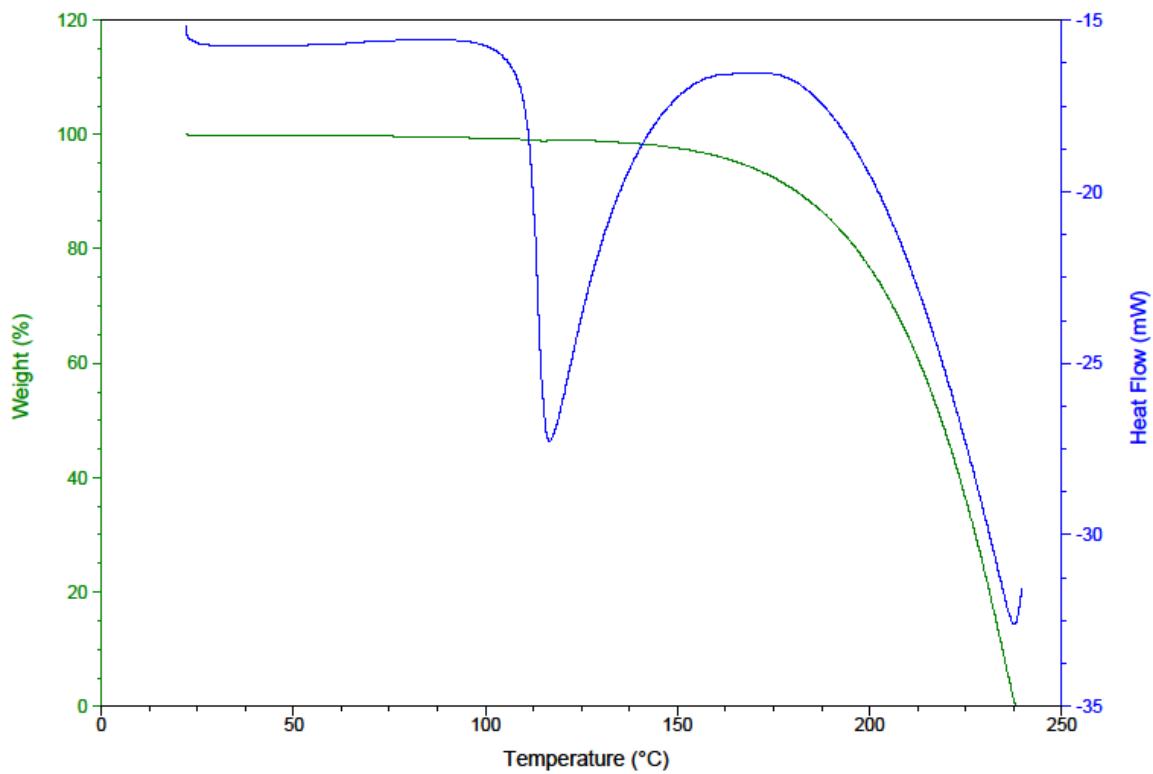
X-RAY DIFFRACTION STUDIES

The grown crystal of semicarbazone of N –phenyl acetamide was subjected to powder X-ray diffraction studies. The sample of harvested grown crystal was carried out by using BRUKER D8 advance powder diffractometer with cu $\text{k}\alpha$ radiation ($\lambda=1.5418\text{\AA}$) at a rate of 1°/min in the range 20-80. The diffraction pattern show the figure .6. The sharp peak gives clear idea about the good crystallinity observe nature of grown crystal. crystal of semicarbazone of N –phenyl acetamide is show the application oriented properties of crystal.



THERMAL ANALYSIS

Thermogram gives the information about decomposition pattern and weight loss of the sample. DTA curve gives information regarding the phase transformation, water crystallization and melting point of the compound. DSC/DTA curve of semicarbazone of N –phenyl acetamide was recorded by utilizing SDTQ 600V 20.9 BUILD 20 instrument between the temperature 0°C to 350°C at a heating rate of 10°C/minute under nitrogen atmosphere. The thermogram is shown in figure .7. Two sharp peak is appeared at 110°C and 240°C. It shows the melting point of the SCPA crystal. The curve indicate that material is fully decomposed . The peak sharpness is refer to the good degree of crystallinity of grown crystal.provide the information about the thermal properties of grown crystal. In thermo gravimetric analysis shows the weight loss at 238.09°C



ANTIBACTERIAL ACTIVITY

In vitro antimicrobial assessment of semicarbazone of N –phenylacetamide compound had been carried out towards 8 bacterial strains, which contain 4 Gram-positive bacteria (*Bacillus subtilis*, *Micrococcus luteus*, *Staphylococcus aureus* and *Streptococcus mutans*) and 4 Gram-negative bacteria (*Escherichia coli*, *Klebsiella pneumoniae*, *Proteus vulgaris* and *Shigella flexneri*). The chosen nonlinear optical compounds have been screened for antimicrobial studies the usage of the Disc Diffusion Assay (Ericsson and Sherris, 1971). The Petri plates (nine cm dia.) were pre-seeded with 10 ml of Muller Hinton Agar and stock tradition became streaked thoroughly to make certain uniform distribution of the micro-organisms. Sterile paper discs (5 mm diameter) containing a 100 μ g/ml of compounds screened for antibacterial activity

Simultaneously, paper discs dipped with pure respective solvents have been used as advantageous controls. The Petri plates were then pre-incubated for 3 h at five°C to allow most diffusion of the compounds into the media. Cefalexin and Gentamycine (10 μ g/ml) was used as terrible manipulate in opposition to gram advantageous and gram bad bacteria respectively (Hailu Tadeg et. al., 2005; Nancy et al., 2000; Zaidan et al., 2005) had been used as reference requirements. After the incubated length the area of inhibition (diameter) become measured with a scale and the information were tabulated.

Table: Antibacterial activity data of semicarbazone of N –phenylacetamide compound (10 μ g) tested against selected human pathogenic bacteria.

Microorganism tested		Zone of inhibition(mm) diameter	
		Nonlinear optical compound	
		PC*	COM5
Gram positive	<i>Bacillus subtilis</i>	10	31
	<i>Micrococcus luteus</i>	12	30
	<i>Staphylococcus aureus</i>	11	27
	<i>Streptococcus mutans</i>	-	-
Gram negative	<i>Escherichia coli</i>	8	26
	<i>Klebsiella pneumonia</i>	9	29
	<i>Proteus vulgaris</i>	13	28
	<i>Shigella flexnari</i>	11	31

PC*= Positive Control Cefalexin and Gentamycine 10 μ g

COM5 = semicarbazone of N –phenylacetamide

Determination of Minimal Inhibitory Concentration (MIC) and minimal bactericidal concentration (MBC)

A modified agar microdilution method of Lorian, (1996) was used to determine the MIC of semicarbazone of N –phenylacetamide. The test tubes contained serially diluted from 1500 μ g/ml to 1.46 μ g/ml were inoculated with the selected bacterial strain suspension and the test tubes were incubated at 35°C for 18 h. Observations were performed in triplicates and results were expressed as the lowest concentration of compounds that produced a complete suppression of colony growth.

Table:Minimum Inhibitory Concentrations (MIC) data of semicarbazone of N –phenylacetamide tested against selected human pathogenic bacteria.

Microorganism tested		Nonlinear optical compounds	
		PC*	COM5
Gram positive	<i>Bacillus subtilis</i>	1.46	187.5
	<i>Micrococcus luteus</i>	5.89	187.5
	<i>Staphylococcus aureus</i>	5.89	46.87
	<i>Streptococcus mutans</i>	2.23	93.75
Gram negative	<i>Escherichia coli</i>	5.87	46.87
	<i>Klebsiella pneumonia</i>	23.4	187.5
	<i>Proteus vulgaris</i>	11.7	93.75
	<i>Shigella flexneri</i>	11.7	187.5

PC*= Positive Control Cefalexin and Gentamycine 10 μ g

COM5 = semicarbazone of N –phenylacetamide

CONCLUSION

The grown crystal of semicarbazone of N –phenyl acetamide was successfully prepared by using semicarbazide and N –phenyl acetamide using methanol as a solvent and the sample was grown by slow evaporation solutions growth technique. The FT-IR spectrum revealed all the characteristics bonds corresponding to different molecular group present in the sample. UV-Vsible spectrum was support the transparency nature of grown crystal. H¹ NMR spectrum provides the structural information of grown crystal. Thermal analysis confirms the thermal stability of SCPA crystal. The purity and crystalline nature is ascertained by powder XRD studies.

ACKNOWLEDGEMENT

The author S.Sasikala gratefully acknowledge the Chairman, Secretary and Principal of Vivekananda College of Arts and Science for women, Sirkali, Tamil Nadu, for their constant encouragement and the Chairman, Secretary and Principal of A.V.C College(Autonomous), Mannampandal, Mayiladuthurai, Tamil Nadu, for providing facilities and also CARISM ,SASTRA University, Thanjavur for providing analytical support.

REFERENCES

1. Boomadevi S and Dhanasekaran RD (2004) Synthesis, crystal growth and characterization of L-pyrrolidone-2-carboxylic acid (L-PCA) crystals. *J. Cryst. Growth.* 261,70-76.
2. Bruice PY (2002) Organic chemistry, Pearson education (Singapore) Pte. Ltd., *first Indian reprint*,Delhi. 534–565.
3. Chemla DS and Zyss J (1988) Non-linear optical properties of organic molecule and crystals. 1 & 2, *Academic Press, NY*.
4. Elmali A, Karaka A and Unver H (2005) Non-linear optical properties of bis[(pbromophenylsalicylaldiminato) chloro] iron(III) and its ligand N-(4 bromo) salicylaldimine. *Chem. Phys.* 309, 251.
5. Frazier CC, Cockerham MP, Chauchard EA and Lee CH (1987) Second-harmonic generation in aromatic organic compounds. *J. Opt. Soc. Am. B.* 4, 1899-1903.
6. Kanis DR, Ratner MA and Marks TJ (1994) Design and construction of molecular assemblies with large second-order optical nonlinearities. *Quantum chemical aspects. Chem. Rev.* 94, 195-242.
7. Babu KR, Deepa M, Nair CMK, Vaidyan VK. Growth of anthracene crystals by gel aided solution technique. *Cryst Res Technol.* 1998;33:817–9.
8. Chakkaravarthi AA, LakshmanaPerumal CK, Santhanaraghavan P, Sivaji K, Kumar P, Muralithar S, Ramasamy P. Preparation of high-quality anthracene crystals using double run selective selfseeding vertical Bridgman technique (DRSSVBT). *J Cryst Growth.* 2002;246:85–9.
9. Karl N. Growth and electrical properties of high purity organic molecular crystals. *J Cryst Growth.* 1990;99:1009–16.
10. Kurtz SK and Perry TT (1968) A powder technique for the evaluation of non-linear optical materials. *J. Appl.phys.* 39, 3798-3813.
11. Madhurambal G, Anbusrinivasan P. Growth of high quality anthracene crystals by simple solution technique. *Cryst Res Technol.* 2006;41:231–5
12. Madhurambal G, Ramasamy P, Anbusrinivasan P, Mojumdar SC. Thermal properties, induction period, interfacial energy and nucleation parameters of solution grown benzophenone. *J Therm Anal Calorim.* 2007;90:673–9.
13. Mojumdar SC, Sain M, Prasad RC, Sun L, Venart JES. Selected thermo analytical methods and their applications from medicine to construction. *J Therm Anal Calorim.* 2007;60:65362.
14. Mojumdar SC, Moresoli C, Simon LC, Legge RL. Edible wheat gluten (WG) protein films: preparation, thermal, mechanical and spectral properties. *J Therm Anal Calorim.* 2011;104:929–36.
15. Santhakumari .R, Ramamoorthy.K. 2011. Structural thermal optical characterization of an NLO material-Benzaldehyde thiosemicarbazone of monohydrate single crystals part A:(78)653-659.
16. William Kemp, 1991. *Organic spectroscopy* –Third edition
17. Kalsi.P, 1987. *Spectroscopy of organic compounds* , New Delhi, *Wiley Eastern*.
18. Rao CNR. 1975. *Ultraviolet and visible Spectroscopy, Chemical applications*, New York *Plenum Press.*

19. Dyer JR. 1987. Application of absorption spectroscopy of organic compounds. *New Delhi Prentice-hall of India.*
20. Kalsi P. Spectroscopy of organic compounds. New Delhi: *Wiley Eastern; 1985.*