

Spectroscopic, Optical, Semiconducting And Thermal Behaviour Of Thiosemicarbazone Of Benzophenone And Benzaldehyde

G.V.PANDIAN, P.ANBUSRINIVASAN

Abstract: The main objective of the present work is to correlate the optical, semiconducting and thermal behaviour of thiosemicarbazone of benzophenone and benzaldehyde. These crystals have been grown by slow evaporation solution growth technique (SESGT) for the first time using methanol as solvent. The grown crystals have been characterized by Fourier-transform Infra-red spectral analysis, UV-Visible spectral analysis, proton nuclear magnetic resonance, band gap energy determination SHG efficiency and thermal studies.

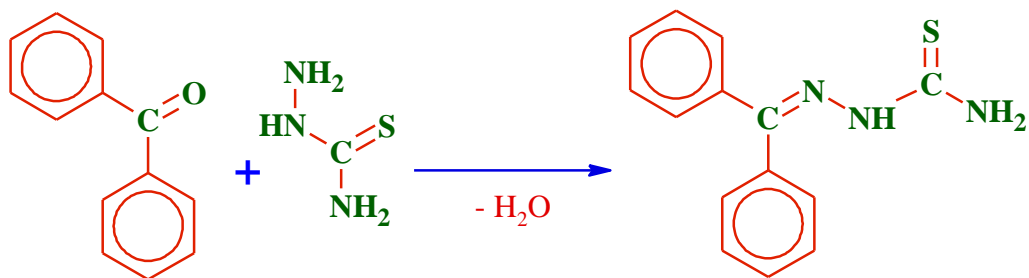
Introduction

For the past three decades, the field of opto electronics, optic communication have experienced tremendous advancements. Recently, the nonlinear material gain more attention due to their enormous application in opto electronic and optic communication technologies. [1-8] Organic compounds are often formed by very weak Vander walls and hydrogen bonds and possess high degree of delocalization. Hence they are optically more nonlinear than inorganic crystals. Today's researches have mentioned that organic crystals are bulk in size, hard, stable, and large Nonlinear optical susceptibilities compared to the inorganic crystals but they have poor mechanical properties. Considering all these parameters the modern scientists have concentrated on the growth of organic crystals. In addition thiosemicarbazone molecules containing π -electron conjugation system asymmetrized by the electron donor and acceptor groups are highly polarizable entities for nonlinear optical applications. Hence the thiosemicarbazone derivatives are considered as the potential organic optical materials. This belongs to the carbonyl group of compounds in which the Ketonic and aldehyde group are having asymmetrical carbon. Therefore in the present study, the preparation, spectral characterization, band gap energy determination and SHG efficiency and thermal stability of thiosemicarbazone of benzophenone and benzaldehyde is reported for the first time. These crystals are prepared and grown by slow evaporation solution growth technique (SESGT). The harvested crystals were characterized by FT-IR, UV, ^1H NMR, Band gap energy determination, SHG efficiency and thermal behavior of the crystals is analyzed systematically and correlated.

Experimental

The organic crystal of thiosemicarbazone derivatives were prepared by adopting the standard procedure [9,10]. To a hot solution of thiosemicarbazide in methanol, a solution of carbonyl compound in methanol was added drop wise during thirty minutes. The mixture was stirred and refluxed for four hours. Then it was filtered and the filtrate was concentrated to half the volume. Then the filtrate allowed for slow evaporation at room temperature, crystals were collected by filtration, washed with cold ethanol and dry the crystals. These crystals are suitable for characterization studies.

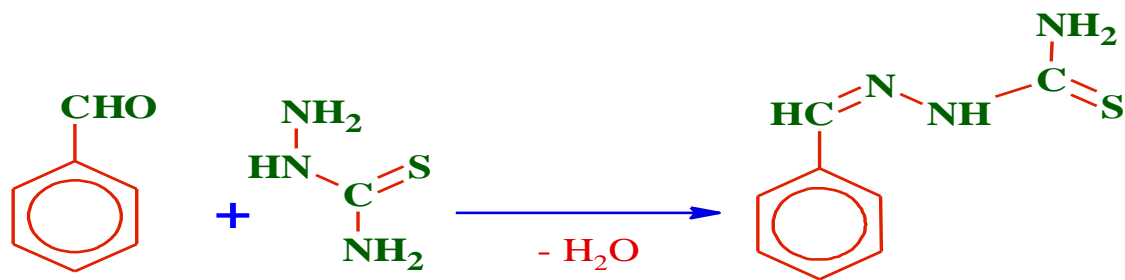
-
- Department of chemistry, T.B.M.L College, Porayar.
 - Department of Chemistry, A.V.C College (Autonomous), Mannampandal,
 - Email: gvpsjatbml@gmail.com



Benzophenone Thiosemicarbazide Thiosemicarbazone of benzophenone



Figure 1. Photograph of thiosemicarbazone of benzophenone



Benzaldehyde Thiosemicarbazide Thiosemicarbazone of benzaldehyde

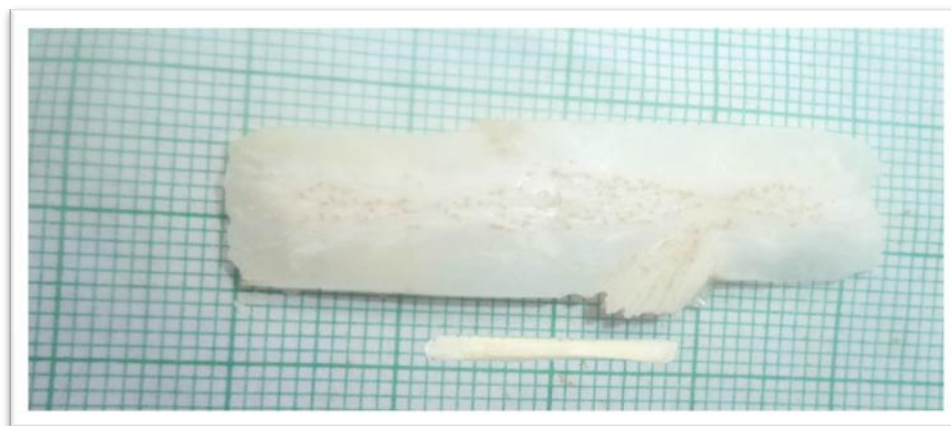


Figure 2. Photograph of thiosemicarbazone of benzaldehyde

Results and Discussion

FT-IR Spectral analysis

Fourier transform infrared (FT-IR) spectrum is an important record, which gives sufficient information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency [11]. The absorption of infrared radiation causes the various bonds in a molecule to stretch and bend with respect to one another [12, 13]. The spectrum was recorded using AVTAR 370 DTGS FT-IR spectrometer in the wave number range from 400 cm^{-1} to 4000 cm^{-1} with KBr pellet technique. The Fourier transform infrared spectrum of thiosemicarbazone of benzophenone and benzaldehyde is shown in figure 3 and 4 respectively.

The peak at 3365 cm^{-1} shows the N-H stretching vibration. The peak at 1482.02 cm^{-1} shows N-N stretching vibration. The peak at 1160.43 cm^{-1} and 1159.23 cm^{-1} shows C=S stretching vibration for thiosemicarbazone of benzophenone and thiosemicarbazone of benzaldehyde. The peak at 1278 cm^{-1} corresponds to aromatic C-H whereas in thiosemicarbazone of benzaldehyde 1298 cm^{-1} . The signal at 999.89 cm^{-1} indicates C-N stretching. The peak at 647 cm^{-1} shows N-H bending. The signal obtained at 1590 cm^{-1} is due to the formation of the imine group between carbonyl group and thiosemicarbazide. Due to the C=N and N-N stretching vibration the peaks observed at below 1540 cm^{-1} . There is no peak observed at 2720 cm^{-1} confirms the C=O functional group in thiosemicarbazone derivatives.

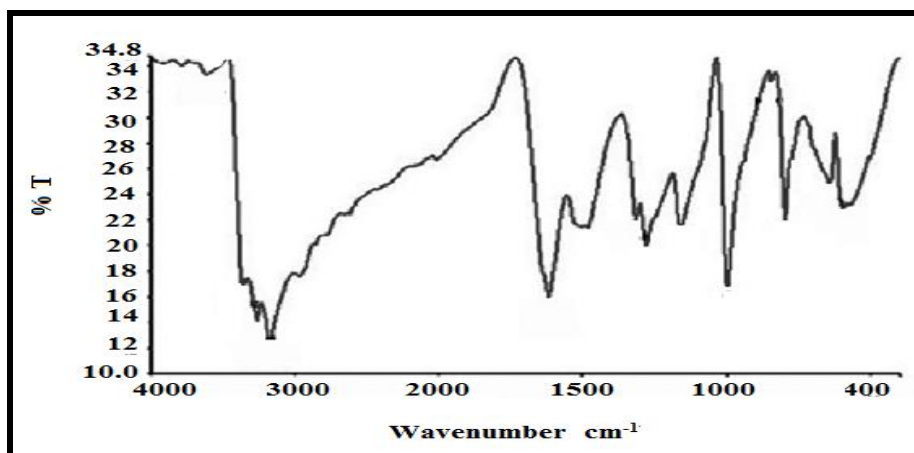


Figure 3. FT-IR Spectrum of thiosemicarbazone of benzophenone.

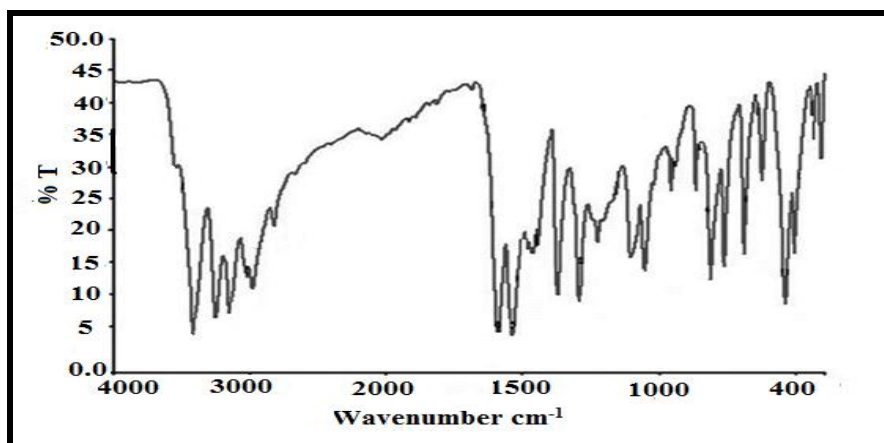


Figure 4. FT-IR Spectrum of thiosemicarbazone of benzaldehyde

UV-Visible spectral studies

UV-Visible spectral study is very useful technique to determine the transparency of a substance. The molecular absorption in the UV-Visible region depends mainly on the electronic structure of the molecule [14, 15]. The UV-Visible spectrum of thiosemicarbazone of benzophenone and benzaldehyde crystals were recorded using a Lambda 25

spectrometer. UV-Visible spectrum is shown in figure 5 and 6. The spectrum shows the characteristic absorbance band between $240\text{--}320\text{ nm}$. There is no characteristic absorbance between $320\text{--}800\text{ nm}$. Because of these properties thiosemicarbazone of benzophenone and benzaldehyde may find applications in opto electronics.

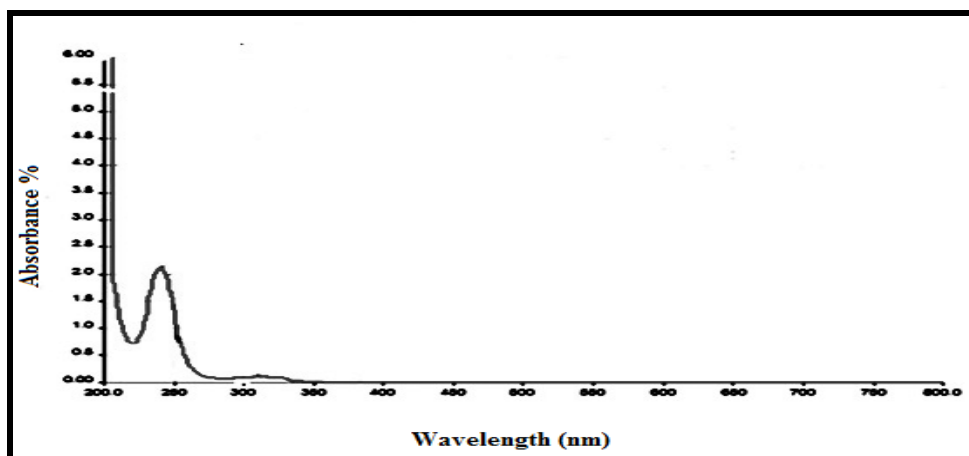


Figure 5. UV-Visible Spectrum of thiosemicarbazone of benzophenone

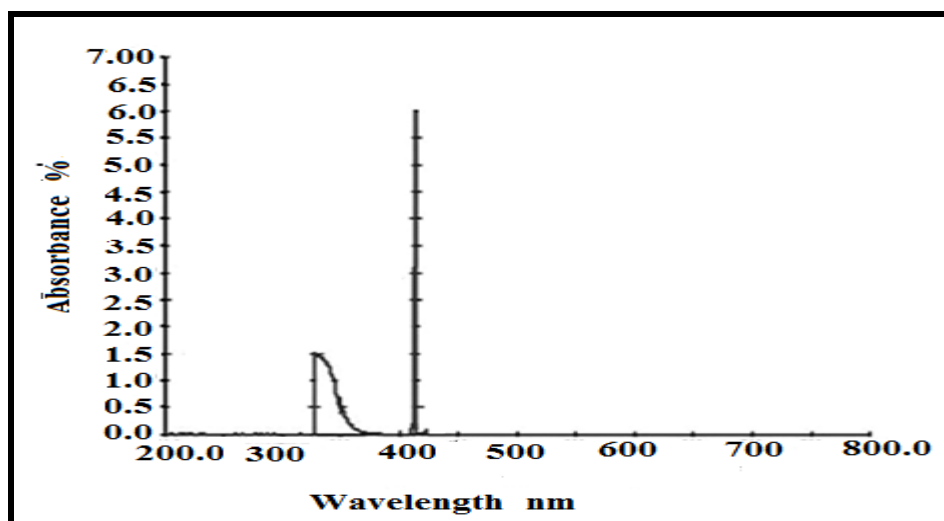


Figure 6. UV-Visible Spectrum of thiosemicarbazone of benzaldehyde

NMR Spectral analysis

^1H NMR Spectral analysis

The Nuclear Magnetic Resonance Spectral analysis is useful in the determination of the molecular structure based on the chemical environment of the magnetic nuclei such as ^1H , ^{13}C , ^{31}P etc., even at low concentrations [14, 15]. The ^1H NMR spectral analysis was carried out on the thiosemicarbazone of benzophenone and benzaldehyde crystals in BRUKER 300NMR spectrometer at 300 MHz using DMSO as solvent. The ^1H NMR spectra of thiosemicarbazone of benzophenone and thiosemicarbazone of benzaldehyde is shown in figure 7 and 8. The ^1H NMR spectrum revealed the presence of an aromatic system. There is a multiplet at $\delta=7.721$ ppm indicates the presence of aromatic protons. The NH_2 proton of hydrazide is observed at 8.658 as broad singlet. The $-\text{NH}$ proton is observed at 7.219 ppm. The ^1H -NMR

Spectrum of thiosemicarbazone of benzaldehyde shows signal observed at $\delta=8.24$ ppm is corresponds to the NH_2 protons of hydrazide group. A singlet at $\delta=8.055$ ppm confirm the NH proton. The multiplet observed between $\delta=7.370$ and 7.801ppm confirms the presence of aromatic protons. The presence of peak at $\delta=4.216$ ppm indicates the $\text{HC}=\text{N}$ protons. The signal at $\delta=3.451$ ppm shows the HOD signals of the solvent. The peaks at $\delta=1.276$ confirms the CH protons. The signal at $\delta=2.501$ indicates the residual protons present in DMSO d6 solvent [16]. The spectral data obtained for the thiosemicarbazone of benzophenone and thiosemicarbazone of benzaldehyde were well in accordance with theoretical and standard spectrum [17,18].

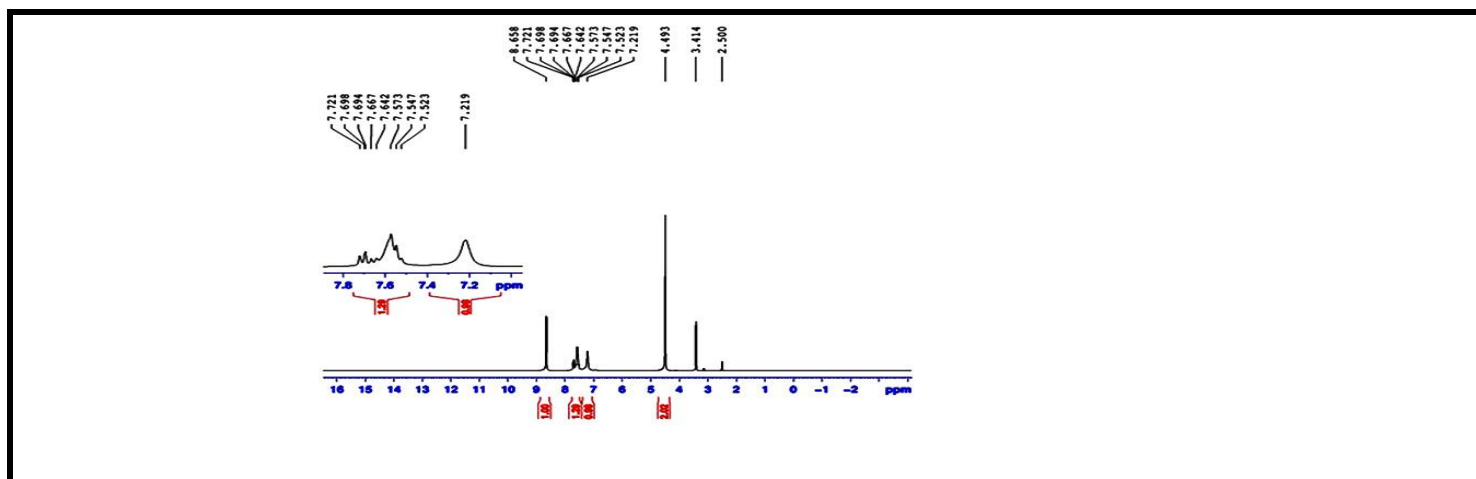


Figure 7. $^1\text{H-NMR}$ Spectrum of thiosemicarbazone of benzophenone

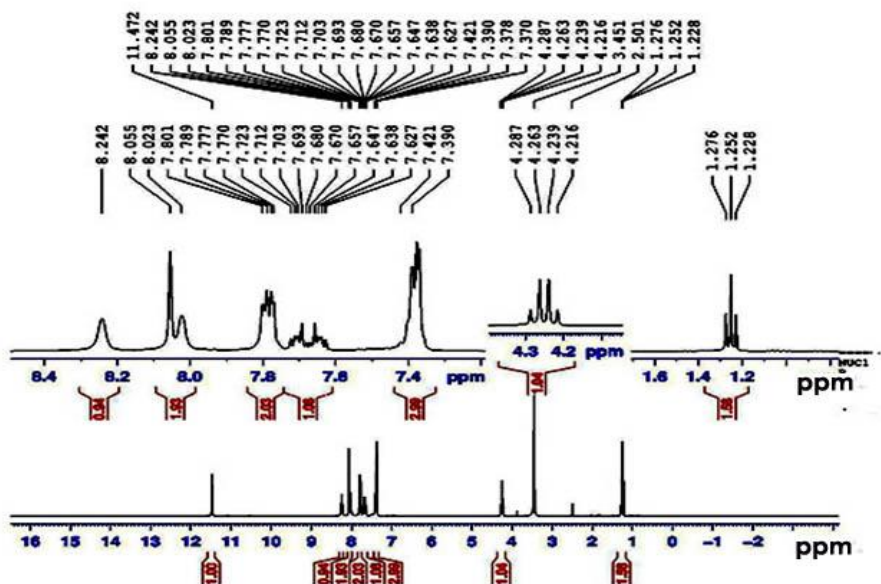


Figure 8. $^1\text{H-NMR}$ Spectrum of thiosemicarbazone of benzaldehyde

Thermal analysis

Thermal properties of harvested crystal of thiosemicarbazone of benzophenone and benzaldehyde were studied in powder form by recording TGA and DSC response curve in the temperature range between 0°C to 500°C . Thermal studies have been carried out using on SDTQ 600R 20.9 BUILD 20 Instrument at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The thermogram of thiosemicarbazone of benzophenone and benzaldehyde is shown in figure 9. In thiosemicarbazone of benzophenone; the sample taken for the measurement is 16.6580 mg.

There is an endothermic peak at 184.14°C shows its melting point. Thermal analysis clearly depicts the thermal stability and crystalline nature of the grown crystal [19]. Thermal and spectral analyses are very useful technique for material characterization [20-23]. The thermogram further shows the thermal stability and crystalline nature of the grown crystal. The other endothermic peak shows the further decomposition. In TGA there is a sharp weight loss at 206.75°C and further the curve shows subsequent weight loss at 246.09°C and 283.93°C .

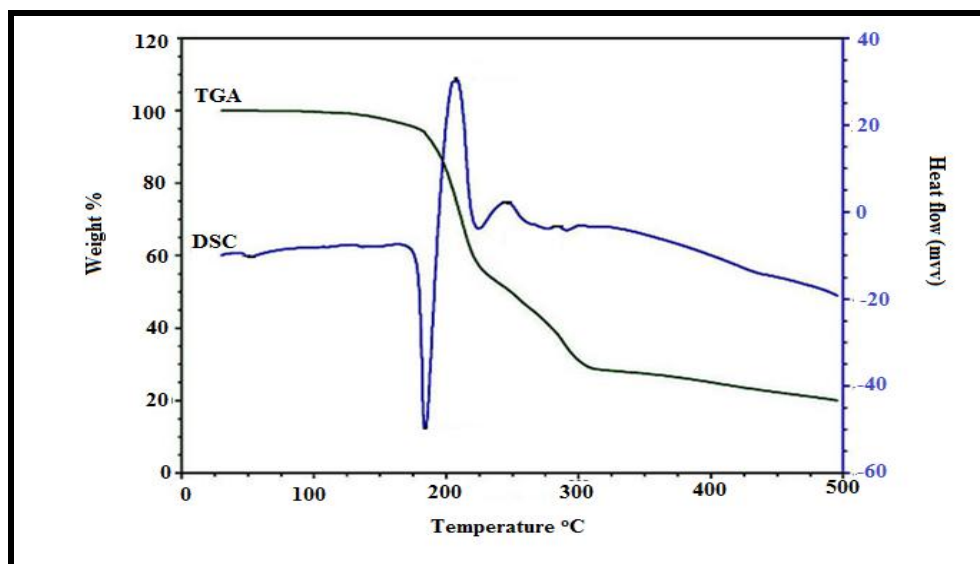


Figure 9. Thermogram of thiosemicarbazone of benzophenone

The thermogram of thiosemicarbazone of benzaldehyde shown in figure 10. The weight of sample taken for the measurement is 10.9750mg. The thermogram shows the endothermic peak at 153.50°C. The grown crystal begins to attain an endothermic transition and begins to decompose. The sharpness of this endothermic peak shows the good degree of crystallinity and purity. In TGA there are three

weight losses noted in the thermogram, first one is due to expulsion of water present in the crystal. The second and third major weight loss is observed just above 200 °C and 300 °C. Because of the sharp endothermic peaks shows the good degree of crystallinity of the thiosemicarbazone of benzophenone and benzaldehyde.

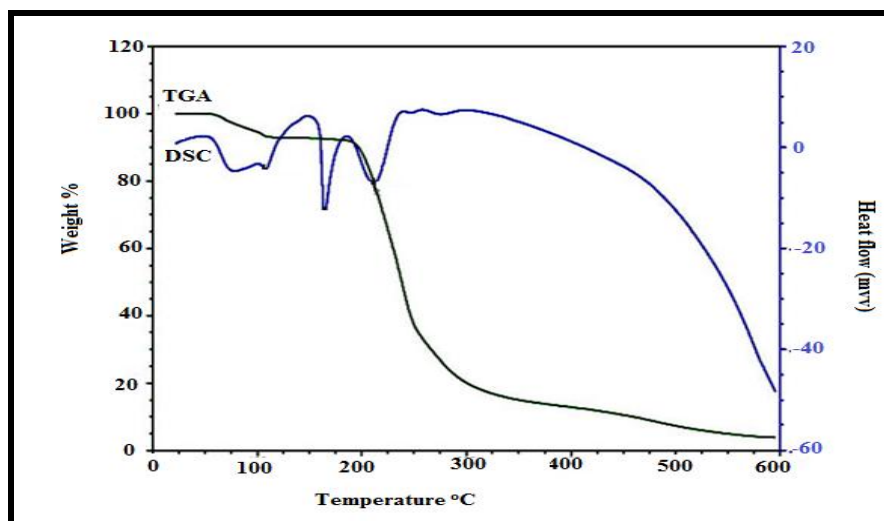


Figure 10 Thermogram of thiosemicarbazone of benzaldehyde

Band gap energy calculation

Band gap refers to the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band in insulators and semiconductors. This is equivalent to the energy required to free an outer shell electron from its orbit about the nucleus to become a mobile charge carrier, able to move freely within the solid material, so the band gap is a major factor determining the electrical conductivity of a solid. The band gap energy of prepared thiosemicarbazone of benzophenone and thiosemicarbazone of benzaldehyde crystals were

evaluated from the relation between absorption coefficient α and photon energy $h\nu$ [24].

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

Where A is a constant, E_g is the band gap and $x = 1/2$ for directly allowed electronic transitions. Figure 11 and 12 shows the plot between $(\alpha h\nu)^2$ and $h\nu$ of the prepared thiosemicarbazone of benzophenone and thiosemicarbazone of benzaldehyde crystals. The extrapolation of linear portion of the curves on $h\nu$ axis gives the direct band gap energy. The value of band gap energy

for thiosemicarbazone of benzophenone crystal is 4.777eV whereas thiosemicarbazone of benzaldehyde crystal is 3.539 eV. The band gap energy determination reveals that

both thiosemicarbazone of benzophenone and of benzaldehyde crystals shows semiconducting property.

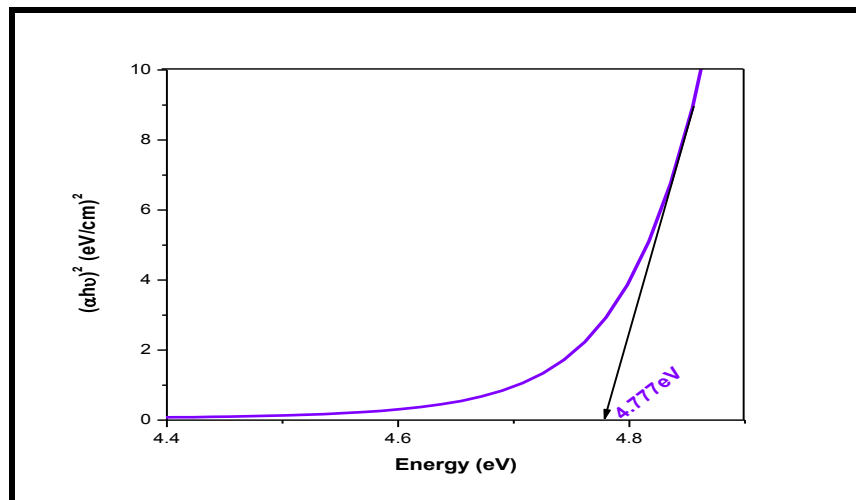


Figure 11. Band gap energy spectrum of thiosemicarbazone of benzophenone

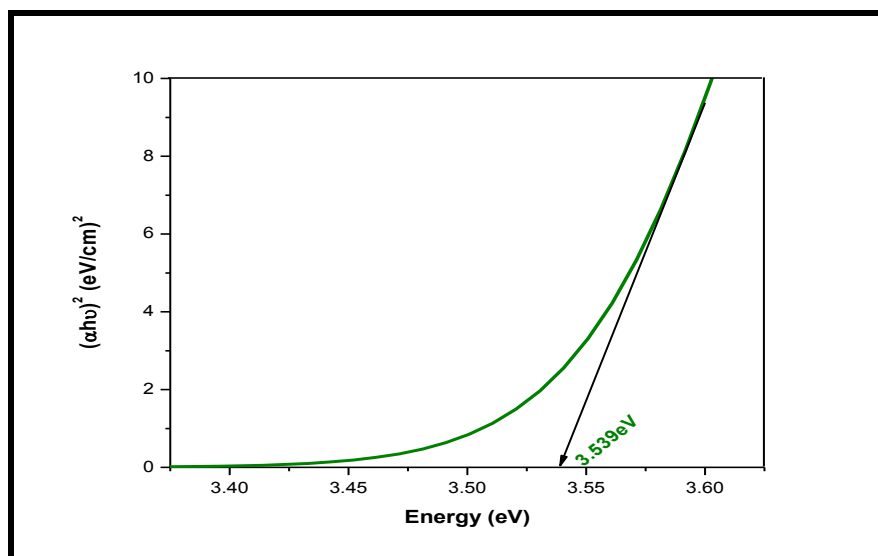


Figure 12. Band gap energy spectrum of thiosemicarbazone of benzaldehyde

Nonlinear optical studies

Kurts and Perry second harmonic generation (SHG) tests [25-27] was performed to determine the NLO efficiency of thiosemicarbazone of benzophenone and of benzaldehyde crystal. The grown crystal was powdered with a uniform particle size and packed in a micro capillary of uniform bore and was illuminated using spectra physics quanta ray DHS2:Nd: YAG laser is used to test second harmonic generation (SHG) of grown crystal. The relative SHG efficiency obtained for thiosemicarbazone of benzophenone is found to be about 2.8 times higher than that of potassium dihydrogen orthophosphate, whereas thiosemicarbazone of benzaldehyde is found to be about 5.1 times higher than that of potassium dihydrogen orthophosphate crystals.

Conclusion

Thiosemicarbazone of benzophenone and of benzaldehyde crystals were successfully grown using slow evaporation solution growth technique, using methanol as a solvent. The FT-IR spectral analysis gives an idea about the presence of functional groups. The UV-Visible spectrum proves the transparent nature of the crystal between 320-800nm. The molecular structure of the thiosemicarbazone derivatives were suitably correlated with the ¹H NMR spectral data. Thermal stability of harvested crystals was analyzed by TGA –DSC studies and found that both are thermally stable upto 150°C. The band gap energy and SHG efficiency of thiosemicarbazone of benzophenone and benzaldehyde were correlated. The non-linearity of the both thiosemicarbazone of benzophenone and benzaldehyde crystals were proved by the Kurts and Perry second harmonic generation test.

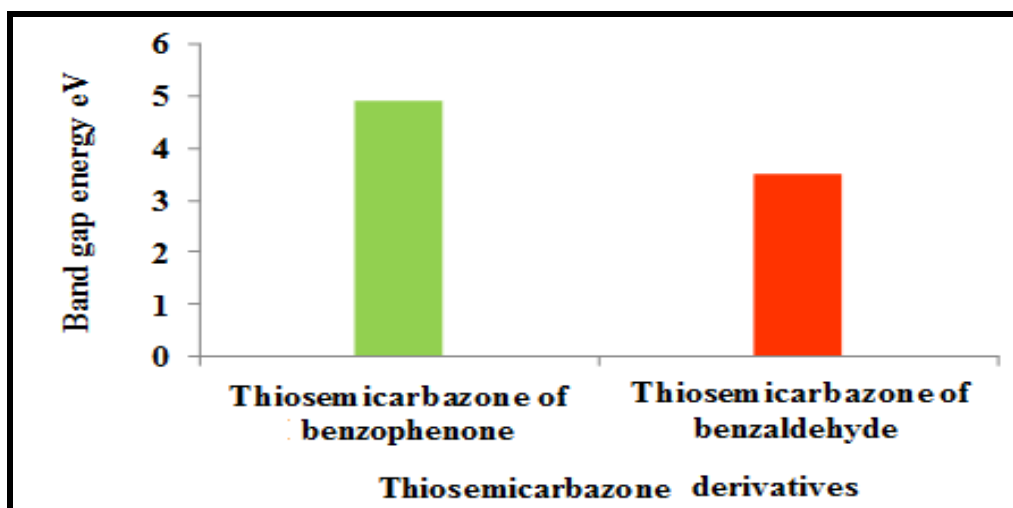


Figure 13. Correlation of band gap energy of thiosemicarbazone of benzophenone and benzaldehyde

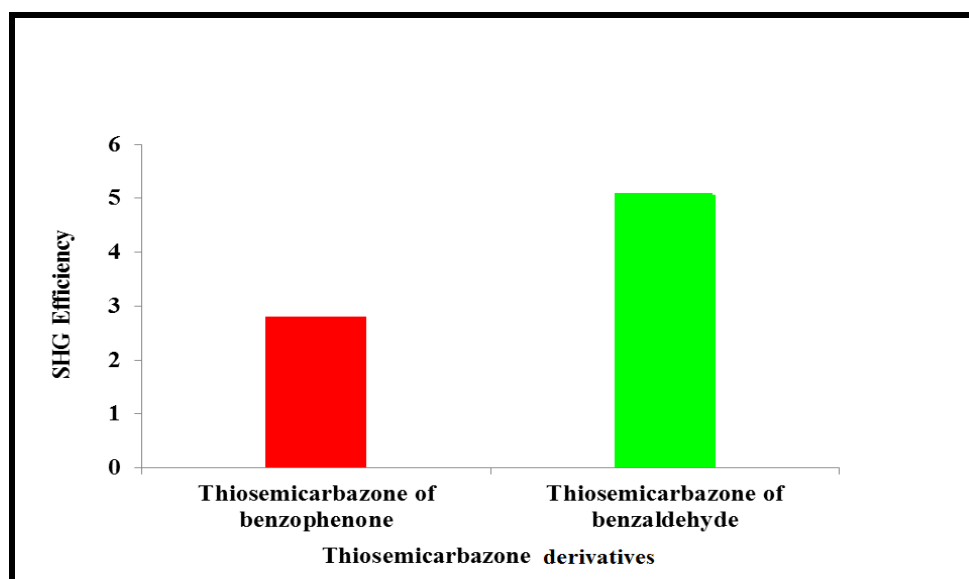


Figure 14. Relative SHG efficiency

The band gap energy of thiosemicarbazone of benzophenone is 4.7 eV and that of thiosemicarbazone of benzaldehyde is 3.5 eV. This may be interpreted as the presence of phenyl ring (π electrons) enhances the band gap energy. The relative band gap energies and SHG efficiencies of thiosemicarbazone of benzophenone and benzaldehyde is shown in figure 13 and 14 respectively. With reference to the literature, as thiosemicarbazone benzophenone and benzaldehyde has an aromatic ring at one end and NH_2 at other end, They possesses high SHG efficiency than that of potassium dihydrogen ortho phosphate. The thiosemicarbazone of benzaldehyde has higher SHG efficiency and lower band gap energy but it is thermally stable up to 150°C whereas the thiosemicarbazone of benzophenone having higher band gap energy and lower SHG efficiency, but it is thermally stable upto 180°C . This correlation and relative thermal stability provides information regarding the application oriented properties of the materials. This also gives an idea

about the selection of suitable thiosemicarbazone derivatives for the fabrication and opto electronics and other similar applications.

References

- [1] B.Narayanamoolaya., S.M.Dharmaprakash., J Crystal Growth **290**,498 (2006).
- [2] P.Anbusrinivasan, G.Madhurambal,SC Mojumdar J Therm Anal calorim **96** ,111(2009).
- [3] G.Vasudevan, P.Anbusrinivasan. G.Madhurambal. S.C,Mojumdar,, J Therm Anal calorim ,**104** ,975(2011).
- [4] K.Sankaranarayana,P. Ramasamy, J cryst growth, **292**,405(2006) .

- [5] P.Anbusrinivasan, S.Kavitha, Asian journal of chemistry,**20** ,979(2008).
- [6] C.RamachandraRaja , K.Ramamoorthi R.Manimekalai, Spectrochimica Acta Part A **99**,23(2012).
- [7] P. AnbuSrinivasan, M.Suganthi, Asian journal of chemistry, **20** ,1775 (2008).
- [8] Yun-zhang, Yonggangwang, Yunxiache, Jiminezheng J crystal growth **299**,120(2007).
- [9] R.Santhakumari, K.Ramamurthy, Spectro chemical Acta part A: **78**, 653 (2011).
- [10] WiliredoHernandez, et.al Bioinorgchem Appl-v **2008**,PMC2615113 (2008).
- [11] JR.Dyer . Applications of absorption spectroscopy of organic compounds. New Delhi Prentice-hall of India(1987).
- [12] P.Kalsi, Spectroscopy of organic compounds, NewDelhi, Wiley Eastern, (1987).
- [13] R.M.Silverstein and G.C.Bassler,Spectrometric identification of organic compounds,Wiley,New York (1964).
- [14] Y.R.Sharma Elementary organic spectroscopy.Reprint (2003).
- [15] William Kemp, Organic spectroscopy-Third edition-(1991).
- [16] C. N. R. Rao, Ultraviolet and Visible Spectroscopy, Butterworths, London, UK, 3rd edition,(1975).
- [17] M.H Dos Santos et.al, Magn. Reson.Chem. **39**,155,(2001).
- [18] Myoung-chongsong et.al, Bull,Koream Chem, Soc,**28(7)** 1209(2007).
- [19] G.Vasudevan,P.Anbusrinivasan,G.Madhurambal, SC.Mojumdar, . J. Therm Anal Calorim **96**,99(2009).
- [20] K.A.Nandekar et.al, Rasayan Journal of Chemistry, **5** ,261(2012).
- [21] D.Jaikumar et.al J. Cryst. Growth. , **312**,120(2009).
- [22] S.C. Mojumdar, et.al. J Therm Anal Calorim **60** 653(2007).
- [23] S. C .Mojumdar, et.al. J Therm Anal Calorim ,**81** 211(2005).
- [24] A.L. Fahrenbruch, R.H. Bube (Eds.), Fundamentals of Solar Cells, Academic, New York, 1993.
- [25] S.K.kurtz,T.T.Perry ,J.Appl.Phys.**39** , 3798(1968).
- [26] P.M.Ushasree, et.al J. Cryst. Growth. **218**, 365(2000).
- [27] T.Balakrishnan , K.Ramamurthi, Spectrochimica Acta part **A 72** 269(2009).