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Research Article

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"Spectral, Optical, Semiconducting and Thermal Characteristics of thiosemicarbazone of Benzaldehyde and Acetaldehyde"

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Abstract

The present work describes to correlate the optical, semiconducting and thermal behavior of thiosemicarbazone of benzaldehyde and acetaldehyde. 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.

Keywords: Slow evaporation, Solution growth technique, Spectral characterization, Thermal analysis, Band gap energy, SHG efficiency.

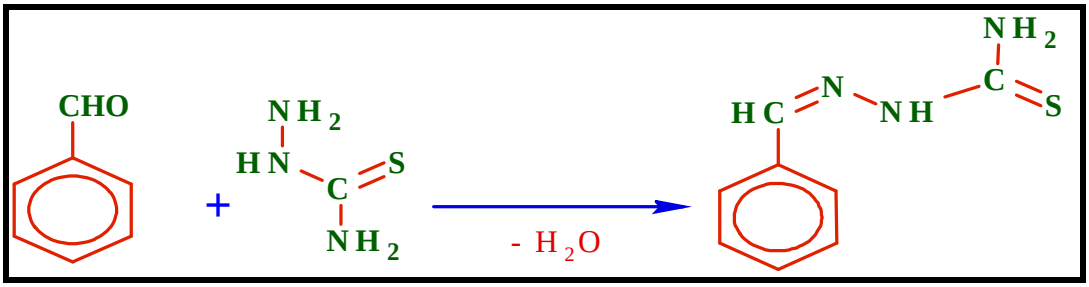
1. Introduction

Recent 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. An Organic nonlinear crystals possess shorter wavelength, optical quality sufficiently larger nonlinear coefficient. Considering all these parameters, the modern scientists have concentrated on the growth of organic crystals [1,2].Organic crystal of thiosemicarbazone of benzaldehyde and acetaldehyde play an important role in application of optical computing and optical communication devices and optical communication processes. This belongs to the carbonyl group of compounds in which the benzaldehyde and aldehyde group are having asymmetrical carbon. Therefore in the present studies, the preparation, spectral characterization, Thermal stability,band gap energy determination and SHG efficiency of thiosemicarbazone of benzaldehyde and acetaldehyde, are 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, ^{1}H NMR, Thermal stability, Band gap energy determination, SHG efficiency of the crystals were analysed systematically and correlated [3-8].

2. Experimental

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.



Benzaldehyde + Thiosemicarbazide =Thiosemicarbazone of benzaldehyde

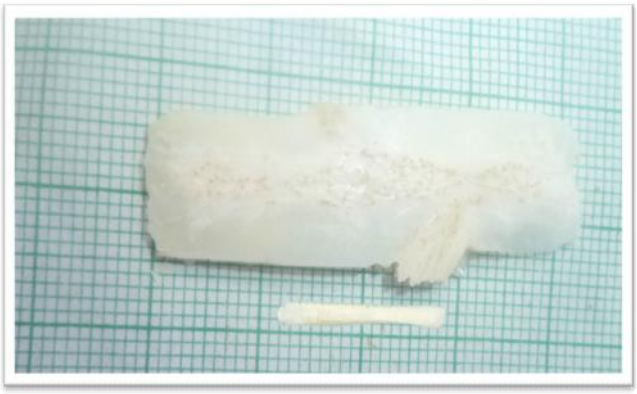
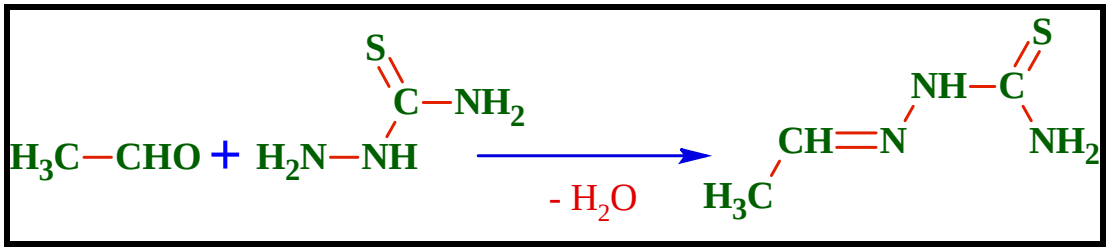


Figure 2.1. Photograph of thiosemicarbazone of benzaldehyde



Acetaldehyde + Thiosemicarbazide =Thiosemicarbazone of acetaldehyde

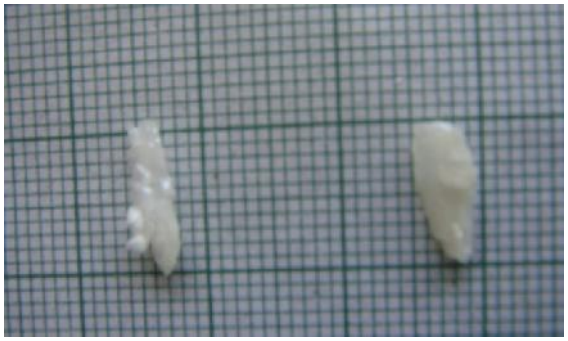


Figure 2.1. Photograph of thiosemicarbazone of acetaldehyde

3. FT-IR Spectral analysis

Fourier transform infrared (FT-IR) spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding to the molecular structure of the 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 4000cm^{-1} with KBr pellet technique.

The Fourier transform Infrared spectrum of thiosemicarbazone of benzaldehyde and acetaldehyde is shown in figure 3 and 4 respectively. The peak at 3365,3366cm^{-1} shows the N-H stretching vibration.The peak at 1482.02cm^{-1},1485cm^{-1} shows N-N stretching vibration. The peak at 1160.43cm^{-1} and 1163cm-^{1} shows C=S stretching vibration for thiosemicarbazone of benzaldehyde and thiosemicarbazone of acetaldehyde. The peak at 1298 cm^{-1} corresponds to aromatic C-H whereas in thiosemicarbazone of acetaldehyde 3177cm^{-1}.The absence of peak at 1298 cm^{-1} in thiosemicarbazone of acetaldehyde shows a aliphatic in nature. The signal at 999.89cm^{-1},1485 cm^{-1} indicates C-N stretching. The band obtained at 1590cm^{-1}and1531 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 absence of -CHO functional group in thiosemicarbazone derivatives.

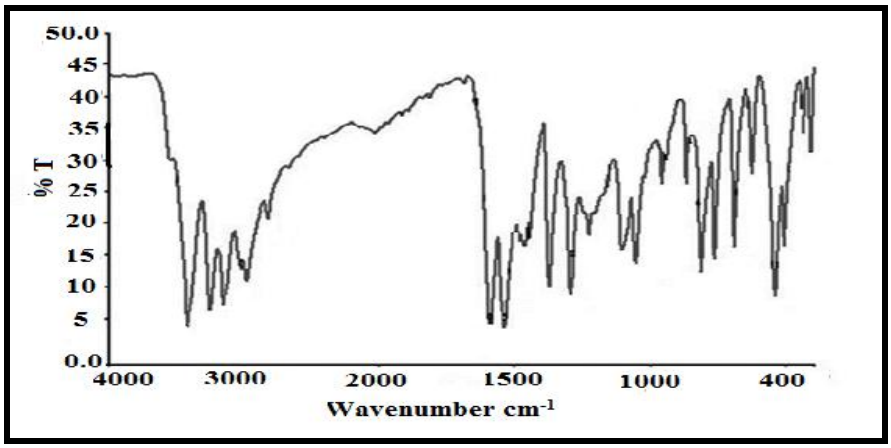


Figure 3.1. FT-IR Spectrum of thiosemicarbazone of benzaldehyde

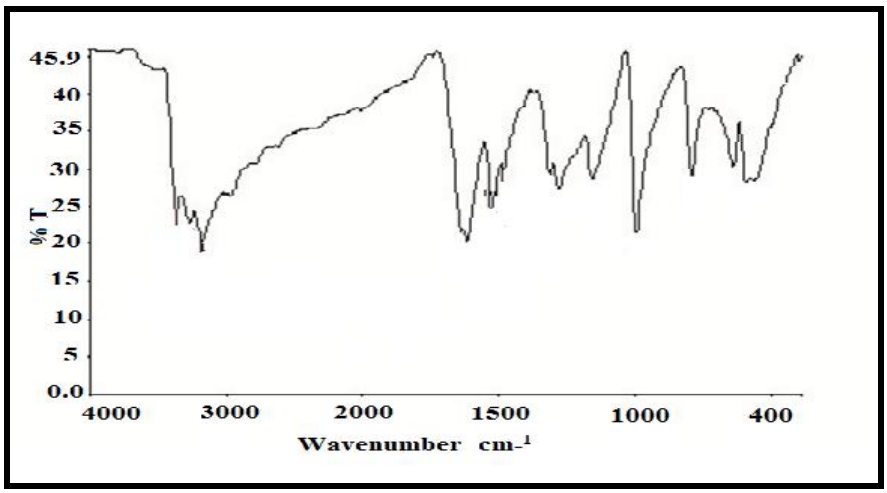


Figure.3.2 FT-IR Spectrum of thiosemicarbazone acetaldehyde

4. UV- Visible spectral analysis

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 [14-16].The UV-Visible spectrum of thiosemicarbazone of benzaldehyde and acetaldehyde 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 260-380nm. There is no characteristic absorbance band between 380-800nm. Because of these properties thiosemicarbazone of benzaldehyde and acetaldehyde may find applications in opto electronics.

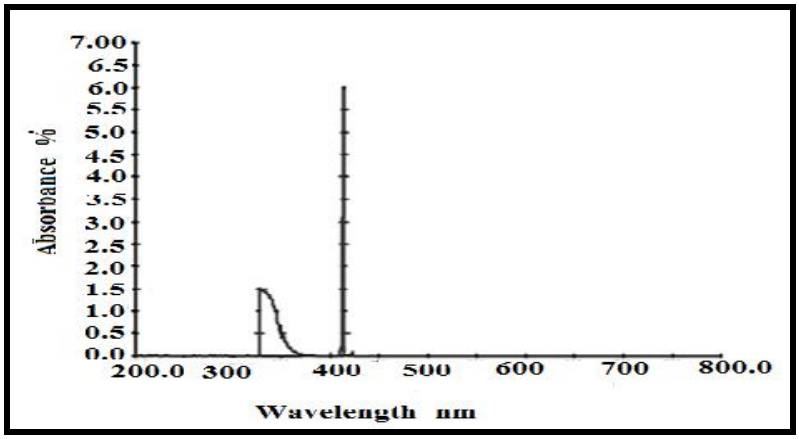


Figure 4.1. UV-Visible Spectrum of thiosemicarbazone of benzaldehyde

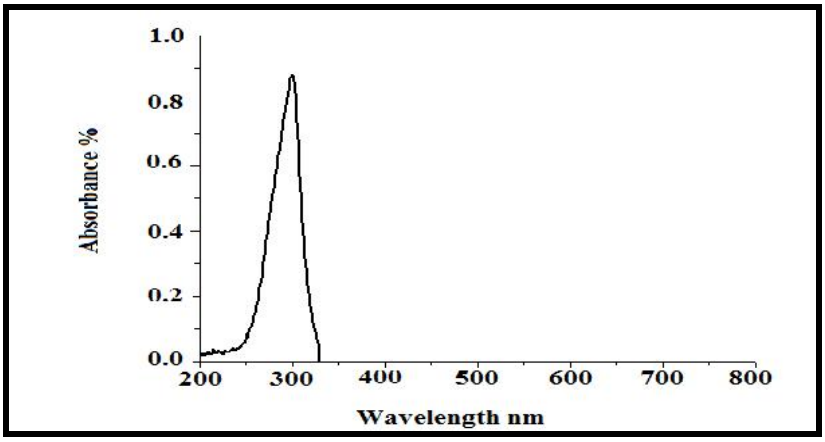


Figure 4 .2 UV- Visible spectrum of thiosemicarbazone of acetaldehyde

5. NMR spectral analysis

5. (a)^{1}H 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 ^{1}H, ^{13}C, ^{31}P etc., even at low concentrations [17,18].The ^{1}H NMR spectral analysis was carried out on the thiosemicarbazone of benzaldehyde and acetaldehyde crystals in BRUKER 300NMR spectrometer at 300 MHz using DMSO as solvent. The ^{1}H NMR spectra of thiosemicarbazone of benzaldehyde and thiosemicarbazone of acetaldehyde is shown in figure 7 and 8. The ^{1}H NMR spectrum revealed the presence of an aromatic system . There is a multiplet at δ=7.370-7.801 ppm indicates the presence of aromatic protons. The NH_2 proton of hydrazide is observed at 8.658ppm as broad singlet. The –NH proton is observed at 7.219 ppm.

The ^{1}H-NMR Spectrum of thiosemicarbazone of acetaldehyde shows signal observed at δ=8.624ppm is corresponds to the NH_2 protons of hydrazide group. A singlet at δ=7.20ppm confirm the NH proton. The CH protons is observed at δ=4.484ppm.The signal at δ=3.413ppm shows the HOD signals of the solvent. The signal at δ=2.498indicates the residual protons present in DMSO d6 solvent. The spectral data obtained for the thiosemicarbazone of benzaldehyde and thiosemicarbazone of acetaldehyde were well in accordance with theoretical and standard spectrum.

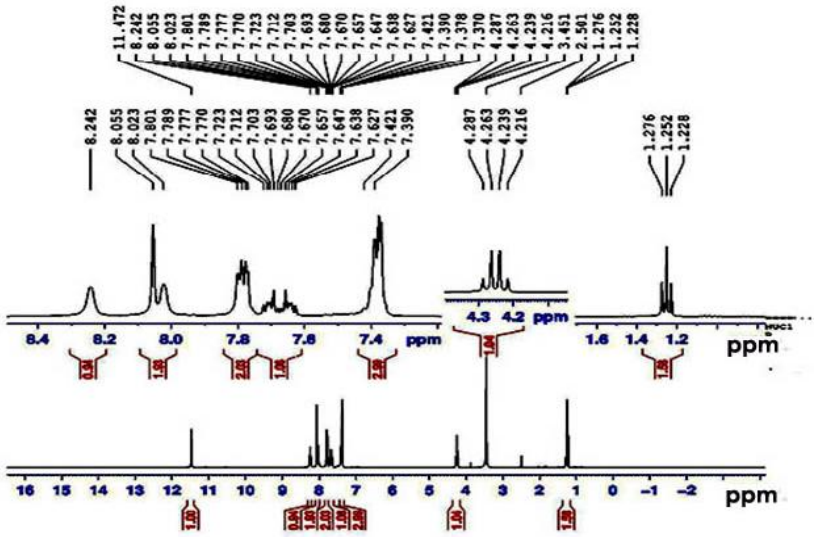


Figure 5.1. ^{1}H-NMR Spectrum of thiosemicarbazone of benzaldehyde

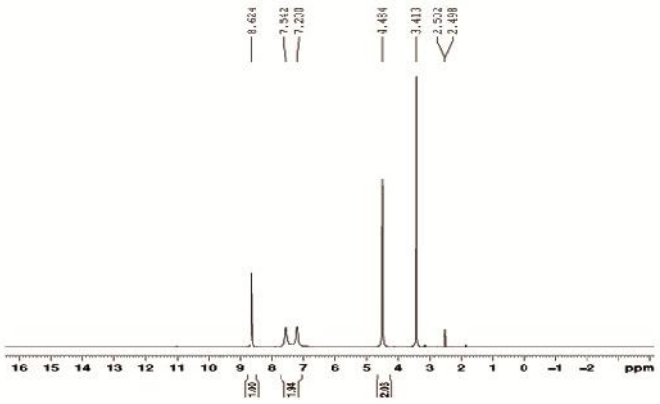


Figure.5.2 (a) ^{1}H NMR Spectrum of thiosemicarbazone of acetaldehyde

6. Thermal analysis

Thermal properties of harvested crystal of thiosemicarbazone of benzaldehyde and acetaldehyde were studied in powder form by recording TGA and DSC response curve in the temperature range between 0^{0}C to 500^{0}C. Thermal studies have been carried out using on SDTQ 600R 20.9 BUILD 20 Instrument at a heating rate of 10 ^{0}C /min under nitrogen atmosphere. The thermogram of thiosemicarbazone of benzaldehyde and acetaldehyde is shown in figure 9.In thiosemicarbazone of benzaldehyde the sample taken for the measurement is 10.9750 mg. There is an endothermic peak at 153.50 ^{0}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 is observed just above 200^{0}C and 300^{0}C.

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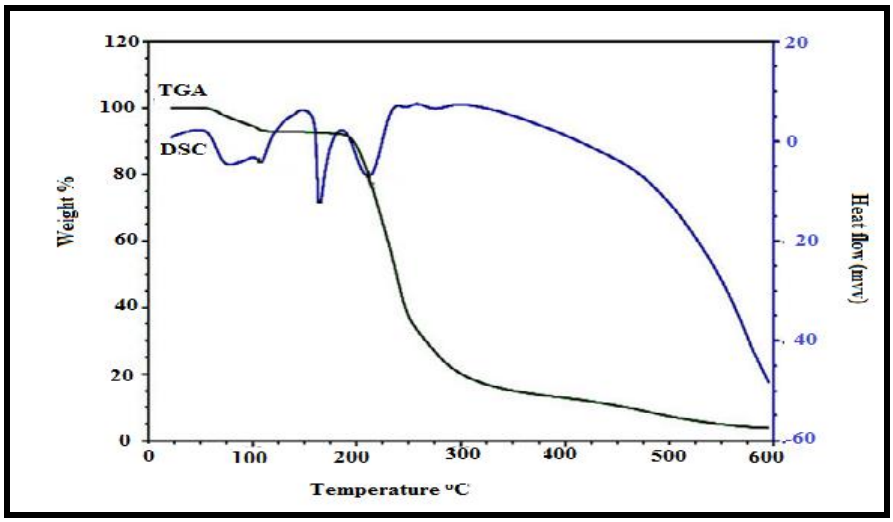

Figure 6. Thermogram of thiosemicarbazone of acetaldehyde

The thermogram of thiosemicarbazone of acetaldehyde shown in figure 10. The weight of sample taken for the measurement is 5.7110mg.The thermogram shows the endothermic peak at 183.64^0C. The grown crystal begins to attain an endothermic transition and begins decompose. In TGA curve decomposition started at around180^0C and subsequent decomposition occur at 217^0C and 260^0C. Because of the sharp endothermic peaks shows the good degree of crystallinity and purity of the thiosemicarbazone of benzaldehyde and acetaldehyde.

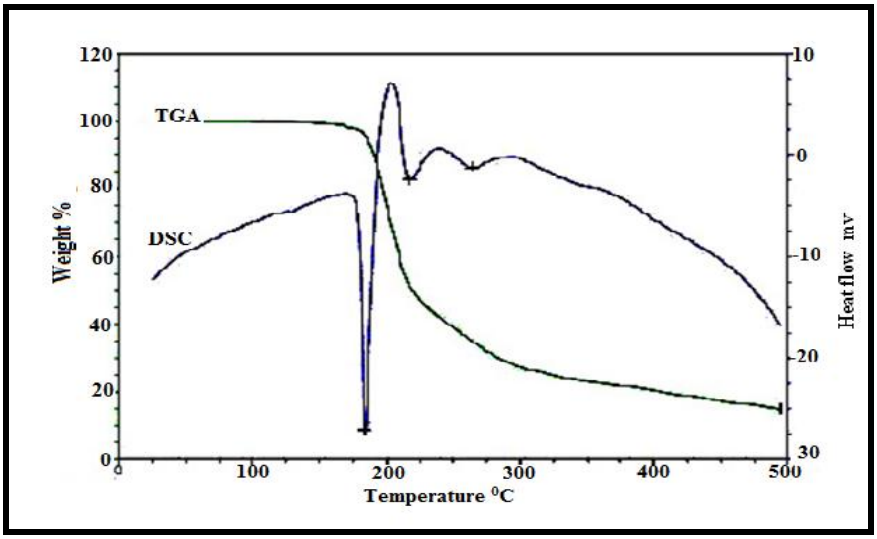

Figure 7. Thermogram of thiosemicarbazone of acetaldehyde

7. 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 benzaldehyde and thiosemicarbazone of acetaldehyde crystals were evaluated from the relation between absorption coefficient α and photon energy ħν [24].

$$(\alpha\hbar\nu) = A\,(\hbar\nu - E_g)^{\chi}$$

Where A is a constant, E_g is the band gap and $\chi = 1/2$ for directly allowed electronic transitions. Figure 11 and 12 shows the plot between $(\alpha\hbar\nu)^2$ and ħν of the prepared thiosemicarbazone of benzaldehyde and thiosemicarbazone of acetaldehyde crystals. The extrapolation of linear portion of the curves on ħν axis gives the direct band gap energy. The value of band gap energy for thiosemicarbazone of benzaldehyde crystal is 3.539eV whereas thiosemicarbazone of acetaldehyde crystal is 3.991 eV. The band gap energy determination reveals that both thiosemicarbazone of benzaldehyde and of acetaldehyde crystals shows semiconducting property.

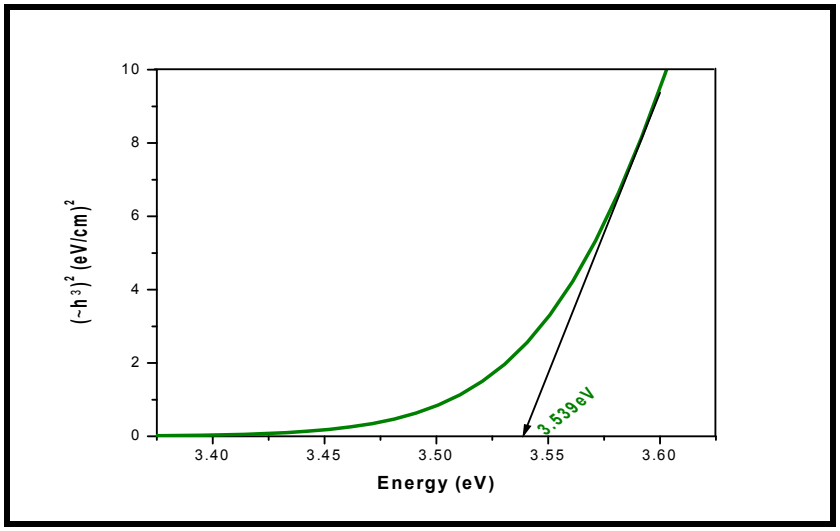

Figure 8. Band gap energy spectrum of thiosemicarbazone of benzaldehyde

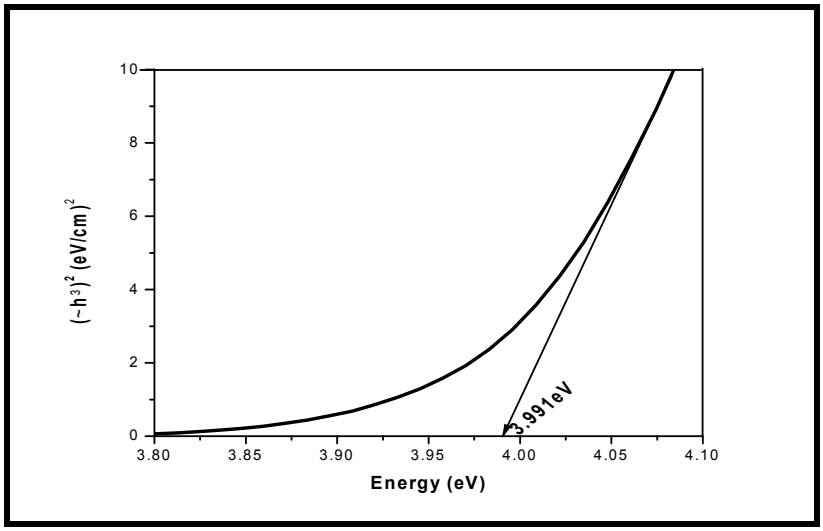

Figure 9. Band gap energy spectrum of thiosemicarbazone of acetaldehyde

8. Nonlinear optical studies

Kurts and perry second harmonic generation (SHG) tests [25-26] was performed to determine the NLO efficiency of thiosemicarbazone of benzaldehyde and of actaldehyde 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 benzaldehyde is found to be about 5.1 times higher than that of potassium dihydrogen orthophosphate, whereas thiosemicarbazone of acetaldehyde is found to be about 1.6 times higher than that of potassium dihydrogen orthophosphate crystals.

Conclusion

Thiosemicarbazone of benzaldehyde and of acetaldehyde 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 380-800nm.The molecular structure of the thiosemicarbazone derivatives were suitably correlated with the ^{1}H NMR spectral data. Thermal stability of harvested crystals was analyzed by TGA –DSC studies and found that both are thermally stable upto 183^{o}C.The band gap energy and SHG efficiency of thiosemicarbazone of benzaldehyde and acetaldehyde were correlated. The non-linearity of the both thiosemicarbazone of benzaldehyde and acetaldehyde crystals were proved by the Kurts and perry second harmonic generation test.

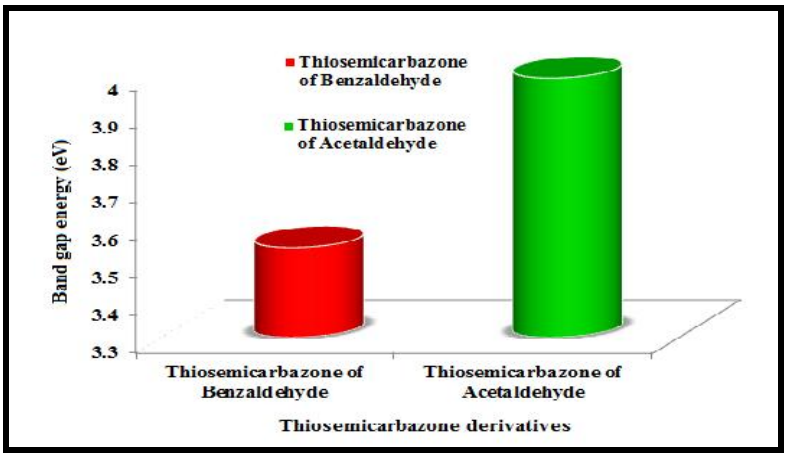

Figure 10. Correlation of band gap energy of thiosemicarbazone of benzaldehyde and acetaldehyde

The band gap energy of thiosemicarbazone of benzaldehyde is 3.539eV and that of thiosemicarbazone of acetaldehyde is 3.991eV. This may be interpreted as the presence of phenyl ring group enhances the band gap energy. The relative band gap energies and SHG efficiencies of thiosemicarbazone of benzaldehyde and acetaldehyde is shown in figure 13 and 14 respectively.

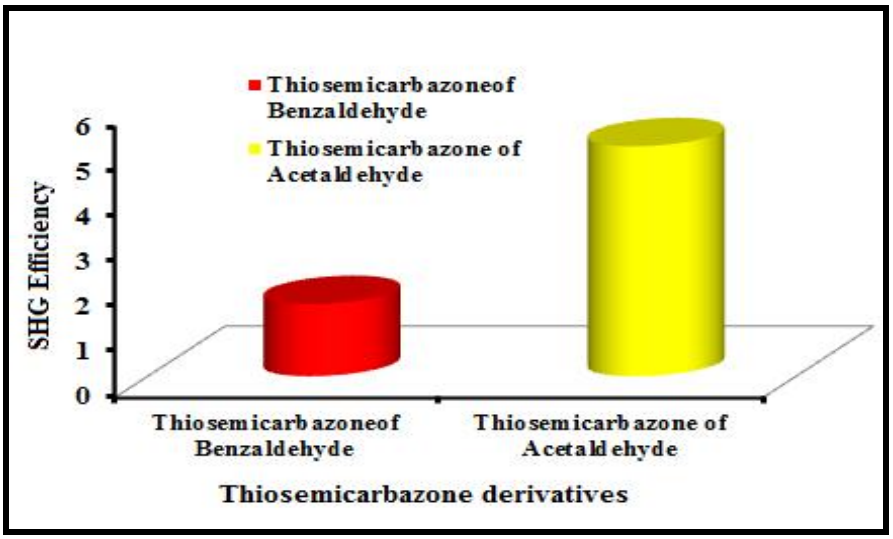

Figure 11. Relative SHG efficiency

With reference to the literature, as thiosemicarbazone 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 153^0C whereas the thiosemicarbazone of acetaldehyde having higher band gap energy and lower SHG efficiency, but it is thermally stable upto 183^0C. 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.

Acknowledgments

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References

1. Sankaranarayanan K, Ramasamy P, Unidirectional crystallization of large diameter benzophenone single crystal from solution at ambient temperature. J cryst growth, 292 (2006) 405-414..
2. Arulchakkaravarthi.A, Jayavel.P, santhanaragavan. P, Ramasamy.P Growth of organic molecular single crystal trans-stilbene by selective self-seeding from vertical Bridgman technique: J cryst Growth 2002(234) 159-5.
3. Vasudevan. G,. Anbusrinivasan. P, Madhurambal. G, Mojumdar. S.C,,Effect of dopant on the characterization of KAP crystal- *J Therm Anal calorim* (2011) 975-979.
4. Narayanamoolaya. B, Dharmaprakash.SM, Synthesis, growth and characterization of nonlinear optical crystal L-tyrosine hydrobromide. *J Crystal Growth* 290(2006) 498-503.
5. Anbusrinivasan. P, Kavitha. S, Growth and characterization studies of 2-Bromo-4-chloroacetophenone crystals; *Asian journal of chemistry*, vol 20 (2008) 2,979-982.
6. Ramachandra Raja C, Ramamoorthi K,R. Manimekalai, Growth and spectroscopic characterization of ethylene diamine tetra acetic acid (EDTA) doped Zinc sulphatehepta hydrate-A semi organic NLO material, *Spectrochimica Acta Part A* 99(2012) 23-26.
7. Madhurambal. G, Ramasamy.P, Anbu Srinivasan. P, Suganthi. M, Vasudevan.G, Mojumdar.S.C, The growth and characterization of 2,4-dinitro phenyl hydrazone of benzophenone and mixed crystals, *Asian journal of chemistry, vol* 20 (2008) 3,1775-1780.
8. Yun-zhang, Yonggangwang, Yunxiache, Jiminezheng. Growth and properties of two new organic nonlinear optical crystals; Hydroxyethylammonium-l-tartrate monohydrate and Hydroxyethylammonium-o-tartratemono hydrate; *J crystal growth* 299(2007) 120-124.
9. WiliredoHermandeza, Juan paz, Abraham Vaisberg, EvgeniaSpodine, Rainer Richter and LotharBeyer.Synthesis,Characterization and in Vitro Cytotoxic Activities of Benzaldehyde Thiosemicarbazone Derivatives and Their Palladium (II) and Platinum (II) Complexes against various Human Tumor cell Lines, *Bioinorgchem Appl-v* 2008,PMC2615113 (2008).

10. Santhakumari.R, Ramamurthy.K, Structural, Thermal and optical characterization of an organic Nlo material –Benzaldehyde Thiosemicarbazone monohydrate single crystals *Spectro chemical Acta part A*: 78 653-659 (2011).
11. Kalsi.P, Spectroscopy of organic compounds, NewDelhi, Wiley Eastern, 1987.
12. Dyer JR. Applications of absorption spectroscopy of organic compounds. New Delhi Prentice-hall of India: 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. C. N. R. Rao, Ultraviolet and Visible Spectroscopy, Butterworths, London, UK, 3rd edition, 1975. Press 1975.
16. William Kemp, Organic spectroscopy-Third edition-1991.
17. Dos Santos M.H, Nagem T.J, Braz-Filho R, ILuta I.S and Speziali N.L Complete assignment of the ^{1}H and ^{13}C NMR spectra of the tetraaisoprenylatedbenzophenone15-epiclusianone *Magn. Reson.Chem.* 39 (2001) :155158.
18. Myoung-chongsong, FikruNigussie, Hye-Joung Yang and Nam-In Back, A New benzophenone from Linderafruticosa, *Bull,Koream Chem, Soc*,28(7) (2007) 1209.
19. Vasudevan. G, Anbusrinivasan. P, Madhurambal. G, Mojumdar.SC, Thermal analysis effect of dopants Spectral characterization and growth aspect of KAP crystals . *J. Therm Anal Calorim* 2009(96) 99-102.
20. Mojumdar.SC, Sain.M, Prasad.RC, Sun.L,Venart.JES. Selected thermoanalytical methods and their applications from medicine to construction. *J Therm Anal Calorim* 60 (2007) 653-662.
21. Jaikumar.D, Kalainathan. Bhagavanarayana. G "Synthesis, growth, thermal, optical and mechanical properties of new organic NLO crystal: L-alanine DL-malic acid ,"*J. Cryst. Growth*, 312(2009) 120–124.
22. Mojumdar SC, Miklovic J, Krutosikova A, Valigura D, Stewart J M. Furopyridine-Ni(II) complexes-Synthesis, Thermal and spectral characterization. *J Therm Anal Calorim.* 2005(81) 211-215.
23. A.L. Fahrenbruch, R.H. Bube (Eds.), Fundamentals of Solar Cells, Academic, New York, 1993.
24. kurtz S.K,Perry T.T,*J.Appl.Phys*.39(1968) 3798-3813.
25. Balakrishnan T, Ramamurthi K, "Crystal growth, Structural, optical, mechanical and thermal properties of a new non linear optical single crystal L-Ornithine monohydrochloride", *Spectrochimica Acta part* A 72 (2009) 269-273.
26. Ushasree.P.M, Muralidharan.R, Jayavel.R, Ramasamy.P,"Growth of bis(thiourea) cadmium chloride single crystals — a potential NLO material of organometallic complex" *J. Cryst. Growth*. 218,(2000) 365–371.

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