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Preparation, spectral and thermal characterization of an organic NLO material [(E)- benzylideneamino] thiourea

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Abstract

A semi-organic crystal–[(E)-benzylideneamino] thiourea (EBAT) was grown by adopting slow evaporation solution growth technique (SESGT) using methanol as a solvent.The functional group of harvested crystals were studied by the Fourier Transform (FT-IR) spectral analysis. The UV Spectra confirms the optical transparency. This is more helpful to use these crystals in opto applications. The harvested crystal of [(E)-benzylideneamino] thiourea was characterized by proton nuclear magnetic resonance and ^{13}C NMR spectra which shows the molecular structure of the crystal. The TGA and DSC confirm the decomposition of the sample at 153.50^{o}C. It further confirms the grown crystal [(E)-benzylideneamino] thiourea (EBAT) is thermally stable up to 153.50^{o}C. The crystalline powder of the grown crystals was examined by X-ray diffraction studies. Second harmonic generation efficiency of the powdered [(E)-benzylideneamino] thiourea was tested using Nd:YAG laser and it is found to be ~5.1 time that of potassium dihydrogen ortho phosphate.

Key words: solution growth, slow evaporation technique, spectral characterization, Thermal analysis, SHG efficiency.

1. Introduction

In recent years, intense research work has been carried out to identify a special variety of thermally stable optical material. In general semi-organic crystals are more stable than inorganic and organic crystals. The slow evaporation solution growth Technique (SESGT) is an important technique because large size, stable, optical crystals are being grown by this technique[1-6]. Hence these crystals are used in the area of optical communication and optical computing and information processes.The grown crystal was characterized by FT-IR spectral analysis, UV, H-1 and carbon -13 Nuclear magnetic resonance spectra, X-ray

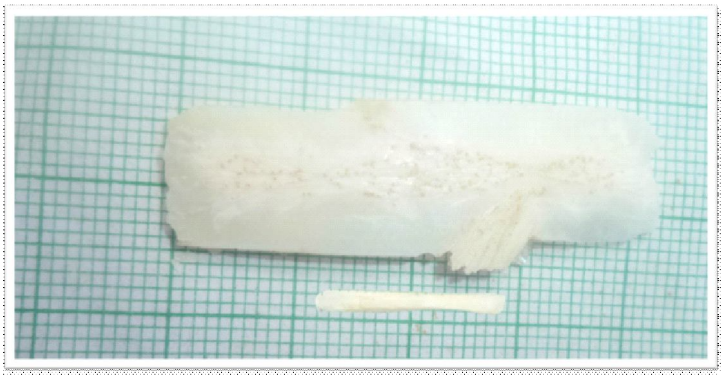


Figure 1. Crystals of [(E)-benzylideneamino] thiourea

diffraction (XRD) and TGA-DSC studies[7-12].

2. Experimental

The semi organic crystal of [(E)-benzylideneamino] thiourea (EBAT) was prepared by adopting general procedure[13-17]. To a hot solution of Thiosemicarbazone in methanol, a solution of benzaldehyde in methanol was added drop wise during 30 minutes. The mixture was stirred and refluxed for 4 hours. It was filtered and the filtrate was concentrated to half the volume. After a slow evaporation of the concentrated solution at room temperature, crystals were collected by filtration, washed with cold ethanol and dried in vacuo. The harvested crystals are shown in Figure 1. These crystals are suitable for characterization studies.

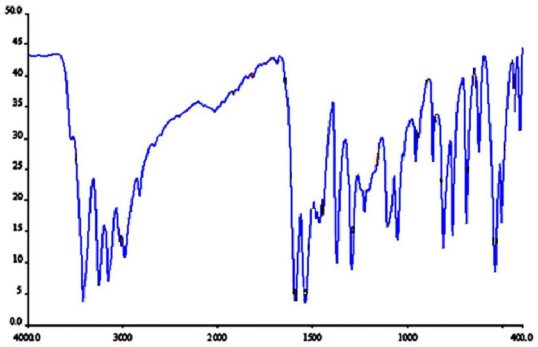
3. Result and Discussion

3.1. FT-IR Spectral analysis :

Functional groups present in the sample were analyzed using Fourier Transform Infrared spectrum[18-22]. The spectrum was recorded using AVTAR370 DTGS FT-IR spectrometer in the wavenumber range from 400-4000cm^{-1} with KBr pellet. The Fourier Infra-red spectrum (FT-IR) of the grown crystal is shown in figure-2. The observed and their corresponding group identification is given in Table-1. The band obtained at 1590cm^{-1} is due to the formation of the imine group between Benzaldehyde and Thiosemicarbazide. Due to the C=Nand N-N stretching vibration the peaks observed at below 1500 cm^{-1}. The peak observed at 1159.23cm^{-1} shows C=S stretching vibration.As expected the peak corresponds to aromatic C-H was observed at 1298cm^{-1}. There is no peak observed at 2720 cm^{-1} confirms the aldehyde functional group in [(E)-benzylideneamino] thiourea (EBAT).

Table 1.

S.No	Frequency cm^{-1}	Group identification
1	1590	C=N imine group
2	1500	N-N Stretching
3	1159	C=S Stretching
4	1298	Aromatic C-H
5	1107	NH_2 rocking



Wavenumber (cm^{-1})

Figure 2. FT-IR Spectrum of
[(E)-benzylideneamino] thiourea

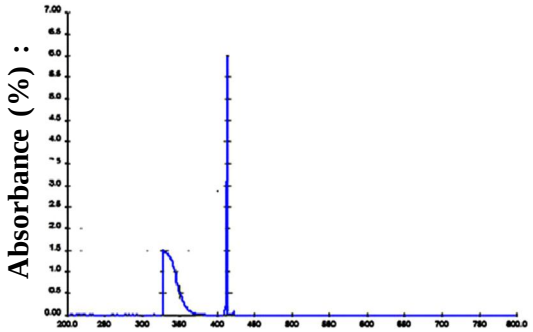


Figure 3. UV-Visible Spectrum of
[(E)-benzylideneamino] thiourea

3.2 UV Visible Spectral studies:

UV-Visible Spectral study is very useful technique to determine the optical properties and transparency of a substance[23-28]. The UV-Visible spectrum of[(E)-benzylidene-amino] thiourea (EBAT)crystal was recorded using Lambda 25 spectrometer is shown in figure 3.

This spectrum shows the characteristic absorption around 325-425nm which is assigned to asubstituted benzene with $–NH_2$ group and $–SO_3H$ group.This spectrum also confirms the aromatic nature of grown crystal. The recorded UV-Visible spectrum proves the highly transparent nature of the material between 425-800nm.This confirms the characteristic property of [(E)-benzylideneamino] thiourea (EBAT), which is suitable for optical application.

3.3 NMR Spectral analysis :

3.3.(a). ^1H NMR spectral analysis :

The proton NMR and Carbon-13 NMR spectra shows the molecular structure of the crystal[29-30]. The ^1H NMR spectral analysis was carried out on the [(E)-benzylideneamino] thiourea (EBAT) crystal in BRUKER NM-474 spectrometer. The ^1H NMR spectra of [(E)-benzylideneamino] thiourea (EBAT) is shown in figure-4. A peak observed at δ=8.24 is corresponds to the NH_2 protons of Hydrazide group. The multiplet at =7.370-7.801 confirms the presence of aromatic protons, there is no band between δ=1.8-1.9 confirms the absence of methylene group, the peak observed at δ=3.451 indicates (N-C=S) the presence of hetero sulphur atom. The peaks observed at δ=1.276 confirms the CH protons. The peak observed at δ=2.501confirms [(E)-benzylide-neamino] thiourea (EBAT) is aromatic in nature.

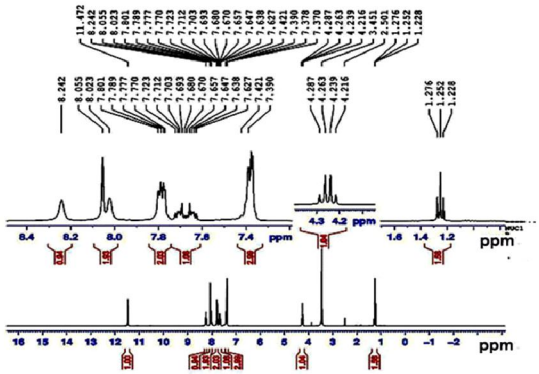


Figure 4. ^{1}H-NMR Spectrum of [(E)-benzylideneamino] thiourea

3.3.(b). ^{13}C-NMR Spectral analysis :

The ^{13}C NMR spectral analysis was carried out on the [(E)-benzylideneamino] thiourea crystal in BRUKER NM474. The ^{13}C NMR Spectra of[(E)-benzylideneamino] thiourea (EBAT) is shown in figure 5. The imine group is represented by the peak atδ=167.01 ppm The multiple peak at δ=127.36-134.74ppm represents the presence of benzene ring. The peak observed at δ=13.94ppm contains the substituted aromatic compound[31]. The presence of hetero sulphur atom from δ=40 ppm. The absence of aromatic aldehydes confirms there is no peak at 25 and 17ppm confirms the absence of methylene aliphatic group. The correlation of the signals observed in 1H and 13 C NMR spectra with the functional group is shown in Table 2.

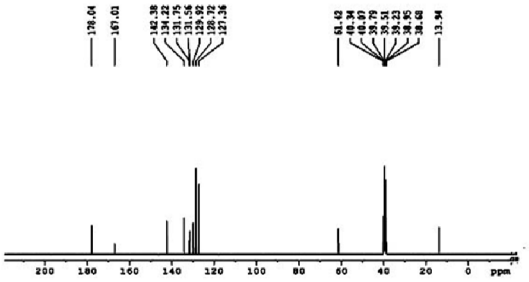


Figure 5. ^{13}C -NMR Spectrum of [(E)-benzylideneamino] thiourea

Table-2

Spectrum	Signal at δ ppm	Group identification
^{1}H	8.24	NH_2 proton of hydrazide
	7.370-7.801	Aromatic protons
	3.451	N-C=S hetero sulphur atom
	1.276	CH protons
	2.501	Aromatic nature
^{13}C	167.01	Imine group
	127.36-134.74	Benzene ring
	13.94	Substituted aromatic compound
	40	Hetero sulphur atom

3.4 *X-ray diffraction studies :*

The X-ray diffraction studies of the grown semi-organic crystal of [(E)-benzylideneamino] thiourea was recorded using BRUKER D8 ADVANCE POWDER diffractometer with Cuα radiation (α=1.5418A^{0}. The sample was scanned at a rate of 1^{o}/min in the range of 10^{0}-70^{o}. The crystalline nature and purity of the grown crystals determined by X-ray diffraction studies[36-41]. The X-ray diffraction pattern of [(E)-benzylideneamino] thiourea (EBAT) is shown in figure 6. The obtained values are in good agreement with standard values, which confirms the purity of the grown crystal and its application oriented properties.

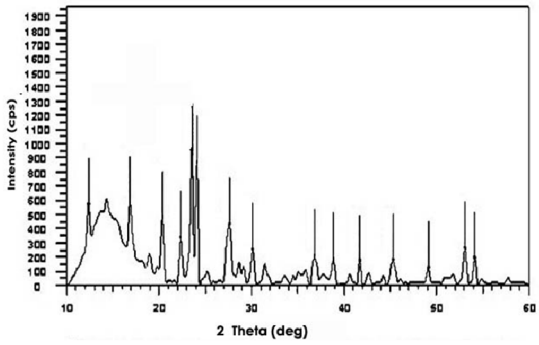


Figure 6. X-ray diffraction pattern of [(E)-benzylideneamino] thiourea

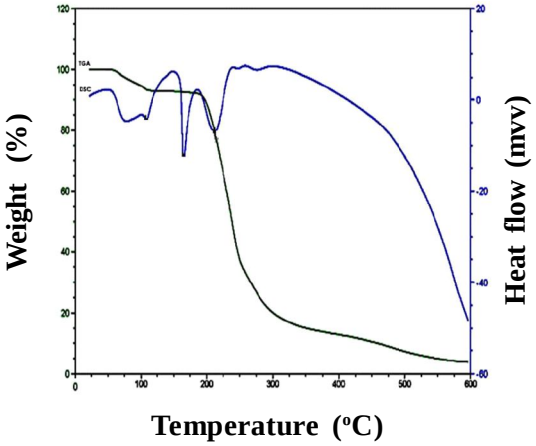


Figure 7. Thermogram of – [(E)-benzylideneamino] thiourea

3.5 Thermal analysis :

Thermal study of [(E)-benzylidene-amino] thiourea (EBAT) was analyzed using SDT Q 600V 20.9 BUILD20 instrument between the temperature o0Cto 600^0Cat a heating rate of 10^0C/minutes under nitrogen atmosphere. The thermal analysis is a very useful technique in the characterization and thermal stability of the crystal[33-35]. The thermograme of [(E)-benzylideneamino] thiourea (EBAT) shown in figure 7. The sample weight is 10.9750mg sample was taken for the measurement The Thermogram shows the endothermic peak at 153.50°C. Further shows the grown crystal has crystalline nature and thermal stability. The grown crystal begins to attain an endothermic transition and begins 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.

3.6 Nonlinear optical studies :

Kurts and perry second harmonic generation (SHG) tests[32] was performed to determine the NLO efficiency of [(E)-benzyli-deneamino] thiourea (EBAT) 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 SHG efficiency obtained for [(E)-benzylideneamino] thiourea (EBAT) is about 5.1 times that of potassium dihydrogen orthophosphate crystal.

Conclusion

[(E)-benzylideneamino] thiourea (EBAT) was prepared by using benzaldehyde and Thiosemicarbazide in methanol solution by adopting standard procedure. The crystal was grown by slow evaporation solution growth technique (SESGT). The presence of benzaldehyde group and the nature of the protons were identified by FT-IRand ^{13}C; ^{1}H NMR Spectral analysis**.** The UV-Visible spectrum reveals that the grown crystal is transparent in the

wavelength region. Thermal stability of the crystal was confirmed byTGA/DSC studies. The crystalline nature of the grown crystal was confirmed by X-ray diffraction studies.The NLO test confirms the SHG efficiency of [(E)-benzylideneamino] thiourea.

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