INFLUENCE OF SILVER NITRATE IN ORGANIC CRYSTAL OF SNTU BY VARIOUS CHARACTERISATION STUDIES

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Abstract

At 32^0c by using Ethyl alcohol is used as the solvent by the method of slow evaporation technique is adopted and a pure transparent solid organic crystal of Silver Nitrate Thiourea Urea (SNTU) was obtained. The optical property of the crystal was carried out by UV-Vis spectral study. The functional group was identified by FTIR spectral analysis. The crystals structure was characterized by XRD analysis .The thermal stability of the crystal was evaluated by thermo gravimetric and differential thermal analysis (TG-DTA). The microhardness also confirmed the stability of the crystal by the Vickers method.

Keywords: SNTU, UV-Vis, FTIR, XRD, TG-DTA

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INTRODUCTION

In the recent research, the non-linear optical (NLO) properties are conformed the various thiourea compounds [1-9]. So the young researches are very much interested to study the properties of thiourea compounds mixed with inorganic metal as dopant. Urea and thiourea represent privileged structures in medicinal chemistry. Indeed, these moieties constitute a common framework of a variety of drugs and bioactive compounds endowed with a broad range of therapeutic and pharmacological properties The non-linearity and other properties are enhanced due to the presence of metal is a key and due to the presence of hydrogen bond in thiourea also enhances the physico chemical properties. The properties of thiourea completely changes by adding various inorganic metals as dopant [10-12]. In this paper the crystal of Silver Nitrate Thiourea Urea (SNTU) are synthesised by slow evaporation technique and the characterisation studies such as UV-VIS, FTIR, XRD, TG-DTA and microhardness are carried out**.**

EXPERIMENTAL

Synthesis

Organic single crystals of SNTU were grown by preparing Silver Nitrate, Thiourea and urea were taken as equimolar ratio and dissolved by using distilled water [8-9] at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was filtered to remove insoluble impurities using Whatmann filter paper of pore size 10 micrometers. Then the solution of SNTU was taken in a beaker with a perforated lid in order to control the evaporation rate and kept at room temperature for crystallization. Finally a well fined single crystal was obtained after 14 days by slow evaporation method.

Characterization

The Shimadzu 2401 UV-VIS spectrophotometer recorded the UV spectrum of SNTU crystals in the spectral range 200 -800nm.

The thermo Nicolet 380 FTIR instrument recorded the FTIR spectrum of SNTU in the range of 400-4000cm^{-1} by the use of KBr pellet method.

The X-ray diffraction studies of the grown crystal of SNTU are carried out by the instrument of X' Per Pro-PAnalyic diffractometer.

The Perkin Elmer Pyris 6 DSC instrument used to found the TG-DTA analysis of the grown crystal of SNTU in the temperature range of 30 to 700^{0}C in the nitrogen atmosphere at the heating rate of 10^{0}C /minutes.

The micro hardness of the grown crystal of SNTU are carried out by Micro Vickers Hardness tester.

RESULTS AND DISCUSSION

The photograph of the grown crystals of urea, thiourea and SNTU are shown in Fig.1.

The physical morphological size of the crystal was 40mm x 15mm.

Fig 1 Crystal of SNTU

UV spectral analysis

The UV spectra of the grown crystal of Barium chloride Thiourea Urea (SNTU) are shown in Fig.2, 3 and 4. The observed bands have been tabulated in table 1. In SNTU, the π- π* absorption band shifted to intermediate wavelength 249.2 nm and 287nm compared to urea (236nm) and thiourea (255nm). The higher UV wavelength of urea 335nm also reduced to 324.2 in SNTU. It may be the formation of bonding between urea and thiourea through Silver metal in SNTU crystal and the decreased bond length of >C=O and >C=S and thus intermediate energy required for this transition and the absorption shows the blue end of the spectrum. Similarly, n- π* transition also shifted to higher wavelength due to less stable non-bonded electron in SNTU.

Table 1 Comparison of absorption band of urea, thiourea with SNTU

S.NO	Crystals	Absorbance	Wavelength in nm
1	Urea	0.013	335
		0.456	236
2	Thiourea	1.416	255
		1.866	240
		0.005	388
3	**SNTU**	3.432	210.2
		0.077	287.0
		0.065	249.2
		0.012	324.2

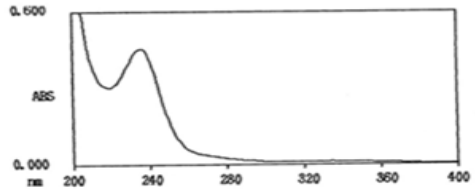

Fig. 2 UV Spectrum of Urea

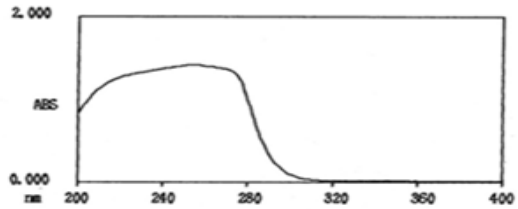

Fig. 3 UV Spectrum of Thiourea

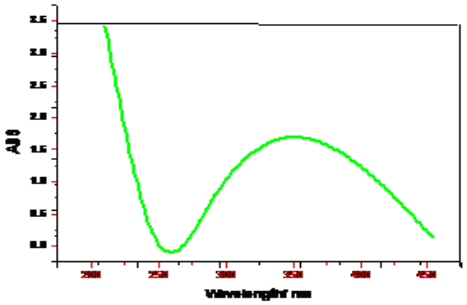

Fig. 4 UV Spectrum of SNTU

FTIR Spectral analysis

The FTIR spectra of SNTU are shown in Fig. 5. The FTIR spectral value of urea, thiourea and SNTU are given in Table 2. The high frequency N-H absorption band in the region 3100-3500cm^{-1} in the spectra of urea was shifted to lower frequencies on the formation of SNTU compound. It can be seen from the table that the bending vibration of C=S at 785cm^{-1} of urea was shifted to lower frequency in SNTU (738cm^{-1}), asymmetric C=S vibration at 1454cm^{-1} of urea was shifted to higher frequency (1467cm^{-1}) in SNTU. Similarly C-N stretching vibration at 1064cm^{-1} of thiourea was shifted to higher frequency in SNTU (1094cm^{-1}). This shows the binding of urea and thiourea is through Potassium.

The formation of hydrogen bond expected to increase the contribution to highly polar character for nitrogen to carbon and sulphur to carbon. The band observed at 2000 to 2700cm^{-1} also confirms the formation of the title compound, because delocalization of pi electrons of urea and thiourea occur at these regions.[10-13] These bands are not observed in single crystal of thiourea which was shown in the fig 5,6 and 7.

Table 2 --- FTIR assignments for urea, thiourea and SNTU

Urea (cm^{-1})	Thiourea (cm^{-1})	SNTU (cm^{-1})	Assignment
3455	3362	3366	ν_s NH_2
1625	1591	1589	γ_{as} N=C=N
---	1478	1467	ν_s C=S
1064	1093	1094	ν_s CN
---	732	738	δ_s C=S

as-asymetric; s-symmetric; δ-deformation; γ-bond stretching

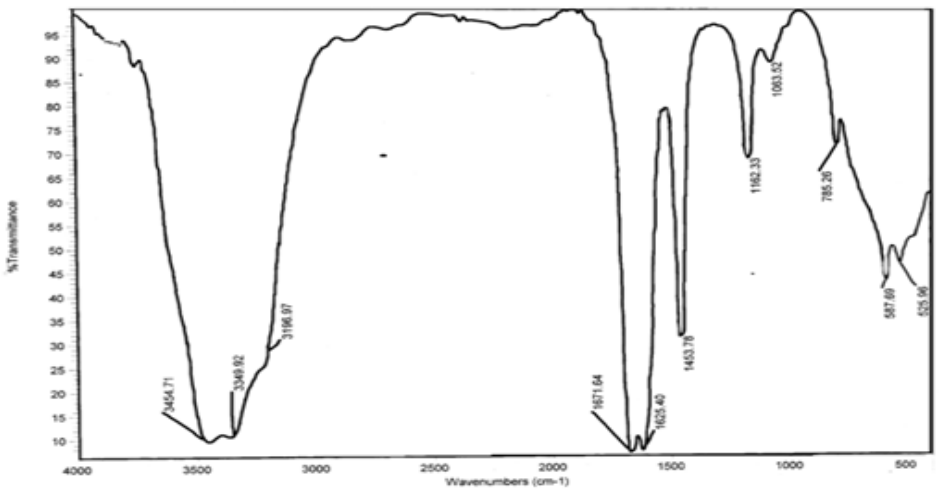

Fig. 5 FTIR Spectrum of urea

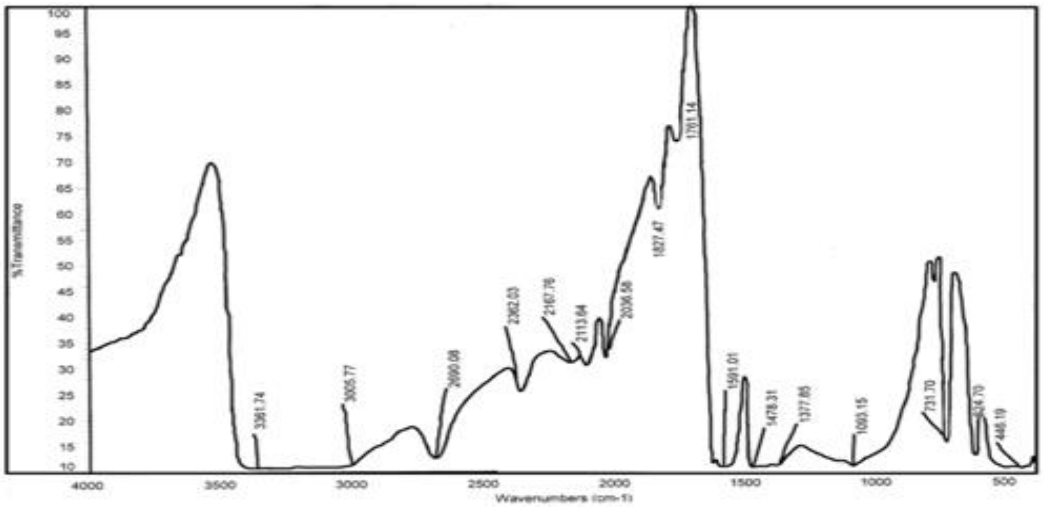

Fig. 6 FTIR Spectrum of thiourea

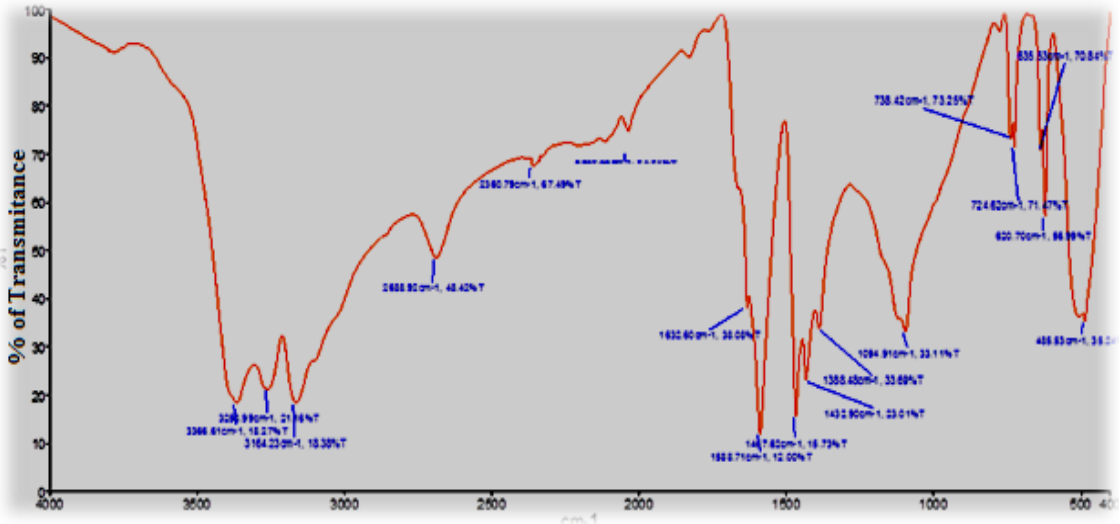

Fig 7 FTIR Specturm of SNTU

XRD Analysis

Figures 8, 9 and 10 shown in the XRD pattern of urea, thiourea and SNTU crystals respectively, the interplanar spacing d and intensity of peaks are recorded in table 2. The XRD pattern of SNTU has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in SNTU (112). The XRD of SNTU shows a up shift of the peak positions compared with urea and thiourea. However, most of the peaks in the XRD peak are not resemble with that of urea and thiourea. The unit cell dimensions of SNTU crystal were determined using RIGAKU AFC7 diffractometer.

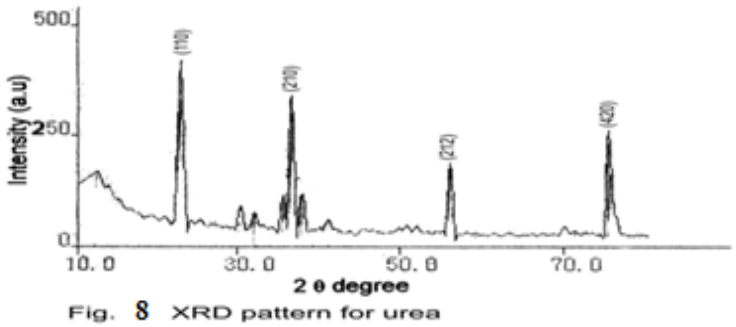

Fig. 8 XRD pattern for urea

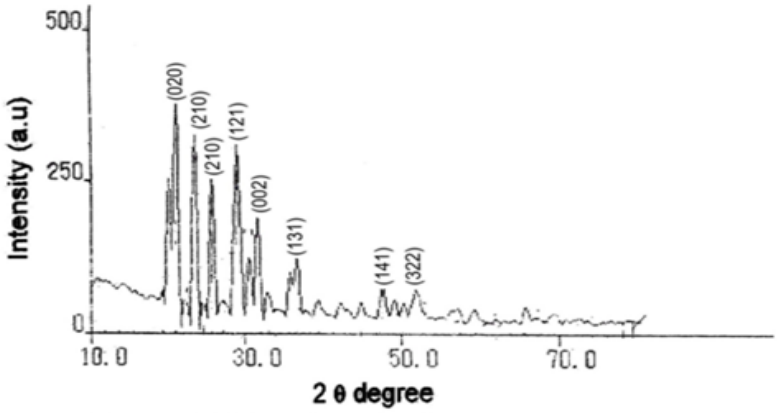

Fig. 9 XRD pattern for thiourea

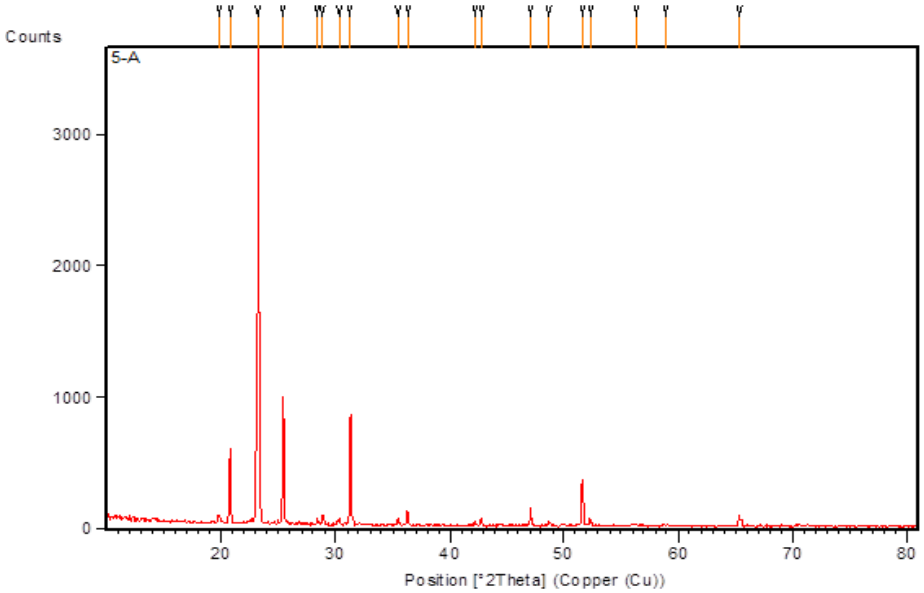

Fig. 10 XRD Pattern of SNTU

NLO test

The SHG behaviour of the powdered material was tested using Kurtz Perry method [14]. The sample was ground into very fine powder and tightly packed in a micro capillary tube. Then it was mounted in the path of Nd:YAG laser beam of 9.6 mj pulse energy obtained by splitting the original laser beam. The output light was passed through monochromator which was detected green light at 534 nm. This confirms the NLO behaviour of the material. The green light intensity registered by a photomultiplier tube and converted into an electrical signal. The same particle size of KDP was used as a reference material [15]. SHG efficiency of Thiourea urea Barium chloride was greater than that of KDP.

TG-DTA Analysis.

Thermal analysis of single crystals powder of SNTU is carried out in nitrogen atmosphere at a heating rate of 10^0C per minuets. The TG–DTA curves of SNTU are shown in Fig. 11. It is seen from the TG curve that the SNTU undergoes complete decomposition between 170 and 550^0C and exhibited three significant mass loss steps [16-18]. The initially the mass loss around 80% at 170 to 225 ^{0}C due to the decomposition of SNTU. This highest loss in the mass is due to the elimination of thiourea and urea. The subsequent mass loss between 226 to 300 and Silver nitrate. It is also confirmed by DTA curve with the corresponding endothermic DTA peak at 175 and 220^0C. The subsequent mass loss step at 251to 550^0 C is due to the elimination of SCN accompanied with 20 % mass loss with exothermic DTA peak at 225^0C. The experimental mass losses are in good agreements with the theoretical expectations. The high thermal stability of SNTU crystals arises due to strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions.

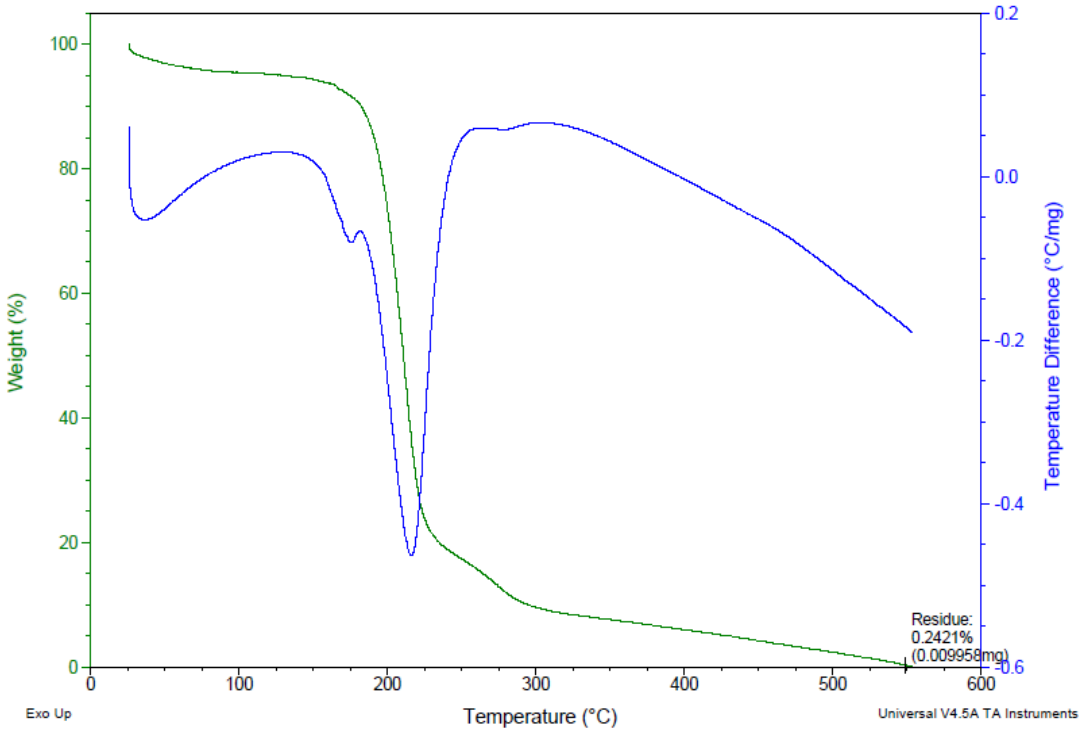

Fig. 11 TG- DTA Curve of SNTU

CONCLUSION

Single crystal of Silver Nitrate Thiourea Urea have been grown by slow evaporation technique. Powder XRD confirms the structure of the crystal. FT-IR analysis confirms the presence of functional groups present in the crystal. SHG efficiency shows that the crystal has a higher efficiency than KDP. The high thermal stability of SNTU crystals arises because of the strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions. TG curve of SNTU undergoes complete decomposition between 170 and 550^{0}C in two steps that is endothermic DTA peak at 175 and 220^{0}C and an exothermic DTA peaks at 225^{0}C which confirm the SNTU crystal has high thermal stability.

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