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Research Article

SYNTHESIS, MECHANICAL AND THERMO GRAVIMETRIC SPECTROSCOPY STUDIES OF NSTU SINGLE CRYSTAL

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ABSTRACT

In the current research, a green coloured Nickel Sulphate Thiourea Urea (NSTU) crystal with physical morphologic size of approximately 3.4 cm width x 3.7cm height size was obtained by slow evaporation method. At room temperature (30°C) distilled water was used as solvent for the prepared NSTU crystal. Various characterization studies such as FT-IR, XRD, microhardness, UV-Vis and TG-DTA were carried out for the above mentioned single crystal. From these characterizations studies the functional group, crystal structure pattern, the hardness stability by applied load, absorption of wavelength and thermal stability are determined.

Keywords: NSTU, FTIR, XRD, UV-Vis, TG-DTA.

1. INTRODUCTION

In the recent research, the non-linear optical (NLO) properties are confirmed by various thiourea compounds [1-8]. The researchers are very much interested to study the properties of thiourea compounds mixed with inorganic metal as dopant. The non-linearity and other properties are enhanced due to the presence of nickel metal bonded with thiourea. The properties of thiourea completely changes by adding various inorganic metals as dopant [9-12]. In this paper, the crystals of Nickel Sulphate Thiourea Urea (NSTU) are synthesized by slow evaporation technique. From the UV-VIS spectrum, the crystal maximum absorbance shifted to lower wavelength. FTIR studies confirmed the presence of NSTU, XRD deal about the pattern of the crystal; the crystal was found to have good thermal and mechanical stability by the help of TG-DTA and microhardness. The crystal may be useful to study antibacterial character due to the presence of sulphur in thiourea.

2. MATERIAL AND METHODS

2.1. Synthesis

Organic single crystals of NSTU were obtained when eqimolar proportion of Nickel Sulphate, Thiourea and urea are dissolved with distilled water. A homogeneous mixture of solution at 30°C was obtained. The solution was filtered to remove insoluble impurities using Whatmann filter paper of pore size 10 micrometers. The solution of NSTU 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 17 days by slow evaporation method. The photograph of the grown crystals of NSTU is shown in Fig.1. The physical morphological size of the crystal is 3.4mm x 3.7mm.

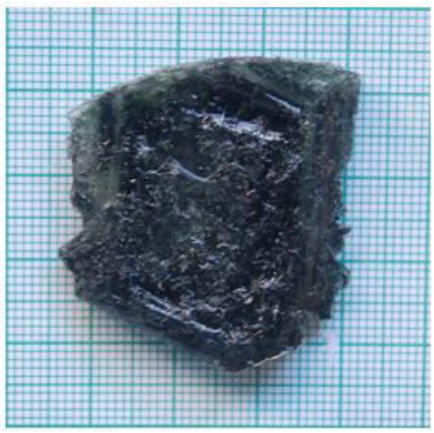

Fig. 1: Crystal of Nickel Sulphate thiourea urea (NSTU)

2.2. Characterization

The thermo Nicolet 380 FTIR instrument recorded the FTIR spectrum of NSTU in the range of 400-4000cm^{-1}

by the use of KBr pellet method. The instrument of X' Per Pro-P Analytic diffractometer was used to find out the X -ray diffraction studies. The micro hardness of the grown crystal of NSTU was carried out by Micro Vickers Hardness tester. The Shimadzu 2401 UV-VIS spectrophotometer recorded the UV spectrum of NSTU crystals in the spectral range 200-800nm. The Perkin Elmer Pyres 6 DSC instrument was used to found the TG-DTA analysis of the grown crystal of NSTU in the temperature range of 30 to 700°C in the nitrogen atmosphere at the heating rate of 10°C/minutes.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectral analysis

The FTIR spectra of NSTU are shown in Fig.2. The FTIR spectral value of urea, thiourea and NSTU are given in Table 1. 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 NSTU 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 NSTU (738cm^{-1}), asymmetric C=S vibration at 1454cm^{-1} of urea was shifted to higher frequency (1467cm^{-1}) in NSTU. Similarly C-N stretching vibration at 1064cm^{-1} of thiourea was shifted to higher frequency in NSTU (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 N-H symmetric stretching band observed at 3455 to 3364cm^{-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.

Table 1: FTIR assignments for urea, thiourea and NSTU

Urea (cm^{-1})	Thiourea (cm^{-1})	NSTU (cm^{-1})	Assignment
3455	3362	3364	ν_s NH_2
1625	1591	1632	$\gamma_{as\ N=C=N}$
---	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

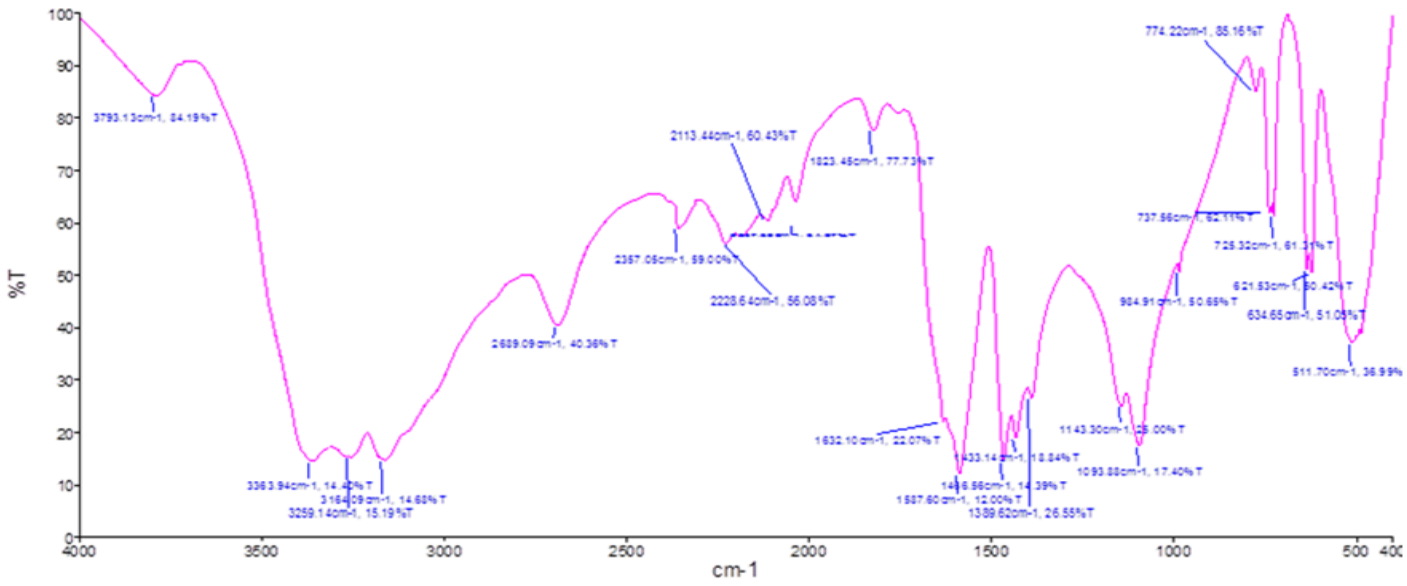

Fig. 2: FTIR spectrum OF NSTU

3.2. XRD Analysis

Figs. 3-5 show the XRD pattern of urea, thiourea and NSTU crystals respectively. The XRD pattern of NSTU has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in NSTU (110). The XRD of NSTU show an up shift of the peak positions compared with urea and thiourea. However, most of the peaks in the XRD peak does not resemble with that of urea and thiourea. The unit cell dimensions of NSTU crystal were determined using RIGAKU AFC7 diffractometer.

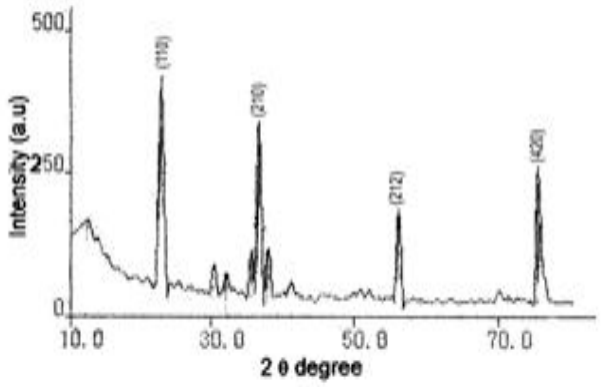

Fig. 3: XRD pattern of Urea

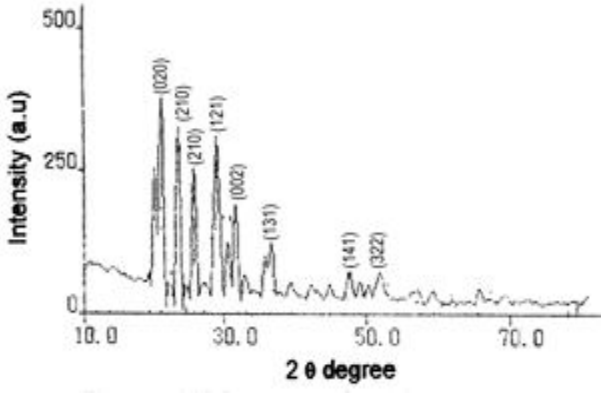

Fig. 4: XRD pattern of Thiourea

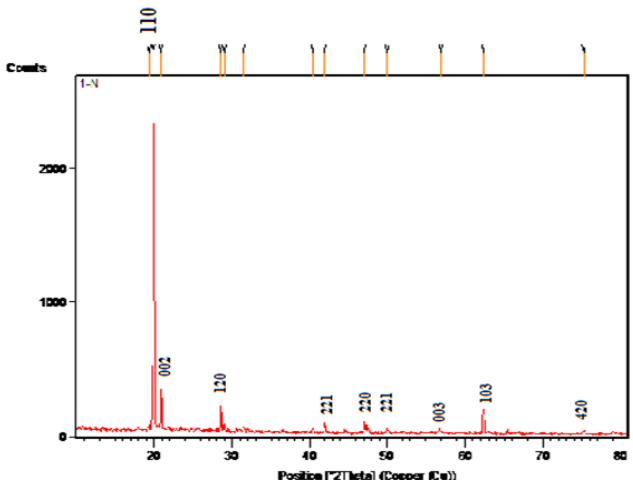

Fig. 5: XRD pattern of NSTU

3.3. Microhardness

P is the applied load and Hv is the Vickers hardness. If P increases Hv values also increases. That is shown the Table 2 and Fig.6.

Table 2: Micro hardness of NSTU

P gm	Hv kg/mm^2
25	24.2
50	45.6
100	91.8

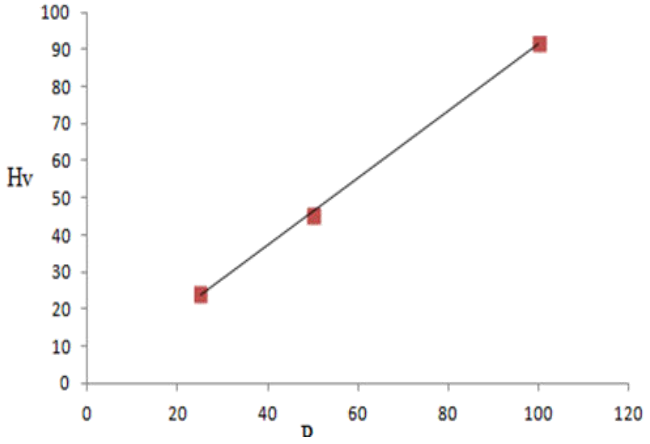

Fig. 6: Plot of HV of NSTU

3.4. NLO test

The SHG behavior 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 532 nm. This confirms the NLO behavior of the material. The emitted light intensity are recorded by a photomultiplier tube and converted into as electrical signal. The same particle size of KDP was used as a reference material [15]. SHG efficiency of NSTU was greater than that of KDP.

3.5. UV spectral analysis

The UV spectra of the grown crystal of Nickel Sulphate Thiourea Urea (NSTU) are shown in Figs.7-9. The observed bands have been tabulated in table 3. In NSTU, the π- π* absorption band shifted to inter-mediate wavelength (244nm) compared to urea (236nm) and thiourea (255nm). This is because of the formation of bonding between urea and thiourea through Nickel metal. The bond length of >C=O in urea and >C=S in Thiourea was decreased due to the presence of Nickel metal. The absorption band shows the UV region of the spectrum. Similarly, n- π* transition also shifted to higher wavelength due to less stable non-bonded electron in NSTU.

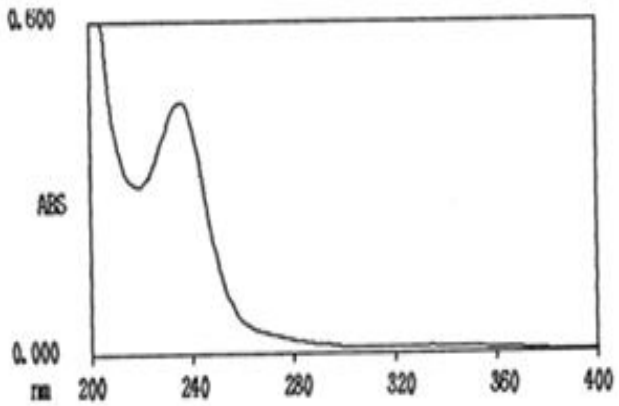

Fig. 7: UV Spectrum of Urea

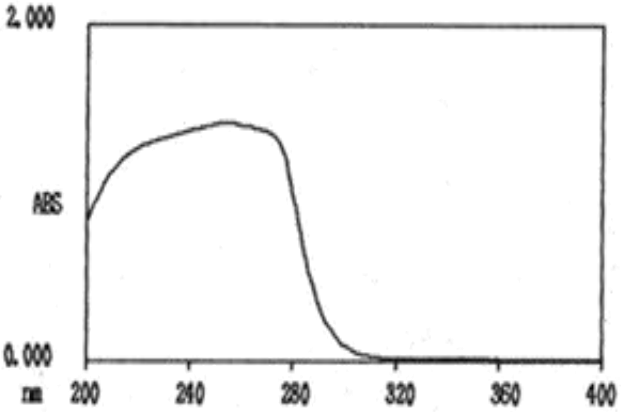

Fig. 8: UV Spectrum of Thiourea

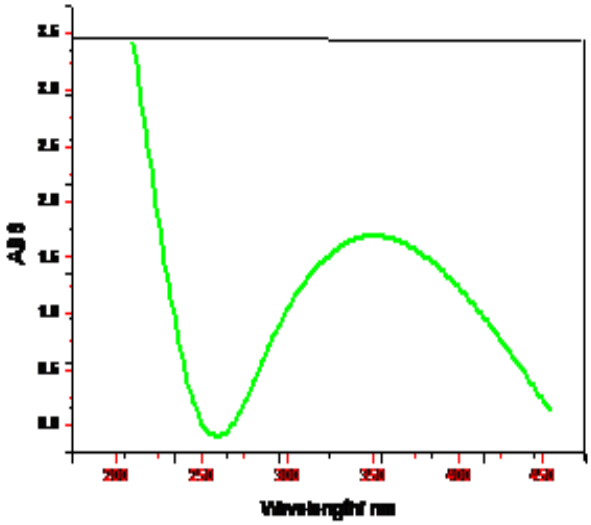

Fig. 9: UV Spectrum of NSTU

Table 3: Comparison of absorption band of urea, thiourea with NSTU

Crystals	Absorbance	Wavelength (nm)
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
NSTU	3.432	210.2
	0.737	287.0
	0.065	249.2
	0.127	324.2

3.6. TG-DTA Analysis

Thermal analysis of single crystals powder of NSTU was carried out in nitrogen atmosphere at a heating rate of 10°C per minuets. The TG-DTA curves of NSTU are shown in Fig. 10. The NSTU powder weight was taken initially 4.0460 mg in the Universal V4.5A TA Instruments. From the total weight nearly 10% of the weight was lost of the NSTU crystal at the temperature range of 175°C.

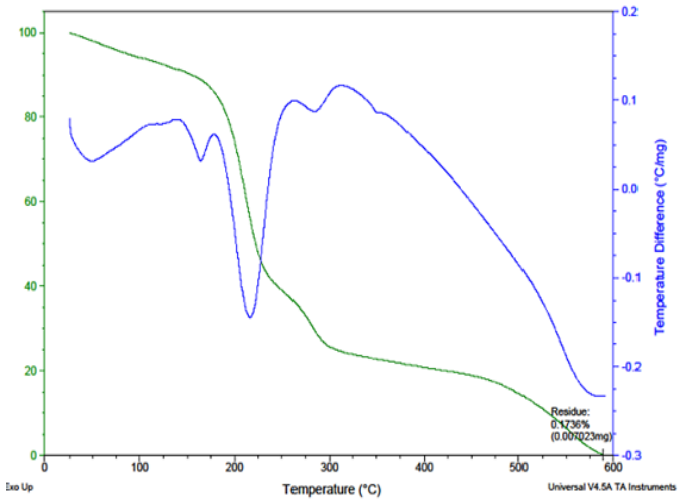

Fig. 10: TG-DTA curves of NSTU

The sample of NSTU undergoes complete decomposition between 175 and 600°C and exhibited three significant mass loss steps. From the total mass of the substance, around 65% of the NSTU was lost between the temperatures of 175 to 300°C due to the decomposition of NSTU. This highest loss in the mass is due to the elimination of thiourea. It is also confirmed by DTA curve with the corresponding endothermic DTA peak at 175 and 225°C. The subsequent loss of mass at 300 to 600°C is due to the elimination of SCN accompanied with NSTU mass loss with exothermic DTA peak at 225 to 325°C. The experimental mass

losses are in good agreements with the theoretical expectations. The high thermal stability of NSTU crystals arises due to strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions.

4. CONCLUSION

A well fined single crystal NSTU was obtained after 17 days by slow evaporation method with the physical morphological size of the crystal is 3.4mm x 3.7mm. FT-IR analysis confirms the presence of functional groups present in the crystal by the band observed in the region 3455 to 3364cm^{-1}. In the XRD studies, major (110) and (020) peak with maximum intensity is shifted in NSTU (110), it confirms that the structure of the crystal is orthorhombic. In the microhardness testing, the crystal showed very good linearity between applied load and the microhardness. In UV-VIS spectral studies, the maximum absorbance was observed in the wavelength of 210.2 nm. An NLO property shows that the crystal has a higher efficiency than KDP. The high thermal stability of NSTU crystals arises because of the strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions. TG curve of NSTU undergoes complete decomposition between 170 and 600°C in two steps that is endothermic DTA peak at 175 and 225°C and an exothermic DTA peaks at 225 to 325°C.

Conflict of interest

The authors wish to declare that there are no conflict of interest associated with this research work and similarly and there has been no financial support involved in this work that could affect its outcome.

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