UV-VIS, FTIR, XRD, TG-DTA AND MICROHARDNESS STUDIES OF NCTU ORGANIC CRYSTAL

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Abstract

The visual morphology size of the NCTU crystal is crystal is approximately 35 mm width and 36mm height size light green colour solid crystal NCTU was obtained after 16 at room temperature by using Ethanol as solvent the method of slow evaporation technique was adopted. The characterization studies were carried out for the NCTU crystal such as UV-Vis FT-IR, XRD, microhardness, and TG-DTA. From these characterizations it was useful to found the absorption of wavelength, functional group, crystal structure pattern, the hardness stability by applied load and thermal stability.

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

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1. INTRODUCTION

In the research of crystal growth, the non-linear optical (NLO) properties were confirmed from the doped thiourea urea compounds [1-8]. The scientists are very much interested to study the properties of thiourea urea compounds mixed with inorganic dopant such as barium chloride, potassium iodide, manganese chloride and nickel sulphate.[9-12] The non-linearity and other properties are enhanced due 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 urea completely changes by adding various inorganic metals as dopant [9-12]. In this paper, the crystal of Nickel Chloride Thiourea Urea (NCTU) are synthesized by slow evaporation technique and the characterization studies such as UV-VIS, FTIR, XRD, TG-DTA and microhardness are carried out**.**

2. MATERIAL AND METHODS.

2.1. Synthesis

Organic single crystals of NCTU were grown by preparing Nickel Chloride, Thiourea and urea was taken as 1:1:1 ratio in ethanol at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was filtered off to remove insoluble impurities using Whatmann filter paper of pore size 10 micrometers. The solution was taken in a beaker with a perforated lid in order to control the evaporation rate and kept aside for few days. Finally, a well fined light green colour single crystal was obtained after 16 days. The photograph of the grown crystal of NCTU is shown in Fig.1. The physical morphological size of the crystal is 35 mm width and 36mm.

Fig. 1: Crystal of Nickel Chloride thiourea urea (NCTU)

2.2. Characterization

By the use of KBr pellet method thermo Nicolet 380 FTIR instrument recorded the FTIR spectrum of NCTU in the range of 400-4000cm^{-1}. The instrument of X' Per Pro-P Analytic diffractometer was used to find out the X -ray diffraction studies.

By Vickers Hardness method the micro hardness of the grown crystal of NCTU was carried out. The Shimadzu 2401 spectrophotometer recorded the UV-Vis spectrum in the spectral range 200-800nm. The TG-DTA analysis of the grown crystal of NCTU was Carried out by Perkin Elmer Pyres 6 DSC instrument in the temperature range of 30˚C 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 NCTU are shown in Fig.2. The FTIR spectral value of urea, thiourea and NCTU 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 NCTU compound. It can be seen from the table that the bending vibration of C=S at 776cm^{-1} of thiourea was shifted to lower frequency in NCTU (737cm^{-1}), asymmetric C=S vibration at 1456cm^{-1} of urea was shifted to higher frequency (1468cm^{-1}) in NCTU. Similarly C-N stretching vibration at 1063cm^{-1} of thiourea was shifted to higher frequency in NCTU (1095cm^{-1}). This shows the binding of urea and thiourea is through Nickel.

The formation of hydrogen bond expected to increase the contribution to highly polar character for nitrogen to carbon and sulphur to carbon. the N=C=N asymmetric stretching vibration of urea 1625cm^{-1} was increased as 1632cm^{-1} in NCTU. The N-H symmetric stretching band observed at 3464 to 3356cm^{-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 NCTU

Urea (cm^{-1})	Thiourea (cm^{-1})	NCTU (cm^{-1})	Assignment
3464	3356	3364	ν_s NH_2
1625	1591	1632	$\gamma_{as\ N=C=N}$
---	1456	1468	ν_s C=S
1063	1093	1095	ν_s CN
---	776	737	δ_s C=S

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

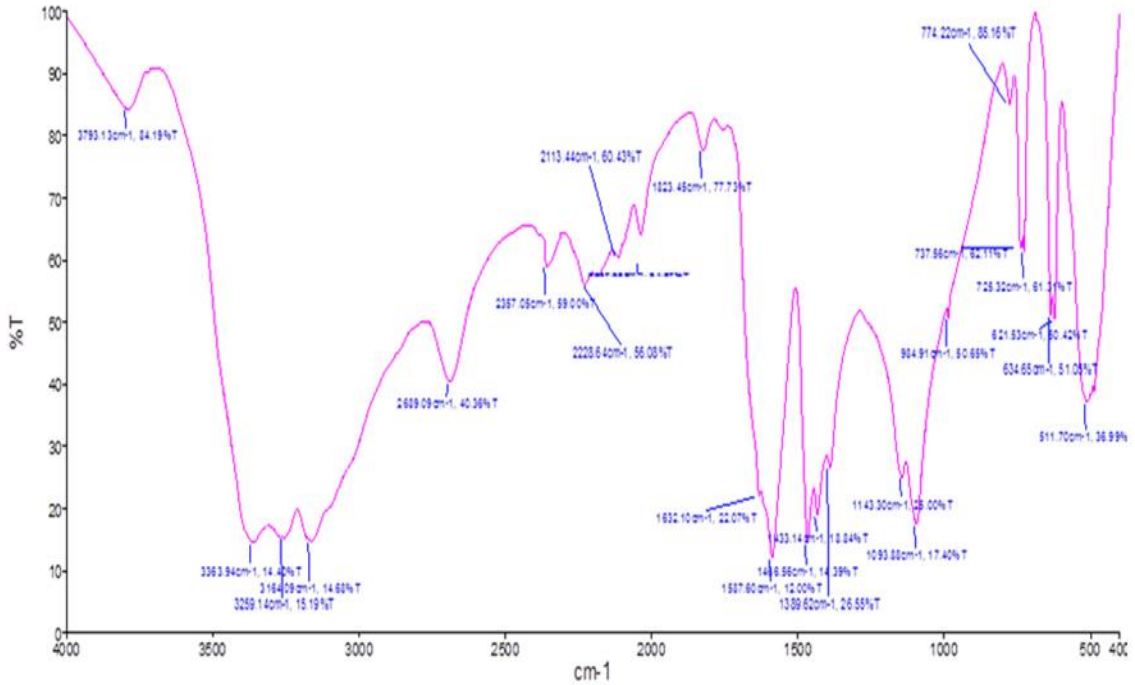


Fig. 2. The FTIR spectrum OF NCTU

3.2. XRD Analysis

The unit cell dimensions of NCTU crystal were determined using RIGAKU AFC7 diffractometer. The following Figures. 3, 4 and 5 are the XRD pattern of urea, thiourea and NCTU crystals respectively. The XRD pattern of NCTU crystal are compared with urea and thiourea where the major peaks such as (110) and (020) with maximum intensity is shifted in NCTU (110). The XRD of NCTU shown 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.

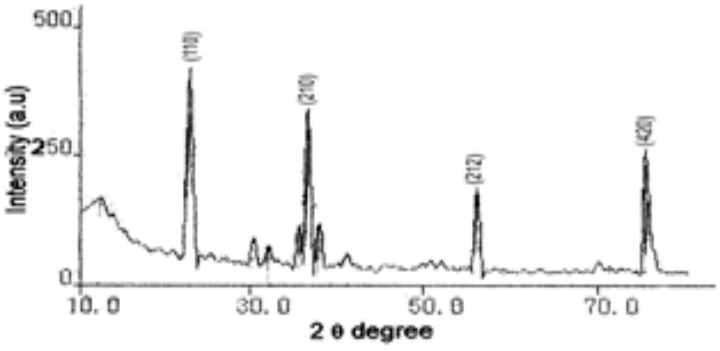


Fig .3 XRD pattern of Urea

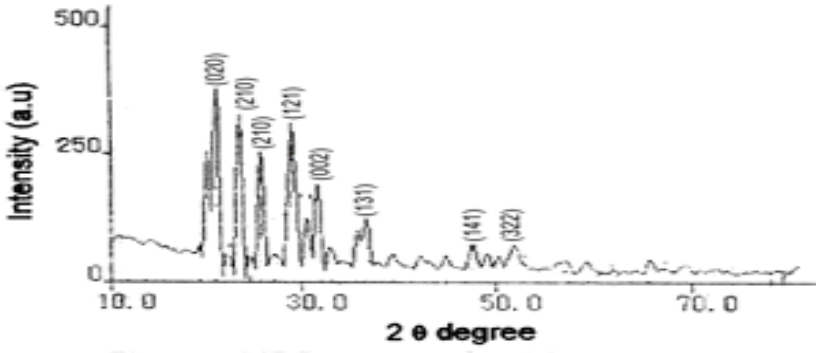


Fig . 4 XRD pattern of Thiourea

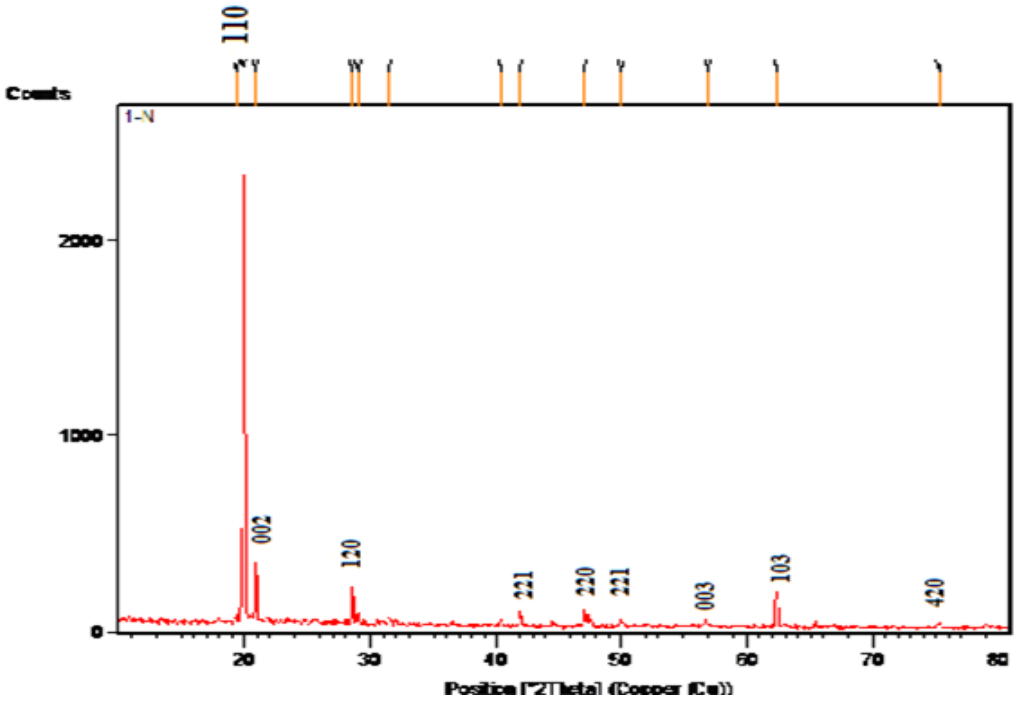


Fig . 5 XRD pattern of NCTU

3.3. Microhardness.

By Vickers Hardness method the micro hardness of the grown crystal of NCTU was carried out. P is the applied load and Hv is the Vickers hardness. If P increases Hv values also increases. That was shown the Table 2 and fig.6. this indicates the crystal have good stability.

Table 2: Micro hardness of NCTU

S.No	P gm	Hv kg/mm^2
1	25	**24.5**
2	50	**45.9**
3.	100	**91.8**

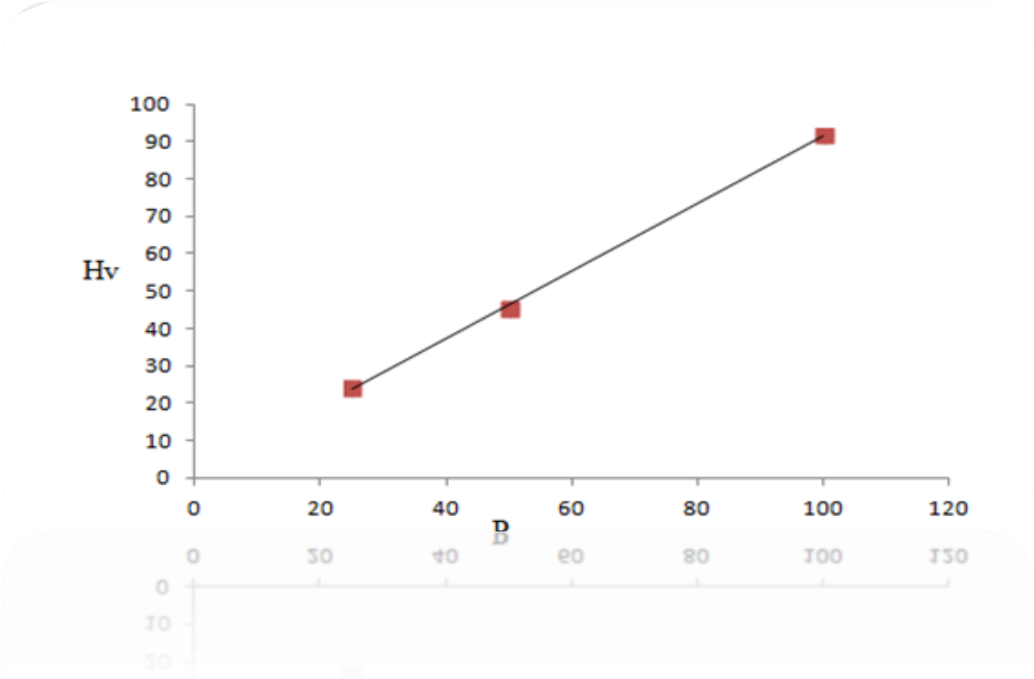


Fig 6 Plot of HV of NCTU

3.4 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 532 nm. This confirms the NLO behavior 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 NCTU was greater than that of KDP.

3.5 UV spectral analysis

The UV spectra of the grown crystal of Nickel Chloride Thiourea Urea (NCTU) are shown in Fig.7, 8 and 9. The observed bands have been tabulated in table 3. In NCTU, the π- π* absorption band shifted to intermediate UV wavelength (243nm) compared to urea (235nm) and thiourea (254nm). In visible region the absorbance are very low in NCTU compared to Urea (335nm and 324.2). 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 NCTU.

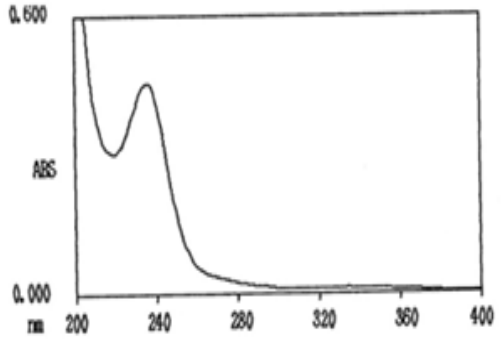


Fig 7 UV Spectrum of Urea

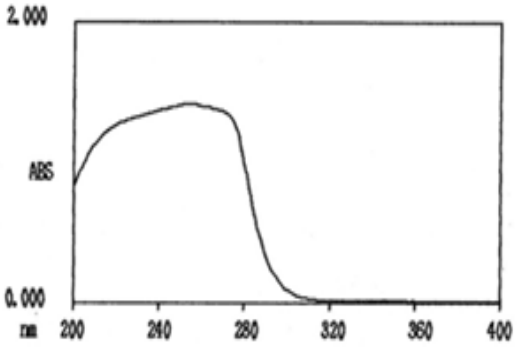


Fig 8 UV Spectrum of Thiourea

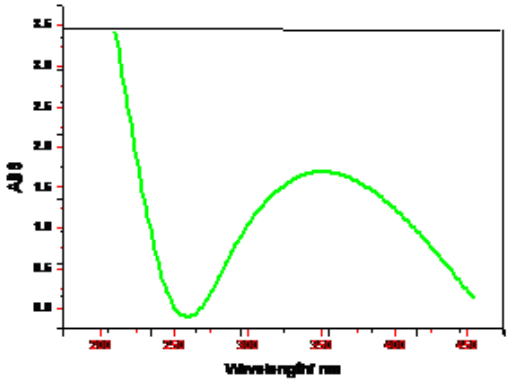


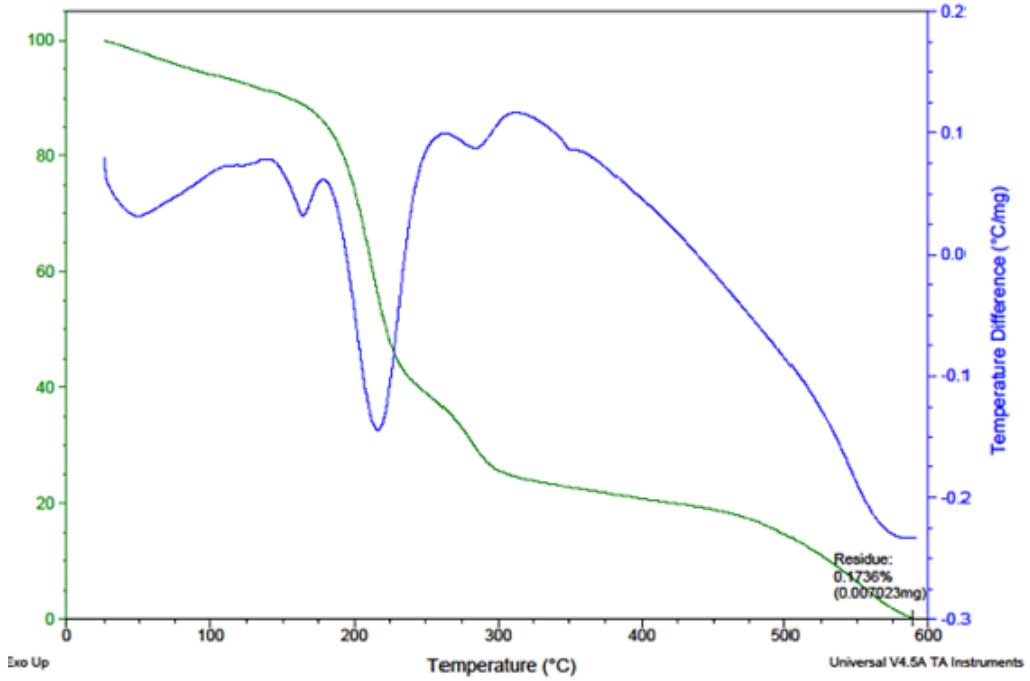
Fig 9 UV Spectrum of NCTU

Table 3. Comparison of absorption band of urea, thiourea with NCTU.

Crystals	Absorbance	Wavelength in nm
Urea	0.013	335
	0.456	243
Thiourea	1.416	235
NCTU	3.432	212.4
	0.737	254.0
	0.065	249.2
	0.127	324.2

3.6 TG-DTA Analysis.

The TG-DTA analysis of the grown crystal of NCTU was Carried out by Perkin Elmer Pyres 6 DSC instrument in the temperature range of 30˚C to 700˚C in the nitrogen atmosphere at the heating rate of 10˚C/minutes. It was shown in Fig. 10. The NCTU powder weight was taken initially 4.0460 mg in the Universal V4.5A TA Instruments the substance up to 175^{0}C gradual weight loss that is only 10% of the total sample size. The sample of NCTU undergoes complete decomposition between 176 and 600^{0}C and exhibited three significant mass loss steps. Form the total mass of the substance around 65% of the NCTU was loss between the temperatures of 176 to 300 ^{0}C due to the decomposition of NCTU. This highest loss in the mass is due to the elimination of thiourea urea. It is also confirmed by DTA curve with the corresponding endothermic DTA peak at 176 and 230^{0}C. The subsequent mass loss step at 300 to 600^0 C is due to the elimination of SCN accompanied with NCTU mass loss with exothermic DTA peak at 231 to 300^{0}C. The experimental mass losses are in good agreements with the theoretical expectations. The high thermal stability of NCTU crystals arises due to strong bond existing between the conjugation layers of thiourea urea molecule and the nickel ions.



4. CONCLUSION

Finally a well fined single crystal NCTU was obtained after 16 days by slow evaporation method with the physical morphological size of the crystal is approximately 35 mm width and 36mm height. FT-IR analysis confirms the presence of functional groups present in the crystal that the band observed in the region 3464 to 3356cm^{-1}. In the XRD studies, major (110) and (020) peak with maximum intensity is shifted in NCTU (110), it confirms the structure of the crystal is belongs to orthorhombic. In the microhardness testing, the crystal showed very good linearity between applied load and the microhardness. In UV-VIS spectral studies of NCTU the maximum absorbance was observed in the wavelength of 212.4nm. An NLO property shows that the NCTU crystal has a higher efficiency than KDP. The high thermal stability of NCTU crystals arises because of the strong bond existing between the conjugation layers of thiourea urea molecule and the Nickel metal ions. TG curve of NCTU undergoes complete decomposition between 176 and 600˚C in two steps that is endothermic DTA peak at 176 and 230˚C and an exothermic DTA peaks at 231 to 300˚C.

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