

# Thermal, UV, XRD and FTIR studies of Thiourea Urea Potassium Iodide single crystal

<sup>1</sup>M. Thendral, \*G. Selvarajan, \*M. Mariappan

<sup>1</sup>Assistant Professor of Chemistry, E.G.S.P. Arts and Science College, Nagapattinam, Tamil Nadu, India.

\*Assistant Professor, PG and Research Department of Chemistry, Thiru.Vi. Ka. Government Arts College, Thiruvavur-610 003, Tamil Nadu, India.

Corresponding authors: mmari101@gmail.com & selvarajangesan2014@gmail.com

**ABSTRACT** - The single crystal of Thiourea Urea potassium iodide (TUPI) was obtained from aqueous solution by a slow evaporation technique at room temperature. The UV-Vis spectral study was carried out to test the optical transmitting property. The functional group of grown crystal was found by FTIR analysis. The crystals were characterized by X-ray diffraction analysis. The nonlinear optical property was confirmed by Kurtz Perry powder technique. The thermal stability of the crystal was evaluated by thermo gravimetric and differential thermal analysis (TG-DTA).

**Keywords:** TUPI, XRD, UV-Vis, FTIR, TG-DTA

## I. INTRODUCTION

Nonlinear optic (NLO) frequency conversion materials have a significant impact on laser technology, optical communication and optical storage technology. The search for frequency conversion materials over the past decades has led to the discovery of many NLO materials with high nonlinear susceptibilities. However their often inadequate transparency, poor optical quality, lack of robustness, low laser damage threshold and inability to grow organic materials in practical device application [1-6]. Moreover, growth of large sized single crystals has excellent mechanical and thermal properties but they possess relatively modest nonlinearity. Due to the above reason, a lot of research has been carried out on semi organic materials which have combined properties of both organic and inorganic materials [7]. In this present work, mixed crystals of Thiourea urea potassium iodide (hereafter abbreviated as TUPI) have been grown by slow evaporation technique at room temperature. The changes in the FTIR, X-ray diffraction (XRD), hardness parameters and thermal stability have been studied.

## II. EXPERIMENTAL

### Synthesis

Single crystals of Thiourea urea potassium iodide was grown by preparing Thiourea, urea and potassium iodide taken in 1:1:1 equimolar ratio in triple 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 Thiourea urea potassium iodide 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 16 days by slow evaporation method.

## III. RESULTS AND DISCUSSION

The photograph of the grown crystals of urea, thiourea and TUPI is shown in Fig.1,2 and 3.



Fig. 1 Urea



Fig. 2 Thiourea



Fig.3 TUPI

### UV spectral analysis

The UV spectra for urea, thiourea and (hereafter Thiourea Urea Potassium Iodide abbreviated as TUIPI) TUIPI are shown in Fig. 4, 5 and 6. The observed bands have been tabulated in table 1. In TUIPI, the  $\pi$ - $\pi^*$  absorption band shifted to longer wavelength compared to urea. This is because of the formation of bonding urea and thiourea through potassium, decreases the bond length of  $>C=O$  and  $>C=S$  and thus smaller energy required for this transition and hence the absorption shows the blue end of the spectrum. Similarly,  $n$ - $\pi^*$  transition also shifted to higher wavelength due to less stable non-bonded electron in TUIPI.

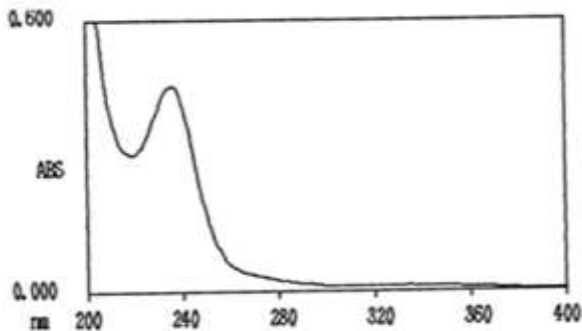


Fig. 4 UV Spectrum of Urea

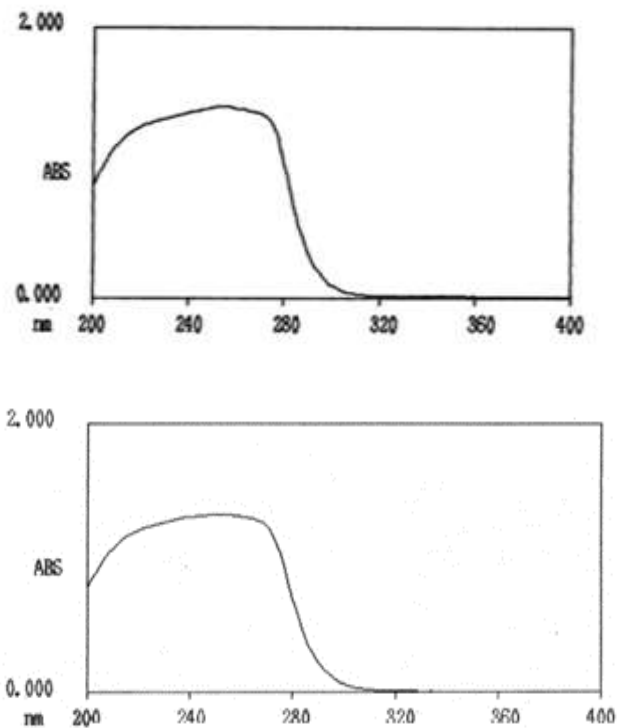


Fig 6. UV-spectrum of TUIPI

**Table 1** Comparison of absorption band of urea, thiourea with TUIPI

Crystals	Absorbance	Wavelength in nm
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
TUIPI	1.480	210
	1.866	240
	0.005	388

### FTIR Spectral analysis

The FTIR spectra for urea, thiourea and TUIPI are shown in Fig. 7, 8 and 9. The high frequency N-H absorption band in the region  $3100$ - $3500\text{cm}^{-1}$  in the spectra of urea was shifted to lower frequencies on the formation of TUIPI compound. It can be seen from the table that the bending vibration of  $C=S$  at  $785\text{cm}^{-1}$  of urea was shifted to lower frequency in TUIPI ( $738\text{cm}^{-1}$ ), asymmetric  $C=S$  vibration at  $1454\text{cm}^{-1}$  of urea was shifted to higher frequency ( $1468\text{cm}^{-1}$ ) in TUIPI. Similarly  $C-N$  stretching vibration at  $1064\text{cm}^{-1}$  of thiourea was shifted to higher frequency in TUIPI ( $1093\text{cm}^{-1}$ ). 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  $2700\text{cm}^{-1}$  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 2 --- FTIR assignments for urea, thiourea and TUIPI

Urea ( $\text{cm}^{-1}$ )	Thiourea ( $\text{cm}^{-1}$ )	TUIPI ( $\text{cm}^{-1}$ )	Assignment
3455	3362	3368	$\nu_s \text{NH}_2$
1625	1591	1589	$\nu_{as} \text{N}=\text{O}=\text{N}$
1454	1478	1468	$\nu_s \text{C}=\text{S}$
1064	1093	1093	$\nu_s \text{CN}$
785	732	738	$\delta_s \text{C}=\text{S}$

*as-asymmetric; s-symmetric;  $\delta$ -deformation;  $\nu$ -bond stretching*

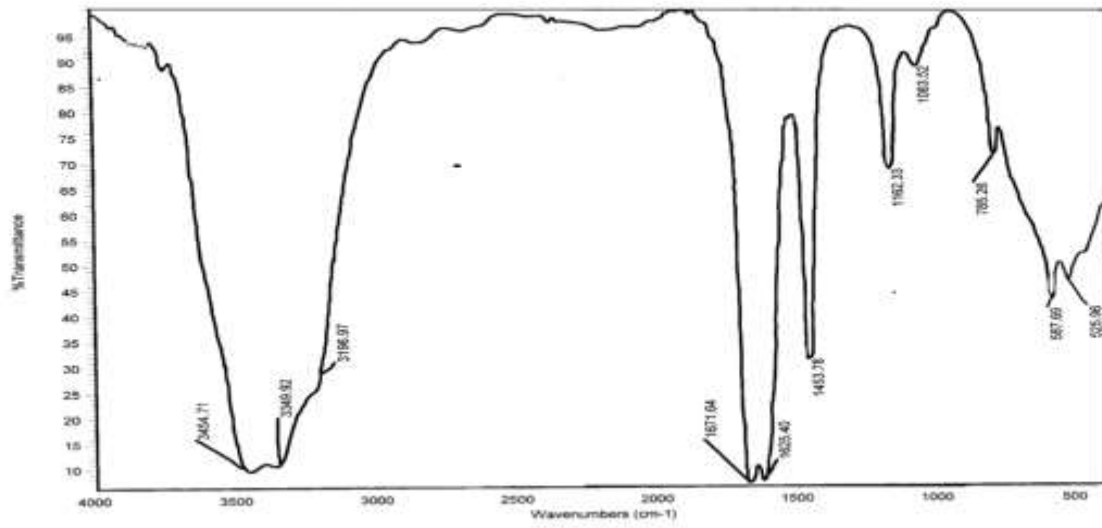


Fig.7 FTIR Spectrum of urea

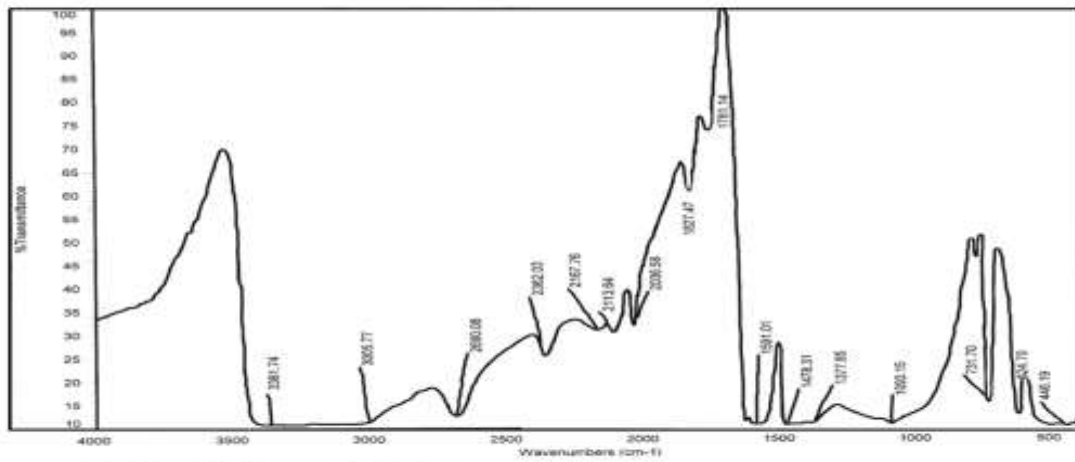


Fig. 8 FTIR Spectrum of thiourea



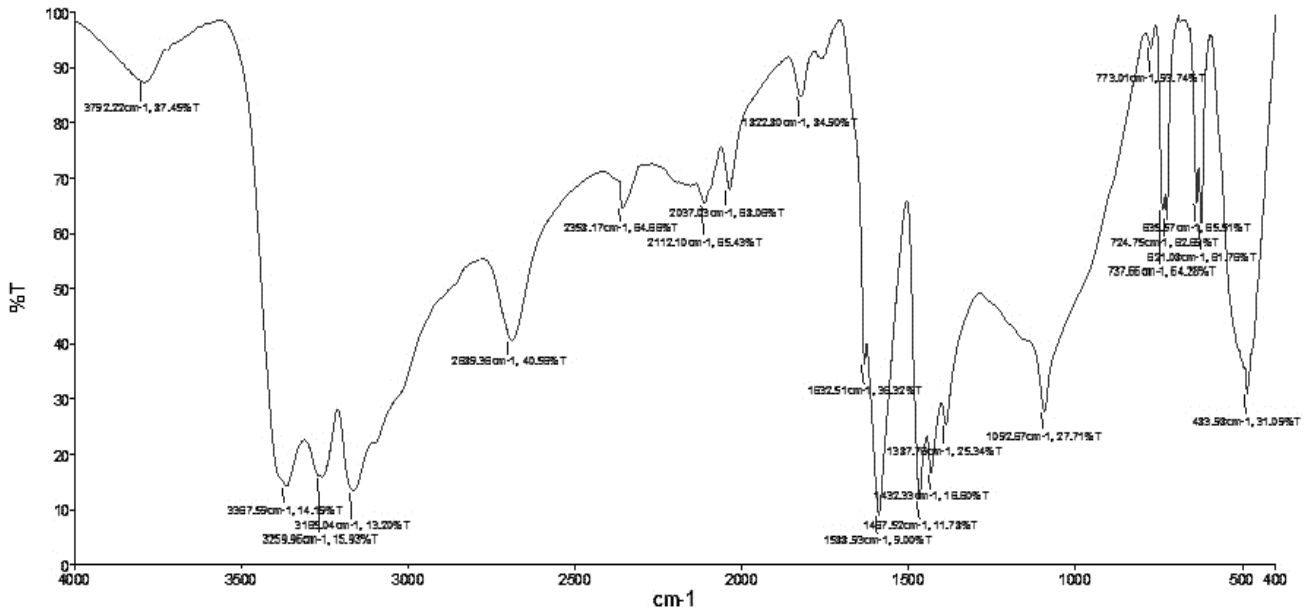


Fig 9 FTIR spectrum of TUPI

### XRD Analysis

Figures 10,11 and 12 show the XRD pattern of urea, thiourea and TUPI crystals respectively, the interplanar spacing *d* and intensity of peaks are recorded in table 2. The XRD pattern of TUPI has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in TUPI (112). The XRD of TUPI show 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 TUPI crystal were determined using RIGAKU AFC7 diffractometer.

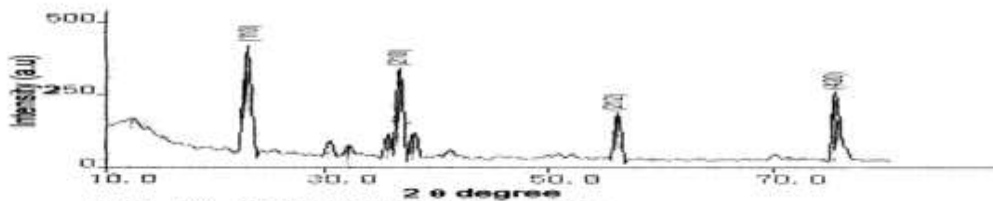


Fig. 10 XRD pattern for urea

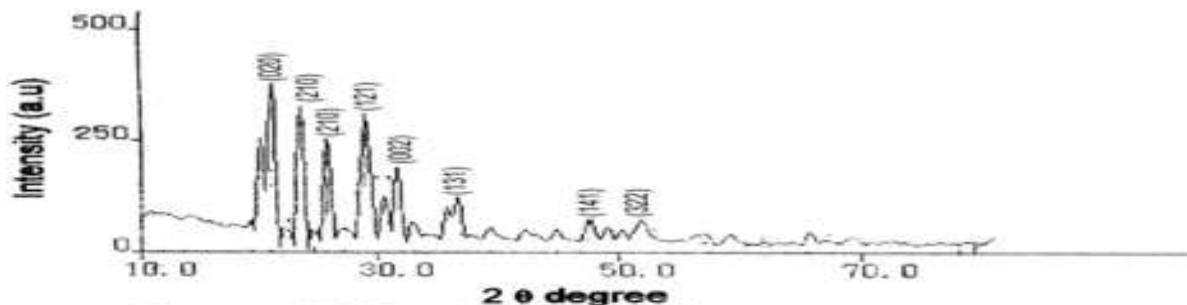


Fig. 11 XRD pattern for thiourea

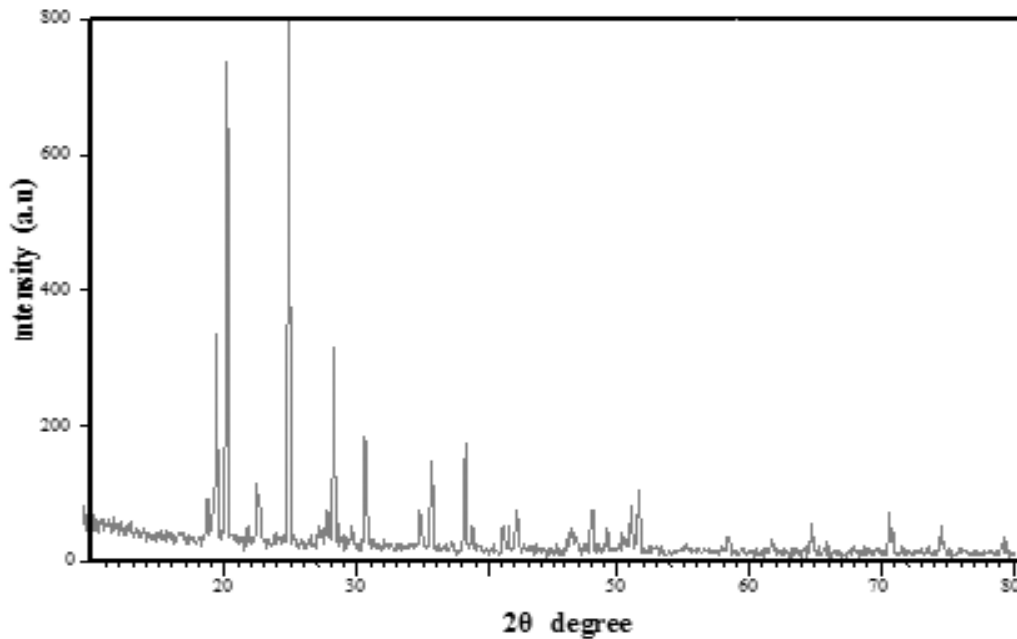


Fig. 12 XRD pattern for TUPI

#### 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 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 potassium iodide was greater than that of KDP.

#### IV. CONCLUSION

Single crystals of Thiourea urea potassium iodide were 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.

#### REFERENCES

- [1] R. Ezhilvizhi, S. Kalainathan, G. Bagavannarayana, *Cryst Res Technol.* 2008, 43, 778.
- [2] S.Sangeetha, G.Selvarajan, *Int. Res. J. Environmental Sci.* 2017, 6(11), 10-15.
- [3] D. Jayalakshmi, J. Kumar, *Cryst Res Technol*, 2006, 41, 37.
- [4] S. Selvakumar, M. Ravikumar, K. Rajarajan, *J Cryst Growth Design*, 2006, 11, 2607.
- [5] K. Selvaraju, R. Valluvan, S. Kumararaman, *Mat Lett.* 2006, 44, 577.
- [6] P.A. Franken, A.E Hill, C.W. Peters, G. Weinreich, *Phys. Rev. Lett.*, 1961, 7, 118.
- [7] G. Madhurambal, M. Mariappan, S. Hariharan, P. Ramasamy, S.C. Mojumdar, *J Therm Anal Calorim.* 2013, 112 (2), 1127.
- [10] A. More, V.M.S. Verenkar, S.C. Mojumdar, *J Therm Anal Calorim.* 2008, 94, 63.
- [11] G.Madurambal, M.Mariappan, G.Selvarajan, S.C. Mojumdar, *J. Therm. Anal and Calorim.*, 2015, 119 (2), 931.
- [12] R. Rajasekaran, K.V. Rajendran, *Mater Chem Phys.* 2003, 82, 273.
- [13] G. Li, L. Xue, g. Su and Y. Ha, *Cryst. Res. Technol.* 40 (2005) 867.
- [14] M.Thendral, M.Mariappan, G.Selvarajan, 2018, *International Journal of Current Research in Life Sciences*, 7, (05), 2121-2125.
- [15] R. Ezhilvizhi, S. Kalainathan, G. Bagavannarayana, *Cryst Res Technol.* 2008, 43, 778.