

Synthesis and Characterisation of a Single crystal of Thiourea Urea Barium chloride

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ABSTRACT - The transparent solid organic crystal of Thiourea Urea Barium chloride (TUBC) was obtained from aqueous solution of water 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 XRD analysis. The thermal stability of the crystal was evaluated by thermo gravimetric and differential thermal analysis (TG-DTA). The nonlinear optical property was confirmed by Kurtz Perry powder technique.

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

I. INTRODUCTION

Crystals have fascinated man from times immemorial by virtue of their brilliant colors, geometrical forms and symmetry. The crystals play a significant role in the present scenario and extensively used as frequency controlled oscillators, radiation detectors, optoelectronics, transistors, tunnel-diodes and also magnetic devices, ultrasonic amplifiers, lasers and lenses. 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 Barium chloride (hereafter abbreviated as TUBC) 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 ANALYSIS

Synthesis

Organic single crystals of Thiourea urea Barium chloride was grown by preparing Thiourea, urea and Barium chloride taken as equal molar ratio in tested 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 Barium chloride 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.

III. RESULTS AND DISCUSSION

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

UV spectral analysis

The UV spectra for urea, thiourea and (hereafter Thiourea Urea Barium chloride abbreviated as TUBC) TUBC are shown in Fig. 4, 5 and 6. The observed bands have been tabulated in table 1. In TUBC, the π - π^* 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 - π^* transition also shifted to higher wavelength due to less stable non-bonded electron in TUBC.



Fig.1 Urea



Fig.2 Thiourea



Fig.3 TUBC

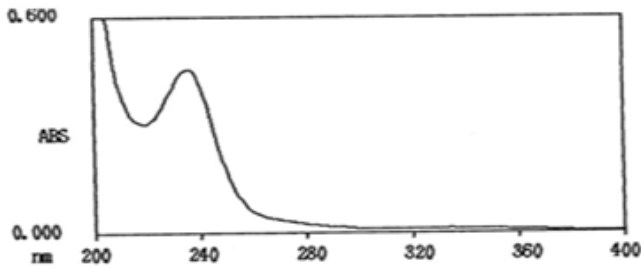


Fig.4 UV Spectrum of Urea

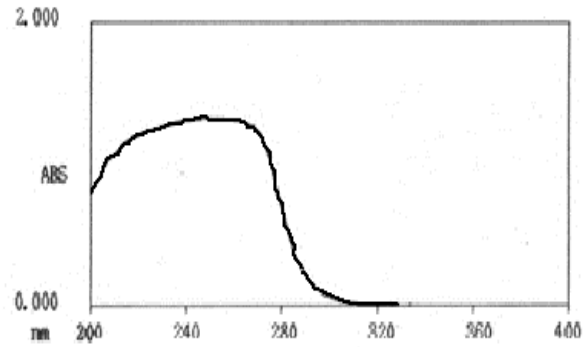


Fig 6. UV - Spectrum of TUBC

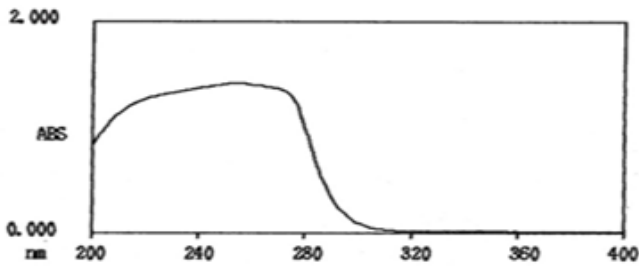


Fig.5 UV Spectrum of Thiourea

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

Crystals	Absorbance	Wavelength in nm
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
TUBC	1.480	212
	1.866	244
	0.005	382

FTIR Spectral analysis

The FTIR spectra for urea, thiourea and TUBC are shown in Fig. 7, 8 and 9. 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 TUBC 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 TUBC (738cm⁻¹), asymmetric C=S vibration at 1454cm⁻¹ of urea was shifted to higher frequency (1486cm⁻¹) in TUBC. Similarly C-N stretching vibration at 1064cm⁻¹ of thiourea was shifted to higher frequency in TUBC (1092cm⁻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.

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

Urea (cm ⁻¹)	Thiourea (cm ⁻¹)	TUBC (cm ⁻¹)	Assignment
3455	3362	3364	ν_s NH ₂
1625	1591	1589	γ_{as} N=C=N
1454	1478	1486	ν_s C=S
1064	1093	1092	ν_s CN
785	732	738	δ_s C=S

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

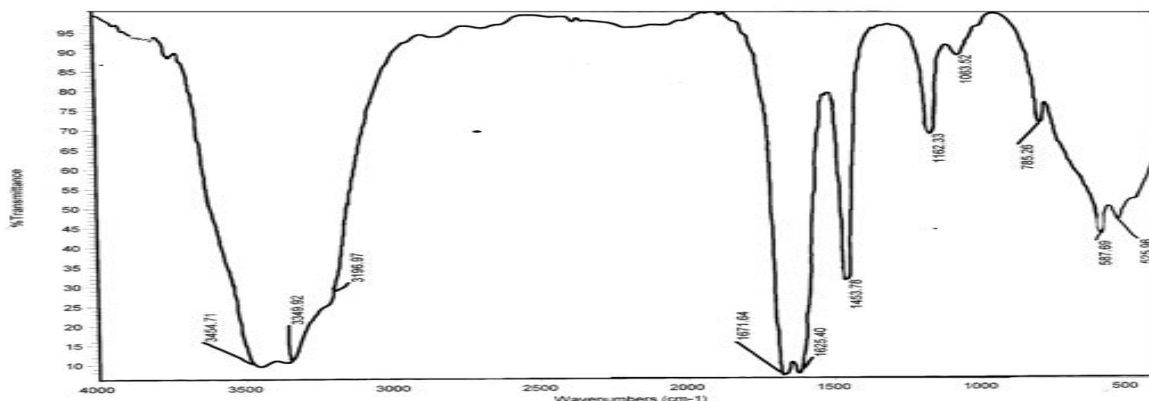


Fig.7 FTIR Spectrum of urea

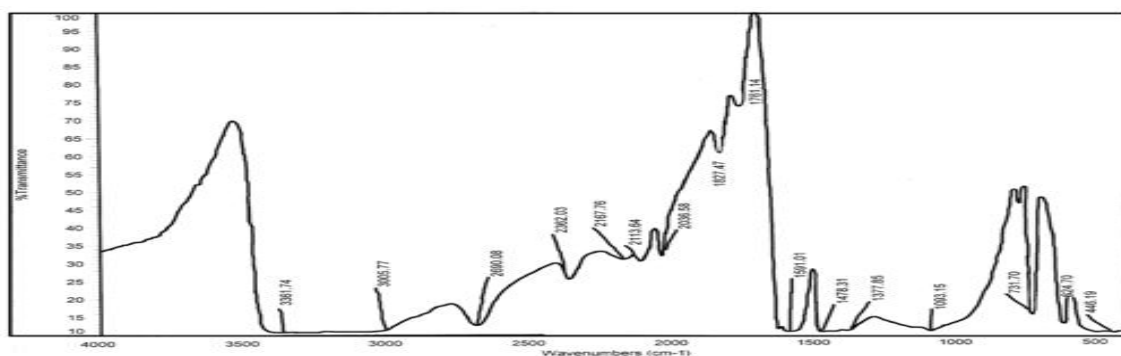


Fig.8 FTIR Spectrum of thiourea

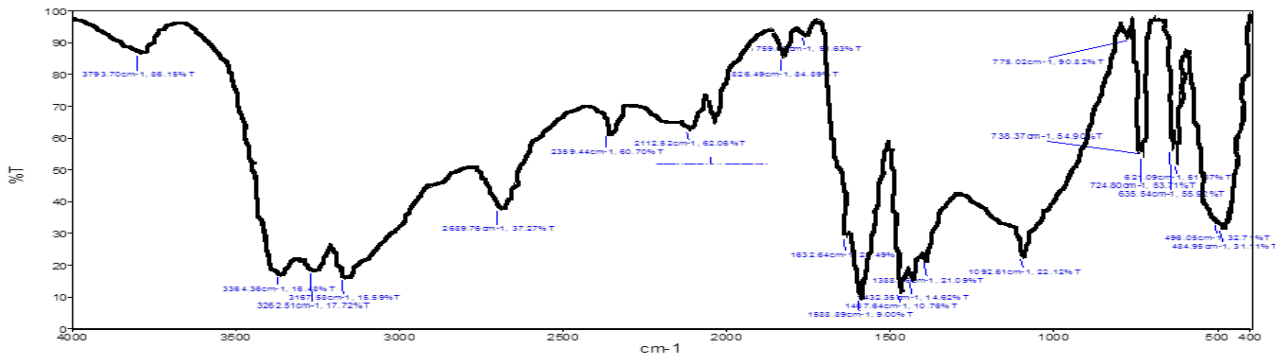


Fig 9 FTIR Spectrum of TUBC

XRD Analysis

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

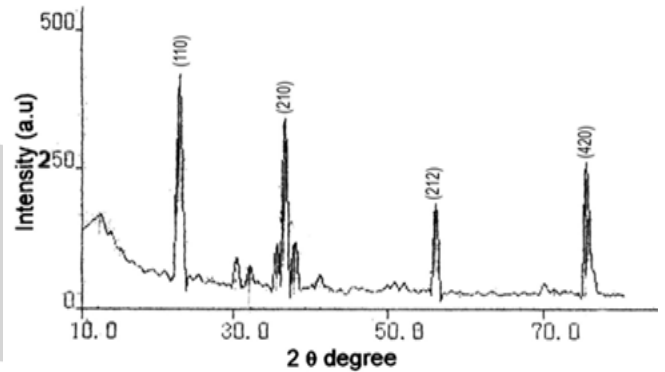


Fig. 10 XRD pattern for urea

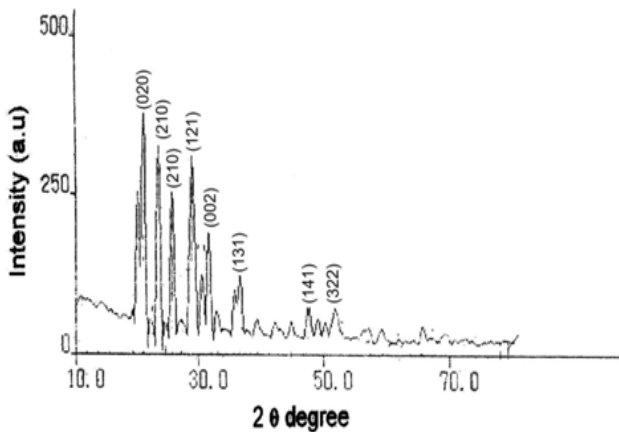


Fig. 11 XRD pattern for thiourea

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 Barium chloride was greater than that of KDP.

TG-DTA Analysis.

Thermal analysis of single crystals powder of TUBC is carried out in nitrogen atmosphere at a heating rate of 10⁰C per minuets. The TG-DTA curves of TUBC are shown in Fig. 13. It is seen from the TG curve that the TUBC undergoes complete decomposition between 170 and 620⁰C and exhibited three significant mass loss steps [16-18]. The initially the mass loss around 80% at 170 to 250⁰C due to the decomposition of TUBC. This highest loss in the mass is due to the elimination of thiourea urea and Barium chloride. It is also confirmed by DTA curve with the corresponding endothermic DTA peak at 170 and 210⁰C. The subsequent mass loss step at 251to 610⁰ C is due to the elimination of SCN accompanied with 20 % mass loss with exothermic DTA peak at 275⁰C. The experimental mass losses are in good agreements with the theoretical expectations. The high thermal stability of TUBC crystals

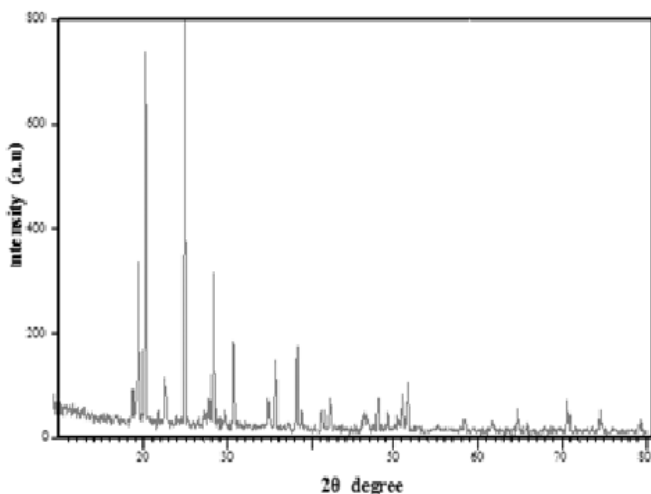


Fig. 12 XRD pattern of TUBC

NLO test

arises due to strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions.

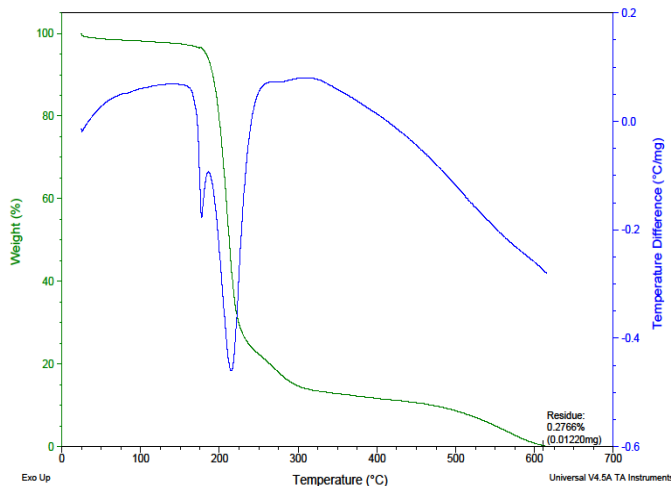


Fig.13 TG - DTA of TUBC

IV. CONCLUSION

Single crystals of Thiourea urea Barium chloride 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. The high thermal stability of TUBC crystals arises because of the strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions. TG curve of TUBC undergoes complete decomposition between 170 and 620°C in two steps that is endothermic DTA peak at 170 and 210°C and an exothermic DTA peaks at 275°C.

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