INFLUENCE OF BARIUM METAL IN ORGANIC CRYSTAL OF BCTU BY VARIOUS CHARACTERISATION STUDIES

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ABSTRACT

A pure transparent solid organic crystal of Barium chloride Thiourea Urea (BCTU) was obtained at room temperature by using distilled water following the method of slow evaporation technique. The optical property of the crystal was studied by UV-Vis spectral study. The functional groups were identified by FT-IR 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: BCTU, UV-Vis, FTIR, XRD, TG-DTA.

1. INTRODUCTION

In the recent research, the non-linear optical (NLO) properties are confirmed by various thiourea compounds [1-9]. Young researches 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 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 barium chloride thiourea urea (BCTU) 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 BCTU were grown by preparing Barium chloride. Thiourea and urea was taken as equimolar ratio and dissolved 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. The solution of BCTU 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 13 days by slow evaporation method. The

photograph of the grown crystals of urea, thiourea and BCTU is shown in Fig.1. The physical morphological size of the crystal is 3.4mm x 3.3mm.

Fig. 1: Crystal of barium chloride thiourea urea (BCTU)

2.2. Characterization

The Shimadzu 2401 UV-VIS spectrophotometer recorded the UV spectrum of BCTU crystals in the spectral range 200-800nm. The thermo Nicolet 380 FTIR instrument recorded the FTIR spectrum of BCTU 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 Perkin Elmer Pyris 6 DSC instrument was used to found the TG-DTA analysis of the grown crystal

of BCTU in the temperature range of 30 to 700ºC in the nitrogen atmosphere at the heating rate of 10ºC/ minutes. The micro hardness of the grown crystal of BCTU was carried out by Micro Vickers Hardness tester.

3. RESULTS AND DISCUSSION

3.1. UV spectral analysis

The UV spectra of the grown crystal of Barium chloride Thiourea Urea (BCTU) are shown in Fig.2, 3 and 4. The observed bands have been tabulated in table 1. In BCTU, the π- $\pi*$ absorption band shifted to intermediate wavelength (244nm) compared to urea (236nm) and thiourea (255nm). This is because of the formation of bonding between urea and thiourea through barium metal. The bond length of >C=O in urea and >C=S in Thiourea was decreased due to the presence of Barium metal. The absorption band shows the UV region of the spectrum. Similarly, n- $\pi*$ transition also shifted to higher wavelength due to less stable non-bonded electron in BCTU.
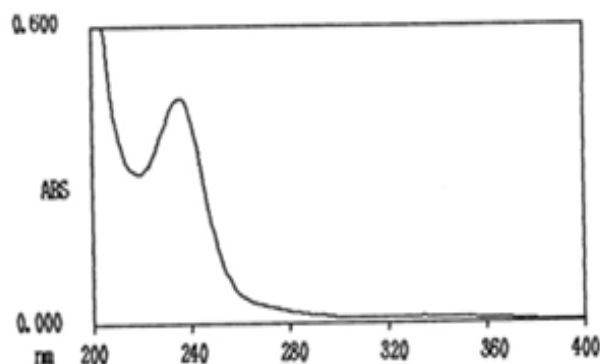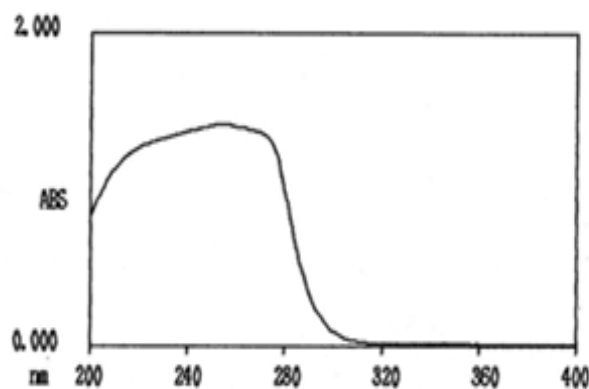

Fig. 2: UV Spectrum of Urea
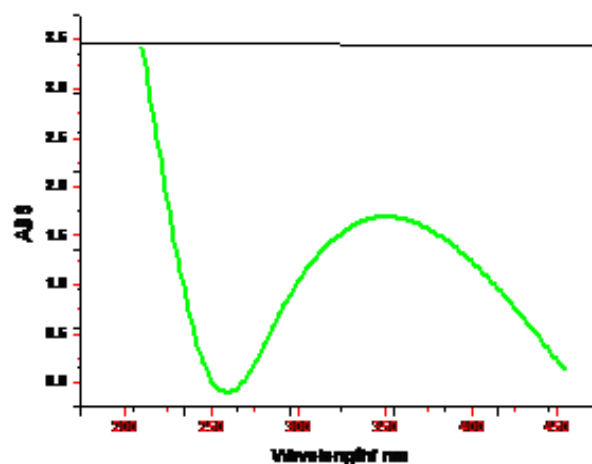

Fig. 3: UV Spectrum of Thiourea

Fig. 4: UV Spectrum of BCTU

Table 1: Comparison of absorption band of urea, thiourea with BCTU

Crystals	Absorbance	Wavelength in nm
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
BCTU	3.413	210.2
	0.737	290.6
	0.065	249.2
	0.137	453.8

3.2. FTIR Spectral analysis

The FTIR spectra of BCTU are shown in Fig. 5. The FTIR spectral value of urea, thiourea and BCTU 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 BCTU 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 BCTU (738cm^{-1}), asymmetric C=S vibration at 1454cm^{-1} of urea was shifted to higher frequency (1486cm^{-1}) in BCTU. Similarly C-N stret- ching vibration at 1064cm^{-1} of thiourea was shifted to higher frequency in BCTU (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.
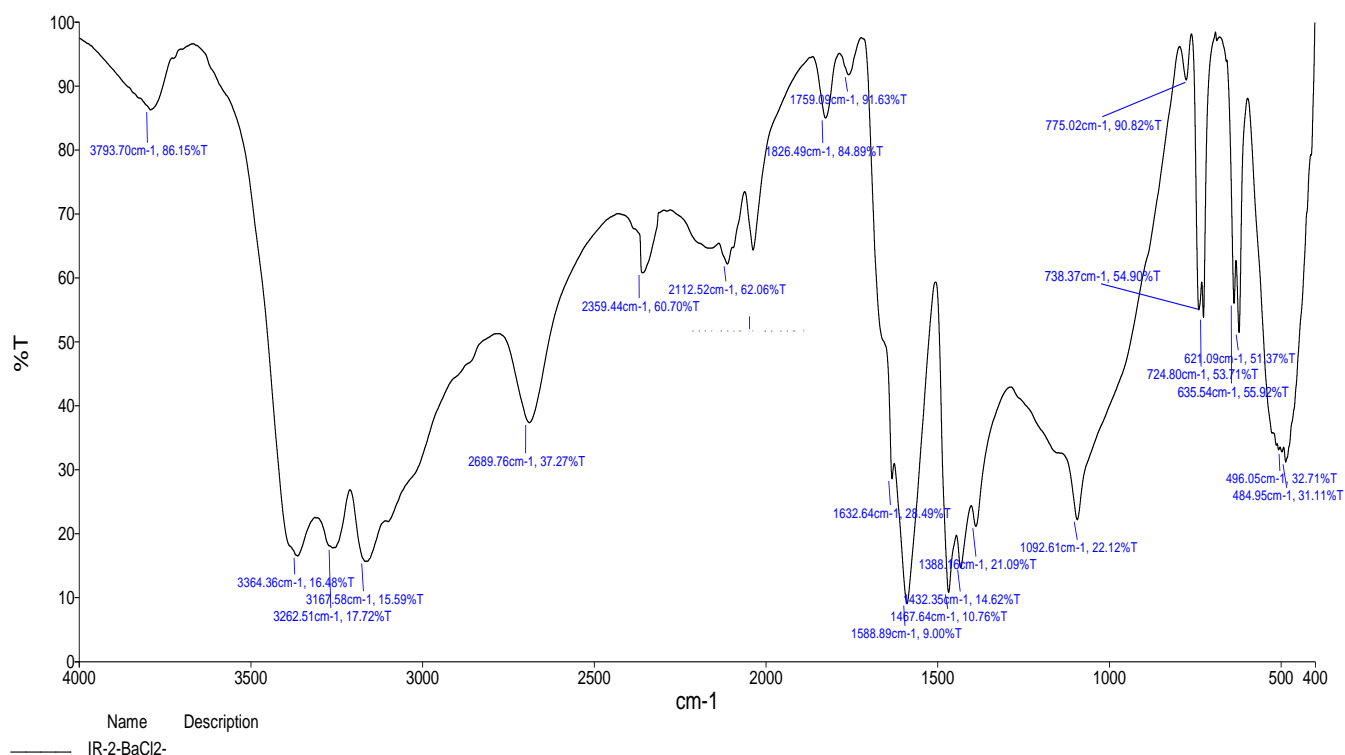
Fig. 5: FTIR spectrum OF BCTU

Table 2: FTIR assignments for urea, thiourea and BCTU

Urea (cm^{-1})	Thiourea (cm^{-1})	BCTU (cm^{-1})	Assignment
3455	3362	3364	$\nu_s\,NH_2$
1625	1591	1589	$\gamma_{as\,N=C=N}$
---	1478	1486	$\nu_s\,C=S$
1064	1093	1092	$\nu_s\,CN$
---	732	738`	$\delta_s\,C=S$

3.3. XRD Analysis

Figs. 6-8 show the XRD pattern of urea, thiourea and BCTU crystals respectively. The XRD pattern of BCTU has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in BCTU (112). The XRD of BCTU 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 BCTU crystal were determined using RIGAKU AFC7 diffractometer.

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 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.

3.5. TG-DTA Analysis

Thermal analysis of single crystals powder of BCTU is carried out in nitrogen atmosphere at a heating rate of 10°C per minuets. The TG-DTA curves of BCTU are shown in Fig. 9. It is seen from the TG curve that the BCTU undergoes complete decomposition between 170 and 620°C and exhibited three significant mass loss steps [16-18]. The initially the weight was loss up to 80% in the temperature range of 170 to 250°C due to the decomposition of BCTU. The loss in the weight in thermal analysis of BCTU is due to decomposition temperature of the molecules like the elimination of thiourea, urea, and Barium chloride. It is also confirmed

by DTA curve with the corresponding endothermic DTA peak at 170 and 210°C. The subsequent mass loss step at 251 to 610°C is due to the elimination of SCN accompanied with 20 % mass loss with exothermic DTA peak at 275°C. The experi-mental mass losses are in good agreements with the theoretical expectations. The high thermal stability of BCTU crystals arises due to strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions.
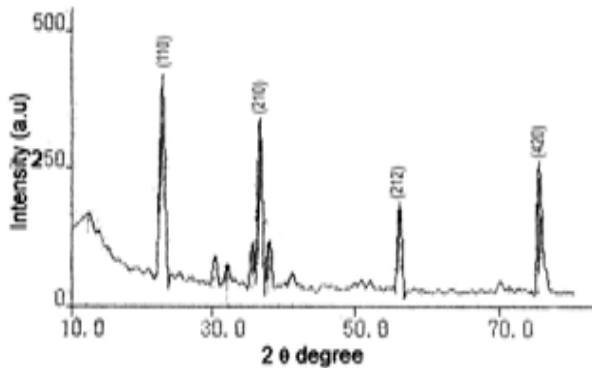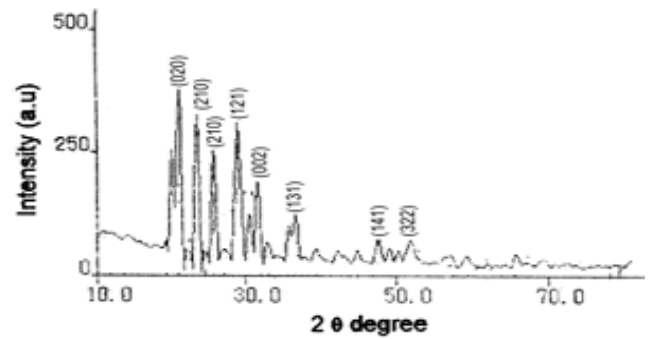

Fig. 7: XRD pattern of Thiourea
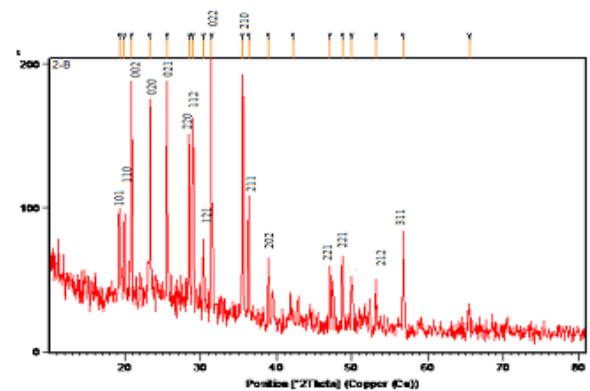

Fig. 6: XRD pattern of Urea
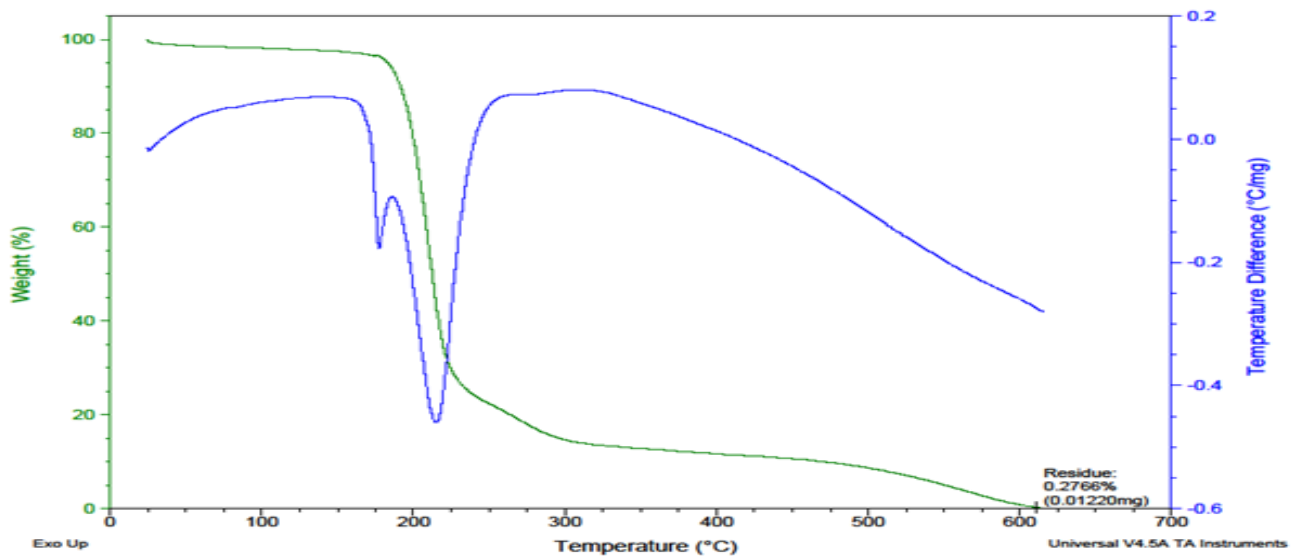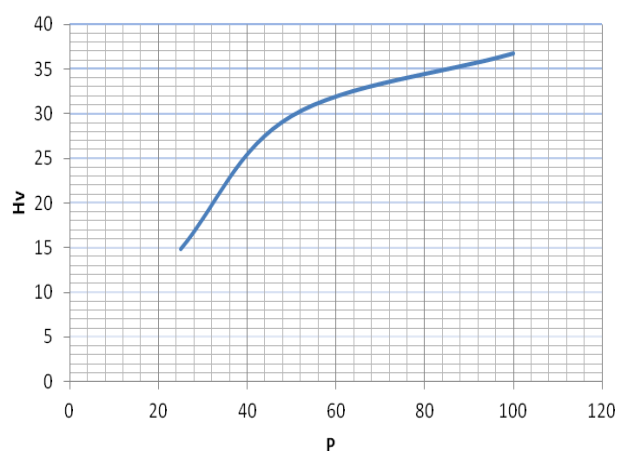

Fig . 8: XRD pattern of BCTU

Fig. 9: TG- DTA of TUBC

3.6. Microhardness

P is the applied load and Hv is the Vickers hardness. If P increases Hv values also increases. That was shown the Table 3 and fig.10.

Table 3: Micro hardness of BCTU

S.No	P gm	Hv kg/mm^2
1	25	14.9
2	50	29.8
3	100	36.8

Fig. 10: Plot of HV of BCTU

4. CONCLUSION

Finally a well fined single crystal was obtained after 13 days by slow evaporation method with the physical morphological size of the crystal is 3.4mm x 3.3mm. In UV-VIS spectral studies, the maximum absorbance was observed in the wavelength of 453.8 nm. FT-IR analysis confirms the presence of functional groups present in the crystal that the band observed in the region between 2000 to 2700cm^{-1}. In the XRD studies, major (110) and (020) peak with maximum intensity is shifted in BCTU (022), it confirms the crystal is orthorhombic. SHG efficiency shows that the crystal has a higher efficiency than KDP. The high thermal stability of BCTU crystals arises because of the strong bond existing between the conjugation layers of thiourea urea molecule and the metal ions. TG curve of BCTU 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. In the microhardness testing, it withstands stability by applying the load up to 100g.

5. REFERENCES

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