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Thermal, FTIR and microhardness studies of bisthiourea-urea single crystal

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Abstract Single crystals of a new nonlinear optical material, bisthiourea-urea have been grown from aqueous solution by slow evaporation technique with a period of 4 weeks. The structure of the grown crystals was confirmed by X-ray diffraction (XRD). The presence of title compound in the crystal lattice has been qualitatively determined by FTIR analysis. The mechanical properties and thermal stability of the grown crystals were evaluated by Vickers microhardness test and TG and DTG, respectively.

Keywords Bisthiourea-urea single crystal · Solution growth · FTIR · TG · DTG

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Introduction

Nonlinear optical (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 [1–15]. Hence, recent research is concentrated on organic materials due to their large nonlinearity, high resistance to laser-induced damage, low angular sensitivity, and good mechanical hardness [16, 17]. Recent metal complexes of thiourea and thiourea analogs have been investigated [18]. Metal complex of thiourea, commonly called semi organics, include the advantage of both organic and inorganic part of the complex. Thermal, XRD and spectral analyses are very useful techniques for materials characterization. Therefore, it is not surprising that many authors have applied these techniques for investigation of many materials [19–32]. In this study, mixed crystals of bisthiourea-urea (BTU) have been grown by slow evaporation technique at room temperature. The changes in the FTIR, XRD, hardness parameters, and thermal stability have been studied.

Experimental

Crystal growth

BTU crystals were grown from the aqueous solution by slow evaporation technique. The starting material was synthesized by dissolving high purity BTU (AR grade) in the molar ratio 2:1, in triple distilled water as a solvent. The following reaction is expected to take place, giving the required compound.

$$2NH_2-CS-NH_2+\ NH_2-CO-NH_2 \\ \rightarrow NH_2-CS-NH_{2\ldots}OC-(NH_2)_{2\ldots}SC(NH_2)_2$$

After successful recrystallization process, transparent and good quality crystals were obtained after a period of 1 month. It was observed that the sample containing thiourea and urea gave good bulk crystals with perfect morphology.

Results and discussions

Solubility

Single crystals of BTU started to grow in about 1 week in the Petri dishes. Figures 1 and 2 show the morphology of the urea, thiourea. The photograph of the BTU crystal is shown in Fig. 3.

Fig. 1 Urea

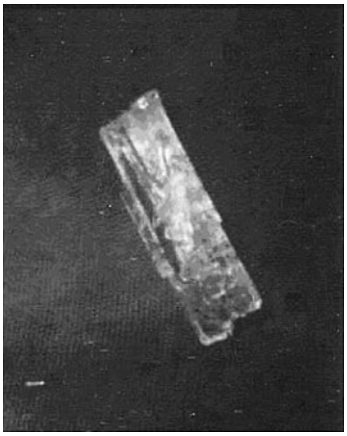


Fig. 2 Thiourea

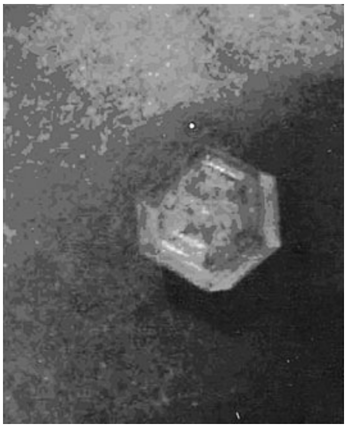


Fig. 3 BTU

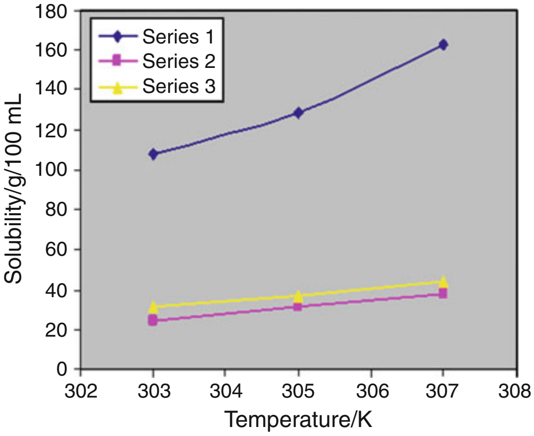


Fig. 4 Solubility of urea, thiourea, and BTU in water. Series 1 urea; Series 2 Thiourea; Series 3 BTU

The variation of solubility with temperature is shown in Fig. 4. The solubility of BTU was expressed in 26.2 g/100 mL and temperature in 303 K, respectively. The solubility of urea and thiourea was found to be 108.2, 24.4 g/100 mL. BTU has a positive temperature coefficient of solubility. Therefore, slow evaporation of aqueous solution of BTU could be attempted to grow bulk crystals.

The UV spectra for urea, thiourea, and BTU crystals are shown in Figs. 5, 6, and 7. In BTU, the $\pi-\pi^*$ absorption band shifted to longer wavelength compared with urea. This is because of the formation of hydrogen bond between >C=O···N–H (of urea, thiourea) increase the bond length of >C=O and thus smaller energy required for this transition and hence the absorption shows the red end of the spectrum. Similarly, $n-\pi^*$ transition also shifted to higher wavelength due to the less stable non-bonded electron in BTU.

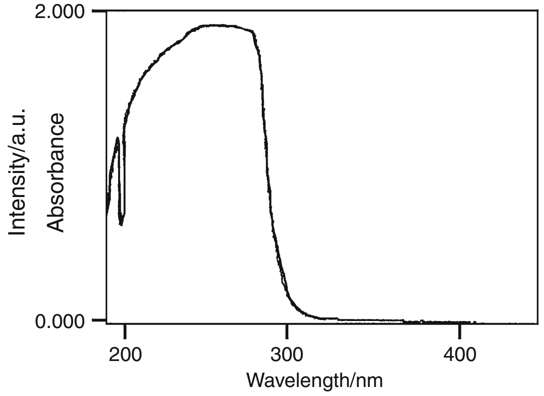


Fig. 5 UV spectrum of urea

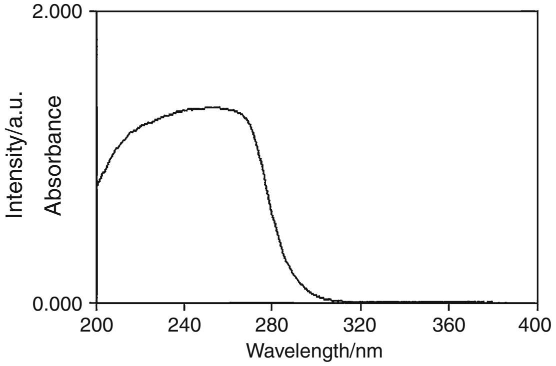


Fig. 6 UV spectrum of thiourea

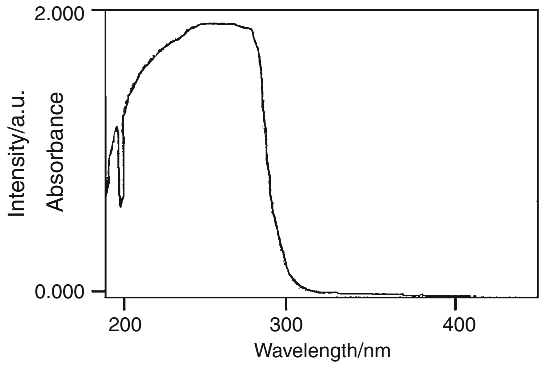


Fig. 7 UV spectrum of bisthiourea-urea single crystal

FTIR analysis

The FTIR spectral analyses of urea, thiourea and BTU crystals have been carried out between 400 and 4000 cm^{-1} on an IFS Brukker 66v spectrometer. The FTIR spectral data are summarized in Table 1 and the spectra are shown in Figs. 8, 9, and 10. The broad band around 3364 cm^{-1} assigned to NH stretching vibration of BTU crystal. The absorption observed at 1488 and 1093 cm^{-1} in the spectrum of BTU corresponds to the 1453 and 1063 cm^{-1} absorption of urea and thiourea, respectively, and can be assigned to the N–C–N stretching vibration. The broad envelope positioned between 2358 and 2888 cm^{-1} of BTU corresponds to the symmetric and asymmetric stretching modes of NH_2 group of thiourea. The absorption at 1785 cm^{-1} is due to C=O stretching of urea. The frequency assigned for NH_2 bending at 1589 cm^{-1}, which shows the presence of urea part of the molecule. All these observations clearly indicate the presence of thiourea and urea in the crystal lattice.

Table 1 FTIR vibrational frequencies of urea, thiourea and BTU crystals/cm^{-1}

Urea	Thiourea	UTMC	Assignments
3455	3362	3364	NH stretching
	1671	1785	C=O stretching
1625	1591	1589	NH bending
1454	1478	1468	CN assymetric stretching
1064	1093	1093	CN stretching
	732	733	C=S rocking

X-ray diffraction studies

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to confirm the crystallinity and also to identify the lattice parameters on an ENRAF–NONIUS CAD4 automatic X-ray diffractometer. The XRD patterns are given in Figs. 11, 12, and 13 and the results are summarized in Table 2. The calculated lattice parameter values are a = 7.9746 Å, b = 8.9361 Å, and c = 5.7140 Å and the crystal belongs to orthorhombic structure. The XRD results are in good agreement with the repeated values and thus confirm the grown crystal.

Thermal analysis

The thermogravimetric analysis of BTU was carried out for sample mass of 15 mg between 50 and 800 °C at heating rate of 10 K/min in nitrogen atmosphere on a NETZCH STA 409C/CD thermal analyzer. The TG-DTG curves of BTU are shown in Fig. 14. Two molecules of ammonia and one molecule of carbon monoxide are eliminated on heating the compound from 180 to 250 °C. This accounts for 81.99% mass loss observed on TG curve. The theoretical mass loss of urea is in good agreement with experimental mass loss. The remaining portion of BTU crystal very slowly decomposed between 615 and 750 °C. The mass loss indicates the presence of urea in BTU. Afterwards, thiourea in BTU begins to split to hydrogen

Fig. 8 FTIR spectrum of urea

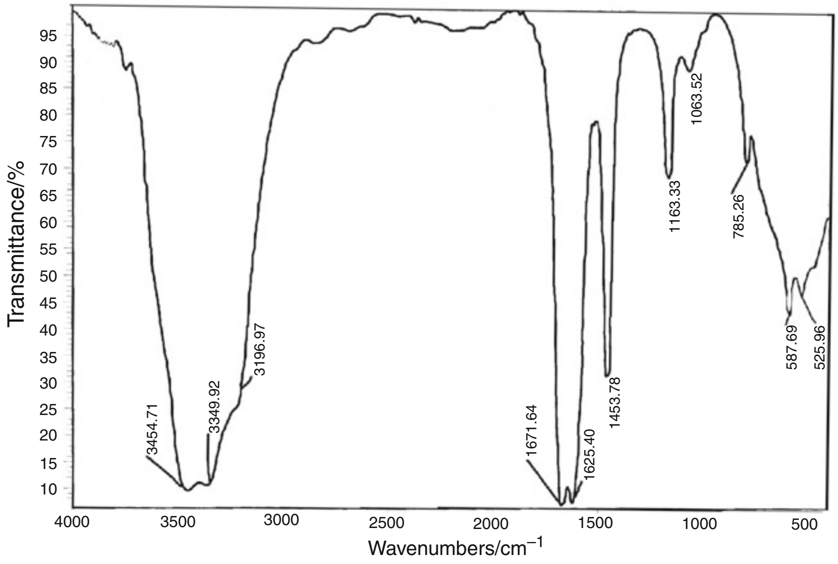
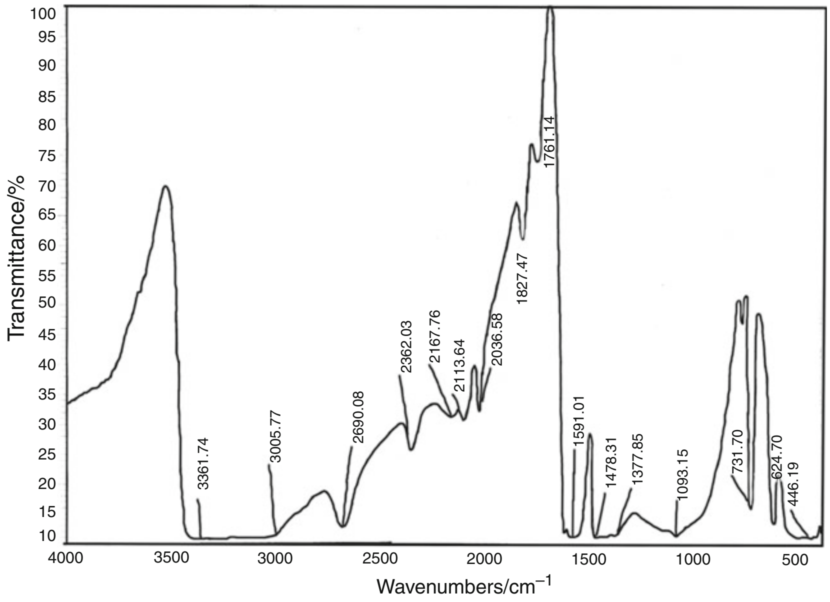


Fig. 9 FTIR spectrum of thiourea

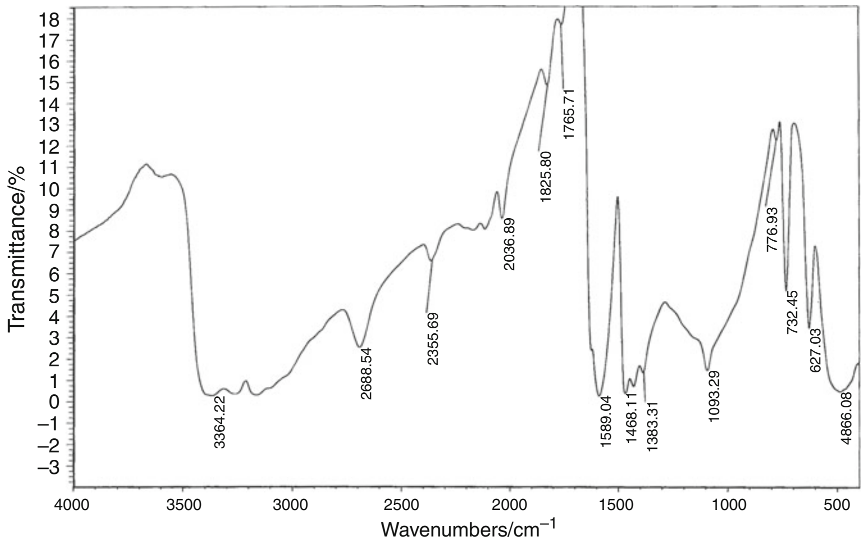


sulfide, nitrogen, and carbon residue. This accounts for 10.41% mass loss observed on the TG curve. The sharp mass loss at 180 °C illustrating the absence of absorbed water in the crystal lattice. The DTA curve recorded for the grown crystal implies that the material undergoes an endothermic peak at 182.4 °C corresponding to the melting point of the crystal. The DTA curve (not shown) also reveals that the sharp endothermic peak coincides with that of TG results and thus confirms the thermal stability of the crystal. This study indicates that the compound could be used for device fabrication below the melting point of the crystal.

Mechanical (micro) hardness

The mechanical strength of BTU crystal was estimated using a Vickers microhardness tester fitted with a diamond indenter. A smooth surface was selected and subjected to this study. Indentations were made for various loads from 5 to 25 g. Several trials were carried out on the prominent

Fig. 10 FTIR spectrum of bisthiourea-urea single crystal



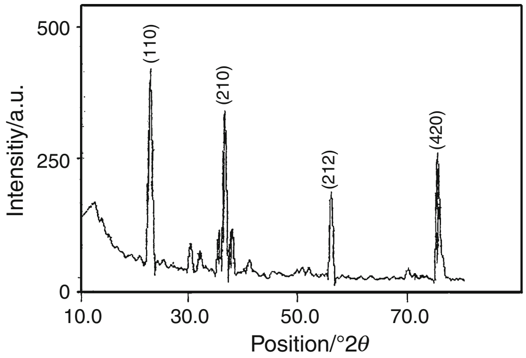


Fig. 11 XRD patterns of urea

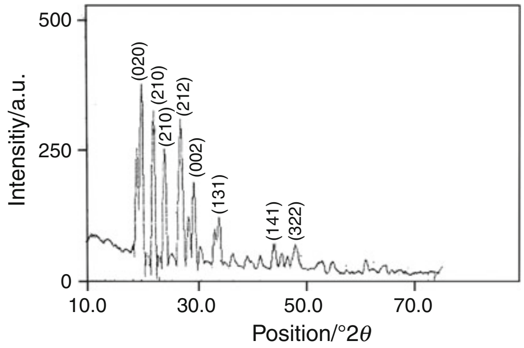


Fig. 12 XRD patterns of thiourea

(110) and the average diagonal length was calculated for an indentation time of 10 s. The Vickers hardness number (Hv) of the crystal was calculated using the relation $Hv = 1.8544\ p/d^2$ where p is the applied load in Kg and d is the average diagonal length of impression in mm. Figure 15 shows the variation of Vickers microhardness value with load. Hardness value decreases with the increase in load and the crystal experiences crack for 30 g.

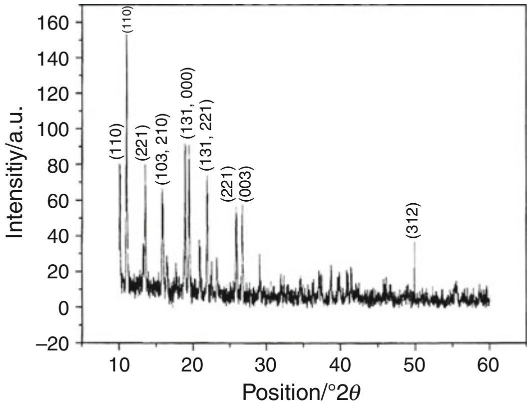


Fig. 13 XRD patterns of bisthiourea-urea single crystal

Table 2 X-ray diffraction data for BTU single crystal

2θ/°	d/Å	h k l		
		Thiourea	Urea	
10.1	4.3963	110	–	
11.0	4.0404	–	110	
15.0	2.9787	221	–	
17.8	2.5218	103	210	
19.0	2.3679	131	002	
20.4	2.2117	221	–	a = 7.9746 Å
22.1	2.0492	–	112	b = 8.9361 Å
25.0	1.8242	–	221	c = 5.7140 Å
29.8	1.5513	–	003	
30.9	1.5013	–	103	
33.2	1.4080		312	
39.3	1.2169	–	421	
41.0	1.1752	–	004	
44.8	1.0493	–	431	
49.8	1.0086	–	312	

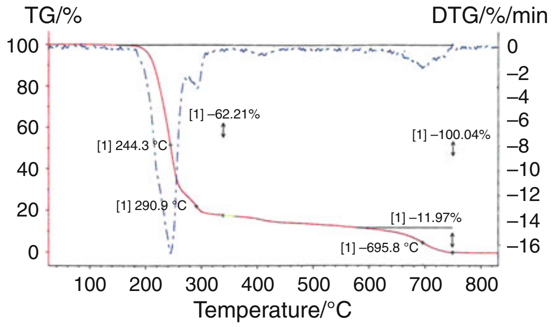


Fig. 14 TG-DTG curves of bisthiourea-urea single crystal

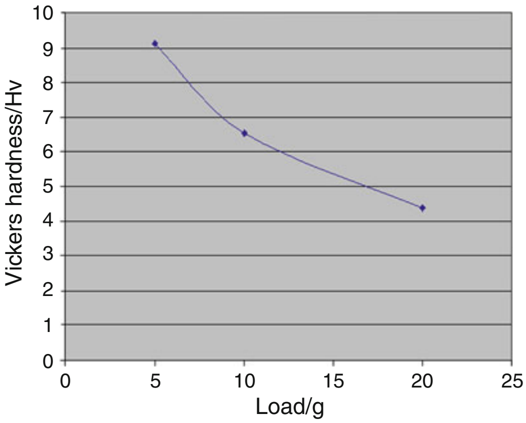


Fig. 15 Plot of microhardness versus load for bisthiourea-urea single crystal

Conclusions

Optically good quality single crystals of BTU were grown by slow evaporation technique under room temperature. Grown crystals were characterized and confirmed that the crystal belongs to orthorhombic system. FTIR analysis was carried out to study the molecular vibration and functional groups of the grown crystals. TG-DTG analyses showed that the crystal retain its texture up to 180 °C. The DTA curve of crystal implies that the material undergoes an endothermic peak at 182.4 °C corresponding to the melting point of the crystal. The DTA curve also reveals that the sharp endothermic peak coincides with that of TG results and thus confirms the thermal stability of the crystal. This study indicates that the compound could be used for device fabrication below its melting point. Mechanical studies reveal that Vickers microhardness value decreases as the load increases.

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