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TG–DTA, UV and FTIR spectroscopic studies of urea–thiourea mixed crystal

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Abstract A mixed crystal of urea–thiourea was grown by slow evaporation of aqueous solution at room temperature. The bright and transparent crystals obtained were characterized by thermogravimetric–differential thermal analysis (TG–DTA), UV and FTIR spectroscopic analyses. A fitting decomposition pattern for the title compound was formulated on the TG curve which shows a two stage weight loss between 200 and 750 °C. In this temperature range DTA curve shows exothermic peaks supporting the formulated decomposition pattern. The UV and FTIR spectra show the characteristic absorption, vibration frequencies due to urea–thiourea mixed crystals. Detailed structural analysis of the compound is under progress.

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Introduction

Nonlinear optical (NLO) materials have a significant impact on laser technology, optical communication and optical storage devices. The search for new frequency conversion materials over the past decade has led to the discovery of many organic materials. Organic material possesses large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical properties [1–3]. Urea is representative of one class of materials which are applicable to photonics and served as a model compound and reference material in the DMOS (Diffusive Mixing of Organic Solutions) experiment in microgravity carried out by NASA [4–7]. Recently metal complexes of thiourea have been explored. Example of these complexes is zinc thiourea sulphate (ZTS), cadmium thiourea chloride (CTC) and zinc thiourea chloride (ZTC). These crystals have better nonlinear properties than KDP [7, 8]. In addition, also many other researchers have investigated various organic–inorganic materials and characterized them using various thermal, optical, microscopic, XRD and spectral analyses [4, 9–26]. Literature survey shows that urea metanitro benzoic acid, urea hydrogen peroxide compounds have been studied. However, there is no reference in literature regarding the work of urea–thiourea mixed crystal (UTMC). This article reports the synthesis, and characterization of UTMC using UV and FTIR spectra as well as TG and DTA studies. A detailed structural analysis of the compound is under progress and will be published in future.

Experimental details

Preparation of urea–thiourea mixed crystal

A UTMC was prepared at room temperature by slow evaporation of aqueous solution containing equimolar proportion of urea and thiourea (Merck, Mumbai). Care was taken to minimise mechanical and thermal variations. Colourless, bright and transparent crystal with an average size of 0.9 × 0.8 × 0.8 mm was obtained.

Measurements

The thermogravimetric and differential thermal analyses of UTMC was carried out using a NETZSCH STA 409C thermal analyser in nitrogen atmosphere. The sample was heated between 30 and 800 °C at a heating rate of 10 °C/min. UV spectral analysis was carried out using a double beam spectrometer. A Bruker IFS 66V spectrometer was used to record the FTIR spectra of the compound, employing KBr pellet technique in the frequency range 400–4,000 cm^{-1}. A detailed structural analysis of the compound will be published later.

Results and discussion

The TG and DTA curves of UTMC are shown in Fig. 1. The TG curve indicates a two step weight loss on heating the compound between 30 and 800 °C.

The following decomposition pattern is formulated for UTMC:

Step 1

$$\ldots H{-}HN{-}CO{-}NH{-}H\ldots S = C(NH_2)_2 \rightarrow 2NH_3 + CO$$

Step 2

$$\ldots HN{-}CS{-}NH\ldots \rightarrow H_2S + N_2 + C$$

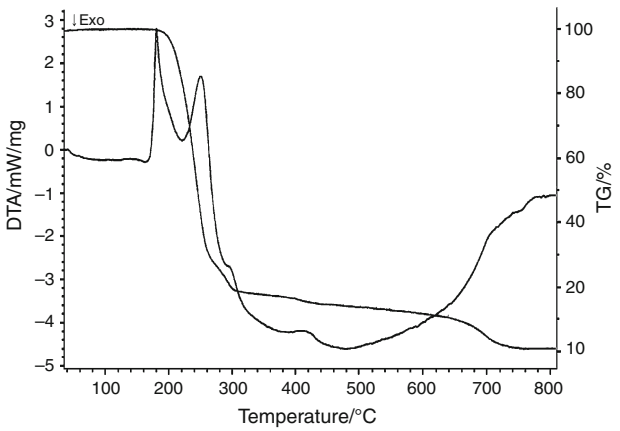

Fig. 1 TG–DTA curves of urea thiourea mixed crystal

Two molecules of ammonia and a molecule of carbon monoxide are lost on heating the compound from 180 to 250 °C. This accounts for 80% weight loss observed in TG curve. The theoretical weight loss of urea is much closed to experimental weight loss. The remaining portion of UTMC very slowly decomposed up to 750 °C. High weight loss indicates that the presence of urea in UTMC. In UTMC, urea is stable up to 180 °C. Above 180 °C urea in UTMC decomposes into two molecules of ammonia and a molecule of carbon monoxide. Urea is slowly vaporises at 250 °C. Afterwards, thiourea in UTMC begins to split to hydrogen sulphide, nitrogen and carbon residue. This accounts for 10.41% weight loss observed in the TG curve. The thermogravimetric study thus confirms the formation of the title compound in the stoichiometric ratio and the decomposition pattern of UTMC. The DTA curve depicted in Fig. 1 shows an exothermic peak at 182 °C corresponds to the first stage decomposition. The second broad exothermic peak at 250 °C is due to the decomposition of thiourea in UTMC.

The UV spectra for urea, thiourea and UTMC are shown in Figs. 2, 3, 4. The observed bands have been summarized in Table 1. In UTMC, the π–π^* absorption band shifted to

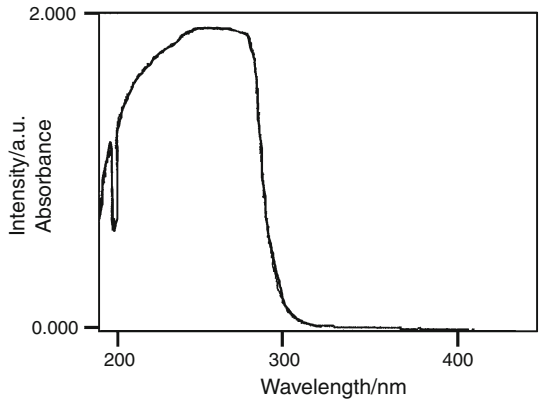

Fig. 2 UV spectrum of urea

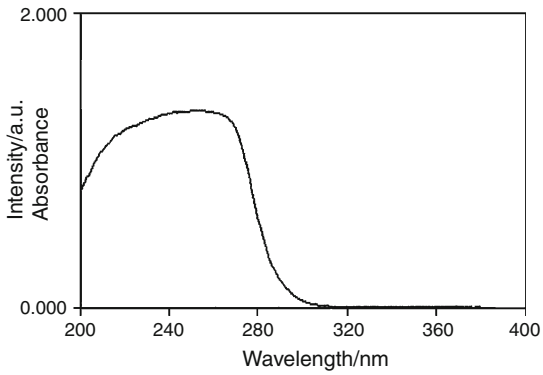

Fig. 3 UV spectrum of thiourea

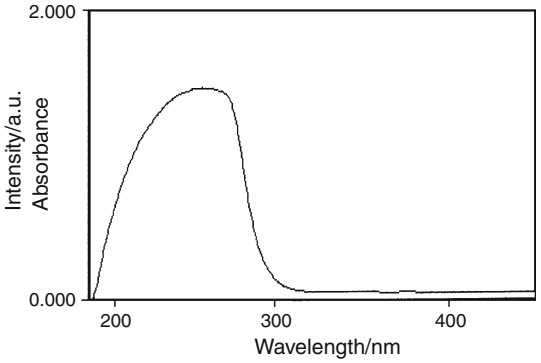

Fig. 4 UV spectrum of urea–thiourea mixed crystal

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

Crystals	Absorbance	Wavelength/nm
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
UTMC	0.008	394
	0.011	380.5
	0.010	347
	1.792	250.5

longer wavelength compared to urea. This is because of the formation of hydrogen bond between >C=O···N–H (of urea, thiourea) increases 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-π* transition also shifted to higher wavelength due to less stable non-bonded electron in UTMC.

The FTIR spectra of urea, thiourea and UTMC are shown in Figs. 5, 6, 7, respectively. The various absorption bands in FTIR spectra and the corresponding assignments are given below.

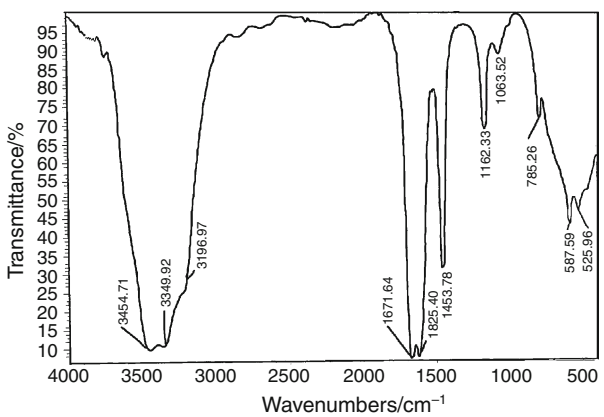

Fig. 5 FTIR spectrum of urea

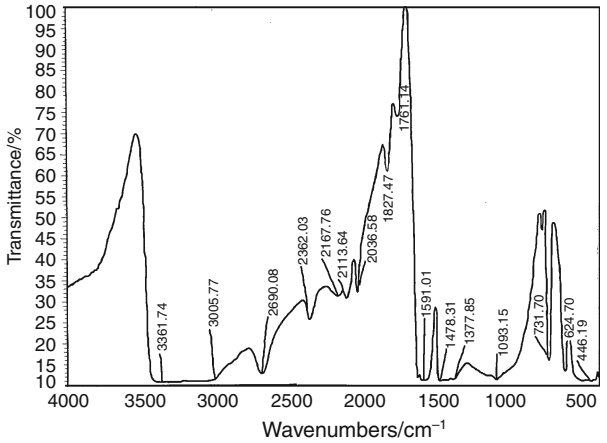

Fig. 6 FTIR spectrum of thiourea

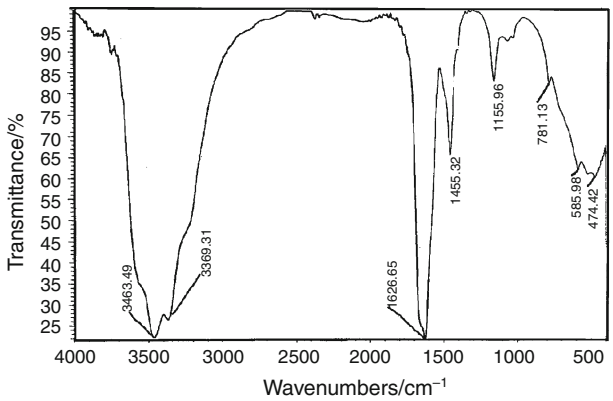

Fig. 7 FTIR spectrum of urea–thiourea mixed crystal

The frequencies at 3362 cm^{-1} is due to symmetric stretching N–H vibration of UTMC. δ_s C=S and ν_{as} C=S bending and asymmetric stretching appear at 722 and 1433 cm^{-1}, respectively. The broad band at 2361 and 2688 cm^{-1} are due to ν_s N=C=O and ν_{as} N=C=O stretching modes. The weak band appearing at 1093 cm^{-1} is due to ν symmetric stretching vibration. The rocking mode of N=C=N found as a peak at 485 cm^{-1}. From this FTIR studies shows the characteristic vibration frequencies due to urea and thiourea. This confirms the formation of UTMC.

Conclusions

Mixed crystal of UTMC was prepared at room temperature by slow evaporation of aqueous solutions. The bright and transparent crystal obtained was characterized. The TG and DTA studies confirm a two stage decomposition of the compound when heated between 180 and 750 °C. The UV spectral analysis confirms the formation of hydrogen bond between urea and thiourea. The FTIR spectra show characteristic vibrational frequencies of urea and thiourea. The

detailed structural analysis of the compound under progress will help to understand the mechanism of the title compound.

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