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NOTE

Thermal, UV and FTIR Spectroscopic Studies of Urea-Thiourea Mixed Crystal

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A mixed crystal of urea thiourea was grown by slow evaporation of aqueous solution at room temperature. The bright and transparent crystals obtained was characterized through thermogravimetric (TG-DTA), UV and FTIR spectroscopic analyses. A fitting decomposition pattern for the mixed crystal was formulated on the TG thermogram which shows a two stage weight loss between 200 and 750 °C. In this temperature range, DTA curve shows exothermic dips supporting the formulated decomposition pattern. The UV and FTIR spectra show the characteristic absorption, vibration frequencies due to urea-thiourea mixed crystals.

Key Words: Urea-thiourea mixed crystal, UV, FTIR, TG-DTA.

Non-linear 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 hardness[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 diffusive mixing of organic solutions (DMOS) experiment in microgravity carried out by NASA[4-7]. Recently, metal complexes of thiourea have been explored [*e.g.*, zinc thiourea sulphate (ZTS), cadmium thiourea chloride (CTC) and zinc thiourea chloride (ZTC)]. These crystals have better non-linear properties than potassium dihydrogen phosphate (KDP)[7-9]. This paper reports the synthesis and characterization of urea-thiourea mixed crystal through UV, FTIR spectra, TG and DTA studies.

A mixed crystal of urea-thiourea (UTMC) was prepared at room temperature by slow evaporation of aqueous solution containing equimolar

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proportion of urea and thiourea (Merck, Mumbai). Precautions were taken to minimize the mechanical and thermal variations. Colourless, bright and transparent crystal with an average size of 0.9 mm × 0.8 mm × 0.8 mm was obtained.

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 K/min. UV spectral analysis was carried out by using a double beam spectrometer. A Burker IFS 66V spectrometer was used to record the FTIR spectra of the compound, employing KBr pellet technique in the frequency range 4000-400 cm^{-1}.

The thermograms indicates a two step weight loss on heating the compound between 30-800 °C. The following decomposition pattern is formulated for urea-thiourea mixed crystal (UTMC):

Step-1: $\cdots\cdot$ -H-HN-CO-NH-H$\cdots\cdot$S=C $(NH_2)_2 \longrightarrow 2NH_3 + CO$

Step-2: $\cdots\cdot$HN-CS-$NH_2\cdots\cdot \longrightarrow H_2S + N_2 + C$

Two molecules of ammonia and a molecule of carbon monoxide are lost on heating the compound from 180-250 °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 to up to 750 °C. High weight loss indicates the presence of urea in UTMC. Urea is vapourized slowly 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. This is consistent with the TG thermogram. The thermogravimetric study thus confirms the formation of the mixed crystal of urea-thiourea in the stoichiometric ratio and the decomposition pattern of UTMC. The DTA curve shows an exothermic dip at 182 °C which corresponds to the first stage decomposition. The second deep and broad exothermic dip in the temperature 250 °C is due to the decomposition of thiourea in UTMC.

The observed bands of the UV spectra for urea, thiourea and UTMC have been tabulated in Table-1. In UTMC, the π-π^* absorption band shifted to longer wavelength compared to 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. This is further confirmed by the presence of the absorption at 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 IR 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

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
	0.010	347
	1.792	250

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.

Conclusion

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

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