J Therm Anal Calorim (2011) 104:885–891
DOI 10.1007/s10973-011-1290-6

Thermal and FTIR spectral studies in various proportions of urea thiourea mixed crystal

G. Madhurambal · M. Mariappan ·
B. Ravindran · S. C. Mojumdar

CTAS2010 Conference Special Chapter

Abstract Mixed crystals of various proportions of urea thiourea were grown by slow evaporation of aqueous solution at room temperature. The bright and transparent crystals obtained were characterized using thermogravimetry–differential thermal analysis (TG–DTA) and FTIR spectroscopic analyses. A fitting decomposition pattern for the title compound was formulated on the TG curve which shows a two-stage mass loss between 175 and 750 °C. In this temperature range, DTA curves show exothermic peaks supporting the formulated decomposition pattern. The FTIR spectra show the characteristic absorption, vibration frequencies due to urea thiourea. Detailed structural analysis of the compound is under progress.

Keywords Solution growth · Urea thiourea mixed crystal · TG-DTA · FTIR

Introduction

Nonlinear optic (NLO) materials have recently attracted much attention because of their potential applications in emerging opto-electronic technologies. The search for new frequency conversion materials over the past decade has led to the discovery of many organic materials [1–25]. Though organic NLO crystals have high nonlinearity, fast responses and tailor made flexibility. Their applications are limited due to inherent poor chemical stability caused by organic π-conjugated system [26, 27]. Many authors investigated various organic and organometallic compounds due to their very important roles in chemical, biological, electrical and environmental sciences and also examined their various properties [5–30]. 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 in organic solutions (DMOS) experiment in microgravity carried out by NASA [28]. Recently metal complexes of thiourea have been explored. Thiourea is an interesting inorganic modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds. It belongs to orthorhombic crystal system. Only few of thiourea complexes, viz., zinc thiourea sulphate, bis thiourea cadmium chloride, triallyl thiourea mercury bromide, thio semicarbazide crystallizes in noncentro symmetry structure, show second harmonic generation (SHG). TG–DTA as well as FTIR spectral analysis have been applied to investigate the physical and chemical properties such as structure, fusion, vaporization, decomposition, oxidation and degradation of the studied compounds.

G. Madhurambal
Department of Chemistry, A D M College for Women,
Nagapattinam, Tamil Nadu, India

M. Mariappan
Department of Chemistry, RVS College of Engineering and
Technology, Karaikal, Pondicherry, India

B. Ravindran
Department of Physics, EGS Pillay Engineering College,
Nagapattinam, India

S. C. Mojumdar
Department of Chemical Technologies and Environment,
Faculty of Industrial Technologies, Trencin University
of A. Dubcek, Púchov, Slovakia

S. C. Mojumdar (✉)
Department of Chemical and Biochemical Engineering, The
University of Western Ontario, London, ON N6A 5B9, Canada
e-mail: scmojumdar@yahoo.com

Experimental

The mixed crystals of various proportions were synthesized, and their purities were checked by standard methods of analysis. As the growth process is slow, the atoms of the constituent particles take definite position during growth. The mixed crystals of a values 0.1, 0.25 and 0.5 were grown by suitable amounts urea and thiourea for desired ‘a’ values (0.1, i.e. 1 g of thiourea, 9 g of urea). The TG–DTA of various proportion of urea thiourea mixed crystal (here after abbreviated as UTMC) was carried out on a NETZSCH ST 409 °C thermal analyser in nitrogen atmosphere. The samples were heated between 30 and 800 °C at a heating rate of 10 K/min. A Burker IFS 66 V spectrometer was used to record the FTIR spectrum of the compounds, employing KBr pellet technique in the frequency range 400–4,000 cm^{-1}. A detailed structural analysis of the compounds will be published later.

Results and discussion

Thermal analysis

The TG–DTA curves of various proportions of UTMC are shown in Figs. 1a, b and 2. The TG curves indicate a two-step mass loss on heating the compounds between 30 and 800 °C. The following decomposition pattern is formulated for various proportions of UTMC.

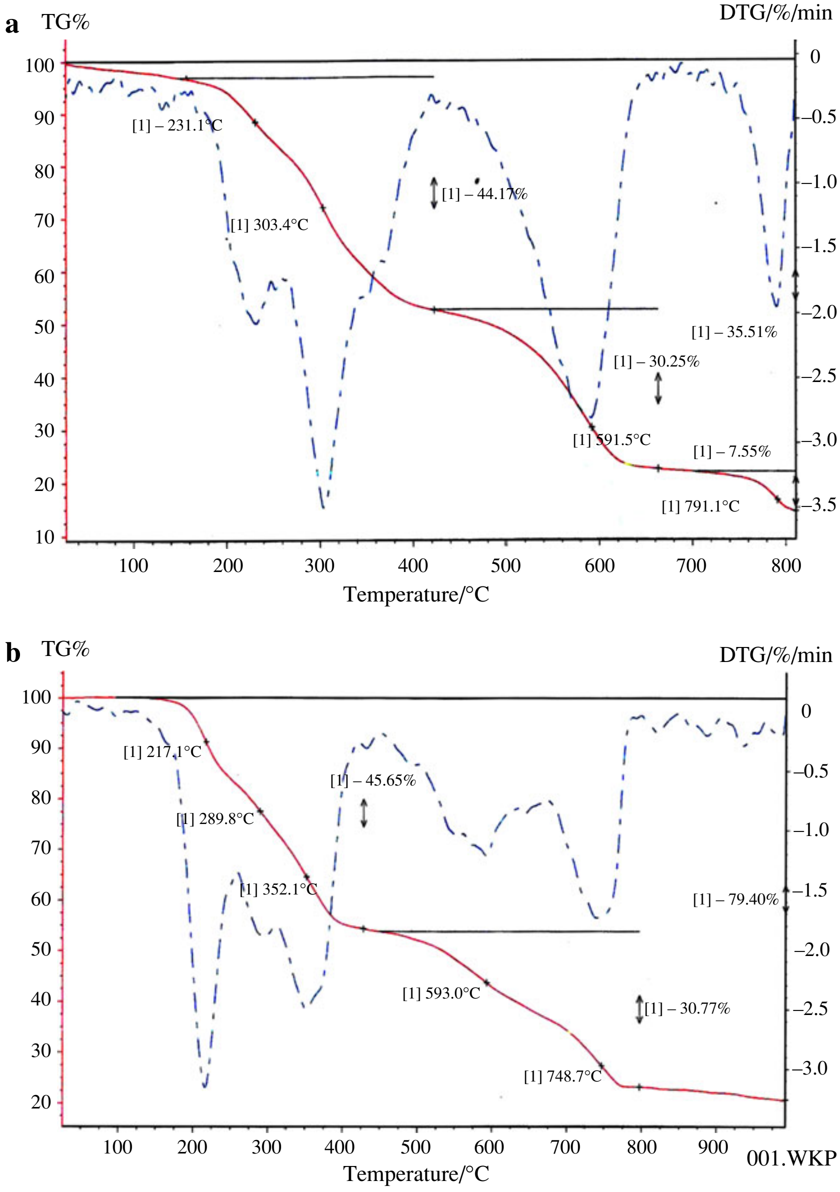


Fig. 1 **a** TG–DTA of 0.1 urea thiourea mixed crystal. **b** TG–DTA of 0.25 urea thiourea mixed crystal

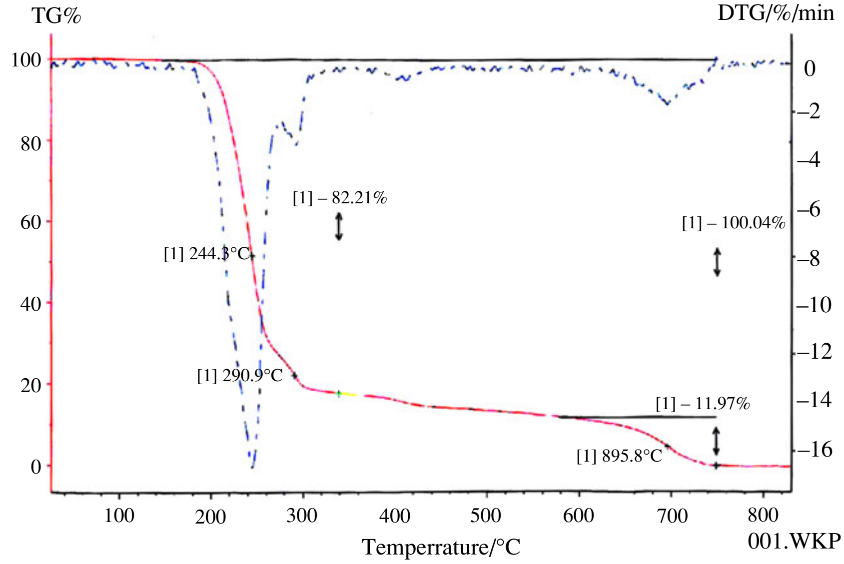


Fig. 2 TG-DTA of 0.5 urea thiourea mixed crystal

Step 1

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

Step 2

$$\cdots \mathrm{HN{-}CS{-}NH_2} \cdots \rightarrow \mathrm{H_2S + N_2 + C}$$

Two molecules of ammonia and a molecule of carbon monoxide are lost on heating the compound 0.5 UTMC from 175 to 295 °C. These accounts for 82.21% mass loss observed on the TG curve. Here the decomposition pattern of 0.1 and 0.25 UTMC is some what different from 0.5 UTMC. This is because of the formation of weak hydrogen bond between C=O……N–H of urea and thiourea. This accounts for 44.17% mass loss occurring in first-stage decomposition and 45.67% of mass loss observed in the temperature between 325 and 450 °C. In the case of 0.5, urea is stable up to 175 °C. Above 175 °C urea in the various proportions of UTMC decomposes into two molecules of ammonia and a molecule of carbondioxide. Afterwards, i.e. when the temperature reaches 625 °C, thiourea in UTMC begins to split to hydrogen sulphide, nitrogen and carbon residue. This accounts for 11.97% mass loss observed on the TG curve. The thermogravimetric studies thus confirm the formation of the title compound. Similarly, in the case of 0.1, 0.25 UTMC, ammonia and carbon monoxide lost on heating the compound from 180 to 250 °C. This accounts for 44.17 and 45.67% mass loss observed on the TG curves. Here the thermal stability of 0.1 and 0.25 UTMC was decreased when compared to 0.5 UTMC. This indicates the higher percentage of urea combines with thiourea. Thiourea in 0.1 and 0.25 UTMC is stable up to 320 °C. After that, thiourea begins to split. This accounts for 30.25 and 30.77% mass loss observed on the TG curves.

Solubility

The literature survey indicates the organic urea, thiourea salts as nonlinear optic materials. The salts used for the experiments are Analar Merck grade. The salts were recrystallized by using deionized water. It is essential to increase purity to a respectable level before proceeding further. Considerably recrystallization will produce material which is pure for crystal growth. Urea, thiourea salts are recrystallized with distilled water. Saturated solutions of urea, thiourea were prepared at 40 °C. The solutions were filtered to avoid any insoluble impurities by using heated apparatus to prevent nucleation. The solutions were cooled down to room temperature in order to obtain maximum yield. The resulted crystals were recrystallized further. The fine powdered crystals were filtered off by suction and air-dried at room temperature. The purity was then checked by standard method analysis like melting point.

Doubly distilled water was used in all experiments. First of all the solubility of the salts was determined. The experimental procedure adopted was as follows.

The saturated urea, thiourea and solutions of A to C (solution A, B and C = 0.1, 0.25 and 0.5, UTMC in water) are prepared individually. Then the empty weight of silica crucible was weighed. 5 mL of saturated solution was taken in a crucible and it was also weighted. From this the solubility of urea in 100 mL of water was found as 108.9 g and that of thiourea was 10.5 g. Similarly the solubility of 0.1, 0.25 and 0.5 UTMC is presented in Table 1.

Table 1 Effect of temperature on solubility of urea thiourea mixed crystal in water

Proportions	Solvent	Temperature/K	Solubility/g/100 mL
0.1	Water	303	91
0.1	Water	305	125
0.1	Water	307	160
0.25	Water	303	73.3
0.25	Water	305	79.5
0.25	Water	307	85.7
0.5	Water	303	48.6
0.5	Water	305	55.2
0.5	Water	307	61.4

It was observed that the salt thiourea is less soluble so the proportions of the crystals were expressed in terms of less soluble salt. The solubility decreases with increase of thiourea proportions. Solubility of the mixed crystals in all proportions increases with increase of temperature.

FTIR Spectral Analyses

The FTIR spectra of the various proportions of UTMC were recorded on a Burker IFS 66 V FTIR spectrometer by KBr pellet technique in the range 400–4,000 cm^{-1} and shown in Figs. 3, 4 and 5. The observed bands along with their vibrational assignments have been given in Table 2. Here the characteristic vibrational absorptions of UTMC have been compared with those of thiourea and urea. The high frequency N–H absorption bands in the region 3,100–3,500 cm^{-1} in the spectra of urea, thiourea were shifted to higher frequencies on the formation of urea thiourea compound indicating that the hydrogen bonding must be between nitrogen atom of urea and hydrogen of thiourea. It can be seen from the table that the symmetric stretching of C=S (in 0.25 UTMC) vibrations at 740 cm^{-1} of thiourea was shifted to lower frequencies (from 724 to 733 cm^{-1}), asymmetric stretching of C=S vibration at 1,417 cm^{-1} was shifted to higher frequencies (1,433, 1,431 cm^{-1}) in 0.25 and 0.5 UTMC. Similarly C–N stretching vibration at 1,089 cm^{-1} was shifted to higher frequency (1,093 and 1,095 cm^{-1}). This shows that binding of urea with thiourea is through nitrogen. The formation of hydrogen bond expected to increase the contribution to highly polar character of the structure of urea and thiourea molecules resulting in a stronger double bond character for the nitrogen to carbon and sulphur to carbon. The band observed at 1,589–1,626 cm^{-1} corresponds to the band of thiourea assigned to the N–C–N stretching vibration. This frequency might be attributed to a stronger double bond character of carbon to nitrogen and carbon to sulphur. The band observed at 2,000–2,700 cm^{-1} also confirms the formation of title compound, because delocalization of π electrons of urea and thiourea occurs at these regions. These bands are not observed in single crystals of urea and thiourea.

SHG efficiency

The nonlinear optical property of various proportions of UTMC was confirmed by shining Nd:YAG laser ($\lambda = 1046$ nm) on thin plate of grown crystal. It is observed that green light is coming out from 0.1, 0.25 and 0.5 UTMC. The frequency of the emitted light was drastically decreased from 0.1, 0.25 to 0.5 and then slightly

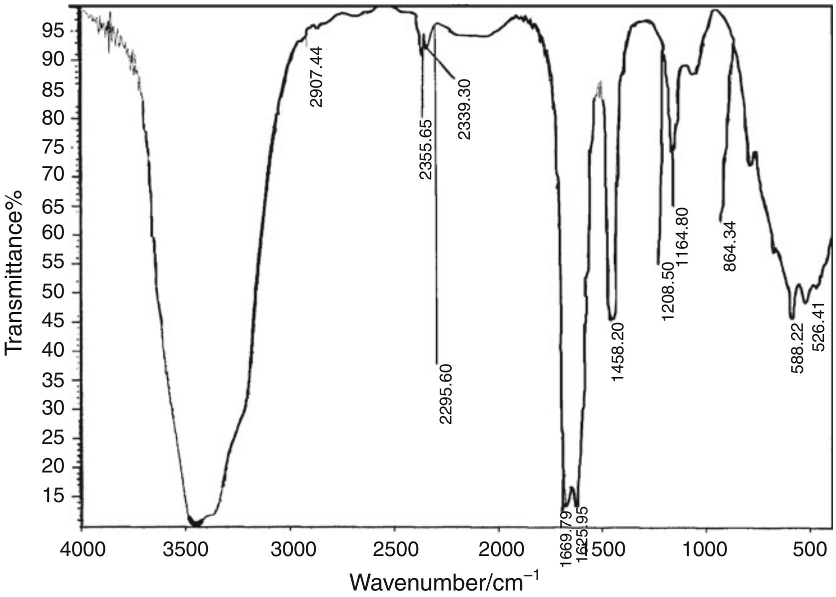


Fig. 3 FTIR spectrum of 0.1 UTMC in water

Fig. 4 FTIR spectrum of 0.25 UTMC in water

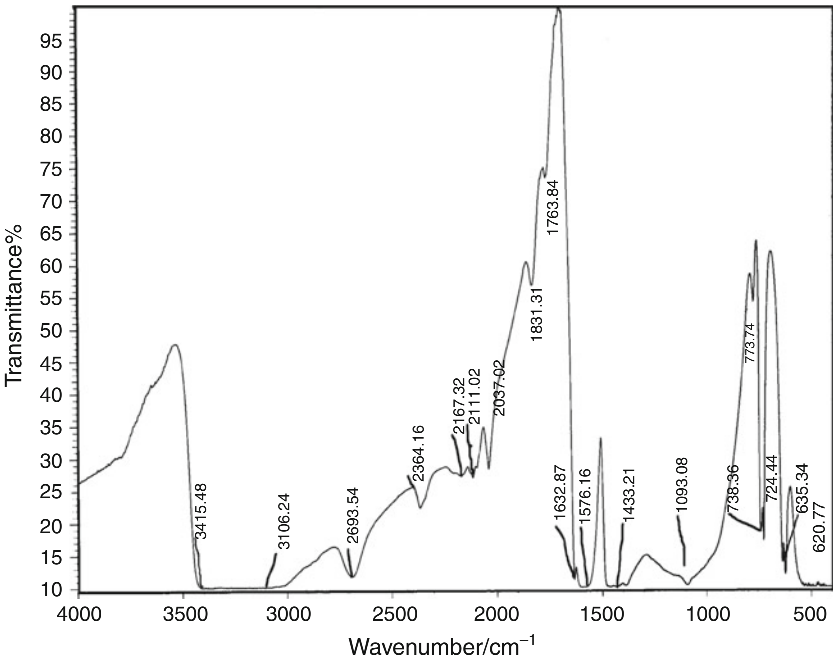
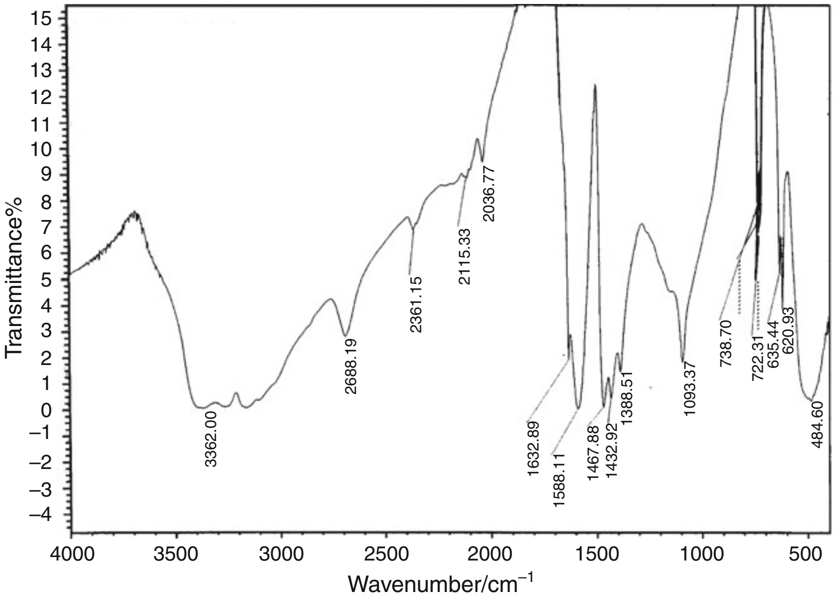


Fig. 5 FTIR spectrum of 0.5 UTMC in water



increased from 0.5. This is due to fact that the oxygen in urea is more electronegative than sulphur in thiourea. This causes the more delocalization of electrons in the case of 0.1, 0.25 UTMC when compared to 0.5. This increase the noncentro-symmetric properties of urea, hence enhance its nonlinearity. The qualitative measurement of the second harmonic conversion efficiency was determined using powder technique developed by Kurtz and Perry. The crystal was ground into powder and density packed between two transparent glass slides. A Nd:YAG laser beam of wavelength 1,064 was made to fall normally on the sample cell. The transmitted fundamental wave was absorbed by a $CuSO_4$ solution and the second harmonic signal was detected by a photomultiplier tube and displayed on storage oscilloscope. An ADP crystal, powdered to the identical size was used as a reference material in the SHG measurement.

X-ray diffraction study

The X-ray diffraction pattern of UTZC is given in Figs. 6, 7 and 8. The American chemical Society for Testing and Materials (ASTM) data of urea and thiourea are also represented.

Table 2 FTIR Spectra of 0.1, 0.25, 0.5 UTMC compared with urea, thiourea

Wave number/cm^{-1}					
Urea	Thiourea	0.1 UTMC	0.25 UTMC	0.5 UTMC	Assignment
–	411	–	–	–	δ_s(S–C–N)
508	494	526	–	485	δ_{as}(N–C–N)
–	–	588	635, 621	635, 621	$\delta_s(NH_2)$
–	740	–	724	722	δ_s(C=S)
790	–	–	774	739	δ_{as}(C=O)
–	–	864	–	–	$\delta_s(NH_2)$
–	1089	–	1093	1093	γ_s(C–N)
–	–	1165	–	–	γ_s(C–O)
–	–	1209	–	–	γ_s(CN & δ_s NH_2)
–	–	–	–	1389	γ_s(CN & δ_s NH_2)
–	1417	–	1433	1433	γ_{as}(C=S)
–	1471	1458	–	1468	γ_s(N–C–N)
–	–	–	1576	1588	γ_{as}(CN & δ_s NH_2)
1631	1627	1626	1633	1633	$\delta_{as}(NH_2)$
–	–	1670	1831, 1764	–	γ_s(C=O)
–	–	–	2037	2036	$\gamma_s(NH^+)$
–	–	–	2112	2115	γ_s(N=C=N)
–	–	–	2167	–	$\gamma_s(NH^+)$
–	–	2296	–	–	γ_s(N=C=O)
–	–	2356, 2339	2364	2361	$\gamma_s(C{=}NH^+)$
–	–	–	2694	2688	$\gamma_s(NH_2^+)$
–	3167	–	3106	–	$\gamma_s(NH_2)$
3320	3280	3364	–	–	$\gamma_{as}(NH_2)$
3422	–	3456	3415	3362	$\gamma_{as}(NH_2)$

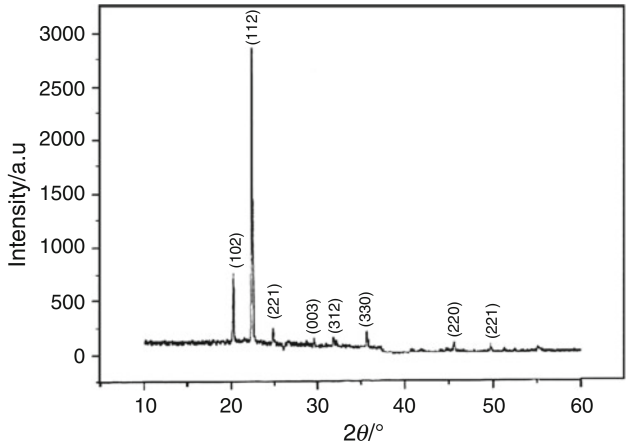


Fig. 6 XRD pattern of 0.1 urea thiourea mixed crystal

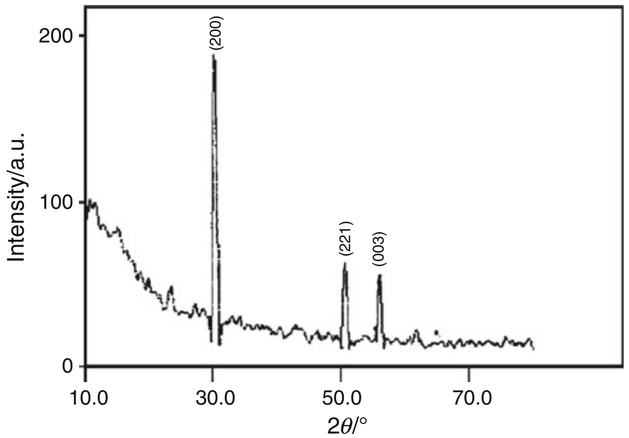


Fig. 7 XRD pattern of 0.25 urea thiourea mixed crystal

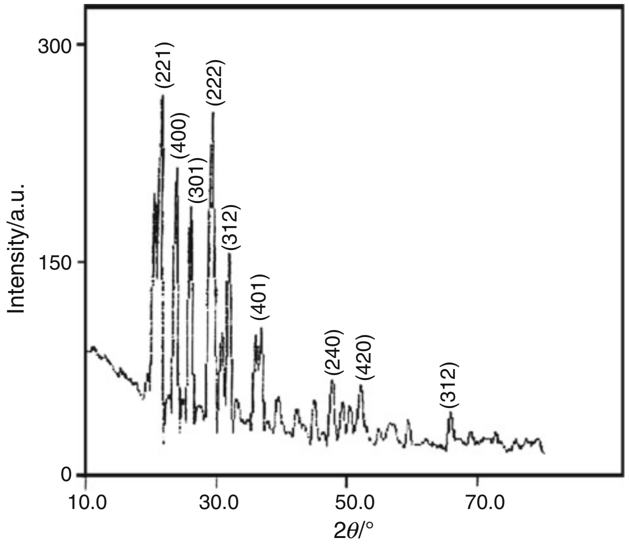


Fig. 8 XRD pattern of 0.5 urea thiourea mixed crystal

From the ASTM values, the different planes absorbed are identified for all the mixed crystals and they are produced. Urea belongs to tetragonal and D_{2D}^{2}–P42$_1$M and thiourea belongs to D_{2H}^{16}–P$_8$MM$_1$ orthorhombic. It is understood that the number of planes absorbed decreased, and d values also decreased. This may be due to the overlapping of planes of urea crystals and reorientation in the structure, and this brings at different morphology of the crystals itself. This is a striking phenomena observed and this mixed combination of mixed crystals will produce a wide range of laser active crystals.

Conclusions

Mixed crystals of various proportions of UTMC were prepared at room temperature by slow evaporation of aqueous solutions. The bright and transparent crystals obtained were characterized. The TG and DTA studies confirm a two-stage decomposition of the compound when heated between 180 and 750 °C. 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.

References

1. Mojumdar SC, Madhurambal G, Saleh MT. A study on synthesis and thermal, spectral and biological properties of carboxylato-Mg(II) and carboxylate-Cu(II) complexes with bioactive ligands. J Therm Anal Calorim. 2005;81:205–10.
2. Mojumdar SC, Melnik M, Jona E. Thermoanalytical investigation of magnesium(II) complexes with pyridine as bio-active ligand. J Therm Anal Calorim. 1999;56:541–6.
3. Madhurambal G, Ramasamy P, Anbusrinivasan P, Vasudevan G, Kavitha S, Mojumdar SC. Growth and characterization studies of 2-bromo-4′-chloro-acetophenone (BCAP) crystals. J Therm Anal Calorim. 2008;94:59–62.
4. Kubranova M, Jona E, Rudinska E, Nemcekova K, Ondrusova D, Pajtasova M. Thermal properties of Co-, Ni- and Cu-exchanged montmorillonite with 3-hydroxypyridine. J Therm Anal Calorim. 2003;74:251–7.
5. Meenakshisundarm SP, Parthiban S, Madhurambal G, Mojumdar SC. Effect of chelating agent (1, 10-phenanthroline) on potassium hydrogen phthalate crystals. J Therm Anal Calorim. 2008;94:21–5.
6. Boomadevi S, Dhanasekaran R, Ramasamy P. Investigation on nucleation kinetics of urea crystals from methanol. Cryst Res Technol. 2002;37:159–68.
7. Shannon JJ, Haris KDM. Phase transitions involving re-ordering of the guest molecules in solid organic compound: heptonic anhydride/urea. J Chem Soc. 1996;92:267–72.
8. Haris KDM, Thomas JM. Structural aspects of urea inclusion compounds and their investigation by X-ray diffraction study. J Chem Soc. 1990;86:2985–96.
9. Madhurambal G, Ramasamy P, Anbusrinivasan P, Suganthi M, Vasudevan G, Mojumdar SC. The growth and characterization of 2, 4 dinitro phenyl hydrazone of benzophenone and mixed crystals. J Therm Anal Calorim. 2008;94:45–51.
10. Rajasekaran R, Rajendran KV. Investigation on nucleation of cadmium thiourea chloride single crystals. Mater Chem Phys. 2003;82:273–80.
11. Kumar K, Ramamurthy K. A novel growth method for zinc thiourea sulphate single crystals. Cryst Res Technol. 2006;41:217–20.
12. Sangwal K, Mielniczek-Brzoska E. Effect of impurities on metastable zone width for the growth of ammonium oxalate monohydrate crystals from aqueous solutions. J Cryst Growth. 2004;267:662–75.
13. George AR, Harris KDM. Computational investigation of surface structural relaxation in crystalline urea. J Mater Chem. 1995;5:133–40.
14. Boomadevi S, Dhanasekaran R, Ramasamy P. Investigation on nucleation kinetics of urea crystals from methanol. Cryst Res Technol. 2002;37:159–68.
15. Verma S, Singh MK, Wadhavan VK, Suresh CH. Growth morphology of zinctris(thiourea)sulphate crystals. J Phys. 2000;54:879–84.
16. Gupte SS, Desai CF. Vickers hardness anisotropy and slip system in zinc(tris)thioureasulphate crystals. Cryst Res Technol. 1999;34:1329–32.
17. Krishnan H, Justin C, Jerome S. Growth and characterization of novel ferroelectric urea-succinic acid single crystals. J Cryst Growth. 2008;310:3313–7.
18. Varshney KG, Agrawal A, Mojumdar SC. Pectin based cerium(IV) and thorium(IV) phosphates as novel hybrid fibrous ion exchangers synthesis, characterization and thermal behaviour. J Therm Anal Calorim. 2005;81:183–9.
19. Zaitseva NP, Rashkovich LN, Bogatyreva SV. Stability of KH_2PO_4 and K(H, D)2PO4 solutions at fast crystal growth rates. J Cryst Growth. 1995;148:276–82.
20. Udayalakshmi K, Ramamurthi K. Optical, mechanical and thermal properties of p-bromoacetanilide. Cryst Res Technol. 2006;41:795–9.
21. Hall SR, Kolinsky PV, Jones R, Allen S, Gordon P, Bothwell B, Bloor D, Norman PA, Hursthouse M, Karaulov A, Baldwin J, Goodyear M, Bishop D. Polymorphism and nonlinear optical activity in organic crystals. J Cryst Growth. 1986;79:745–51.
22. Nyvlt J, Rychly R, Gottfried J, Wurzelova J. Metastable zone-width of some aqueous solutions. J Cryst Growth. 1970;6:151–62.
23. Kurtz SK, Perry TT. A powder technique for the evaluation of nonlinear optical materials. J Appl Phys. 1968;39:3798–813.
24. Madhurambal G, Mojumdar SC, Hariharan S, Ramasamy P. TG, DTC, FT-IR and Raman spectral analysis of Zn_a/Mg_b ammonium sulfate mixed crystals. J Therm Anal Calorim. 2004;78:125–33.
25. Ushasree PM, Jayavel R, Ramasamy P. Growth and characterization of phosphate mixed ZTS single crystals. Mater Sci Eng B. 1999;65:153–8.
26. Bhagavannarayana G, Choubey A, Shubin YV, Lal K. Study of point defects in as-grown and annealed bismuth germanate single crystals. J Appl Cryst. 2005;38:448–54.
27. Jayalakshmi D, Kumar J. Growth and characterization of bis thiourea zinc acetate. Cryst Res Technol. 2006;41:37–40.
28. Anie S, Cyriac M, Ittyachen MA. Growth and characterization of a new metal organic crystal: Potassium thiourea bromide. Mater Lett. 2001;49:299–302.
29. Shahil S, Stella S, P Mythili. Growth and characterization of pure and doped cadmium thiourea acetate single crystals. J Cryst Growth. 2008;310:2555–62.
30. Bhagavannarayana G, Kushwaha SK, Parthiban S. Influence of inorganic and organic additives on the crystal growth, properties and crystalline perfection of tris (thiourea) copper (I) chloride crystals. J Cryst Growth. 2008;310:2575–83.