Crystal growth and characterization of 0.1urea thiourea mixed crystal

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ABSTRACT
Mixed crystals of 0.1urea thiourea have been grown in solution by slow evaporation technique at ambient temperature (30ºC). 0.1Urea thiourea mixed crystal (UTMC) crystallizes in tetragonal system with unit cell parameters a = b = 5.7012 c =5.0369. A powder X-ray diffraction pattern has been recorded and indexed. The UV and FTIR Spectrum have been recorded in the range 200-400nm and 400-4000cm⁻¹ respectively. The presence of functional groups has been confirmed by FTIR analysis. 0.1UTMC crystals are thermally stable up to 160°C and shows optical nonlinearity for Nd:YAG laser at 1064μm wavelength. The preliminary data indicate that the harmonic generation efficiency of 0.1UTMC is greater than that of pure thiourea.

Keywords: Crystal growth, 0.1UTMC, FTIR.

1. INTRODUCTION
Urea crystals attract the attention of both theoreticians and experimentalist due to the non-linear optical piezoelectric properties. Urea is representative of clears of materials which are applicable to photonics and reference material in the DMOS (diffusive mixing of organic solution) experiment in microgravity carried out by NASA. Thiourea, urea possesses a large dipole moment which are potentially useful material for frequency doubling of near IR laser radiation. It is also significant impact on laser technology, optical communication and optical data storage. In the modern world, the development of science in many areas has been achieved through the growth of mixed crystals. Nonlinear optical (NLO) materials are expected to play a major role in the technology of photonics including optical information processing. Many research efforts are undertaken to synthesize and characterize new molecules for second-order nonlinear optical (NLO) applications such as high-speed information processing, optical communications and optical data storage.

2. EXPERIMENTAL
0.1Urea mixed thiourea crystals were grown by slow evaporation technique at room temperature. 9g of urea and 1g of thiourea (AR Merck grade) was dissolved in triple distilled water. The proportion of the mixed crystal is expressed interms of less soluble salt. Mixed solutions were properly stirred for two hours and filtered to remove the suspended particles. The filtered solutions were poured in to petridishes and kept for evaporation at ambient temperature. In solution growth technique, the size of a crystal depends on the amount of the material available in the solution, which in turn is decided by the solubility of the material in the solvent. The solubility of synthesized 0.1UTMC material has been determined in water. This was performed by adding water maintained at constant temperature to a known quantity of the material till the material is dissolved. Using this technique, the magnitude of solubility of 0.1UTMC has been evaluated for various temperatures between 303-305K.

Infrared spectroscopic studies were carried out on the grown crystals in order to understand the solubility and bonding in them. The FTIR spectrum of 0.1UTMC crystal was recorded on a Shimadzu spectrometer using KBr pellet technique in the wavelength range 400-4000cm⁻¹. The powder XRD pattern of the grown crystal was recorded using Cu Kα radiation (λ = 1.5418Å).

Thermogravimetric (TGA) and differential analysis (DTA) of 0.1UTMC were made employing Netzch STA 409 thermal analyzer at a heating rate of 10°C/min under nitrogen atmosphere.

The nonlinear property in urea doped thiourea crystal was confirmed by shining Nd:YAG laser (λ = 1046nm) on the plate of the grown
crystal. It is observed that green light is coming out from the crystal. 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 densely packed between transparent glass slides. An Nd:YAG laser beam of wavelength of 1064 nm was made to fall on the sample cell. The transmitted fundamental wave was absorbed by a CuSO₄ solution and the second harmonic signal was detected by a photo multiplied tube and displayed on a storage oscilloscope. An ADP crystal, powdered to the identical size was used as reference material in the SHG measurement.

1. RESULTS AND DISCUSSION

Mixed crystals of 0.1UTMC started to grow in about one week in the Petri dishes. The photograph of the 0.1UTMC crystal is shown in Fig. 3. Fig. 1 and 2 shows the morphology of the urea, thiourea.

Fig. 1 Urea

Fig. 2 Thiourea

Fig. 3 0.1UTMC
The variation of solubility with temperature is shown in Fig. 4. The solubility of 0.1 UTMC was expressed in 79.8 g/100 ml and temperature in 303 Kelvin respectively. The solubility of urea and thiourea was found to be 108.2 g/100ml, 24.4 g/100ml. 0.1 UTMC has a positive temperature coefficient of solubility. Therefore, slow evaporation of aqueous solution of 0.1 UTMC could be attempted to grow bulk crystals.

![Fig. 4: Solubility of urea, thiourea and 0.1 UTMC in water](image)

Series 1 – urea; Series 2 – Thiourea; Series 3 - 0.1 UTMC

The UV spectra for urea, thiourea and 0.1 UTMC are shown in Fig. 5, 6 and 7. The observed bands have been tabulated in Table 1. In 0.1 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 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 0.1 UTMC.

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

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Absorbance</th>
<th>Wavelength in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>0.013</td>
<td>335</td>
</tr>
<tr>
<td></td>
<td>0.456</td>
<td>236</td>
</tr>
<tr>
<td>Thiourea</td>
<td>1.416</td>
<td>255</td>
</tr>
<tr>
<td></td>
<td>1.480</td>
<td>210</td>
</tr>
<tr>
<td>0.1 UTMC</td>
<td>1.866</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>0.005</td>
<td>388</td>
</tr>
</tbody>
</table>

The FTIR spectra for urea, thiourea and 0.1 UTMC are shown in Fig. 8, 9 and 10. The high frequency N-H absorption bands in the region 3100-3500 cm⁻¹ in the spectra of urea was shifted to higher frequencies on the formation of urea thiourea compound indicating that hydrogen bonding must be between nitrogen atom of urea with hydrogen of thiourea. It can be seen from the table that the bending vibration of C=S at 785.26 of urea was shifted to higher frequencies in 0.1 UTMC (864), asymmetric C=S vibration at 1453.78 of urea was shifted to higher frequency (1458 cm⁻¹) in 0.1 UTMC. Similarly C-N stretching vibration at 1063.52 of thiourea was shifted to higher frequencies in urea and 0.1 UTMC (1093.15, 1165 cm⁻¹). This shows the binding of urea with thiourea is through nitrogen. 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 2700 cm⁻¹ also confirms the formation of the title compound, because delocalization of pi electrons of urea and thiourea occur at these regions. These bands are not observed in single crystal of urea.

**Table 2: FTIR assignments for urea, thiourea and UTMC**

<table>
<thead>
<tr>
<th>Urea (cm⁻¹)</th>
<th>Thiourea (cm⁻¹)</th>
<th>UTMC (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3455</td>
<td>1625</td>
<td>1064</td>
<td>ν₃ NH₂</td>
</tr>
<tr>
<td>3362</td>
<td>1591</td>
<td>1093</td>
<td>ν₃ N=NC=S</td>
</tr>
<tr>
<td>1591</td>
<td>1454</td>
<td>1458</td>
<td>ν₃ C=S</td>
</tr>
<tr>
<td>1626</td>
<td>1478</td>
<td>1165</td>
<td>ν₁ CN</td>
</tr>
<tr>
<td>785</td>
<td>732</td>
<td>864</td>
<td>δ₃ C=S</td>
</tr>
</tbody>
</table>

as-asymmetric;  s-symmetric;  d-deformation;  γ-bond stretching
Fig. 8 FTIR Spectrum of urea
Fig. 9 FTIR Spectrum of thiourea
Figures 11, 12 and 13 show the XRD pattern of urea, thiourea and 0.1UTMC crystals respectively, interplanar spacing d and intensity of peaks are recorded in table. The XRD pattern of 0.1UTMC has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in 0.1UTMC(112). XRD of 0.1UTMC show a up shift of the peak positions compared with urea and thiourea. However, most of the peaks in the XRD peak are not resemble with that of urea and thiourea. The unit cell dimensions of 0.1UTMC crystal were determined using RIGAKU AFC7 diffractometer. 0.1Urea thiourea mixed crystal (UTMC) crystallizes in tetragonal system with unit cell parameters parameters a = b = 5.7012 c = 5.0369.
Fig. 11 XRD pattern for urea
Fig. 12  XRD pattern for thiourea
Fig. 13 XRD pattern for 0.1UTMC
The TG and DTA of UTMC is shown in Fig. 14. The TG curve indicates a two step weight loss on heating the compound between 30-800°C. The following decomposition pattern is formulated for UTMC:

**Step 1**

\[ \ldots \text{H-N-CO-NH-H} \ldots \text{S=C (NH}_2\text{)}_2 \rightarrow 2\text{NH}_3 + \text{CO} \]

**Step 2**

\[ \ldots \text{HN-CS-NH}_2 \ldots \rightarrow \text{H}_2\text{S + N}_2 + \text{C} \]

Two molecules of ammonia and a molecule of carbon monoxide are lost on heating the compound from 160-240°C. This accounts for 53.28% 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 280 to 380°C. This weight loss indicates the presence of urea and thiourea in UTMC. In UTMC, urea is stable up to 160°C. Above 160°C urea in UTMC decomposes in to two molecules of ammonia and a molecule of carbon monoxide. Urea is slowly vaporises to the temperature of 240°C. Afterwards, thiourea in UTMC begins to split to hydrogen sulphide, nitrogen and carbon residue. This accounts for 41.19% weight loss observed in the TG. This is consistent with the thermogram. The thermogravimetric study thus confirms the formation of the title compound in the stachiometric ratio and the decomposition pattern of UTMC. The DTA curve depicted in Fig. 14 shows an exothermic dip at 137.5 and 241 °C corresponds to the first stage decomposition. The second deep and broad exothermic dip in the temperature and 380.8°C is due to the decomposition of thiourea in UTMC.

**CONCLUSION**

Mixed crystals of 0.1 urea thiourea were prepared at room temperature by slow evaporation of aqueous solution. The TG-DTA studies confirm the two stage decomposition of the compound when heated between 133°C-800°C. The FTIR spectra show the characteristic vibrational frequencies of urea thiourea mixed crystal. Detailed structural analysis of the compound under progress.

**REFERENCES**