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# Crystal growth, thermal, optical studies of Urea Thiourea Magnesium Sulphate (UTMS)

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**Abstract:** The semi-organic non-linear optical crystal thiourea magnesium sulphate (UTMS) has been grown by slow evaporation technique using waster as solvent. Good quality single crystals with size 7 x 6 x 4 $mm^3$ were grown within three weeks. The lattice parameters of the grown crystals have been determined by X-ray diffraction studies. Vibrational spectrum was recorded to determine the symmetries of molecular vibrations. The TGA, DTA and DSC show that the material has good thermal stability. The UV-Vis spectrum shows the transmitting ability of the crystal in the entire visible region. The non-linear nature of the crystal was confirmed by SHG test.

**Keywords**: thiourea magnesium sulphate, Infrared and UV spectra; Optical transmission; Second harmonic generation.
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## Introduction

Nonlinear optical (NLO) materials have attracted much attention due to their major role in the emerging photonic and opto electronic technologies[1,2].To be useful in this technology the materials should possess large second order optical nonlinearities, short transparency cutoff wavelength and thermal stability. Organic materials possess good optical non-linearity but they are thermally unstable. Inorganic materials are having excellent mechanical and thermal properties with moderate non-linearities. The search for new and efficient NLO materials has resulted in the development of a new class of materials called semiorganics. Semiorganics are formed by combining organic molecules of high polarizability[3] with mechanically strong and thermally stable inorganic molecules. These materials combining the chemical flexibility and nonlinearity of organics and favorable physical properties of inorganics[4,5] . Here, an attempt is made to grow and characterize a single crystal of thiourea magnesium sulphate (TMS) by slow evaporation. Large single crystals can be grown from slow evaporation solution growth[6].

## Experimental

From the solubility test, TMS is more soluble in water. The required quantities of the component salts were very well dissolved in double distilled water and thoroughly mixed for about 4 hours using a magnetic stirrer to ensure homogeneous temperature and concentration through out the volume of the solution. The $P_H$ of the solution is 4. The saturated solution was covered with transparent polythene paper and left undisturbed for slow evaporation. Good quality single crystals were grown within three weeks and are shown in Figure 1.

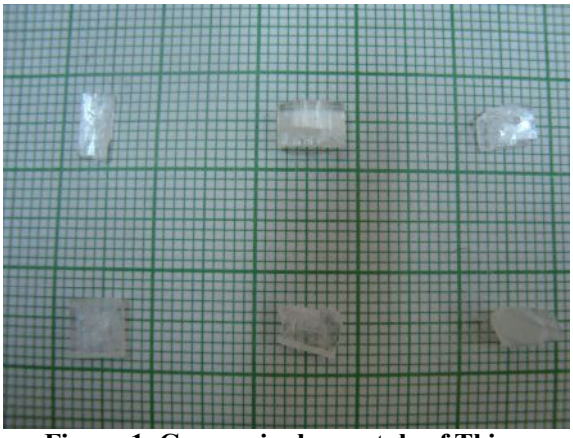

**Figure 1. Grown single crystals of Thiourea Magnesium Sulphate**

## Characterization

### Powder X-ray diffraction analysis

Powder X-ray diffraction analysis has been carried out using Philips Powder X-ray diffractometer using CuKa (λ = 1.5418 Å) radiation to identify the lattice parameters. The sample was scanned over the range 10 to 60° at a scan rate of 1°/min. The XRD pattern of the crystal is shown in Figure 2. The obtained XRD pattern was analyzed using PROSZKI software package[7] and the diffraction peaks are indexed. The peak corresponding to (200) has a minimum count of 1680 cps. From the results it is observed that the crystal belongs to orthorhombic system with the following cell dimensions: a = 7.6212 Å, b = 8.5427 Å, c = 5.5019 Å, and cell volume, V = 358.202 $Å^3$.

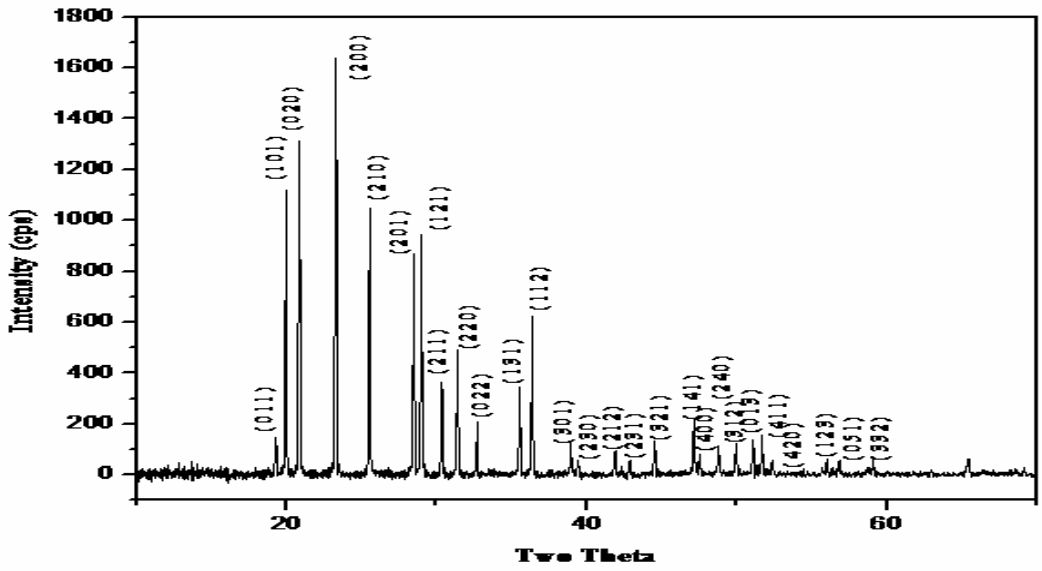


**Figure 2. XRD pattern of UTMS crystal**

## FTIR spectral study

Infrared spectroscopy is effectively used to determine the molecular structure and the identification of the functional groups in the synthesized compound. FTIR spectrum was recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4000 – 400 cm-1 and shown in Figure 3. The characteristic vibrational frequencies are assigned and compared with urea, thiourea (YAMAUCHI etal, 1950).. The symmetric and asymmetric C=S stretching vibrations at 740 and 1417 cm-1 of Thiourea are shifted to 730 and 1412 cm-1 respectively[8] . The N-H absorption bands in the high frequency region 3400 – 3000 cm-1 in the thiourea were not shifted to lower frequencies on the formation of metal-thiourea complex indicating that nitrogen to magnesium bonds are not present and bonding must be between sulphur and magnesium atoms[9]. he band at 1473 cm-1 is assigned to N-C-N stretching vibration and other characteristic vibrational frequencies are assigned in Table 1.

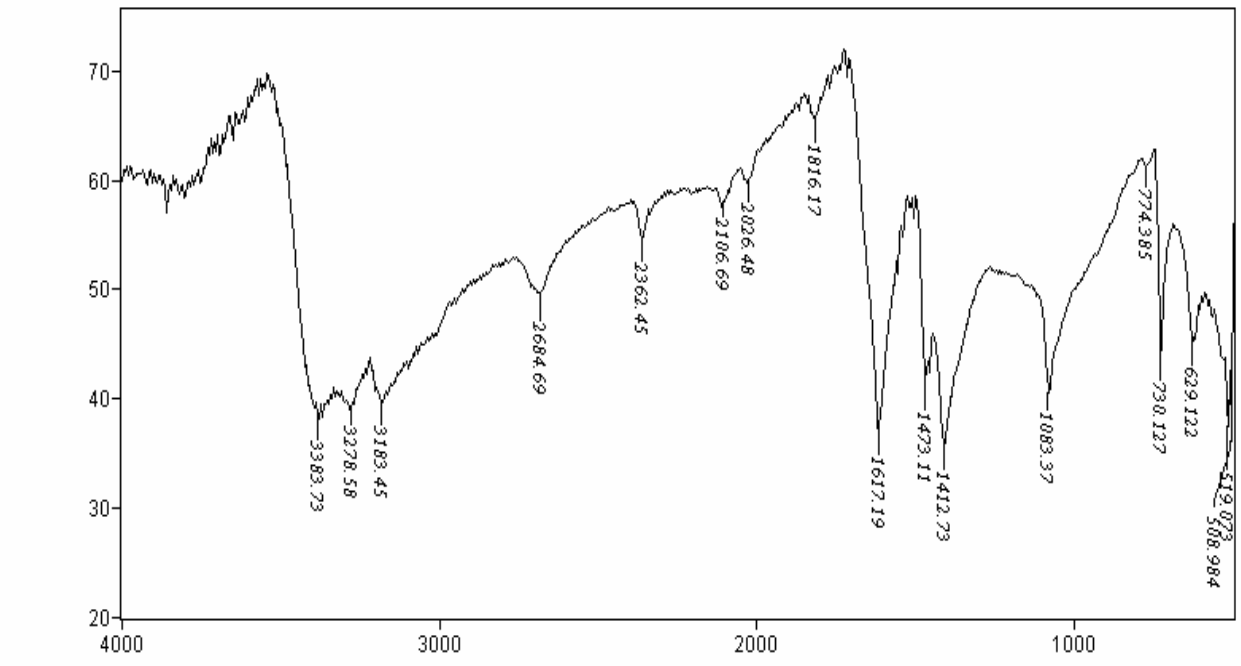


**Figure 3. FTIR spectrum of UTMS crystal**

**Table 1 Comparison of Absorption IR bands of TUMS with Urea, Thiourea**

| Urea | Thiourea | TUMS | Assignments |
|---|---|---|---|
| - | 469 | - | δ(S-C-N) |
| 508 | 494 | 509 | δ (N-C-S) |
| - | 740 | 730 | ν(C=N) |
| 790 | - | | |
| 1008 | - | - | |
| - | 1089 | 1083 | $\rho(NH_2)$ |
| - | 1417 | 1412 | $\nu_S$ (C=S) |
| 1454 | - | | |
| - | 1471 | 1473 | ν(N-C-N) |
| 1631 | 1627 | 1621 | δ $(NH_2)$ |
| 3320 | 3167 | 3178 | $\nu_S$ $(NH_2)$ |
| 3422 | 3280 | 3283 | $\nu_S$ $(NH_2)$ |
| | 3376 | 3388 | $\nu_S(NH_2)$ |

## UV-Vis spectral studies

The optical transmittance range and transparency cut off are important in optical applications. The optical absorption spectrum of UTMS was recorded using Varion Cary 5E UV-Vis-NIR spectrophotometer in the range 200 – 400 nm with high resolution and is shown in Figure 4. The significant absorption was found at 235 nm. The lower cut off wavelength is below 250 nm, which is an advantage in semi organic non linear materials. The absorbance of the crystal over inorganic material is less that one unit in the entire visible region. The transparent nature in the visible region is a desirous property for NLO application and enables it to be a good candidate for optoelectronic applications.

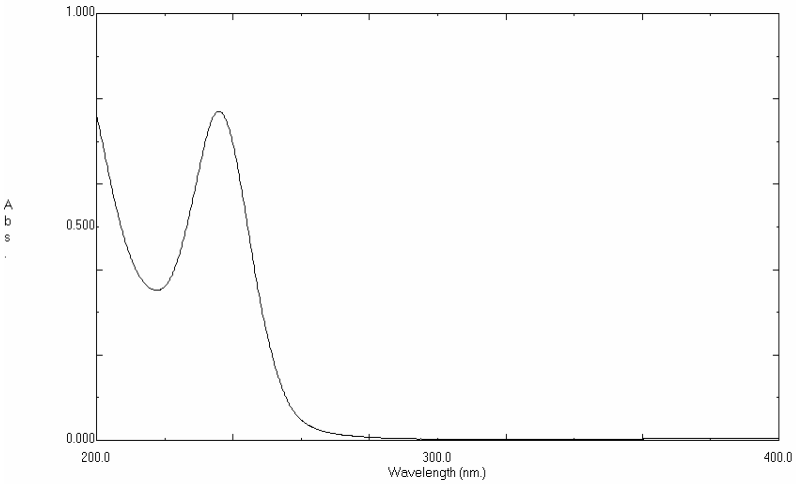


**Figure 4. UV-VIS spectrum of UTMS crystal**

## Second Harmonic Generation testing (SHG)

The SHG conversion efficiency of the crystal was carried out using the Nd:YAG laser beam of wavelength 1064 nm, using Kurtz Powder technique[10] . The second harmonic generation was confirmed by the emission of green radiation of wavelength of 532 nm. Second harmonic generation efficiency of UTMS is compared with KDP and it is found to be 1/4$^{th}$ of KDP material.

## Thermal studies

Thermogravimetry (TGA) when complemented with differential thermal analysis (DTA) and differential scanning studies (DSC) gives valuable information about decomposition patterns of materials and weight loss[11] can be got. Simultaneous TGA and DTA were carried out for the UTMS crystals. A powder sample of 3.08 mg was used for the analysis in the temperature range of 28°C to 1100°C with a heating rate of 20 K/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Fig. 5 . There is no loss of weight observed around 100°C showing the absence of any absorbed water molecules in the sample. There is a sharp endotherm at 228.73°C which has no corresponding weight loss in the TGA trace. Hence, this endotherm is assigned to melting of this compound. Major weight loss occurs in two stages between 242°C and 300°C. The first stage weight loss corresponds to 73.58% at 242.05°C another weight loss follows at 298.64°C corresponds to 82.23%. The weight loss in this range may be due to decomposition of thiourea present in UTMS. The increase in decomposition temperature compared to the decomposition temperature of thiourea which is 182°C[12] may be due to the formation of metal complex. This shows the thermal stability of UTMS.

The DSC analysis was done between 28°C and 1000°C. the DSC trace is shown in Fig. 6. There is a sharp endotherm at 229.79°C which represents its melting point. The sharpness of this peak shows good degree of crystallinity of the sample. The TGA, DTA and DSC study of UTMS crystal is stable upto its melting point.

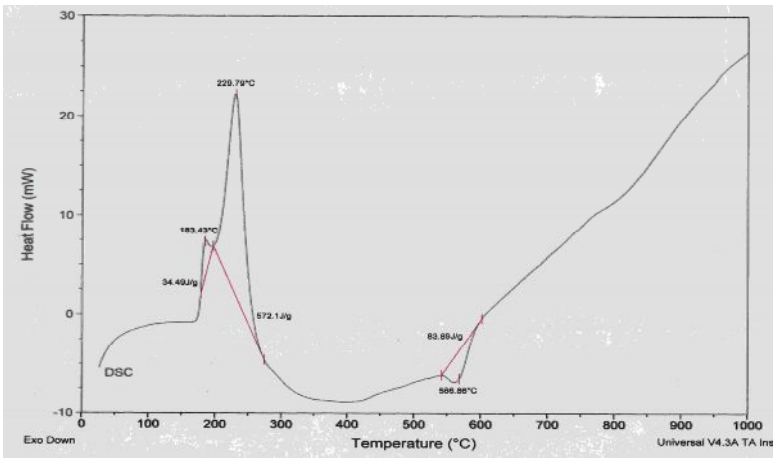


**Figure 5. TGA and DTA of UTMS crystal**

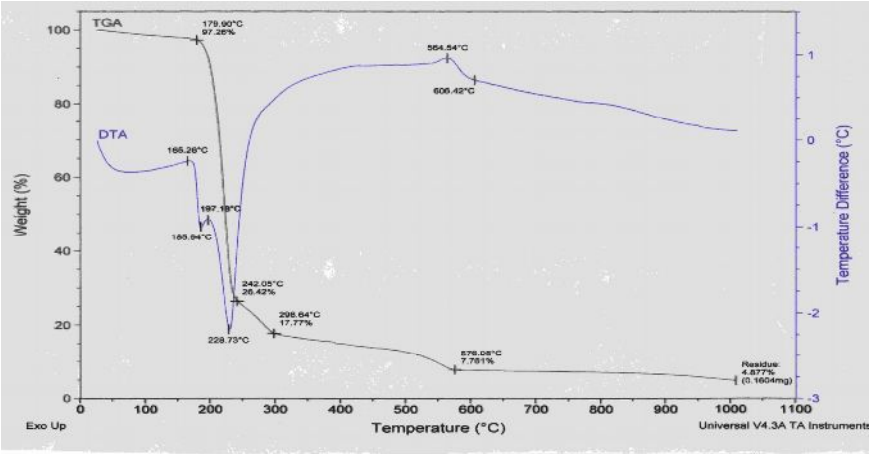


**Figure 5. DSC of UTMS crystal**

## Conclusion

1. Single crystals of UTMS have been grown by slow evaporation technique at room temperature.
2. Unit cell parameters have been evaluated by XRD technique. XRD analysis confirmed that the UTMS belongs to orthorhombic system.
3. The functional groups present in UTMS have been confirmed by FTIR spectral analysis.
4. UV-Vis spectrum shows the good optical transmittance of the crystal and proves the suitability of the crystal for NLO applications
5. The powder SHG measurement confirms the frequency doubling.
6. The UTMS crystal is found to be thermally stable upto 228°C.

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