

## Synthesis growth and characterization of a new NLO material: Thiourea urea manganese chloride

<sup>1</sup>Thendral M, <sup>2</sup>Mariappan M and <sup>2</sup>Selvarajan G\*.

<sup>1</sup> Assistant Professor, Department of Chemistry, E.G.S.P. Arts and Science College, Nagapattinam, Tamilnadu, India.

<sup>2</sup> Assistant Professor, PG and Research Department of Chemistry, Thiru.Vi. Ka. Government Arts College, Thiruvavur, Tamilnadu, India.

\*Corresponding Author: E-Mail: selvaa\_00@rediffmail.com

Received: 26<sup>th</sup> Dec 2016, Revised and Accepted: 28<sup>th</sup> Dec 2016

### ABSTRACT

A new NLO material Thiourea urea manganese chloride was grown from aqueous solution by a slow evaporation technique at room temperature. Crystals were characterized by X-ray diffraction analysis whose results they crystallize on tetragonal system. The functional group of grown crystal was found by FTIR analysis. The nonlinear optical property was confirmed by Kurtz Perry powder technique. The detailed structural analysis of the compound is under progress.

**Keywords:** Thiourea urea manganese chloride, XRD, UV-Visible Spectroscopy, FTIR, NLO.

### 1. INTRODUCTION

Materials with second order of non-linear optics have greatly attracted due to their possible applications in new technologies of optoelectronics [1-3]. Organic materials have been of particular interest, since non-linear optical responses on these materials are of microscopic origin, thus offering an opportunity to utilize theoretical models along with synthesis flexibility to design and produce new materials [4,5]. Most of the organic crystals have inadequate transparency, poor optical quality and low laser damage threshold [6]. Moreover, growth of large sized single crystals has excellent mechanical and thermal properties but they possess relatively modest nonlinearity. Due to the above reason, a lot of research has been carried out on semi organic materials which have combined properties of both organic and inorganic materials [7].

### 2. EXPERIMENTAL

#### 2.1. Synthesis

Single crystals of Thiourea urea manganese chloride was grown by preparing Thiourea, urea and manganese chloride taken in 1:1:1 equimolar ratio in triple distilled water [8-9] at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was filtered to remove insoluble impurities using

Whatmann filter paper of pore size 10 micrometers. Then the solution of Thiourea urea manganese chloride was taken in a beaker with a perforated lid in order to control the evaporation rate and kept at room temperature for crystallization. Finally a well defined single crystal was obtained after 15 days by slow evaporation method.

### 3. RESULTS AND DISCUSSION

The photograph of the grown crystals of urea, thiourea and TUMC is shown in figure 1, 2 and 3.

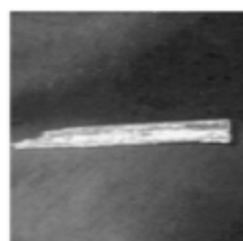


Figure - 1: urea.

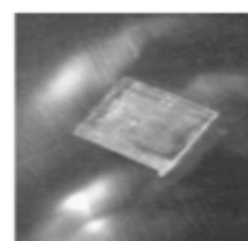


Figure -2: Thiourea

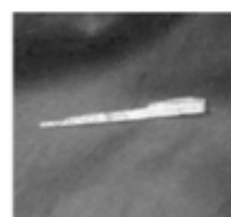


Figure - 3: UTMC

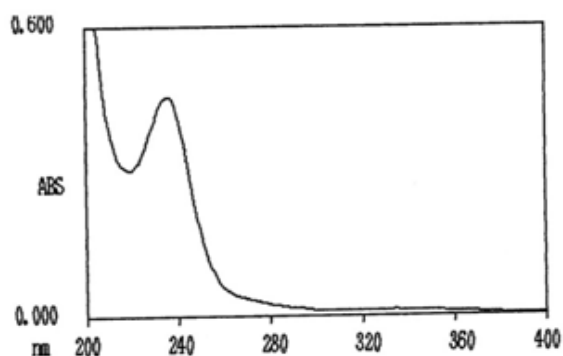


Figure - 4: UV Spectrum of Urea.

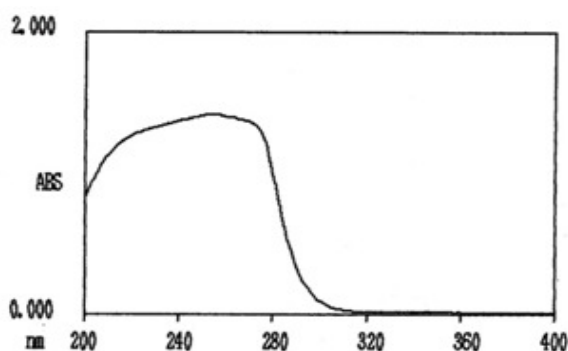


Figure - 5: UV spectrum of Thiourea.

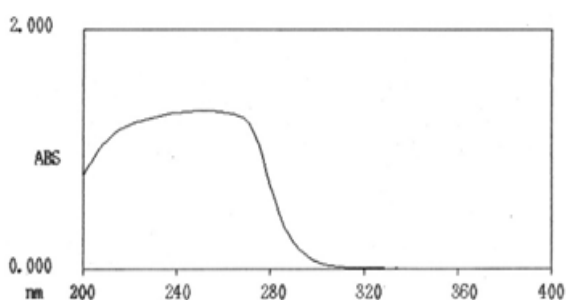


Figure - 6: UV Spectrum of UTMC.

Table - 1: Comparison of absorption band of urea, thiourea with TUMC

Crystals	Absorbance	Wavelength (nm)
Urea	0.013	335
	0.456	236
Thiourea	1.416	255
	1.480	210
TUMC	1.866	240
	0.005	388

### 3.1. UV spectral analysis

The UV spectra for urea, thiourea and (hereafter Thiourea urea manganese chloride abbreviated as TUMC) TUMC are shown in figure 4, 5 and 6. The observed bands have been tabulated in table 1. In TUMC, the  $\pi$ - $\pi^*$  absorption band shifted to longer wavelength

compared to urea. This is because of the formation of bonding urea and thiourea through manganese, decreases the bond length of  $>C=O$  and  $>C=S$  and thus smaller energy required for this transition and hence the absorption shows the blue end of the spectrum. Similarly,  $n$ - $\pi^*$  transition also shifted to higher wavelength due to less stable non-bonded electron in TUMC.

### 3.2. FTIR Spectral analysis

The FTIR spectra for urea, thiourea and TUMC are shown in Fig. 7, 8 and 9. The high frequency N-H absorption band in the region  $3100-3500\text{cm}^{-1}$  in the spectra of urea was shifted to lower frequencies on the formation of TUMC compound. It can be seen from the table that the bending vibration of  $C=S$  at  $785\text{cm}^{-1}$  of urea was shifted to higher frequency in TUMC ( $961\text{cm}^{-1}$ ), asymmetric  $C=S$  vibration at  $1454\text{cm}^{-1}$  of urea was shifted to higher frequency ( $1466\text{cm}^{-1}$ ) in TUMC. Similarly  $C-N$  stretching vibration at  $1064\text{cm}^{-1}$  of thiourea was shifted to higher frequency in TUMC ( $1095\text{cm}^{-1}$ ). This shows the binding of urea and thiourea is through manganese. 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  $2700\text{cm}^{-1}$  also confirms the formation of the title compound, because delocalization of pi electrons of urea and thiourea occur at these regions.<sup>[10-13]</sup> These bands are not observed in single crystal of urea.

Table - 2: FTIR assignments for urea, thiourea and TUMC

Urea ( $\text{cm}^{-1}$ )	Thiourea ( $\text{cm}^{-1}$ )	TUMC ( $\text{cm}^{-1}$ )	Assignment
3455	3362	3162	$\nu_s \text{NH}_2$
1625	1591	1587	$\gamma_{as} \text{N}=\text{C}=\text{N}$
1454	1478	1466	$\nu_s \text{C}=\text{S}$
1064	1093	1095	$\nu_s \text{CN}$
785	732	961	$\delta_s \text{C}=\text{S}$

as-asymmetric; s-symmetric;  $\delta$  deformation;  $\gamma$ -bond stretching

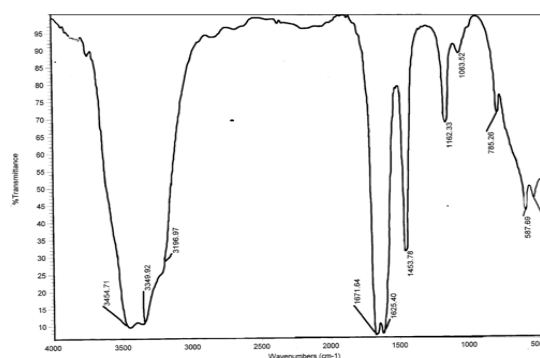


Figure - 7: FTIR Spectrum of urea.

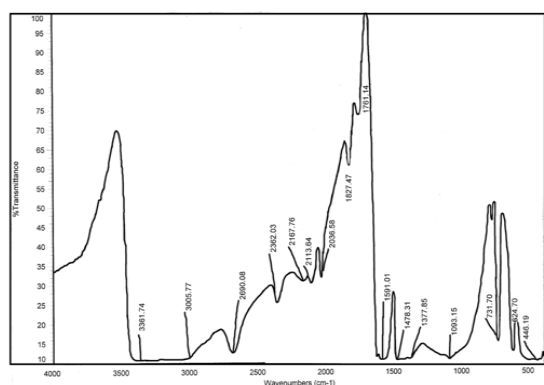


Figure - 8: FTIR Spectrum of thiourea.

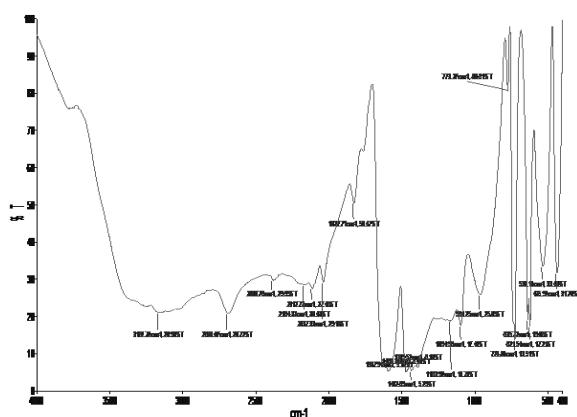


Figure - 9: FTIR Spectrum of UTMC.

### 3.3. XRD Analysis

Figures 10, 11 and 12 show the XRD pattern of urea, thiourea and TUMC crystals respectively, the interplanar spacing *d* and intensity of peaks are recorded in table 2. The XRD pattern of TUMC has been compared with those of urea and thiourea. Major (110) and (020) peak with maximum intensity is shifted in TUMC (112). The XRD of TUMC 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 TUMC crystal were determined using RIGAKU AFC7 diffractometer.

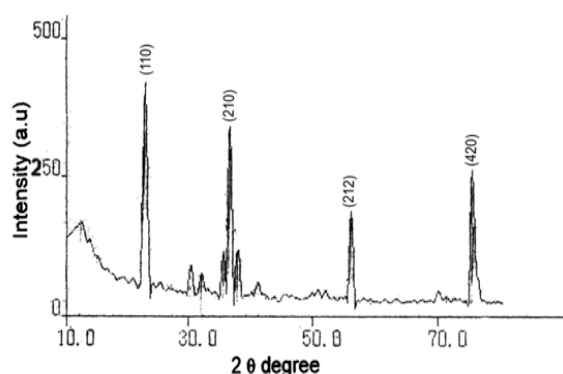


Figure - 10: XRD pattern for urea.

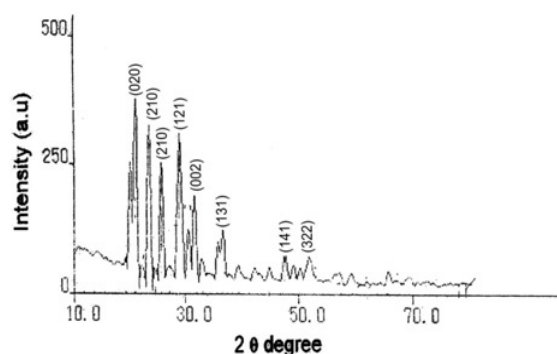


Figure - 11: XRD pattern for thiourea.

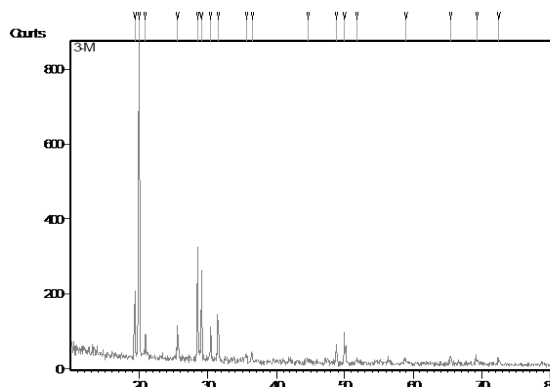


Figure - 11: XRD pattern for UTMC.

### 3.4. NLO test

The SHG behaviour of the powdered material was tested using Kurtz Perry method [14]. The sample was ground into very fine powder and tightly packed in a micro capillary tube. Then it was mounted in the path of Nd:YAG laser beam of 9.6 mj pulse energy obtained by splitting the original laser beam. The output light was passed through monochromator which was detected green light at 532 nm. This confirms the NLO behaviour of the material. The green light intensity registered by a photomultiplier tube and converted into an electrical signal. The same particle size of KDP was used as a reference material. SHG efficiency of Thiourea urea manganese chloride was greater than that of KDP.

### 4. CONCLUSION

Single crystals of Thiourea urea manganese chloride were grown by slow evaporation technique. Powder XRD confirms the structure of the crystal. FT-IR analysis confirms the presence of functional groups present in the crystal. SHG efficiency shows that the crystal has a higher efficiency than KDP.

### 5. REFERENCES

1. Madhurambal G, Mariappan M, Hariharan S, Ramasamy P and Mojumdar SC. *J. Therm. Anal and Calorim.*, 2013; 112(2): 1127.

2. Madhurambal G, Ravindran B, Mariappan M, Ramamurthi K and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2011; 104(3): 875.
3. Sangeetha MK, Mariappan M, Madhurambal G and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2012; 108(3): 887.
4. Mojumdar SC, Madhurambal G, Mariappan M and Ravindran B. **J. Therm. Anal and Calorim.**, 2011; 104(3): 901.
5. Mariappan M, Selvarajan G and Madurambal G. **International Journal of Pharmaceutical and Chemical Sciences.**, 2013; 2(4) 1949.
6. Ravindran B, Madhurambal G, Mariappan M, Ramamurthi K and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2011; 104 (3): 909.
7. Franken PA, Hill AE, Peters CW and Weinreich G. **Phys. Rev. Lett.**, 1961; 7: 118.
8. Selvarajan G. **Nagapattinam Water Quality Assessment, Monitoring and Mentoring with Various Adsorbent Treatment Measures.** Ph.D., Thesis, Bharathidasan University, Tiruchirappalli, India, 2010.
9. Selvarajan G, Mariappan M, Madurambal G and Thendral M. **International Journal of Chemical and Pharmaceutical Sciences.** 2013; 4(4): 45.
10. Sangeetha MK, Mariappan M, Madhurambal G and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2013; 112(2): 1059.
11. Madurambal G, Mariappan M, Selvarajan G and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2015; 119(2): 931.
12. Sangeetha MK, Mariappan M, Madhurambal G and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2013; 112(2): 1059.
13. Mariappan M, Selvarajan G and Madurambal G. **International Journal of Pharmaceutical and Chemical Sciences.** 2013; 2(4): 1943.
14. Madhurambal G, Mariappan M, Hariharan S, Ramasamy P and Mojumdar SC. **J. Therm. Anal and Calorim.**, 2013; 112(2): 1031.