



## RESEARCH ARTICLE

### NUCLEATION AND SPECTROSCOPIC STUDIES OF MANGANESE DOPED NEW NLO ORGANIC CRYSTAL

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#### 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.

**Key words:** Thiourea urea manganese chloride, XRD, UV-Visible Spectroscopy, FTIR, NLO

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#### INTRODUCTION

Materials with second order of non-linear optics have greatly attracted due to their possible applications in new technologies of optoelectronics (Ezhilvizhi, 2008; Sangeetha, 2017 and Jayalakshmi, 2006). 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 (Selvakumar, 2006 and Selvaraju, 2006). Most of the organic crystals have inadequate transparency, poor optical quality and low laser damage threshold (Franken, 1961). Moreover, growth of large sized single crystals have excellent mechanical and thermal properties but they possess relatively modest nonlinearity. Due to the above reasons, a lot of research has been carried out on semiorganic materials which have combined properties of both organic and inorganic materials (Madhurambal, 2013).

#### Experimental

##### 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 distilled water at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was filtered to remove insoluble impurities using Whatman filter paper of pore size 10 micrometers.

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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.

#### RESULTS AND DISCUSSION

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

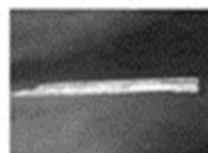


Fig. 1. Urea

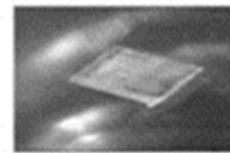


Fig. 2. Thiourea

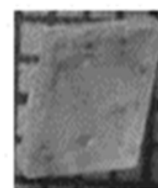


Fig. 3. TUMC

#### UV spectral analysis

The UV spectra for urea, thiourea and (hereafter Thiourea urea manganese chloride abbreviated as TUMC) are shown in Fig. 4, 5 and 6.

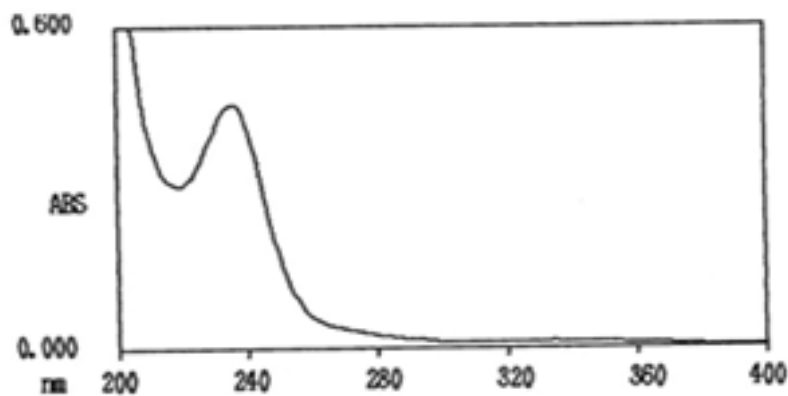


Fig. 4. UV Spectrum of Urea

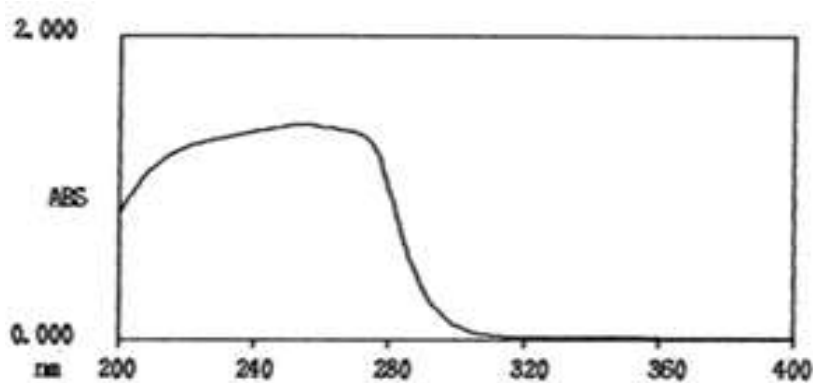


Fig. 5. UV Spectrum of Thiourea

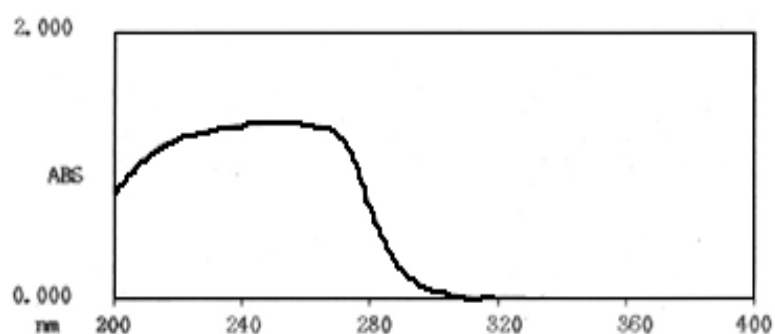


Fig. 6. UV Spectrum of TUMC

Table 1. Comparison of absorption band of urea, thiourea with TUMC

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

Table 2. FTIR assignments for urea, thiourea and TUMC

Urea (cm <sup>-1</sup> )	Thiourea (cm <sup>-1</sup> )	TUMC (cm <sup>-1</sup> )	Assignment
3455	3362	3162	$\nu_s$ NH <sub>2</sub>
1625	1591	1587	$\gamma_{as}$ N=C=N
1454	1478	1466	$\nu_s$ C=S
1064	1093	1095	$\nu_s$ CN
785	732	961	$\delta_s$ C=S

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

The observed bands have been tabulated in Table 1. In TUMC, the  $\pi$ - $\pi^*$  absorption band shifted to longer wavelength compared to urea [8]. This is because of the formation of b 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 [9]. Similarly,  $n$ - $\pi^*$  transition also shifted to higher wavelength due to less stable non-bonded electron in TUMC.

### 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 bands 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  $785$  of urea was shifted to higher frequency in TUMC ( $961$ ), asymmetric  $C=S$  vibration at  $1454$  of urea was shifted to higher frequency ( $1466\text{cm}^{-1}$ ) in TUMC.

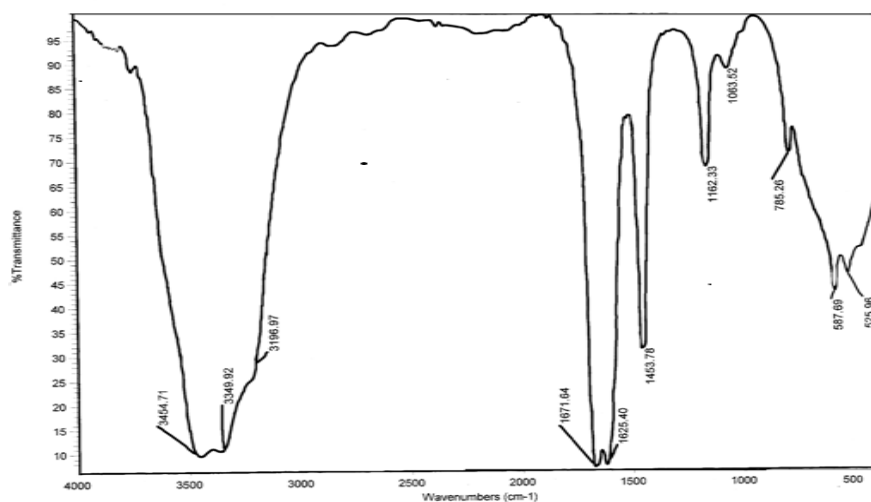


Fig. 7. FTIR Spectrum of urea

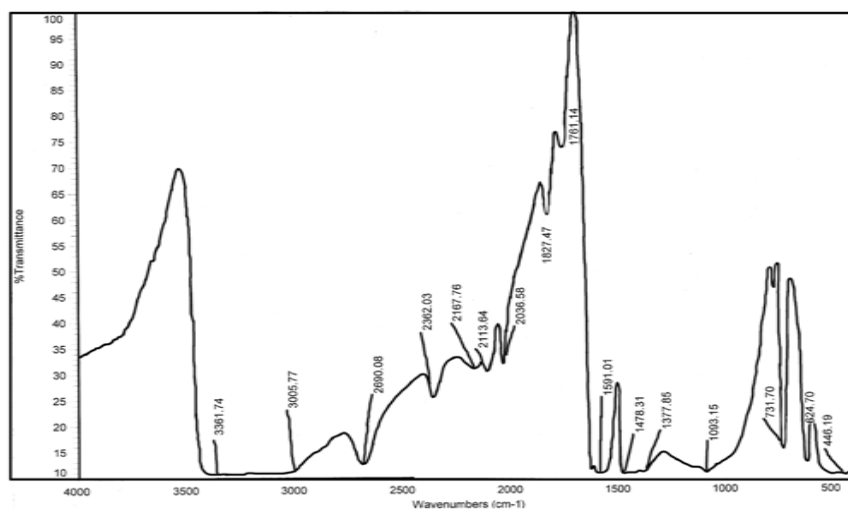


Fig. 8. FTIR Spectrum of thiourea

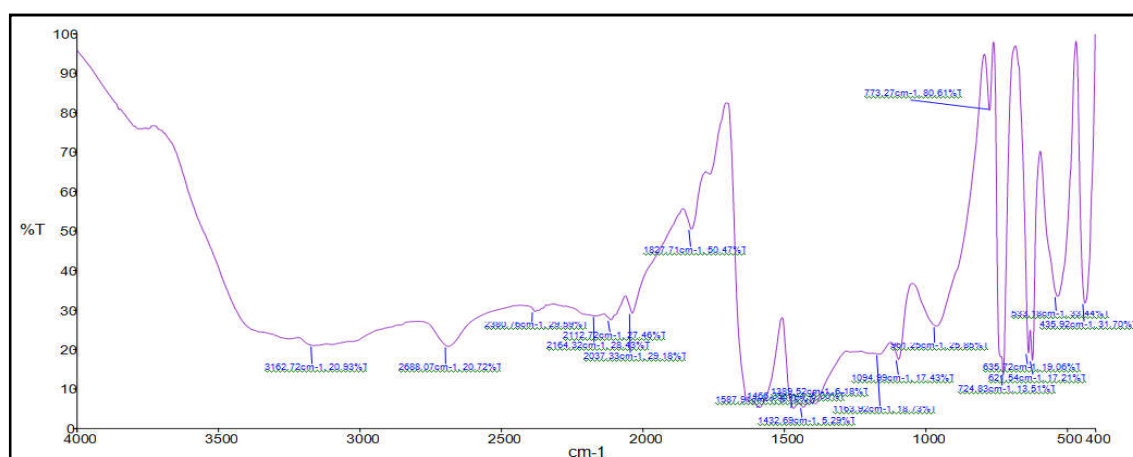


Fig. 9. FTIR spectrum of TUMC

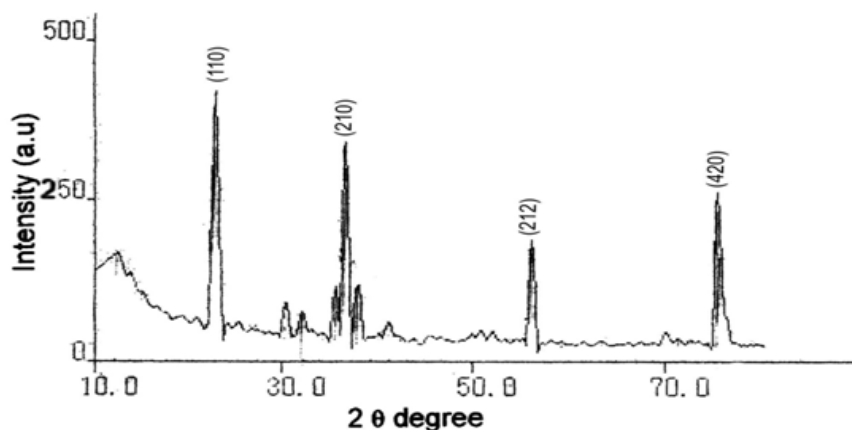


Fig. 10. XRD pattern for urea

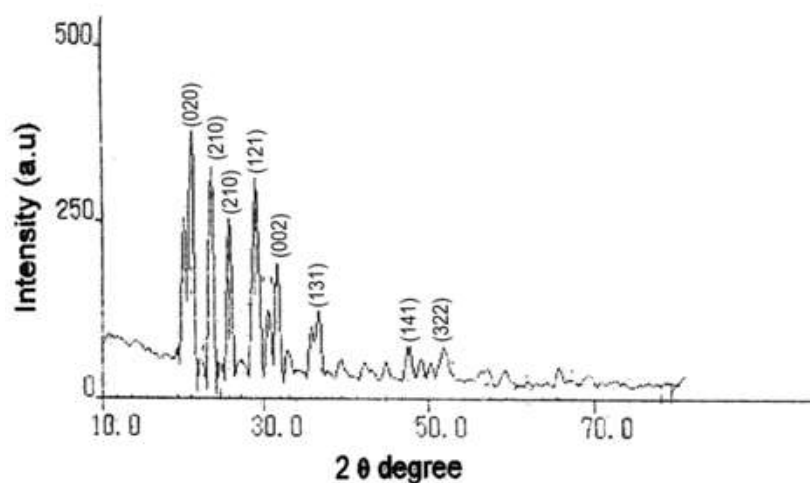


Fig. 11. XRD Pattern for thiourea

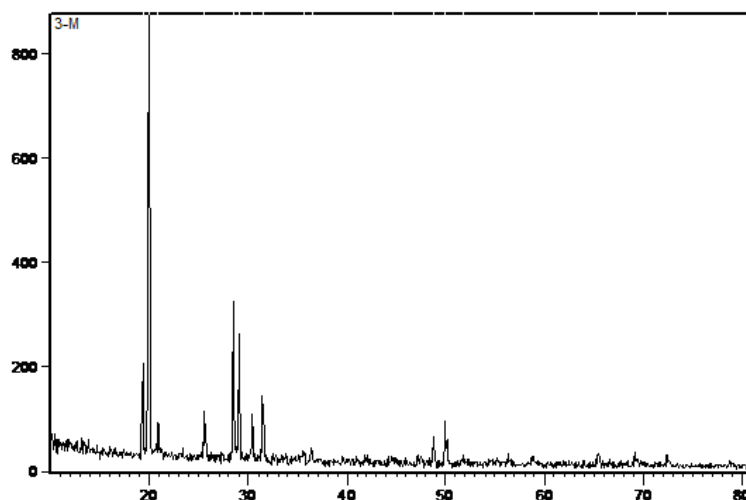


Fig. 12. XRD Pattern for TUMC

Similarly C-N stretching vibration at 1064 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 [10]. 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. These bands are not observed in single crystal of urea.

#### XRD Analysis

Figures 10,11 and 12 show the XRD pattern of urea, thiourea and TUMC crystals respectively, 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 UTMC (112). 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.

### NLO test

The SHG behaviour of the powdered material was tested using Kurtz Perry method (Madurambal, 2015). 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. These confirm the NLO behaviour of the material (Rajasekaran, 2003). 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 (Li, 2005). SHG efficiency of Thiourea urea manganese chloride was greater than that of KDP.

### 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 (Thendral, 2016). SHG efficiency shows that the crystal has a higher efficiency than KDP.

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