

Growth And Characterization Of Novel Thiourea Based NTS, MTS And NMTS Crystals

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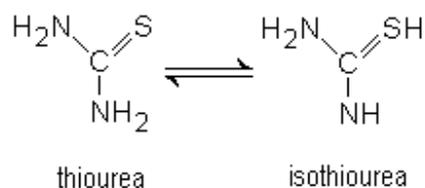
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Abstract: Thiourea Crystals as such do not have any nonlinear optic property of its own. But Thiourea crystals grown as Nickel Thiourea Sulphate (NTS), Magnesium Thiourea Sulphate (MTS), and bimetallic Nickel Magnesium Thiourea Sulphate (NMTS) have many interesting NLO properties. The growth of single crystals of NTS, MTS and NMTS are discussed in detail. The crystals were confirmed by XRD techniques and analysed for structural, mechanical and spectroscopic properties. Further the crystallinity of the grown crystals were determined using High Resolution X-Ray Diffraction (HRXRD) analysis. Some interesting results are presented in this paper.

Keywords: Thiourea, novel materials, properties.

1. Introduction

Thiourea is a white crystalline solid [1,2,3]. It is soluble in water, and in most organic solvents. Thiourea (CAS No. 62-56-6; IUPAC name 2-thiourea; also known as thiocarbamide, sulfourea) is a white crystalline solid [4,5]. Thiourea (CH₄N₂S) occurs in two tautomeric forms:



and thus has three functional groups: amino, imino, and thiol [6]. The substance does not have a sharp melting point, as rearrangement to ammonium thiocyanate (NH₄SCN) occurs at temperatures above

about 135 °C. Data on melting between 167°C and 182°C are reported in the literature [7]. Information on the boiling point is not available, as decomposition occurs. The temperature of decomposition is not yet known. Single crystals of Thiourea and NTS, MTS and NMTS were grown by the solution growth technique by slow evaporation method and characterized by structural and spectroscopic techniques.

2. Solubility studies

Dissolved substances are recoverable in solid form by precipitation upon evaporation or removal of the solvents. In solution growth the crystals are grown from the selected solvents operating at temperatures far below its melting points. A convenient unit of solubility is the mass of solute per unit mass of solvent, or commonly gram

solute/100ml of the solvent. Inter-conversions with molal units and mol fractions are made readily when densities of the solutions are known. The solubility of a chemical species in a solvent refers to the amount of solute that can be dissolved at constant temperature, pressure, and solvent composition (including the presence of other solutes). In other words, it is the concentration of the solute in the solvent at equilibrium. Solubility curves of Thiourea and NTS, MTS and NMTS were studied from 20 - 45°C using a cryostat and it was noted that at room temperature (Fig.1). pure thiourea had a solubility of 22 grams/100 ml.

3. Metastable zonewidth

It is the measure of stability of a solution during crystal growth in its supersaturated region where the largest width implies the substance having higher stability. 100 ml of the saturated solution was kept in the cryostat and the temperature reduced at 5°C per hour while the solution was stirred continuously. The temperature of formation of the

first speck or nuclei corresponds to the width of the metastable zone. The metastable zone width of Thiourea (Fig.2) was observed to be almost uniform in the lower temperature gradients and also in the higher gradients maintaining a gentle slope.

4. Induction period

The time of formation of the first speck or nuclei (induction period) were studied in pure Thiourea, and for NTS, MTS and NMTS. It was found that the maximum induction period (Fig.3) was found at concentration 1.1 which was 375 seconds for thiourea and for a concentration 1.5 a minimum induction interval was observed as 85 seconds for NMTS. This illustrates that undoped thiourea had slowest induction time period and bimetallic Nickel Magnesium Thiourea had the fastest induction period. It was observed that impurities and dopants decreased the duration of the nuclei formation and crystal growth thereby enabling faster crystal growth rates.

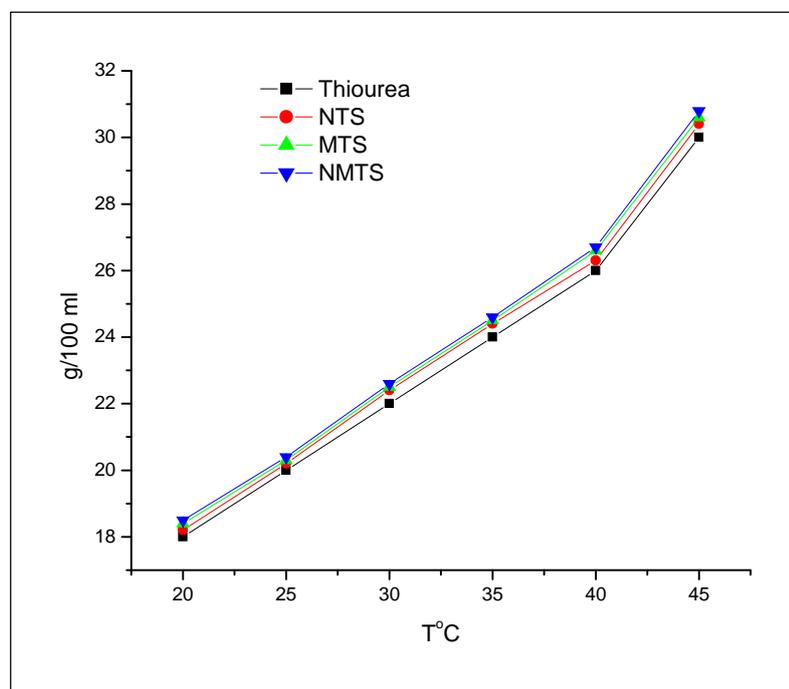


Fig.1 Solubility curves of TU, NTS, MTS and NMTS

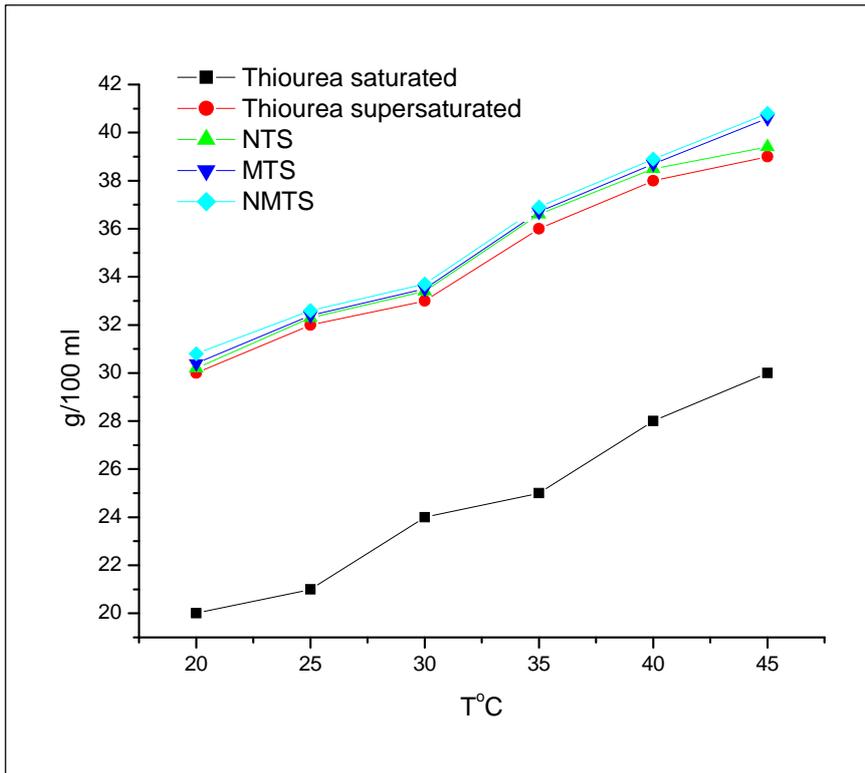


Fig.2 Metastable zone width of TU, NTS, MTS and NMTS

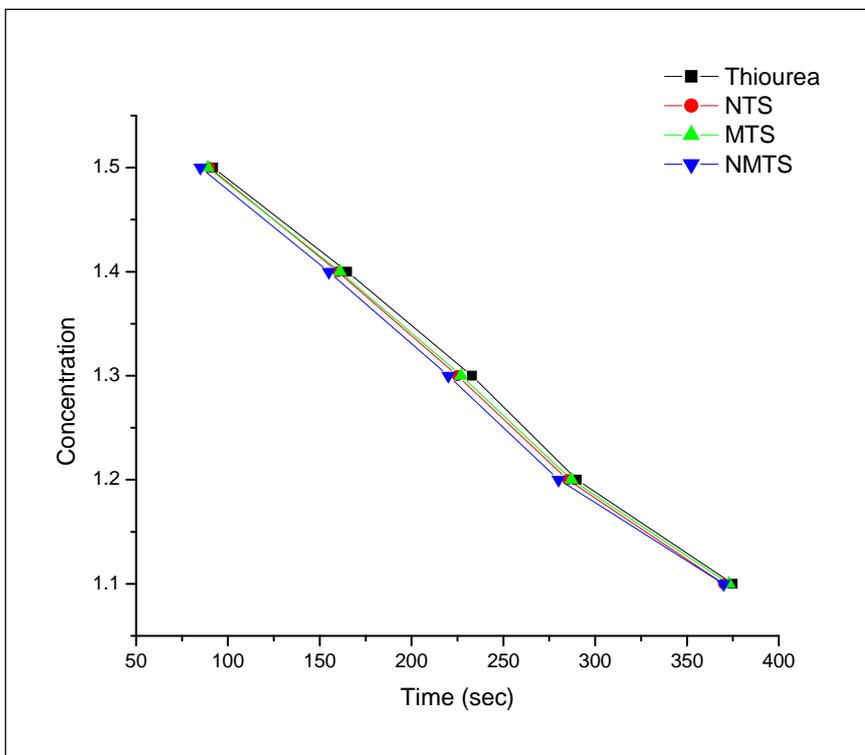


Fig. 3 Induction periods of TU, NTS, MTS and NMTS

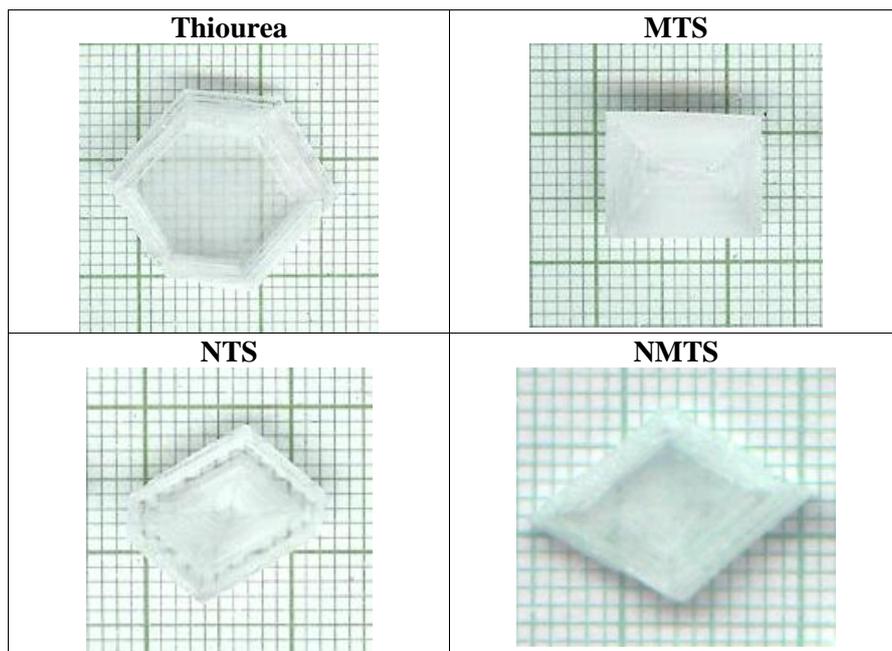


Fig. 4 Crystals of Thiourea, NTS, MTS, NMST

5. Synthesis and Crystal Growth

The starting materials were Thiourea, Nickel or Magnesium Sulphate (G.R.Merck) taken in the ratio 3:1 and used as solute. For bimetallic crystallization Thiourea, Nickel Sulphate and Magnesium Sulphate were taken in the ratio 3 : 0.5 : 0.5. Twice distilled water was used as the solvent. Nickel and Magnesium in the form of Nickel sulphate and Magnesium sulphate in the stoichiometric ratios was used as additive. In the present study, slow evaporation technique was used to grow Thiourea, NTS, MTS and NMST crystals. Room temperature saturated solution was prepared in the individual cases. The solution was filtered and then allowed to evaporate in a dust free atmosphere. After one week, optically transparent Thiourea, NTS, MTS and NMST single crystals of size $20 \times 10 \times 5 \text{ mm}^3$ are obtained. The grown crystals are shown in the figure 4.

6. XRD confirmations

XRD studies were carried out with the grown crystals in powdered form. The powder samples were loaded into a Rigaku X-Ray diffraction apparatus using $\text{CuK}\alpha$ radiation having $\lambda = 1.5405$ and analysed. Results were compared with the ICDD data and also with JCPDS database file number 31-1934 where the prominent peaks of the reported values coincided with the investigated patterns. The powder XRD pattern (Fig. 5) of Thiourea as well as NTS, MTS and NMST had three prominent peaks at (020), (210), (211) respectively.

The cell parameters were found to be $a = 7.664 \text{ \AA}$, $b = 8.559$, $c = 5.492 \text{ \AA}$ and the cell volume was 360.25 \AA^3 , which was in good agreement with the reported values [8].

7. FTIR analysis

The physical principles underlying infrared Spectroscopy [9] have been appreciated as one of the few techniques that can provide information about the chemical bonding in a material, it is particularly useful for the nondestructive analysis of solids and thin films, for which there are few alternative methods.

FTIR spectra of the Thiourea, NTS, MTS and NMST were done on a Perkin-Elmer 781 spectrophotometer in the range $400\text{--}4000\text{cm}^{-1}$ using a KBr pellet. Many useful correlations have been found in the mid-infrared region. This region is divided into the 'group frequency' region, $4000\text{--}1300 \text{ cm}^{-1}$, and the fingerprint region, $1300\text{--}650 \text{ cm}^{-1}$. In the group frequency region the principal absorption bands are assigned to vibration units consisting of only two atoms of a molecule: in the interval from 4000 to 2500 cm^{-1} , the absorption is characteristic of hydrogen stretching vibrations with elements of mass 19 or less. The intermediate frequency range, $2500\text{--}1540 \text{ cm}^{-1}$ (*unsaturated* region) contains triple bond frequencies which appear from 2500 to 2000 cm^{-1} and double bond frequencies from 2000 to 1540 cm^{-1} . In the region between 1300 and 650 cm^{-1} there are single bond stretching frequencies and bending vibrations (skeletal frequencies) of polyatomic systems that

involve motions of bonds linking a substituent group to the remainder of the molecule. The region $667\text{--}10\text{ cm}^{-1}$ contains the bending vibrations of carbon, nitrogen, oxygen and fluorine with atoms heavier than mass 19, and additional bending motions in cyclic or unsaturated systems. In pure thiourea, and also in NTS, MTS and NMTS (fig. 6) the 3300 cm^{-1} region is badly obscured by intense OH absorption. When small molecules (e.g. N_2 , O_2 and H_2) are linked to metal ions a symmetry change occurs which has a strong influence on the infrared spectra. This undergoes a stretching vibration at 2631 cm^{-1} . Metal–ligand vibrations are also metal sensitive and are shifted by changing the metal or its oxidation state which is applicable only to isostructural metal complexes.

The observed frequencies for the diatomic molecule O_2 stretching was at 1408 cm^{-1} . Dopants like Mg had absorption peaks at 731 cm^{-1} , Ni^{3+} at 492 cm^{-1} and strong absorption bands for lattice water (antisymmetric and symmetric OH stretchings) at 3381 cm^{-1} were also observed. It was observed that Ni^{3+} and Mg^{2+} in NMTS attributed for the absorbance peaks at 498 cm^{-1} and 729 cm^{-1} (for nickel and magnesium) and also some additional absorbance peaks at 1086 cm^{-1} and 1414 cm^{-1} which

implies that the inclusion of Nickel and Magnesium modifies the transparency of the bimetallic crystal.

Nickel and Magnesium can coordinate with thiourea in two possible ways, through nitrogen or through sulphur. The high frequency N-H absorption bands in the region $3100\text{--}3400\text{ cm}^{-1}$ in the spectrum of thiourea were not shifted to lower frequencies on the formation of metal-thiourea complex indicating the absence of nitrogen to zinc bonds and confirming that bonding must be between sulphur and zinc atoms [10]. It can be seen from table that the symmetric and asymmetric C=S stretching vibrations at 740 cm^{-1} and 1417 cm^{-1} of thiourea are shifted to lower frequencies in all the cases of NTS, MTS and NMTS. The C-N stretching vibration at 1089 cm^{-1} is shifted to higher frequencies. This shows that binding of zinc with thiourea is by sulphur [11]. The symmetric S-C-N stretching is shifted to higher frequency, whereas the asymmetric S-C-N stretching is shifted to a lower frequency. The formation of Ni-S and Mg-S bonds are expected to increase the contribution to the highly polar character of the structure of thiourea molecule, resulting in a stronger double bond character for the carbon to sulphur bond. The stretch vibrations (table.1) of NTS, MTS and NMTS are compared with the available data for thiourea [12].

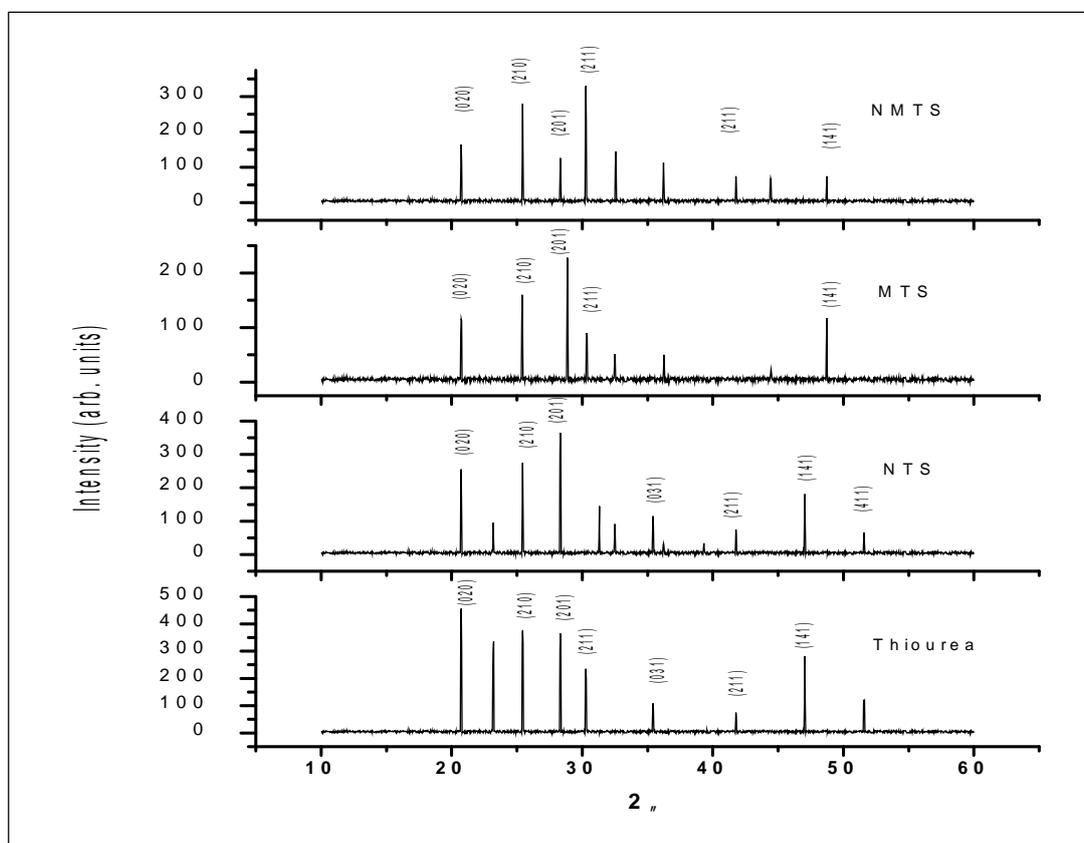


Fig. 5 XRD of TU, NTS, MTS, NMTS

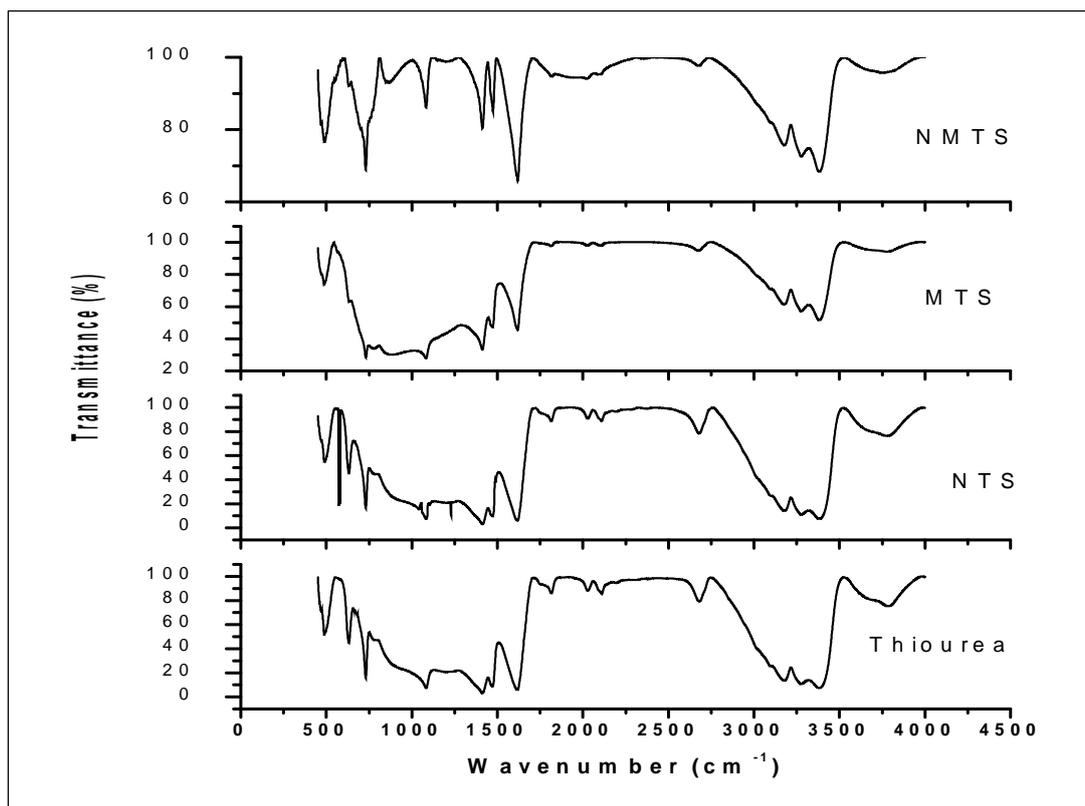


Fig. 6 FTIR of TU, NTS, NMTS

Table 1.

Thiourea (cm ⁻¹)	NTS (cm ⁻¹)	MTS (cm ⁻¹)	NMTS (cm ⁻¹)	
469	480	486	485	δ_s (S - C - N)
494	498	496	496	δ_{as} (N - C - N)
740, 1417	733, 1410	721, 1411	729, 1414	γ_s (C = S)
1089	1090	1098	1096	γ_{as} (C = S)
3280	3295	3303	3300	γ_s (NH ₂)

δ_s - Symmetric Bending, δ_{as} - Asymmetric Bending

γ_s - Symmetric stretching, γ_{as} - Asymmetric stretching

8. High Resolution X-Ray Diffraction Analysis

The high-resolution diffraction curves recorded for specific diffracting planes which are mentioned in the curved brackets with the multicrystal X-ray diffractometer [13] in symmetrical Bragg geometry. A well-collimated and monochromated MoK₁ beam obtained from a set of three plane (111) Si monochromator crystals set in dispersive (+,-,-) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,-,-,+) configuration. Due to

dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant.

All the curves were found to have single peaks (fig 7,8,9,10). This diffraction curve shows that though the quality of this crystal is very good, the specimen contains one *very low* angle boundary. The general crystalline quality of the specimen were found to be reasonably good. Thiourea in the pure form had a full width half maximum of 23'' where

NTS, NMTS had FWHM's of 27'' and 28''. MTS had the broadest curve at 80''. This comparative study reveals that the quality of the crystals other

than MTS is better where the crystalline quality of MTS requires refinement.

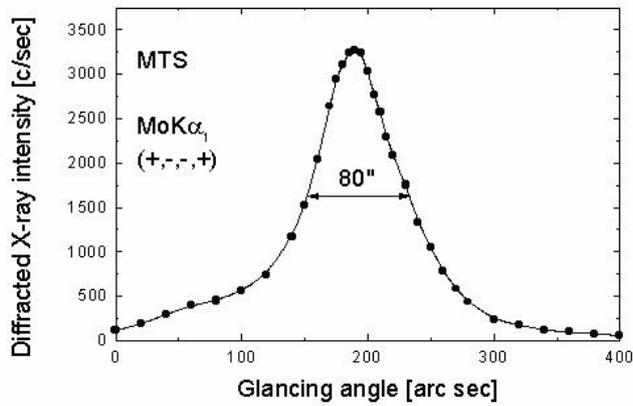


Fig. 7 HXRD pattern of MTS

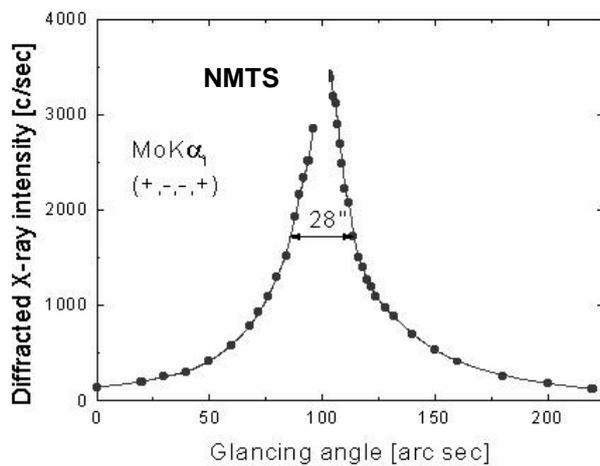


Fig. 8 HXRD pattern of NMTS

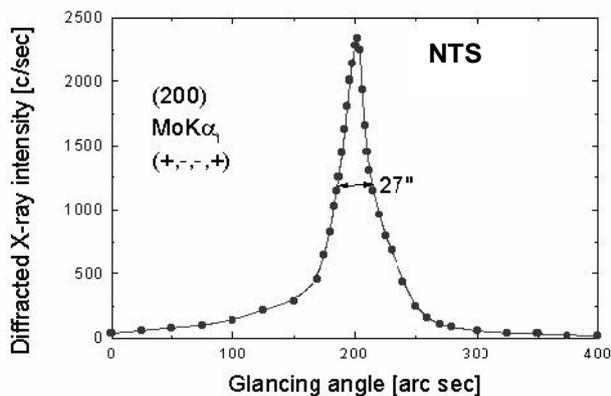


Fig. 9 HXRD pattern of NTS

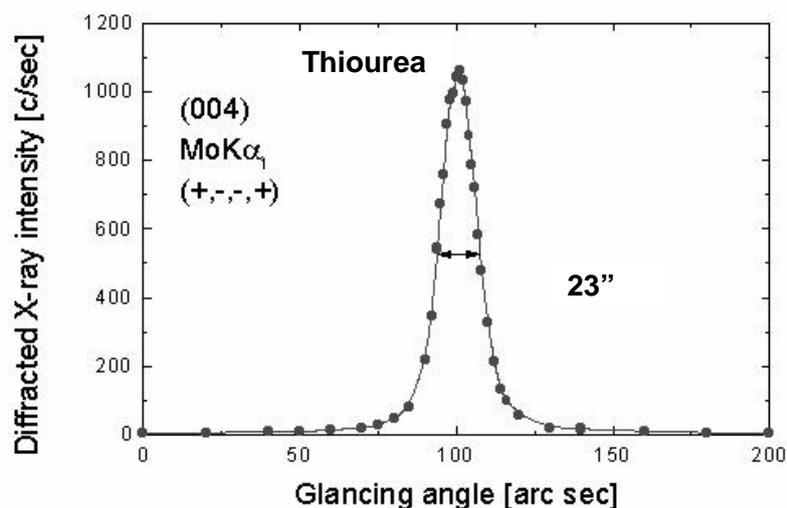


Fig. 10 HXRD pattern of Thiourea

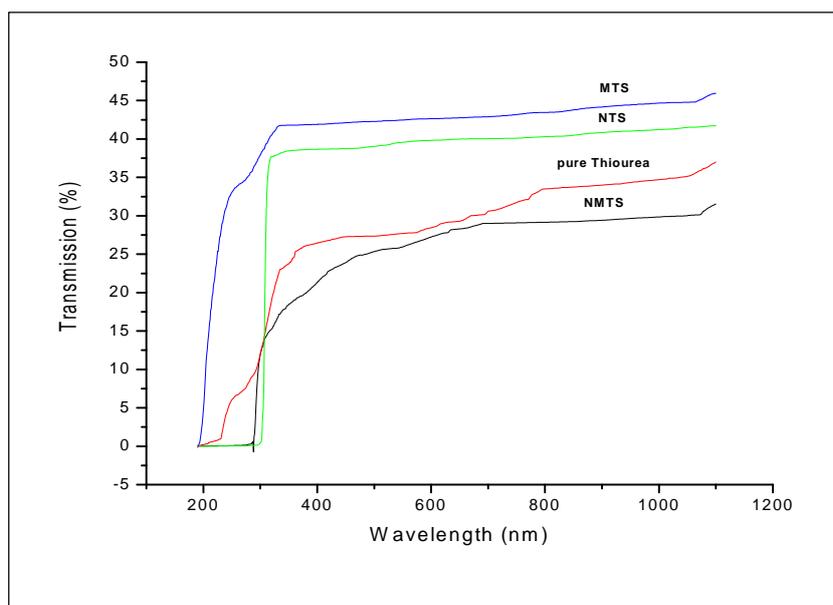


Fig. 11. UV-Vis spectra of TU, NTS, MTS and NMTS

9. UV-VIS-NIR Analysis

The UV-Vis-NIR spectral transmittance was studied using a Shimadzu UV-1061 UV-Vis spectrophotometer with a single crystal of 2 mm thickness in the range of 200-1200 nm. The recorded spectrum is shown in figure 11. The crystal has

sufficient transmission in the entire visible and IR region. The lower cut off wavelength is around 350 nm; the transmission percentage of Thiourea crystal is around 30%, as compared to NTS, which is around 45%. The transmission percentage is around 27% for MTS crystal and 40 % for NMTS crystal.

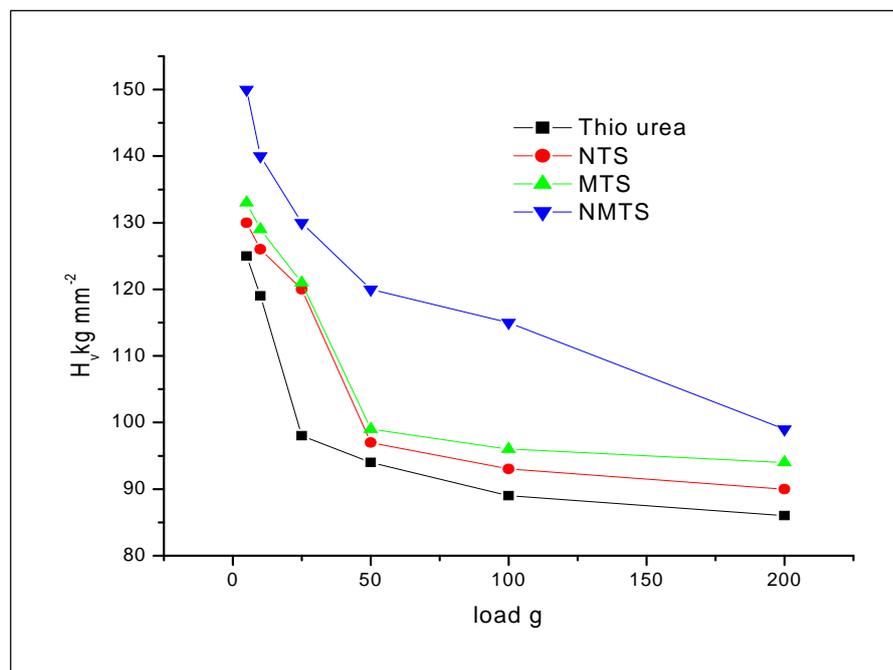


Fig. 12 Comparative microhardness of TU, NTS, MTS and NMTS

10. Hardness Tests

Microhardness tests are essential to find the hardness of the material grown and to estimate the amount of maximum mechanical stress it can withstand. Samples of Thiourea, NTS, MTS and NMTS were indented using a Lietz-Wetzler P1191 Microhardness tester fitted with a Vickers pyramidal indenter with an optical angle of 136° between the opposite pyramidal faces. Observations of the various indentation tests were done using the Metallux-II Metallurgical Microscope.

An indentation time of 10 seconds were applied uniformly for loads 5,10,25,50,100g. The hardness value of the thiourea crystal samples were found to increase proportionally (fig. 12) with the applied loads until 50g. Beyond 50g the samples developed mild cracks on the pyramidal indentation edges. Further increase in the load evolved large prominent cracks. The hardness values were calculated using the formula

$$H_v = \frac{1.8544 \times P}{D^2} \text{ kg mm}^{-2}$$

In the present study, it is observed that pure Thiourea is more brittle than that of NTS, MTS and NMTS crystals. This could be possibly due to the incorporation of the impurities deep into the crystal lattices strengthening the sample.

11 Conversion efficiency

The conversion efficiency of the crystal was checked using the powder SHG technique developed by Kurtz and Perry [14]. The crystal was ground into powder and densely packed in between two glass slides. An Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The emission of green light qualitatively confirms the second harmonic generation of NTS, MTS and NMTS crystals.

12 Conclusion

The solubility of Thiourea, NTS, MTS and NMTS was analyzed in the temperature range 20-45°C. The solubility curve indicates moderate solubility in water with a positive moderate solubility temperature gradient. Single crystals of Thiourea, NTS, MTS and NMTS have been grown by slow evaporation technique at room temperature. Powder XRD pattern confirmed the formation of the respective compounds. The functional groups present in the grown crystal have been confirmed by FTIR spectral analysis. It is evident from both XRD and FTIR studies that binding of thiourea with Nickel and Magnesium occurs through sulphur. The good optical transmittance in the visible-IR region and SHG conversion efficiency makes the crystal a potential material for NLO applications.

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