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Growth and studies of thiourea urea magnesium chloride (TUMC) single crystals

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Abstract A new semi organic Non-linear optical (NLO) crystal thiourea urea magnesium chloride (TUMC) was grown by slow evaporation technique at room temperature. Good quality single crystals were grown within 20 days. The FTIR spectrum of title compound was recorded and vibrational assignments were made. The recorded UV–vis spectrum shows the optical transmission property of the crystal. The Second harmonic generation (SHG) of TUMC crystal was tested by Kurtz–Perry method using Nd:YAG laser and the result confirms that the grown crystal exhibits NLO property. To analyse the thermal stability of the crystal TG/DTA analysis were made. Detailed structural analysis of the compound is under progress.

Keywords Crystal growth · FTIR · UV–vis · TG/DTA · SHG

Introduction

Non-linear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [1–3]. The search for new NLO materials has led to the discovery of many organic NLO materials. A few of the organic materials have good non-linearity, mechanical hardness, high resistance to laser damage threshold, and ultra fast non-linear response time [4–7]. Owing to its thermal instability, certain of them is found to be useless [8]. Therefore, researchers focused their attention on semi organic crystals. Recently thiourea–urea complexes have been explored. Some of the complexes are urea–thiourea [9], Bis thiourea–urea [10], thiourea urea zinc chloride [11], urea thiourea magnesium sulphide [8], urea thiourea mercury sulphide [8], and urea thiourea mercury chloride [14]. These crystals have better non-linear optical property. In this study an attempt is made to combine thiourea with urea and magnesium chloride to grow a new semi organic non-linear optical material.

Experimantal

Synthesis

A single crystal of thiourea urea magnesium chloride (TUMC) was prepared by dissolving the required quantities of thiourea, urea, and magnesium chloride in Millipore water. Using a magnetic stirrer the solution was thoroughly mixed. Then the solution was left for slow evaporation. A crystalline substance was formed. No further purification was done.

The TUMC solution was prepared in water and maintained at 30 °C with continuous stirring to insure homogeneous temperature and concentration. On reaching saturation, the content of the solution was analysed gravimetrically. This process was repeated for every 5 °C in water from 30 to 50 °C. The solubility curve thus obtained is shown in Fig. 1.

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Crystal growth

Large single crystals of TUMC crystals were grown by slow evaporation method. The TUMC salt solution was prepared by dissolving required quantities of thiourea, urea, and magnesium chloride in Millipore water. All the salts were GR grade and E Merck products. The solution was stirred continuously for 9 h. The saturated solution was filtered and poured into a petri dish covered with paper. The solution was left undisturbed for slow evaporation. Good quality single crystals can be obtained within 20 days. The grown crystals are shown in Fig. 2. The crystals are semitransparent in nature. The size of the crystal is about 8 × 6 × 2 mm^3.

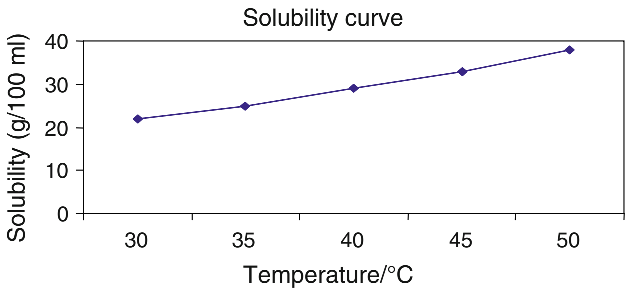


Fig. 1 Solubility curve of TUMC solution

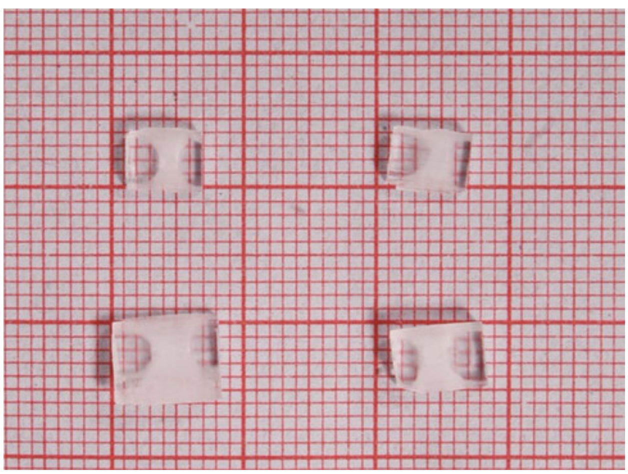


Fig. 2 As grown TUMC crystals

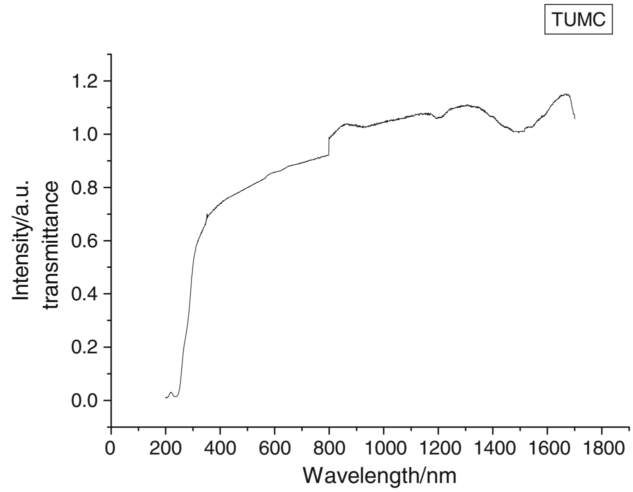


Fig. 4 UV spectrum of TUMC crystals

Characterization

FTIR spectral analysis

In order to identify the functional groups present in the title compound, FTIR spectrum was recorded using Perkin Elemer Spectrum RXI spectrophotometer by KBr pellet

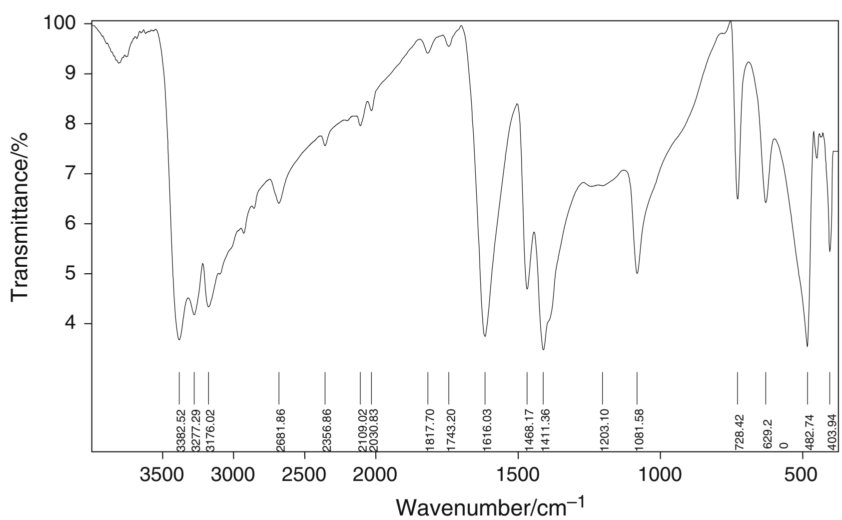


Fig. 3 FTIR spectrum of TUMC crystals

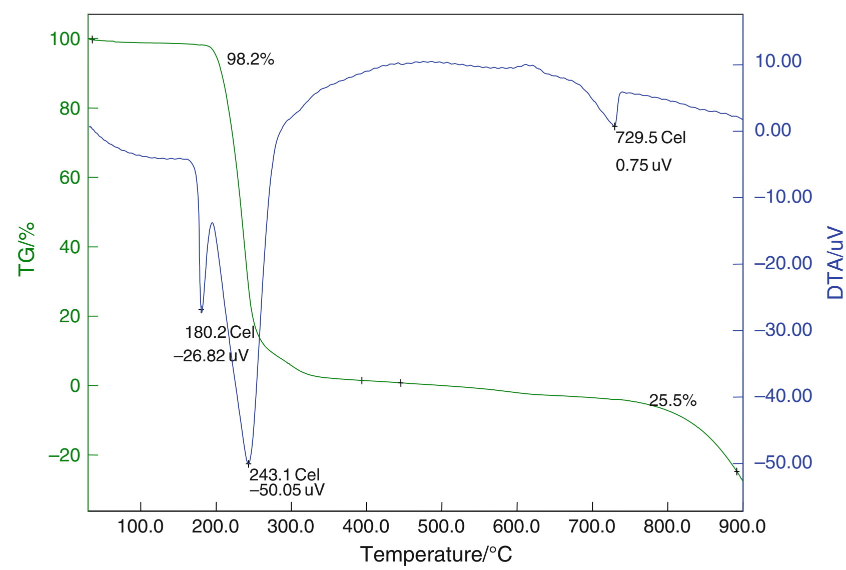
technique in the region 400–4000 cm^{-1}. The recorded FTIR spectrum of TUMC is shown in Fig. 3.

In the metal complexes of thiourea, there are two possibilities of the coordination of the metal with thiourea that can occur. The coordination with metal may occur through either nitrogen or sulphur of thiourea [12, 13]. The peak at 480 cm^{-1} is due to rocking mode of N=C=N. The symmetric and asymmetric C=S stretching vibrations are observed at 740 and 1417 cm^{-1} of thiourea. These peaks are obtained at 728 and 1411 cm^{-1}, respectively, for TUMC crystal. This indicates that the bonding of metal with thiourea is only through sulphur [13, 15].It is evident that the N–H absorption bands in the region 3000–3400 cm^{-1} in thiourea were not shifted to lower frequencies on the formation of metal–thiourea complex. This indicates that nitrogen to metal bond is not present and the bonding must be between sulphur and metal. The band at 1473 cm^{-1} may be assigned to N–C–N stretching vibration [13, 14]. The peaks between 1700 and 2700 cm^{-1} were due to overtone and combination bands [14]. The peak at 3382 cm^{-1} is due to N–H vibration of TUMC.

Optical absorption studies

For device applications of NLO materials, the optical transmittance range and lower cut off wavelength are the main requirements. The optical transmission spectrum of TUMC crystal was recorded in the region 200–1600 nm,

Fig. 5 TG/DTA of TUMC crystals



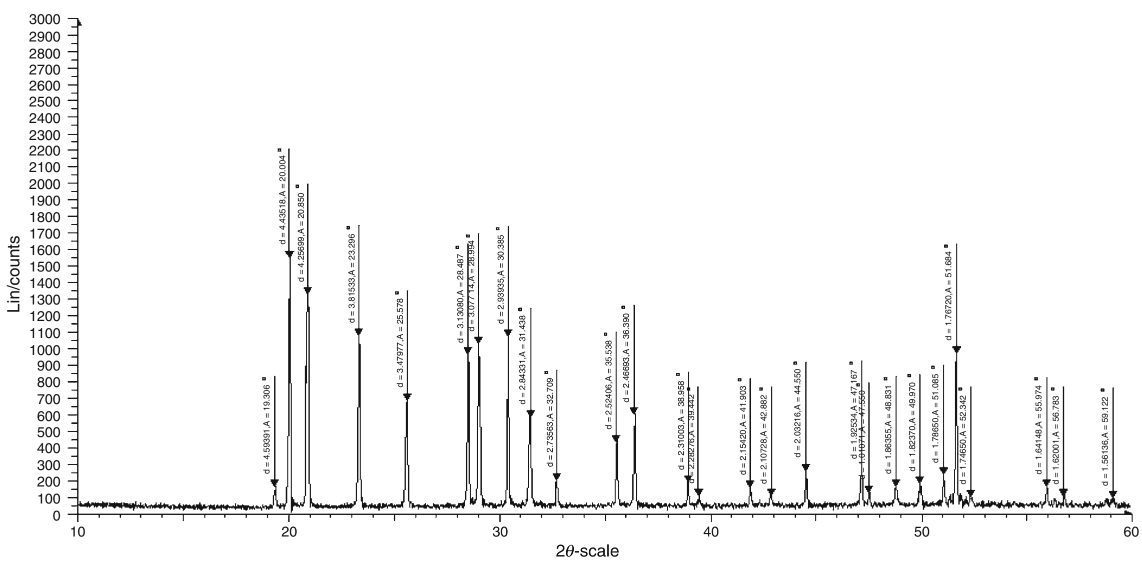


Fig. 6 Powder XRD pattern of TUMC crystals

using a VARIAN CARY 5000 spectrophotometer. The recorded optical absorption spectrum of TUMC is shown in Fig. 4. The lower cut off wavelength is at 210 nm. It is observed that the TUMC crystal has good transmittance window in the visible and IR region.

Second harmonic generation testing (SHG)

The SHG conversion efficiency of the crystal was carried out using the Nd:YAG laser beam at 1064 nm, using Kurtz Powder technique. A pulse of energy of 680 mJ/pulse, pulse width of 10 ns, and repetition rate of 10 Hz was used. The second harmonic generation was confirmed by the emission of green radiation of wavelength at 532 nm. Second harmonic generation efficiency of TUMC is compared with KDP and it is found that the SHG efficiency is 0.35 times as that of KDP.

Thermal analysis

The thermogravimetry (TG) and Differential thermal analysis (DTA) of TUMC was carried out using a Seiko TG/DTA 6200 model thermal analyzer in nitrogen atmosphere. A powder sample of 4 mg was used for the analysis in the temperature range of 0–800 °C with a heating rate of 20 °C/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Fig. 5. From the TG curve, it is observed that there was no loss of weight around at 100 °C. This confirms the absence of water molecule in the sample. TUMC crystal has thermal stability up to 180 °C. Above 180 °C, urea in TUMC decomposes into two molecules of ammonia and one molecule of carbon monoxide [10] and it vaporizes completely at 300 °C. Then thiourea starts to decompose into hydrogen sulphide, nitrogen, and carbon residue [10]. The remaining compounds of TUMC decompose very slowly up to 800 °C. In DTA curve, the exothermic curve at 180 °C corresponds to the urea decomposition and the exothermic curve at 243 °C is due to the decomposition of thiourea [10].

XRD analysis

The powder X-ray diffraction data were collected for grown TUMC crystals. The grown crystals were grounded using an agate mortar and pestle. The XRD pattern was recorded using Bruker D8 advance model instrument with Cu Kα radiation. The sample was scanned in the range of 10°–60° at a scan rate of 0.02 count per minute. The X-ray powder diffraction pattern of TUMC crystal is shown in Fig. 6. The prominent well-resolved Bragg's peak at specific 2θ angle reveals the high crystalline nature of the crystal.

Conclusions

A new NLO material Thio urea magnesium chloride was successfully grown by solution growth method at room temperature. The various functional groups are observed from FT–IR spectrum. The TUMC is transparent for entire region of visible spectrum and has lower cut off wavelength at 210 nm. The TUMC crystal is having good thermal stability up to 180 °C. The non-linear optical studies confirmed the SHG property. Thus, TUMC seems to be a promising material for NLO application in view of its superior optical properties. The prominent well-resolved Bragg's peak at specific 2θ angle reveals the high crystalline nature of the crystal.

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