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Growth and characterization of semiorganic crystal

Urea thiourea sodium chloride

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Abstract Single crystals of urea thiourea sodium chloride (UTNC) were grown from aqueous solution by slow evaporation technique. FTIR spectra were recorded to identify the functional groups. The crystals were characterized by recording the powder X-ray diffraction that revealed the crystalline nature of the crystal. The UV–Vis spectral study was carried out to test the optical transmitting property. The second harmonic generation test (SHG) was carried out, and it shows the non-linear nature of the crystal. The thermal stability of the crystal was analyzed by thermogravimetric and differential thermal analysis (TG-DTA).

Keywords Crystal growth · Powder XRD · FTIR · UV–Vis · TG-DTA · SHG

Introduction

Extensive research has been made over the past few decades on the growth of non-linear optical (NLO) crystals. NLO materials have their potential applications in the field of laser technology, optical communication, optical signal processing and switching. Recent researchers focus their attention on developing new semiorganic non-linear optical (NLO) materials, as they have the advantages of both organic and inorganic materials. Among the semiorganic NLO materials, metal complexes of thiourea have low cutoff wavelengths, applicable for high-power frequency conversion [1]. Thiourea is a centro-symmetric molecule. When it is coordinated with metal ions, it becomes non-cento-symmetric material and exhibits non-linear optical activity [2–4]. Many authors investigated various thiourea complexes and also examined their various properties [5–8]. In this paper, we presented a preliminary report on growth, thermal and optical studies of UTNC crystals.

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Experimental

Synthesis

UTNC salt was synthesized by dissolving urea (GR grade), thiourea (GR grade) and sodium chloride (GR grade) in the appropriate ratio in Millipore water. The solution was stirred continuously for 9 h at homogeneous temperature and concentration. The saturated solution was filtered using Whatman filter paper and then poured into petri dishes. Then, the solution was left for slow evaporation. A crystalline substance was formed. No further purification was done. The harvested crystals were found to be transparent as shown in Fig. 1. The size of the crystal is around 10 mm × 10 mm × 1 mm.

The solubility of UTNC has been determined at different temperatures from 30 to 50 °C at the interval of 5 °C. The solubility curve thus obtained is shown in Fig. 2. It shows the positive solubility temperature gradient.

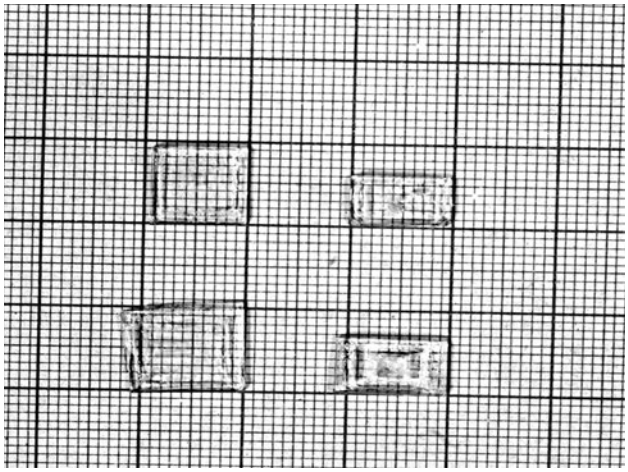

Fig. 1 As grown UTNC crystals

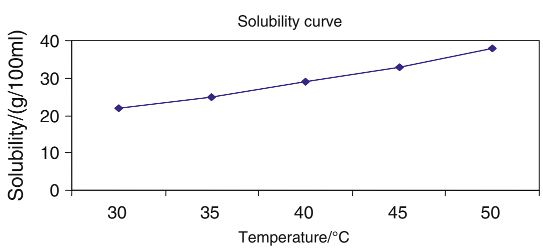

Fig. 2 Solubility curve of UTNC solution

Characterization

To identify the functional groups present in the UTNC, FTIR spectrum was recorded using Perkin Elmer Spectrum RXI spectrophotometer by KBr pellet technique in the region of 400–4000 cm^{-1}. The XRD pattern was recorded using Bruker D8 advance model instrument with Cu Kα radiation. Using a VARIAN CARY 5000 spectrophotometer, the optical transmittance was examined in the region of 200-1600 nm. The SHG efficiency of the grown crystal was measured by Kurtz powder method [6] using Nd: YAG laser of 1064-nm wavelength. The thermal stability of UTNC is analyzed on a Seiko TG-DTA 6200 model thermal analyzer in nitrogen atmosphere.

Results and discussions

FTIR spectra

The recorded FTIR spectrum of UTNC is shown in Fig. 3. In the metal complexes of thiourea, there are two possibilities of the coordination of the metal with thiourea. The coordination with metal may occur through either nitrogen or sulfur of thiourea [9, 10]. The symmetric and asymmetric

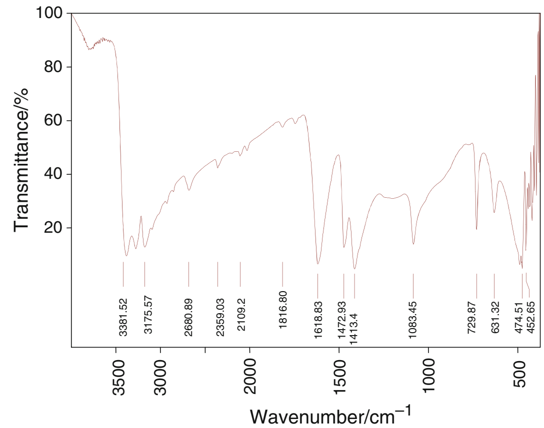

Fig. 3 FTIR spectrum of UTNC crystals

C=S stretching vibrations are observed at 740 and 1417 cm^{-1} of thiourea. These peaks are shifted to 730 cm^{-1} and 1413 cm^{-1}, respectively, for UTNC crystal. As the bonds of thiourea are shifted to lower frequency in C=S stretching vibrations, the bonding of the metal with thiourea is only through sulfur [9–13]. It is evident that the N–H absorption bands in the region of 3000–3400 cm^{-1} in thiourea were not shifted to lower frequencies on the formation of metal thiourea complex. Also the absorption peak at 1618 cm^{-1} due to NH_2 deformation modes is not shifted. This indicates that nitrogen to metal bond is not present and the bonding must be between sulfur and metal [14]. The asymmetric N=C=N bending vibration is observed at 475 cm^{-1}. The peaks between 1700 and 2700 cm^{-1} were due to overtone and combination bands [15]. The other modes of vibrations of UTNC are compared with thiourea and presented in Table 1.

Powder X-ray diffraction studies

The powder X-ray diffraction data were collected for grown UTNC 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 Ka radiation. The sample was scanned in the range of

Table 1 FTIR assignments for thiourea and UTNC (*as* asymmetric, *s* symmetric, δ bending, *v* bending)

Wave number of thiourea/cm^{-1}	Wave number of UTNC/cm^{-1}	Assignments
640	631	δ_{as} (N–C–S)
1089	1083	v_s (CN)
1472	1473	v_{as} (CN)
3100–3200	3176	v_s (NH_2)
3280	3381	v_{as} (NH_2)

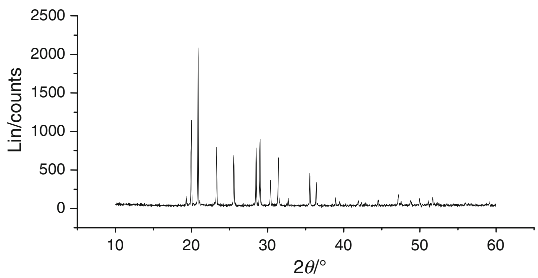

Fig. 4 Powder XRD of UTNC crystals

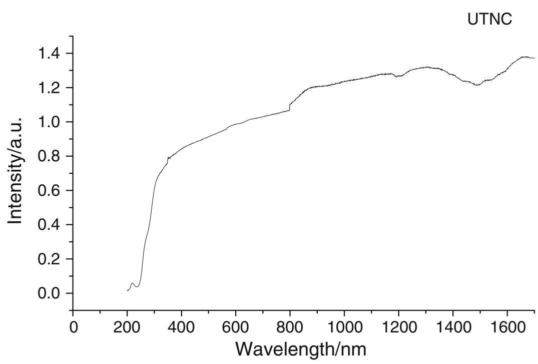

Fig. 5 UV spectrum of UTNC crystals

10°–60° at a scan rate of 0.02 counts per minute. The X-ray powder diffraction pattern of TUMC crystal is shown in Fig. 4. The prominent well-resolved Bragg's peak at specific 2θ angle reveals the high crystalline nature of the crystal.

Optical absorption studies

The optical transmission spectrum of UTNC crystal was recorded in the region of 200–1600 nm. The recorded optical absorption spectrum of UTNC is shown in Fig. 5. The lower cutoff wavelength of UTNC is at 250 nm. The lower cutoff wavelength of urea is 200 nm [16] and that of thiourea is 210 nm [17]. It is observed that the UTNC crystal has good transmittance window in the visible and IR region.

SHG efficiency

The SHG conversion efficiency of the crystal was carried out using the Nd: YAG laser beam at 1064 nm, using Kurtz powder technique**.** The crystal was finely powdered and packed between two glass slides. A pulse of energy of 680 mJ/pulse, pulse width of 10 ns and repetition rate of 10 Hz were made to fall on the sample. The second harmonic generation was confirmed by the emission of green radiation of wavelength at 532 nm.

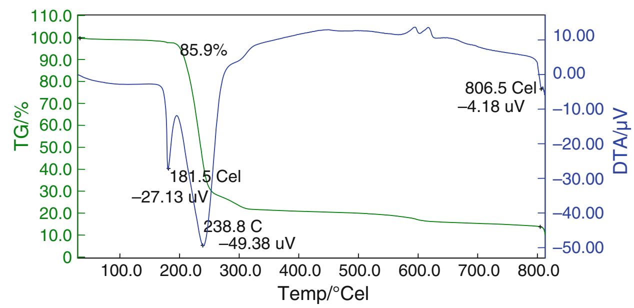

Fig. 6 TG-DTA of UTNC crystals

Thermal analysis

The thermogravimetry (TG) and differential thermal analysis (DTA) of UTNC were carried out. A powder sample of 4 mg was used for the analysis in the temperature range of 30–800 °C with a heating rate of 20 °C/min in the nitrogen atmosphere. The thermogram and differential thermogram are shown in Fig. 6. 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. UTNC crystal has thermal stability up to 181.5 °C. Above 181.5 °C, urea in UTNC decomposes into two molecules of ammonia and one molecule of carbon monoxide [18–21] and it vaporizes completely at 300 °C. Then, thiourea starts decomposing into hydrogen sulfide, nitrogen and carbon residue [18–21]. The remaining compounds of UTNC 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 238.8 °C is due to the decomposition of thiourea [18–21]

Conclusions

A new NLO material UTNC was grown by solution growth method at room temperature. Its solubility curve shows moderate solubility of UTNC in water, and it has positive solubility temperature gradient. The FTIR spectra confirm the various functional groups present in the crystal. The crystalline nature of the sample is confirmed by powder XRD analysis. The UTNC is transparent for entire region of visible spectrum and has lower cutoff wavelength at 250 nm. The UTNC crystal is having good thermal stability up to 180 °C. The non-linear optical studies confirmed the SHG property. Thus, UTNC is a potential material for NLO application.

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