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# Bulk size growth, FT-NMR, FT-IR and thermal studies of TTPI single crystal

A. Subashini[b], K. Sendil Kumar[b], V. Ramesh[b], K. Rajarajan[a,*]

[a] Department of Physics, Rajeswari Vedachalam Government Arts College, Chengalpet 603 001, India
[b] Research and Development Centre, Bharathiar University, Coimbatore 641 046, India

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ABSTRACT

In the present work, bulk size (20 mm × 16 mm × 7 mm) single crystal of tetrakis thiourea potassium iodide [$K(N_2H_4CS)_4I$]; (TTPI) has been grown from an aqueous solution using simple slow evaporation solution growth (SEST) technique. The XRD results proved that the compound crystallizes in tetragonal crystal system. The FT-IR spectrum of TTPI has clearly identified the functional groups of thiourea in the resulting compound. The chemical shift observed at 182.04 ppm of FT-NMR profile has clearly established the one type of carbon atom which is due to the incorporation of thiourea in TTPI. The TGA–DTA studies revealed that the sample undergoes weight loss in two major decomposition stages. Further, DSC study indicates that there is no adsorbed water of crystallization in the sample and the sample is found to be stable up to the melting point 197.9 °C, which is comparable to the value (193.2 °C) as indicated in the DTA peak. It is also inferred that the melting point of TTPI is far better than ATZC (58 °C), CMTG (100 °C), CMTD (150 °C), BTCoC (110 °C) and comparable to CMTC (198.5 °C) and TMTM (199.06 °C).



## 1. Introduction

In recent years, material scientists have thirst to synthesize and grow crystals with an optically good quality and better physico-chemical properties so that they can be used for device fabrications in modern industries including photonics. In this context, the feasibility of forming metal–organic coordination compound of thiourea is an attractive strategy for obtaining good quality non-linear optical crystals. Thiourea is an interesting matrix modifier capable of forming coordinate bonds through sulfur (S) and nitrogen (N). The π-orbital electron delocalization in thiourea that arises from the mesomeric effect is responsible for their nonlinear optical response and the absorption in the near ultraviolet region [1–5]. In the present research work, effort was made to combine thiourea with potassium iodide and succeeded in growing a relatively bigger size tetrakis thiourea potassium iodide (TTPI) single crystals using slow evaporation solution growth technique and successfully grown a bulk size (20 mm × 16 mm × 7 mm) single crystal of TTPI. The grown crystals of TTPI were subjected to single crystal X-ray diffraction analysis, Fourier transform infrared analysis in order to understand the crystalline property and the functional groups of the fragments involved in the resulting compound of TTPI. Further the samples were also subjected to TG–DTA and DSC studies to understand the thermal behavior as well.

## 2. Synthesis and crystal growth

Tetrakis thiourea potassium iodide [$K(N_2H_4CS)_4I$; TTPI] is a second harmonic generation crystalline material of thiourea-halogen family. In order to obtain TTPI, as purchased analytical reagent grade chemical of thiourea and potassium iodide were incorporated in the stoichiometric equation with the molar ratio 4:1 and stirred well to avoid the co-precipitation of thiourea. The resulting solution was carefully filtered and kept for nucleation. The crystalline material of TTPI was obtained in a week time. The product was collected and purified by repeated recrystallization in acetone. From the recrystallized material, seed crystal of good quality was selected as a seed and the same was used to grow bulk size TTPI single crystal. To achieve good size crystal, the seed was hung using a suitable thread in the supersaturated solution of TTPI with the optimum pH value adjusted to 4.0. Over a period of three weeks, the bulk size (20 mm × 16 mm × 7 mm) single crystal of TTPI was grown from an aqueous solution using slow solvent evaporation technique and presented. It is quite interesting and impressive that the crystal picture clearly depicts how the bulk crystal gets developed as layer by layer with its best morphological features during crystal growth. The piercing out of inner portion and wedge shaped portions on the side faces of the crystal add beauty to the crystal and it resembles the shape of a small tortoise. The as grown single crystal of TTPI is shown in Fig. 1.

* Corresponding author. Tel.: +91 44 27427816; fax: +91 44 27431257.
*E-mail address:* drkrr2007@gmail.com (K. Rajarajan).

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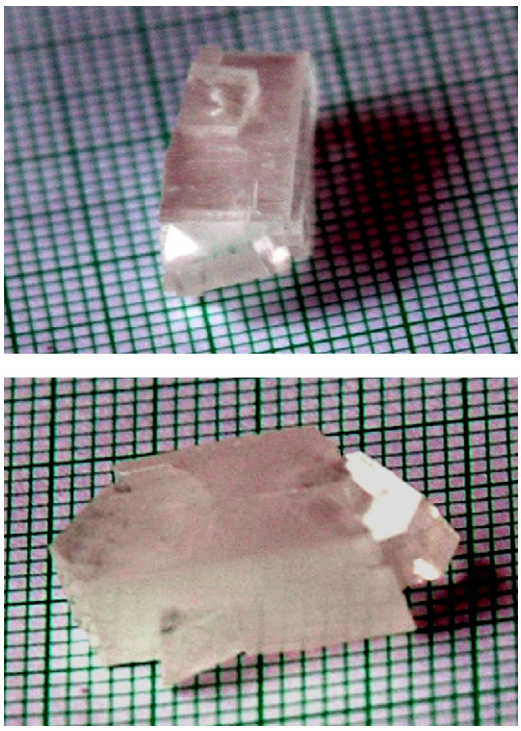

**Fig. 1.** The as grown single crystal of TTPI.

## 3. Results and discussion

### 3.1. Single crystal X-ray diffraction analysis

TTPI crystal was subjected to single crystal XRD studies using ENRAF NONIUS CAD-4F single crystal X-ray diffractometer. The complete structure was solved by the least-squares technique using SHELXL program. It belongs to tetragonal crystal system with space group $P4_1$. The cell parameters are $a = b = 20.1284$ Å, $c = 8.2163$ Å. The cell parameters obtained in the present work are in good agreement with the earlier reported work [6].

### 3.2. Fourier transform infrared analysis

The functional groups of TTPI were confirmed by recording the FTIR spectrum in the range of 4000–400 $cm^{-1}$ using BRUKER IFS-66V spectrometer. Fig. 2 shows the FT-IR transmission spectrum of TTPI crystal in the region 4000–400 $cm^{-1}$. The various functional groups of TTPI were well identified and compared with frequency components of thiourea as listed in Table 1.

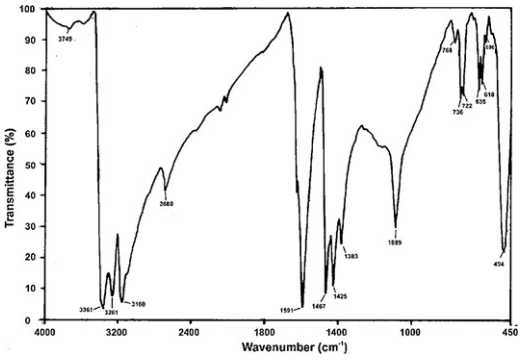


**Fig. 2.** FT-IR spectrum of TTPI single crystal.

**Table 1**
The wave number assignments of TTPI in comparison with thiourea.

| Wave number ($cm^{-1}$) | | Assignment |
|---|---|---|
| Thiourea | TTPI | |
| 469.0 | 494.0 | NCS symmetric bending |
| 640.0 | 600.0, 618.0, 635.0 | NCS asymmetric bending |
| 740.0 | 722.0, 736.0, 768.0 | CS symmetric stretching |
| 1089.0 | 1090.0 | CN symmetric stretching |
| 1417.0 | 1425.0 | CS asymmetric stretching |
| 1472.0 | 1467.0 | CN asymmetric stretching |
| 1627.0 | 1591.0, 1629.0 | $NH_2$ symmetric stretching |
| 3100–3200 | 3160.0 | $NH_2$ symmetric stretching |
| 3280, 3384 | 3261.0, 3364.0 | $NH_2$ asymmetric stretching |

### 3.3. FT-NMR studies

The Fourier transform nuclear magnetic resonance spectrum of TTPI was recorded using Jeol GSX 400 NB 400 MHz FT-NMR spectrometer in the range 0–220 ppm and shown in Fig. 3. The sample was kept in a homogeneous magnetic field and further subjected to a radio frequency pulse of very short duration and the decay of the signal called the free induction decay (FID) was monitored. A Fourier transform of FID gives the frequency domain NMR spectrum. Since the spread of the signal is so wide, two $C^{13}$ nuclei will have identical chemical shifts unless they are equivalent or enantiotopic. If the carbon atoms present in the resulting compound are different then only individual carbon atoms can be observed in the spectrum. Since TTPI contains one type of carbon atom belonging to thiourea [$(N_2H_4CS)_4$], the spectrum has only one signal. It is evident that the chemical shift observed at 182.04 ppm corresponds to the carbon atom belonging to thiourea. Interestingly, the above signal acts as a strong evidence for the existence of thiourea ligand in the resulting compound of TTPI.

### 3.4. Optical studies

The optical absorption spectrum of TTPI was recorded in the range 200–1200 nm using Varian Carry 5E model spectrophotometer (Fig. 4). The spectrum shows that the UV cut off wavelength is about 230 nm and interestingly the absorption value is less than two units from 230 nm to 1200 nm. The above facts clearly show that TTPI possesses a wide optical transparency window from IR to UV region.

### 3.5. TGA–DTA and DSC analysis

The TG–DTA and DSC studies of TTPI crystal were carried out in the temperature range 28–1200 °C and 24–220 °C by using NETZSCH STA 409C thermal analyzer and NETZSCH DSC 204 instrument, respectively, under nitrogen atmosphere, at a heating rate of 10 K/min. Initially, 14.360 mg and 9.160 mg samples were loaded

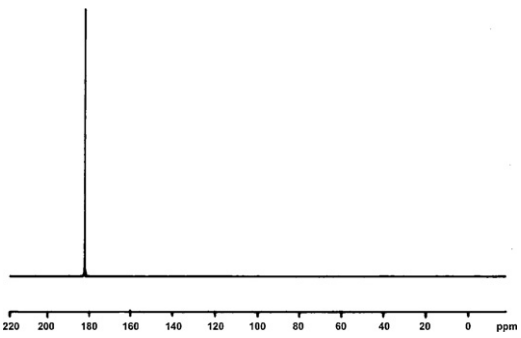


**Fig. 3.** FT-NMR studies of TTPI single crystal.