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The growth and characterization of a metal organic crystal, potassium thiourea thiocyanide

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Abstract The growth and characterization of a new non-linear organometallic crystal, potassium thiourea thiocyanide (PTT) is reported. The growth of single crystals was accomplished by the slow evaporation solution growth method. The grown crystals were characterized by XRD, TG–DTA, UV, and FTIR spectral analyses. PTT has good optical transmission in the entire visible region which is an essential requirement for a non-linear crystal. TG curve of PTT undergoes complete decomposition between 176 and 1,000 °C in three steps with corresponding three DTA peaks. The high thermal stability of organometallic crystals are due to strong bonding existing between the conjugation layers of thiourea molecule and the potassium ions.

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Introduction

In recent years, the non-linear optical (NLO) properties of some products of thiourea [1–15] have attracted great interest because semiorganic materials have the potential for combining high optical non-linearity and the chemical flexibility of organics with the physical ruggedness of inorganics. Thiourea molecule has large dipole moment [16] and has the ability to form extensive network of hydrogen bonds. The centro-symmetric thiourea molecule, when combined with inorganic salts yields non-centro-symmetric complexes which has non-linear optical properties. Metal complexes of thiourea include advantages of both organic and inorganic part of the complex. A variety of crystals of this class have been grown by several groups [17–19]. TG–DTA, XRD, optical, and spectral analysis are very important techniques for materials characterization. It is not surprising that many authors have used these techniques for investigation of various materials [12, 20–39]. In this article, we report the growth of single crystals of potassium thiourea thiocyanide, a new semiorganic NLO material by slow evaporation method and its characterization by thermal, XRD, optical, and spectral analyses.

Experimental

Preparation

Raw material for the growth of PTT was synthesized by mixing methanol solutions of potassium thiocyanide

and thiourea in 1:2 ratio. The proposed chemical reaction is

$$KSCN + 2CS(NH_2)_2 \rightarrow K\{[CS(NH_2)_2]_2\}SCN$$

Since thiourea has the coordinating capacity to form different phases of metal thiourea complexes, the mixture of the reactants had to be stirred well and the product was purified by repeated recrystallization before it is used for the growth of PTT crystal. The slow evaporation technique was used to grow single crystals of PTT in methanol solution. A good transparent single crystal of PTT was obtained in 7–10 days.

Characterization

The grown crystals of PTT were subjected to single crystal X-ray diffraction studies on an ENRAF NONIUS CAD4 diffractometer.

The FTIR spectra of PTT crystals were recorded in the range of 400–4,000 cm^{-1} on a Bruker 66 V FTIR instrument using the KBr pellet method in order to reveal the metal complex co-ordination.

The UV spectrum of PTT crystals was recorded on a Hitachi UV–VIS spectrophotometer in the spectral range 180–800 nm.

The TG–DTA analysis was carried out between 30° and 1,000 °C in the nitrogen atmosphere at a heating rate of 10 °C/min on a STA 409C analyzer.

Table 1 Crystallographic parameters of PTT

Chemical formula	K {[$CS(NH_2)_2$]$_2$} SCN
Cell parameters/Å	$a = 5.4891$
	$b = 7.6560$
	$c = 8.5505$
System	Orthorhombic

Results and discussion

XRD analysis

The single crystal XRD data of the PTT single crystal was obtained using a single crystal X-ray diffractometer and the crystallographic data are given in Table 1. From the single crystal XRD analysis, it is confirmed that the grown PTT crystals belong to orthorhombic crystal system and the space group is $P2_12_12_1$. The crystallographic data reveal the change in lattice parameters indicating the influence of dopant potassium.

FTIR spectral analysis

The FTIR spectrum of PTT is shown in Fig. 1. The FTIR spectral data of thiourea and PTT are summarized in Table 2. When it was compared with the spectra of thiourea, several peaks were found to be slightly shifted. In the complex, there are two possibilities by which co-ordination of potassium with thiourea can occur. The co-ordination of

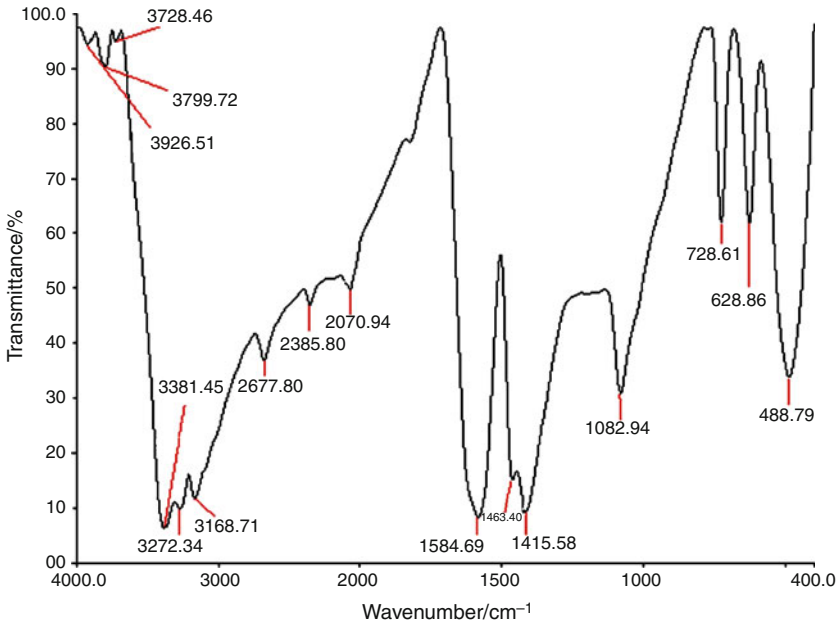

Fig. 1 FTIR spectrum of potassium thiourea thiocyanide

Table 2 Assignments of FTIR band frequencies/cm^{-1} of thiourea and PTT

Thiourea	PTT	Assignments
1,625	1584.69	δNH_2
1,470	1463.40	γ_{as} (N–C–N)
1,417	1415.58	γ_s (C=S)
1,083	1082.94	γ_s (N–C–N)
730	728.61	δs (C=S)

potassium may occur either through nitrogen or sulfur of thiourea [40].

The broad envelope positioned between 2,677 and 3,381 cm^{-1} corresponds to symmetric and asymmetric stretching modes of NH_2 group of thiourea. The bonds of thiourea were shifted to lower frequencies on the formation of potassium thiourea complex. This indicates that nitrogen to potassium bonds is not present in the co-ordination compounds. The absorption observed at 1463.40 and 1082.94 cm^{-1} in the spectra of PTT corresponds to the 1,470 and 1,083 cm^{-1} absorption of thiourea, can be assigned to N–C–N stretching vibration. The decrease in wave number can be attributed to the greater double bond character of the C to N bond on complex formation. Comparison of vibration spectra of thiourea and PTT is shown in Table 2.

UV spectral analysis

The UV spectra for thiourea and PTT are shown in Figs. 2 and 3, respectively. In PTT, the π–π^* absorption band shifted to lower wavelength (236.98 nm) compared to thiourea (255 nm). This is because of the formation of co-ordinated bond between metal with thiourea. Thus, greater energy required for this transition and hence the absorption shows the blue end (shift) of the spectrum.

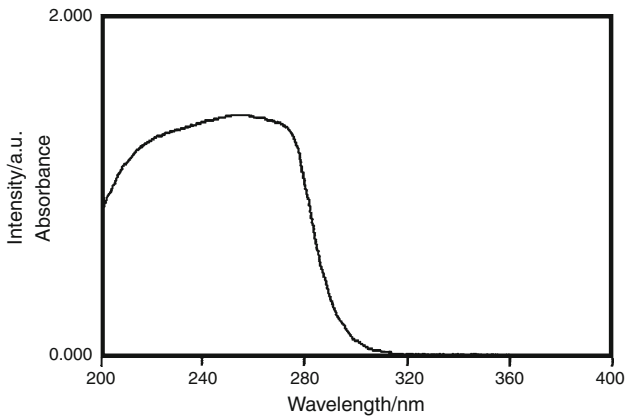

Fig. 2 UV spectrum of thiourea

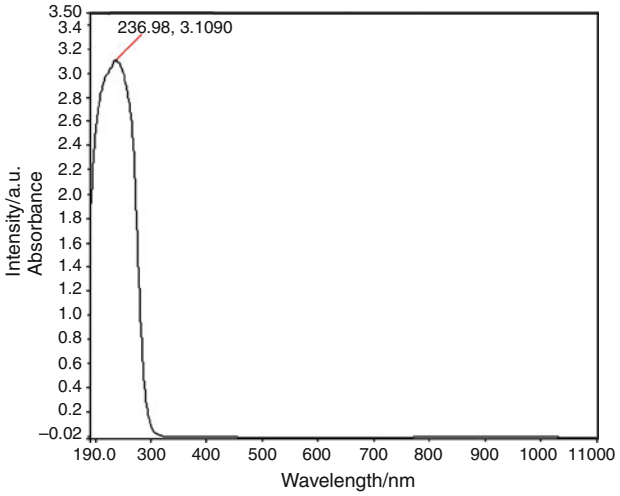

Fig. 3 UV spectrum of potassium thiourea thiocyanide

Thermal analysis

TG–DTA analysis of dried powder of single crystals of PTT is carried out in nitrogen atmosphere at a heating rate of 10 °C/min. The TG–DTA curves of PTT are shown in Fig. 4. It is seen from the TG curve that the PTT undergoes complete decomposition between 176 and 1,000 °C and exhibited three significant mass loss steps. The first step of decomposition at 176–220 °C produces a maximum mass loss around 62% compared to subsequent steps. This mass loss step is due to the elimination of thiourea and is also confirmed by DTA curve with the corresponding endothermic DTA peak at 210.18 °C. The second mass loss step at 222–510 °C is due to the elimination of SCN accompanied with 23% mass loss with corresponding exothermic DTA peak at 468.94 °C. The third and final mass loss step took place at 510–1,000 °C and is responsible for the decomposition of potassium accompanied with 15% mass loss with corresponding exothermic DTA peak at 539.31 °C. The experimental mass losses are in good agreements with the theoretical expectations. The high thermal stability of organometallic crystals arises due to strong bond existing between the conjugation layers of thiourea molecule and the metal ions.

NLO test

In order to confirm the NLO property, the grown crystal was subjected to NLO test using high intensity Nd-YAG laser. The out put from the Nd-YAG laser was used as the source and it was illuminated to the crystal specimen. Pulse energy was 300 mJ/s. The out put could be seen as a bright green flash emission from the sample.

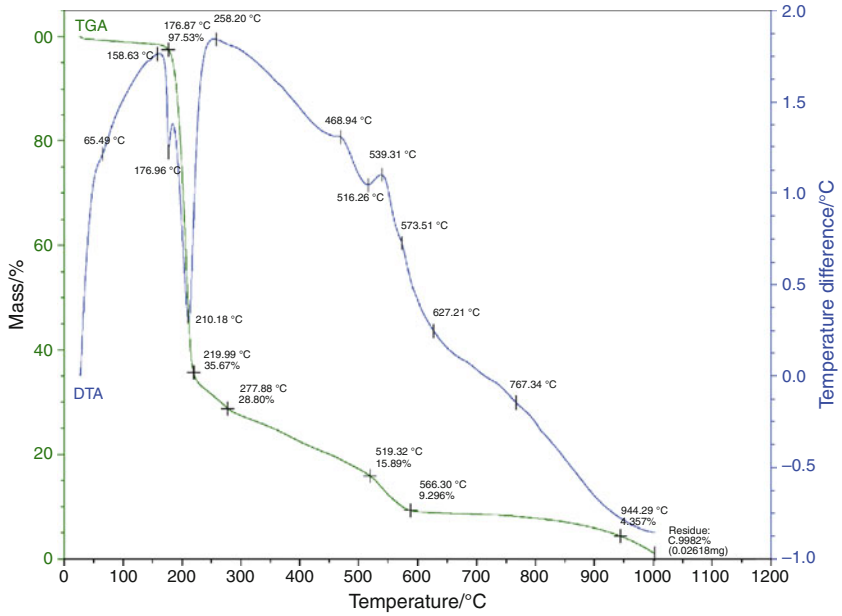

Fig. 4 TG–DTA (exo up) curves of potassium thiourea thiocyanide

Conclusions

Single crystals of PTT were grown using the slow evaporation technique. The lattice parameters were found using the single crystal XRD technique. The FTIR spectrum reveals the functional group of the grown crystal. SHG efficiency makes the crystal potential material for NLO application. The high thermal stability of organometallic crystals arises because of the strong bond existing between the conjugation layers of thiourea molecule and the metal ions. TG curve of PTT undergoes complete decomposition at 176–1,000 °C in three steps with corresponding one endothermic DTA peak at 210.18 °C and two exothermic DTA peaks at 468.94 and 539.31 °C.

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