

A comparative study on the spectral properties of thiourea potassium chloride and thiourea tartarate single crystals

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Abstract : Single crystals of thiourea potassium chloride and thiourea tartarate were grown by slow evaporation of aqueous solutions containing 1 mol of thiourea and 1 mol of either potassium chloride or tartaric acid. The UV-Visible spectra were recorded for both the crystals which show a slight change in the lower cut off value due to some change in the functional group formation between the two crystals. The IR spectra were recorded for the grown crystals, to study the functional groups, which show a marked difference between the two spectra. A comparative report was made between the two crystals for non linear optical applications. The UV visible spectra show a good transmission in the entire visible region which is primary requirement of good non linear optical crystal.

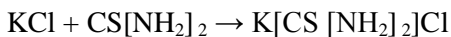
Key words: Thiourea, crystal growth, Spectral studies, UV-Visible spectra, IR spectra.

Introduction:

Due to the recent surge in the advancement of optical communication technology, laser technology and optical data storage, the need for new nonlinear optical materials with good optical transmission and stability increases. Initially organic compounds attracted attention for frequency conversion applications because of their good conversion efficiency ¹ but the disadvantage in pure organic compounds is their low damage threshold. Recently semi organic single crystals for optical applications allured the interest of scientists because of their better properties like large nonlinearity, high laser damage threshold and good mechanical strength ^{2,3}. One of the basic requirements for NLO materials is non centro symmetry. Thiourea is a centro symmetric molecule at room temperature but can be converted into noncentro symmetry by forming metal complex or organic compounds. It is well known that thiourea can easily form compounds with metal complexes and growing optical quality single crystal is quite easy by low temperature solution growth. It has also been reported that thiourea metal complex materials are ideal for frequency conversion applications as they have low angular sensitivity ⁴. Even though the crystal structure and properties of many thiourea metal complexes have been reported ⁵⁻⁹, a comparative study of the optical properties is missing in the literature. The present manuscript compares the optical properties of the semi organic potassium thiourea chloride and organic thiourea tartarate single crystals for second harmonic generation applications.

Crystal Growth:

In our present work potassium thiourea chloride and thiourea tartarate single crystals have been grown by the slow evaporation method. Saturated solutions of thiourea with either potassium chloride or tartaric acid are mixed with thiourea in triple distilled water in the molar ratio of 1:1 as per the equation below for KCl

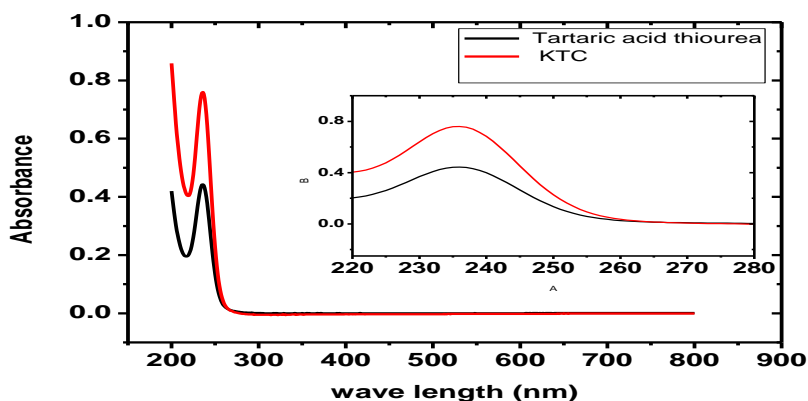


By repeated recrystallization process the purity of the salts were further increased and the super saturated solutions were kept undisturbed at room temperature. Optically transparent defect free seed crystal was obtained within the period of 15 days. Large size single crystals were grown by slow cooling method using a homemade constant temperature bath. The structure of the grown crystals was estimated by the XRD studies which confirm there is a small change in the lattice parameter values of the grown crystals.

UV-Visible Spectroscopy:

The bonding electrons, the electrons associated with more than one nucleus are susceptible to energy level transitions under stimulus to appropriate radiation. The presence of nitrogen increases the likelihood of π bonds. The n to π^* and π to π^* transitions are lower energy transitions and will be induced by UV or Visible region. The UV-visible studies of Thiourea potassium chloride and tartaric acid measured in a solution medium taking ultra pure water as solvent were investigated using Shimadzu UV-2450 spectrophotometer in the range of 200-900 nm. The recorded transmittance spectra are shown in (Figure-1) and the inset inside shows the cutoff wavelength of the two grown crystals. There is a very small change in the cut off wave length and grown films are highly transparent in the entire UV region with cut off wave length of 259 nm and 261 nm for potassium thiourea chloride and thiourea tartarate single crystals. The optical band gap calculated from the UV-Visible spectrum is around 4.75 eV and 4.78 eV for the grown potassium thiourea chloride and thiourea tartarate respectively.

Figure 1: Recorded Transmittance spectra

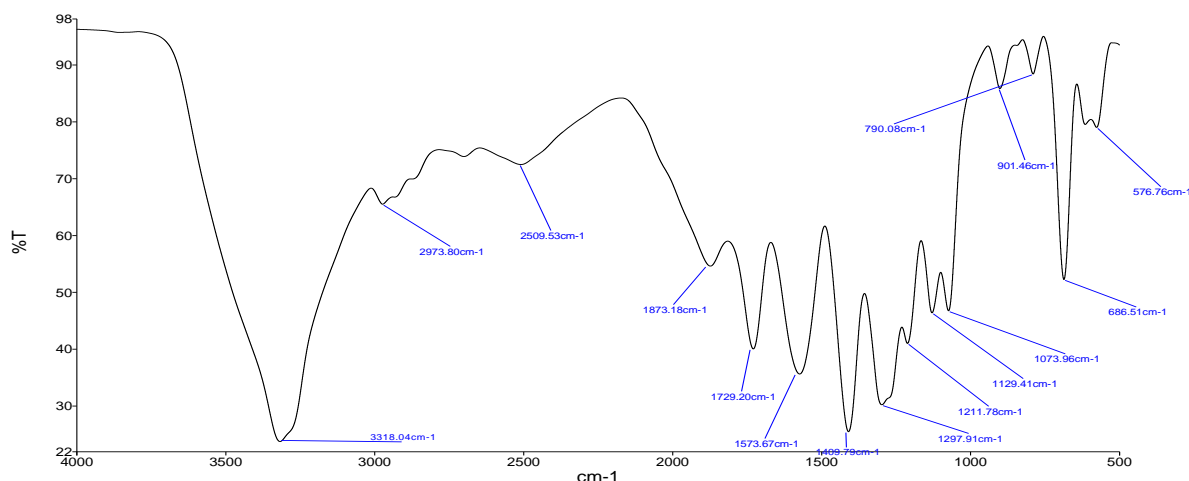
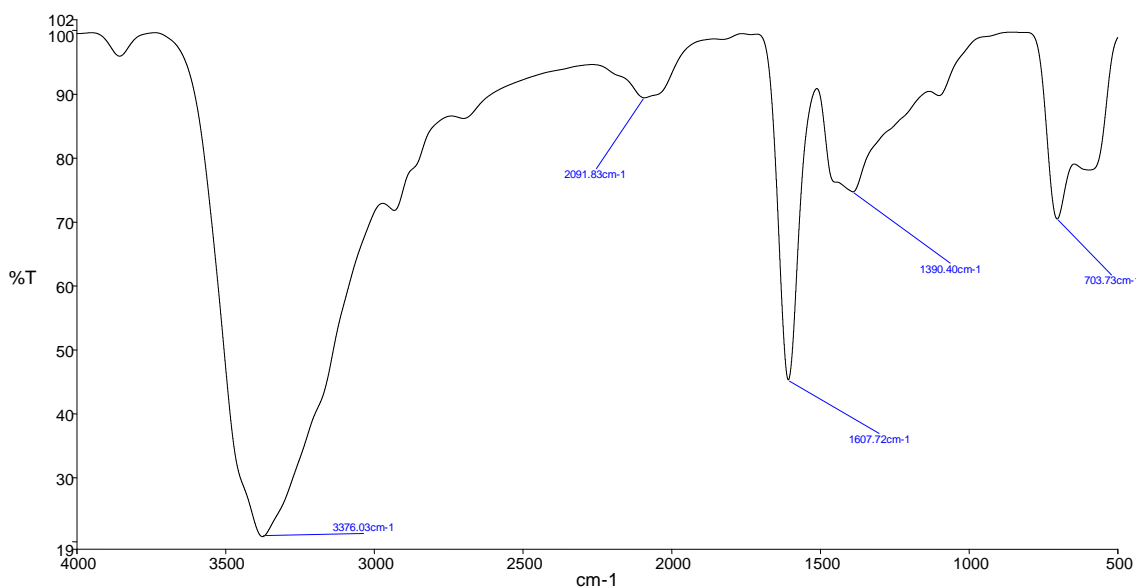


Infrared spectroscopy studies:

The vibration of the atoms in the molecule is the base for the IR spectra and it is commonly obtained by passing infrared radiation through a sample. The functional groups in the molecules are determined by the fraction of the absorbed incident radiation and the energy at which the absorption occurs related to the frequency of the vibration of the functional group of the sample molecule. The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. In general the IR spectrum can be split up into far- IR ($<400\text{ cm}^{-1}$), mid- IR ($4000\text{ to }400\text{ cm}^{-1}$) and near- IR spectrum ($13000 - 4000\text{ cm}^{-1}$).

In the present study, the mid-IR spectra were recorded for the grown crystals in the range of $4000\text{--}400\text{ cm}^{-1}$ using Perkin Elmer instrument by KBr pellet technique as shown in (Figure- 2 & 3). The mid-IR region are generalized as follows¹⁰

4000-2500 cm^{-1} range represents X-H stretching mode
 2500-2000 cm^{-1} range represents the triple bond region.
 2000-1500 cm^{-1} range represents the double region and
 1500-600 cm^{-1} range represents the finger print region.

Figure 2: IR-Spectra of thiourea potassium chloride**Figure 3: IR-Spectra of thiourea tartaric acid**

In both the (Figures- 2 & 3), the absence of any pronounced absorption peak around 2000 – 2500 cm⁻¹ confirms the absence of any triple bond in the grown samples. There are two possibilities by which the metal ion can form complex with thiourea, either through nitrogen or through sulphur in thiourea. The formation of S-M bond can increase the polarity of thiourea molecule ¹¹.

In the IR spectrum of thiourea potassium chloride (Figure-2), the absorption peak around 3319 cm⁻¹ corresponds to N-H stretching mode. The peak around 780 cm⁻¹ is assigned to C=S bond and the peak around 1410 cm⁻¹ may correspond to C-N bond.

There is a slight variation in the peak position for thiourea tartarate single crystals as shown in (Figure-3). The small absorption peak around 3700 may be assigned to O-H bond due to the presence of tartaric acid. The presence of absorption band around 1607 cm⁻¹ can be assigned to C=O stretching mode, the absence of these bands in potassium thiourea chloride confirms the absence of oxygen in the grown crystal. The identified functional groups in pure thiourea, potassium thiourea chloride and thiourea tartarate crystals are systematically assigned with corresponding wavenumber, as shown in (Table-1). The prominent shifts in the vibrational frequencies from pure thiourea confirms the formation of new functional groups or difference in environment than pure thiourea single crystal.

Table 1: Functional Group Identification with Wave number

Thiourea (cm-1)	Potassium thiourea chloride (cm-1)	Thiourea tartarate (cm-1)	Assignment (cm-1)
494	570		N-C-N Stretching
740	780	703	C=S Stretching
1089	1029	1050	C-N Stretching
1417	1410	1360	C=S Stretching
1627	1728	1607	NH ₂ Bending
3376	3319	3376	NH ₂ Stretching

Conclusion:

The potassium thiourea chloride and thiourea tartarate single crystals have been grown by slow solution evaporation technique. The XRD studies confirms a change in cell parameter. The prominent shifts in the vibrational frequencies of the identified functional groups confirmed the formation of thiourea metal complex and thiourea tartarate single crystals. The grown single crystals showed high optical transparency, large transmission and wide optical band gap (4.75 eV) than pure thiourea confirming its suitability for distinct optical applications. Comparison of the optical properties of two crystals suggest that they both have more or less the same property but as the mechanical stability of semiorganic potassium thiourea chloride will be better than the pure organic crystals, it is suggested that the potassium thiourea chloride can be a better candidate for frequency conversion applications.

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