

FTIR Spectroscopy and DSC-Based Thermodynamic Characterization of Nonlinear Optical Thiourea Crystals

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Abstract—Nonlinear optical (NLO) crystals are vital for applications in photonics and optoelectronics. Thiourea, an organic NLO material, is particularly attractive due to its optical nonlinearity, stability, and hydrogen bonding network. In this study, single crystals of thiourea were investigated using Fourier Transform Infrared (FTIR) spectroscopy and Differential Scanning Calorimetric (DSC). FTIR spectra confirmed the characteristic vibrational modes of functional groups, validating molecular integrity and crystal quality. DSC analysis was employed to evaluate the thermal response and calculate key thermodynamic parameters, including enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The results indicate strong intermolecular interactions and favorable thermal stability, making thiourea suitable for nonlinear optical device applications. This combined spectroscopic and calorimetric approach provides insight into the structure–property relationship of thiourea crystals and establishes their potential in advanced photonic applications.

Index Terms— FTIR Spectroscopy, Differential Scanning Calorimetry, Thermodynamic Parameters, Vibrational Analysis, Thermal Stability, Photonic Applications

I. Introduction

Nonlinear optical (NLO) materials have attracted considerable attention in recent decades due to their wide-ranging applications in optoelectronics, photonics, laser technology, and frequency conversion devices. Among the various organic and semi-organic crystals, Thiourea [$\text{CS}(\text{NH}_2)_2$] has emerged as an important candidate for NLO applications owing to its large dipole moment, hydrogen-bonding capability, and favorable crystal growth characteristics. Its ability to form semi-organic complexes with metal salts further enhances its optical nonlinearity, making it a versatile material in nonlinear optics.

A thorough understanding of the structural, spectroscopic, and thermodynamic properties of thiourea is essential to evaluate its stability and suitability for device fabrication. Spectroscopic techniques such as Fourier Transform Infrared (FTIR) spectroscopy provide insight into the vibrational modes of the functional groups, hydrogen-bonding interactions, and molecular arrangements within the crystal lattice. This information is vital in confirming the purity and molecular integrity of the grown crystals.

On the other hand, Differential Scanning Calorimetry (DSC) is a powerful thermal analysis technique used to determine phase transitions, enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG). The evaluation of such thermodynamic parameters provides a quantitative measure of the crystal's thermal stability and the spontaneity of phase transitions, which are critical factors in determining the operational limits of NLO materials.

II. FTIR Spectroscopic Analysis

The FTIR spectrum of thiourea crystals was recorded in the range of 4000–400 cm^{-1} (Fig. 1). The observed absorption bands and their assignments are summarized in Table 1.

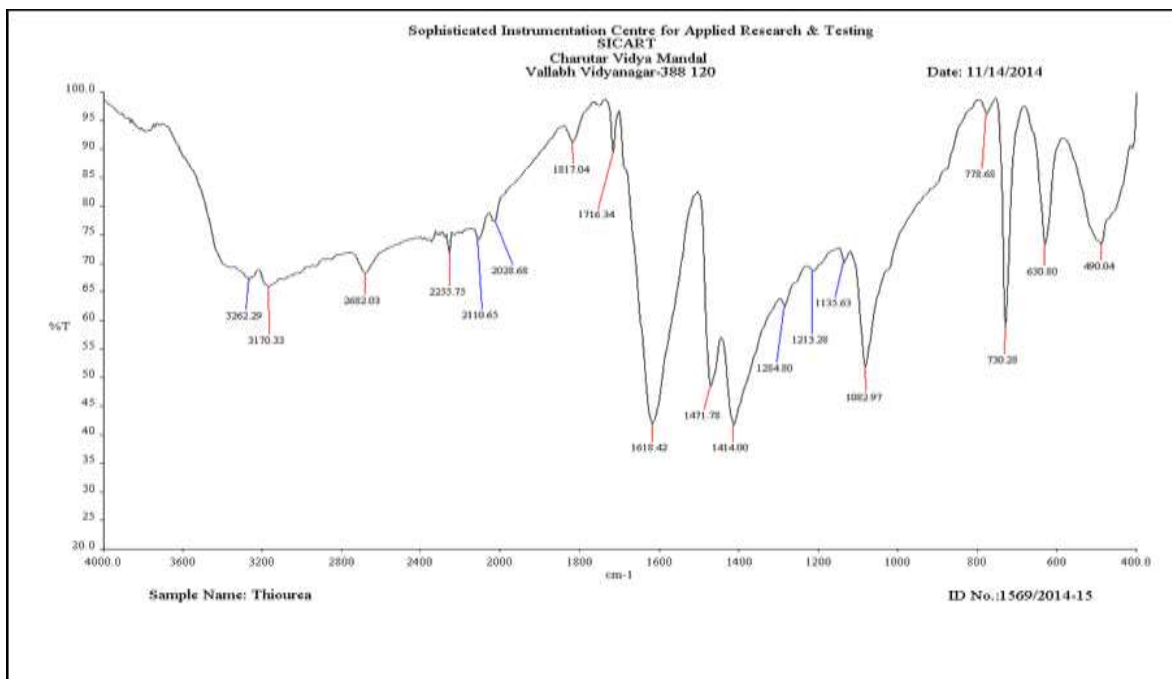


Figure 1 FTIR Spectra for Thiourea

Observed Peaks & Assignments:

Table 1 Observed Peaks & Assignments

Wavenumber (cm^{-1})	Assignment
3262, 3170 cm^{-1}	N–H symmetric and asymmetric stretching vibrations ($-\text{NH}_2$ group)
2682 cm^{-1}	Possible overtone / weak C–H type vibration or combination band
2355, 2110, 2028 cm^{-1}	Weak bands (may correspond to overtones, combination vibrations, or impurities/atmospheric CO_2 interactions)
1817, 1716 cm^{-1}	Overtone / Fermi resonance (not typical of thiourea fundamentals; may be due to coupling of NH_2 bending)
1618, 1471 cm^{-1}	N–H bending vibrations (scissoring mode of NH_2 group)
1414 cm^{-1}	C–N stretching vibration
1234, 1213 cm^{-1}	C=S stretching coupled with N–C–N bending
1135 cm^{-1}	C–N stretching mode
1083 cm^{-1}	In-plane NH_2 rocking
730, 630 cm^{-1}	Out-of-plane NH_2 wagging/twisting vibrations
490 cm^{-1}	Skeletal vibration involving C=S and N–C–N linkage

The broad peaks observed at 3262 and 3170 cm^{-1} correspond to the symmetric and asymmetric N–H stretching vibrations of the –NH_2 groups. A weak band near 2682 cm^{-1} may be attributed to overtone or combination modes. The bands at 2355 , 2110 , and 2028 cm^{-1} are associated with weak overtone/combination absorptions.

The amide region displays characteristic bands at 1618 and 1471 cm^{-1} , which can be assigned to N–H bending (scissoring) of the amino groups. A distinct peak at 1414 cm^{-1} arises from C–N stretching vibrations. The C=S stretching vibration, a signature mode of thiourea, appears strongly in the region $1234\text{--}1213\text{ cm}^{-1}$, coupled with N–C–N bending. Further absorptions at 1135 and 1083 cm^{-1} correspond to C–N stretching and in-plane rocking of –NH_2 , respectively. The low-frequency region exhibits peaks at 730 and 630 cm^{-1} , assigned to out-of-plane NH_2 wagging/twisting, while the band at 490 cm^{-1} corresponds to skeletal vibrations involving the C=S bond.

The presence of all characteristic vibrational modes of thiourea indicates that the grown crystal retains its structural integrity and molecular identity without significant impurities. These assignments are in good agreement with reported literature values, confirming the high quality of the sample.

III. DSC Thermodynamic Analysis

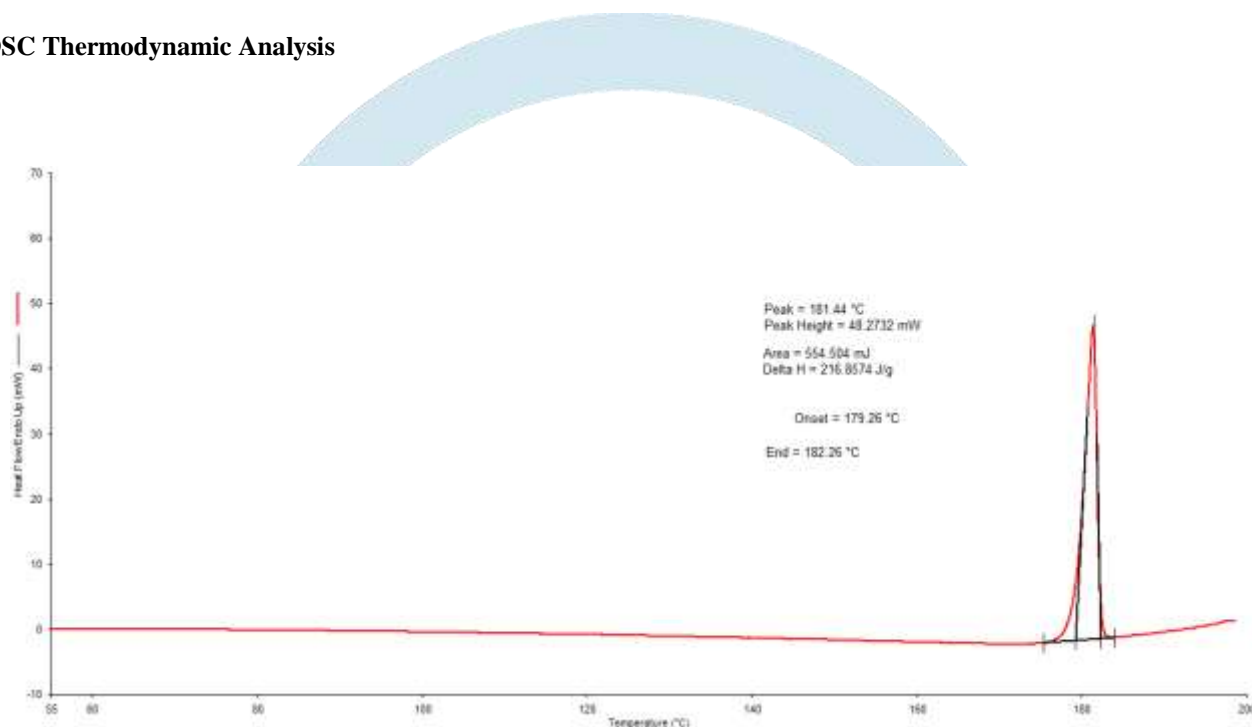


Figure 2- DSC thermogram of Thiourea

The thermal stability and phase transition behavior of thiourea crystals were investigated using Differential Scanning Calorimetry (DSC). The DSC thermogram (Fig.2) shows a sharp endothermic peak at $181.44\text{ }^{\circ}\text{C}$ (454.59 K), with an onset at $179.26\text{ }^{\circ}\text{C}$ (452.41 K) and completion at $182.26\text{ }^{\circ}\text{C}$ (455.41 K). The sharp nature of the peak confirms the well-defined phase transition corresponding to the melting of thiourea.

From the integrated peak area, the enthalpy change (ΔH) was obtained as 216.86 J/g . On molar basis (molar mass = 76.12 g/mol), the enthalpy of transition was calculated as 16.52 kJ/mol .

The corresponding entropy change (ΔS) was evaluated using the relation:

$$\Delta S = \Delta H / T \text{ ----- (1)}$$

At $T = 454.59\text{ K}$, ΔS was found to be $0.477\text{ J/g}\cdot\text{K}$ or $36.3\text{ J/mol}\cdot\text{K}$.

The Gibbs free energy change (ΔG) at the transition temperature was calculated using the relation:

$$\Delta G = \Delta H - T\Delta S \text{ ----- (2)}$$

Which yielded a value close to 0 J/mol , indicating the equilibrium nature of the melting transition.

From DSC, ΔC_p is obtained from baseline shift before and after transition. In graph, the baseline looks flat (no visible step), meaning ΔC_p is negligible for this transition.

Final Thermodynamic Parameters of Thiourea (from DSC)

Table 2 Calculated Thermodynamic Parameters of Thiourea

ΔH (per gram):	216.86 J/g
ΔH (per mole):	16.52 kJ/mol
ΔS (per gram):	$0.477\text{ J/g}\cdot\text{K}$
ΔS (per mole):	$36.3\text{ J/mol}\cdot\text{K}$
ΔG (per gram at T_p):	$\approx 0\text{ J/g}$
ΔG (per mole at T_p):	$\approx 0\text{ J/mol}$
ΔC_p :	negligible

IV. Discussion

The FTIR analysis confirmed the vibrational signatures of thiourea functional groups (NH_2 , $\text{C}=\text{S}$, $\text{C}-\text{N}$), verifying the purity and structural stability of the grown crystals. The DSC results revealed a sharp endothermic transition corresponding to melting, with well-defined thermodynamic parameters. The relatively high enthalpy and entropy values highlight the stability of thiourea crystals up to their melting point, which is a desirable property for nonlinear optical applications where thermal endurance is critical.

The combined spectroscopic and thermodynamic investigations demonstrate that thiourea is a structurally stable and thermally reliable material, making it a promising candidate for device-level applications in nonlinear optics.

V. REFERENCES

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