Growth and characterization of Thiourea single crystals doped with Nickel Sulphate and Ammonium Sulphate

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ABSTRACT: Nonlinear optical thiourea single crystals doped with Nickel Sulphate and Ammonium Sulphate were conveniently grown by slow evaporation method at room temperature. The sample confirmed by powder XRD studies. The grown crystals were subjected to optical characterization by FT-IR, UV-Vis and Photoluminescence techniques. Crystal system and lattice parameters have been estimated by powder x-ray diffraction analysis. The prominent peaks of powder XRD pattern have been indexed and diffraction data have been presented. The presence of various functional group were identifies with the help of FT-IR analysis. The UV analysis reveals the absorption phenomenon and also bandgap energy. The impurities of the absorptions were detected by PL spectra.

Key words: Slow evaporation, XRD, Optical studies.

1. INTRODUCTION

Thiourea is a sulfur-containing organic compound widely used as raw materials in the synthesis of pharmaceuticals, dyes, and resins [1,2], as well as a vulcanization accelerator for rubber [3], a flotation agent for metal minerals [4,5], and an organic catalyst [6]. The common production of thiourea crystals is to generate thiourea solutions through the reaction of lime nitrogen with hydrogen sulfide and calcium hydroxide, subsequently, a batch crystallization process is employed to cool the solutions from 35 °C to 15 °C, finally yield the aimed products by solid-liquid separation [7]. The resultant products frequently exhibit a broad crystal size distribution (CSD), primarily spanning from 0.15 mm to 0.9 mm, with a substantial presence of fine crystals, which causes moisture absorption and agglomeration [8,9], thereby affecting the production of downstream industries. To tackle the above problems, the crystallization process of thiourea has been investigated. For example, employing classical nucleation theory to scrutinize the nucleation process of thiourea crystallization reveals that at high supersaturation, thiourea is susceptible to homogeneous nucleation, whereas at low supersaturation, it tends to undergo heterogeneous nucleation [10]. It was also found that the addition of sodium polystyrene sulfonate can inhibit the nucleation, with the apparent order of nucleation increasing from 0.99–1.65 to 1.54–3.44, and the width of the metastable zone significantly increasing [11]. Compared with the crystal nucleation process, the crystal growth has a more important impact on regulating crystal size, morphology, *etc.* [12,13]. In general, crystal growth encompasses two fundamental processes: bulk diffusion and surface reaction [14]. For instance, the crystal growth of pentaerythritol is controlled by the complex mechanisms of surface reaction and diffusion limitation [15], while the controlling step for the growth of mesalazine and allopurinol is the surface reaction [16]. Hence, an investigation into the kinetics and mechanisms of crystal growth can elucidate the governing steps in growth, thereby strengthen the crystallization process and achieve CSD and morphology control [[17], [18], [19]]. However, there are few relevant research reports on the growth process of thiourea crystals. Here, our objective is to scrutinize the impact of temperature variations on the growth kinetics of thiourea crystals. We aim to determine the kinetic parameters of crystal growth at different temperatures using the power law model and two-step growth model, to explore the influence of cooling process on the growth mechanism of thiourea crystals, to identify key factors limiting crystal growth and then conduct corresponding process optimization, thus to provide theoretical reference for improving the particle size of thiourea crystals.

2. EXPERIMENTAL

2.1 Growth of Nickel Sulphate doped Thiourea (TNS) and Ammonium Sulphate doped Thiourea (TAS)

Bulk growth of TNS and TAS single crystal has been carried out in the aqueous solution by slow evaporation method, using a constant temperature bath. The ratio in which the constituent compounds were added in each cases 1:1 respectively. A saturated solution of the salts was prepared and stirrer well for 2 hours then the solutions was filtered. The filtered solutions were transferred into the petri dishes which were closed in the thick papers with fine pores in order to minimize the rate of evaporation. The solutions were allowed to evaporate completely and single crystals of TNS and TAS well transparent crystals were harvested in 25 days.

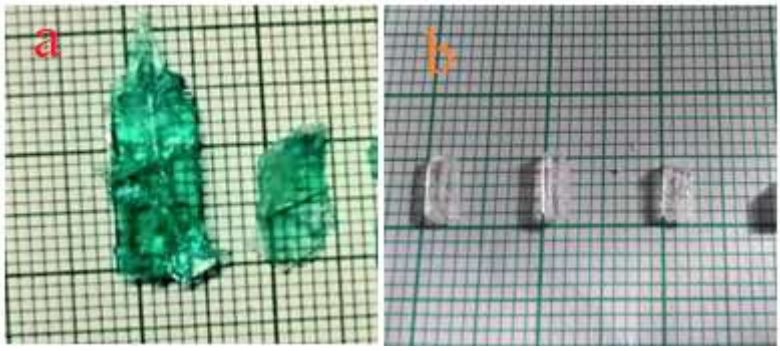

Fig 1 a) Nickel Sulphate doped Thiourea b) Ammonium Sulphate doped Thiourea Single crystals

3. RESULTS AND DISCUSSION

3.1 POWDER XRD ANALYSIS

The cell parameter and geometry of the TNS and TAS were determined by powder X-ray diffraction analysis. The prominent peaks obtained in the powder XRD analysis. The below figure of grown crystals of TNS and TAS confirm the crystalline nature that can be shown below figure 2. The crystal structure in orthorhombic. The lattice parameters of grown crystals were tabulated. That can be shown in the table 1.

Table 1 Lattice parameters of grown crystals

Crystal	a(Å)	b(Å)	c(Å)	Volume (cm^3)
Nickel Sulphate doped Thiourea	8.5069	9.1487	10.5024	817.37
Ammonium Sulphate doped Thiourea	8.5967	7.7117	9.3712	621.26

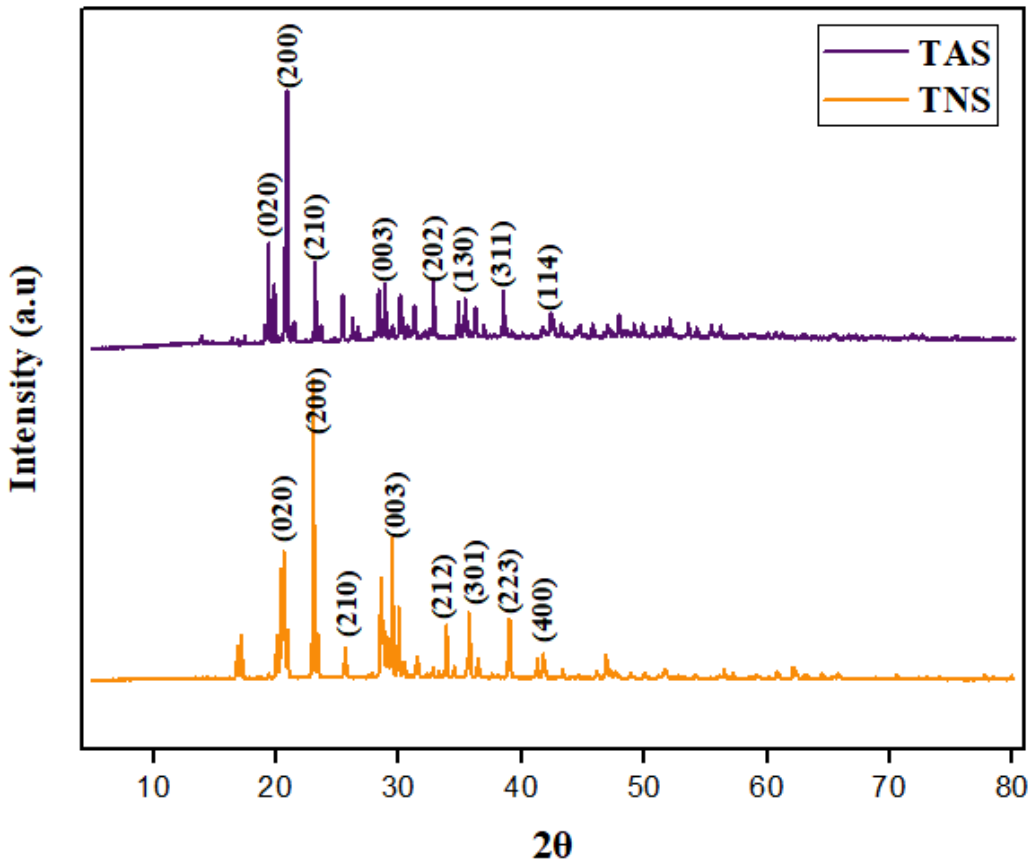

Figure 2 XRD Spectrum of TNS and TAS single crystals

3.2 FTIR ANALYSIS

The FTIR absorption spectrum in the infrared region 400-4000cm^{-1} was recorded for TNS and TAS crystals. Observed vibrational wave numbers and their assignments are listed in the table 2 and the spectrum shown in figure 3. In the FTIR spectra of pure Thiourea, the N-C-N asymmetric bending occurs at 487.25cm^{-1}. For Thiourea doped Nickel Sulphate and Thiourea doped ammonium Sulphate the N-C-N asymmetric is at 487cm^{-1}. The C-N stretching occurs at 1250-1020 cm^{-1} .For pure Thiourea this C-N stretching appear at 1088.12 cm^{-1} This appears at 1093 cm^{-1} for Thiourea doped Nickel Sulphate and Thiourea doped Ammonium Sulphate crystal .The O-H stretching presence at 3200-3550 cm^{-1}. The
O-H stretching vibrations appear at 3362 cm^{-1} for Nickel Sulphate doped Thiourea and Ammonium Sulphate doped Thiourea crystals. The C=O stretching mode of vibrations occurs at 1685 -1666cm^{-1}. For Thiourea doped Nickel Sulphate and Thiourea doped Ammonium Sulphate crystals the C=O stretching vibrations appears at 1671 cm^{-1} . The C-H bending occurs at 1478cm^{-1} for the Thiourea doped Nickel Sulphate and Thiourea doped Ammonium Sulphate crystal. The C=Cl stretching occurs at 850–550cm^{-1}. For Thiourea doped Nickel Sulphate and Thiourea doped Ammonium Sulphate crystal, C=Cl stretching appears at 732cm^{-1}. The C-I stretching occurs at 600-500 cm^{-1}, For Thiourea doped Ammonium Sulphate crystals the C-I stretching appears at 601cm^{-1}.

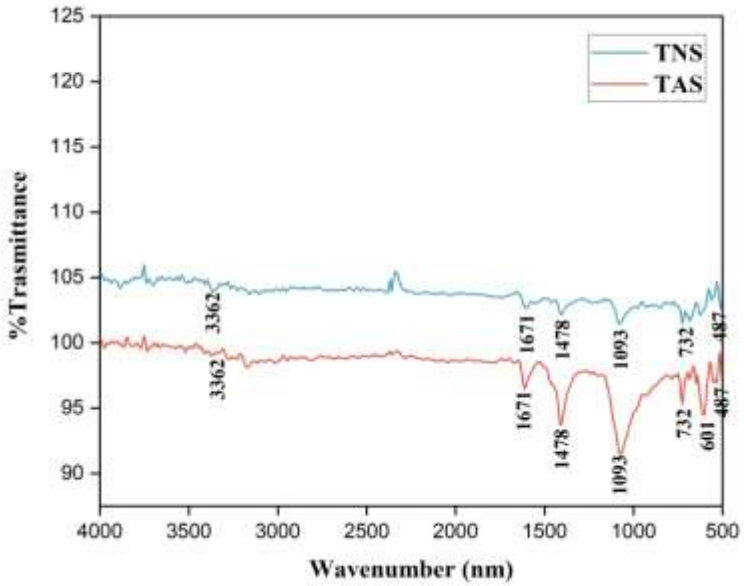

Figure 3 FTIR Spectrum of TNS and TAS single crystals

Vibrational assignments of TNS and TAS single crystals

Wavenumber (cm^{-1})		ASSIGNMENT
Nickel sulphate doped Thiourea	Ammonium sulphate doped Thiourea	
3362	3362	O-H STRETCHING
1671	1671	C=O STRETCHING
1478	1478	C-H BENDING
1093	1093	C-N STRETCHING
732	732	C=CL STRETCHING
-	601	C-I STRETCHING
487	487	N-C-N ASYMMETRIC BENDING

3.3 UV ANALYSIS

The optical activity of titled crystals was studied by UV-Vis spectrometer. UV absorption was carried out by the spectrometer. UV-Vis study is the important tool to determine the transparency, which is an important requirement for a material to be optically active. Low absorption in the entire visible and near infrared region. Absorption and bandgap energy are shown in figure 4 and 5. With low cut off wavelength of TNS and TAS were 235nm and 237nm respectively suggest that the materials are suitable for optoelectronic applications.

The bandgap of the crystals were calculated by plotting $(\alpha h\nu)^2$ against the hv and extrapolating the linear portion near the onset of absorption edge to the energy X-axis. The bandgap energy of TNS and TAS were found to be 5.02eV and 4.97eV.

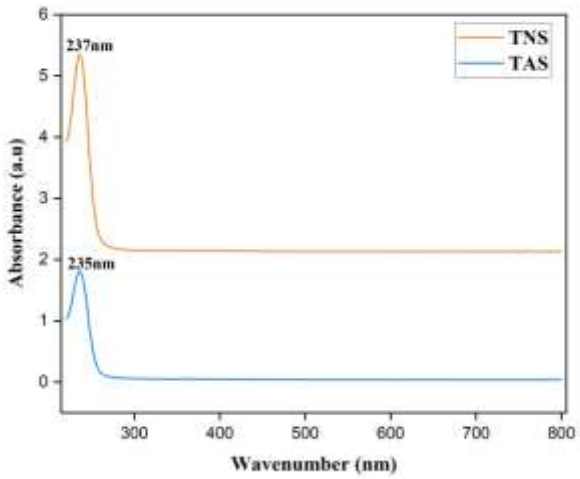

Figure 4 Absorption spectra of TNS and TAS single crystals

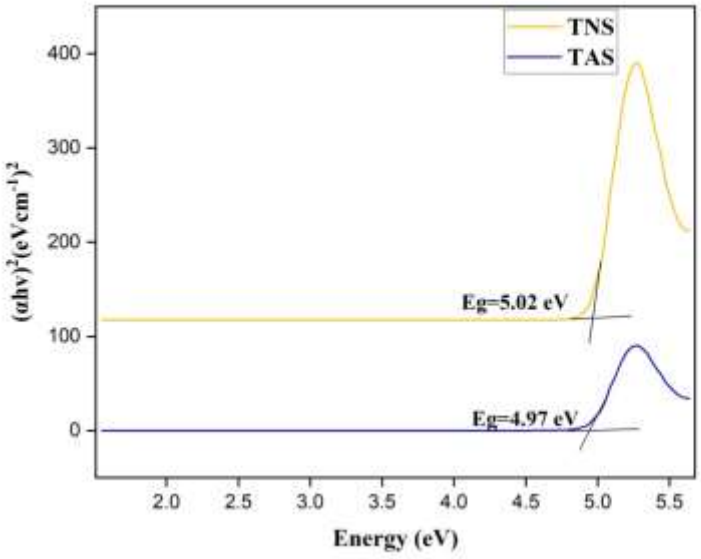

Figure 5 Bandgap energy of TNS and TAS single crystals

3.4 PL ANALYSIS

In order to probe the electronic structure of grown crystals emission spectrum was recorded from 200nm to 700nm and is shown the below figure. The spectrum exhibited broad emission peak from 300nm to 400nm, which shows the materials has blue emission on excitation at 369nm. Emission Peaks & Energy Transitions observed PL peaks indicate the electronic transitions occurring in the doped thiourea crystal and its shown figure 6. If a strong emission is seen in the UV region (~369 nm in your spectrum), it suggests a band-to-band transition or excitonic recombination. Ni^{2+} can introduce defect states or trap levels within the bandgap, leading to quenching or enhancement of PL intensity depending on defect density. NH_4^+ can influence the hydrogen bonding network in thiourea, potentially altering the crystal field and shifting emission peaks. It may enhance or suppress luminescence by affecting charge carrier recombination dynamics. Higher PL intensity suggests better crystallinity and fewer non-radiative defects. Reduced intensity might indicate increased defect density, phonon interactions, or quenching effects from dopants The PL spectrum confirms that doping with $NiSO_4$ and $(NH_4)_2SO_4$ significantly influences the optical properties of thiourea. The presence of a strong UV peak suggests good .crystallinity, while intensity variations indicate changes in defect states due to doping. These findings can be useful for optimizing thiourea-based materials in photonic and optoelectronic applications.

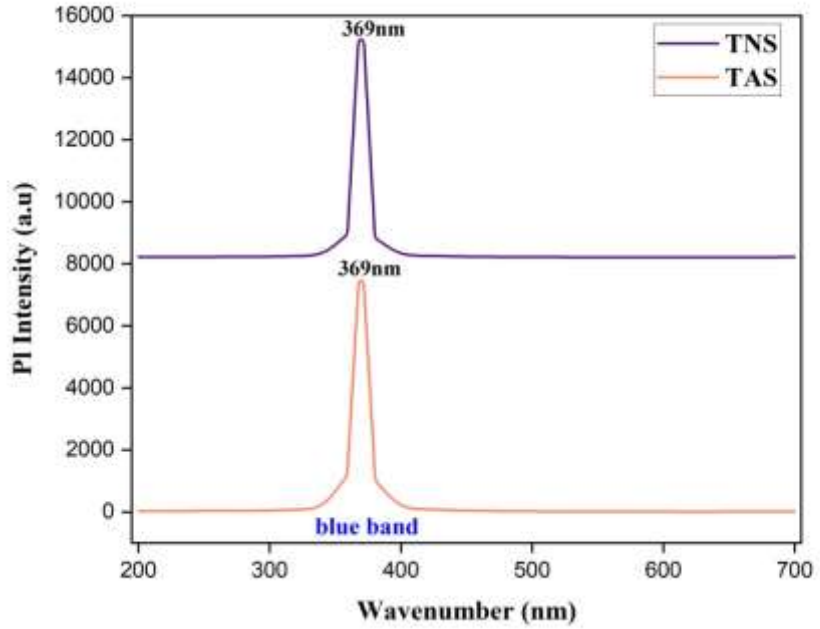

Figure 6 PL spectrum of TNS and TAS single crystals

4. CONCLUSION

The good qualities of single crystals were successfully grown by slow evaporation method at room temperature. The XRD analysis reveals the crystalline structure and the crystals were orthorhombic structure. FT-IR analysis confirmed the presence of functional groups in the grown crystals. The UV-Vis spectra showed the crystals had a wide optical window and a good absorption in the entire visible region. From the result of PL spectrum shows the blue emission and the sharp peak indicates the crystallinity. The optical results suggest that the crystals were suitable for optoelectronic, NLO, and light emitting applications.

5. ACKNOWLEDGEMENT

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