



INVESTIGATIONS ON THE SYNTHESIS AND CHARACTERISATIONS OF THIOUREA BARIUM CHLORIDE SINGLE CRYSTALS

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Abstract

In the current study, solvent evaporation was used to create Thiourea barium chloride (TUBC) single crystals at room temperature. Using powder X-ray diffraction, the structural study of the TUBC crystal was investigated. UV-Visible, FT-IR, Raman, and photoluminescence (PL) spectra were used to analyse the optical characteristics of TUBC crystals. The crystal exhibits absorbance maxima at 209 nm and is transparent between 300 and 900 nm in the visible spectrum. The evaluation of the numerous optical constants, including refractive index, reflectance, light-speed, extinction coefficient, electrical susceptibility, dielectric constant, and optical and electrical conductivity. Results showed that the absorption spectrum was also used to study all these optical constants, including extinction coefficient and reflectance. The deformation of NH₂ caused the absorption mode at 1618 cm⁻¹, which demonstrates the lack of a nitrogen-metal connection because it had no effect on crystallization. The TUBC crystal was exposed to 50–800 cm⁻¹ of Raman scattering. Two emission peaks are visible in the blue region of the Photoluminescence (PL) investigation of TUBC crystals (419 nm-S and 441 nm-Ba).

Key words

Powder XRD, UV-Visible, FT-IR, Raman scattering and Photoluminescence

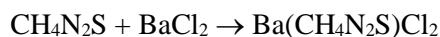
1.0 Introduction

Due to its potential use in a variety of industries, including medical diagnosis, undersea communication, telecommunication, high optical data storage, and color display devices, nonlinear optical (NLO) materials have attracted a lot of attention [1, 2]. The introduction of new technologies into technological society has been made possible by the emergence of several application-oriented single crystals. As frequency-controlled oscillators, radiation detectors, optoelectronics, transistors, tunnel-diodes, as well as magnetic devices, ultrasonic amplifiers, lasers, and lenses, crystals play a crucial part in today's world. For their numerous uses in semiconductors, superconductors, and photonic devices, organic crystals are widely recognized [3,4]. The foundation of organic NLO materials is the long-range -bond system of the molecule, which may be easily changed by substituting electron-donating and -withdrawing groups surrounding the aromatic moieties to improve optical nonlinearity[5-8]. Thiourea barium chloride (TUBC) single crystals were produced in the current study at room temperature using a slow evaporation approach. Using UV-Vis spectral analysis, the generated crystals' transparency was investigated. By using FTIR analysis, the existence of functional groups was investigated. The power crystal X-ray diffraction (XRD) was used to analyze the crystal structure. The Raman scattering spectrum was taken on TUBC to study the functional bonds. The photoluminescence (PL) studies were carried out to know the electronic structure.

2.0 Materials and Methods

2.1 Synthesis and growth of TUBC crystal

Thiourea and barium chloride were combined in a 1:1 molecular ratio to create a single crystal of thiourea barium chloride (TUBC). To create a saturated solution, both were dissolved in double-distilled water and agitated for 5 hours. To eliminate any suspended particles the mixture was filtered and then kept at a constant temperature of 30°C in a constant temperature bath for slow evaporation. As shown in figure, high-quality crystals might be harvested in 3 to 4 weeks. The following chemical process resulted in the formation of TUBC crystals.



Synthesized single crystal of Thiourea barium chloride. (TUBC)

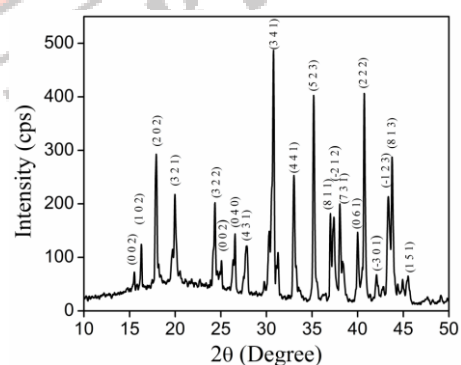
2.2 Characterization

The produced TUBC crystal was analysed using powder crystal XRD (PXRD) (Rigaku 600) with $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) and a scanning rate of 2° per minute. The characteristics of absorbance and transmittance in the spectral region of 200 nm to 800 nm were investigated using an Ocean Optics USB 4000 UVV spectrometer. Shimadzu FTIR Spectrometer was used to record the FT-IR spectrum in order to investigate the basic molecular vibrations. The LabRAM HR(UV) system with 325 nm laser and CCD detector was used to record the Raman spectra in the 50 cm^{-1} to 800 cm^{-1} range. With the help of the Horiba Scientific-Fluoromax-4 spectrophotometer TCSPC, the photoluminescence spectrum was analysed. Using a KEITHLEY 2410-c 1100V Source Meter, the DC resistivity is estimated in the 40V to -40V range while the current is measured in the 26°C to 115°C temperature range.

3.0 Results and Discussion

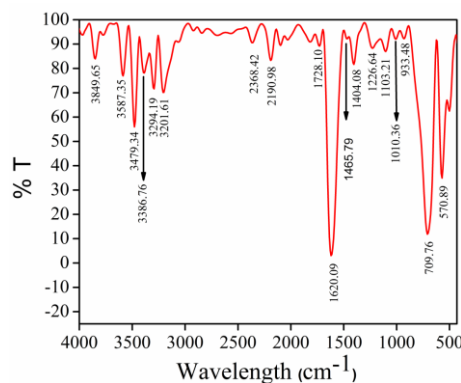
3.1. Powder crystal XRD analysis

For powder crystal X-ray diffraction (XRD) analyses, the synthesized TUBC crystal sample was ground into a fine powder. The result of the powder crystal XRD pattern synthesized material is shown here. The peaks seen in the XRD pattern attest to crystalline nature of the grown crystals. Using the treor iteration approach and the X-pert high score plus program, the peaks were indexed. The crystal has the following cell parameters: $a = 6.69 \text{ \AA}$, $b = 7.11 \text{ \AA}$, $c = 10.83 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90.14^\circ$, $\gamma = 90^\circ$ and volume = 514.925 \AA^3 .



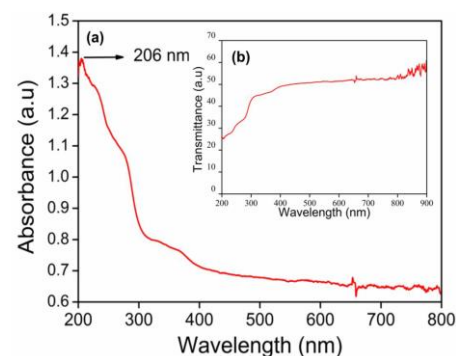
3.2. FTIR spectral analysis

The FTIR spectrum of the TUBC crystal is shown here. The peaks were seen to be shifted in the spectrum of Thiourea as a result of inclusion of Barium. When inorganic salts are added to Thiourea, the metal (Barium) atoms from the salts form complexes with the Sulphur of Thiourea, which caused the FTIR peaks to shift [9–12]. Therefore, compared to the conventional spectra of Thiourea, it is predicted that the C-N stretching frequency must rise and the C-S stretching frequency should fall on complex formation. The deformation of NH_2 caused the absorption mode at 1618 cm^{-1} , which demonstrates the lack of a nitrogen-metal connection because it had no effect on crystallization. The absence of a metal-nitrogen connection was indicated by a shift in the NH_2 rocking vibration mode from 1082 cm^{-1} to 1103.21 cm^{-1} . Thiourea standard peaks at 1412 cm^{-1} and 730 cm^{-1} were shifted to lower frequencies at 1404.08 cm^{-1} and 709.76 cm^{-1} , respectively, due to a metal-Sulphur bond.



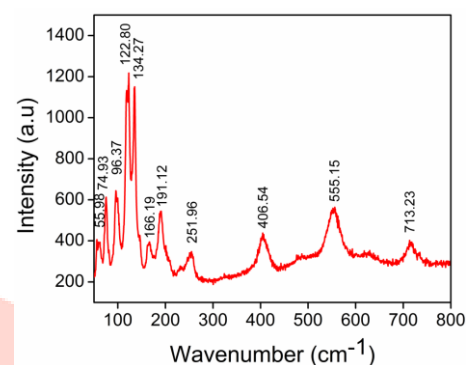
3.3. UV-Visible spectral analysis

The TUBC crystal's transmission and absorbance spectra are presented here. The crystal exhibits low visible-band absorbance, with maximum absorbance at 206 nm. This might be caused by the electronic transition in Thiourea molecules [13]. According to the transmittance spectrum, the crystal exhibits approximately 50% transmittance in the entire visible and near-IR region with lower cut-off wavelength of 308 nm. The applicability of the crystal for optoelectronic and optical communications is demonstrated by its sufficient transmittance [9, 10]. The TUBC crystal exhibits an adequate transmission in the visible region when compared to earlier findings. This supports the good quality crystal. The TUBC crystal exhibits marginally higher transmission in the visible region compared to previously reported materials [11, 12] with less loss in the visible region suitable for optoelectronic applications.



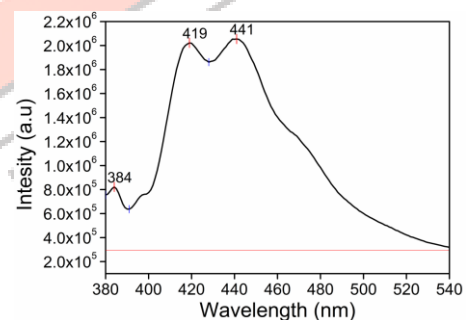
3.4. Raman analysis

The TUBC crystal was subjected to 50 to 800 cm^{-1} of Raman scattering. The peaks were allocated to the various modes of vibration in order to validate the existence of functional bonds, as is demonstrated above. BaCl_2 scissoring and Thiourea translation are responsible for the scattering peak at 55.98 cm^{-1} , which supports the presence of Ba in the crystal. The peak at 96.37 cm^{-1} further supported the evidence of C-S symmetric stretching vibration. The 122.80 cm^{-1} C-S stretching mode and the 406.54 cm^{-1} NH_2 rocking mode were assigned to the C-S asymmetric stretching and Thiourea rocking modes respectively. The peak, which was present at 406.54 cm^{-1} [14], supported the C-S bending. Similar to this, the asymmetric vibration was observed at 251.96 cm^{-1} and the Cl-Ba-Cl scissoring, stretching vibration was observed at 191.12 cm^{-1} . The peaks at 555.15 cm^{-1} , NH_2 twisting, and 713.23 cm^{-1} , NH_2 wagging, confirmed the presence of the amine (NH_2) group in TUBC.



3.5. Photoluminescence studies

This photoluminescence (PL) spectrum of TUBC crystals is displayed here. The 350 nm wavelength radiation was used to excite the TUBC crystal, and emission measurements were made between 380 and 550 nm. In the ultraviolet and blue portions of the electromagnetic spectrum, TUBC crystal produced fluoresces. The interstitial atoms of Ba and S may be viewed respectively as acceptor and donor states, while the vacancies of Ba and S might be treated as localized donor and acceptor states. The synthesized TUBC crystal exhibited significant intensity PL emission spectra with a tiny emission peak at 384 nm between 419 and 441 nm. The vacancy of Barium sites are responsible for the emission at 441 nm [15, 16]. S²⁻ vacancies are responsible for the 419 nm emission peak [17]. Hyper luminescence is the name used to describe a tiny emission band that is found in the TUBC crystal in the UV region at 384 nm and is a part of the material's electrical structure [18].



4. Conclusions

Using a slow evaporation technique, single TUBC crystals were synthesised at a constant temperature of 30°C. From the solution, flawless translucent crystals were extracted. The crystalline nature of the grown crystals is confirmed by powder crystal XRD analyses. FTIR analysis and Raman analysis were used to demonstrate the presence of functional groups of Thiourea and the inclusion of metal. By using FTIR, it was determined that metal atom bonds with Thiourea are made through Sulphur. Raman spectroscopy was used to establish the presence of barium and Thiourea, and the spectrum confirmed the vibrational modes noted in the FTIR spectrum. According to UV-Visible spectrum, the transmission is present in the visible region whereas absorption is present in the UV region. The TUBC crystals exhibited an absorption maximum at 209 nm and about 50% transmission in the visible spectrum. The theoretical band-gap was determined to be 3.83 eV, which is consistent with the actual data. The optical band-gap was estimated to be 3.89 eV. The produced TUBC crystals' emission is seen in the blue area of PL spectra. The principal two peaks are the vacancies of Barium and Sulphur, respectively.

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