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Analysis on linear and nonlinear optical properties of an efficient semi-organic crystal: Thiourea borate

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ABSTRACT

Single crystals of thiourea borate, a novel semi organic nonlinear material has been grown by slow evaporation method at ambient temperature. The compound has been subjected to single crystal XRD to characterise the lattice parameters. Results show that the crystal belongs to Triclinic crystal structure. FTIR spectra were recorded to identify the functional groups present in the sample. The transparency of the optical material was analysed by the UV–Vis-NIR studies. The absorption studies illustrate the UV cut-off wavelength to be 255 nm. The transmission studies indicate rapid and intensive transition to maximum transmission at the cut-off wavelength. The third order nonlinear optical properties of the crystal were studied by Z scan technique using continuous wave 532 nm diode pumped Nd:YAG laser. Closed aperture Z scan studies reveal the crystal to possess negative nonlinearity. Open aperture Z scan pattern indicate saturation absorption within the material. The nonlinear optical parameters such as nonlinear refractive index n_2, nonlinear absorption coefficient β and nonlinear susceptibility $\chi^{(3)}$ were also determined.

1. Introduction

Over the years, technology has taken a quantum leap with crystals playing a prominent role in the field of material science. In this tech savvy era, the science of crystal growth has indeed catapulted the demand for solid state materials which finds application in photonic, electronic, computer, semiconductor industries, data processing and imaging, communication systems to name a few. In particular, the nonlinear optical property of the crystal has unlocked the electromagnetic spectrum to a range of laser frequencies and intensities which are utilised in diverse fields such as fibre optics, astronomy, biochemistry, colour display, optoelectronics, frequency conversion, optical memory storage, data processing, optical switching, optical sensors, data imaging and quantum computing [1–3]. The search for novel NLO material has led researchers to investigate many organic and inorganic materials. Another class of materials namely, the semiorganic materials have gained profound interest as they combine the high nonlinearity and structural flexibility of the host organics with the physical and chemical hardness of the additive inorganics. In addition, these metal organics can be easily grown into large three- dimensional crystals from their aqueous solutions. The diverse molecular structure of these organic inorganic complexes enables to utilise the linear and nonlinear optical properties of the crystal most effectively. Also, the nonlinear coefficient and phase matching ability of the crystal are the parameters that determine the nonlinear optical process [4,5].

Thiourea is a well-known organic ligand with a large dipole moment and centrosymmetric structure. Its characteristics as an inorganic matrix modifier and ability to form network of hydrogen bonds has made it a preferred NLO material. It is used extensively in electro-optic, electro-acoustic devices, ultraviolet deduction, infrared imaging, and in optical communication systems [6,7]. The Borate family crystals have garnered a lot of attention owing to their excellent ultraviolet nonlinear optical properties, second and third order harmonic efficiencies and high nuclear radiation resistance. The variability of borate structures, low cut-off wavelength down to 200 nm, high laser damage threshold up to 40 GW/cm^2 have escalated the demand for borate crystals in NLO studies [8,9]. In the present work, both Thiourea and Boric acid are combined to synthesize and grow a novel semiorganic NLO material and investigate its third order harmonic generation capabilities utilised in high frequency ultrafast optical processing techniques [10].

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2. Experimental procedure

Bulk thiourea borate single crystal was formed by slow evaporation technique at room temperature. The advantage of this method is that the crystals can be grown at a fixed temperature. Thiourea borate single crystals were formed by dissolving analytical grade reagents thiourea and boric acid powder in the molar ratio 3:1 in double distilled water. The solution was stirred continuously for 3 h using a magnetic stirrer, filtered using Whatman filter paper and left to evaporate. Tiny seed crystals were formed by spontaneous nucleation after a period of 30 days. The synthesised material was further purified by repeated recrystallization process. A defect free seed was taken and suspended in the mother solution to evaporate. Large size single crystals were formed once nucleation and growth process were completed. Thiourea borate crystal of dimension $8 \times 4 \times 2\ mm^3$ was harvested after a period of 20 days and its photograph is shown in Fig. 1. The chemical equation for the reaction is given as

$$CS(NH_2)_2 + H_3BO_3 + H_2O \rightarrow H_2NCSNHH \cdots OHB(OH)_2$$

3. Results and discussion

3.1. Single crystal XRD analysis

Single crystal X ray diffraction is a non-destructive analytical technique which provides a detailed insight into the internal lattice of crystalline substances. Unit cell dimensions, bond length, bond angle and the structure of the crystal can be determined from this study. Single crystal XRD study was carried out using Bruker Kappa 2 CCD X-ray diffractometer to identify the crystal structure and the lattice parameters of the thiourea borate single crystal. The single crystal XRD studies indicated that the cell parameters of thiourea borate single crystals as, a = 6.67 Å, b = 6.99 Å, c = 7.02 Å and α = 60.4°, β = 76.7°, Υ = 79.3°. The volume of the cell was 276 $Å^3$. The study shows that the grown crystal belongs to triclinic crystal system. Single crystal XRD pattern of the grown sample thiourea borate is shown in Fig. 2

3.2. FTIR spectral analysis

FTIR technique is a quantitative and qualitative analytical tool for detecting functional groups and characterizing the covalent bonding information. The infrared spectroscopy determines the molecular structure and identifies the functional groups present in the thiourea borate crystal. Functional groups with strong dipole gives rise to sharp absorption peaks in the IR region. FTIR spectrum was recorded on Bruker FTIR spectrophotometer using KBr pellet technique in the region 400–4000 cm^{-1} and is shown in Fig. 3.

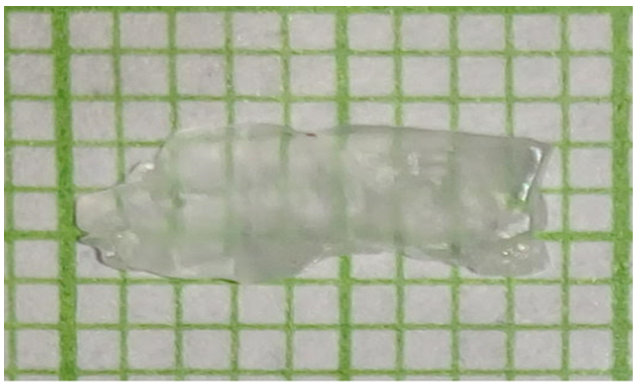

Fig. 1. Photograph of grown crystal of thiourea borate.

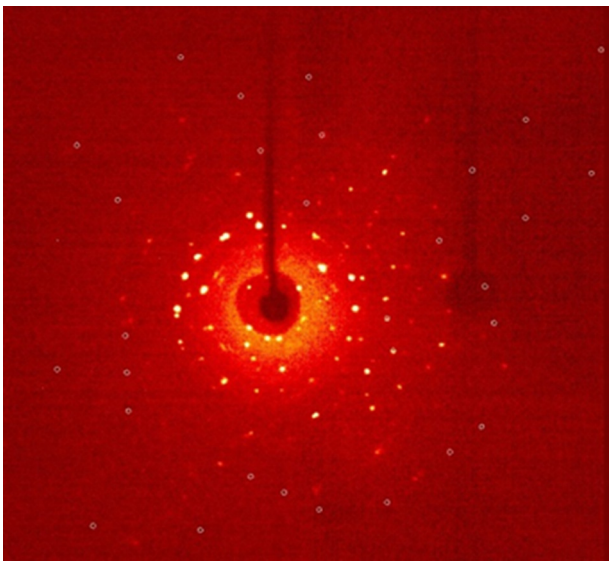

Fig. 2. Single crystal XRD pattern of grown crystal of thiourea borate.

FTIR spectrum of thiourea borate shows an absorption peak at 541.95 cm^{-1} corresponding to N-C-N bending vibrations of thiourea while the peak at 730.38 cm^{-1} corresponds to C═S symmetric stretching vibrations [11]. The steep peak at 1625.46 cm^{-1} corresponds to NH_2 bending vibrations, while the sharp peak at 769.66 cm^{-1} corresponds to in plane wagging of NH_2. The low intensity absorption of C-N symmetric stretching mode was observed at 1082.78 cm^{-1} and 2031.80 cm^{-1} [6]. The B-O symmetric vibrations of the borate group were identified at 769.66 $cm^{-1}$and the B-O asymmetric vibrations at 1398.45 cm^{-1}. The OH group from the boric acid was observed at 3631.34 cm^{-1} [8,12]. The presence of the above functional groups in the sample confirms the presence of Thiourea and Boric acid in the sample.

3.3. Linear optical studies

3.3.1. UV–VIS-NIR absorption analysis

NLO crystals must possess wide transparency range for optimum utilization in optical devices. The optical absorption spectrum gives information about band gap energy and cut-off wavelength of the crystal. Identifying the absorption edge of the crystal helps in elucidating its optical properties. UV–Vis absorption spectrum for the grown crystal was carried out between 200 and 1100 nm by UV-1800 series spectrophotometer and is shown in Fig. 4. The spectrum shows low absorption in the entire visible region (400–600 nm) and near IR region (600–800 nm). The absorption of light is due to excitation of electrons in the σ and π orbitals from the ground state to the higher excitation states [13]. Wide transmittance in the entire visible region enables a very good optical transmission of second harmonic frequencies. A steep fall in absorption can be seen around 255 nm and this corresponds to the UV lower cut-off wavelength or the fundamental frequency of the crystal. The wide transparency in the visible region and the low cut-off wavelength ensures that the thiourea borate crystal is most applicable for higher harmonic generation and optoelectronic applications [14].

3.3.2. Determination of energy band gap from linear optical spectrum

Optical absorption study is a useful technique to understand the electronic band structure of the grown material. The fundamental absorption of photon energy corresponds to the optical excitation of the electrons from the valence to the conduction band and