Optical, optical band gap and nonlinear optical properties of Thiourea Ammonium Chloride single crystal for nano applications

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Abstract - Single crystals of Thiourea Ammonium Chloride (TAC) were grown by a slow evaporation technique. The modes of vibrations of different molecular groups present in the TAC crystal have been identified by FTIR spectral analysis. The UV–vis–NIR spectral analysis is used to study the optical behaviors like absorption and transmission properties of the crystal. The optical band gap of the TAC crystal is calculated to be cut off wavelength 290nm at photon energy of 4.327eV. Finally the Non Linear Optics (NLO) property of TAC crystal was confirmed by Second Harmonic Generation (SHG) test using the Nd:YAG laser of fundamental wavelength 1064 nm.

Key words - Thiourea Ammonium Chloride crystal, Optical band gap, Nonlinear optics, Photon energy, Second Harmonic Generation.

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1. Introduction

Great interest has been evinced by researchers in crystal semiconductors for solar cell devices and thin crystal transistors for flat panel displays [1-3]. Non LinearOptical (NLO) crystals have been studied to meet the needs of laser developments. The crystals of organic NLO materials have shown a higher figure of merit than that of inorganic NLO materials because of large second order nonlinear susceptibilities and quick response, and have been investigated also for their potential applications [4-6]. Further the binary organic materials have shown an improvement over their parent components [7-8]. These crystals have excellent physical properties and good record for long term stability in devices [9-13]. Tuning of band gap in semiconductor materials is an important tool in optoelectronic and photonic integration [14]. Knowledge of optical constants

of a material such as optical band gap and extinction coefficient is vital to scrutinize the material potential for optoelectronic applications [15]. The electrical properties of semiconductors strongly depend upon the band gap [16-17]. The crystal growth is a frontier area of science and nanotechnology, which plays a major role in the technology of photonics [18-21]. The fast developments in the field of nanotechnology, optoelectronics and photonics necessitate the search for new and efficient Nonlinear Optical (NLO) materials that can be utilized for optical computing, optical communications, electro-optic frequency shifting and optical data storage for developing technologies in telecommunications, treatment of HIV and signal processing [22-24]. We report the growth and characterization of Thiourea Ammonium Chloride crystal; Fourier transforms infrared spectroscopy, UV–vis–NIR spectral studies and optical band gap studies. Finally the second harmonic generation is calculated and reported for this title compound.

2. Materials and Methods
2.1 Crystal Synthesis

The starting materials were prepared by dissolving of aqueous solution thiourea and Ammonium chloride 1:1 ratio at room temperature and stirred well to enable homogenization of the solution. The seed crystals are prepared by the slow evaporation technique. Good quality seed was chosen and kept suspended in the super-saturated solution. The product was purified by repeated recrystallization before it was used for growth of TAC crystal. The optically transparent crystals of size were obtained in a period of 25 days. The crystals were subjected to spectral analysis for the investigation of optical and nonlinear optical properties.

2.2 Characterization Studies

The TAC single crystal is subjected to various methods of FTIR spectrum analysis, UV spectral analysis, optical band gap, Second Harmonic Generation measurements (SHG).

3 Results and Discussion
3.1 Fourier transform infrared spectroscopic studies of TAC crystal

The FTIR spectrum was measured within the 400–4000cm^{-1} region using a Perkin-Elmer Spectrophotometer by KBr pellet technique. The FTIR spectrum of TAC crystal is shown in Figure 1. In FTIR spectrum of TAC crystal, the strong absorption bands in the region 3288, 3395cm^{-1} corresponds to symmetric and asymmetric stretching vibration of OH group. The C–N stretching vibrations were observed at wave numbers 1119cm^{-1} and 1127cm^{-1}. The in- plane and out plane

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vibrations of C–H group are identified at 966cm^{-1} and 713cm^{-1} respectively [27]. A sharp intense peak was observed at 1615 cm^{-1}, which is due to the NH$_2$ stretching of the benzene ring. The band due to the C=N of TAC crystal was observed as a sharp and intense one at 1436cm^{-1} [28]. The NO$_2$ rocking vibration is observed at 475cm^{-1} and 503 cm^{-1}. The asymmetric and symmetric stretching vibrations of methyl groups in TAC crystal appear at 3108cm^{-1} and 2698 cm^{-1} respectively. The C–H asymmetric and symmetric deformation modes of methyl groups appear at 1491cm^{-1} and 1472cm^{-1} respectively [25].
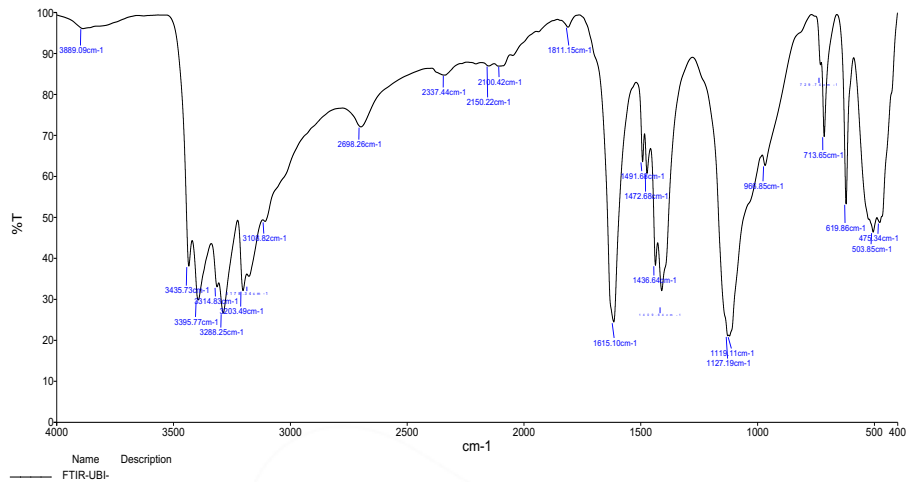


Figure 1 Fourier transform infrared spectrum of TAC crystal

3.2 Optical studies of TAC crystal
3.2.1 Optical absorption studies

The spectra were recorded in the wavelength region 190-1100nm using a Lambda 35 Spectrophotometer. In the UV, visible and IR regions, the materials are found to be transparent. The transparent nature facilitates the application of TAC in photonics and optoelectronics. The UV cut-off wavelength of TAC crystal occurs at 290nm. It is well known that an efficient NLO crystal has an optical transparency lower cut-off wavelength between 200nm and 400nm .
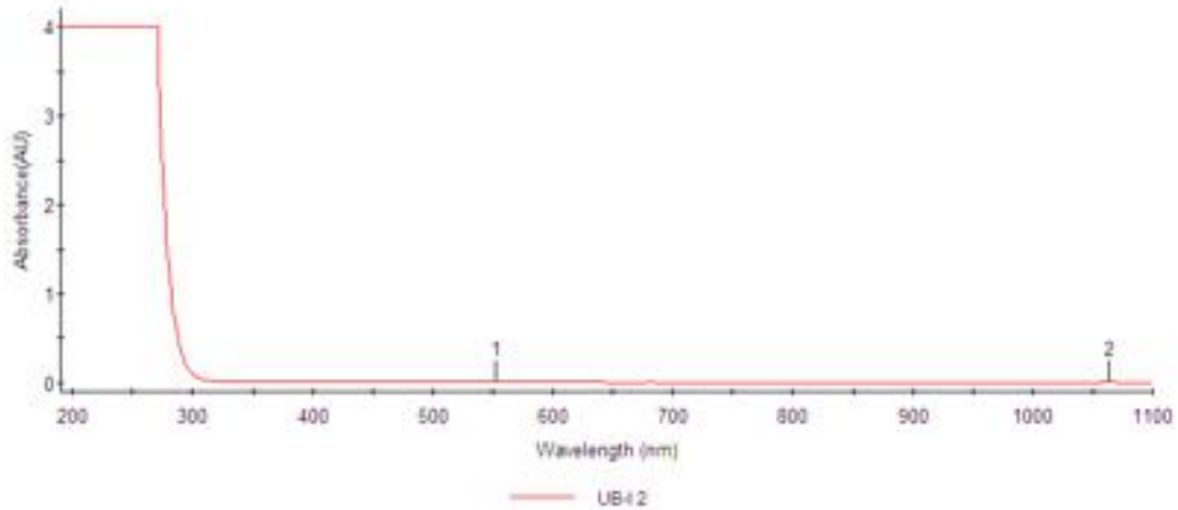
Figure 2 Optical absorbance spectrum of TAC crystal

3.2.2 Optical transmission studies
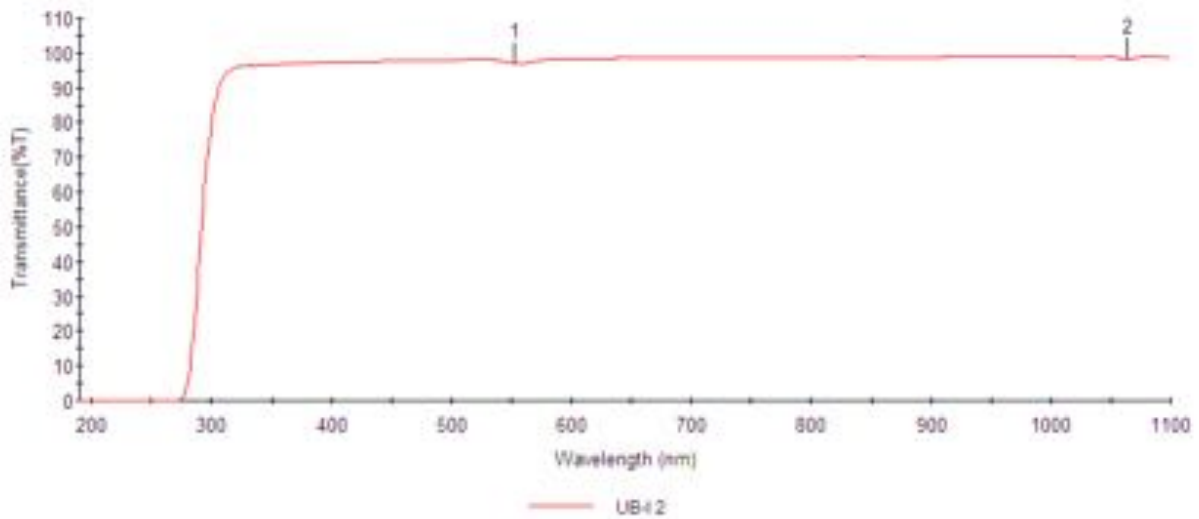
**Figure 3** Optical transmittance spectrum of TAC crystal

Optical transmission spectrum of TAC single crystal is shown in Figure 3. TAC crystal highly transparent in the considerable region of wavelength 290nm [25-26]. The good transmissions of the crystal in entire visible region suggest its suitability for second harmonic generation devices [27-28]. The UV absorption edge for the grown crystal was observed to be around 290nm. The dependence of optical absorption coefficient on the photon energy helps to studying the band structure and the type of transition of electrons [29]. The optical absorption coefficient (α) was calculated from the transmittance using the following relation:

$$\alpha = \frac{\sqrt{2.3036 \log(1/T)}}{d}$$

where, T is the transmittance and d is the thickness of the crystal.

As a direct band gap material, the crystal under study as an absorption coefficient (α) obeying the following relation for high photon energies hν:

$$\alpha = A \frac{\sqrt{h\nu - E}}{h\bar{\nu}}$$
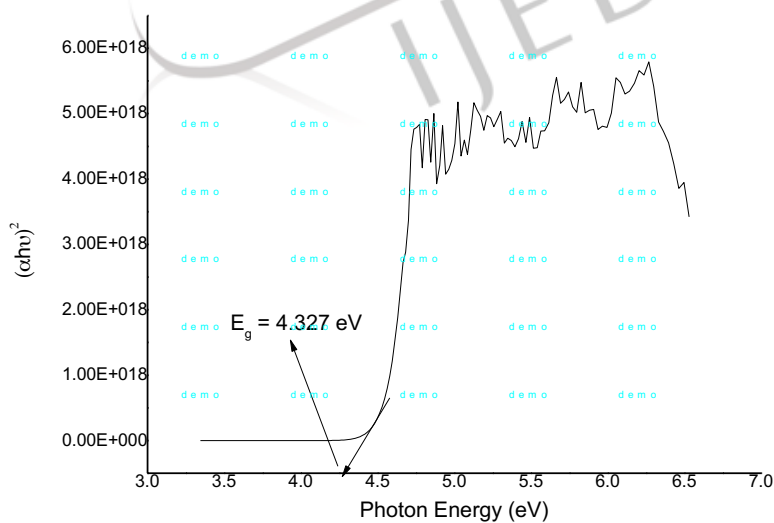
Figure 4 (αhν)^2 versus photon energy of TAC crystal

where, E_g is optical band gap of the crystal and A is a constant. The plot of variation of (αhν)^2 versus photon energy is shown in Figure 4. E_g was evaluated by the extrapolation of the linear part [30]. The band gap is found to be 4.327eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [31].

3.2.3 Second harmonic generation studies of TAC crystal

The second harmonic generation efficiency was determined by the modified version of the powder technique developed by Kurtz and Perry [32], using an Nd-YAG, 10ns laser with a pulse repetition rate of 10Hz working at 1064nm. The sample was ground into fine powder and tightly packed in a micro-capillary tube. It was mounted in the path of the laser of 9.6-mJ pulse energy obtained by splitting the original laser beam. The output light was passed through a monochromator transmitting only the second harmonic (green) light at 532nm. The green light intensity was registered by a photo multiplier tube and converted in an electrical signal. The signal was displayed on the oscilloscope screen. The generation of the second harmonic was confirmed by the emission of green light [33-36].

4 Conclusion

Optical single crystals of TAC have been grown successfully by the slow evaporation technique. The presence of functional groups is confirmed by FTIR spectral analysis. The optical absorption studies show that the crystal possesses very low absorption in the entire visible and NIR region. The optical transmittance of the crystal confirms the transparency of the crystal obtained, by tailoring and tuning the optical band gap of the materials. The finally the second harmonic generation for the crystals suggests that the TAC crystals are suitable for fabrication of nano-materials, optoelectronic, electroscopic and photonic devices.

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