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Synthesis, growth and characterization of S-benzyl isothiouronium chloride single crystals

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S-Benzyl isothiouronium chloride single crystals were grown at room temperature by slow evaporation solution growth technique. Single crystal X-ray diffraction study has been carried out to find the crystal system and unit cell parameters. Various functional groups present in the grown material have been identified using FTIR spectra. The transparency of crystal was tested using UV-visible spectra. The grown crystal exhibits second harmonic generation (SHG). TGA/DTA analysis also carried out.

1 Introduction

Organic crystals have been extensively studied due to their non-linear optical (NLO) coefficients being often larger than those of inorganic materials. Many new organic crystals have been found, based on the predictive molecular engineering approach and have been shown to have potential applications in non-linear optics. Some interest has been shown in the search for ultra violet laser materials [1]. The organic NLO materials play an important role in SHG, frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability, etc. [2]. In recent years, considerable research efforts have been made in exploring novel organic materials for their potential use in a variety of devices. The materials, which could produce green/blue laser light and could withstand high-energy light radiation, are of vital importance for their use in devices. Organic materials have been known for their applications in semiconductors [3], superconductors [4] and NLO devices [5,6].

Recently, a large number of organic compounds with non-localized π electron systems and a large dipole moment have been synthesized to realize the non-linear susceptibilities larger than the inorganic optical materials. However, their potential applications are limited by, poor chemical stability and red cut off wavelength caused by large birefringence, which results from the layer stacking of the structure and other factors [7]. The basic structure of organic NLO materials is based on π bonding systems. Due to the overlap of π bonding electrons, delocalization of the charge distribution takes place, which leads to a high mobility of the electron density. In the present study, S-benzyl isothiouronium chloride was synthesized and the crystals were grown by slow evaporation solution growth technique. The crystals were characterized using UV-Vis, FTIR, Mass spectrum, Single crystal XRD, thermal studies and SHG studies.

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2 Experimental procedure

Synthesis S-Benzyl isothiouronium chloride was synthesized from thiourea and benzyl chloride in the presence of ethanol. The chemicals used were of AnalaR grade. The melting point of the recrystallized sample was found to be 148°C, which is coinciding with the available literature [8].

Crystal growth A saturated solution of 100 ml of S-benzyl isothiouronium chloride was prepared in 0.2 M HCl at 50°C and the solution was filtered. The filtrate was taken in a beaker, which was hermetically sealed to avoid the evaporation of the solvent. Within few days, seed crystals were found. Good quality seeds were hung in the solution with the help of a nylon thread. Growth was carried out at room temperature. The grown crystals were harvested after a typical growth period of 15 days. Thus, transparent and high optical quality crystals were obtained. The seed crystals and the grown crystal are shown in figure 1a and b respectively.

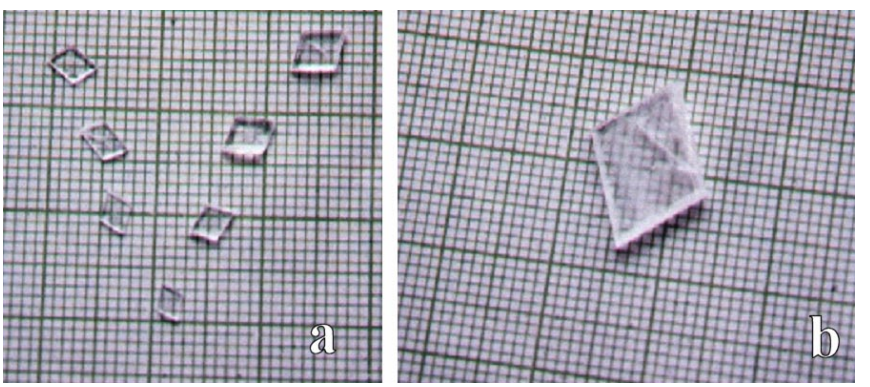

Fig. 1 a) Seed crystals of S-benzyl isothiouronium chloride. b) Grown crystal of S-benzyl isothiouronium chloride.

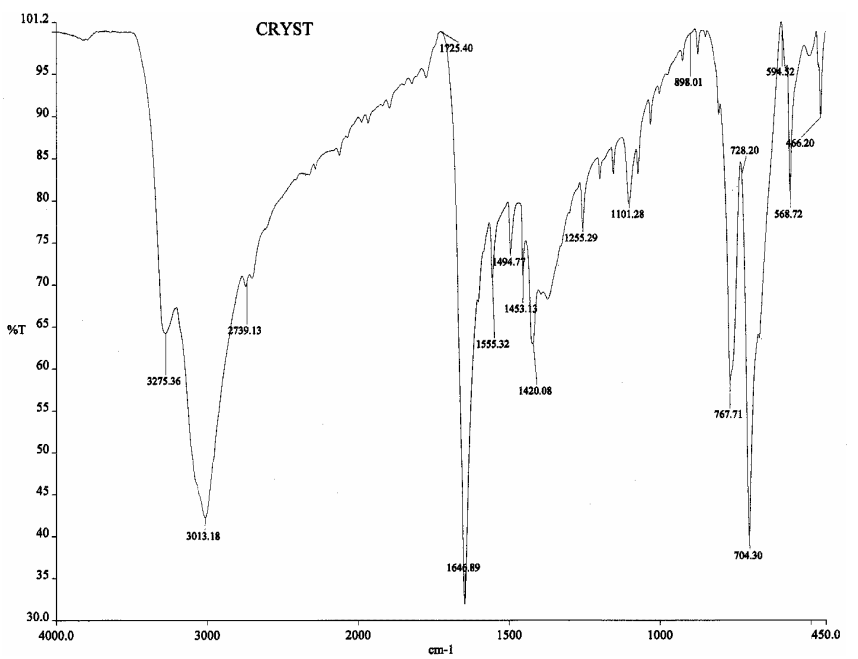

Fig. 2 FTIR spectrum of S-benzyl isothiouronium chloride.

Table 1 The crystallographic data of S-benzyl isothiouronium chloride.

Chemical formula	$C_8H_{11}N_2SCl$
Cell parameters	a = 8.4188 Å; b =11. 3642 Å; c = 20.5225 Å α = 90.06°; β = 90°; γ = 89.98°
Volume	1963.4365 $Å^3$
Molecular weight	202 gm
System	Orthorhombic

3 Results and discussion

Single crystal X-ray diffraction analysis The crystallographic data of S-benzyl isothiouronium chloride were obtained using single crystal X-ray diffraction analysis (Model: ENRA NO NIUS CAD 4). It was observed that the crystal belongs to orthorhombic system. The crystallographic data of S-benzyl isothiouronium chloride is given in table 1.

FT-IR analysis In order to analyze qualitatively the presence of functional groups in the crystals, FT-IR spectrum was recorded using BRUKER IFS 66V FT-IR spectrometer in the wavelength range 4000 – 450 cm^{-1} by KBr pellet technique. The infrared spectrum of the S-benzyl isothiouronium chloride material is shown in figure 2. The absorption at 3275.36 cm^{-1} and 3013.18 cm^{-1} is due to N-H and C-H stretching vibration. The first one corresponds to N-H and C-H anti symmetric stretching and the second peak corresponds to N-H and C-H symmetric stretching. The peak at 1646.89 cm^{-1} represents the NH_2 bending. Stretching of benzene ring is revealed at 1555.32 cm^{-1}. The absorption peaks at 1494.77 cm^{-1} and 1101.28 cm^{-1} are due to N-C-N anti symmetric and symmetric stretching vibration. The peak at 1453.13 cm^{-1}represents the aromatic ring vibration. CH_2 asymmetric deformation is conformed due to the peak at 1420.08 cm^{-1}. The peaks at 1255.29 cm^{-1} and 568.72 $cm^{-1}$are due to C-S-C stretching and C-S-C bending respectively. The sharp and intense absorption of S-benzyl isothiouronium chloride at 728.20 cm^{-1} corresponds to the 730.00 cm^{-1}absorption of thiourea. The peak at 767.71 cm^{-1} is due to NH_2 out of plane. The peak at 704.30 cm^{-1} is due to Ar-H bending. The peak 466.20 cm^{-1} represents the N-C-N bending. The comparison between S-benzyl isothiouronium chloride and thiourea are shown in table 2.

Table 2 Comparison of FT-R data of S-benzyl isothiouronium chloride with thiourea.

Thiourea (cm^{-1})	S-Benzyl isothiouronium chloride (cm^{-1})	Assignment
1625	1647	NH_2 bending
1470	1495	N-C-N anti symmetric and stretching
1417	1420	C-S anti symmetric stretching
1083	1101	N-C-N symmetric and stretching
730	728	C-S symmetric stretching

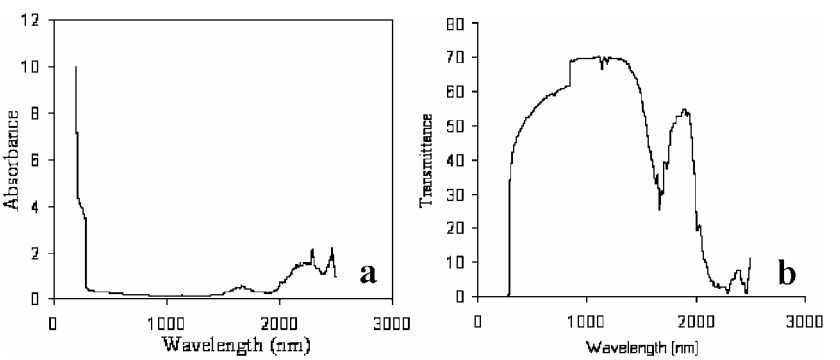

Fig. 3 UV-Vis absorbance and transmittance spectra.

UV-Vis study Optical absorption spectrum was recorded using VARIAN CARRY 5E – UV-Vis-NIR spectrometer in the wavelength range of 190 nm and 2500 nm. The plot of absorbance vs wavelength is shown in figure 3a. The figure illustrates the absorbance behaviour in the entire UV, visible and near IR region, it is an important requirement to a material for NLO applications. The absornbance is maximum at 204 nm is noticed. The less absorbance behaviour in the entire visible region also conforms to the colourless nature of the crystal.

Transmittance spectra are very important for any NLO material, because, an NLO material can be of practical use only if it has wide transparent window. To find the transmission range of S-benzyl isothiouronium chloride optical transmittance spectra were recorded for the samples grown by slow evaporation method. The recorded transmittance spectrum is shown in figure 3b. It can be seen that the optical transmission efficiency is very good.

Mass spectrum The mass spectrum of S-benzyl isothiouronium chloride was recorded using mass spectrometer. The molecular weight of the compound is found to be 202. From the mass spectrum it was found

that, the molecular weight of the compound reduced to 166.This difference in the molecular weight may be due to decomposition of HCl.

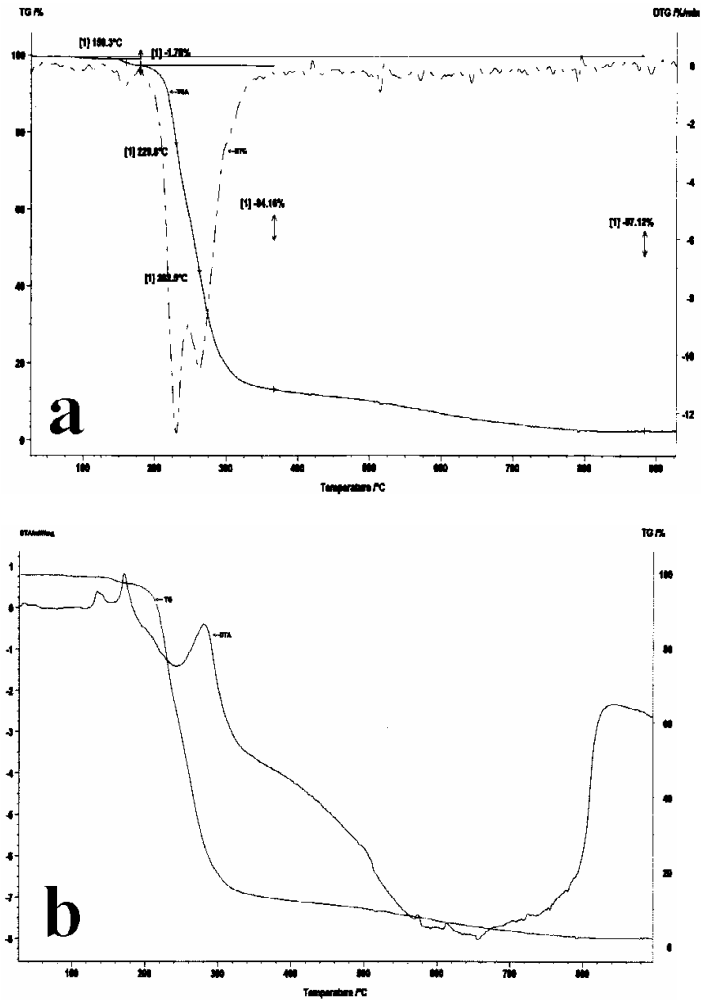

Fig. 4 a) TGA/DTG of S-benzyl isothiouronium chloride. b) TGA/DTA of S-benzyl isothiouronium chloride.

Thermal gravimetric analysis (TGA) Thermal gravimetric analysis of S-benzyl isothiouronium chloride was carried out in METTLER – TA4000 system between 28°C and 1000°C at a heating rate of 10.0 K/min in nitrogen atmosphere. The thermogram and the trace due to differential thermogram are illustrated in Fig. 4a. There is no loss of water below 158°C illustrating the absence of any absorbed water in the sample. The weight loss of 57% between 158°C and 265°C is due to the elimination of thiourea hydrochloride from the compound. The temperature between 265°C and 365°C represents the elimination of cyclobutene from the remaining compound. The residual mass above 365°C corresponds to 5% of carbon present in the compound. This study indicates that the compound could be used for any application below its melting point. The sharpness of the thermo gram is also illustrative of the crystal purity without association of any impurities. [9,10]

The DTA analysis was also performed between 28°C and 1000°C at a heating rate of 10.0 K/min in nitrogen atmosphere. The resulting trace is shown in figure 4b. The TGA trace is also shown in the same figure for comparison. There are two endotherms; one between 150°C and 170°C and the second between 270°C and 300°C. The first endotherm is assigned to the elimination of thiourea hydrochloride based on the results obtained with TGA trace. The second endotherm represents the elimination of cyclobutene from the compound.

Nonlinear optical test The grown crystals were characterized for their NLO property. For this purpose, the output from Nd: YAG laser of fundamental wavelength at 1064 nm was used as source and it was illuminated to the crystal specimen. The output could be seen as a bright green flash emission from the sample.

5 Conclusions

Single crystals of S-benzyl isothiouronium chloride, a new organic NLO material, have been grown by slow evaporation solution growth technique for the first time. The lattice parameters and crystal structure have been determined from the single XRD. It was found that it has orthorhombic crystal structure. The functional groups of the compound have been determined from the FTIR spectrum. The molecular weight of the compound was compared with the mass spectrum. TGA/DTA spectrum illustrates that there was no inclusion of any impurities. S-benzyl isothiouronium chloride crystals generate optical second harmonic frequency of an Nd: YAG laser.

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