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Growth and characterization of a new metal-organic crystal: Sodium thiourea bromide

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ABSTRACT

Sodium thiourea bromide (STB), a new semiorganic nonlinear optical material, has been synthesized and single crystals were grown from aqueous solution. The FT-IR spectrum confirms the compound formation. Single crystals of STB have been grown by slow evaporation of solvent at room temperature. The grown crystal was subjected to single crystal X-ray diffraction, UV-Vis-NIR, TG/DTA and DSC analyses. The second harmonic generation of STB was measured by Kurtz and Perry powder technique. The laser damage threshold value was determined using a Q-switched Nd:YAG laser operating at 1064 nm with 65 ns pulses in single shot mode. The mechanical property of the grown was determined by Vicker's hardness test.

Key words: Sodium thiourea bromide; Solution growth; Single crystal XRD; Nonlinear optical material.

INTRODUCTION

Nonlinear optical (NLO) materials find extensive opto electronic applications such as optical frequency conversion, optical data storage and optical switches in the inertially confined laser fusion systems. Materials with second-order optical nonlinearities, short transparency cut-off wavelength, high thermal and mechanical properties are needed to realize many of these applications. Inorganic materials are widely used in these applications due to their high melting point, high mechanical strength and high degree of chemical inertness. But the optical nonlinearity of these materials is poor. Organic compounds are often formed by weak van der Waal and hydrogen bonds and possess high degree of delocalization. Hence, they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials are flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity and high damage resistance etc., A major drawback of crystalline organic materials are difficult in growing bulk size, optical quality single crystals and also, the fragile nature of these crystals makes them for difficult for the process in device applications. The inherent limitations on the maximum attainable nonlinearity in an inorganic materials and the moderate success in growing device grade organic single crystals have made scientists to adopt alternate strategies. The obvious one was to develop hybrid organic-inorganic materials with some trade off in their respective advantages. This new class of materials has come to be known as semi-organic [1-3] with metal-organic coordination compounds [4]. In the case of metal-organic coordination complexes, the organic ligand is usually more dominant in the NLO effect. As for the metallic part, focus in on the group (IIB) metals (Zn, Cd, Na and Hg) as these compounds have a high transparency in the UV region, because of their closed d^{10} shell. Regarding the organic ligands, small π -electron systems such as thiourea [$CS(NH_2)_2$], thiocyanate (SCN) and urea have been used with remarkable success. Further, thiourea is one

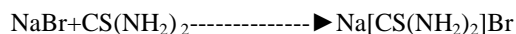
of the few simple organic compounds with high crystallographic symmetry. It crystallizes in the rhombic bipyramidal division of rhombic system and acts as a good ligand [5]. The centro symmetric thiourea molecule, when combined with inorganic salt yields noncentro symmetric complexes, which have the NLO properties [6]. Thiourea possesses large dipole moment and it forms number of NLO active metal coordination compounds [7-11]. In this paper, we are presenting a preliminary report on the growth and characterization of sodium thiourea bromide single crystals.

MATERIALS AND METHODS

2. Experimental

2.1 Synthesis and crystal growth

Raw material for the growth of the title compound was synthesized by mixing aqueous solutions of sodium bromide and thiourea in the ratio of 1:4 and the corresponding chemical reaction is given below as



Since thiourea has the coordination capacity to form different phases of metal-thiourea complexes, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. The product was purified by repeated recrystallization before it is used for the crystal growth. Single crystals of sodium thiourea bromide were obtained from aqueous solution by slow evaporation technique after a period of two weeks. The seed crystals of STB thus obtained were used to grow bulk size and it is depicted in Fig. 1.

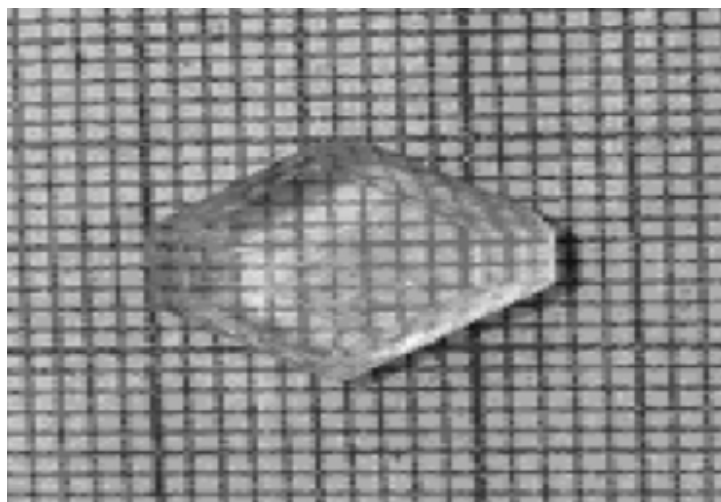


Figure 1 As grown sodium thiourea bromide single crystal

2.2 Characterization techniques

The single crystal X-ray diffraction studies of the crystals were carried out using ENRAF NONIUS CAD4 single X-ray diffractometer with $\text{MoK}\alpha$ ($\lambda=0.717 \text{ \AA}$) radiation. Least square refinement of 25° reflections were done in the range $20\text{--}30^\circ$. The FT-IR was recorded in the range of $4000\text{--}400\text{cm}^{-1}$ using BERKIN ELMER RX1 spectrometer. The optical transmission spectrum was recorded in the range of $190\text{--}1100\text{nm}$ using BERKIN ELMER LAMBDA 35 spectrometer. The NLO efficiency of the crystal was evaluated by Kurtz and Perry powder technique using a Q-switched, mode locked Nd:YAG laser emitting 8 ns pulses with spot radius of 1 mm. DTA/TGA and DSC studies of the crystals were carried out using the instrument STD Q600 V8.3 Build 101.

RESULTS AND DISCUSSION

3.1. Single crystal XRD

The single crystals of STB have been subjected to X-ray diffraction studies using NONIUS CAD4 X-ray diffractometer. The structures were solved by the full matrix least squares technique using the SHELXL program. The calculated values are tabulated in Table 1. It is observed that the grown crystals are in orthorhombic system.

Table. 1. Crystallographic parameters

Chemical formulae	Na[CS(NH ₂) ₂]Br
Cell parameters	a=5.491(1)Å
	b=7.654(1)Å
	c=8.550(0)Å
	α=β=γ=90°
Volume	359.3(3)Å ³
System	Orthorhombic

3.2. FT-IR spectral studies

The FTIR spectrum of the grown crystal is shown in the Fig. 2. A number of reports are available on the IR absorption studies of thiourea [12-14]. When the STB spectrum was compared with the spectra of thiourea, a shift in the peaks observed confirmed the metal coordination with thiourea. In the complex, the coordination of sodium with thiourea may occur either through nitrogen or through sulfur [15]. Most of the metals form a complex through sulfur [16]. The study of the spectra of STB shows a shift in the low frequency region and also agrees with the literature [17, 18]. The peaks at 3781 cm⁻¹, 3368 cm⁻¹ and 3161 cm⁻¹ are due to the N-H vibrations of thiourea. It is further observed that the N-H absorption band in the higher frequency region 3000-3400 cm⁻¹ in the thiourea were not shifted to lower frequencies on the formation of metal – thiourea complex indicating thus nitrogen to sodium bonds are not present and that the bonding must be between sulfur and sodium atoms. The other frequencies of STB are assigned and compared with thiourea in Table 2.

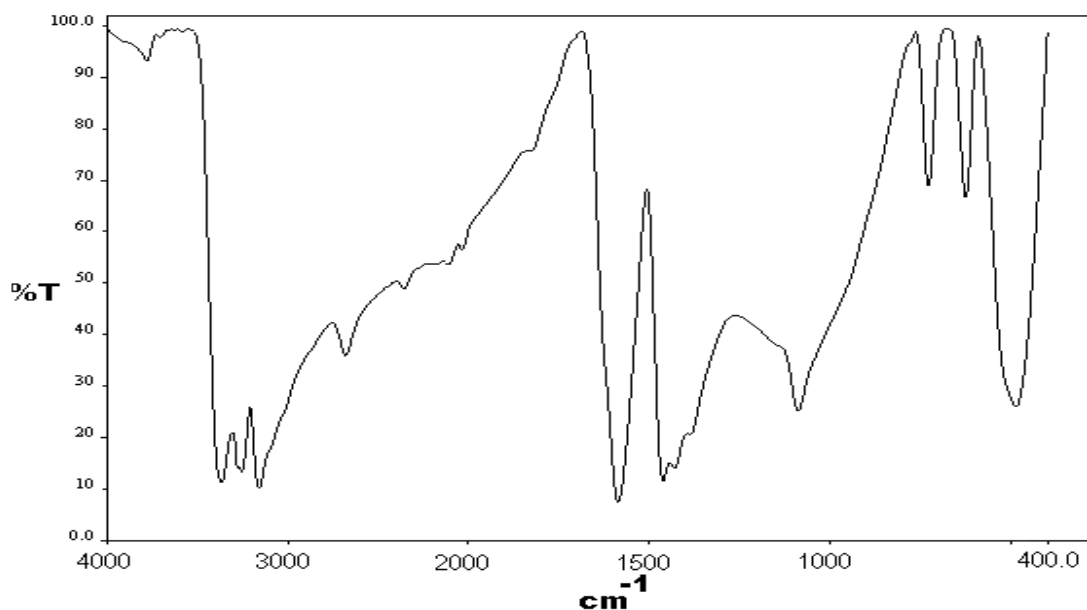


Figure 2. FT-IR spectrum of STB single crystal

Table. 2. Assignments of IR band frequencies (cm⁻¹) of thiourea and STB

Thiourea [15] (cm ⁻¹)	STB(cm ⁻¹)	Assignments
1627	1587	ν(NH ₂)
1470	1473	δ(N-C-N)
1417	1420	ν(CS)
1089	1086	ν(C-N)
740	729	ν(CS)
494	488	ν(N-C-N)

δ- bending, ν - stretching.

3.3 UV-Vis-NIR studies

To determine the transmission range and hence to know the suitability of STB single crystals for optical applications, UV-Vis analysis was made between 190nm and 1100nm using BERKIN ELMER LAMBDA 35 spectrometer. It covered a broad region which near ultra violet (200nm to 400nm), visible (400nm to 800nm) and

far-infra red (800nm to 1100nm). The plot of % transmittance Vs wavelength (nm) is shown in the Fig. 3. The absorbance is not registered in the measured wavelength range starting from 280nm to 1100nm. At 263.45 nm a sharp fall of transmittance to zero was observed indicating a single transition in the near UV region of STB. The nearly sharp fall in the transmittance at 263.45nm suggests nearly similar distribution of energies among all molecules of STB single crystal. Absence of absorption in the region between 280nm to 1100nm is an advantage as it is the key requirement for materials having NLO properties [19,20].

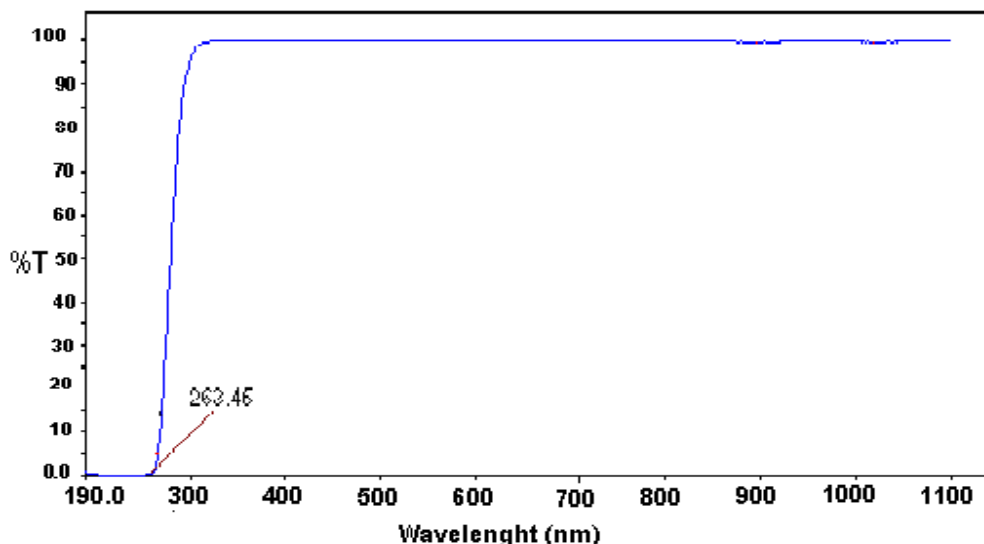


Figure 3. Optical transmission spectrum of STB single crystal

3.4 Nonlinear optical test

3.4.1 Second harmonic generation measurement

Kurtz [21] second harmonic generation (SHG) test was performed to find the NLO property of STB crystal. The crystal was grained into powder and densely packed in the microcapillary tube of uniform diameter (1.0 mm). A Quanta Ray Spectra Physics Nd:YAG laser producing pulses with a width of 8ns and a repetition rate of 10Hz was used. The laser was focused to fall on the powder sample. The SHG was confirmed by the emission of green radiation (532 nm) and the optical signal was controlled by photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output in the CRO. The measured output of STB is 47mV at given pulse energy 11.4mJ/pulse. The SHG efficiency of grown crystal is comparable with the standard reference material, KDP (63mV).

3.4.2 Laser induced damage threshold studies

In nonlinear optical, crystal the harmonic conversion efficiency is proportional to the power of the fundamental beam. Hence, a way to increase the efficiency is to focus the beam into the crystal. The laser damage threshold of an optical crystal is an important factor of affecting its applications. The laser damage threshold depends on specific heat, thermal conductivity, optical absorption etc., If the material has high heat, the laser damage threshold will be high and vice versa [22]. In the present study, an actively Q-switched diode array side pumped Nd:YAG laser is used for the laser induced damage threshold studies. The pulse width and the repetition rate of the laser pulses are 65 ns and 10 KHz respectively; at 1064 nm radiation. For this measurement, 32 μ m diameter beam was focused on the crystal with lens of 8 cm focal length. A well polished sample with clear surface was taken for the present study. The laser damage threshold of STB is 0.871 J/cm². The subject of material damage is of great importance to the design and successful operation of nonlinear devices.

3.5 Thermal studies

3.5.1 Melting point

The melting point of STB was directly determined as 176 °C using a melting point apparatus, Guna [23]. The apparatus works on calorimetric principle to specify the melting point of the chosen substance with good accuracy. The unit has an arrangement to hold the capillary containing the sample in uniform media. The thermocouple

attached in the capillary shows the temperature by means of a digital display with appreciable accuracy. At the point when the sample melts, the display shows the melting point of the substance with accuracy of 0.3%.

3.5.2 TGA and DTA studies

A powder sample weighing 2.5990mg was used for the TGA and DTA analyses. It is carried out simultaneously in nitrogen atmosphere at a heating rate of 20°C /minute for a temperature range of 0 °C -1100 °C and it is represented in Fig. 4. The thermo gravimetric analysis shows that the material has very good thermal stability up to 175.60 °C. The weight loss about 19.63% in the temperature range 175 °C -239°C is may be due to liberation of volatile substances like sulfur oxide in the compound. It is further observed that the DTA curve shows that the endothermic peak at around 175 °C is assigned to melting point of the title compound. It is followed by decomposition and volatilization of the compound above 500 °C. Hence, it may be useful for making the NLO devices below its melting point.

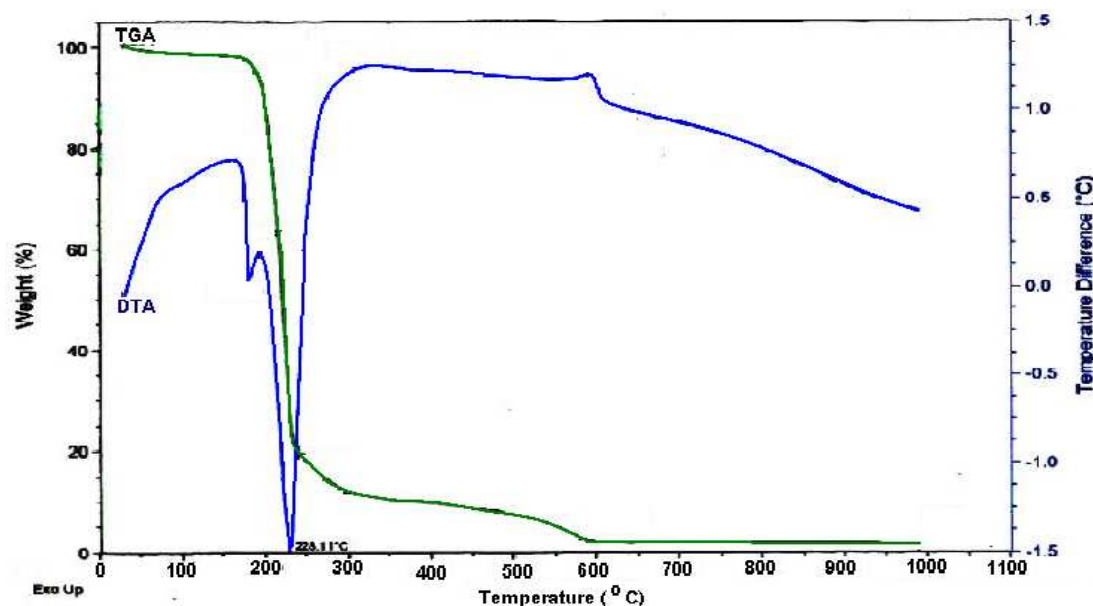


Figure 4. TG/DTA spectrum of STB single crystal

3.5.3 Differential scanning calorimetry

The Differential Scanning Calorimetry (DSC) of STB was carried out in nitrogen inert atmosphere between 0 °C and 1000 °C. It is shown in Fig. 5. The DSC trace shows exactly the same changes shown by differential thermogravimetric analysis. From the study of both thermo grams it is clear that the melting point of grown crystal is near 175°C.

3.6 Hardness test

To evaluate the Vicker's hardness number, several indentation were made on (100) plane of the crystal. The Vicker's micro hardness number was then calculated using the following expression:

$$H_v = 1.8544P/d^2 \text{ Kg/mm}^2$$

Where, H_v is the Vicker's micro hardness number in gmm^{-2} , P the applied load in g and d is the average diagonal length of the indentation in mm. The Vicker's hardness value was measured to be 17.6 gmm^{-2} . Fig. 6 shows load versus Vicker's hardness number for STB. At lower load, there is decrease in the hardness of the material. After that the hardness number is increase with the higher loads, which can be attributed to the work hardening of the surface layers. Beyond the load 100gm, significant cracking occurs, which may be due to the release of internal stresses generated walls indentation.

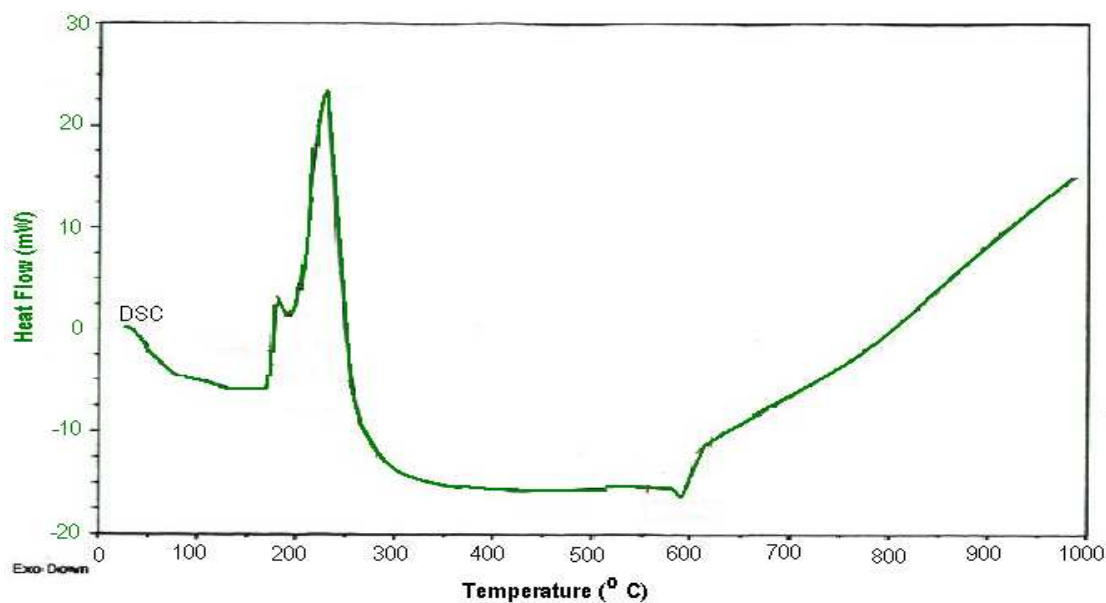


Figure 5. DSC spectrum of STB single crystal

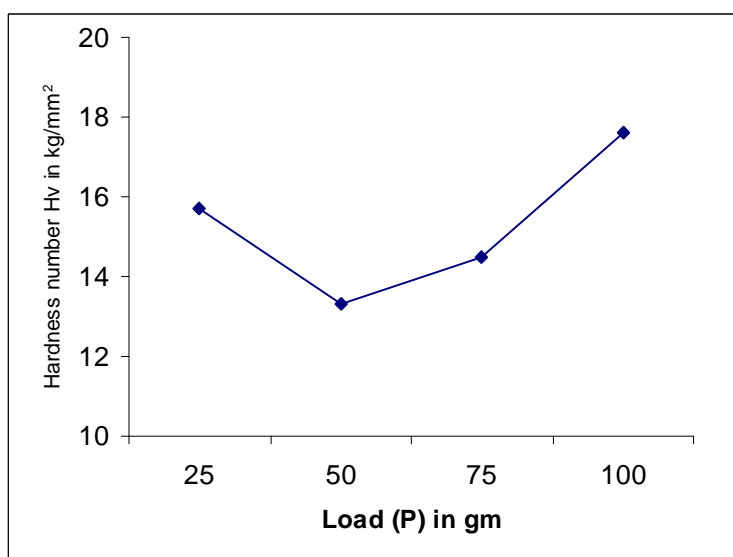


Figure 6. Hardness studies of STB single crystal

CONCLUSION

Single crystals of sodium thiourea bromide crystal have been grown by slow evaporation technique for the first time. The lattice parameters were found by single crystal XRD technique. FT-IR spectrum reveals that the functional groups of the grown crystals are up to the expectation. The crystal has good optical transmittance in the visible IR region. The SHG efficiency assures that the crystal is a potential material for NLO applications. TG/DTA and DSC studies reveal that the materials starts melting temperature at 175°C, thereby indicating the thermal stability of the material to withstand the high temperature encountered in laser experiments.

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