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SYNTHESIS, GROWTH AND CHARACTERIZATION OF BIS THIOUREA SODIUM ZINC SULPHATE SINGLE CRYSTALS-A SEMI ORGANIC NLO MATERIAL

K. Uma[1] --- R. Manimekalai[2] --- G. Pasupathi[3†]

[1,2,3]*PG and Research Department of Physics, A.V.V.M. Sri Pushpam College, Poondi, Thanjavur, Tamilnadu, India*

ABSTRACT

The slow evaporation of the solvent technique is used to grow transparent nonlinear optical (NLO) single crystals of bis thiourea sodium zinc sulphate (BTSZS). The grown crystal is characterized by single crystal X-ray diffraction analysis to confirm the crystallization of the synthesized materials and to determine its unit cell parameters. The crystalline nature and purity of the grown crystals are confirmed by powder X-ray diffraction pattern. The FT-IR and FT-Raman spectra are recorded to identify the functional groups present in BTSZS crystals. The UV-VIS-NIR transmission spectrum of BTSZS crystals are recorded in the wavelength range 190 - 1100 nm to determine the lower cut-off wavelength, percentage of the transmittance and the optical constants such as bandgap, refractive index, extinction coefficient, reflectance etc., Fluorescence study confirms the green emission of BTSZS which indicates the grown crystal is well suited for NLO applications. The thermo gravimetric analysis and differential thermal analyses are used to identify the melting point and the thermal stability of the grown crystals. The second harmonic generation efficiency is measured by Kurtz powder method and it is found to be 1.3 times that of potassium dihydrogen orthophosphates (KDP).

Keywords: Solution growth, FTIR studies, Nonlinear optics, Thermal studies.

Contribution/ Originality

This study is one of very few studies which have investigated the synthesis, growth and characterization of Bis thiourea Sodium Zinc Sulphate, single crystals using slow evaporation technique. Thus grown crystals are having very good optical transmittance. Fluorescence study confirms the green emission and also that NLO property.

† Corresponding author

1. INTRODUCTION

In recent years, growth and studies of the organic NLO materials have been emphasized due to their important physical and chemical properties essential for electro - optic modulation, optical switching, high laser damage threshold, second harmonic generation and nonlinear optical applications [1-5]. Even though organic materials possess high non-centro symmetric behaviour, wide bandwidth potential and high nonlinear activity but they have lesser thermal and mechanical stability. Hence, it is decided to grow semi organic crystals to overcome those demerits. Urea is one of the simplest biological molecules used in organic chemistry because of its capability of forming transition metal complexes. In search of compounds for better optical and mechanical properties, many scientists have studied the derivatives of urea. On the other hand, thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moments and its ability to form extensive nature of hydrogen bonds. Further thiourea, which is centro-symmetric, yields excellent non-centro symmetric materials when it is incorporated into the respective inorganic salt [6-8]. Motivate by the above consideration, in the present study is made an attempt to combine thiourea with sodium sulphate anhydrate and zinc sulphate hepta hydrate, to grow a semi- organic nonlinear optical material.

2. EXPERIMENTAL PROCEDURE

2.1. Crystal Growth

Bis thiourea sodium zinc sulphate (BTSZS) crystals were synthesized by mixing thiourea (Merck), zinc sulphate heptahydrate (Qualigense) and sodium sulphate monohydrate (Qualigense) in the ratio 2:1:1 according to the chemical reaction given below.

$$2[CH_4N_2S] + Na_2SO_4 + 2[ZnSO_4.7H_2O] \rightarrow 2[Na.CH_4N_2S.Zn]\ 3[SO_4]\ .14H_2O$$

The calculated amount of the starting materials was dissolved in doubly distilled water and it was continuously stirred for obtaining homogenous mixer solution. Then the solution was filtered by Whatman filter paper. After filtration, the solution was kept in a water bath maintained at constant temperature (40°C). The purity of the synthesized salt was further improved by successive recrystallization process. The good quality transparent crystals were harvested within the period of 2-3 weeks and is shown in Fig.1

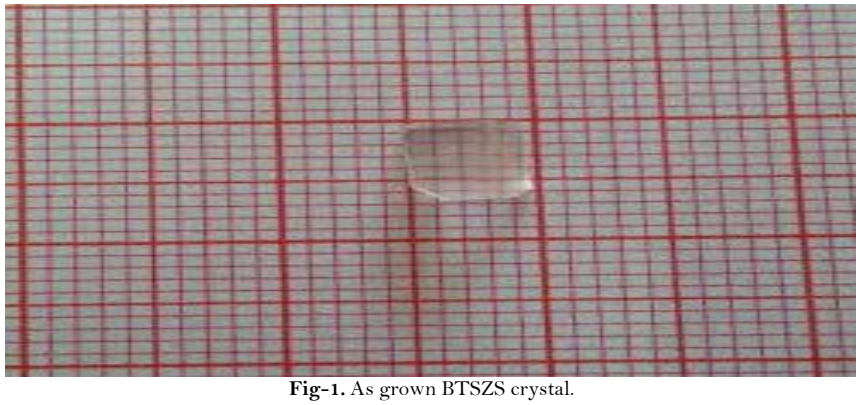

Fig-1. As grown BTSZS crystal.

3. RESULTS AND DISCUSSION

3.1. Single Crystal X-Ray Diffraction

The single crystal X-ray diffraction analysis of the grown crystals was carried out using ENRAF NONIUS CAD-4 automatic X-ray diffractometer. It reveals that the grown crystal belongs to orthorhombic system. The cell parameters of BTSZS crystals are calculated and compared with that of thioura, zinc sulphate and sodium sulphate single crystals and it is tabulated in Table 1.

Table-1. Lattice parameters of BTSZS single crystal.

Crystallographic data	BTSZS*	Sodium Zinc sulphate [9]	Thiourea [10]
a (Å)	7.78	9.1609	5.493
b (Å)	11.13	12.6764	7.655
c (Å)	15.51	9.6868	8.561
α	90	90	90
β	90	90	90
γ	90	90	90
System	Orthorhombic	Orthorhombic	Orthorhombic

*Present study

3.2. FT-IR and FT-RAMAN Analyses

The FT-IR spectrum was recorded using Perkin Elmer RX1 spectrometer in the range of 4000 to 400cm^{-1} (Fig.2). From the FTIR spectrum, the frequencies at 3783 cm^{-1} is due to OH bending of water molecules in the grown crystal. The symmetric and asymmetric C=S stretching vibration of thiourea at 740 and 1470 cm^{-1} are shifted to lower frequencies at 715 and 1402 cm^{-1} indicating the coordination of thiourea with metal ions [11, 12]. The broad peak at 1135 cm^{-1} is attributed to SO_4 groups [13, 14].

The FT-RAMAN spectrum of BTSZS is recorded using Perkin Elmer spectrometer in range of 4000 to 400 cm^{-1}. The presence of functional groups of the title compound were confirmed and compared with FT-IR spectrum and it is tabulated in Table 2.

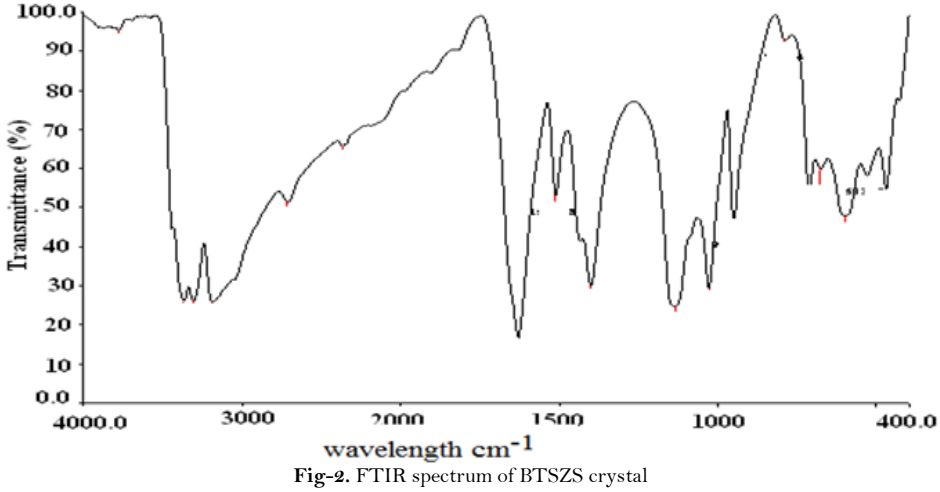

Fig-2. FTIR spectrum of BTSZS crystal

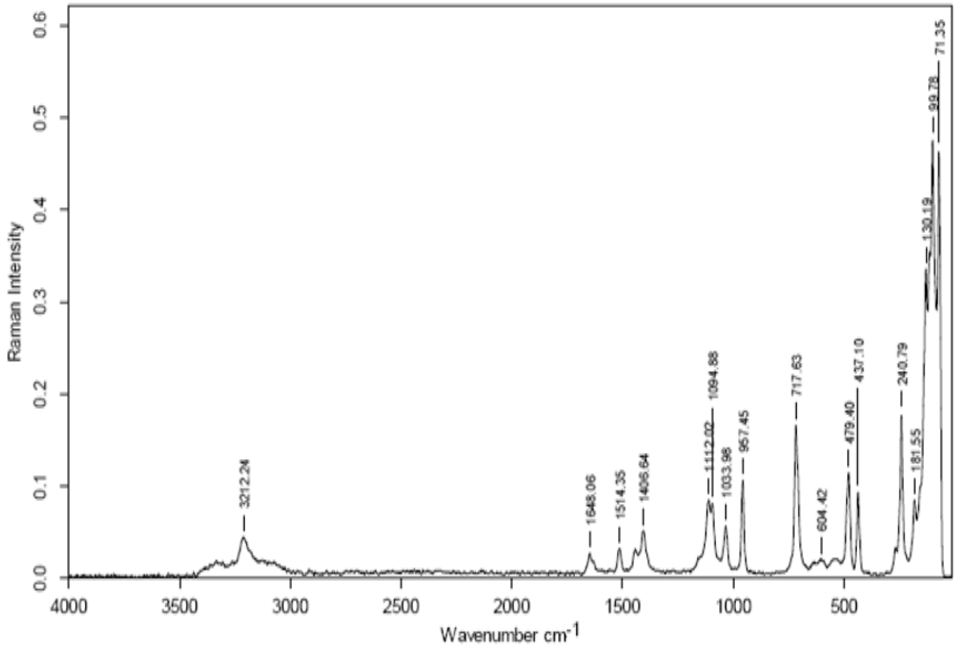

Fig-3. FT-Raman spectrum of BTSZS crystal

Table-2. Vibrational assignments of BTSZS crystal

FTIR	FT Raman	Assignment
3189	3212	NH_2 stretching
1630	1648	C=O stretching
1513	1514	C=S stretching
1402	1406	γ_{ss} CH
1037	1033	γ_{ss} SO_4
952	957	γ_{as} SO_4
715	717	γ_{ss} SO_4 (symmetric)
473	479	γ_{sb} SO_4 (symmetric bending)

3.3. Thermal Analysis

Differential thermogram analysis (DTA) and thermogravimetric analysis (TGA) of the grown crystals were carried out between 30°C to 800 °C in nigtrogen atmosphere at a heating rate 5c /min.The recorded TGA/DTA trace of BTSZS is shown in Fig. 3. On a careful examination of the chart, there are two stages of weight loss, one occurring below 230 °C may be due to weakly entrapped lattice water and the other occurring above it may be due to the removal of strongly entrapped lattice water. From the DTA curve, it was observed that the compound start to decompose at 250 °C and undergoes an irreversible endothermic transition till 300°C which is assigned to the melting point of the compound. There is another endothermic phase transition at 366 °C due to the liberation of volatile substances like sulphur and other impurities in the compound [15-17]. From the DTA/TGA trace, it is seen that the compound is stable upto 251 °C. Hence, the title compound can be used to fabricate the devices that can withstand temperature upto 250 °C.

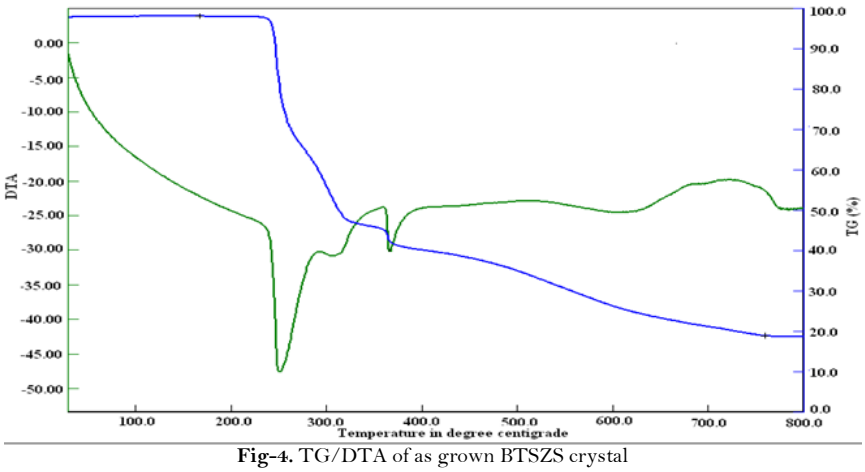

Fig-4. TG/DTA of as grown BTSZS crystal

3.4. UV-VIS-NIR Spectral Analysis

The UV-VIS-NIR transmission spectrum of BTSZS is recorded using Perkin Elmer lambda 35 spectrophotometer in the range of 190 to 1100 nm and is depicted in Fig.4. From the spectrum, it is observed that the cutoff wavelength is around 299 nm. Further the grown crystals have significant absorptions in the entire visible region in the optical transmittance spectrum.

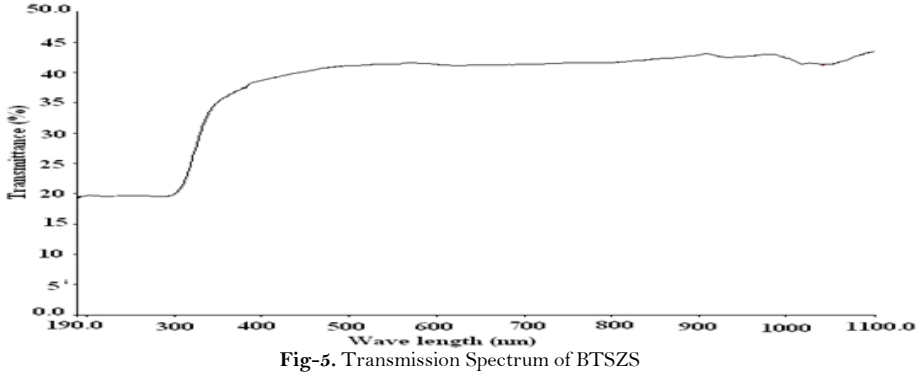

Fig-5. Transmission Spectrum of BTSZS

The transmission extends neatly from 299 nm to 1100 nm similar to that of urea, makes it valuable for those applications requiring blue/green light and the title compound is the good candidate for the fabrication of nonlinear optical devices. Using the optical transmittance data, the optical absorption co-efficient (α) is calculated from the following relation

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \qquad \text{---------- (1)}$$

Where, 'T' is the transmittance and't' is the thickness of the crystal.

Optical band gap (Eg) was evaluated from the transmission spectrum and optical absorption coefficient (α) near the absorption edge is using the equation.

$$h\nu\alpha = A(h\nu - E_g)^{\frac{1}{2}} \qquad \text{----------} (2)$$

where 'A' is the arbitrary constant, Eg is the optical band gap, 'h' is the Plank's constant and 'ν' is the frequency of incident photons [18].

The band gap of BTSZS crystal was estimated by plotting hν Vs $(\alpha h\nu)^2$ (Fig. 5) and it was found to be 3.6 eV.

Extinction coefficient (k) can be obtained from the following equation

$$k = \frac{\alpha\lambda}{4\pi} \qquad \text{----------} (3)$$

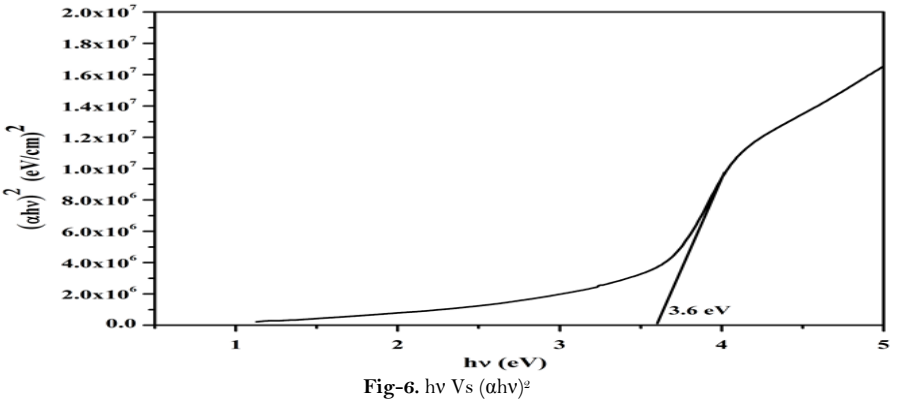

Fig-6. hν Vs $(\alpha h\nu)^2$

A graph was plotted between wavelength and the extinction co-efficient and it is shown in Fig.6.

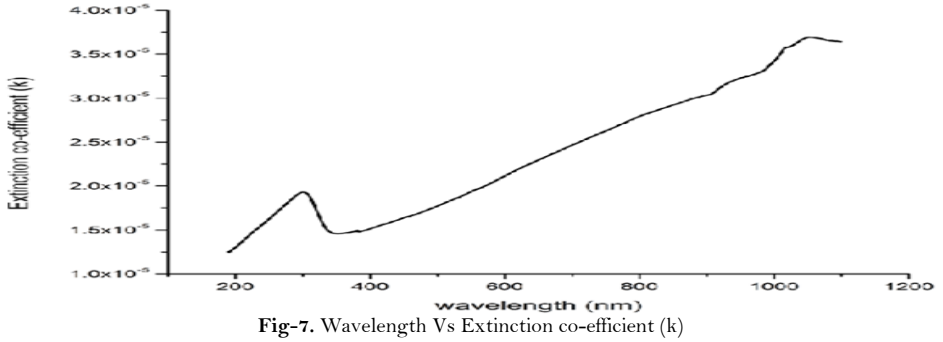

Fig-7. Wavelength Vs Extinction co-efficient (k)

The transmittance (T) is given by

$$T = \left(\frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \right) \qquad \text{----------} (4)$$

The reflectance (R) in terms absorption co-efficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \qquad \text{----------} (5)$$

Refractive index (n) can be determined from the reflectance data using the following equation

$$n = \frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \qquad \text{---------- (6)}$$

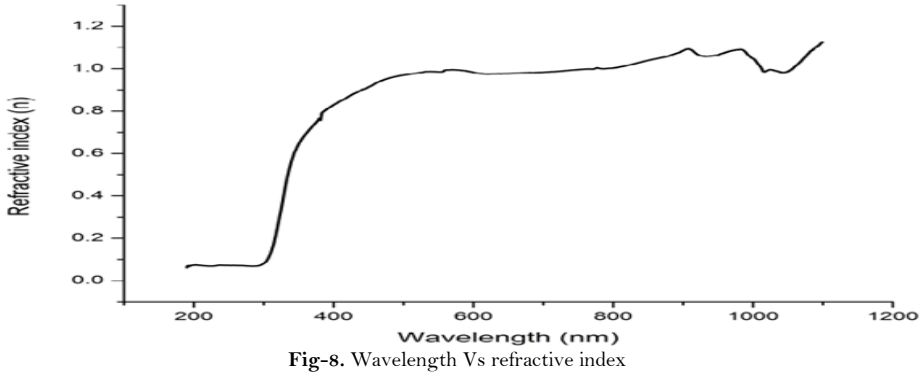

Fig-8. Wavelength Vs refractive index

The variations of extinction coefficient, refractive index are sequentially shown in Fig. 6 and Fig. 7. The least absorption and significantly lower index of refraction in entire visible region exhibited by the grown crystal is most desirable property for antireflection coating in solar thermal devices [19].

3.5. Fluorescence Spectral Analysis

Fluorescence in solids is the phenomenon in which the electronic states of solids are excited by optical photons particular energy. The fluorescence spectrum is recorded in the range of 300-600nm with an excitation wavelength of 350nm as shown in Fig. 9. The first peak that corresponds to the wavelength of ~320 nm is the lower cut off wavelength, from this wavelength, optical band gap is calculated. It is found to be 3.7 eV. The optical band gap determined from this fluorescence spectrum is similar to that obtained from UV-VIS-NIR spectrum of the sample. The other peak observed at 595 nm confirms the green emission that may be due to the non-centro symmetric nature of the grown crystal and may be assigned as π-π* transition due to the interaction between the metal (Zn^{2+}) and the ligand molecule [20]. Thus, the grown BTSZS crystals possess the nonlinear optical properties and it is counter -checked by Kurtz Perry SHG test.

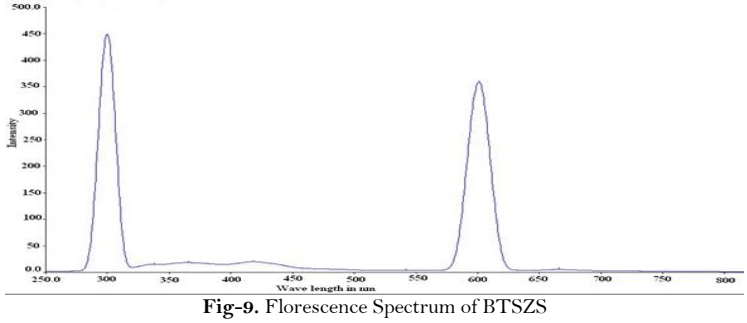

Fig-9. Florescence Spectrum of BTSZS

3.6. Second Harmonic Generation Study (SHG)

The modified version of Kurtz powder technique is well accepted to measure the SHG efficiency of NLO materials [21]. The crystalline powder is illuminated using Q switched Nd:YAG laser with the wavelength 1064 nm of pulse width 8 ns with the frequency rate 10Hz . The SHG is confirmed by the emission of green radiation of 532 nm and the SHG efficiency is found to be 1.3 times that of the reference material KDP.

4. CONCLUSION

Bisthiourea sodium zinc sulphate crystals are grown by slow evaporation technique. The unit cell parameters are determined by single crystal X-ray diffractometer. The crystalline nature and purity of grown crystal is confirmed by power XRD technique. FTIR and FT-Raman spectral studies confirmed the presence of functional groups of thiourea and sulphate. The melting point and decomposition temperatures are analyzed by TG /DTA technique. The optical band gap (Eg), the absorption co-efficient (α), extinction co-efficient (k), the reflectance co-efficient (R) are also determined from UV-VIS-NIR spectrum. The fluorescence of the grown sample is confirmed by nonlinear optical property. The SHG efficiency of the powdered BTSZS crystal is nearly 1.3 times that of standard KDP material.

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