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Growth, optical, elemental and spectral characterization of semiorganic Non Linear Optical zinc thiosemicarbazide sulfate (ZTSCS) single crystals

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Abstract: A semiorganic crystal of zinc thiosemicarbazide sulfate (ZTSCS) has been grown aqueous solution by slow evaporation technique at room temperature. The material was subjected to various characterization techniques such as UV-Visible, non linear optical test, photoluminescence study, elemental analysis and Fourier transform infrared (FTIR) techniques. Cut off wavelength and band gap of the grown crystal were observed using UV-Visible spectrophotometer. The NLO property of the ZTSCS crystal was confirmed by Kurtz-Perry SHG test. FTIR spectral studies have been performed to identify the functional groups. Chemical composition of the title compound was estimated by elemental analyser.
Keywords: Growth, optical, elemental, spectral characterization, semiorganic Non Linear, Optical zinc thiosemicarbazide sulfate (ZTSCS), single crystals.

1. Introduction

Non Linear Optical (NLO) material play a vital role in opto electronics, optical modulation, fibre optic communication, optical computing, optical disk storage, laser fusion reaction, laser remote sensing, colour display, medical diagnostics etc [1].Researchers are take more effort to growing organic, inorganic and semiorganic materials with wide range of transparency and higher non linear coefficient which make them suitable for device fabrication [2, 3]. Most of the organic NLO crystal have poor mechanical, thermal properties and susceptible to damage during processing. Also it is difficult to grow large size of optical quality crystals of these materials for device application. Semiorganic NLO crystal have good thermal, mechanical properties and large non linear coefficient [4, 5]. Single crystals of thiosemicarbazide complexes have more attention in the last few years due to their non linear optical properties [6-9]. Thiosemicarbazide is a centrosymmetric in nature but when combined with inorganic material it produces complexes that are non-centrosymmetric [10].

In the present work zinc sulfate heptahydrate is combined with thiosemicarbazide to form a new semiorganic ZTSCS non linear optical material. This paper reports the crystal growth and characterization of zinc thiosemicarbazide sulfate single crystal using slow evaporation solution growth method. The grown ZTSCS crystal was subjected to various characterization techniques such as UV-Visible spectroscopy, non linear optical test, photoluminescence study, elemental analysis and FTIR techniques. The results are discussed in detail.

2. Experimental

Analtical grade thiosemicarbazide (NH_2- NH-CS-NH_2) and zinc sulfate heptahydrate ($ZnSO_4 .7H_2O$) are taken in equal molar ratio were used to grow zinc thiosemicarbazide sulfate (ZTSCS) crystal and the chemical reaction is given by,

NH_2- NH-CS-NH_2+$ZnSO_4$ .7H_2O→Zn (NH_2- NH-CS-NH_2) SO_4+7H_2O

The 14.3 g of zinc sulfate heptahydrate and 4.55 g of thiosemicarbazide were dissolved in double distilled water at room temperature. The mixture of solutions were stirred with a magnetic stirrer in a tightly closed beaker about 5 hour under room temperature.

The resulting solution was filtered and transferred into a beaker and then kept undisturbed to initiate nucleation. After 165 days, a transparent, colourless and needle shape crystals were collected of size about 16 X 4 X 3 mm³. The photograph of title compound is shown in figure 1.

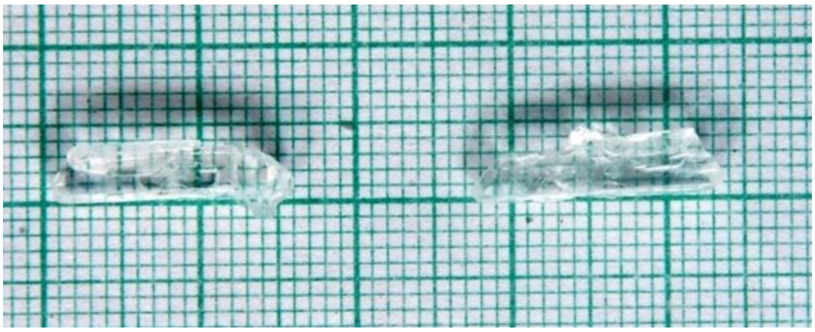

Fig.1 Photograph of ZTSCS Crystal

3. Results and Discussion

3.1 UV-Visible Analysis

In order to reveal the optical properties of the zinc thiosemicarbazide sulfate (ZTSCS) single crystal, UV- Visible spectrum was recorded in the range of 190 – 1100 nm using Lamda 35 UV- visible spectrometer.

The absorption spectrum of ZTSCS as shown in figure 2.The UV cut off wave length for the growth crystal has been found to be 205 nm. The absorption property of the grown crystal in the entire visible region suggests its suitability for second harmonic generation. The band gap or energy gap (E_g) of ZTSCS crystal is found by the following relation,

$$E_g = h\, c/\lambda$$

Where, h is the Planck constant (6.625×10^{-34} JS), c is the velocity of light (3×10^{8}m/s) and λ is the cut off wavelength of grown crystal (nm). The band gap energy of ZTSCS was found to be6.039 eV. From the above results reveals that the grown ZTSCS crystal is belongs to the category of insulating materials.

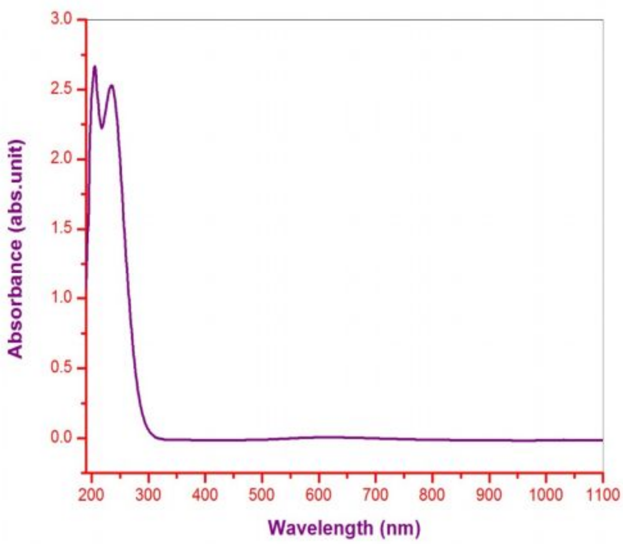

Fig.2 UV-Visible absorption spectrum of ZTSCS crystal

3.2 Non linear optical test

Second harmonic generation efficiency of the crystal was assessed by Kurtz and Perry technique [11, 12]. In this method the powdered sample of ZTSCS with an average particle size of 100 – 150 µm was illuminated using fundamental wavelength of 1064 nm with pulse width 10 ns. The SHG was confirmed by the emission of green radiation.

3.3 Photoluminescence study

Photoluminescence studies can be used to identify the excitation and emission properties of the single crystal [13]. Most of the semiorganic compounds are promising photoluminescence materials because of their high thermal stability, structure and metal dependent emission. In the present work, photoluminescence properties of ZTSCS crystal was recorded in the wavelength 300-1000 nm as shown the figure 3.From the spectrum, a strong peak is observed the wavelength 407 nm. This indicates that the title compound has a violet emission property. The violet emission of zinc thiosemicarbazide sulfate crystal implies that it may be potentially applicable as materials for violet emitting diode device.

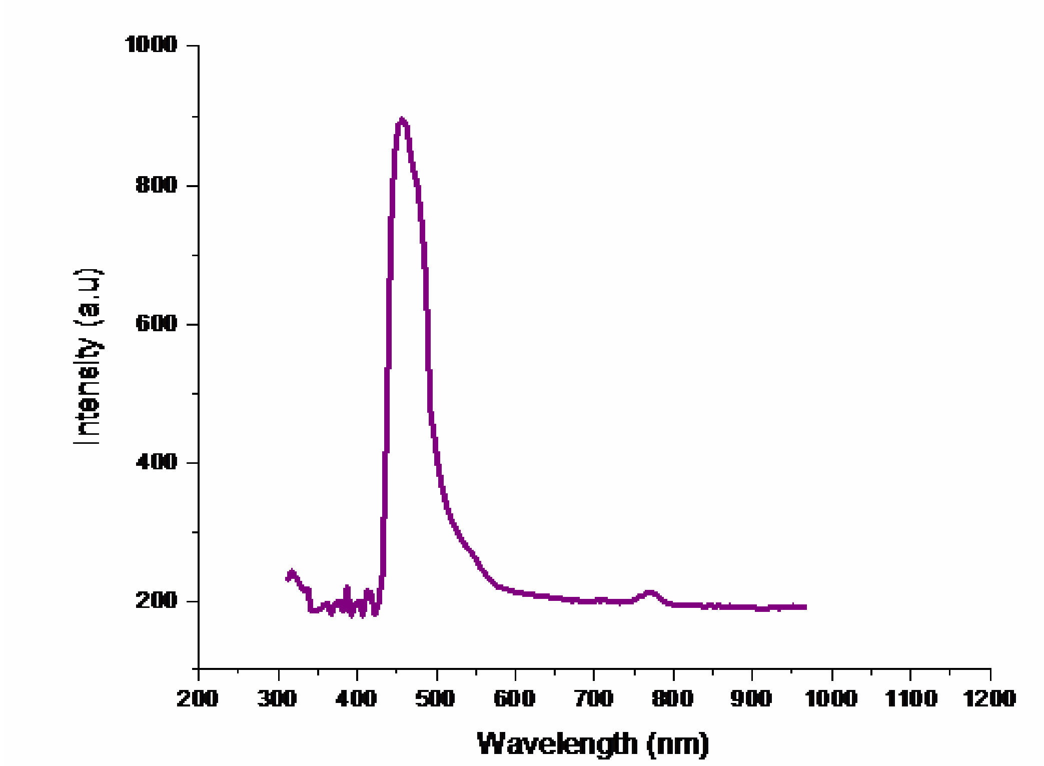

Fig.3 PL spectrum for ZTSCS crystal

3.4 EDAX Analysis

To identify the weight percentage of major and minor elements present in the samples were done using Energy Dispersive X-ray (EDAX) spectrometer by JEOL model JSD-5610 LV with an accelerating voltage of 20KV. The EDAX analysis of grown crystals is shown in figure 4. The atomic and weight percentage of ZTSCS are shown in table 1. Trace elements are estimated by determining the percentage abundance of elements such as Zn, N, O, C and S present in the sample. Table 1 indicates that the results of corresponding elements present in the grown crystal in atomic and weight percentage.

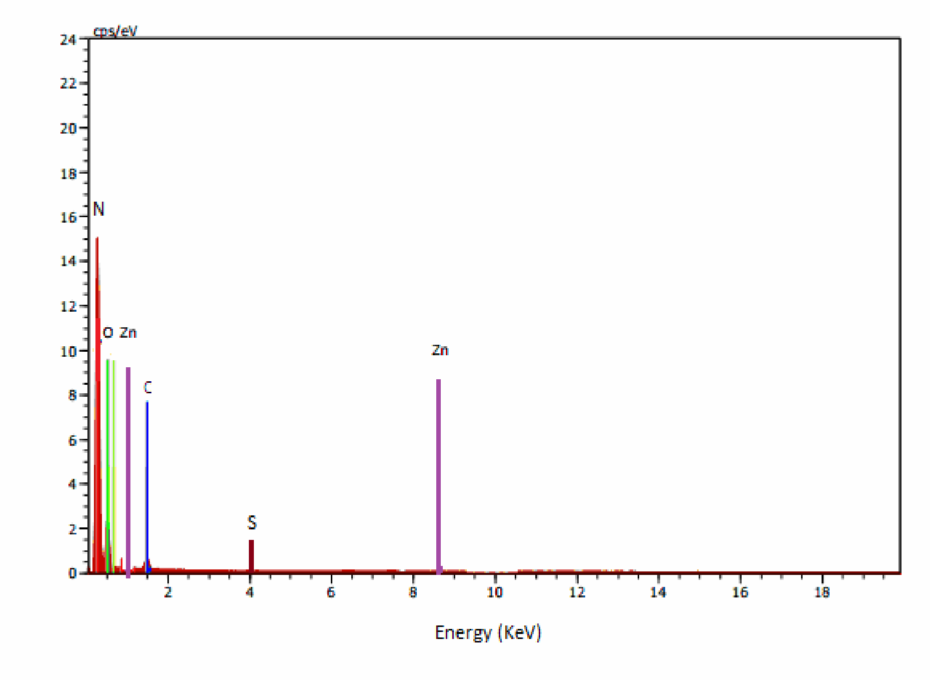

Fig.4 EDAX spectrum of ZTSCS crystal

Table 1: EDAX Parameters of ZTSCS crystal

Element	Weight (%)	Atomic (%)
Zn	49.10	52.10
N	36.24	35.14
O	10.30	8.20
C	2.24	2.16
S	2.12	2.40

3.5 Fourier Transforms Infrared Spectroscopy

Fourier transforms infrared spectrum is important evidence that provides more information about the structure of the compound. To analysis the presence of functional groups in ZTSCS qualitatively, we recorded the FTIR spectrum in the range 400-4000 cm^{-1} using PERKIN ELMER FTIR spectrometer using KBr pellet technique. The observed FTIR spectrum is shown from figure 3. The observed frequencies and their assignment of the grown crystal as given in table.1.The characteristics peaks of zinc thiosemicarbazide sulfate crystal can be described as follows. The peak at 3348 cm^{-1} represents O-H stretching mode of vibration. The weak band at 3182 cm^{-1} is assigned to N-H stretching vibrations. The peak at 2957 cm^{-1} indicates the presence of C-H stretching vibrations [14]. The broad band at 1646 cm^{-1} is assigned to NH_3 asymmetric bending vibrations [15]. The vibration modes at 1407 cm^{-1} and 1353 cm^{-1} are assigned as C-H bending and C= S stretching vibrations respectively [16].

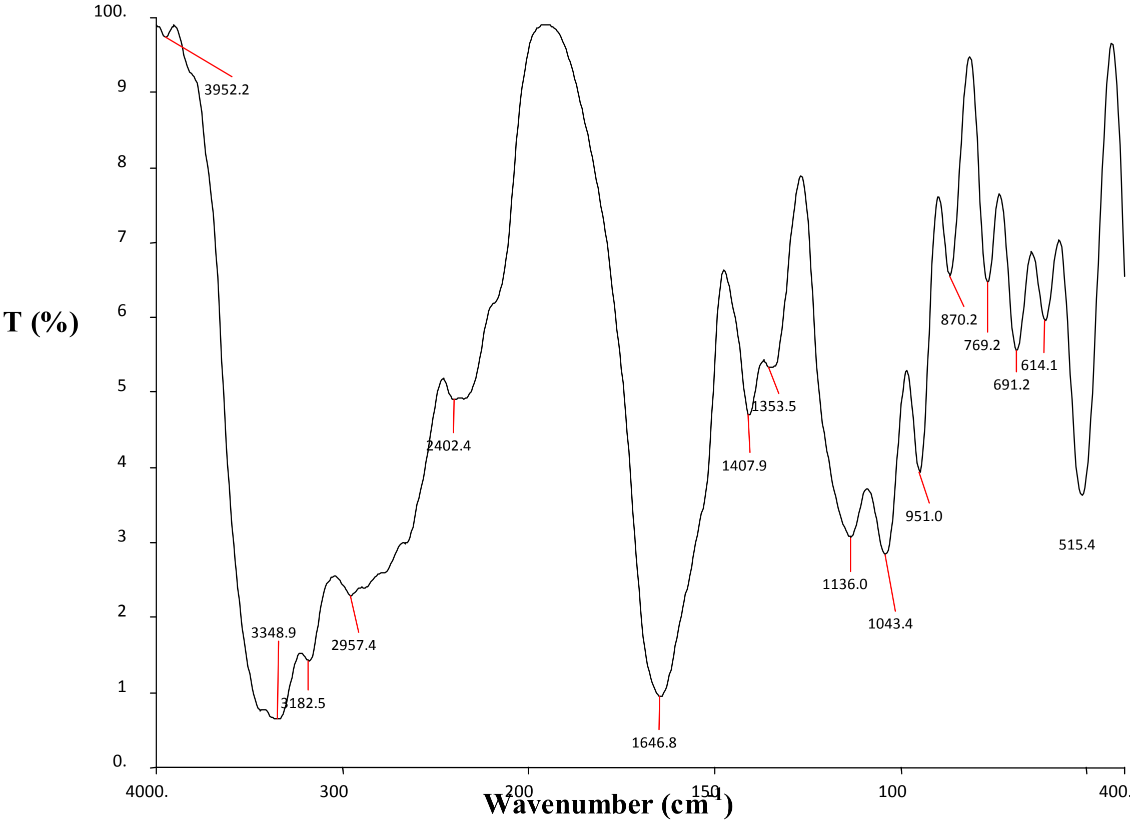

Fig 5 FT-IR spectrum of ZTSCS crystal

A peak at 1136 cm^{-1} is due to NH_3 stretching vibrations [17]. The wavenumber observed at 1043 cm^{-1} and 951 cm^{-1} respond to CCN stretching and C-C asymmetric stretching vibration present in the sample respectively. The vibration mode at 870 cm^{-1} represent symmetric stretching of SO_3^{2-}.The peaks around 769 cm^{-1}, 691 cm^{-1} and 641 cm^{-1} have been attributed to C –S stretching, C-H deformation and carboxylic group respectively.

Table 2: FTIR spectral data of ZTSCS

Observed Wave number (cm^{-1})	Mode Assignment
3348	O-H stretching
3182	N-H stretching
2957	C-H stretching
1646	NH_3 asymmetric stretching
1407	C-H asymmetric stretching
1353	C=S stretching
1136	NH_3 asymmetric stretching
1043	CCN stretching
951	C-C asymmetric stretching
870	C-O asymmetric stretching
769	C-S stretching
691	C-H deformation
614	COO stretching

Conclusion

Single crystals of zinc thiosemicarbazide sulfate have been successfully grown by low temperature solution growth technique. The optical band gap was measured from the UV- visible spectrum for ZTSCS was found to be 6.03eV. The photo luminescence spectrum obtained in the present study indicates violet emission of crystal at 407 nm. EDAX spectrum of ZTSCS crystal confirms the presence of Zn, N, O, C and S in the sample. Owing to its low cut off wavelength, high value of band gap, second harmonic generation efficiency and luminescence properties, the grown ZTSCS crystal have been effectively utilized for photonic applications.

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