

Investigation on the Properties of Zinc Thiourea Sulphate Crystal for NLO Application

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ABSTRACT: A semi-organic non-linear optical single crystal of zinc thiourea sulphate has been grown by slow evaporation solution growth technique. The single crystal XRD analysis confirms that the crystal belongs to the orthorhombic system with non-centrosymmetric space group Pmmm. Powder X-ray diffraction analysis was carried out for the grown crystal in the range 20°-80°. The presence of functional groups was confirmed by using FTIR spectral analysis. The UV-Vis spectrum shows that it has a good transmittance in the entire visible region with the lower cut-off wavelength at 253 nm. The thermal characteristics of zinc thiourea sulphate were analyzed by thermogravimetric (TGA) and differential thermal analysis (DTA). The mechanical behavior of the grown crystal was studied using Vickers microhardness tester. Nonlinear optical characteristics of zinc thiourea sulphate have been studied using Q-switched Nd:YAG laser ($\lambda=1064$ nm). The second harmonic generation conversion efficiency of zinc thiourea sulphate is 0.8 times that of standard KDP crystal.

KEYWORDS: Nonlinear optical, crystal growth, mechanical properties, thermal analysis

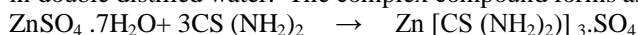
I. INTRODUCTION

The nonlinear optical properties of the organic molecular crystals have received a great deal of interest for the past two decades due to their extensive application in the fields like laser technology, telecommunication, optical information processing and storage [1-2].

The semi-organic materials have the potential for combining the high optical nonlinearity and flexibility of organics with temporal, thermal stability and excellent transmittance of inorganics [3-7]. Zinc thiourea sulfate (ZTS) is an efficient semiorganic nonlinear material for type II second harmonic generation [8-10]. Zinc Thiourea Sulfate having molecular formula $Zn(NH_2CSNH_2)_3SO_4$ is one such a novel promising non-linear optical metal organic crystal having essential applications in the area of second harmonic generation device as well as laser tuned experiments [11]. While, a centro symmetric Thiourea molecule combines with inorganic material, it turns into non centro symmetric (NLO) complexes [12] which include both organic and inorganic advantages which known as semi organic material. This makes ZTS as a good candidate for non linear optical applications having 0.8 times more SHG efficiency than KDP crystal. The growth and various studies of doped and undoped ZTS crystals have been reported in a number of publications [13-17]. In the present work, zinc thiourea sulphate has been grown by slow evaporation technique and investigated the optical, thermal, and mechanical properties through various characterization studies such as X-ray diffraction, UV-Vis, FTIR and TGA and DTA.

II. MATERIALS AND METHODS

Single crystal of zinc thiourea sulphate was grown by slow evaporation solution technique. The high purity zinc sulphate heptahydrate ($ZnSO_4 \cdot 7H_2O$) and thiourea ($CS(NH_2)_2$) were taken in the molar ratio of 1:3 and were dissolved in double distilled water. The complex compound forms as follows:



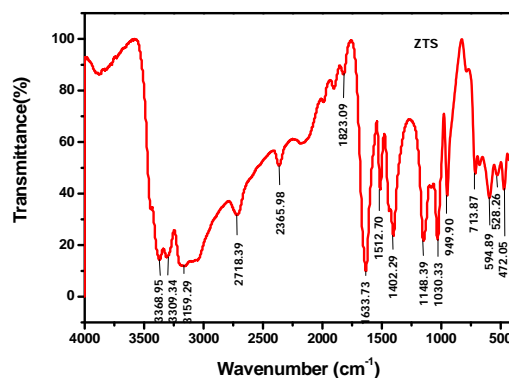


Fig.2. FTIR Spectrum of the grown ZTS Crystal

The absorption band observed at 1633cm^{-1} in the spectrum of ZTS corresponds to that of thiourea of about the same frequency 1625cm^{-1} and can be assigned to the NH_2 bending vibration. The absorption observed at 1519cm^{-1} and 940cm^{-1} in the spectrum of ZTS corresponds to the 1470 and 910cm^{-1} absorption of thiourea, respectively and can be assigned to the N-C-N stretching vibration. The increase in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation. The absorption band at about 1402cm^{-1} corresponds to 1417cm^{-1} of thiourea and can be assigned to the C=S stretching vibration. On coordination through sulfur, nature of vibration is slightly changed. The sharp and intense absorption of ZTS at 713cm^{-1} corresponds to the 730cm^{-1} absorption of thiourea. The lowering of frequency can be attributed to the reduced double bond character of the C=S bond on coordination. The absorption bands assigned to the particular vibrations indicate the presence of sulfur to metal bonds in ZTS.

UV-VIS SPECTRAL ANALYSIS

The optical transmission spectrum of ZTS single crystal was recorded in the wavelength region $200\text{-}1000\text{nm}$ and it is shown in Fig.3. For optical fabrications, the crystal should be highly transparent in the considered region of wavelength. The favorable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation. The UV absorption edge for the grown crystal was observed to be around 253nm . The lower cut off wavelength is found to be 253nm for ZTS which infinity good agreement with reported value [20].

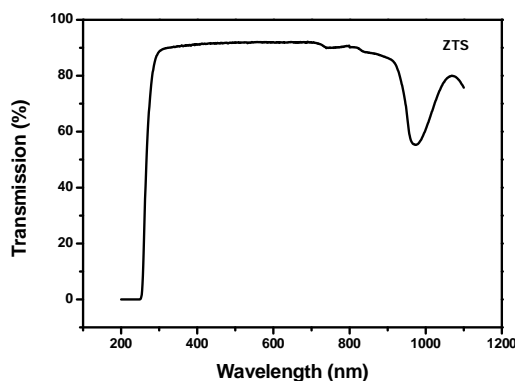


Fig.3. UV transmittance spectrum of the grown ZTS crystal

The optical absorption coefficient (α) was calculated from transmittance using the following relation [18]

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right)$$

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where, T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$) [19].

$$\alpha = \frac{A[h\nu - E_g]^{\frac{1}{2}}}{h\nu}$$

where, E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Fig.4.

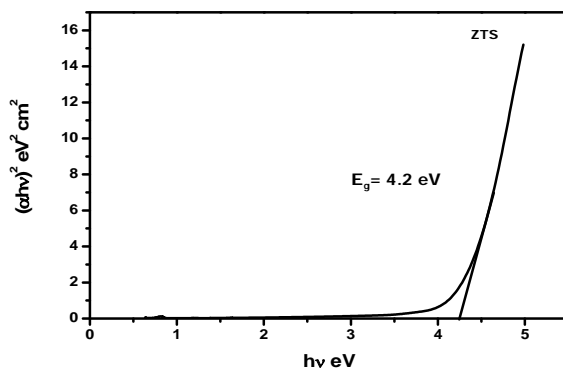


Fig.4. Variation of photon energy ($h\nu$) with $(\alpha h\nu)^2$ of the grown ZTS crystal

E_g is evaluated using the extrapolation of the linear part [21]. Using Tauc's plot, the energy gap E_g was calculated as 4.2eV and the large band gap clearly indicates the wide transparency of the crystal. This high band gap value indicates that the grown crystal possesses dielectric behavior to induce polarization when powerful radiation is incident on the material.

THERMAL ANALYSIS

The thermal analysis are used to find out the weight loss (TGA), melting and decomposition point (DTA) of the grown ZTS crystal. The TG/DTA curves were shown in Fig.5. There occurs no weight loss up to first x-axis (250°C) in the TG curve. This indicates that there is no inclusion of water in the crystal lattice. A major weight loss observed at 250°C in the TG curve is assigned to the decomposition of the title compound. During this transition mass of sample reduces by 51%. The first phase of weight loss begins at 223.04°C which is attributed to the decomposition as well as the evaporation of the sample. The second phase of weight loss at 312.22°C is may be due to the degradation of the sample itself.

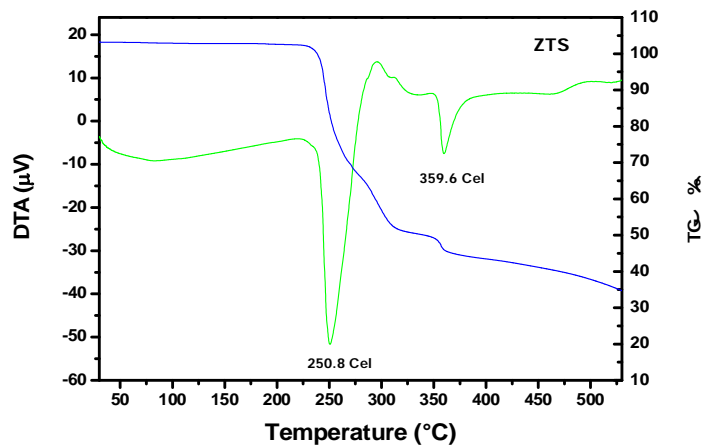


Fig.5. TGA/DTA of curve grown ZTS crystal

DTA curve shows that pure ZTS melts at 231°C which was also confirmed by earlier literature. In the present work, DTA curve shows that ZTS starts to soften at 231.7°C and it undergoes endothermic transition (peaks) at 250.86°C, 205.3°C and 359.6°C. Also, the plot shows no endothermic or exothermic transitions below 250°C indicating the absence of other phase transitions before the melting point. The sharpness of endothermic peaks in DTA curve shows good degree of crystallinity of the grown crystals. No decomposition up to its melting point at tests the stability of this material for application in lasers, where the crystals are required to withstand high temperatures.

MICROHARDNESS

Microhardness is the measure of strength of the material and is an important mechanical property of the optical materials in the formation of the fabrication of devices. Physically hardness is the resistance offered by the material to localized plastic deformation caused by scratching or indentation. Vickers microhardness studies were carried out on ZTS crystal by applying load of differed magnitudes. The indentation time was fixed constant for each trial. Repeated trials were performed to ascertain the correctness of the observed results.

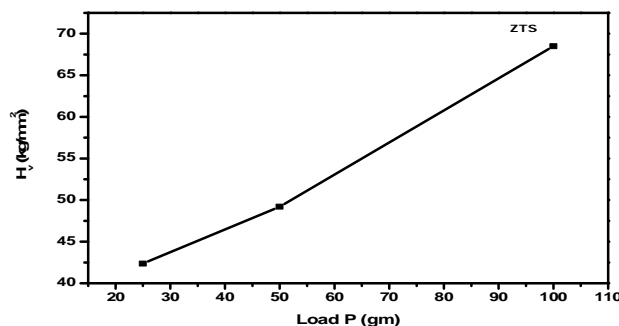


Fig.6. Plot of load versus hardness number

The Vickers microhardness number H_v was calculated using the relation,

$$H_v = 1.8544 (P/d^2) \text{ kg/mm}^2$$

where,

P is the load in kg and d is the diagonal length of indentation impression in mm. The plot of load (P) versus Vickers hardness number (H_v) is shown in Fig.6. It is observed that the hardness number increases with increasing load. The

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increase in hardness with the load could be attributed to the heaping up of materials at the edges of impression made by the diamond pyramid.

The hardness value of ZTS crystal is found to 68.9 kg/mm^2 for a load of 100g which confirms the good mechanical stability of the crystal. The relation between load and size of the indentation is given by Meyer's law: $P = k_1 d^n$ where, k_1 is a constant for a given material and n is the work hardening coefficient. Fig.7. shows the least square fit plot of $\log(d)$ versus $\log(P)$.

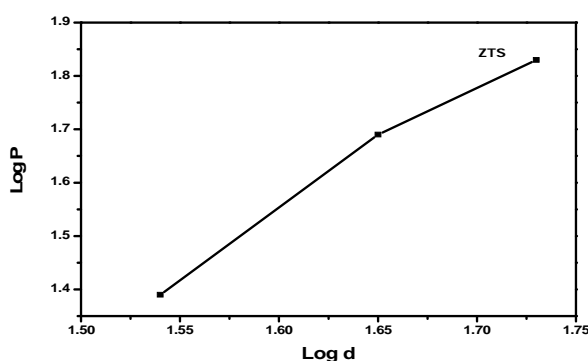


Fig.7. Plot of $\log d$ versus $\log P$

The slope of the straight line gives the work hardening coefficient (n). According to Onitsch, n should lie between 1 and 1.6 for hard materials and should be greater than 1.6 for soft materials. Since n is 2.6 for ZTS, it is concluded that the ZTS crystal is a soft material and hardness number increases with the load and it is useful for nonlinear applications.

SECOND HARMONIC GENERATION EFFICIENCY MEASUREMENTS

The most widely used technique for confirming the SHG efficiency of NLO materials to identify the materials with non-centrosymmetric crystal structures is the Kurtz Powder technique. Fine powder of ZTS crystals were exposed under 1064nm laser beam from a pulsed Nd:YAG laser having a repetition rate of 10Hz and pulse width of 8ns to test the second harmonic generation (SHG) efficiency of the ZTS crystal was evaluated by taking the microcrystalline powder of KDP as the reference material. The output light was passed through a monochromator which detected green light at 532nm. This confirms the NLO behavior of the material. The relative conversion efficiency was calculated from the output power of ZTS crystals with reference to KDP crystals. It is observed that the conversion efficiency of ZTS is 0.8 times that of KDP crystal.

VI. CONCLUSION

Good quality single crystals of zinc thiourea sulphate were grown by the slow evaporation solution growth technique. The molecular structure was established by single crystal XRD analysis. The presence of functional groups was identified by FTIR spectral analysis. The UV-visible spectrum suggests the suitability of the grown crystal for various optical applications. The thermal stability of the title crystal was determined by TG/DTA studies. Vickers microhardness was calculated in order to understand the mechanical stability of the grown crystal. The powder SHG measurement shows that the grown zinc thiourea sulphate crystal has SHG efficiency.

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