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Crystal Growth and Synthesis of Tristhiourea Zinc(II) Sulpate (ZTS)

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***Abstract*—** Tristhioureazinc(II)sulphate (ZTS) potential semiorganic Non-linear optical material with high SHG efficiency, application in laser technology and photonic applications are grown as pure single crystals by slow evaporation solution growth technique, one of the best method at room temperature bythe crystallization process is furtheranalysed by single crystal XRD which infers that the ZTS crystal has orthorhombic system. The surface morphology was studied by SEM. Powder XRD reveals that there is increase in the intensity of the peaks for pure ZTS crystal inferring some slight changes in structural parameters. FTIR reveals some slight variation in vibrations frequencies and secondary vibrational bands found. UV-Visible spectra shows better transmittance with high optical properties, The SHG measurement shows the increased NLO efficiency for ZTS specimen.

***Keywords*—** SEST, SEM-EDS, Non-linear optic, ZTS.

INTRODUCTION

Non-linear optic (NLO) material showing second harmonic generation have been in demand over the last few decades due to technological importance in fields of optical communication single processing and instrumentation [1]. Recently ZTS has got a wide application in the production of crystal analyser for long wave X-ray spectrometer. Being a good non-linear optical material, ZTS possess piezoelectric, pyroelectric and elastic properties [2]. The NLO properties of metal complexes of thiourea have attracted singnificant attention in the last few years, because both inorganic and organic components contribute specifically to the process of SHG. Metal-organiccomplexes offer higher environment stability combined with greater diversity of tunable electronic properties by virture of the co-ordinated metal center. Many metal thiourea complexes possessing second-order NLO avtivities [3] and some of them centosymmetric in nature have been reported [4]. Tristhioureazinc(II)sulphate (ZTS) is a promising semiorganic NLO with high SHG efficiency and high laser damage threshold suitable for Nd:YAD laser. The relative SHG and laser damage threshold values for ZTS are comparable with that of KDP [5]. ZTS belongs to the orthorhombic system with the space group PCa21, (point group mm2) [6]. Investigation on SHG, laser induced damage, thermal properties, influence of PH on morphology, optical properties and growth rate of ZTS crystals have been reported [7]. Also the growth vibrational studies and defect characterization were reported in the literature [8]. The effect of doping on the properties of ZTS has been extensively studied [9]. Recently the effect of organic additives[10-11], Mn(II)[12],Ce(IV)[13], Cs(I5)[14], Mg(I)[15], organic solvent on ZTS on picric acid[16], are ported. In this paper ZTS mixed crystal is synthesized and grown by slow evaporation technique at room temperature. The effect 0f ZTS is studied using optical, single crystal XRD, powder XRD, FTIR, and SEM-EDS.

EXPERIMENTAL DETAILS

Crystal growth and Synthesis

Crystals were grown by slow evaporation solution growth technique. ZTS is prepared by mixing zinc sulphate hepta hydrate (EM) and thiourea(SQ) in the ratio 1:3 according to the chemical reaction---1 in the aqueous medium.

$$ZnSO_4 + 3[CS(NH_2)_2] \rightarrow Zn[CS(NH_2)]_3SO_4$$

Zinc Sulphate Thiourea Tristhiourea Zinc(II) Sulphate

In order to avoid decomposition, low temperature is maintained during thepreparation using deionised water. The product is purified by repeated crystallization. The crystal is grown by adding triply distilled water to zincsulphate and thiourea in a conical flask and stirred using magnetic stirrer for 3 hours then the contents in conical flask are filtered and the filtrate is kept for slow evaporation covered with holes on polythene sheet covered over the 450ml beaker. Bulk crystals are grown using optimized growth parameters after the formation of seed crystsls and harvested in

around 16to 25 days. Figure 1 shows photograph of Tristhioureazinc(ll)sulphate crystal.

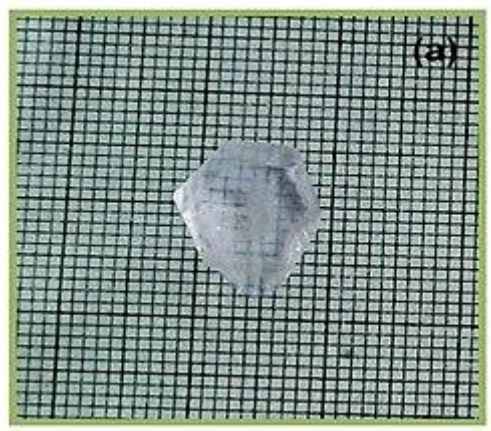

Fig.1. *Images of (a) Pure ZTS*

Characterization Technique

The surface morphology was observed using a JEOL JSM 5610 LVScanning electron microscope which has a resolution of 3.0nm and an acceleration voltage of 0.3 to having the maximum magnification of 2,00,000 times. EDS is a chemical microanalysis technique performed in conjucation with a SEM. The EDS X-ray detector measured the number of emitted X-ray photons and their energy. Single crystal X-ray diffraction studies were carried out using Bruker AXS (Kappa APEX II) X-ray diffractometer. Powder XRD can provide information about crystalline structure (or lack thereof) in a sample even when the crystal size is too small for single crystal X-ray diffraction. Fourier transform infrared spectra were recorded using AVATAR 370 FTIR spectrometer. UV-Visible spectra were recorded using spectrophotometer JASCO V530. The second harmonic generation test on the crystal was performed by the Kurtz powder SHG method.

MATERIALS AND METHODS

Scanning Electron Microscopy (SEM) With Energy Dispersive X-Ray Spectroscopy (EDS)

[SEM study JEOL JSM 5610lv] gives information about the surface nature and its suitability for device fabrication, also used to check the presence ofimperflections. The effectiveness of different impurities in changing the surface morphology is different has been reported [17]. Figure 2. shows the scanning electron micrographs recorded for undoped and as grown ZTS crystals. The micrograph (a) depicts the surface features of the undoped specimen and shows a resonably good uniform surface with some roughness which could be due to impurities.

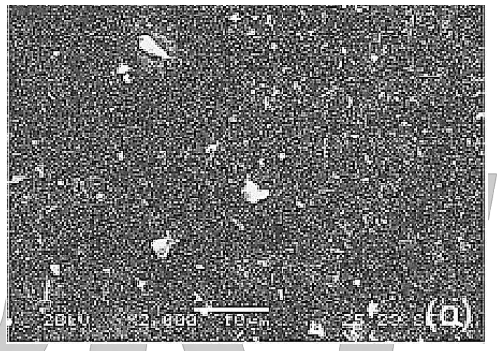

Fig 2. *SEM graph of (a) Pure ZTS*

The doping of zinc resulting in its incorporation into the crystalline matrix is well confirmed by EDS picture 3. The higher concentration of Zn into the thiourea crystalline matrix can be clearly seen in the graph. The accommodating cabability of Zinc on the surface of the crystal in also non-uniform.

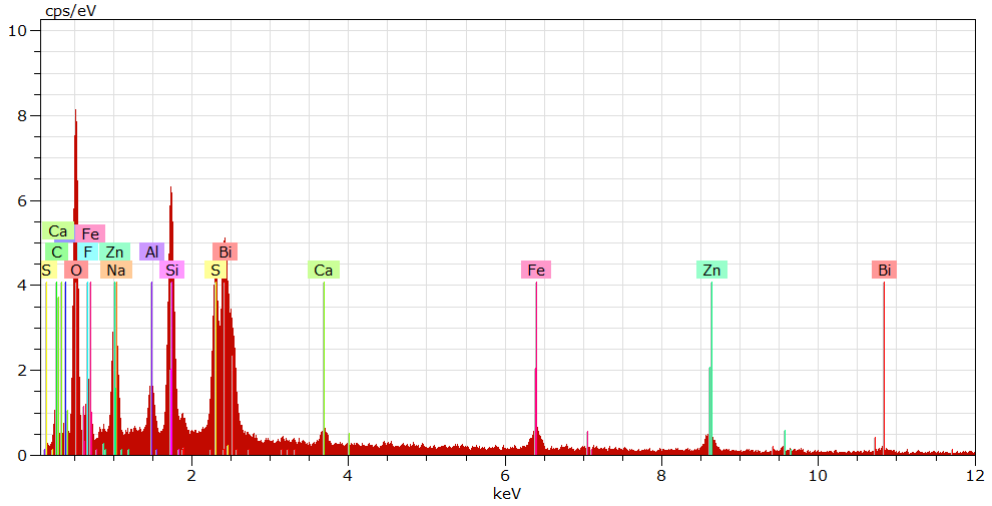

Fig 3. *EDS graph of Zn doped TU crystal*

Single Crystal X-Ray Diffraction

Single crystal X-ray diffraction studies were carried out using Bruker AXS (Kappa APEX II) X-ray diffractometer. Data were collected on a diffractionsystem, which employs graphite mono chromated Mo Kαradiation (λ = 0.71073Å). The table - 1 shows the cell parameters values for pure and Bismuth doped ZTS crystals. The pure ZTS crystal belongs to orthorhombic system with a =7.794A0, b=11.152A0, c=15.49A0, and space group Pca21.

Table 1. *The cell parameter values of ZTS and Bi doped ZTS crystal*

Lattice Parameter Values	**a**	**b**	**c**	**v**	**System**
ZTS	A^0	A^0	A^0	A^{03}	Orthorhombic
	7.794	11.152	15.49	1348	

Powder X-Ray Diffraction Analysis

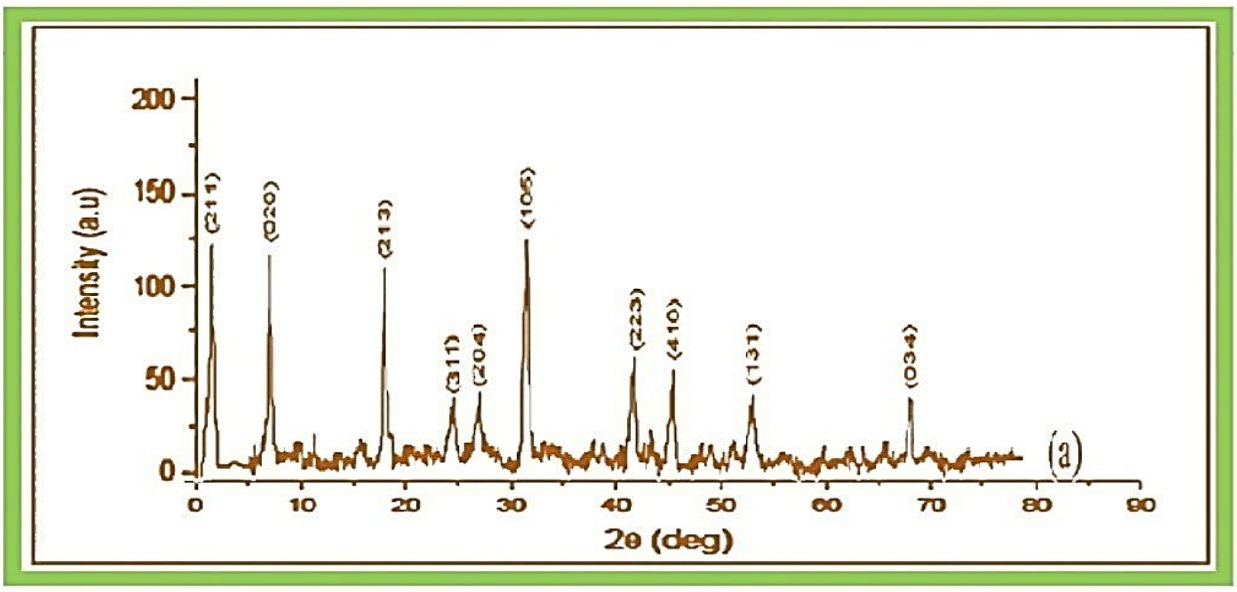

Fig 4. *Powder XRD graph of Pure ZTS*

The powder X-ray diffraction analysis was performed with a graphite mono chromate Cukα radiation. The XRD pattern of ZTS crystal grown rapidly shows in the case of pure ZTS crystal, there is no change in basic structure except for the slight variation, increase intensity in peaks may be due to zinc on TU (Figure 4). The XRD data is analysed with Rietveld method with RIETAN-2000. From XRD, the slight increase in intensity of ZTS specimen could be due to large particle size which could be calculated using scherrer equation.

t= K λ/(β cosθ).

Where

t-averaged dimension of crystallities

k- scherrer constant (assumed to be)

λ-wavelength of x-ray

Ø-peak position measured in radiation

β-integral breath of reflection (in radian2θ)

The granularity of the doped crystal is 18.9nm. It appears that the Zinc doping does not inhibit the growth of the crystals, and also the preferred orientations for the specimens.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra are recorded for pure ZTS crystals by using AVATAR 330 FT-IR instrument by KBr pellet technique in the range 400-4000cm-1Fig 5, shows the prominent peaks in the FTIR pattern of pure ZTS crystals. The peak obtained at 3376cm-1 in pure is due to N-H stretching. A peak at 3306cm-1 is due to O-H stretching in specimen. The peak 1627cm-1 indicates the c=o stretching. The vibrational frequencies obtained in the range 1398 to 1123cm-1 in the pure specimen is shifted to higher frequency range 1435.74 to 1126cm-1 which could be due to sulphate part of the molecule in the specimen.

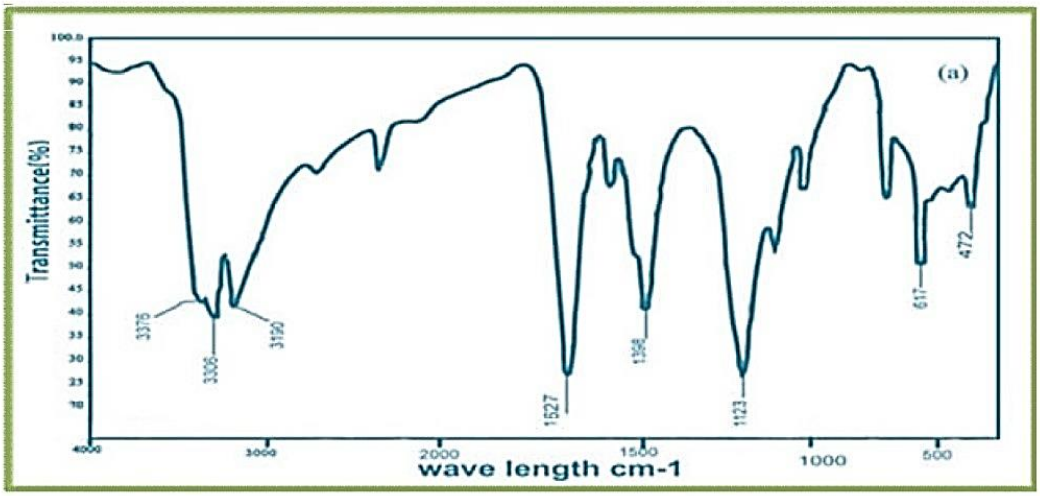

Fig.5 *FTIR Spectra of (a) pure ZTS*

UV-Visible – NIR Spectroscopy:

UV-visible absorption spectrum of pureZTS crystal in the range 200-800nm is shown in figure 6. The high transmittance in the visible region could lead to the applications of this crystal in optical window. The lower cut off wavelength of pure ZTS is 250~nm. The band gap energy for doped and pure specimen is calculatedas 4.972ev for pure ZTS using the formulae.

$$E_g = h c / \lambda_{max}$$

$E_g = 1.243 \times 103 / \lambda$ max

Where

h – Plank constant

c – Velocity of light

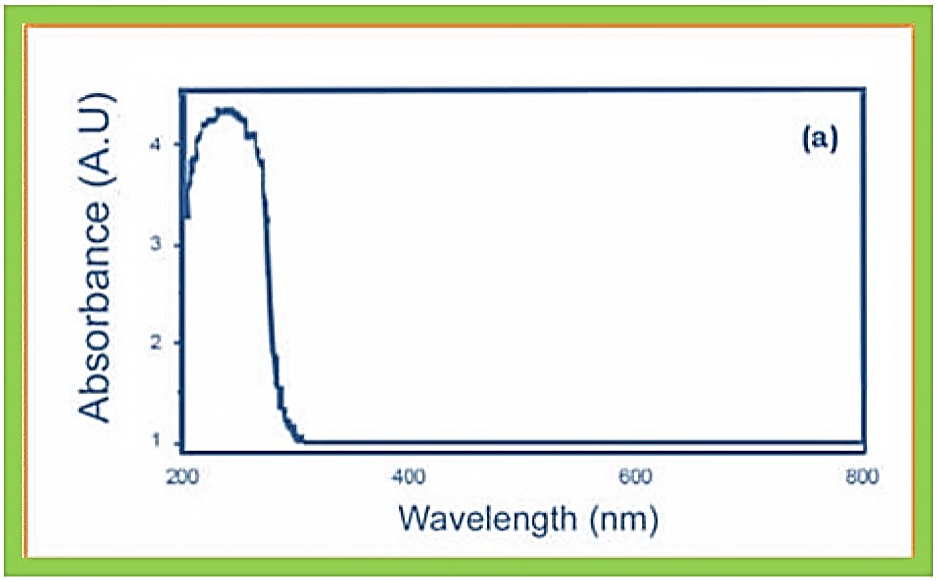

Fig.6 *UV Spectra of (a) pure ZTS*

SHG efficiency

SHG test on the crystals well performed by Kurtz powder SHG method [18]. An Nd:YAG laser with a modulated radiation of 1064nm was used as theoretical source and directed on the powdered sample through a filter. The doubling of frequency was confirmed by the green radiation of532nm.The SHG output for the specimen of ZTS is given in table-2. The input radiation used is 5milliboise | pulse output intensity of SHG gives relative value of NLO efficiency of the material. From the table-2 it is clear that the NLO efficiency of doped ZTS crystal is better.

Table 2. SHG Output

SYSTEM	I2GƆ(mV)
ZTS	48-49

CONCLUSION

Using XRD, FT-IR, SEM-EDS, and kurtz powder techniques, the effect of ZTS crystals has been investigated in our present study. The surface morphology of the crystal was studied from SEM and EDS Confirmthe presence of Zinc in the ZTS specimen and a slight variation in the intensity of the pure ZTS specimen, it also exhibits decreased vibrational peaks in FT-IR of pure ZTS. The single crystal XRD shows that ZTS belongs to orthorhombic system. A better transmittance with high band gap energy obtained for ZTS specimen gives the application in optical windows.

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