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Growth, optical, theoretical and dielectric studies on ZTS single crystals

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ABSTRACT

Semi organic single crystal of pure and doped ZTS are grown by slow evaporation method from its aqueous solution. It's a very good non linear optical material. The fully grown crystals were then characterized by Single crystal XRD to determine the cell parameters, space group and the system to which it belongs. Basic data such as valance electron plasma energy, Penn gap, Fermienergy and electronic polarizability were calculated. The optical absorption spectrum recorded in the wavelength range 200nm to 2500nm and its energy gap (Eg) was also calculated. The dielectric measurement was carried out to study the different polarization mechanism and conductivity of the crystal.

Keywords*:* Solution growth; XRD; Optical; Dielectric.

INTRODUCTION

NLO materials play an important role in the field of fiber optical communication laser technology, optical single processing and also used in the area of opto-electronics, telecommunication, and optical storage devices due to their potential applications in emerging optoelectronic technologies[1 to 6]. In the order to satisfy the day to day technological requirements, many scientists focused their attention on the growth of materials which have a good nonlinear optical behavior and be optically transparent in the visible and near IR regions. Recent works shows that the organic crystals have been very large nonlinear susceptibilities than the inorganic one, but it has low laser damage threshold, inadequate transparency, poor optical quality, lack of robustness, inability to produce large crystals. In the case of inorganic NLO materials, through they have relatively modest optical linearity's due to the lack of extended π – electron delocalization [7,9]. Hence in the several years research is focused on new types of NLO materials which combine the advantages of organic and inorganic materials called semi organic materials. Two types of semi organic material include organic and inorganic salts and metal organic coordination complexes. Due to the high optical nonlinearity and chemical flexibility of organics combined with temporal and thermal stability and excellent transmittance in UV visible region metal organic complexes have great attention in NLO field. The thiourea is an inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bon. ZTS is a potential semi organic nonlinear material and crystallizes in the non centrosymmetric orthorhombic space group $Pca2_1$, and point group mm2. Though the SHG efficiency of ZTS is

reported to be greater than that of ZTC. Fundamental parameters like plasma energy, Penngap, Fermi energy, particle size, dislocation density and strain values were calculated.

MATERIALS AND METHODS

ZTS single crystals were grown from aqueous solution by slow evaporation technique using water as a solvent. The crystals was synthesized with a ratio of 1:3 using the following equation

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

The solution of zinc sulfate was added to Tris thiourea and the mixture is stirred vigorously to avoid precipitation of other phases. The solution is placed at room temperature for evaporation process. After a time span of 45 days a good quality single crystal was harvested from the mother solution.

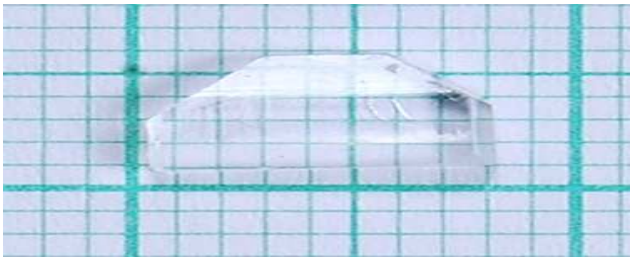

Fig. 1. Photograh of as growth ZTS crystal

RESULTS AND DISCUSSION

1. X-ray diffraction analysis

Diffraction analysis was carried out by ENRAF NONIUS CAD -4 X-RAY diffractometer.The XRD study reveals that the crystal belongs to orthorhombic system with space group Pca21 and lattice parameters a =11.159Å, b =7.792Å, c =15.527Å, cell volume V =1351Å3 and $\alpha=\beta=\gamma=90^0$ which is in agreement with that of reported values [10-12]. The molecular weight of the grown crystal is M = 389.8 g, and total number of valence electron is Z = 102. The density of the grown crystal was found to be 1.91 mg/m^3 and dielectric constant at 1 MHz is εr =126.29. The plasma energy , ħωp is

$$\hbar\omega_p = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \quad (1)$$

where
Z =102 valence electrons, ρ is the density and M is the molecular weight of the ZTS single crystal. The plasma energy is terms of Penn gap and Fermi energy [13] as,

$$E_p = \frac{\hbar\omega_p}{(\varepsilon_r-1)^{\frac{1}{2}}} \quad \text{and} \quad (2)$$

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (3)$$

Polarizability ,α is obtained using the relation [14]

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2}\right] X \frac{M}{\rho} X 0.396 X 10^{-24}\ cm^{-1} \quad (4)$$

where S_0 is a constant for a particular material , and is given by.

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2 \quad (5)$$

The value of α so obtained agrees well with that of Clausius – Mossotti equation ,which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho} \frac{\varepsilon_r - 1}{\varepsilon_r + 2} \quad (6)$$

where N is avagadro number and the fundamental data on the grown crystal of ZTS are listed in table 1. The pure ZTS have been charcterized by powder X-ray diffractiometer to verify the single phase nature of the sample. Table 2 gives the structural parameters from powder X-ray analysis. It shows that the FWHM increases towards increase in strain value and particle size and dislocation density also decrease.

Table 1 Some theoretical data for ZTS Single Crystal

Parameters	Values
Plasma Energy	20.36
Penn gap (eV)	1.82
Fermi gap (eV)	16.39
Polarizability (cm^3) Penn analysis	$7.83x10^{-23}$
Clasius Mossottiequation	$7.901x10^{-23}$

Table 2 gives the structural parameters from powder X-ray analysis.

The particle size

$$D = \frac{0.94\lambda}{\beta cos\theta} \quad (7)$$

Where $\lambda = 1.5405X10^{-10}$

β = Full width half maximum

Dislocation density

$$\delta = \left(\frac{1}{D^2}\right) lin/m^2 \quad (8)$$

and strain value is

$$\varepsilon = \left(\frac{\beta cos\theta}{4}\right) lin^2\, m^{-4} \quad (9)$$

Table 2 Structural Parameters for ZTS

S.no	FWHM(β) deg	Particle Size (D) nm	Dislocation density(δ) kg/m^3	Stain(ε) $lin^{-2}m^{-4}$
1	0.04	$3.67*10^{-9}$	$7.41*10^{16}$	0.009855028
2	0.08	$1.83*10^{-9}$	$2.98*10^{17}$	0.019755824
3	0.12	$1.24*10^{-9}$	$6.53*10^{17}$	0.02963784
4	0.16	$9.29*10^{-10}$	$1.16*10^{18}$	0.058610583

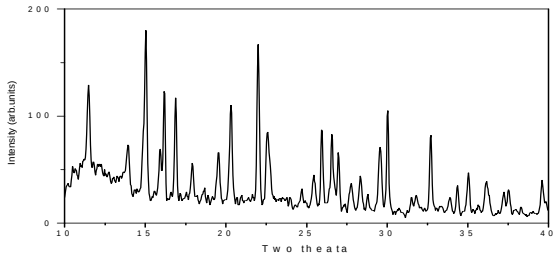

Fig. 2. Powder XRD Pattern of ZTS

4. Optical absorbance

Fig 3 shows optical absorption spectrum of single crystal recorded in the wave length region 230 -2500 nm using VARIEN CARY 5E UVV- VIS NIR spectrometer. The absorption spectrum reveals that the crystal has lower

cutoff wavelength at 273 nm. The absorption near UV region is associated electron with absorption within thiourea units of ZTS . The optical absorption coefficient (α) was calculated using the following relation

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 the relation for high photon energy (hν).

$$\alpha = \frac{A(h\nu - E_g)^{\frac{1}{2}}}{h\nu} \quad (10)$$

where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h_\nu)^2$ against hν is shown in figure 4. The band gap is found to be 4.453 eV.

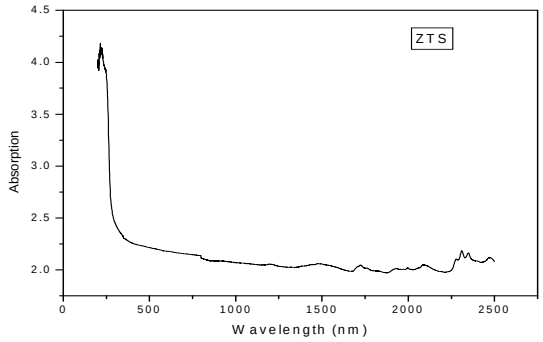

Fig. 3. Optical absorption spectrum

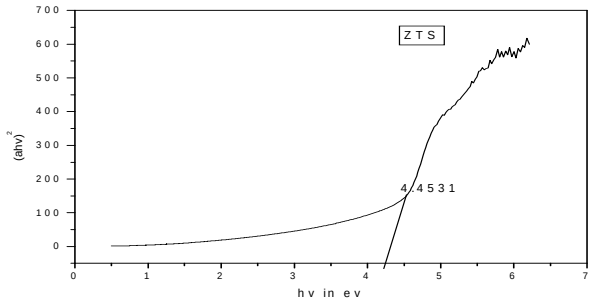

Fig. 4. Tauc's plot for hν versus $(\alpha h_\nu)^2$

5. Dielectric studies

Single crystals of ZTS of dimensions 8X4X6 mm^3 were subjected to dielectric studies for different temperature and various frequencies ranging from 1 KHz to iMHz using HIOKI 3532-50 LCR HITESTER. The dielectric parameter as a function of frequency is described by the complex permittivity in the form.

$$Є(\omega) = Є_r(\omega) – Є'(\omega) \quad (11)$$

Where $Є_r$ real part and $Є'(\omega)$ imaginary part are the components for the energy storage and energy loss respectively in each cycle of the electric field.

For the dielectric characteristic of pure ZTS sample, the measured capacitance C(ω) was used to calculate the dielectric constant Є(ω) using the following expression.

$$\varepsilon(\omega) = \frac{Cd}{\varepsilon_0 A} \quad (12)$$

Where d is thickness of the sample and A is surface area of the sample and $Є_0$ is premitivity of free space. Where as for dielectric loss Є' (ω);

Є'(ω)=Є(ω)tanδ(ω) and (13)

We can find dielectric modulus from calculated the above the relation. In complex form dielectric modulus is

$$M^* = \frac{1}{\varepsilon^*} = M' + iM'' \quad (14)$$

Where M' real part of the dielectric modulus is given by

$$M' = \frac{\varepsilon'}{((\varepsilon')^2+(\varepsilon'')^2)} \quad (15)$$

And M'' imaginary part of the dielectric modulus is given by

$$M'' = \frac{\varepsilon''}{((\varepsilon')^2+(\varepsilon'')^2)} \quad (16)$$

The relaxation time of the orientation of dipoles can be calculated using the imaginary part of the dielectric modulus

$$\tau = \frac{1}{\omega} \quad (17)$$

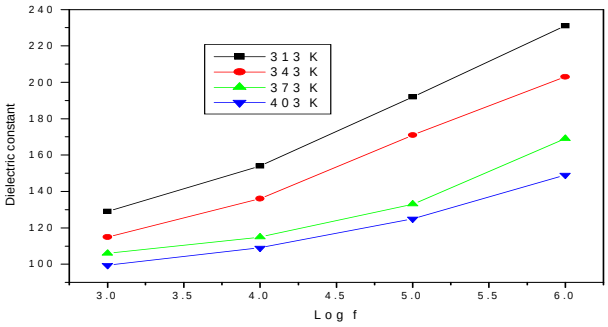

Fig. 5. Log f against Dielectric constant

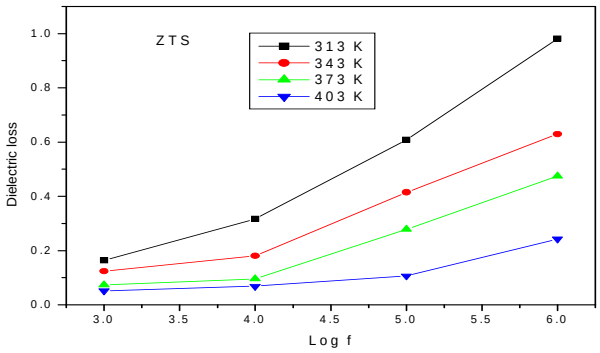

Fig. 6. Log f against Dielectric loss

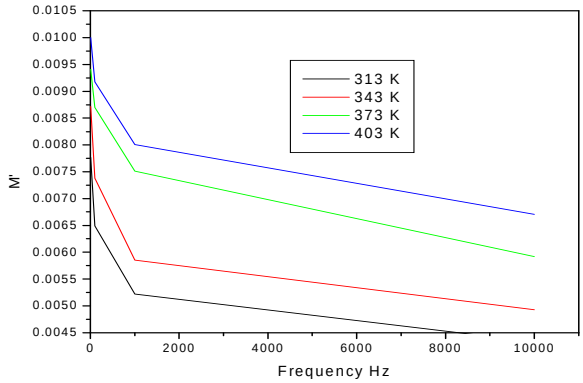

Fig. 7(a). Variation of frequency with real part of modulus

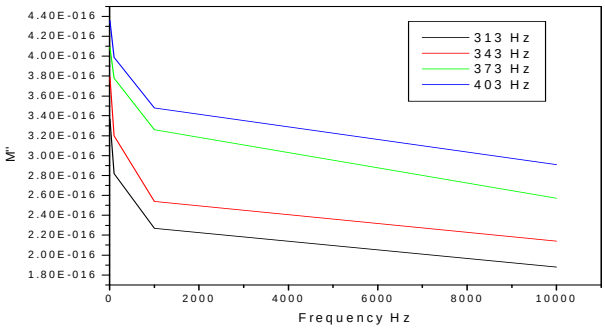

Fig. 7(b). Variation of frequency with imaginary part of modulus

The variation of dielectric constant and frequency at different temperature is shown in figure 5. From the figure the dielectric constant increases with the increase in frequency. The higher value of dielectric constant at higher frequency is important for the fabricatioin of materials. The value of dielectric constant at lower frequency may be due to the presence of all the polarization, namely electronic, ionic, orientatiional, space charge polarization and its higher values at higher frequencies may be due to the increase of significance of these polarization gradually. The dielectric loss also studied as a function of frequency at different temperature and is shown in figure 6. These curves suggest that the dielectric loss is independent of frequency of the applied field, similar to that of dielectric constant. Figure 7(a) and (b) show the estimated value of the real and imaginary part of electrical modulus. The value at low frequency region (below 1KHz for real and imaginary modulus) indicates the removal of electrode polarization [15,16]. The relaxation time is $1.57X10^{-7}$.

CONCLUSION

Single crystals of ZTS have been successfully grown by slow evaporation from aqueous solution. Single crystal XRD analysis confirmed that the crystals belong to orthorhombic system with the space group Pca21. The band gap energy of ZTS calculated from the optical absorption spectrum is about 4.453 eV. The basic parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal are also been estimated. The dielectric constant increases with increasing frequency at different temperatures. Dielectric modulus of real and imaginary part calculated from dielectric constant and loss factor and relaxation time estimates is $1.57\ X10^{-7}$.

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