Growth, Optical and Electrical Properties of zinc tris (thiourea) sulphate (ZTS) Single Crystals

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ABSTRACT

Single crystals of Zinc Tris (thiourea) Sulphate (ZTS) exhibiting high transparency were grown by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic system. The optical absorption study reveals the transparency of the crystal and is noticed in the entire visible region and the cut-off wavelength has been found to be 270 nm. The optical band gap was found to be at 3.55 eV. The dependence of extinction co-efficient (K) and the refractive index (n) on the wavelength have been observed. The electrical properties of the grown crystal have also been studied using the Cole–Cole plot.

Keywords

Single crystal, slow evaporation technique, Single crystal X-ray diffraction.

1. 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 nonlinear response of the crystal is due to the application of strong sources of electric field which gives rise to the second and higher order nonlinear properties like second harmonic generation, d-c rectification, frequency mixing, sum generation and self focusing [3]. One can explore all these nonlinear effects from the asymmetric systems by attributing them into high intense optical beam. The performance of the organic NLO materials in the optical region placed a great demand on these materials owing to which, several attempts have been made by the scientists to identify the good quality nonlinear organic crystals. The search for new frequency conversion materials in recent years has concentrated on semi-organic complexes in which many optically active organic amino acids are mixed with the inorganic salts in order to enhance their physical and chemical properties. 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 [4-8]. In this present investigation we report the growth, optical and electrical properties of semi-organic Zinc Tris (thiourea) Sulphate (ZTS) single crystals.

2. SYNTHESIS

The starting materials Zinc sulphate heptahydrate and thiourea (AR grade) were dissolved in millipore water (18.2 MΩ cm^{-1}) in mole ratio of 1:3 at room temperature. The prepared solution was stirred well for 3 hours using a magnetic stirrer to avoid coprecipitation of the material and clear solution was obtained. The solution was taken in a covered container for controlled evaporation and kept at room temperature. After 25 days the ZTS material was crystallized at the bottom of the container. The synthesized material was purified by repeated recrystallization process and used for the growth of crystals. The grown ZTS crystals are shown in figure 1.

3. RESULTS AND DISCUSSIONS
3.1 Single Crystal X-ray Diffraction Studies

Single crystal X-ray diffraction analysis for the grown crystal has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer with MoKα radiation (λ=0.71703 Å). It is found that the grown crystal belongs to orthorhombic crystal system with space group Pca2$_1$ and the lattice parameters are a = 11.126 Å, b= 7.773 Å and c= 15.491 Å which agree well with the reported literature [9].

3.2 Optical Transmission Studies

The UV–Vis transmission spectrum of ZTS crystal has been recorded in the range 200–1000 nm by varian 5E UV-Vis-NIR spectrophotometer and the spectrum is shown in figure 2. Low absorbance is observed throughout the visible and IR region. The cutoff wavelength of the ZTS crystal is found to be 270 nm.

The optical absorption co-efficient (α) was calculated using the following relation

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

where 'T' is the transmittance and 'd' is the thickness of the crystal.

As a direct band gap material, the crystal under study has absorption co-efficient (α) obeying the following relation for high photon energies ($h\nu$)

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

where E_g is band gap and A is constant.

The graph between $(\alpha h\nu)^2$ and $(h\nu)$ is shown in figure 3 and the band gap (E_g) of the crystal was calculated as 3.55 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [10].

3.3 Determination Of Optical Constants

The optical constants, refractive index (n) and extinction coefficient (K) were determined from the transmission (T) spectrum. The transmittance of the crystal [11] is

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \qquad (3)$$

where t is the thickness and α is related to extinction coefficient K by

$$K = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Figure 4 shows the plot of extinction co-efficient (K) as a function of wavelength. From the graph it is clear that the value of extinction coefficient (K) decreases with the increase of wavelength. The refractive index (n) can be determined from the reflectance (R) using the relation [12].
The Reflectance (R) is written in terms of refractive index (n)

as $$R = \frac{(n-1)^2}{(n+1)^2} \qquad (5)$$

It can also be written in terms of absorption coefficient as

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \qquad (6)$$

From the above equation, the refractive index n can be derived as

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \qquad (7)$$

It is clear from the figure 5 that refractive index (n) decrease as the wavelength increases. Thus both the values of extinction coefficient (k) and refractive index (n) depend on

wavelength. The internal efficiency also depends on photon energy. Hence by tailoring the photon energy, one can achieve the desired material for optical device fabrications.

3.4 Electrical Conductivity Studies

Electrical conduction takes place as a result of electron jump from the low valence state to high valence state as well as movement of ions. The d.c electrical conductivity (σ_{dc}) of the grown crystal at room temperature is determined using the relation

$$\sigma_{dc} = \frac{d}{AR_{dc}} \qquad (8)$$

where 'd' is the thickness of the grown crystal and 'A' is the area of the grown crystal and R_{dc} is the d.c resistance of the same crystal. The value of R_{dc} is evaluated from the Cole–Cole plot drawn between $Z' = Z \cos\theta$ and $Z'' = Z \sin\theta$ and is shown in figure 6. The d.c conductivity (σ_{dc}) determined from the Cole–Cole spectra at room temperature is found to be 10.66×10^{-5} mho m^{-1}. The low value of electrical conductivity of the crystal is due to a decrease in the mobility of the charge carriers by ion size, which leads to change in the electronic band structure [13].
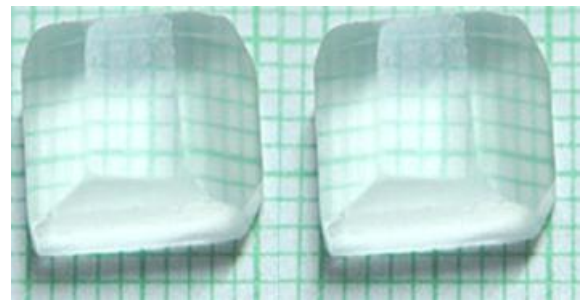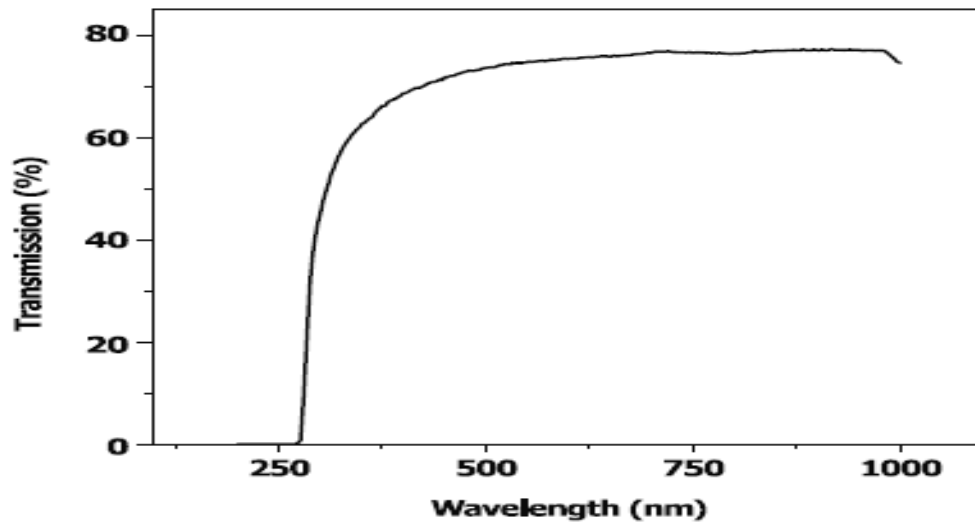

Figure.1 As grown ZTS crystal
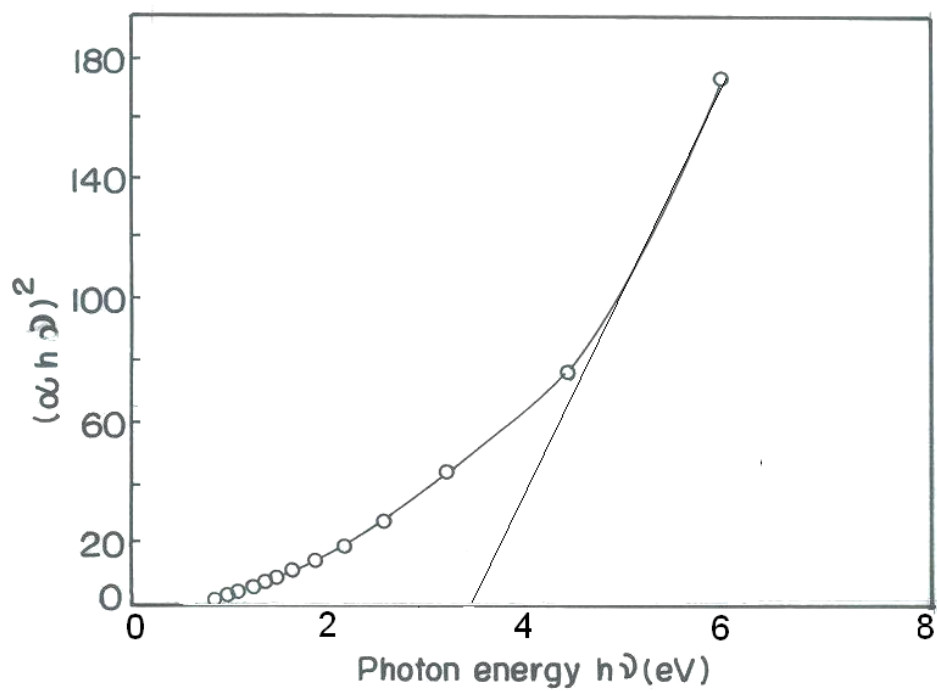
Figure 2. UV–Vis transmission of the ZTS crystal

Figure 3. $(\alpha h v)^2$ versus (hv) for ZTS crystal.

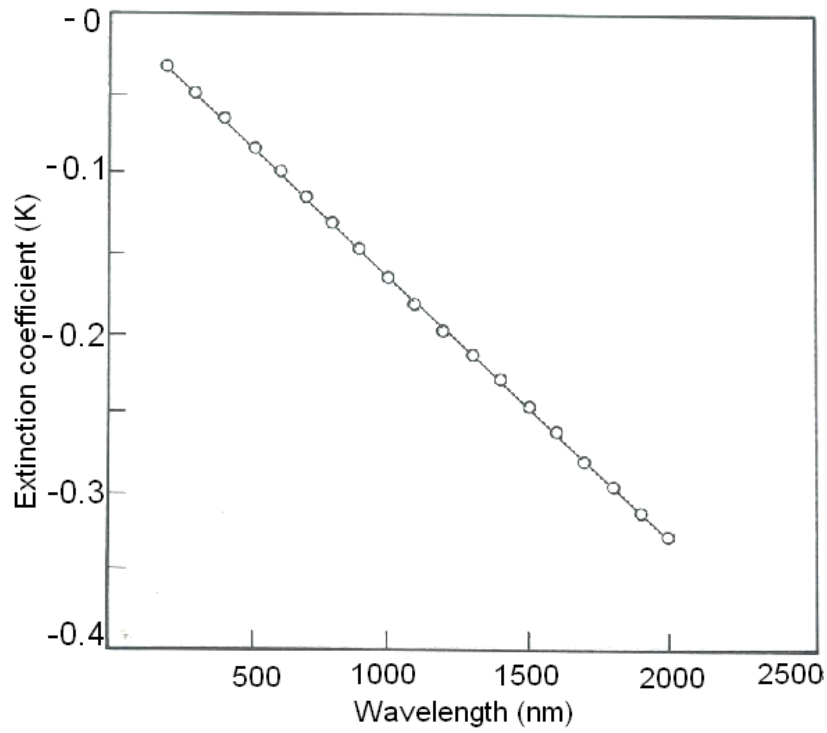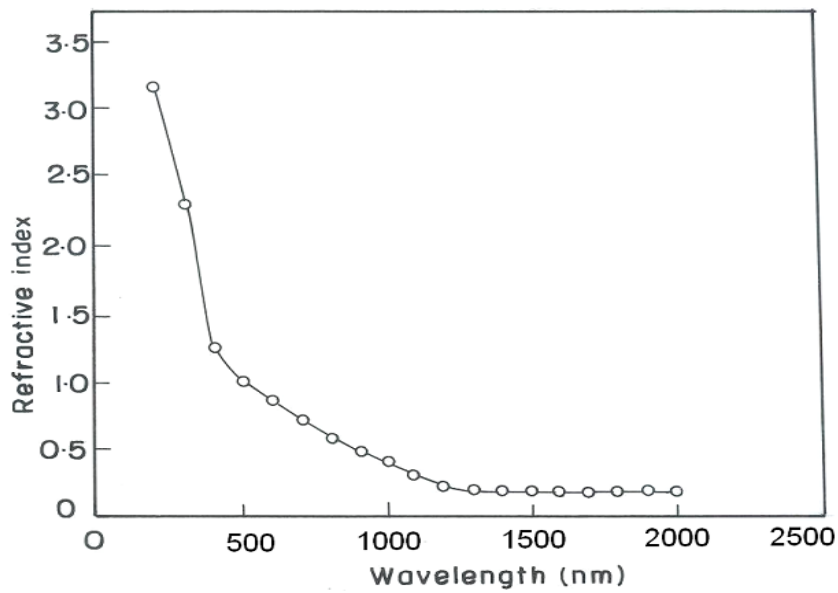Figure 4. Plot of extinction coefficient (K) versus wavelength

Figure 5. Refractive index (n) versus wavelength

coefficient (K) and refractive index (n) indicated the transparency of the crystal and confirmed its suitability for optical device fabrication.
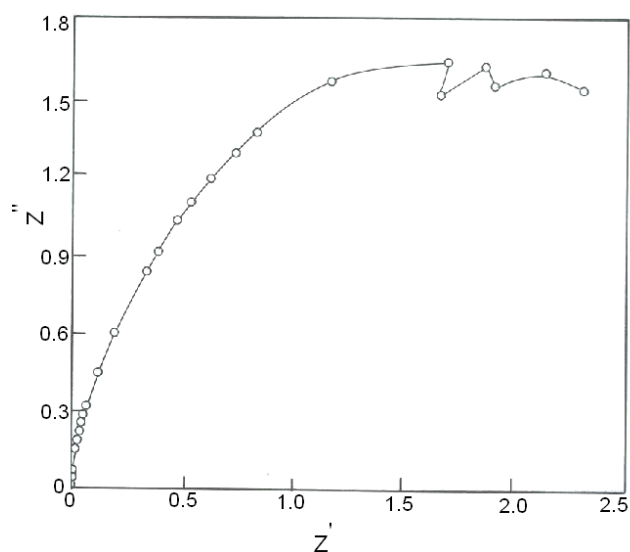

Figure 6. Cole–Cole plot.

4. CONCLUSION

Optically good quality single crystals of ZTS were grown by slow evaporation technique within a period of three weeks. The lattice parameters were determined from the single crystal XRD and it has been found that ZTS belongs to orthorhombic crystal system with space group $Pca2_1$. From UV transmission study, the band gap energy was found to be 3.55 eV. The optical investigation such as extinction

5.REFERENCES

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