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Synthesis, Growth and characterization of semi-organic zinc (tris) thiourea chloride crystal

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Abstract

Zinc (Tris) Thiourea chloride (ZTTC) a semi organic nonlinear optical material has been grown by slow evaporation process from its aqueous solution. The grown crystals were subjected to characterize by Single crystal X-ray diffraction, Powder X-ray diffraction, Fourier transform infrared spectroscopy, optical transmission spectrum and Dielectric studies. Single crystal X-ray diffraction studies confirm the orthorhombic structure. The FTIR spectrum analysis has confirmed the functional groups in the ZTTC. Its optical behavior was examined by UV-Vis and found that the crystal is transparent in the region between 841-2000 nm. Dielectric study shows that the dielectric constant decreases with increase in frequency.

Keywords: ZTTC, semiorganic crystal, slow evaporation process; dielectric studies

INTRODUCTION

Non linear optical (NLO) materials find wide applications in the area of optical devices such as optical communication, optical computing, harmonic generator, medical diagnostics, frequency mixing and optical switching [1-3]. The investigation on organic NLO materials show large optical nonlinearities due to polar and highly conjugated p electron system terminated with donor and acceptor groups. However, due to poor mechanical and thermal properties most of the organic materials are susceptible to damage [4]. Hence, in last several years search 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 [5–10]. The metal organic complexes attracting great attention in nonlinear optical field due to high optical nonlinearity.Among the semi organic nonlinear optical materials, metal complexes of thiourea which have low UV cut off wavelengths, applicable for high power frequency conversion have received much attention [11-13]. These materials are potential semi organic material with high laser damage threshold and large NLO coefficient [14], because of the presence of large dipole. Thiourea can form number of coordination compounds like Bis thiourea zinc chloride (BTZC), Bis thiourea cadmium chloride(BTCC), Copper thiourea chloride(CTC), Zinc (tris) thiourea sulphate (ZTS), Bis thiourea cobalt chloride(BTCoC), Tetra thiourea copper chloride (TTCC), Tris (thiourea) cadmium sulphate (CTS), Potassium thiourea bromide(PTB) etc are of metal organic coordination. In this paper we report the results of our work on the growth of ZTTC crystal along with the characterization by single XRD, powder XRD, Fourier transform infrared spectroscopy (FTIR), UV visible spectral study and dielectric studies.

EXPERIMENTAL PROCEDURE

Single crystal of ZTTC was grown from a saturated aqueous solution containing thiourea and zinc chloride in a molar ratio 3:1. A necessary quantity of thiourea is taken in a beaker and dissolved in deionised water at room temperature. After preparing clear solution of thiourea, the proportional amount of zinc chloride is added little by little with continuous stirring of the solution for bringing a homogenous mixture. The prepared solution of pH value 3 was filtered and allowed to evaporate slowly at room temperature. Colorless good optical single crystal of ZTTC with size 20×7×3 mm^3 was harvested. Purity of the crystal was improved by successive recrystallization process. The photograph of the as grown single crystal is shown in Fig1. The expected chemical reaction is as follows,

$$3[CS\,(NH_2)_2] + ZnCl_2 \rightarrow Zn.\,[CS\,(NH_2)_2]_3).Cl_2 \quad \text{---- (1)}$$

Fig 1. As-grown crystal of ZTTC

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Characterization studies

The crystalline nature of the grown crystals was confirmed with powder X-ray diffraction pattern recorded using PHILIPS 'X'Pert Pro Radiation CuK$_\alpha$ X-ray diffractometer.The crystalline phase and size of the products were determined by X–ray powder diffraction (XRD) by using a Seifert (JSO-DEBYEFLEX 2002) diffractometer with Cu-Kα radiation (λ=0.1540nm). To identify the elements and the functional groups present in the grown crystal, FTIR spectrum was recorded using Perkin Elmer FTIR spectrometer. The optical transmission spectrum of the ZTTC crystal was recorded using Carry 5E UV-Vis-NIR spectrophotometer in the range of 350 - 2000 nm. Transparent polished crystals of rectangular dimension 5x3x1 mm^3 was selected for dielectric studies using HIOKI 3532-50 LCR HITESTER.

RESULTS AND DISCUSSION

Single Crystal X-Ray Diffraction

X-ray diffraction studies were performed to reveal the crystal structure of the grown crystal. The calculated lattice parameters are a=13.02 Å, b=12.76 Å, c=5.891 Å and the crystal belongs to the orthorhombic system.

Powder X-Ray Diffraction Analysis

The grown crystal of ZTTC has been subjected to powder X-ray diffraction. Powder form of the above mentioned crystal was taken for the analysis with a scan speed of 1 °/min. The indexed powder X-ray diffraction pattern of the grown crystal is given in fig 2. The obtained 2θ values are used for indexing using the PROSZKI software package. The well defined and sharp peaks signify the good crystalline nature of the sample.

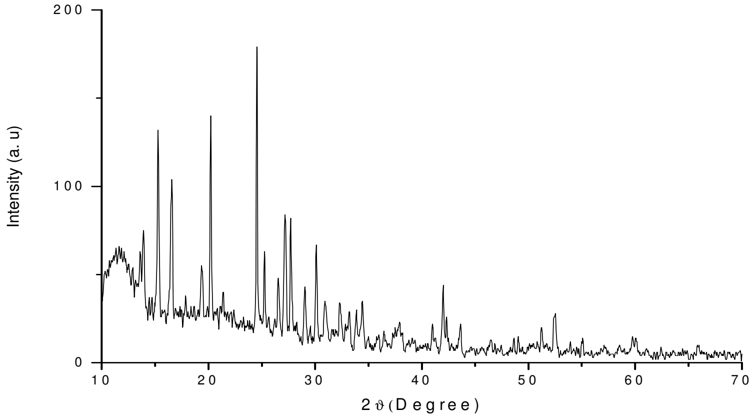

Fig 2. Powder X-ray diffraction pattern.

Fourier Transform Infrared Analysis

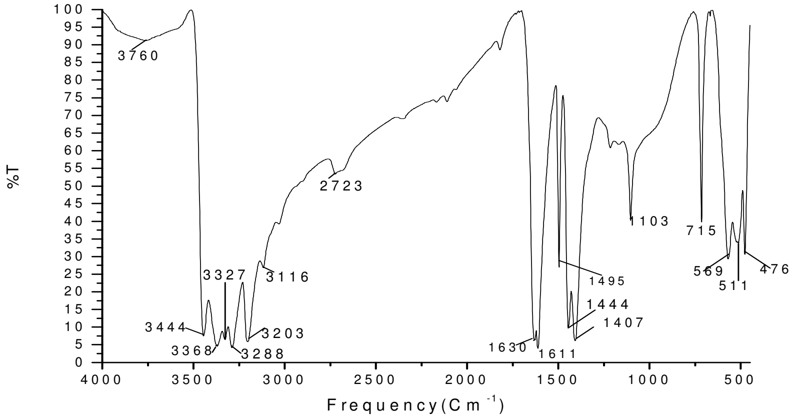

Fig 3. FTIR spectra of ZTTC crystal

The FTIR spectral analysis for the grown crystal was recorded in the range 400-4000cm^{-1} Using KBr pellet technique and the resultant spectrum is depicted in Fig 3. The broad band lying in the range 3500-1600 cm^{-1} corresponds to NH stretching of thiourea due to its hydrogen bonding interaction with chlorine site of the neighboring complex. The peak at 569 cm^{-1} in the spectra is assigned to symmetric NH$_2$ wagging vibration. Strong absorption band at 1103 cm^{-1} in the spectra due to NH$_2$ rocking vibration. In ZTTC crystals, C=S is bonded to Zn^{2+} whereas in pure thiourea it is bonded to NH$_2$. Therefore C-S bonding mode is also shifted to lower values from 730 to 715 cm^{-1}. The peaks at 1611 and 1631 cm^{-1} in the spectra are attributed to NH$_2$ asymmetric bending vibrations. Absorption band at 511 cm^{-1} is due to symmetric NH$_2$ bending vibrations. Peak appears at 1495 cm^{-1} due to N-C-N asymmetric stretching vibration. The peak at 476 cm^{-1} is due to N-C-N bending vibration. The absorption at 1444 and 1407 cm^{-1} can be assigned to C=S asymmetric stretching vibration of thiourea.

Optical transmission studies

The optical property of the ZTTC crystal was assessed by using UV-Vis spectrometer. The crystal is well polished and the specimen 2mm thick was subjected to transmission measurement in the spectral range of 350-2000 nm. The UV-Vis spectrum gives limited information about the structure of the molecule, because the absorption of UV and visible light involves promotion of the electron in σ and π orbital from the ground state to higher energy states [15]. Fig 4 shows the transmission curve, in which the lower cut off wavelength is obtained at 356 nm. Further it is found that the maximum transmission of the grown ZTTC single crystal is in the visible NIR region than that of the visible region.

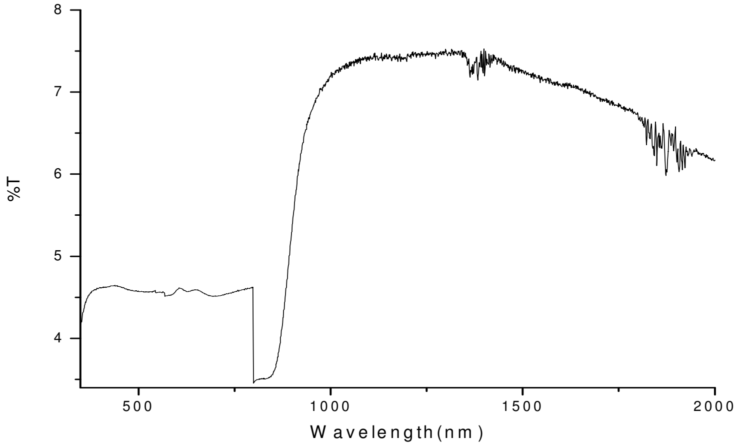

Fig 4 . Transmission spectrum of ZTTC.

Dielectric Studies

Dielectric measurements were carried out on a ZTTC crystal of dimensions 5×3×1 mm^3.

The dielectric constant and dielectric loss have been calculated using the equation (2) and (3).

$\varepsilon = Cd/A\varepsilon_0$ --- (2)

$\varepsilon' = \varepsilon \tan\delta$ --- (3)

where d is the thickness of the specimen, and A is the area of the sample. The observations are made in the frequency range 50 Hz-5 MHz at different temperature (308, 313.318 and 323 K). Dielectric constant and dielectric loss measurements of ZTTC crystal are shown in Fig 5 and 6. It is noted from the Fig 5 that the dielectric constant decreases exponentially with increasing frequency and attains lower values at different temperature. The value of ε_r at lower frequency may be due to the presence of all the polarization, namely electronic, ionic, orientational and space charge polarization and its low value at higher frequencies may be due to the loss of significance of these polarization gradually. The very high value of ε_r at lower frequency might be due to the space charge polarization. It is observed that the dielectric constant of the material is most probably same within the temperature range 308-313K and 318-323 K. It is evident from the Fig. 6 that the crystal has very low dielectric loss in higher frequency region, which indicates the enhanced optical quality of the sample with lesser defects. The variation in the value of ε_r is marginal in the frequency range 1 KHz-5 MHz. It is further noted that the dielectric constant (Fig 7) decreases with temperature.

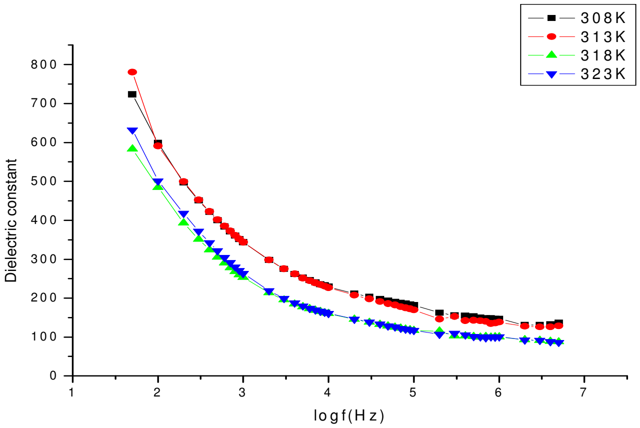

Fig 5 . Variation of dielectric constant of ZTTC with log frequency.

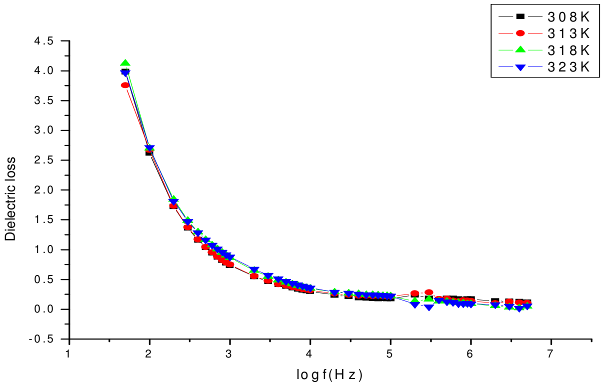

Fig 6 . Variation of dielectric loss of ZTTC with log frequency.

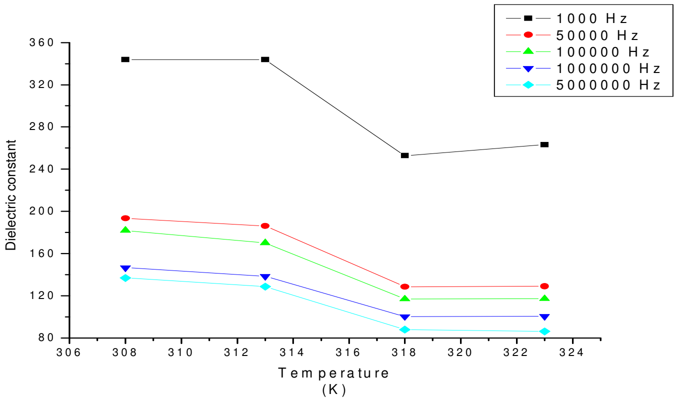

Fig 7. Temperature dependence of dielectric constant for ZTTC single crystal

CONCLUSIONS

Transparent, colorless, crystal of Zinc (tris) thiourea chloride was successfully grown using the slow solvent evaporation technique. The single crystal X-ray diffraction studies confirm that the ZTTC crystal belongs to orthorhombic system. The functional groups were confirmed by FTIR analysis. UV-Vis spectrum reveals the optical transparency of the grown crystal. Dielectric studies show that the dielectric constant decreases with increase in frequency.

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