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Zinc (tris) thiourea sulphate (ZTS): A single crystal neutron diffraction study

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Abstract. The crystal structure of ZTS has been determined by neutron diffraction with a final R-value of 0.026. Using the structural parameters, the contributions from the structural groups to the linear optical susceptibility and linear electro-optic coefficients have been evaluated. Results showed a significant contribution from the hydrogen bonds in the structure.

Keywords. Crystal structure; neutron diffraction; electro-optical.

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1. Introduction

Non-linear optical crystals of inorganic salts incorporated with urea analogs have better chemical flexibility and good mechanical properties for use as devices. Zinc (tris) thiourea sulphate, $Zn(SC(NH_2)_2)_3SO_4$ (ZTS) is one such metal-organic crystal which is used for electro-optical (EO) applications and frequency doubling of near IR laser radiations. In this study, the crystal structure of ZTS has been obtained in detail by single crystal neutron diffraction technique. Using the structural parameters and an existing formalism [1] based on the theory of bond polarizability, the contributions from each of the structural groups in the unit cell to the total values of the EO coefficients of ZTS are estimated. Results are discussed.

2. Experiment

The ZTS crystal used in our experiment was grown by the research group at CAT, Indore [2]. Three-dimensional neutron intensities with $(\sin\theta)/\lambda \leq 0.51$ (Å)$^{-1}$ were recorded on a computer-controlled 4-circle neutron diffractometer at Dhruva reactor, BARC. Data were processed and corrected for absorption resulting in a set of 824 unique squared structure factors $(F_0)^2$. Starting from the reported [3] X-ray structural parameters (S.G. $Pca2_1$, cell parameters: $a = 11.126(5)$ Å, $b = 7.773(4)$ Å, $c = 15.491(5)$ Å), and using the $(F_0)^2$ values, the structure of ZTS has been

Table 1. Bond distances (in Å units) in ZTS.

Zn–O(1)	1.984(6)	S(1)–O(1)	1.463(7)	H(2)–O(3)	1.987(8)	H(7)–O(4)	1.843(7)
Zn–S(2)	2.330(4)	S(1)–O(2)	1.490(8)	H(4)–O(2)	1.868(9)	H(10)–O(4)	1.930(9)
Zn–S(3)	2.308(5)	S(1)–O(3)	1.458(9)	H(5)–O(3)	2.164(6)	H(11)–O(3)	2.035(9)
Zn–S(4)	2.310(5)	S(1)–O(4)	1.474(6)	H(6)–O(2)	2.056(9)	H(12)–O(1)	1.926(5)
	S–C	C–N					
tu_1	1.724(9)	1.31(1)	1.32(1)				
tu_2	1.723(9)	1.31(1)	1.31(1)				
tu_3	1.723(8)	1.30(1)	1.32(1)				

refined to a final $R(F^2)$ of 0.026 by the method of full-matrix least-square refinement. Parameters involving hydrogen atoms are determined in more detail than in the previous X-ray study [3]. Interatomic distances and angles (table 1), calculated from the refined parameters, are within the acceptable limits as found in similar structures reported.

3. Structure of ZTS

ZTS crystallizes in non-centrosymmetric symmetry with four formula units in the unit cell. The structure comprises three thiourea (tu) groups (tu_1, tu_2, tu_3) and $(SO_4)^{2-}$ ions (see figure 1). Each tu group consists of one carbon atom bonding to one sulphur and two nitrogen atoms. Each of the two nitrogen atoms in turn is connected to two hydrogens. Likewise, each Zn^{2+} ion is tetrahedrally coordinated to three sulphur atoms (in the three tu groups) and to an oxygen atom in the sulphate ion. This Zn-tetrahedral group is more distorted than $(SO_4)^{2-}$ ion group. The structure of ZTS also contains an interesting hydrogen bonding network. Some of the total 12 hydrogen atoms (in the asymmetric unit) which were identified in the present study form a ring of intramolecular H-bonds involving thiourea groups and sulphate ion.

4. Electro-optic coefficients

The linear EO coefficients (r_{ijk}) are given by

$$(r_{ijk}) = (r_{ijk})^{\text{ion}} + (r_{ijk})^{\text{el}}, \tag{1}$$

where the RHS terms are ionic and electronic contributions

$$(r_{ijk})^{\text{ion}} = (A_{kk}/B_{ij}) \sum (\beta_n/r_0)[F_{ijk} + G_{ijk}], \tag{2}$$

where

$$A_{kk} = \varepsilon_0(\varepsilon_{dck} - \varepsilon_k),\ B_{ij} = N(e_c)^* \varepsilon_i \varepsilon_j,\ F_{ijk} = f\alpha_{ni}\alpha_{nj}\alpha_{nk},$$
$$G_{ijk} = 1/2(\alpha_{ni}\delta_{jk} + \alpha_{nj}\delta_{ik}). \tag{3}$$

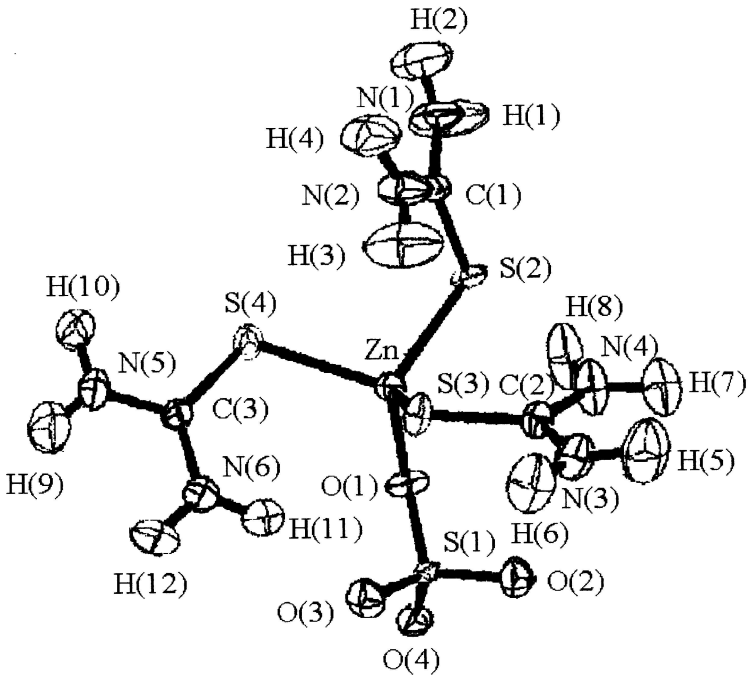

Figure 1. ORTEP drawing of the structure of ZTS.

The summation in eq. (2) is done over all the bonds in the unit cell. α_{ni}, α_{nj}, α_{nk} are the direction cosines and β_n is the bond susceptibility along the bond direction of the nth bond. $\varepsilon_{i,j,k}$ are the optical permittivities, N is the number of pairs of atoms in the cell, $(e_c)^*$ is the Callen effective charge which is related to the plasma frequency $\hbar w_{\mathrm{p}}$, f is the ionicity factor which is a function of Thomas–Fermi factor and bond covalency $f_c(=(E_h/E_g)^2$ where the E_h, E_g are the energy gaps). Further details on the formalism are described in [1].

5. Calculation of the EO coefficients of ZTS

The unit cell of ZTS contains 30 atoms in the asymmetric unit making a total of 148 bonds: Zn–O (4 No.), Zn–S (12 No.), S–O (16 No.), S–C (12 No.), C–N (24 No.), N–H (48 No.), H–O (32 No.) with each tu group consisting two C–N, one C–S and four N–H bonds. Several bond parameters (as described above) are estimated for each type of the bonds in the unit cell (table 2). The ionic components of the coefficients are computed using eq. (2) and the reported [4,5] dielectric constants.

The total linear susceptibility (χ) and the ionic components $(r_{ijk})^{\mathrm{ion}}$ for the crystal are estimated by summation of the respective values for each bond. The electronic components $(r_{ijk})^{\mathrm{el}}$ are calculated from the measured NLO coefficients d_{ijk} given in [5]. Results are given in table 3 in which a close agreement between the calculated and measured χ and r_{ijk} can be noticed. It can be seen that the

Table 2. Some bond parameters of ZTS.

	Zn–S	Zn–O	S–O	C–S	C–N	N–H	H–O
E_g (eV)	11.0	16.7	17.2	12.3	20.6	41.6	9.42
f	−0.3	−0.42	−0.15	−0.16	−0.045	−0.13	−0.23
hw_{p} (eV)	13.7	14.6	26.9	23.7	29.7	40.3	13.8
$f.\sum(\alpha_3)^3 + \alpha_3$	2.54	−2.07	0.45	1.01	−0.54	−1.05	2.28

Table 3. Linear susceptibility (χ) and EO coefficients (r_{ijk}) of ZTS.

	r_{33}	r_{23}	χ
Ionic comp. (cal.)	1.59	1.73	
Electronic comp. (cal.)	−0.1	−0.16	
Total (cal.)	1.49 ± 0.05	1.57 ± 0.07	0.16
Experimental	1.52 ± 0.12	1.49 ± 0.11	0.15

Experimental values [4] are at a wavelength of 514.5 nm and 2 kHz frequency of the applied field.

total coefficients arise more significantly from the ionic components than from the electronic ones.

Contributions to χ and EO coefficients from the individual molecular groups in the structure are given in table 4. These results showed that the tu_1, tu_2, tu_3 and $(SO_4)^{2-}$ groups contribute about 17% to the total value of χ whereas a maximum of about 25% contribution arises from the H-bonds alone. Similarly, a major contribution to the r_{33} coefficient comes from the tu_2 group and the H-bonds whereas the maximum contribution to r_{23} coefficient arises from the $(SO_4)^{2-}$ groups.

Thus the present work points out the molecular groups which are relatively more sensitive to the EO coefficients. This helps to grow crystals with better linear optical and EO properties. It also demonstrates the importance of neutron diffraction technique, which gave better information on the H-atoms.

Table 4. Contributions from structural groups to χ and r_{ijk} (pm/V).

	χ	$(r_{33})^{\mathrm{ion}}$	$(r_{23})^{\mathrm{ion}}$
Zn–T	0.012	0.48	−0.37
$(SO_4)^{2-}$	0.023	−0.43	2.61
tu_1	0.028	−0.61	0.60
tu_2	0.029	0.89	−0.93
tu_3	0.029	0.24	−0.63
H-bonds	0.040	1.02	0.45
Total	0.161	1.59	1.73

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