INTERNATIONAL JOURNAL OF CURRENT RESEARCH IN CHEMISTRY AND PHARMACEUTICAL SCIENCES
(p-ISSN: 2348-5213: e-ISSN: 2348-5221)
www.ijcrcps.com
(A Peer Reviewed, Referred, Indexed and Open Access Journal)
DOI: 10.22192/ijcrcps Coden: IJCROO(USA) Volume 13, Issue 3- 2026

Research Article

DOI: http://dx.doi.org/10.22192/ijcrcps.2026.13.03.001

Investigations of structure, Thermal stability and Optical properties of a Tristhiourea Zinc acetate single crystals

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Abstract

A single crystal of tris(thiourea) zinc(II) acetate was grown by the slow evaporation solution growth method. The synthesized crystal was characterized using elemental analysis, powder X-ray diffraction (PXRD), thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and nonlinear optical (NLO) studies. Elemental analysis confirms the stoichiometric ratio of the crystal. The thermal stability was investigated through TG and DSC analysis. The crystalline nature of the crystal was evidenced by the sharp and well-defined Bragg peaks observed in the PXRD pattern. The absorption peak observed at 210 nm is attributed to electronic transitions. A thermal anomaly observed at 185.45°C during the cooling cycle indicates the presence of a first-order phase transition. The infrared spectrum revealed the various chemical bonds present in the crystal. The second harmonic generation (SHG) efficiency of the crystal was evaluated by using the powder SHG method and the emission of green light confirms that the crystal possesses NLO properties.

Keywords: Crystal growth, Single crystal, Powder XRD, Thermal analysis, FTIR spectrum, NLO property.

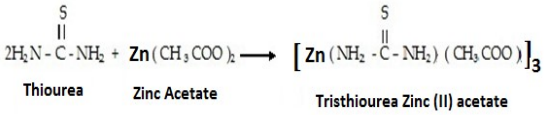
1. Introduction

Non-linear optical (NLO) materials have played an important role in laser science and technology, and the search of new NLO materials-particularly for UV and far-IR applications is on the rise. In recent years the search for new NLO materials included semi-organic and coordination compounds due to their advantages over traditional inorganic and organic compounds. There are three main types of interest in the study of NLO semi-organic and coordination compounds thus far. The first interest is to find transparent second harmonic generation (SHG) materials to be used for the frequency doubling of a semi-conductor laser. [1] NLO crystals are central parts of real time holography, optical correlator devices, phase-conjugator, thresholding devices, optical communication optical modulations, optical data storage, electro-optical switches, nuclear fusion experiments and many more [2]. These materials need to have large optical nonlinearity, large laser induced damaged threshold, low angular sensitivity and good mechanical and thermal stabilities [3]. NLO materials are used in frequency conversion, which is a popular technique for extending the useful wavelength range of lasers with wide spectrum of frequency generated through second harmonic generation (SHG), third harmonic generation (THG) or higher harmonic generation, parametric oscillations, wave mixing, etc. processes [4-7]. Organometallic materials have the combined advantages of high optical nonlinearity and chemical flexibility of organic materials with the thermal stability and mechanical sturdiness of inorganic NLO materials. Thiourea possesses a large dipole moment and it forms a number of coordination compounds like bisthiourea cadmium chloride (BTCC) and tris thiourea zinc sulfate (ZTS) . Metal ion doped semi-organic materials have excellent mechanical and thermal properties [8].Examples of such crystals include cadmium thiourea acetate [9], bisthiourea zinc chloride [10] and bisthiourea lithium chloride [11].

In the present work, tris(thiourea) zinc (II) acetate crystals were grown from an aqueous solution and systematically characterized using C H N S analysis, powder X-ray diffraction, UV-Vis-NIR optical transmittance, TGA, DSC, FTIR and nonlinear optical studies.

2. Growth of single crystals of TTZA

Single crystals of tristhiourea zinc(II) acetate (TTZA) were grown by the slow evaporation solution growth method at room temperature. Thiourea and zinc(II) acetate were taken in a molar ratio of 2:1 respectively. Aqueous solutions of analytical-grade of thiourea and zinc(II) acetate were prepared separately using doubly distilled water. The two solutions were then mixed together and stirred continuously for about 3 hours using a mechanical stirrer to ensure homogeneity. The resulting clear solution was filtered through filter paper into a clean, dry beaker to remove any impurities. The beaker was covered with ordinary filter paper and kept undisturbed in a dust-free environment to allow slow evaporation of the solvent. After a suitable period, well-defined single crystals of TTZA were obtained. The formation of TTZA crystals can be represented by the following reaction:



Under the experimental conditions, bright, transparent, and colourless TTZA crystals were obtained. Crystallization occurred within a period of 10-15 days. The grown crystals were carefully collected from the mother liquor using well-cleaned forceps. To improve crystal quality the harvested crystals were subjected to repeated recrystallization.

2.1. Characterization techniques

Elemental analysis of the crystal was carried out by using a Vario EL III CHNS analyzer at the Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Cochin. The powder X-ray diffraction pattern of the crystal was recorded

using an X'PERT-PRO diffractometer at STIC, Cochin. The UV-visible spectrum was obtained using a JASCO V-670 UV-Vis spectrophotometer at VIT University, Vellore. Thermal analysis (TGA) was performed at SAIF, Chennai, using an SDT Q600 (V20.9 Build 20) instrument. The crystal was heated from room temperature to 500°C under a nitrogen atmosphere. Low-temperature differential scanning calorimetry (DSC) measurements of the crystal was studied by using a METTLER TOLEDO DSC instrument under a nitrogen atmosphere at a heating rate of 10 K min^{-1}. The samples were cooled from 30°C to -150°C and subsequently heated from 0°C to 500°C. The FTIR spectrum of the crystal was recorded using a Perkin Elmer RXI spectrometer with the KBr pellet technique in the frequency range 4000-400 cm^{-1} at the Archbishop Casmir Instrumentation Centre, St. Joseph's College, Trichy. The second harmonic generation (SHG) efficiency of the crystal was evaluated using the modified Kurtz-Perry powder technique with a Nd:YAG laser at IISc, Bangalore.

3. Results and Discussion

3.1 Elemental analysis

The experimental percentages of carbon, nitrogen, hydrogen, and sulphur were found to be C 25.38%, N 19.78%, H 4.97%, and S 22.67%, which are in close agreement with the calculated values (given in brackets) of C 25.56%, N 19.88%, H 4.86%, and S 22.72%, respectively. The close correspondence between the experimental and calculated values confirms the formation of the crystal in the expected stoichiometric ratio.

3.2. Powder X-ray diffraction pattern analysis

The sharp and well-defined Bragg peaks observed at various 2θ angles indicate the good crystalline nature of the compound. The powder X-ray diffraction pattern of the crystal is shown in Figure 1. The unit cell parameters were determined as a = 17.2689 Å, b = 9.3478 Å, c = 5.4781 Å with $\alpha \neq \beta \neq \gamma \neq 90°$, and a unit cell volume of 598.58 $Å^3$. These lattice parameters confirm that the grown crystal belongs to the triclinic crystal system.

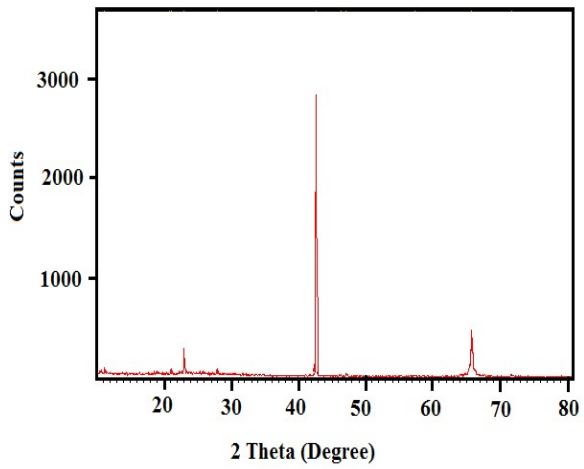


Figure 1. Powder X-ray diffraction pattern of TTZA crystal.

3.3. UV-Visible transmittance spectral study

Transmittance spectra are crucial for evaluating the suitability of single crystals for practical applications, as a wide transparency window is essential. The UV-visible transmittance spectrum of the TTZA crystal is shown in Figure 2. An absorption peak observed at 210 nm is attributed to electronic transitions. No absorption is observed in the wavelength range from 300 nm to 1200 nm, indicating a wide transparency window. Hence, the TTZA crystal is a suitable for nonlinear optical applications.

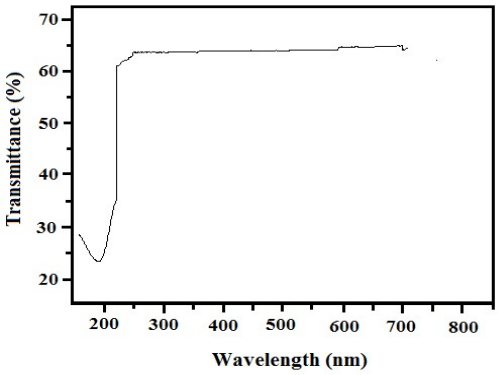


Figure 2. UV-visible spectrum of TTZA crystal.

3.4. Thermogravimetric analysis

The TGA thermogram of the crystal is shown in Figure 3. When the crystal was heated from 0°C to 500°C, it is decomposed in a single stage. The first stage of decomposition occurred between 0°C and 500°C. The weight loss in this stage is due to the loss of methyl groups, sulfur, nitrogen, carbon dioxide and zinc (Zn). The experimental weight loss was 97.20%, The calculated weight loss of 97%. The slight differences in weight loss may be due to the presence of occluded or absorbed water molecules in the crystal. Thus, the TGA also study confirms that the crystal is formed in a stoichiometric ratio.

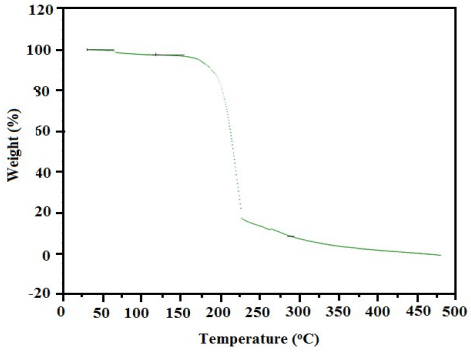


Figure 3. TG thermogram of TTZA crystal.

3.5. Low temperature DSC analysis

The low-temperature DSC of the TTZA crystal is shown in Figure 4. During the heating cycle, the crystal exhibits a thermal anomaly at 185.45 °C. However, no corresponding anomaly is observed in the cooling cycle (not shown in the curve). This thermal hysteresis suggests the occurrence of a second-order phase transition, which is attributed to the gradual ordering of Zn^{2+} and NH_4^+ ions in the crystal lattice.

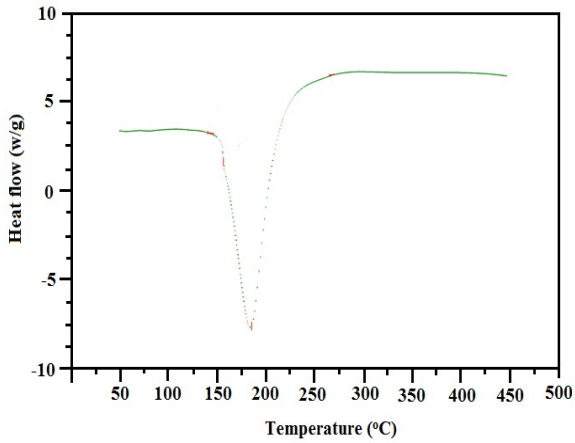


Figure 4. Low temperature DSC curve of TTZA crystal.

3.6. FTIR spectral analysis

The FTIR observed spectrum of the title crystal is shown in Figure 5. The asymmetric stretching of NH_2 molecule peak observed at 3790 cm^{-1}. The peaks at 394 and at 3298 cm^{-1} are due to the NH stretching vibrational bands in NH_2. The NH_2 group associated with broad band is found at 3132 cm^{-1}. The peak at 2688 cm^{-1} is due to asymmetric stretching vibration in NH molecule. The peak at 2334 cm^{-1} is presence of NH stretching vibration. The stretching vibration of CH_2 is observed at 2211 cm^{-1}. The peak at 2035 cm^{-1} is due combination band of NH_2. The band observed at 1546 cm^{-1} is presence of asymmetric stretching of NH^+. The wagging of CH_2 is found at 1342 cm^{-1}. The peak at 1416 cm^{-1} is due to symmetric stretching of COO^-. The rocking of NH^+ occurs at 1074 cm^{-1}. The peak at 1018 cm^{-1} is due to -CN stretching vibration. The peak at 890 cm^{-1} and 928 cm^{-1} indicates the rocking of CH_2. The C=S stretching vibrations peak observed at 768 cm^{-1}. The peak at 729 cm^{-1} is presence of C=S symmetric stretching vibrations. The rocking of COO^- is found at 661 cm^{-1}. The peak at 613 cm^{-1} indicates that presence of symmetric N-C-N stretching. The peak at 482 cm^{-1} skeletal vibration may be due to $Zn(CH_3COO)$.

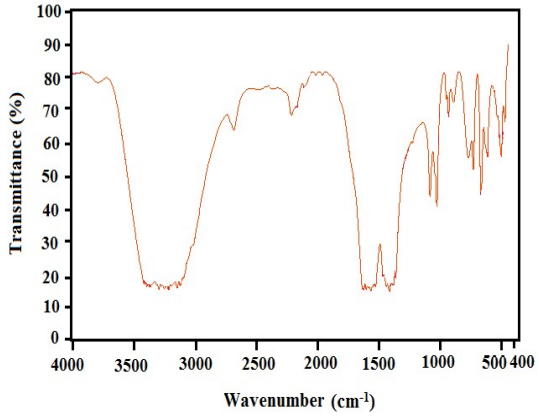


Figure 5. FTIR spectrum of TTZA crystal

3.7. Non linear optical study

The Kurtz-Perry test was performed to investigate the nonlinear optical (NLO) properties of the TTZA crystals. The Kurtz technique is commonly used as a screening method to identify materials capable of phase matching and to determine whether a crystal possesses a non-centrosymmetric structure. For the experiment, the crystals were ground into a fine powder and densely packed between two glass slides. A Nd:YAG laser with a pulse width of 10 ns, a wavelength of 1064 nm, and a repetition rate of 10 Hz was directed normally onto the sample. The emission of green light from the sample confirmed the occurrence of second harmonic generation (SHG), indicating that the grown TTZA crystal exhibits measurable NLO efficiency.

4. Conclusions

Single crystals of tris(thiourea) zinc(II) acetate (TTZA), a semi-organic nonlinear optical material, was successfully grown from an aqueous solution using the slow evaporation technique at ambient temperature. The CHNS elemental analysis was carried to ascertain stoichiometric ratio of the crystals was confirmed through CHNS elemental analysis. The crystalline nature and unit cell parameters of the grown crystals were determined using X-ray powder diffraction technique. UV-Vis-NIR spectroscopic study was studied to reveal the optical property of the title material and it indicates which is suitable for optoelectronic applications. The thermal stability of TTZA crystal was investigated by using thermogravimetric (TG) analysis, while differential scanning calorimetry (DSC) was used to study the first-order phase transition of the material. The functional groups present in the crystal were identified through FTIR spectral study. The NLO response of TTZA single crystal was confirmed by using a Nd:YAG laser for demonstrating their potential for nonlinear optical applications.

Acknowledgments

The authors acknowledge the services of Sophisticated Test and Instrumentation Centre (STIC), Cochin University of Science and Technology, Cochin and Indian Institute of Science, Bangaluru for their carrying NLO instrumental facilities. The one of author (T.Dhanabal) acknowledges the Chairman and Secretary of Muthayammal Engineering College (Autonomous), Rasipuram, Tamil Nadu, India for their constant encouragement and support to carry out this work.

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DOI: 10.22192/ijcrcps.2026.13.03.001	

How to cite this article:
T.Dhanabal, M.Thangarasu, K.Umamaheswari, D.M.Muniraj. (2026). Investigations of structure, Thermal stability and Optical properties of a Tristhiourea Zinc acetate single crystals. Int. J. Curr. Res. Chem. Pharm. Sci. 13(3): 1-7.
DOI: http://dx.doi.org/10.22192/ijcrcps.2026.13.03.001

