Growth and characterization of tris thiourea zinc nitrate: An organo metallic single crystal

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Abstract: Single crystals of tris(thiourea) zinc nitrate (Zn (NH₂CSNH₂)₃(NO₃)₂, abbreviated as TZNN, a organo metallic single crystal have been grown successfully by slow evaporation method. Crystal of dimensions 1.122 cm³ was harvested after a period of 45 days and is reported. X-ray diffraction analysis has been carried out to confirm orthorhombic system and etching studies for their growth orientation and perfection. The powder x-ray diffraction of the crystal recorded and the various planes of reflections are identified. The presence of functional group and the coordination of metal ions to thiourea were confirmed by FTIR analysis. The transmission spectrum reveals that the crystal has low UV cutoff of 302 nm and has a good transmittance in the entire visible region enabling its use in optical applications. The thermal behavior of the crystal has been investigated using thermogravimetric analysis (TGA) and differential thermal analysis (DTA), which indicates that the material does not decompose before melting. Mechanical strength of the crystal has been analyzed using Vickers’ micro-hardness test. Studies of dielectric properties like dielectric constant and dielectric loss as function of frequencies for varying temperatures in the range 303 – 433 K suggests these crystals are good candidates for electro optic modulators and frequency convertors.

Keywords: thiourea zinc nitrate, FTIR, UV-Vis, TGA/DTA, Micro hardness, Dielectrics.

Introduction and Experimental

Metal complexes of thiourea, commonly called organo-metallics, include the advantages of both organic and inorganic part of the complex. These metal complexes of thiourea, which have low UV cutoff wavelength, have received much attention in the field of optical storage industry. Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network.
of hydrogen bonds. Also metals with d^{10} configuration like zinc, cadmium, mercury readily combine with thiourea resulting in stable compounds with high optical nonlinearity, good physiochemical behavior and hence applications in electro optics and piezoelectricity[1-3].

**Crystal Growth**

Tris thiourea zinc II nitrate was synthesized by mixing aqueous solutions of thiourea (AR grade) and sodium nitrate (AR grade) in the molar ratio 3:1. The chemical reaction is as follows

\[\text{[Zn(NH}_2\text{CSNH}_2\text{)}_3\text{]}\text{SO}_4 + 2\text{NaNO}_3 \rightarrow \text{[Zn(NH}_2\text{CSNH}_2\text{)}_3\text{]}\text{(NO}_3\text{)}_2 + \text{Na}_2\text{SO}_4\]

The synthesized salts were dissolved in double distilled water and purified by repeated re-crystallization and used for preparation of growth solution. The grown single crystals of TZNN are shown in the Figure 1.

![Fig 1. The as grown crystal of TZNN single crystal](image)

**Results and discussion**

The crystal belongs to orthorhombic crystal system. The etching studies were carried out on the as grown crystals of TZNN to study the symmetry of the crystal face from the shape of the etch pits, and the distribution of the structural defects in the grown crystals[4] Fig 2. a shows the surface of the crystal without etchant. Fig. 2b-2e, shows the steps on the etched surface when etched with water. Thus the etch pits indicates the grown crystal will have perfect orientation. The most widely used technique for confirming the SHG efficiency of NLO materials, to identify the materials with non-centrosymmetric crystal structures, is the Kurtz powder technique [5]. FTIR spectrum was recorded using Bruker IFS 66V spectrophotometer by KBr pellet technique in the region 4000 – 400 cm^{-1} and shown in Figure 3. The characteristic vibrational frequencies are assigned and given in Table 1. The crystals show good transmittance in the entire visible region. As seen in the spectra there are no significance absorption after 302 nm. Simultaneous TGA and DTA were carried out for the TZNN crystals to study thermal stability and found to be stable.

The mechanical characterization of the TZNN crystals was done by Vickers and Knoop microhardness studies carried out at room temperature. The elastic stiffness constant (c_{11}) was calculated using Wooster’s empirical relation as c_{11} = H^{3/4}. The dielectric study on TZNN single crystal was carried out on (100) plane using HIOKI 3532-50 LCR HITESTER in the frequency range from 50 Hz – 5 MHz at different temperatures. The measurement of dielectric loss and dielectric constant has been done as a function of frequency.

![Fig 2. Surface of as grown TZNN single crystal a) without etchant, b) etching with water for 30sec, c) 45 sec, d) 1 min, e) 2 min [20 x magnification]](image)
Fig. 3 The FTIR spectrum of TZNN single crystal

Table 1: Comparison of Absorption IR bands of TUMS with Urea, Thiourea

<table>
<thead>
<tr>
<th>Thiourea</th>
<th>UTMS</th>
<th>UTHS</th>
<th>TZNN</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>1412</td>
<td>1413</td>
<td>1400</td>
<td>$\nu_s$ (C=S)</td>
</tr>
<tr>
<td>1471</td>
<td>1473</td>
<td>1473</td>
<td>1465</td>
<td>$\nu$(N-C-N)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1627</td>
<td>1621</td>
<td>1611</td>
<td>1629</td>
<td>$\delta$ (NH$_2$)</td>
</tr>
<tr>
<td>3167</td>
<td>3178</td>
<td>3183</td>
<td>3188</td>
<td>$\nu_s$ (NH$_2$)</td>
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<tr>
<td>3280</td>
<td>3283</td>
<td>3273</td>
<td>3307</td>
<td>$\nu$ (NH$_2$)</td>
</tr>
<tr>
<td>3376</td>
<td>3388</td>
<td>3383</td>
<td>3383</td>
<td>$\nu_d$(NH$_2$)</td>
</tr>
</tbody>
</table>

$\nu$ – Stretching, $\rho$ – Rocking, $\delta$ – Bending $\nu_s$ – symmetric stretching, $\nu_{as}$ – asymmetric stretching

Conclusion

The crystallographic data indicates that the TZNN crystallize under orthorhombic structure. FTIR analysis confirmed the coordination of metal complex with thiourea in the crystal lattice. Growth pattern were observed using etch pits on the flat surface of the crystal using water as etchant. The vickers’ hardness shows the crystal have good mechanical strength and calculated elastic stiffness constant shows these crystals can be used for device fabrication. The crystal has lower cut off wavelength at 302 nm and dielectric constant and dielectric loss at different temperature shows the grown crystals are typically a normal dielectric material.

References