Electro-optic, piezoelectric, and dielectric properties of zinc tris thiourea sulfate

Uma B. Ramabadraran and David E. Zelmon

Materials Directorate, Wright Laboratories, Wright-Patterson AFB, Ohio 45433-6533

Gretchen C. Kennedy

Cleveland Crystals, Inc., Cleveland, Ohio 44110

(Received 10 January 1992; accepted for publication 16 March 1992)

Recently, it has been demonstrated that semiorganic materials have potential for very efficient nonlinear optical devices. Among many recently reported materials is zinc tris thiourea sulfate. We report measurements of the electro-optic, piezoelectric, and dielectric constants of this new material.

Performance requirements for nonlinear optical devices have placed severe demands on the materials used in those devices. For several years, an intense search for new materials has been carried out by many workers and a wide variety of both organic and inorganic materials has been developed. Problems with both classes of materials have resulted in the investigation of semiorgansics. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with the physical ruggedness of inorganics. Zinc tris thiourea sulfate (ZTS) was recently grown in bulk form and second harmonic generation measurements indicate that its second harmonic generation efficiency is comparable to that of potassium dihydrogen phosphate (KDP). More important, ZTS has an exceptionally wide acceptance angle for second harmonic generation, a very low power threshold, and can be grown from aqueous solution at moderate temperatures.

ZTS is an orthorhombic semiorganic crystal belonging to the mm2 point group. X-ray analysis by Andreiti, et al. shows that a zinc ion is tetrahedrally bonded to three sulfur atoms from the thiourea and one oxygen from a sulfate ion. The crystal is biaxial with refractive indices of $n_x = 1.667$, $n_y = 1.734$, and $n_z = 1.740$ at 510 nm. Marcy, et al. have recently completed measurements of the nonlinear optical constants for second harmonic generation in ZTS and compared them to that of the $d_{14}$ coefficient for KDP. They have demonstrated that $d_{31}$, $d_{32}$, and $d_{33}$ are 0.79, 0.90, and 0.59 times that of KDP's $d_{14}$ respectively. ZTS's second harmonic capability also makes it potentially useful for electro-optic applications. We report the first measurements of the electro-optic, piezoelectric, and dielectric constants for this material and discuss the figure of merit.

Crystals of ZTS were grown from aqueous solution by Cleveland Crystals, Inc. Six 5 mm cubes were cut along the principal crystallographic axes for the measurements. X-ray analysis confirmed that the orientation of the cubic faces were within 2 degrees of the crystallographic axes. All six faces of the cubes were polished and electrodes of SPI No. 5002 high-purity silver paint were applied to the appropriate faces.

The electro-optic coefficients were measured by applying an electric field to the samples and using a Mach-Zehnder interferometer similar to that described by Duffourne, et al. to measure the change in the optical path caused by the applied field. The light source, a Spectra-Physics 2045 argon ion laser set at a wavelength of 514.5 nm. The polarization of the input beam was controlled externally to the interferometer. The polarization and propagation directions of the input light for the measurement of each component of the electro-optic tensor are given in Table I. The zero-field phase difference between the two arms of the interferometer was set to $\pi/2$ modulo 2$\pi$. This ensured the maximum sensitivity for the measurement. The sample was put into the test arm of the interferometer and modulated by a 2 kHz sinusoidal electric field which was varied from 1000 to 1800 V/cm $p-p$. The change in the intensity of the center fringe was measured as a function of the applied electric field using an EGG model SGD-20 silicon photodetector. The modulated signal was fed to an SRI Model 510 lock-in amplifier with the time constant set to 300 ms. The dynamic range of the interferometer was measured by adjusting the compensator and measuring the maximum and minimum intensity of the center fringe before each experiment. From this data, the phase shift due to the application of the field was determined and was used to calculate the combined contribution of the electro-optic effect and the piezoelectric effect to the change in optical path. The relative phase difference between the arms of the interferometer was checked before and after each experiment to be sure it had not drifted from its zero-field value. An example of the data is shown in Fig. 1.

In order to separate the electro-optic effect and the piezoelectric effect, an independent measurement was made of the piezoelectric coefficient. We measured the piezoelectric coefficient by evaporating a mirror onto one surface of each sample and using the sample as one of the

---

TABLE I. Polarization chart.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Light pol.</th>
<th>E field dir.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{31}$</td>
<td>$x$ axis</td>
<td>$z$ axis</td>
</tr>
<tr>
<td>$r_{32}$</td>
<td>$y$ axis</td>
<td>$z$ axis</td>
</tr>
<tr>
<td>$r_{33}$</td>
<td>$z$ axis</td>
<td>$z$ axis</td>
</tr>
<tr>
<td>$r_{42}$</td>
<td>$y$-z plane</td>
<td>$y$ axis</td>
</tr>
<tr>
<td>$r_{51}$</td>
<td>$x$-z plane</td>
<td>$x$ axis</td>
</tr>
</tbody>
</table>

---

81 Also with: Systran Corporation, 4126 Linden Ave., Dayton, Ohio.
FIG. 1. Change in the intensity of the center fringe is plotted vs applied voltage. The straight line represents a least squares fit to the data.

mirrors in a Michelson interferometer, shown in Fig. 2. The phase shift resulting in the physical change in the dimensions of the crystals was measured and the piezoelectric coefficients calculated using:

\[ \Delta L_k = d_{k\ell} E L_k \]  

and

\[ \Delta \phi = \frac{2\pi}{\lambda} \Delta L_k. \]

We checked the accuracy of the apparatus by measuring a sample of strontium barium niobate and comparing our results with those in the published literature. Our calibration data are shown in Table II along with the data for ZTS.

The dielectric constants were found by measuring the capacitance of the samples with HP 4274 and 4275 LCR meters and calculating the dielectric constant assuming that each sample behaves like a parallel plate capacitor. Measurements were made at room temperature at frequencies from 100 Hz to 10 MHz. The data presented in Table III are those obtained at 10 MHz. Very small variations in capacitance were seen over the frequency range used. The apparatus was carefully checked for stray capacitance and data obtained for similarly shaped test samples of KDP were obtained and are shown in Table III.

PIEZOELECTRIC COEFFICIENT MEASUREMENT

FIG. 2. Schematic diagram of the Michelson interferometer. BS is a 50/50 beam splitter, LIA is the lock-in amplifier.

### TABLE II. EO and PZ coefficients.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>SBN (pm/V)</th>
<th>ZTS (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>eo r11</td>
<td>51.96 ± 2.6</td>
<td>2.60 ± 0.01</td>
</tr>
<tr>
<td>eo r21</td>
<td>⋯</td>
<td>1.49 ± 0.11</td>
</tr>
<tr>
<td>eo r31</td>
<td>⋯</td>
<td>1.52 ± 0.12</td>
</tr>
<tr>
<td>pz d11</td>
<td>30.37 ± 1.7</td>
<td>0.65 ± 0.20</td>
</tr>
<tr>
<td>pz d21</td>
<td>⋯</td>
<td>7.49 ± 0.66</td>
</tr>
</tbody>
</table>

The intensity of the center fringe of the Mach–Zehnder interferometer is

\[ I = I_1 + I_2 + 2 \sqrt{I_1 I_2} \cos[\phi_0 + \phi(E)] \]  

where \( \phi_0 \) is the phase difference between the two arms of the interferometer when no field is applied and \( \phi(E) \) is the phase shift due to the applied electric field and \( I_1 \) and \( I_2 \) are the intensities in the reference and sample arm of the interferometer respectively. Differentiating Eq. (1) with respect to the electric field gives

\[ dI/dE = -2 \sqrt{I_1 I_2} \sin[\phi_0 + \phi(E)] d\phi(E)/dE. \]

If we assume that \( \phi(E) \ll \phi_0 \), this expression becomes

\[ dI/dE = -2 \sqrt{I_1 I_2} \sin(\phi_0) d\phi(E)/dE. \]

From the slope of the intensity versus electric field data, \( \phi(E) \) can be determined. This figure can then be used in combination with the piezoelectric data to calculate the electro-optic coefficients. Using this procedure and combining results with data obtained from the piezoelectric measurements, the electro-optic coefficients can be calculated.

The measured electro-optic and piezoelectric are summarized in Table II and are the combined results of five measurements performed on each of four samples. The figures for \( r_{13}, r_{23}, \) and \( r_{33} \) are smaller than similar figures for KDP. Although crystal symmetry indicates that \( r_{42} \) and \( r_{51} \) should be nonzero, we were unable to observe any fringe shift associated with these coefficients, despite repeated checks of the measurement apparatus and many experiments. In the absence of any other evidence, we believe that these coefficients are smaller than \( 5 \times 10^{-14} \) m/V, which is the current limit of sensitivity of our apparatus.

The dielectric constant data, shown in Table III, are the result of fifteen measurements in each crystallographic direction on each of two samples. The dielectric constants showed a very small variation with frequency over the range 100 Hz to 10 MHz and are about 25% that of KDP. All of the samples tested show a very small frequency dependence for the dielectric constant for frequencies over 120 Hz.

### TABLE III. Dielectric constants

<table>
<thead>
<tr>
<th>Dielec. const.</th>
<th>KDP</th>
<th>ZTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_{11} )</td>
<td>⋯</td>
<td>5.87 ± 0.51</td>
</tr>
<tr>
<td>( \varepsilon_{22} )</td>
<td>⋯</td>
<td>5.35 ± 0.46</td>
</tr>
<tr>
<td>( \varepsilon_{33} )</td>
<td>21.76 ± 0.15</td>
<td>5.80 ± 0.22</td>
</tr>
</tbody>
</table>

Ramabadran, Zelmon, and Kennedy 2590
We have measured the electro-optic, piezoelectric, and dielectric constants of ZTS. The figures for the electro-optic coefficients are smaller than those for KDP, although the overall figure of merit for ZTS, defined as $n_1 r_{ij} / \varepsilon$, is 22% higher than that for KDP due to ZTS's relatively low dielectric constant and higher refractive index. We were unable to see any fringe shift which should have resulted from $r_{42}$ and $r_{51}$ and we are conducting further experiments to determine the reason for this null result.

The authors wish to thank Dr. F. Kenneth Hopkins for his helpful suggestions during the course of this study.