Electrical Measurements on Zinc – Magnesium Tris(Thiourea) Sulphate (ZMTS) Single Crystals

A. Darlin Mary A, K. Jayakumari B, C. K. Mahadevan c

a Department of Physics, Annai Velankanni College, Tholayavattam – 629174, Tamil Nadu, India
b Department of Physics, Sree Ayyappa College for Women, Chunkankadai - 629174, Tamil Nadu, India
c Department of Physics, S.T. Hindu College, Nagercoil - 629002, Tamil Nadu, India

Abstract

Pure and magnesium sulphate mixed zinc tris(thiourea) sulphate single crystals were grown by the slow evaporation method from aqueous solutions. The grown crystals were characterized by X-ray powder diffraction. The cell parameters of the grown crystals were estimated by single crystal X-ray diffraction technique. The observed results show that the small amount of magnesium molecules were incorporated in the crystalline matrix of ZTS crystals. DC and AC (with five different frequencies, viz. 100 Hz, 1 kHz, 10 kHz, 100 kHz, and 1 MHz) electrical measurements were carried out at various temperatures. The present study shows that the DC conductivity and dielectric parameters (viz. dielectric constant, dielectric loss and AC conductivity) increase with the increase in temperature for all the grown crystals. Activation energies were also determined.

1. Introduction

Zinc tris(thiourea) sulphate (ZTS), Zn[CS(NH$_2$)$_2$]$_3$SO$_4$, is a relatively new and promising semiorganic nonlinear optical material for frequency conversion of high power lasers. ZTS crystal shares the favourable polarizable property of the organic material and the mechanical properties of the inorganic material. Special features of this material are that it has a high laser damage threshold, a low UV cut off and 1.2 times higher second harmonic generation (SHG) efficiency than potassium dihydrogen orthophosphate (KDP). Also, ZTS crystal has excellent mechanical properties when compared to other semiorganic nonlinear optical crystals. Moreover, it is less hygroscopic than KDP [1]. ZTS belongs to the orthorhombic crystal system with the point group of mm2 and the lattice parameters are $a = 11.130$, $b = 7.773$ and $c = 15.490$ Å [2].

In the present work, ZTS has been mixed with various molar percentages of magnesium sulphate to improve the SHG efficiency to find its suitability as better alternative to other NLO materials for optoelectronics applications [3]. Magnesium tris(thiourea) sulphate (MTS), Mg[CS(NH$_2$)$_2$]$_3$SO$_4$, is a semiorganic nonlinear optical material. MTS belongs to the monoclinic crystal system and the lattice parameters are $a = 7.67$, $b = 5.48$ and $c = 8.56$ Å and $\beta = 13.11^\circ$ [4].

Anandakumari and Chandramani [5] have recently reported that KDP crystals containing alkali halide impurities have shown appreciable increase in second harmonic generation efficiency compared to pure KDP crystals. It can be expected that impurity addition to ZTS makes this material more useful. Moreover, forming solid solutions with similar materials may also bring fruitful results. Aiming at discovering new useful materials, in the present study, we have made an attempt to grow and characterize mixed crystals based on ZTS and MTS. Even though the lattices of ZTS and MTS mismatch, the precursors molecules are isomorphous. As the mixed crystals are proposed to be grown from the precursors mixed in the required proportion, it is expected to be possible for the formation of ZTS – MTS mixed crystals. We report, herein, the results of our study.

2. Experimental

The ZMTS salt was synthesized by the stoichiometric incorporation of AnalyR grade (AR) zinc sulphate heptahydrate + magnesium sulphate heptahydrate and thiourea in the molar ratio 1:3. The component salts were very well dissolved in
deionized water, which was thoroughly mixed using a magnetic stirrer and the mixture was heated at 50°C till a white crystalline salt of ZMTS was obtained. Temperature was maintained at 50°C to avoid decomposition as followed by the previous workers [6]. ZMTS salt was synthesized according to the reaction.

\[
\text{Zn}_x\text{Mg}_{1-x}\text{SO}_4 \cdot 7\text{H}_2\text{O} + 3\text{CS (NH}_2\text{)}_2 \rightarrow \text{Zn}_x\text{Mg}_{1-x}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4
\]

where \(x=0.0\) to \(1.0\) in steps of 0.1

Single crystals of ZMTS were grown by the solution growth employing slow evaporation technique at room temperature (31°C). Transparent and colourless ZMTS crystals of size \(7\times7\times4\) mm\(^3\) were harvested in 20-25 days except MTS crystal. The MTS crystal of size \(9\times8\times5\) mm\(^3\) was harvested in 30-35 days.

The grown ZMTS crystals were subjected to single crystal XRD analysis using an ENRAF NONIUS CAD4 diffractometer with MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å) to determine the unit cell dimensions.

DC electrical conductivity measurements were carried out in all the grown ZMTS crystals using the conventional two-probe technique at various temperatures ranging from 40 to 120°C in a way similar to that followed by Perumal and Mahadevan [7]. The resistances of the crystals were measured using a million megohm meter. The observations were made while cooling the sample. The samples were cut into rectangular shape to the desired thickness of \(1-2\) mm and polished. For good conduction opposite faces of the sample crystals were coated with good quality graphite. The samples were annealed in the holder assembly at \(\sim 120^\circ\text{C}\) before making observations. The dimensions of the crystals were measured using a traveling microscope (L.C. = 0.001 cm). The DC conductivity (\(\sigma_{dc}\)) of the crystal was calculated using the relation \(\sigma_{dc} = d/(RA)\), where \(R\) is the measured resistance, \(d\) is the thickness of the sample, and \(A\) is the area of the crystal in contact with the electrode.

The capacitance (\(C_{cryst}\)) and dielectric loss factor (\(\tan \delta\)) measurements were carried out on all the grown crystals using an LCR meter (Agilent 4284A) with five different frequencies such as \(10^2\), \(10^3\), \(10^4\), \(10^5\) and \(10^6\) Hz at various temperatures ranging from 40-120°C in a way similar to that followed by Mahadevan and his co-workers [7-9]. The samples were annealed up to 120°C to remove water molecules, if present. The observations were made while cooling the sample. Air capacitance (\(C_{air}\)) was also measured. The sample crystal was prepared as in the case of DC conductivity measurements. The dielectric constant of the crystal was calculated using Mahadevan’s relation [8,9](as the crystal area was smaller than the plate area of the cell).

\[
\varepsilon_r = \left( \frac{A_{air}}{A_{cryst}} \right) \frac{C_{cryst} - C_{air}}{C_{air} \left(1 - A_{cryst}/A_{air}\right)},
\]

where \(A_{cryst}\) is the area of the crystal touching the electrode and \(A_{air}\) is the area of the electrode.

The AC conductivity (\(\sigma_{ac}\)) was calculated using the relation

\[
\sigma_{ac} = \varepsilon_\theta \varepsilon_r \omega \tan \delta
\]

where \(\varepsilon_\theta\) is the permittivity of free space (\(8.85 \times 10^{-12}\) C\(^2\) N\(^{-1}\) m\(^{-3}\)) and \(\omega\) is the angular frequency.

The activation energy values were estimated using the relations

\[
\sigma_{dc} = \sigma \exp\left(-\frac{E_a}{kT}\right)
\]

\[
\sigma_{ac} = \sigma \exp\left(-\frac{E_a}{kT}\right)
\]

Here, \(k\) is the Boltzmann’s constant, \(T\) is the absolute temperature, and \(\sigma\) is a constant depending on the material.

### 3. Results and Discussion

#### 3.1 Crystals grown and lattice parameters

A photograph of the grown ZMTS, \(\text{Zn}_x\text{Mg}_{1-x}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\) (where \(x=0.0\) to \(1.0\) in steps of 0.1) crystals is shown in Figure 1. The external appearance of the grown crystals is found to be different when magnesium content increases. The Lattice parameters obtained for the grown ZMTS crystals are given in Table 1. Except MTS all the other crystals belong to orthorhombic system and the lattice parameters are found to be in line with those of ZTS crystals. The lattice parameters of ZTS and MTS crystals compare well with those reported in the literature [10, 4]. The grown crystals are represented as:

- **ZTS** → Pure ZTS
- **ZTS9** → \(\text{Zn}_{0.9}\text{Mg}_{0.1}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS8** → \(\text{Zn}_{0.8}\text{Mg}_{0.2}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS7** → \(\text{Zn}_{0.7}\text{Mg}_{0.3}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS6** → \(\text{Zn}_{0.6}\text{Mg}_{0.4}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS5** → \(\text{Zn}_{0.5}\text{Mg}_{0.5}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS4** → \(\text{Zn}_{0.4}\text{Mg}_{0.6}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS3** → \(\text{Zn}_{0.3}\text{Mg}_{0.7}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS2** → \(\text{Zn}_{0.2}\text{Mg}_{0.8}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **ZTS1** → \(\text{Zn}_{0.1}\text{Mg}_{0.9}[(\text{CS (NH}_2\text{)}_2)_3]\text{SO}_4\)
- **MTS** → Pure MTS
Figure 1. Photograph showing sample crystals grown. [Top row: from left are ZTS1, ZTS2, ZTS3, ZTS4, ZTS5. Middle row: from left are ZTS6, ZTS7, ZTS8, ZTS9. Bottom row: from left are ZTS and MTS ]

3.2 Electrical properties

The DC electrical conductivities ($\sigma_{dc}$) observed in the present study are shown in Figure 2. The dielectric parameters, viz. dielectric constant ($\varepsilon_r$), dielectric loss factors (tan $\delta$), and AC electrical conductivities ($\sigma_{ac}$) observed are shown in Figures 3-5. All the electrical parameters, viz. $\sigma_{dc}$, $\varepsilon_r$, tan $\delta$ and $\sigma_{ac}$ are found to increase with the increase in temperature in the temperature range considered in the present study. Further, $\varepsilon_r$ and tan $\delta$ values decrease whereas the $\sigma_{ac}$ value increases with the increase in frequency. Moreover, as expected, the $\sigma_{ac}$ values are found to be more than the $\sigma_{dc}$ values. So, it can be understood that all the eleven crystals grown in the present study exhibit normal dielectric behaviour.

Table 1. Lattice parameters and volumes of the grown ZMTS crystals

<table>
<thead>
<tr>
<th>crystal</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V ($Å^3$)</th>
<th>Angle $\alpha=\beta=\gamma=90^\circ$</th>
<th>Crystal system</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTS</td>
<td>7.77</td>
<td>11.11</td>
<td>15.48</td>
<td>1340 [1340]</td>
<td></td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>ZTS9</td>
<td>7.78</td>
<td>11.12</td>
<td>15.47</td>
<td>1341 [1341]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS8</td>
<td>7.77</td>
<td>11.13</td>
<td>15.46</td>
<td>1339 [1339]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS7</td>
<td>7.76</td>
<td>11.14</td>
<td>15.45</td>
<td>1338 [1338]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS6</td>
<td>7.75</td>
<td>11.15</td>
<td>15.48</td>
<td>1337 [1337]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS5</td>
<td>7.77</td>
<td>11.14</td>
<td>15.47</td>
<td>1340 [1340]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS4</td>
<td>7.78</td>
<td>11.13</td>
<td>15.46</td>
<td>1338 [1338]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS3</td>
<td>7.77</td>
<td>11.12</td>
<td>15.45</td>
<td>1337 [1337]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS2</td>
<td>7.76</td>
<td>11.11</td>
<td>15.44</td>
<td>1339 [1339]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>ZTS1</td>
<td>7.74</td>
<td>11.08</td>
<td>15.42</td>
<td>1337 [1337]</td>
<td>$\alpha=\beta=\gamma=90^\circ$</td>
<td></td>
</tr>
<tr>
<td>MTS</td>
<td>7.66</td>
<td>5.49</td>
<td>8.55</td>
<td>359 [360]</td>
<td>$\alpha=\gamma=90^\circ, \beta=138.1^\circ$</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>

Reported [10, 4] values are given in parenthesis.
Figure 3: Dielectric constants observed for the ZM7S crystals
Figure 4: Dielectric loss factors observed for the ZMTS crystals
Electrical conductivities of pure ZTS crystal observed in the present study are found to be in good agreement with the reported values [11]. Electrical conductivity of ZMTS crystals can be understood as due to the proton transport within the framework of hydrogen bonds. Also, the conductivity can be associated with the incorporation into the crystal lattice of impurities and the formation of corresponding defects in ionic crystals. The proton conduction may be accounted for by motion of protons accompanied by a D defect (excess of...
positive charge). Migration of these defects may only modify electric polarization and may not change the charge at an electrode. The motion of defects occurs by some kind of rotation in the bond with defects. The speed of displacement $v = va$, where $v$ and $a$ are the frequency and distance respectively of the jump (hopping of charge) from one bond to the other [12]. So, the increase of conductivity (both DC and AC) with the increase in temperature observed for the ZMTS crystals in the present study can be understood as due to the temperature dependence of the proton transport. Moreover, the conductivity increases smoothly through the temperature range considered in the present study.

The AC and DC activation energies ($E_{ac}$ and $E_{dc}$ respectively) observed in the present study are given in Table 2. $E_{dc}$ value is found to be more than the $E_{ac}$ value, as expected. Both the $E_{dc}$ and $E_{ac}$ values do not vary in a systematic way with the composition. The nonlinear composition dependence is felt for all the electrical parameters considered in the present study. This is similar to that reported in the literature for alkali halide mixed crystals [7, 13-15]. As done in the case of alkali halide mixed crystals, the nonlinear variation with composition of the electrical parameters observed in the present study for the ZMTS crystals can be attributed to the enhanced diffusion of charge carriers along dislocations and grain boundaries.

Table 2. DC and AC activation energies observed for the ZMTS crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$E_{dc}$ (ev)</th>
<th>$E_{ac}$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTS</td>
<td>0.209</td>
<td>0.094</td>
</tr>
<tr>
<td>ZTS9</td>
<td>0.472</td>
<td>0.087</td>
</tr>
<tr>
<td>ZTS8</td>
<td>0.625</td>
<td>0.093</td>
</tr>
<tr>
<td>ZTS7</td>
<td>0.457</td>
<td>0.081</td>
</tr>
<tr>
<td>ZTS6</td>
<td>0.411</td>
<td>0.077</td>
</tr>
<tr>
<td>ZTS5</td>
<td>0.571</td>
<td>0.086</td>
</tr>
<tr>
<td>ZTS4</td>
<td>0.675</td>
<td>0.081</td>
</tr>
<tr>
<td>ZTS3</td>
<td>0.572</td>
<td>0.074</td>
</tr>
<tr>
<td>ZTS2</td>
<td>0.605</td>
<td>0.079</td>
</tr>
<tr>
<td>ZTS1</td>
<td>0.666</td>
<td>0.066</td>
</tr>
<tr>
<td>MTS</td>
<td>0.598</td>
<td>0.073</td>
</tr>
</tbody>
</table>

The dielectric constant of a material is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. It is well established that the space charge polarization is very predominant at lower frequencies. This polarization is known to arise from charged defects or impurities present and also due to the creation and distribution of dipoles either within the bulk or at the surface of the crystal. The dipole orientational effect can sometimes be seen in some materials up to $10^{10}$ Hz. The ionic and electronic polarizations always exist below $10^{13}$ Hz. The large value of $\varepsilon_r$ at low frequency is due to the presence of space polarization, which depends on the purity and perfection of the sample. Results obtained in the present study show that ionic polarization is dominating in ZMTS crystals. Moreover, Varotsos [16] has shown that the electronic polarizability practically remains constant in the case of ionic crystals. The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability.

### 4. Conclusions
Single crystals of ZMTS were grown by the slow evaporation method and characterized by single crystal X-ray diffraction and electrical (both AC and DC) measurements. The grown crystals were transparent and with well defined external appearance. The obtained unit cell parameters of pure ZTS and MTS crystals are in agreement with the literature values. The unit cell parameters values show that both pure and MgSO$_4$ mixed ZTS crystals are in an orthorhombic structure. The MTS crystal belongs to monoclinic structure. The electrical measurements of ZMTS crystals were carried out at different temperatures with various frequencies and it is observed that DC conductivity ($\sigma_{dc}$), dielectric constant ($\varepsilon_r$), dielectric loss (tan $\delta$) and AC conductivity ($\sigma_{ac}$) values increase with the increase in temperature and also these values increase in the case of the MgSO$_4$ added ZTS crystals. All the electrical parameters considered in the present study ($\sigma_{dc}$, $\varepsilon_r$, tan $\delta$, $\sigma_{ac}$, $E_{dc}$ and $E_{ac}$) are found to vary nonlinearly with the composition (x values).
References