CHAPTER- 3

Transition metal doping effects: Influence of Ni(II)/Pd(II) doping effects on tris(thiourea)zinc(II) sulphate crystals*

ABSTRACT

Single crystals of Ni(II)/Pd(II) doped tris(thiourea)zinc(II)-sulphate (ZTS) are grown from an aqueous solution by conventional slow evaporation solution growth technique. The characteristic functional groups are identified by FT-IR analysis. Crystal stress is indicated by powder XRD patterns and FT-IR analysis. Incorporation of dopant into the crystalline matrix during crystallization process is evidenced by energy dispersive X-ray spectroscopy and quantified by inductively coupled plasma technique. The surface morphological changes are observed in the doped specimen. Mechanical stability of the as-grown specimen is analyzed by Vickers microhardness analysis. Thermal studies reveal no decomposition upto the melting point. Lattice parameters determined by single crystal XRD analysis reveal only minor variations as a result of low doping levels. Ni(II)/Pd(II) doping has a catalytic effect on the second harmonic generation efficiency of metal thiourea complex.

3.1. INTRODUCTION

Tris(thiourea)zinc(II) sulphate is a semi-organic nonlinear optical material which finds applications in the area of laser

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technology, optical communication, data storage and optical computing because it has a high resistance to laser induced damage, high nonlinearity, wide transparency, low angular sensitivity and good mechanical hardness compared to many organic NLO crystals\textsuperscript{1-4}. ZTS is a good engineering material for second harmonic generation (SHG) device applications. It is a novel metal organic crystal with potential application in electro-optic modulation\textsuperscript{5}. It crystallizes in orthorhombic system with noncentrosymmetric space group $P\text{ca}2_1$ (point group mm2). Metal ion doped materials are currently receiving a great deal of attention due to the rapid development of laser diodes\textsuperscript{6,7}. Transition metal impurity in the crystalline matrix generally influences the physical properties of the crystal\textsuperscript{8-13}. Palladium doping enhances the gas sensing properties of nanoparticles\textsuperscript{14-19}. Incorporation of palladium strongly affects the manganese reducibility and shifts the reduction process to lower temperature\textsuperscript{20}. Also, palladium doping enhances the stability of gold cluster\textsuperscript{21}. Hexacoordinated bivalent nickel complexes usually show three spin-allowed absorption bands in the near infrared, visible and near ultraviolet regions\textsuperscript{22}. The dielectric constant of the base compositions increased with the addition of NiO upto 2 mol \%\textsuperscript{23}. Widening of the band gap with increased Ni doping was also discussed with Burstein-mass effect and the Ni doped ZnO can be considered a suitable candidate for DSSC applications\textsuperscript{24}.

Recently, we have investigated the effect of doping organic additives\textsuperscript{25-27}, Mn(II)\textsuperscript{28}, Ce(IV)\textsuperscript{29}, Cs(I)\textsuperscript{30}, Mg(II)\textsuperscript{31} and benzene\textsuperscript{32} on ZTS crystals. In the present investigation, the effect of Ni(II)/Pd(II) doping
on ZTS crystals has been studied using FT-IR, XRD, SEM and EDS, microhardness thermal, dielectric studies and Kurtz powder SHG measurements.

3.2. EXPERIMENTAL

3.2.1. Synthesis and crystal growth

ZTS was synthesized\textsuperscript{33} using zinc sulphate heptahydrate (EM) and thiourea (SQ) in a stoichiometric ratio of 1:3. To avoid decomposition, low temperature (<70°C) was maintained during the preparation of solution in deionized water.

\[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + 3\text{CS(NH}_2\text{)}_2 \rightarrow \text{Zn(CS(NH}_2\text{)}_2)_3\text{SO}_4 \]

After successive recrystallization processes, crystals were grown by slow evaporation solution growth technique\textsuperscript{26, 29}. Doping of nickel (5 mol %) in the form of nickel sulphate and palladium (5 mol %) in the form of palladium chloride was done during the crystallization process. The crystallization took place in 20-23 days and the macroscopic defect-free crystals were harvested. Photographs of as-grown nickel(II)/palladium(II) doped ZTS crystals are shown in Fig. 3.2.1.
Fig. 3.2.1. Photographs of (a) pure (b) Ni(II) doped and (c) Pd(II) doped ZTS crystals
3.3. RESULTS AND DISCUSSION

3.3.1. FT-IR

A close observation of FT-IR spectra (Fig. 3.3.1) of the doped specimens reveals that the doping results in small shifts in some of the characteristic vibrational frequencies (Table 3.3.1). The CN stretching frequencies of thiourea (1089 cm\(^{-1}\) and 1472 cm\(^{-1}\)) are shifted to higher frequencies for Ni(II)/Pd(II) doped ZTS (1152 cm\(^{-1}\) and 1514 cm\(^{-1}\)/1157 cm\(^{-1}\) and 1505 cm\(^{-1}\)). The CS stretching frequencies (1417 cm\(^{-1}\) and 740 cm\(^{-1}\)) are shifted to lower frequencies (1403 cm\(^{-1}\) and 716 cm\(^{-1}\)/ 1430 cm\(^{-1}\) and 713 cm\(^{-1}\)) for Ni(II)/Pd(II) doped specimens.

**Table 3.3.1.** FT-IR frequencies (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Thiourea ZTS</th>
<th>Ni(II) doped ZTS</th>
<th>Pd(II) doped ZTS</th>
<th>Assignment of vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3376</td>
<td>3399</td>
<td>3370</td>
<td>3406 (\nu_{as}(NH_2))</td>
</tr>
<tr>
<td>2</td>
<td>3167</td>
<td>3195</td>
<td>3177</td>
<td>3196 (\nu_{as}(NH_2))</td>
</tr>
<tr>
<td>3</td>
<td>1627</td>
<td>1624</td>
<td>1631</td>
<td>1626 (\delta(NH_2))</td>
</tr>
<tr>
<td>4</td>
<td>1089</td>
<td>1122</td>
<td>1152</td>
<td>1157 (\nu_{s}(C-N))</td>
</tr>
<tr>
<td>5</td>
<td>1472</td>
<td>1502</td>
<td>1514</td>
<td>1505 (\nu(N-C-N))</td>
</tr>
<tr>
<td>6</td>
<td>1417</td>
<td>1398</td>
<td>1446</td>
<td>1430 (\nu_{as}(C=S))</td>
</tr>
<tr>
<td>7</td>
<td>740</td>
<td>712</td>
<td>716</td>
<td>713 (\nu_{as}(C=S))</td>
</tr>
<tr>
<td>8</td>
<td>648</td>
<td>619</td>
<td>---</td>
<td>619 (\nu_{as}(N-C-S))</td>
</tr>
<tr>
<td>9</td>
<td>492</td>
<td>471</td>
<td>533</td>
<td>476 (\delta_{as}(N-C-N))</td>
</tr>
</tbody>
</table>
An absorption band in the region 2750 to 3400 cm\(^{-1}\) corresponds to the symmetric and asymmetric stretching frequencies of NH\(_2\) group of zinc(II) coordinated thiourea. Spectral studies suggest that the metal coordinate with thiourea through sulfur atom.

**Fig. 3.3.1.** FT-IR spectra of (a) pure (b) Ni(II) doped and (c) Pd(II) doped ZTS
3.3.2. XRD analysis

A comparison of powder XRD patterns of pure and doped Ni(II)/Pd(II) specimens clearly reveal the intensity variations (Fig. 3.3.2). Diffraction patterns indicate no phase changes and narrow peaks indicate good crystallinity. However, a slight variation in intensity is observed as a result of doping. The most prominent peaks with maximum intensity of the XRD patterns of pure and doped specimens are quite different. These observations could be attributed to the strains in the lattice. The grown crystal belongs to the monoclinic system and the cell parameters of pure and doped specimens are given in the Table 3.3.2. Minor variations in cell parameters are justified because of low doping levels.

Table 3.3.2. Lattice parameters

<table>
<thead>
<tr>
<th>Crystal</th>
<th>a/(Å)</th>
<th>b/(Å)</th>
<th>c/(Å)</th>
<th>Volume/(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ZTS*</td>
<td>11.21</td>
<td>7.72</td>
<td>15.60</td>
<td>1350.23</td>
</tr>
<tr>
<td>Ni(II) doped ZTS</td>
<td>11.08</td>
<td>7.75</td>
<td>15.42</td>
<td>1323.00</td>
</tr>
<tr>
<td>Pd(II) doped ZTS</td>
<td>11.32</td>
<td>7.80</td>
<td>15.51</td>
<td>1369.00</td>
</tr>
</tbody>
</table>

*JCPDS No. 76-0778
Fig. 3.3.2. Powder XRD patterns of (a) pure (b) Ni(II) doped and (c) Pd(II) doped ZTS
3.3.3. SEM and EDS

The effect of the influence of dopant on the surface morphology of ZTS crystal faces reveals structure defect centers and voids as seen in the SEM micrographs (Fig. 3.3.3.1). SEM micrographs of the doped specimen show more scatter centers than that of the undoped specimen. A small quantity incorporation of Ni(II)/Pd(II) in the doped specimen was confirmed by EDS as clearly seen in Fig. 3.3.3.2.

![SEM micrographs of (a) pure (b) Ni(II) doped and (c) Pd(II) doped ZTS](image)

**Fig. 3.3.3.1. SEM micrographs of (a) pure (b) Ni(II) doped and (c) Pd(II) doped ZTS**

Inductively coupled plasma (ICP) analysis indicates that the palladium incorporation (1.2 ppm) is small but significant. The dopant concentration in the host lattice is not proportional to the concentration taken during the crystallization process since the host crystal can accommodate the dopant only to a limited extent. Ease of incorporation even by small quantity doping is justified by comparing the ionic radii of Zn$^{2+}$ (74 ppm) with that of Pd$^{2+}$ (78 ppm).
3.3.4. Thermal studies

The simultaneous TG/DTA curves in nitrogen recorded for doped ZTS specimens are given in the Fig. 3.3.4. The absence of water of crystallization in the molecular structure is indicated by the absence of weight loss around 100°C. The melting point of sample is
slightly increased in the case of Ni(II) doping whereas it is slightly decreased in the case of Pd(II) doped ZTS suggesting the incorporation. No decomposition up to the melting point ensures the suitability of the material for the application in lasers where the crystals are required to withstand high temperatures.

**Fig. 3.3.4. TG/DTA curves of (a) Ni(II) doped and (b) Pd(II) doped ZTS**

### 3.3.5. Mechanical studies

Transparent crystals free from cracks were selected for microhardness measurements. Before indentation, the crystals were
carefully lapped and washed to avoid surface effects. The Vickers hardness indentations were made on the as-grown surface of the Ni(II)/Pd(II) doped crystal at room temperature with the load ranging from 25 to 100 g, keeping the time of indentations kept as 10 sec for all trials. The Vickers hardness number $H_v$ was calculated from the following equation,

$$H_v = 1.8544\left(\frac{P}{d^2}\right) \text{kg/mm}^2$$

where $P$ is the applied load in kg and $d$ is the mean diagonal length of the indentation impression in micrometer.

![Graph](image)

**Fig. 3.3.5. Plot of Vickers hardness number vs Load**

A plot of Vickers hardness number ($H_v$) versus load ($P$) reveals that the hardness of the grown crystal increases as the load increases (**Fig. 3.3.5**). Cracks started developing around the indentation mark beyond a load of 100 g. This may be due to the internal stresses
released during the indentation. The hardness of the material is found to increase with the increase of load confirming the prediction of Onitsch\textsuperscript{34}.

### 3.3.6. Dielectric properties

Fig. 3.3.6(a-c) is the plot of dielectric constant ($\varepsilon_r$), dielectric loss (tan $\delta$) and AC conductivity ($\sigma_{ac}$) versus temperature at different frequencies for both pure and Ni(II) doped specimens. It can be seen that dielectric parameters are temperature dependent. It is observed that both $\varepsilon_r$ and tan $\delta$ are inversely proportional to frequency. The dielectric constant of a material is generally composed of four different types of contributions like ionic, electronic, orientational and space charge polarizations. The large value of dielectric constant at low frequencies may be due to contribution of all these polarizations. The decreased dielectric constant at higher frequencies could be due to the reduction in the space charge polarization. Space charge polarization is generally active at lower frequencies and high temperatures indicating the purity and perfection of the grown crystal\textsuperscript{35}. The increase in conductivity could be attributed to reduction in the space charge polarization at higher frequencies\textsuperscript{36}. In the present study, dielectric constant varying proportionally with temperature is essentially due to the temperature variation of the polarizability\textsuperscript{37}. The low $\varepsilon_r$ value dielectric materials have potential applications in microelectronic industries.
Fig. 3.3.6. Dielectric measurements for pure and Ni(II) doped ZTS

(a) Plot of dielectric constant vs temperature

(b) Plot of dielectric loss vs temperature

(c) Plot of AC electrical conductivity vs temperature
3.3.7. SHG efficiency

The SHG of the specimens were measured by the Kurtz powder technique\textsuperscript{38}. An Nd:YAG laser with modulated radiation of 1064 nm was the optical source. Uniform particle size (125-150 μm) specimens were exposed to laser and the output was monochromated to collect the intensity of the 532 nm component. In order to confirm the influence of doping on the SHG-activity and as a comparative measure the pure and Ni(II)/Pd(II) doped specimens were subjected to SHG test. The output SHG intensities give the relative efficiencies of the measured specimens \textbf{(Table 3.3.3)}. The effect of various metal dopants on the SHG efficiency of ZTS has been listed in \textbf{Table 3.3.4}. From this data, it is clear that the metal doping enhances the SHG efficiency. Metals can behave as electron donors or acceptors and it appears that they facilitate the charge transfer thereby nonlinearity. A favorable molecular alignment for nonlinearity is achieved by incorporation of small quantity of metal into the crystalline matrix. Small quantity incorporation of Ni(II)/Pd(II) doping has a catalytic effect on SHG efficiency of ZTS.

\textbf{Table 3.3.3.} SHG outputs

<table>
<thead>
<tr>
<th>System</th>
<th>$I_{2\omega}$ (mV)</th>
<th>Input energy (mJ/pulse)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure ZTS</td>
<td>2.7</td>
<td>8.8</td>
</tr>
<tr>
<td>Ni(II) doped ZTS</td>
<td>3.9</td>
<td>8.8</td>
</tr>
<tr>
<td>Pure ZTS</td>
<td>14</td>
<td>2.5</td>
</tr>
<tr>
<td>Pd(II) doped ZTS</td>
<td>25</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Table 3.3.4. SHG outputs of ZTS doped with metals

<table>
<thead>
<tr>
<th>System</th>
<th>Relative efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTS doped with Ni(II)</td>
<td>~1.4 times of ZTS</td>
<td>Present work</td>
</tr>
<tr>
<td>ZTS doped Pd(II)</td>
<td>~1.7 times of ZTS</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZTS doped with Mn(II)</td>
<td>~2.1 times of ZTS</td>
<td>28</td>
</tr>
<tr>
<td>ZTS doped with Ce(IV)</td>
<td>~1.6 times of ZTS</td>
<td>29</td>
</tr>
<tr>
<td>ZTS doped with Cs(I)</td>
<td>~1.2 times of ZTS</td>
<td>30</td>
</tr>
<tr>
<td>ZTS doped with K(I)</td>
<td>~1.2 times of KDP</td>
<td>39,40</td>
</tr>
<tr>
<td>ZTS doped with Na(I)</td>
<td>Slightly greater than ZTS</td>
<td>41</td>
</tr>
<tr>
<td>ZTS doped with Li(I)</td>
<td>Green light emission</td>
<td>42</td>
</tr>
<tr>
<td>ZTS doped with Cd(II)</td>
<td>Greater than ZTS</td>
<td>43</td>
</tr>
</tbody>
</table>

3.4. CONCLUSIONS

The influence of Ni(II)/Pd(II) doping on tris(thiourea)zinc(II)-sulphate has been systematically investigated. A close observation of XRD and FT-IR profiles of doped specimens reveal some minor variations, indicating the crystal stress. Doping results in surface roughness and defects. The transition metal can act as an electron donor or acceptor and doping is advantageous since it improves the SHG efficiency of the host crystal to an appreciable extent. Pd(II) is a more effective dopant than Ni(II) in enhancing the efficiency and it is quite likely due to the varied electronic configurations.
REFERENCES


[18] H. H. Liang, J. Y. Lee, Enhanced Electro-Optical Properties of Liquid Crystals Devices by Doping with Ferroelectric Nanoparticles, Department of Materials Science and Engineering, University of Science and Technology, Taiwan


