Growth, Structural, Spectral and Optical Characterization of Pure and Lithium Chloride Doped Triglycine Zinc Sulphate Single Crystals

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ABSTRACT

Single crystals of pure and 1 mol\% lithium chloride doped triglycine zinc sulphate were grown from aqueous solution employing the slow evaporation technique at room temperature. The grown crystals were subjected to single crystal and powder X-ray diffraction analysis to determine the crystal structure and to confirm the crystallinity and phase purity. The functional groups present in the grown crystals were identified by Fourier transform infrared studies. The UV-Visible transmission spectra were recorded to study the optical transparency of the grown crystals. The various studies indicate changes in structural and optical properties of triglycine zinc sulphate crystals due to incorporation of the dopant lithium chloride into the triglycine zinc sulphate crystals.

Keywords: slow evaporation, NLO crystal, PXRD, FTIR

1. INTRODUCTION

Non Linear Optical (NLO) materials for optical second harmonic generation (SHG) have received much attention owing to their practical application in the domain of optoelectronics and photonics [1,2]. Semionic NLO crystals are attracting a great deal of attention due to their high NLO efficiency, high damage threshold and high mechanical strength than organic NLO crystals. In semi organic materials the organic ligand is ionically bonded with inorganic host and hence semi organic crystals are having higher chemical stability and mechanical strength [3]. Aminoacids with inorganic compounds are promising materials for non linear optical applications, as the high optical nonlinearity of the purely organic amino acids tend to combine with the favourable mechanical and thermal properties of the inorganic salt. It has been reported that some complexes of amino acids with simple inorganic salts exhibit ferroelectric properties [4,5]. Glycine is the simplest amino acid and it is a centro symmetric material. Glycine mixed semi-organic material is of special interest as a fundamental building block to develop many complex crystals with improved NLO properties. Crystals of triglycine sulphate are ferroelectric materials [6,7] and pyroelectric materials which find application in the fabrication of infrared detectors, capacitors, transducers and sensors [8,9]. It has been reported in the literature that doping NLO crystals with various dopants can alter physical and chemical properties and doped-NLO crystals may find wide applications in opto-electronic devices compared to undoped NLO crystals [10,11]. In view of this, an attempt has been made to investigate the effect of lithium chloride on the structural, spectral and optical properties of triglycine zinc sulphate crystal.

2. EXPERIMENTAL PROCEDURE

2.1 Crystal Growth

Single crystals of pure and 1 mol\% lithium chloride doped triglycine zinc sulphate (TGZS) were grown from aqueous solution by slow evaporation technique at room temperature. To grow single crystals of triglycine zinc sulphate, the saturated solution was prepared by dissolving glycine and zinc sulphate in deionized water in the ratio 3:1. The solution was stirred continuously for an hour using a magnetic stirrer to
obtain a homogenous solution. Then it was filtered and transferred to a borosil glass beaker which was porously sealed and placed in a dust free atmosphere for slow evaporation. Good quality single crystals of triglycine zinc sulphate were harvested within 25-30 days. For the growth of 1 mol% lithium chloride doped triglycine zinc sulphate crystals, the saturated solution was prepared by mixing triglycine zinc sulphate and lithium chloride in the ratio 1: 0.01 in deionized water. Single colourless crystals of triglycine zinc sulphate doped with lithium chloride were harvested after a growth period of about 30 days. The photographs of the grown pure and 1mol% lithium chloride doped triglycine zinc sulphate crystals are shown in Fig. 1: (a) and (b) respectively.

Fig. 1: Photographs of (a) pure and (b) 1mol% lithium chloride doped TGZS crystals

3. RESULTS AND DISCUSSION

3.1. Single crystal XRD studies

Single crystal X-ray diffraction analysis has been carried out to confirm the crystallinity and to determine the lattice parameters. The grown single crystals of pure and 1mol% lithium chloride doped triglycine zinc sulphate crystals were subjected to single crystal XRD studies using a Bruker Nonius CAD-4/MACH3 single crystal diffractometer. The unit cell parameters of pure triglycine zinc sulphate crystals are $a=7.039\,\text{Å}$, $b=7.039\,\text{Å}$, $c=5.448\,\text{Å}$, $\alpha=\beta=90^{\circ}$, $\gamma=120^{\circ}$, $V=233.02\,\text{Å}^3$ and the unit cell parameters of lithium chloride added triglycine zinc sulphate crystals are $a=7.042\,\text{Å}$, $b=7.042\,\text{Å}$, $c=5.426\,\text{Å}$, $V=234.82\,\text{Å}^3$, $\alpha=\beta=90^{\circ}$, $\gamma=120^{\circ}$. From the data, it is observed that pure and lithium chloride doped triglycine zinc sulphate crystals crystallize in hexagonal system with the space group of $P3\bar{2}$. Slight changes of lattice parameters have been noticed for the lithium chloride doped sample compared to the pure triglycine zinc sulphate crystals.

3.2. Powder X-ray Diffraction Analysis

The powder X-ray diffraction analysis is useful for confirming the identity of a crystal and determining the crystallinity and phase purity. Powder X-ray diffraction (PXRD) studies were carried out on the grown pure and 1mol% lithium chloride doped triglycine zinc sulphate crystals using XPERT-PRO diffractometer with copper (K- Alpha 1) radiation of wavelength $1.54056\,\text{Å}$. Fig. 2: (a) and (b) show the PXRD patterns of pure triglycine zinc sulphate and 1mol% lithium chloride doped triglycine zinc sulphate crystals respectively. The sharp peaks in the XRD patterns of pure and lithium chloride doped triglycine zinc sulphate show that the grown crystals have good crystallinity.

![Powder XRD patterns](image)

Slight shifts in $2\theta$ and variation in the peak intensity is observed between the XRD patterns of pure and lithium chloride doped triglycine zinc sulphate crystals indicating the
entry of lithium chloride molecules in to the triglycine zinc sulphate crystal lattice.

3.3. Fourier Transform Infrared Analysis

Fourier transform infrared (FTIR) spectra were recorded for the powdered samples of pure and 1mol% lithium chloride doped triglycine zinc sulphate crystals in the frequency range of 400 - 4000 cm\(^{-1}\) using Perkin Elmer Fourier transform infrared spectrometer by KBr pellet technique. Figures 3(a) and 3(b) represent the obtained FTIR spectra for pure and 1 mol% lithium chloride doped triglycine zinc sulphate crystals respectively. Assignments were made on the basis of the magnitudes of the frequencies compared with the literature data [12,13]. The frequency assignment for the various absorption peaks observed in FTIR spectra for both pure and 1 mol% lithium chloride doped triglycine zinc sulphate crystals are tabulated in table 2. Fourier transform infrared studies show shift and absence in the frequencies due to the interaction and the incorporation of the dopant lithium chloride into the triglycine zinc sulphate crystal lattice.

![Figure 3](image)

### TABLE - 1

<table>
<thead>
<tr>
<th>Pure TGZS (cm(^{-1}))</th>
<th>1 mol % doped TGZS (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3168</td>
<td>3175</td>
<td>NH(_2)(^+) stretching vibration</td>
</tr>
<tr>
<td>3009</td>
<td>3058</td>
<td>NH(_2)(^+) stretching</td>
</tr>
<tr>
<td>2611</td>
<td>2619</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>1598</td>
<td>-</td>
<td>COO(^-) Asymmetric stretching</td>
</tr>
<tr>
<td>1501</td>
<td>-</td>
<td>NH(_3)(^+) stretching</td>
</tr>
<tr>
<td>1405</td>
<td>1409</td>
<td>COO(^-) symmetric stretching</td>
</tr>
<tr>
<td>1332</td>
<td>1335</td>
<td>CH(_2) wagging</td>
</tr>
<tr>
<td>1193</td>
<td>1111</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>1113</td>
<td>-</td>
<td>C-C stretching</td>
</tr>
<tr>
<td>1035</td>
<td>1031</td>
<td>SO(_4) (^2) vibrations</td>
</tr>
<tr>
<td>892</td>
<td>896</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>690</td>
<td>696</td>
<td>COO(^-) bending</td>
</tr>
<tr>
<td>504</td>
<td>505</td>
<td>COO(^-) rocking</td>
</tr>
</tbody>
</table>

3.4. Optical Transmission Spectral Analysis

The UV-Vis transmission spectra of the pure and 1mol% lithium chloride doped triglycine zinc sulphate single crystals were recorded using a Perkin-Elmer Lambda 35 UV-Visible spectrometer in the range 180-800nm. The UV-Vis transmission spectra obtained for grown samples are shown in figures 4(a) and 4(b) respectively. From the UV spectra, it is evident that the UV cut off wave length for pure TGZS is around 260 nm and it has 86 % transmittance. But in the case of 1mol % lithium chloride doped TGZS, the UV cut off wave length is found to be around 240 nm and the transmittance is 92%. This shows that the addition of 1mol% lithium chloride has increased the optical transparency of the crystal. From the spectra, it is inferred that both pure and lithium chloride doped crystals have the potential to be used for SHG in the case of Nd- YAG laser to emit a second harmonic signal in the green region.
The grown crystals have a wide transmission window in the entire visible region which enables them to be potential candidates for opto electronic applications [14].

4. CONCLUSION

Single crystals of pure and 1 mol% lithium chloride doped triglycine zinc sulphate were grown from aqueous solution using slow evaporation technique. Slight changes of lattice parameters have been noticed for the lithium chloride doped crystals compared to the pure triglycine zinc sulphate crystals. Powder XRD studies confirm that the lattice of triglycine zinc sulphate crystal is slightly distorted due to the addition of lithium chloride. However the hexagonal structure has been retained. Fourier transform infrared studies show shift and absence in the frequencies due to the incorporation of the dopant lithium chloride into the TGZS crystal lattice. From the UV-Vis spectral analysis it is noted that addition of lithium chloride has increased the transparency in the visible region. The crystals grown in the present study can be considered as promising NLO crystals as they have lower cut off wavelengths.

REFERENCES