Crystal Growth, Thermal, and Optical Studies: Thiourea Glycyl-L-Alanine Single Crystals

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Single crystals of pure and thiourea substituted Glycyl-L-Alanine (TU-GLA) were successfully grown by the slow evaporation solution growth method at constant temperature of 35 °C. The effect of thiourea dopant on the crystal properties has been studied. Single crystal XRD analysis confirms the structure and change in the lattice parameter values for the doped crystals. The crystals were characterized by the FTIR and UV-Vis-NIR techniques. The presence of all the elements was confirmed by EDAX analysis. Thermal stability of the grown crystals was tested by TGA/DTA. Hardness studies on the as-grown crystals of GLA and TU-GLA were carried out by a static indentation test at room temperature using a Leitz Wetzlar Vickers microhardness tester. The dielectric response of the crystals was also investigated and reported.

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I. INTRODUCTION

Recently, the growing of single crystals has helped advance modern technology. Nonlinear optical (NLO) materials have been studied extensively for their possible applications and are expected to play a major role in photonic technology, such as telecommunication, optical computing, optical data storage, and optical information processing [1–3].Interestingly, amino acids exhibit specific features such as (1) molecular chirality, which secures eccentric crystallographic structures; (2) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (3) zwitterionic nature of molecules, which favors crystal hardness [4]; (4) amino acids can be used as chiral auxiliaries for nitro aromatics and other donor-acceptor molecules with large hyperpolarizabilities; and (5) as a basis for synthesizing organic and inorganic compounds [5]. Single crystals of GLA have already been reported [6]. Amino acid crystals are widely used and thoroughly studied as NLO crystals. Many researchers have tried to modify the properties and the growth rates of the amino acid crystal by either changing the growth conditions or by adding different impurities. It is very clear from the previous reports that the physical properties of NLO crystals can be enhanced by doping with organic additives [7–10]. In this paper we report on the study of the effect of thiourea on various physical properties of Glycyl-L-Alanine single crystals.

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II. MATERIAL AND METHODS

II-1. Crystal Growth

In the present study Glycyl-L-Alanine (GLA) and thiourea doped GLA (TU-GLA) crystals are grown by the slow evaporation solution growth method. The stoichiometrically synthesized material was taken as the raw material for growth. A saturated solution of GLA was prepared at room temperature with water as the solvent, and the prepared solution was filtered using a micro filter. The filtered solution was taken in beakers and dried in a dust free atmosphere at 35 °C. In this process 3 drops of hydrogen peroxide were added to the mother solution of GLA to inhibit the growth of microbes [11, 12]. Single crystals of optimum size were grown in 40 days. Similarly crystals were also grown with thiourea as a dopant. A saturated solution of GLA was prepared at room temperature and the solution was filtered and thiourea was doped in 2wt%, after adding the dopant the solution was again stirred well in a closed vessel for more than an hour, and then the solution was filtered and dried in a dust free atmosphere at 35 °C. The crystals obtained with urea as dopant had no observable morphological changes. The as-grown crystals are shown in Figs. 1 and 2.

![Photographs of as-grown pure GLA crystals.](image)

FIG. 1: Photographs of as-grown pure GLA crystals.

II-2. Synthesis

The recrystallized salts of Glycine and L-Alanine (AR grade chemicals from E-Merck India Ltd) were used in the present crystal growth experiment. The GLA seed crystals were prepared by dissolving equimolar ratio Glycine and L-Alanine in Millipore water. The synthesized material was further purified by repeated recrystallization, and it was used for the growth of GLA crystals.

The reaction that took place in L-Alanine and Glycine in water medium is as follows:
Similarly 0.2M of urea and thiourea salts were used for the growth of TU-GLA crystals. The structural formula for the doped crystal is:

III. RESULTS AND DISCUSSION

III-1. XRD Study

Single crystal X-ray diffraction studies have been carried out using an ENRAF NONIUS CAD4 single X-ray diffractometer to calculate the lattice parameters of the grown crystals. It was observed that both pure and thiourea doped GLA crystallize in the monoclinic system. Both samples belong to the $P2_12_12_1$ space group which is recognized as being

FIG. 2: Photographs of as-grown TU-GLA crystals.
non-centrosymmetric, thus satisfying one of the basic and essential material requirements for the SHG activity of the crystals [13]. The lattice parameter values were calculated as $a = 9.695$ Å, $b = 9.564$ Å, and $c = 7.437$ Å and compared with the literature values [14]. In the case of thiourea doped GLA crystals slight variations in the lattice parameters as well as cell volume values are observed, and this is shown in Table I.

### Table I: Single crystal XRD data of pure and Thiourea doped GLA crystals.

<table>
<thead>
<tr>
<th>Crystal sample</th>
<th>Cell Parameters (Å)</th>
<th>Unit cell Volume (Å$^3$)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure GLA (Reported)</td>
<td>9.693 9.524 7.537</td>
<td>693.79</td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
<tr>
<td>Pure GLA (Present work)</td>
<td>9.695 9.564 7.437</td>
<td>695</td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
<tr>
<td>Thiourea-doped GLA</td>
<td>9.698 9.574 7.512</td>
<td>699.4</td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
</tbody>
</table>

### III-1-1. FTIR Spectral Study

FTIR studies confirm the various functional groups and their vibration interactions. It establishes the presence of the NH$_3^+$ group in the crystal, confirming the protonation of the amino acid group leading to the formation of the GLA molecule. The FT-IR analysis was recorded in the region 400 – 4000 cm$^{-1}$ using a BRUKER IFS 66V spectrometer to confirm the presence of the functional groups in the grown crystal. The middle IR spectrum of pure and thiourea doped GLA is shown in Figs. 3 and 4. It is observed that the broad envelope between 2508 cm$^{-1}$ and 3081 cm$^{-1}$ is due to overlapping of the NH$_3$ and CH stretching modes. The symmetric and asymmetric NH$_3^+$ stretching vibrations appear at frequencies 2938 cm$^{-1}$, respectively. The NH$_2$ group is protonated by the COOH group, giving rise to NH$_3^+$ and COO$^-$ groups. In the overtone region, there is a sharp intense peak at 2112 cm$^{-1}$, which is assigned to the combinational and asymmetrical bending vibration of NH$_3$. The bending modes of CH$_3$ are well resolved sharp peaks positioned at 1362 cm$^{-1}$ and 1505 cm$^{-1}$. The peak at 1114 cm$^{-1}$ is due to C-O stretch, and the O-H bend of COOH group is observed at 1236 cm$^{-1}$. The lack of any strong IR band at 1700 cm$^{-1}$ clearly indicates the existence of the COO$^-$ ion in zwitterionic form [15]. The C-H and N-H bending frequency is observed at 1307 cm$^{-1}$, and the absorption peak at 1594 cm$^{-1}$ confirms the presence of NH$_3$ bending [16]. A peptide bond CO-NH is formed between the carboxyl group COOH in L-alanine and the amino group NH$_2$, which is clearly visible in the spectrum at 1620 cm$^{-1}$ [17]. It is due to this peptide bond formation that the O-H symmetric stretching vibration of water is seen at 1455 cm$^{-1}$. The characteristic absorption for the -NH group in the aromatic ring is observed at 1306 cm$^{-1}$ for GLA. The broad absorption around 3080 cm$^{-1}$ indicates the co-presence of C=O stretching and O-H stretching. The broad envelope between 2150 cm$^{-1}$ and 3900 cm$^{-1}$ includes overlapping of the stretching modes due to N-H and C-H. The peaks at 1568 cm$^{-1}$ and 1454 cm$^{-1}$ are due to the symmetric and asymmetric stretching modes of NH$_3^+$ and COO$^-$, respectively. The FTIR spectra and the corresponding band assignment clearly indicate that the functional groups of pure GLA are...
not altered by the addition of the thiourea. Moreover the C=S stretching is observed at 820 cm$^{-1}$, which confirms that the dopant has entered into the GLA. The wave numbers observed from the recorded spectra are found to be in close agreement with the literature values [18–20].

FIG. 3: FTIR spectra of pure GLA crystals.

III-1-2. UV-Vis-NIR Study

Figures 5 and 6 show the UV-Vis-NIR spectrum of GLA and TU-GLA recorded with a highly transparent and defect free single crystal of thickness 2 mm. It is evident from the spectrum that both the grown samples have a wide transmission window between 250 and 1550 nm, with a lower cut-off wavelength starting at 270 nm. It is also noted that the percentage of transmittance was slightly higher in the TU-GLA crystal than in the pure crystal. The optical transmission study plays an important role in identifying the usefulness of an NLO material both in the visible and blue regions.

III-1-3. SHG Study

In order to find out the NLO property of the grown crystals, a second harmonic efficiency test was performed by the Kurtz and Perry powder technique [21] using a Q-switched, mode locked Nd – YAG laser operating at the fundamental wavelength 1064 nm, generating about 2.5 mJ / pulse. This laser can be operated in two modes. In the single shot mode the laser emits a single 8 ns pulse. In the multishot mode, the laser produces a continuous train of 8 ns laser pulses at a repetition rate of 10 Hz. In the present study, the single shot mode of 8 ns laser pulses with a spot radius of 1mm was used. The experimental setup used a mirror and 50 / 50 beam splitter to generate a beam with a pulse energy of
6 mJ. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The light emitted by the sample was detected by a photo diode detector and oscilloscope assembly. For the SHG efficiency measurements, a microcrystalline material of KDP was
used for comparison. The second harmonic generation was confirmed by the green emission of wavelength 532 nm from the crystalline sample. Both pure and thiourea doped GLA crystals were found to possess SHG efficiency. The results obtained by this method show that the SHG efficiency for pure and doped samples is about 18% and 20% as that of KDP. Hence the SHG efficiency of pure GLA is increased by the inclusion of thiourea.

### III-1-4. EDAX Analysis

Energy dispersive X-ray analysis (EDAX) used in conjunction with all types of electron microscopes has become an important tool for characterizing the elements present in the crystals. In the present study, the grown crystals were analyzed by an FEI QUANTA 200 F energy dispersive X-ray analyzer. The results obtained in EDAX of the pure and doped crystal are shown in Figs. 7 and 8. This confirms the presence of thiourea in the doped sample as it contains a sulphur atom. From the EDAX spectra the presence of sulphur in the thiourea doped GLA crystal is identified.

### III-1-5. Thermal Studies

The thermal stability of pure and doped GLA single crystals were estimated by the TGA and DTA techniques. Simultaneous thermo gravimetric analysis and differential thermal analysis were carried out for the crystal using a NETZSCH STA 409C/CD thermal analyzer. A powder sample of 20.100mg was kept in a nitrogen atmosphere in the temperature range 25 °C – 1200 °C with a heating rate of 10 K/min. The crucible used was of alumina (Al₂O₃), which served as a reference for the sample. Thermal characteristic curves for pure and doped GLA crystals are shown in Figs. 9 and 10. The TGA curve of GLA
indicates that the sample is stable from ambient up to 242 °C with a weight loss of 33.62%. A systematic weight loss was observed as the temperature further increases above the melting point. The total weight loss of the sample is 98.4% at 300 °C. The DTA curve indicates that the material has an exothermic peak at 235 °C, which represents the melting point. It
is observed that there is no phase transition or decomposition up to the melting point (235 °C), and also there is no mass reduction or decomposition up to 200 °C, indicating that one can crystallize this material by the slow evaporation solution growth technique. The crystal is found to be stable in the nitrogen atmosphere under normal humidity conditions. The stability of this crystal is a useful property for its possible NLO applications. However in TU-GLA, the DTA peak is largely shifted to 261 °C. This increment in the decomposition temperature is evident for the doped crystals, suggesting that the substitution of thiourea enhances the thermal stability of the GLA crystal. Another important observation is that there is no phase transition till the material melts, and this enhances the temperature range for the utility of the crystal for NLO applications.

![FIG. 9: TG and DTA curves of pure GLA crystals.](image)

III-1-6. Micro Hardness Analysis

Hardness studies on as-grown crystals of GLA and TU-GLA were carried out by a static indentation test at room temperature using a Leitz Wetzlar Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter attached to an incident light microscope. Several indentations were made on the crystal by varying the loads from 10 gm to 50 gm and the hardness number (Hv) was determined. The indentation time was kept as 15 s for all the loads. As micro cracks were developed on the crystal surface at higher loads, the maximum applied load was limited to 50 gm. Variation of the hardness number (Hv) with the applied load for GLA and TU-GLA are shown in Figs. 11 and 12. Hardness is a measure of the resistance to plastic deformation. The plot suggests that GLA crystal has an Hv value of 42 Kg/mm² whereas TU-GLA has a fairly high Hv value of 47 Kg/mm² for an applied load of 40 gm. This indicates that doped GLA has a higher VHN value when compared to pure GLA. Also the higher the hardness value, the greater the stress
required to form a dislocation, thus confirming greater crystalline perfection. Hence it may be suggested that the grown crystals may be used for device applications below the applied load of 40 gm.

FIG. 10: TG and DTA curves of TU-GLA crystals.

FIG. 11: Variation of Vickers hardness number with load for pure GLA crystals.
III-1-7. Dielectric Studies

The dielectric analysis is an important characteristic that can be used to obtain knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and the capability of transferring the electric charges can be assessed. Dielectric properties are correlated with electro-optic properties of the crystals, particularly when they are non-conducting materials [22]. The microelectronics industry needs low dielectric constant materials to use as an interlayer dielectric [23]. Figs. 13 and 14 and show plots of the dielectric constant for GLA and TU-GLA crystals as a function of log frequency. It is observed that as the frequency increases, the dielectric constant values are found to decrease exponentially and attain lower values. The dielectric constant becomes almost a constant over the wide frequency range of 5Hz to 5MHz. This is because of the impedance to the motion of the charge carriers at the electrodes, space charge, and macroscopic distortion results, which may cause larger values of a dielectric constant at lower frequencies.

IV. CONCLUSION

Single crystals of pure GLA and thiourea doped GLA were grown by the slow evaporation technique in a period of 45 days. XRD analysis confirms that both crystals belong to the orthorhombic system with the space group P2₁2₁2₁. However there is a slight increase in the lattice parameter and volume for the TU-GLA crystals. Functional groups and the modes of vibrations have been identified by the FTIR spectrum and the peak at 1620 cm⁻¹.
FIG. 13: Dielectric curves of pure GLA crystals.

FIG. 14: Dielectric curves of TU-GLA crystals

reveals the formation of a peptide bond CO-NH between the carboxyl group COOH in L-alanine and the amino group NH$_2$ in glycine, which ascertains the coordination of glycine with alanine. The minimum absorption in the entire visible range 272–280 nm for both crystals shows the suitability of these materials for NLO applications. The NLO property
analysed with the Kurtz Powder technique confirms that the grown crystals are non-linear in nature. The SEM analysis shows the surface morphology of the grown crystals. The thermal analysis reveals that the GLA is thermally stable up to 235 °C and its thermal stability is slightly increased when doped with thiourea. It is interesting to note that the incorporation of the thiourea dopant has improved the thermal stability and SHG efficiency of the GLA crystals. The dielectric studies reveal the low dielectric constant of the crystal at high-frequency regions. These preliminary studies suggest that thiourea doped GLA crystal is a candidate material suitable for photonic device fabrication.

References