GROWTH AND CHARACTERIZATION OF NLO SINGLE CRYSTAL (GLYCINIUM OXALATE)

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ABSTRACT

an organic material, Glycinium oxalate (GOX) was synthesized with two different molar ratios (1:1 and 10:1) and were successfully grown by solvent evaporation method. The grown crystal size and growth rate were compared for the two different molar ratios. The transparent crystals of dimensions 20mm x 10mm x 4mm were obtained. The powder X-ray diffraction analysis was taken to confirm the grown crystal. The FTIR study was carried out. The optical properties were examined and compared by UV-vis-NIR analysis which shows the crystals were transparent between the wavelength 400 nm and 1000 nm. The mechanical properties of the two different crystals grown with different molar ratio were measured and compared.

Keywords: organic crystal, NLO single crystal.

1. Introduction

Nonlinear optics (NLO) has emerged as forefront of current research in view of its vital application such as frequency shifting, optical modulations, optical switching [1-3]. Nonlinear Optical properties of semi-organic materials are currently under intense investigation because of inherent advantage of both organic and inorganic materials. Amino acids are playing vital role in the field of nonlinear optics. Many of amino acids exhibit NLO properties, among them Glycine (NH$_2$CH$_2$COOH amino acetic acid) is the simplest amino acid. The complex of amino acids and the carboxylic acid are expected to throw light on the geometrical features of bio-molecular interactions and aggregation patterns. The reaction between the glycine with oxalic acid yields glycinium oxalate (GOX) [4]. The glycine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The oxalic acid molecule exists in a mono-ionized state in the crystals. The hydrogen bonds that stabilize the molecules are interconnected between the amino and carboxyl groups of adjacent molecules, in a head to tail arrangement. Glycine molecules form columns around 21 screw axes parallel to b. Semi-oxalate ions also form columns parallel to b. Adjacent molecules are related by a cell translation and interconnected by an O–H—O hydrogen bond. Each such column and its equivalent generated by a centre of inversion connect two glycine columns giving rise to a double layer parallel to (102) plane. In each layer, the unlike molecules are connected through an O–H—O hydrogen bond between the carboxyl group of the amino acid and the carboxylate group of the semi-oxalate ion, and their symmetry equivalents. The double layer is further stabilized by hydrogen bonds of the amino group of glycine with the semi-oxalate ion. The double layers are held together by possible C–H—O and vander waal’s interactions. The present communications emphasizes the growth of single crystals of GOX with different molar ratio and the results of characterization studies of GOX are discussed.
2. Experimental

2.1 Growth of glycinium oxalate (GOX)

The commercially available Glycine (AR grade) and oxalic acid were used for growth of the titled compound using the following reaction mechanism.

$$\text{C}_2\text{H}_4\text{NO}_2 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{C}_2\text{H}_6\text{NO}_2 + \text{C}_2\text{HO}$$

The GOX compound was prepared by taking two different molar ratios and thoroughly dissolving equimolar ratio of Glycine (purity 99%), oxalic acid and 10:1 molar ratio in double distilled water and stirred well using a temperature controlled magnetic stirrer to get homogeneous mixture of solution. The substances were purified by successive crystallization process. After repeated crystallization, saturated solution was prepared at 32°C using the synthesized salts. The solution was finally filtered twice using micro-whatmann filter papers to eliminate unwanted impurities. The filtered solution was kept in a crystallizing vessel, covered with a perforated sheet and placed in a dust free atmosphere. A good quality single crystal of optimum size was obtained within a period of 4 weeks at room temperature (32 °C). The grown crystals of different molar ratio of Glycinium oxalate crystals are shown in Fig. 1.

![1:1 GOX](image1)

![10:1 GOX](image2)

Fig.1. photograph of different molar ratio Glycinium oxalate single crystals.

2.2 Characterisation

The grown crystals were confirmed by taking the XRD study and FTIR. The optical properties and mechanical properties of the final product of the sample were studied for the both the samples using UV-visible, micro hardness studies and the results were discussed in detail.

3. Results and Discussion

3.1 Powder X-Ray diffraction analysis

Grown GOX crystals were subjected to different characterization. Finely crushed powder of glycinium oxalate crystal was subjected to powder X-ray diffraction analysis employing a SIEFERT 3003 TT diffractometer with a characteristic CuKα (1.540589 Å) radiation for structural analysis. The sample scanned in the 2θ values from 10° to 60° at a rate of 2° min⁻¹. Fig 2 shows the Powder XRD spectrum of the grown crystal. The characteristic peak has appeared at around 25.36° (2θ). This study confirms that the synthesized material and as grown crystals contain a single phase of glycinium oxalate. It crystallizes in the monoclinic crystal system and the space group is P21/c. The determined lattice parameters are a=10.5700 Å, b=5.550 Å, c=12.083 Å, and β=113.830°, γ=90° and V=708.83 Å and Z=4. The lattice parameters are in good agreement with the reported values [4].
3.2 **FTIR Vibration analysis**

To confirm the formation of the compound the FT-IR spectrum of GOX was taken the spectrum reveals the characteristic vibrations of the zwitter ionic group, \(-\text{NH}^3+\) and the carboxylate ions. The primary \(\text{NH}^3+\) group has N–H stretching frequencies coinciding with the saturated C–H absorption frequencies. Hence the vibrations of the saturated C–H absorption to be observed around 3100 cm\(^{-1}\) are masked by the vibrations of the \(-\text{NH}^3+\) ion and cause a broadened band in this range. This broadening is further widened due to the presence of N-H-O hydrogen bonding. The \(\text{NH}^3+\) absorption, characteristic of amino acids, occurring in the range 3130–3100 cm\(^{-1}\) is more often shifted to lower wave number side, due to the formation of amino salts, and in GOX, it occurs at 3080 cm\(^{-1}\). The \(\text{NH}^2+\) group present in the free acid is converted into the \(-\text{NH}^3+\) ion during the formation of the salt.

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Vibration assignment</th>
</tr>
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<tbody>
<tr>
<td>505.01</td>
<td>Carboxylate group</td>
</tr>
<tr>
<td>887.60</td>
<td>Carboxylate group</td>
</tr>
<tr>
<td>1125.68</td>
<td>Absorption due to (\text{NH}^2+)</td>
</tr>
<tr>
<td>1286.95</td>
<td>C-N Symmetric stretching</td>
</tr>
<tr>
<td>1392.23</td>
<td>COO group</td>
</tr>
<tr>
<td>1495</td>
<td>Absorption due to (\text{NH}^2+)</td>
</tr>
<tr>
<td>1598.81</td>
<td>Strong asymmetric CO(_2) stretching</td>
</tr>
<tr>
<td>2898</td>
<td>(\text{NH}^3+) symmetric</td>
</tr>
</tbody>
</table>

Table 1 Frequencies of absorption observed in FTIR spectra of Glycinium oxalate

From Fig. 3, the peaks are observed at 683, 5847 and 505 cm\(^{-1}\) indicated the presence of carboxylate group. The \(\text{NH}^3+\) group is revealed by the peaks observed at 2609, 1495 and 1125 cm\(^{-1}\). These observations confirmed that the glycine molecule exists as zwitterionic form inside the crystal, in which the carboxyl group is present as a carboxylate ion and the amino group is present as an ammonium ion. Thus, the present study evidences the existence of glycine in phase. The peaks at 887, 1392 and 2965 cm\(^{-1}\) are attributed to CCN, COO– and CH\(_2\) stretching groups, respectively. The assignment of vibrations of glycinium oxalate crystal is given in Table 1 and these are in good agreement with those in literature [5].
3.3 UV-Vis spectroscopy

The UV-Visible spectrum gives the limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in σ and π orbital’s from the ground state to higher energy states. This less absorbance in the entire visible and near-IR region is an important requirement for NLO applications. Transmittance spectra are very important for any NLO material because a non linear optical material can be of practical use only if it has wide transparency window. To find the transmittance range of GOX, the optical transmittance spectrum for the wavelengths range between 200nm to 1200nm was recorded. A crystal of thickness 2mm was used for this analysis. A graph of transmission versus wavelength is shown in Fig. 4. From the spectra it can be observed that both ratio of GOX has same cutoff wavelength but the GOX crystal with molar ratio 10:1 has higher transmittance than equimolar ratio crystal.

3.4 Vickers micro-hardness study

The micro-hardness measurements were made on GOX crystals for the loads ranging from 5 to 30g. The Vickers hardness number $H_v$ is calculated using the relation, $H_v = 1.8544 \times (P/d^2)$ kg/mm², where $P$ is the applied load in kg and $d$ the mean diagonal length in mm. It is found that the GOX is harder than the other glycine doped crystals [6, 7]. This may be due to the C-H-O bonding. It is observed from Fig. 5, that the hardness number is lesser in the molar ratio 10:1 GOX and both the crystals exhibits reverse
indentation size effect while the work hardening co-efficient values of both crystals are calculated which reveals that GOX belong to soft material category.

![Variation of hardness with load for 1:1 and 10:1 ratio Glycinium oxalate crystals.](image)

**Fig. 5.** Variation of hardness with load for 1:1 and 10:1 ratio Glycinium oxalate crystals.

**4. Conclusions**

The GOX crystals were grown from the slow evaporation solution growth technique. The grown crystals were confirmed by powder crystal X-ray diffraction analysis and the FT-IR studies. The UV-visible spectrum reveals that the grown crystals have the cut-off wavelength of 305 nm and transmittance range slightly increased for ratio 10:1GOX than equimolar GOX. From this observation the compound can be employed in the NLO applications in the entire visible region and the near IR region. The Vickers micro-hardness measurement reveals that the hardness of 1:1 ratio GOX is moderately harder.

**References**


