Comparative study of nonlinear semi-organic crystals: Glycine Sodium Nitrate

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ABSTRACT. Glycine Sodium Nitrate (GSN) crystals were grown using slow evaporation technique at ambient temperature. Good quality crystals were obtained in the time interval of 5-6 weeks. Energy Dispersive X-ray Analysis (EDAX) and CHN analysis were carried out to check the purity of the grown crystals. Surface morphologies, smoothness and defects were observed by scanning electron microscope. GSN crystals were characterized by powder X-ray diffraction and indexing was done based on monoclinic system. UV-Vis study of the crystals showed that there is a wide range of transparency in the visible region. We also studied Raman and Fourier transform infrared spectra of GSN crystals. The results and their implications are discussed in the paper in detail.

1. INTRODUCTION
Over the last few years, researchers are extensively investigating the amino acid based semi-organic crystals because of their nonlinear optical (NLO) property. NLO effect is interaction of an electromagnetic field of high intensity laser with a material [1-4]. NLO materials have applications in many fields like laser technology, optical communication, and electro optics. Dealing with organic materials like amino acid provides one the advantage of (1) fine-tune chemical structure [4] (2) zwitterionic nature of molecule which favors crystal hardness (3) absence of strongly conjugated bonds, leading to wide transparency window in UV-Visible spectrum [5-8]. In the present research work, Glycine sodium nitrate crystal were grown with molar ratio of Glycine: Sodium nitrate (2:1) and (3:1). Inorganic material like sodium nitrate was added to glycine because of its excellent mechanical and thermal properties so that it can withstand at higher temperatures in technological applications [9]. The grown crystals were studied by different characterization techniques such as CHN, EDAX, SEM, Powder XRD, UV-Vis, FTIR and Raman spectroscopy.

2. EXPERIMENTAL
2.1 Growth: Most suitable and the simplest method to grow crystals of compound materials which are soluble in liquid media is slow evaporation method. For synthesis, glycine (99.5% pure) and sodium nitrate (99% pure) were taken in the specific molar ratio in double distilled water. GSN crystals were synthesized according to the reaction:

\[2(\text{NH}_2\text{CH}_2\text{COOH}) + (\text{NaNO}_3) \rightarrow \text{NH}_2\text{CH}_2\text{COOH} \cdot \text{NaNO}_3\]

\[3(\text{NH}_2\text{CH}_2\text{COOH}) + (\text{NaNO}_3) \rightarrow \text{NH}_2\text{CH}_2\text{COOH} \cdot 2\text{NaNO}_3\]

Prepared solution was filtered using the Whatman filter paper. Then the solution was filled in petry dish and was covered with parafilm to control the rate of evaporation and kept in vibration free housing. Under these conditions, we could obtain better quality GSN crystals in 5-6 weeks of time. Figure 1 and 2 shows the photographs of as grown GSN 2:1 and GSN 3:1 crystals. The SEM photographs of the grown GSN crystals shown in the figure 3 (a, b, c) shows visible cracks and island growth in the sample.
2.2 EDAX and CHN Analysis: CHN and EDAX analysis were done to authenticate the presence of chemical elements. EDAX analysis was carried out using JEOL JSM-5600 scanning electron microscope and the elements like Sodium, Carbon, Oxygen and Nitrogen were traced which are shown in Figures 4 and Figure 5 for GSN 2:1 and GSN 3:1 crystals respectively. Atomic percentage and weight percentage of traced elements are shown in Table 1. CHN analysis was done using Perkin Elmer 2400 CHNS analyzer. Table 2 shows the percentage of carbon, hydrogen, nitrogen, and oxygen. The oxygen percentage was determined by considering 100% composition of the sample. It is observed from both the analysis that no other elements are present in the grown crystals thereby proving their quality.

<table>
<thead>
<tr>
<th>Table 1: Weight % and atomic % from EDAX</th>
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<tbody>
<tr>
<td>Weight%</td>
</tr>
<tr>
<td>Element</td>
</tr>
<tr>
<td>C K</td>
</tr>
<tr>
<td>N K</td>
</tr>
<tr>
<td>O K</td>
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<tr>
<td>Na K</td>
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Figure 4: EDAX spectrum of GSN 2:1 crystal

Figure 5: EDAX spectrum of GSN 3:1 crystal

Table 2: Percentage of the C, H, N, and O

<table>
<thead>
<tr>
<th>Element</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
<th>O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>GSN 2:1</td>
<td>19.57</td>
<td>3.74</td>
<td>17.03</td>
<td>59.66</td>
</tr>
<tr>
<td>GSN 3:1</td>
<td>28.63</td>
<td>5.71</td>
<td>17.47</td>
<td>48.19</td>
</tr>
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X-ray Diffraction: X-ray diffraction pattern were recorded using Bruker D8 Advance X-ray diffractometer. Diffraction patterns were indexed based on monoclinic system by Powder-X software. The lattice parameter were taken as a=14.323 Å, b=5.2573 Å, c=9.1156 and β=119.030 with space group Cc [10-12]. X-ray diffractograms of both the crystals are shown in Figure 6 and Figure 7 indicating good crystalline nature as seen from the strong and sharp diffraction peaks.

Figure 6-7: X-ray diffractogram of GSN crystals
UV-Vis absorption spectra: GSN 2:1 crystal of thickness of 1.80 mm and GSN 3:1 crystal of 0.56 mm were used to record the optical absorption spectra between 180-800 nm. UV-Vis absorption spectra for both the samples are shown in **figure 8**. From the absorption spectra it is clear that UV cut off for GSN 2:1 is near 303 nm for the sample which matches with reported data [10,13] and UV cut off for GSN 3:1 is near 218 nm. In order to find the optical energy bandgap graph of \((\alpha h\nu)^2\) vs. \(h\nu\) was plotted as shown in **figure 9-10**. The insulating behavior of material was confirmed from the optical energy bandgap value which comes out to be 3.67 eV and 4.89 eV for GSN 2:1 and GSN 3:1 crystal respectively. UV-Vis absorption spectra show excellent transmission in the visible region suggesting that the samples are appropriate for optoelectronic applications [14].

![Figure 8: UV-Vis absorption spectra of both the crystals](image1)

![Figure 9-10: Plots of \((\alpha h\nu)^2\) vs. \(h\nu\)](image2)

3. **RAMAN AND FTIR**

Raman Spectra of GSN crystals were recorded using Jobin Yvon Horibra LABRAM-HR micro Raman system from 180-3500 cm\(^{-1}\) using Argon laser (488 nm) source. The Raman spectra is shown in **figure 11** whereas FTIR spectra are shown in **figure 12-13** for both crystals recorded by Perkin Elmer Spectrum GX from 400-4000 cm\(^{-1}\). Small shifts in wavenumber were observed in Raman spectra when matched with reported data [4, 15].
Table 3 shows the comparative chart of Raman and IR analysis for both the samples and it was matched with the reported data. Raman peaks below 500 cm⁻¹ were observed because of lattice vibrations. It was also observed that near 508, 677, 895, 1052, 1143, 1329, 1448 and 1508 cm⁻¹ both the samples were IR as well as Raman active. Presence of NH₃⁺ group was confirmed near 1614 and 1508 cm⁻¹. CH₂ Rocking, Twisting, Wagging and Scissoring were observed near 939, 1143, 1329 and 1448 cm⁻¹ for both the samples respectively.
4. CONCLUSIONS

GSN 2:1 and GSN 3:1 semi organic crystals were grown at ambient temperature by the slow evaporation method. Good quality, optically clear crystals were obtained within 5-6 weeks time. Purity of the material was checked by EDAX and CHN. Optical energy bandgap for both the samples was calculated from the UV-Vis data and it was found that for GSN 2:1 it was 3.67 eV and for GSN 3:1 it was 4.89 eV. These crystals showed excellent transparency in visible region of the spectrum. From the XRD it was confirmed that both the crystals belongs to the monoclinic system. The various vibrational groups associated with these crystals were studied using FTIR and Raman spectroscopy.

References


