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

Vivek P Gujarati, M P Deshpande, Kamakshi Patel, S H Chaki

Department of Physics, Sardar Patel University, Vallabh-Vidyanagar, Gujarat-India

Email address: vivekgujarati@gmail.com

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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;

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.

Figure 1: Photograph of GSN 2:1 crystal

Figure 2: Photograph of GSN 3:1 crystals.

Figure 3(a)

Figure 3(b)

Figure 3(c)

Figure 3 (a, b and c) SEM photographs of both crystals

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 1: Weight % and atomic % from EDAX

Element	Weight%		Atomic%	
	GSN 2:1	GSN 3:1	GSN 2:1	GSN 3:1
C K	18.57	21.11	22.77	25.36
N K	27.07	28.19	28.46	29.03
O K	49.84	50.3	45.87	45.36
Na K	4.53	0.4	2.9	0.25

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

Element	C%	H%	N%	O%
GSN 2:1	19.57	3.74	17.03	59.66
GSN 3:1	28.63	5.71	17.47	48.19

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 $\beta=119.030$ 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 303nm for the sample which matches with reported data [10,13] and UV cut off for GSN 3:1 is near 218nm. 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 3.67eV and 4.89eV 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

Figure 9-10: Plots of $(\alpha h\nu)^2$ vs. $h\nu$

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 spectras 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].

Figure 11 Raman spectra of GSN crystals

Figure 12 FTIR spectra of GSN 2:1 crystals

Figure 13 FTIR spectra of GSN 3:1 crystals

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 NH_3^+ group was confirmed near 1614 and 1508 cm^{-1} . CH_2 Rocking, Twisting, Wagging and Scissoring were observed near $939, 1143, 1329$ and 1448 cm^{-1} for both the samples respectively.

Table 3:

GSN 21 FTIR ν cm^{-1}	GSN 31 FTIR ν cm^{-1}	GSN 21 Raman ν cm^{-1}	GSN 31 Raman ν cm^{-1}	GSN [4,15-16] Raman ν cm^{-1}	Assignment
-	-	220	220	-	-
-	-	261	-	-	-
-	-	362	-	-	-
-	-	-	-	398	NH_3^+ Torsion
505	502	504	506	508	COO^- Rocking
-	557	558	566	-	-
587	-	-	-	588	COO^- Deform
-	607	605	-	-	-
677	685	685	692	677	NO_3^- Inplane Deform
-	-	-	-	723	COO^- Deform
890	889	893	890	895	C-C stretch
934	929	-	-	939	CH_2 Rocking
1039	1024	1047	1047	1052	NO_3^- Symmetric stretch
1116	1126	-	-	1114	NH_3^+ Rocking

1135	1154	1139	1132	1143	CH ₂ Twisting
1348	1334	1326	1339	1329	CH ₂ Wagging
-	1385	1394	1405	1397	NO ₃ ⁻ Asymmetric stretch
1451	1437	1439	1437	1448	CH ₂ Scissoring
1503	1497	1501	1501	1508	NH ₃ ⁺ Symmetric Bend
-		1578	1576	-	-
1631	1632	-		1614	NH ₃ ⁺ Asymmetric Bend
-		1677	1674	1659	Overtone
2017	2169				-
-	2602	-		2616	Overtone
2719		-		2725	Overtone
-		-		2884	N-H...O Symmetric Stretch
-	2924	2963	2970	2976	CH ₂ Symmetric stretch
-		3000	3004	3000	?-Glycine
-		3100	3104	-	-
3252		-	3260	-	-
3427	3438	-		-	-

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.

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