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# Growth and Characterization of L-Glycine Sodium Nitrate Single Crystal for Electro-optic Applications

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**Abstract**

Single crystals of semiorganic nonlinear optical material of L-Glycine Sodium Nitrate (LGSN) have been successfully grown by slow evaporation solution growth technique. Cell parameters of the grown crystal were identified using single crystal X-ray diffraction analysis and it was found that the material crystallizes in monoclinic system with space group Cc. The presence of functional groups and the spectral properties were assessed by FTIR analysis. Optical transparency of the grown crystals was investigated by UV-Vis-NIR spectrum. The scanning electron microscope analysis was carried out to determine the surface morphology of the grown crystal. Second harmonic generation efficiency of the grown crystal have been measured by Kurtz and Perry technique and it was found to be 2.5 times greater than that of KDP. The obtained results show that L-Glycine Sodium Nitrate crystals are potential materials for NLO device fabrication.

**Keywords:** Solution growth, UV-Vis-NIR, SEM, SHG test.

## 1. Introduction

In recent years, non-linear optical (NLO) crystals with high conversion efficiencies are needed for optical second harmonic generation (SHG) because of their applications in opto-electronics, photonics, high speed information processing, telecommunications and optical information storage devices [1]. Amino acid family crystals are promising materials for these applications and it depends on the properties such as transparency, birefringence, refractive index, dielectric constant and thermal, photochemical and chemical stability [2]. Amino acids are considered to be interesting organic materials for NLO devices as they contain donor carboxylic (COOH) group and the proton acceptor amino acid ($NH_2$) group known as zwitterions which create hydrogen bonds. Considerable efforts have been made on amino acid mixed complex crystals in order to make them suitable for device fabrications [3–6]. Glycine has no centre of chirality and is optically inactive. Glycine family crystals have been subjected to extensive research by several researchers for their efficient non-linear optical properties [7-10]. Since the glycine molecule can exist in zwitterionic form, it is capable of forming compounds with anionic, cationic and neutral chemical compounds. Thus a large variety of glycine coordinated compounds can be formed. However, only those complexes of glycine, which crystallizes in non-centrosymmetric structure, are expected to exhibit nonlinear optical second harmonic generation [11].

Most of the organic NLO crystals usually have poor mechanical and thermal properties whereas the inorganic NLO materials have excellent mechanical and thermal properties, but possess relatively modest optical nonlinearity. Therefore semi organic crystals are those which combine the positive aspects of organic and inorganic materials resulting in desired nonlinear optical properties [12]. The properties of large nonlinearity, high resistance,

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low angular sensitivity, good mechanical hardness and further significance are centred on semi organic crystals. Hence, investigations were done to develop various semi-organic crystals which are more suitable for device fabrication [13,14]. A series of semi-organic compound such as L-Alanine potassium chloride [15], L-Alanine sodium nitrate [16], L-Histidine tetrafluroborate [17] have been reported earlier. The present manuscript reports on the crystal growth of L-Glycine sodium nitrate crystals from aqueous solution followed by the characterizations like single crystal X-ray diffraction, Fourier transform infrared spectroscopy, optical absorption, scanning electron microscopy, second harmonic generation efficiency and the results are discussed.

## 2. Experimental

### 2.1. Materials and method

Analytical reagent grade (AR) samples of glycine and sodium nitrate were used as a precursor materials. Double deionized water (Merck) was used as a solvent. Slow evaporation solution growth technique was adopted for the growth of single crystals. Equimolar ratio of L-glycine and sodium nitrate were taken and stirred well for 4 hours separately and mixed. The solution was then filtered and kept in a vibration free ambiance. Transparent seed crystals were obtained by spontaneous nucleation. Among them, defect free seed crystal was suspended in the mother solution. Single crystals of dimension 9×8×2 $mm^3$ have been grown within the period of 30 days. The photograph of the as grown glycine sodium nitrate crystal is shown in Figure 1.

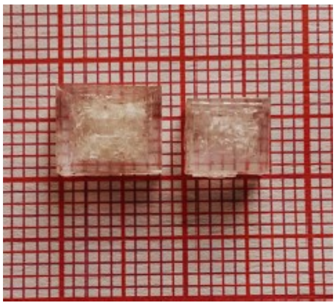

**Figure 1.** As grown LGSN single crystal

### 2.2. Characterization techniques

The grown crystals were subjected to various characterization analyses to test their suitability for optical device applications. Single crystal X-ray diffraction analysis was carried out using Four-circle Enraf Nonius CAD4/MACH3 single crystal diffractometer to determine the lattice parameters and space group. The presence of functional groups in the grown crystal was identified using Fourier Transform Infrared spectral analysis using a PERKIN ELMER SPECTROMETER by KBr pellet technique within the range of 400-4000 $cm^{-1}$.

In order to examine the optical properties of the grown crystal in the UV-Vis-NIR regions of electromagnetic spectrum, the linear optical study was carried out using PERKIN ELMER LAMBDA 35 UV-Visible spectrophotometer within the range of 200-1000 nm. SEM analysis was carried out by using CARL ZEISS SIGMA VP scanning electron microscope to analyse the crystal surface morphology. Second Harmonic Generation efficiency test for the grown samples was performed by Kurtz and Perry powder technique using a Q - switched high energy Nd:YAG Laser (QUANTA RAY Model LAB-170-10) Model HG-4B- High efficiency with repetition rate at 10 Hz.

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## 3. Results and discussion

### 3.1. Single crystal XRD analysis

The L-Glycine sodium nitrate crystal was subjected to single crystal X-ray diffraction analysis to determine the lattice parameters and space group. The title compound crystallizes into monoclinic system with space group Cc [18]. From the XRD data, the calculated lattice parameter values are found to be a = 14.32Å, b = 5.25Å, c= 9.11Å, and are tabulated in Table 1.

**Table 1**. Single crystal XRD analysis data of L-GSN

| L-Glycine SN | Crystal data |
|---|---|
| Crystal System | Monoclinic |
| Space group | Cc |
| Unit Cell dimensions | a = 14.32 Å<br>b = 5.25 Å<br>c = 9.11 Å |

### 3.2. Fourier Transform Infrared spectral analysis

Fourier transform infrared spectral studies were carried out for the samples to identify the functional groups. The presence of functional groups in the compound L-Glycine sodium nitrate was identified and was shown in Figure 2. The vibration peak at 3441 $cm^{-1}$ represents $(NH_3)^+$ asymmetric stretching vibration. The absorption peak at 2098 $cm^{-1}$ shows asymmetrical $NH_3$ bending vibration.

The absorption band at 1614 $cm^{-1}$ represents C=O stretching vibration. The sharp peak at 1392 $cm^{-1}$ is due to $NO_3^-$ asymmetric stretching vibration. The peak at 938 $cm^{-1}$ is due to $CH_2$ rocking vibration. The C-C stretching vibration is attributed to 837 $cm^{-1}$. The absorption band at 665 $cm^{-1}$ shows $NO_3^-$ in plane bending vibration. The vibration peak at 503 $cm^{-1}$ represents COO- rocking vibration [19]. The observed bands along with their vibration assignment are presented in Table 2.

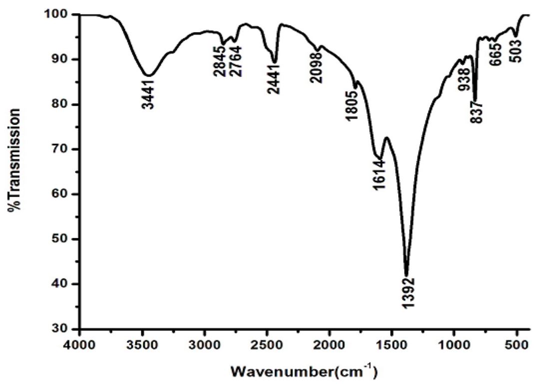


**Figure 2**. FTIR Spectrum of L-Glycine SN

**Table 2.** Tentative assignments of L-Glycine SN

| Wavenumber ($cm^{-1}$) | Assignment |
|---|---|
| 3441 | $(NH_3)^+$ asymmetric |
| 2098 | Asymmetric $NH_3$ bending |
| 1614 | C=O stretching |
| 1392 | $NO_3^-$ asymmetric stretching |
| 938 | $CH_2$ rocking |
| 837 | C-C stretching |
| 665 | $NO_3^-$ in plane bending |
| 503 | COO- rocking |

### 3.3. UV-Visible NIR Spectral analysis

Optical transparency in the entire visible region with a good percentage of transmission is the key properties of an NLO material. The transmission spectrum of L-Glycine sodium nitrate is shown in Figure 3. From the figure it was observed that the material has high transmittance in the entire visible region of about 70% and the lower cut off wavelength was observed at 200 nm. This is one of the most desirable properties of the NLO material for device fabrication.

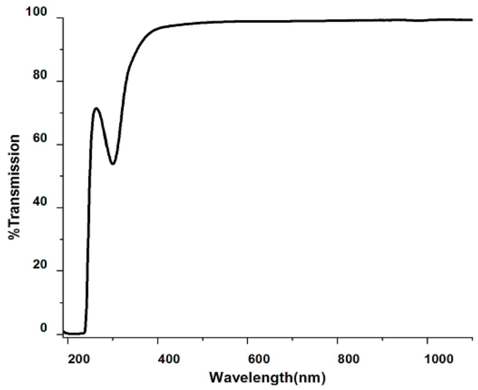


**Figure 3.** UV-Visible-NIR transmission spectrum of L-Glycine SN

### 3.4. Morphological study

Scanning electron microscopy (SEM) analysis has been carried out for the grown crystal to study the nature, surface morphology and the presence of imperfections in the grown crystals. The transparent regions of the crystals are cut into few mm for examining the surface morphology. From the SEM micrograph it can be observed that the grown crystal has cracks and few inclusions which may be due to the impact of growth conditions and was shown in Figure 4.

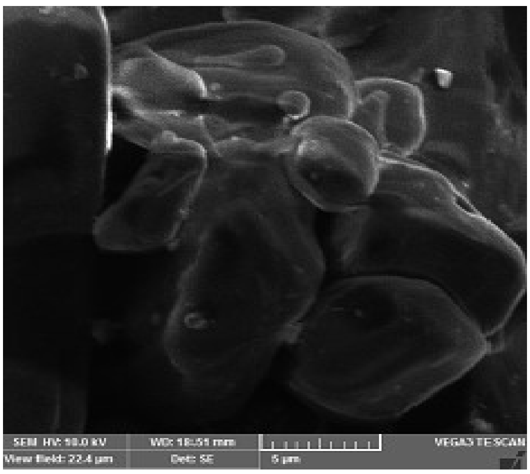

**Figure 4.** SEM image of LGSN

### 3.5. Second Harmonic Generation

Second Harmonic Generation efficiency of L-glycine sodium nitrate crystal was determined by Kurtz and Perry technique. Finely powdered samples are packed tightly in a micro capillary tube. The SHG efficiency of the LGSN crystal is measured with compared to the efficiency of the KDP crystals. A Q-switched Nd:YAG laser emitting fundamental wavelength of 1064 nm is allowed to strike on the powdered sample. The experiment is carried out at room temperature [20]. The SHG efficiency of L-glycine SN crystal was observed to be 2.5 times greater than that of KDP and it confirms the suitability of LGSN crystals in NLO applications.

### 4. Conclusion

A Semi-organic NLO material LGSN has been grown by slow evaporation solution growth technique. The harvested crystals of size 9×8×2 $mm^3$ were obtained after a period of 30 days. Unit cell parameters were by single crystal X-ray diffraction analysis, which confirmed that the grown crystal belongs to monoclinic system with space group Cc. The various functional groups and their vibrational interactions of the grown crystal were confirmed by Fourier transform infrared analysis. The optical study shows that the lower cutoff wavelength is below 200 nm and possess good transparency in the entire visible region. SEM study reveals the crystal morphology of the grown crystal. The estimated SHG efficiency of L-glycine SN was found to be 2.5 times greater than that of KDP. Thus L-GSN crystal can be exploited as a potential material for photonics, electro-optic and SHG device applications.

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