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# EFFECT OF pH ON THE GROWTH AND CHARACTERIZATION OF GLYCINE SODIUM NITRATE (GSN) SINGLE CRYSTAL

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**ABSTRACT**

Single crystals of semi-organic non-linear optical Glycine Sodium Nitrate (GSN) have been successfully grown from three different pH (1.1, 6.0, and 10.8) solutions by evaporation solution growth. In this report we bring out the influence of pH on the optical, structural and NLO properties of the grown crystals. The grown crystals have been subjected to powder X-ray diffraction studies to identify the crystalline nature. Single crystal X-ray diffractometer was utilized to measure the cell parameters and morphology of the grown crystals. The FTIR spectra for the crystals grown at different pH values show variations in the peak intensity. The NLO property is found to be varying with the change in the pH values.

**Keywords**: Re-crystallization; Seed crystals; Semi-organic; Nonlinear optical materials.

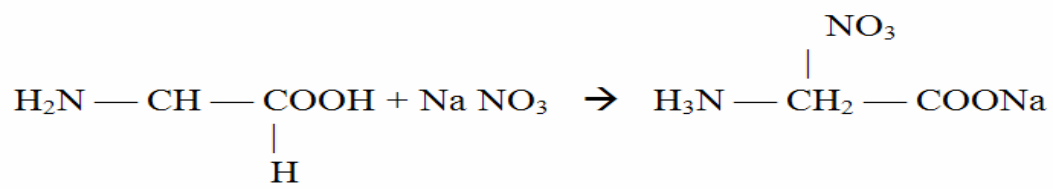
## INTRODUCTION

Non-linear optical materials (NLO) have wide applications in the area of laser technology, optical communication and in storage technology. The high nonlinearity makes it possible for organic crystals to double the frequency of Ga-Al-As diode lasers for generating blue light which is an important coherent light source. However, the short comings of the aromatic crystals such as poor physico-chemical stability, low hardness and cleavage tendency hinder their device applications[1,3]. In order to keep the merits and overcome the shortcomings of organic materials some new classes of NLO crystals such as LAP, GSC, GSB, GSN and KDP (semi-organic complex crystals) to combine the advantages of inorganic crystals such as good stability, with the advantages of organic crystals such as high nonlinearity, are of special interest. Among the semi-organic complex NLO crystals the nonlinearity of GSN is relatively high (GSN). GSN belongs to the face centered monoclinic system with the molecular formula $H_3NNO_3CH_2COONa$. The cell dimensions are a = 37.6433A°, b = 5.2620A°, c = 9.1178A°and β = 93.9215°[10]. The SHG intensity of GSN is 1.5 times that of KDP. In the present study, the effect of pH on the growth and properties, such as NLO, structure of crystal, and optical are studied.

## EXPERIMENTAL

### Preparation of GSN solution at different pH values

The commercial reagent of Glycine (purity 99%) procured from Merck company was purified by the repeated re-crystallization using hot de-ionized water solution by slow cooling. At pH 6.0, essentially the glycine is in the zwitterionic form. Glycine and Sodium Nitrate in the equimolar ratio 1:1 were taken in a beaker containing double distilled Millipore water at room temperature and the saturation solution is brought to pH 6.0. The reaction takes place based on the following equation and the salt is formed.



The purity of the synthesized salt was further increased by successive re-crystallization process. The saturated GSN solutions of different pH (1.1, 6.0, and 10.8) have been prepared using doubly re-crystallized salt. The solution was filtered using a sintered glass filter of 1μ porosity. The solution is transferred to three Petri dishes and covered by a porous paper and kept for slow evaporation process.

**Growth of crystals**

Seed perfection and selection of solvents are very important for growing single crystals of high quality[6,7]. Defects in seed crystal could cause spurious crystallization and flaws during the crystal growth. To ensure good quality crystals, a seed was obtained by spontaneous nucleation in supersaturated solution of GSN at room temperature. Transparent and good quality seeds were selected for the growth. The grown crystals were harvested after a typical growth period of 30 days.

**Structure and morphology**

In order to confirm the crystallinity of the grown crystals, powder X-ray diffraction (XRD) pattern has been recorded using a Rich Seifert Diffactometer (Model 2002) using Cu Kα (λ = 1.5418 Aº)radiation The samples were scanned over the angle range 10-50º at the rate of 0.05º /min. The changes in the unit cell parameters and the morphology of the grown crystals have been observed from single crystal XRD analysis using ENRAF NONIUS CAD4-F (FR 590) single crystal diffractometer (Table 1).

**FTIR spectral studies (Figures 1, 2 and 3)**

The infrared spectra were taken using Brukker IFS66V FTIR spectrometer by KBr pellet technique to confirm the presence of different organic groups along with the inorganic materials presence (Table 2)

**XRF studies**

The X-ray Fluorescence is taken for the samples to study the abundance of Na to be present in the crystals. (Table 3)

**NLO efficiency**

The comprehensive analysis of second order non-linearity of GSN crystals, grown from different pH was performed by Kurtz powder method[8]. The single crystals of GSN grown from different pH values were irradiated by an incident radiation (1064 nm)of pulse width 8ns and pulse energy of 10-800mJ from a Q-switched quanta RAY GCR Nd:YAG laser. KDP was used for calibrating the SHG intensity. A concave mirror, collimated and focused onto the monochromator slit collected the SHG emitted from the crystal sample**.** The output power of the crystal was measured using OPHIR power meter model DG with power head model OPHIR 30A**.** The error in the measured SHG was typically about 5-10%. The NLO property of the crystal was confirmed from the estimation of strong green radiation of the crystal. The results of SHG efficiency of GSN are summarized in Table 4. The GSN crystals grown at different pH values showed very good stability under laser irradiation and no signs of decomposition; crack or fracture were observed even for continued irradiation with laser power of 800 mW.

## RESULTS AND DISCUSSION

The growth kinetics and the quality of the crystals grown from solutions are considerably influenced by pH of the solution. The amino acids contain both acidic ($-NH_3$) and basic (-COO) groups, they are amphoteric. The predominant form of the amino acid depends on the pH of the solution. In an acidic solution, the COOH group and the molecule has an overall positive charge. As the pH is lowered, the -COOH loses its proton at about pH 2. This point is called $pK_{a1}$, the first acid-dissociation constant. As the pH is raised, the $-NH_3^+$ group loses its proton at about pH 9.6. This point is called $pK_{a2}$, the second acid - dissociation constant. Above this pH, the molecule has an over all negative charge (8). So, we have grown crystals of GSN at: (1) pH of 1.1 which is less than pH 2 and (2) pH of 10.6 which is greater than pH 9.6. At pH 1.1 the GSN crystals show high intensity of SHG, the crystal structure is Hexagonal. At pH

6.0 the GSN crystals show very low intensity of SHG, the crystal structure is monoclinic. At pH 10.6 the GSN crystal shows still lower intensity of SHG and the crystal structure is Hexagonal. From the FTIR studies we find for pH = 1.1, the absorption peak at 3444 $cm^{-1}$ rather than OH may indicate the presence of NH bond. NH stretching (amide) may be indicated by the absorption band at 1632 cm and second peak of absorption at 1495 $cm^{-1}$ may confirm the NH stretching. The C=O presence may be indicated by the absorption bands at 1331 $cm^{-1}$ and 1254 $cm^{-1}$. The $CH_2$ vibrations are indicated by the absorption bands at 887 $cm^{-1}$, 672 $cm^{-1}$ and 502 $cm^{-1}$[9]. The FTIR for pH = 10.6 shows, the presence of NH bond is indicated by the absorption peak at 3436 $cm^{-1}$ and NH stretching (amide) is indicated by the absorption at 1672 $cm^{-1}$ and the second peak of absorption at 1481 $cm^{-1}$, confirms the NH stretching. The C=O presence is indicated by the absorption band at 1333 $cm^{-1}$. The $CH_2$ vibrations are indicated by the absorption bands at 893 $cm^{-1}$ 686 $cm^{-1}$ and 501 $cm^{-1}$[9].From the XRF studies we find the existence of $NO_3$ in the GSN pH = 1.1 and this enhances the NLO property. Further the existence of Na is more in the in the GSN, pH = 10.8 and this lowers the NLO property (Table 3)

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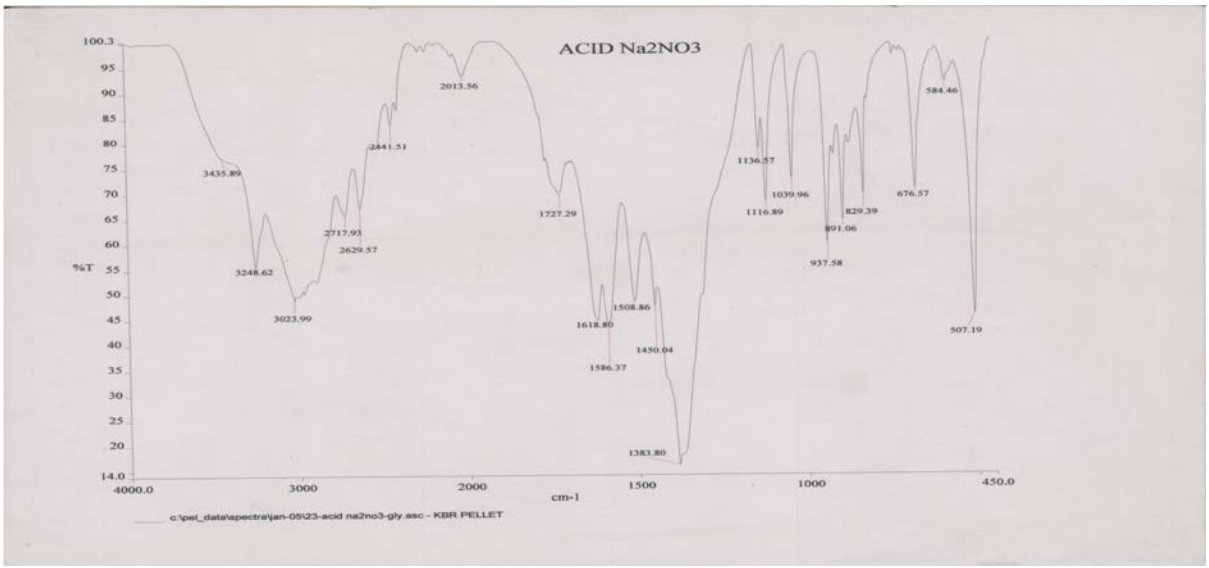


**Fig.-1:** FTIR Spectrum of GSN at pH = 1.1

**Table-1:**The cell parameters of GSN at pH 6

| Compound | a Å | b Å | c Å | α | β | γ | Cell volume Å$^3$ |
|---|---|---|---|---|---|---|---|
| GSN PH=6 | 37.6433 | 5.2620 | 9.1178 | 90 | 93.92 | 90 | 1801.7957 |

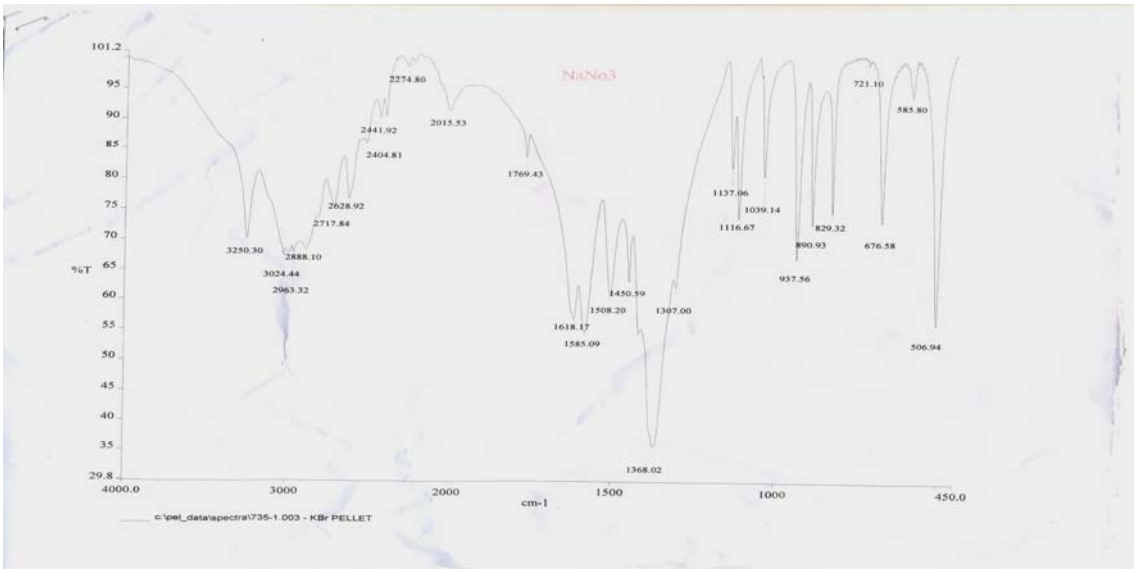


**Fig.-2:** FTIR Spectrum of GSN- at pH = 6.0

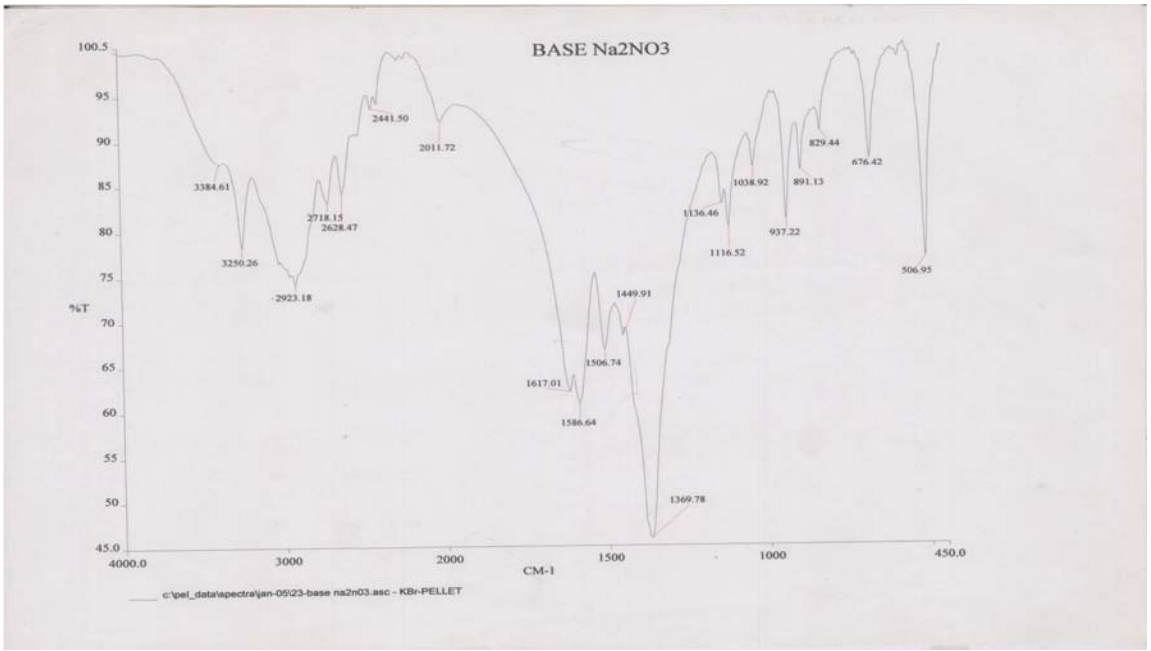


**Fig.-3:** FTIR Spectrum of GSN at pH = 10.6

**Table-2**

| **GSN at pH=10.6** | |
|---|---|
| **Frequency $cm^{-1}$** | **Assignment of vibration** |
| 3385 (w) | Cisoid secondary amide |
| 3250 (m) | N-H stretching (bonded asymmetry) |
| 2923 (m) | $CH_2$ symmetry stretching |
| 2718 (m) | C-H stretching (Fermi resonance stretching of C-Hand First overtone of C-H plane bending |
| 2628 (m) | C-H out of plane bending |
| 2441 (w) | $NH_3^+$ stretching |
| 2012 (w) | $R_2C=N=N$ stretching |
| 1617 (s) | C=O stretching |
| 1587(s) | $COO^-$ asymmetric stretching |
| 1505(s) | N-H plane bending |
| 1450(s) | N-H plane bending |
| 1370(s) | $NO_2$ symmetry stretching |
| 1137(m) | $N_3$ symmetry stretching |
| 1117(m) | C-N stretching |
| 1039(w) | C-N stretching |
| 937(m) | N-O stretching |
| 891(w) | N-O stretching (aliphatic nitric group) |
| 829(w) | N-O stretching (aliphatic nitric group) |
| 676(w) | N-H out of plane bending |

| **GSN at pH = 6** | |
|---|---|
| **Frequency $cm^{-1}$** | **Assignment of vibration** |
| 3250 (m) | N-H stretching (bonded asymmetry) |
| 3024 (m) | $CH_2$ symmetry stretching |
| 2963 (m) | $CH_3$ symmetry stretching |
| 2888(m) | $CH_3$ symmetry stretching |
| 2717 (m) | C-H stretching (overtones & combinations of O-H in plane bending& C-O stretching vibrations) |
| 2628 (m) | C-H stretching (overtones & combinations of O-H in plane bending& C-O stretching vibrations) |
| 2404 (w) | $NH_2$ symmetry stretching |
| 2441 (w) | $NH_3$ stretching |
| 2274 (w) | N=C=O asymmetric stretching |
| 2015 (w) | $R_2C=N=N$ stretching |
| 1769 (w) | C=O stretching |
| 1618 (s) | C=O stretching |
| 1585 (s) | $-COO^-$ asymmetric stretching |
| 1508 (s) | N-H plane bending(secondary amide) |
| 1450(s) | N-H in plane bending |
| 1368(s) | $NO_2$ symmetry stretching |
| 1307(s) | O-H bending |
| 1137(w) | $N_3$ stretching symmetry |
| 1116(m) | C-N stretching |
| 1039(w) | C-N stretching |
| 937(s) | N-O stretching |
| 890(m) | C-N stretching (aliphatic nitro group) |
| 829(m) | C-N stretching (aliphatic nitro group) |

| | |
|---|---|
| 676(m) | N-H out of plane bending |
| **GSN at pH = 1.1** | |
| **Frequency $cm^{-1}$** | **Assignment of vibration** |
| 3435 (s) | Cisoid secondary amide |
| 3248 (m) | N-H stretching |
| 3024 (s) | $CH_2$ symmetry stretching |
| 2718 (m) | C-H stretching |
| 2630 (m) | C-H stretching (overtones & combinations of O-H in plane bending& C-O stretching vibrations) |
| 2441 (w) | $NH_3$ Stretching |
| 2013(w) | $R_2C=N=N$ stretching |
| 1727 (w) | C=O stretching |
| 1628 (s) | C=O stretching |
| 1586 (s) | $-COO^-$ asymmetric stretching |
| 1508 (s) | N-H plane bending(secondary amide) |
| 1450 (s) | N-H in plane bending |
| 1384(s) | $NO_2$ symmetry stretching |
| 1137(m) | $N_3$ stretching symmetry |
| 1116(m) | C-N stretching |
| 1040(m) | C-N stretching |
| 938(m) | N-O stretching |
| 891(m) | C-N stretching (aliphatic nitro group) |
| 829(m) | C-N stretching (aliphatic nitro group) |
| 676(m) | N-H out of plane bending |

**Table-3**

| Sample | | acidNa2NO3 | | | | |
|---|---|---|---|---|---|---|
| Compound Formula | nZ | Concentration | Prepared Elt. | Line 1 | Concentr. 1 | Stat. Dev. 1 |
| Mg | 12 | 74 | 74 | Mg KA1-HS-Min | 74 | 7.8 |
| Fe | 26 | 10 | 10 | Fe KA1-HS-Min | 10 | 0.67 |
| Pd | 46 | 16 | 16 | Pd KA1-HS-Min | 16 | 4.9 |
| **Sample** | | **baseNa2NO3** | | | | |
| Compound Formula | nZ | Concentration | Prepared Elt. | Line 1 | Concentr. 1 | Stat. Dev. 1 |
| Se | 34 | 0.0025 | 0.0025 | Se KA1-HS-Min | 0.0025 | 0.00017 |
| Pd | 46 | 0.02 | 0.02 | Pd KA1-HS-Min | 0.02 | 0.0063 |
| **Sample** | | **Na2NO3baseNaOH** | | | | |
| Compound Formula | nZ | Concentration | Prepared Elt. | Line 1 | Concentr. 1 | Stat. Dev. 1 |
| Mg | 12 | 49 | 49 | Mg KA1-HS-Min | 49 | 5.2 |
| Fe | 26 | 1.3 | 1.3 | Fe KA1-HS-Min | 1.3 | 0.13 |
| Mo | 42 | 1.15 | 1.15 | Mo KA1-HS-Min | 1.15 | 0.04 |
| Na | 11 | 49 | 49 | Na KA1-HS-Min | 49 | 1.9 |

**Table-4**: Power output of SHG signal developed in the KDP and the GSN crystals (grown from different pH)

| KDP | GSN at pH = 1.1 | GSN at pH = 6.0 | GSNat pH = 10.8 |
|---|---|---|---|
| mW | mW | mW | mW |
| 150 | 425 | 400 | 200 |
| 290 | 510 | 475 | 300 |
| 330 | 815 | 700 | 310 |

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