The Role pH on the Second Harmonic Response of GSN

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Abstract

In this work we have done a study of RAMAN spectroscopy on glycine sodium nitrate crystals. This study was supported with the respective X ray diffraction and Second-Harmonic Generation signal detection. The goal of this work is to modify the charge of glycine sodium nitrate in order to obtain three electric behaviors (Zwitterionic, Cationic, and Anionic) and perform the vibrational study on the characteristic peaks that appear in RAMAN spectra. Furthermore with the change on the charge of aminoacid it is observed how it modifies the optical properties in the glycine sodium nitrate complex.
Introduction

Nonlinear optical (NLO) materials have wide applications in the area of laser technology, optical communication and electro optics application. The nonlinear optical effect is the interaction of an electromagnetic field of high intensity laser light with a material [8, 10, 15]. The development of photonic and optoelectronic technologies rely heavily on growth of NLO materials with the high light nonlinear responses. NLO material need to have a large NLO coefficient, large birefringence, wide transparency range, high damage threshold, broad spectral and temperature bandwidth, good chemical and mechanical stability, ease of growth and low cost [13, 16, 17]. One of the advantages in working with organic materials is that they allow one to fine-tune the chemical structures and properties for the desired nonlinear optical properties. Additionally, they have large structural diversity. The properties of organic compounds can be refined using molecular engineering and chemical synthesis [17]. The second harmonic generation SHG is a phenomenon produced by the second order nonlinearities in a material when it is exposed to high intensity and monochromatic light source. Given glycine amino acids as an amphoteric, it can be assumed as cationic, anionic and zwitterionic configurations, i.e. the charge distribution is determinate by the pH and the pKa of the carboxylic group (pKa= 2.34) and the amino group (pKa=9.6). Thus, in the pH range between 2.34 and 9.6, most of molecules are zwitterionic with both ends charged NH$_3^+$ and COO$^-$ [4, 7, 15].

The zwitterinonic form is given by following reaction:

\[
\text{NH}_2\text{RCOOH} \longleftrightarrow \text{NH}_3^+\text{RCOO}^- 
\]
In presence of an acid, the reaction occurs from right to left and takes cationic configuration:

\[
\text{NH}_3^+\text{RCOOH} \leftrightarrow \text{H}^+ + \text{NH}_3^+\text{RCOO}^-
\]

And in presence of a base, the reaction occurs from left to right and takes an anionic configuration [4, 6, 18]:

\[
\text{NH}_3^+\text{RCOO}^- \leftrightarrow \text{H}^+ + \text{NH}_2\text{RCOO}^-
\]

**Experimental Details**

The GSN crystals were obtained by using 99.9% purity sigma Aldrich glycine (NH2-CH2-COOH) with FW=75.57g/mol, and sigma Aldrich sodium nitrate (NaNO₃) (99.9%) with FW=4.99g/mol. A stoichioimetric mixture of glycine and sodium nitrate in equimolar ratio was dissolve in 100ml of water distillated with stirrer magnetic in a thermoplate. In order to modify the charge of GSN molecule, seven samples different pH (1,3,4,7,9,10,11) were prepared [18]. In this sense we have obtained three electric glycine configurations (Zwitterionic, Cationic, and Anionic). The pH was adjusted with nitric acid concentrate HNO₃ and ammonium hydroxide NH₄OH. As follow step the crystals ware retired of the solution are watched with distillated water and immediately drying to prevent clusters formation, crystalline inclusions and eliminate impurities on surfaces. Hence, the size and quality of crystals depend of the molar ratio in the reagents compared with the solvent, i.e. for low concentrations, crystals are big and for high concentrations, crystals are small.
RESULTS AND DISCUSSION

**Crystal Growth**

GSN crystals were obtained by a slow evaporation technique for aqueous solutions. The crystals were prepared with distilled water containing Glycine, Sodium Nitrate [NaNO3] in molar ratio 1:1 with a starting pH of 6.4, and then changing the pH of the solution at 1, 3, 4, 7, 9, 10, 11. Transparent crystals of different size and shapes were obtained in about two to three weeks at room temperature.

The size of the crystals was found to be depending on the amount of material available in the solution which in turn is decided by the solubility of the material in solvent. The shapes were found to be determinate by the pH of the solution.

**RAMAN Spectroscopy**

The RAMAN spectroscopy is a powerful technique used for the analysis of organic compounds which is useful for any state of matter and especially in biological samples. Other advantage of RAMAN spectroscopy is the use of visible radiation, this allows narrow down the warming effects in the sample[14]. The RAMAN spectra can be identified as roto-vibrational spectra, this because the lines of RAMAN frequency correspond to the distance between energy levels. Hence, the main transitions are due to the normal vibrational modes and determinate the modes that change the polarization in the molecule, this characteristic is the main reason why RAMAN is useful in the analysis of GSN [19].
In the present work the RAMAN spectra was carried out at room temperature in frequency range 400- 4000 cm\(^{-1}\) with Xplora RAMAN microscope HORIBA system. The figure 1 shows the symmetric and asymmetric of the functional group NH\(_3^+\) and the stretching vibrations found in 3244 y 2884 cm\(^{-1}\) frequency. Furthermore, the position and broadness of this mode, NH\(_3^+\) asymmetric stretching frequency, indicate the formation of both, intra and intermolecular strong N-H---O hydrogen bonding of the NH\(_3^+\) group, with the oxygen of both, the carbonyl group and inorganic nitrates. Hence, the presence of this bonds make that are found lowering frequencies 2884cm\(^{-1}\)[13, 20]. The crystal structure of GSN show that the organic molecular units are located between layers of NaNO\(_3\) chains and linked to sodium nitrate by strong intramolecular hydrogen bonds of N-H---O type. This structural organization of infinite chains of highly polarity entities connected in a head to tail arrangement in GSN is behalf in contribution to the NLO properties of the crystal. The study of symmetry and stretching vibration of CH\(_2\) group is observed around 3023 and 2969 cm\(^{-1}\). The CH and NH bending observed in 1616 and 1510 cm\(^{-1}\) frequency. The absorption peaks at 2009 and 1615 cm\(^{-1}\) confirmed the presence of NH\(_3^+\) bending. The peak at 1408, 586 and 509 cm\(^{-1}\) is assigned to the symmetric stretching C-COO carboxyl group. The band around 1118 cm\(^{-1}\) is also indicative of the NH3 rocking modes. The band around 178 cm\(^{-1}\) it is indicative of torsion of Na. The wavelength was observed and the proposed allocation of spectrum is shown in the following Table.
**X ray Diffraction**

In order to obtain the structural parameters of the crystal under study, we also achieve a powder X ray diffraction to confirm the phase. The analysis of the observed spectra was performed using X'Pert data collector, powder diffraction data interpretation and indexing software program X'Pert Highscore Plus. Version 2.2a. The XRD peaks were indexed and the unit cell was found to have monoclinic symmetry with cell parameters a=14.326 Å, b=5.261 Å, c=9.115 Å, \( \beta = 119.07^\circ \) and unit cell volume of 600.45 Å\(^3\). The figure showed that basic pH obtained the major phase of GSN compared with acid pH. This is because, as the pH becomes more acid the diffraction patterns show that it reduces the phase of GSN and other compounds are generated.

**Second-harmonic generation**

Second-harmonic generation (SHG), or frequency doubling, can be defined as the conversion of a specific wavelength of light into half its original \( \lambda_1 \rightarrow 1/2 \lambda_1 \), or with respect to frequency \( \omega, \omega_1 \rightarrow 2 \omega_1 \). A typical setup for power SHG measurements is made for modified Kurtz- Perry method. Also, a low energy laser, pulsed or continuous, is needed.[10, 11, 21] Usually Nd-YAG laser (1064 nm output) is used and the sample is a polycrystalline powder. With normal size of 70 µm each crystal, is shown the SHG measurements with respect to different pH of GSN from 1 to 11. The SHG efficiencies are pH 3 this due is closer to pKa = 2.3 of glycine and the dipole moment is major due the change of charge of the molecule, however the change in the dipole moment of the molecule above of pKa=9.7 also shows a good efficiency, it
is given that the sample with more acid pH showed that contain γ-glycine and the more basic pH showed that contains GSN phase in more concentration.

**Conclusions**

The transparent glycine sodium nitrate crystals (GSN crystals) were successfully obtained using slow evaporation technique at room temperature and we characterized by various techniques. The presence of fundamentals groups was verified by a RAMAN microscope. The GSN structure was characterized using XRD powder, the X ray pattern showed that the samples of GSN to basic pH contained the GNS phase and the more acid pH is observed that is obtained GSN on minor concentration but too obtain sub products like γ-Glycine which increase the efficiency of SHG.

**Acknowledgments**

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References


Table Captions

Table 1. Frequencies of RAMAN spectra

Figure Captions

Figure 1. Optical microscopy images of GSN crystals to different pH

Figure 2. The RAMAN spectra of GSN to different pH

Figure 3. Efficiency of the SHG signal of GSN to different pH taken at different power of the Nd:YAG laser

Figure 4. The X ray diffraction pattern of GSN to different pH
<table>
<thead>
<tr>
<th>Frequency RAMAN/cm⁻¹</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>3243</td>
<td>NH₃⁺ Asym Strech</td>
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<tr>
<td>3024</td>
<td>CH₂  Asym Strech</td>
</tr>
<tr>
<td>3000</td>
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<tr>
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<td>CH₂  Sym Strech</td>
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<td>2884</td>
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<tr>
<td>109</td>
<td>N…O Vibrations</td>
</tr>
</tbody>
</table>

Table 1
Figure 2.
Figure 3.
Figure 4

X Ray Powder

Intensity (a.u.)

(200) (111) (20-2)(11-1) (311) (220) (31-3)(22-2) (400) (33-3) (222) (600) (523) (622)

pH 11

pH 10

pH 9

pH 7

pH 4

pH 3

pH 1