The role of pH on the second harmonic response of glycine sodium nitrate (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 the amino acid it is observed how it modifies the optical properties in the glycine sodium nitrate complex.

Keywords: RAMAN, glycine sodium nitrate (GSN), nonlinear optical (NLO), second-harmonic generation (SHG), pKa.

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 (Singer, 1987; Bhat, 2002; Ramesh and Raj, 2009). The development of photonic and optoelectronic technologies rely heavily on growth of NLO materials with the high light no linear 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 (Dhas et al., 2008; Vijayakumar et al., 2008; Peter and Ramasamy, 2010). One of the advantages of 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 (Dhas et al., 2008). 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, that is, the charge distribution is determined 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 the molecules are zwitterionic with both ends charged NH_3^+ and COO^- (Pradhan and Vera, 1998; Ramesh and Raj, 2009; Johan et al., 2009). The zwitterionic form is given by the following reaction:

$$NH_2RCOOH \leftrightarrow NH_3^+RCOO^-$$
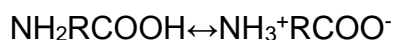
In presence of an acid, the reaction occurs from right to left, and takes cationic f configuration:

$$NH_3^+RCOOH \leftrightarrow H^+ + NH3^+RCOO^-$$
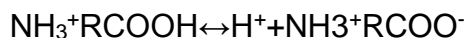
In the presence of a base, the reaction occurs from left to right and takes an anionic configuration (Fuchs, 2006; Bouchard et al., 2007; Johan et al., 2009):
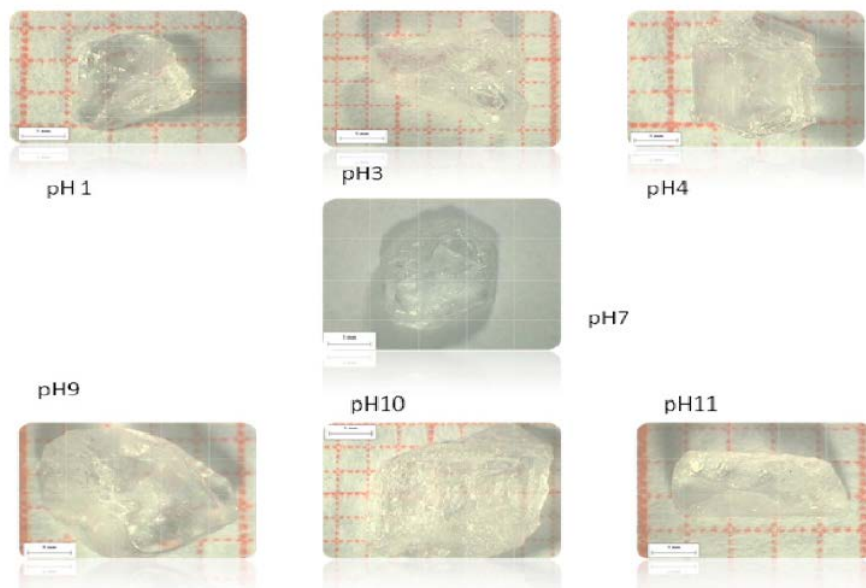
$$NH_3^+RCOO^- \leftrightarrow H^+ + NH_2RCOO^-$$
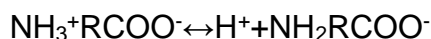
Figure 1. Optical microscopy images of GSN crystals to different pH.

Materials and methods

The glycine sodium nitrate (GSN) crystals were obtained by using 99.9% purity sigma Aldrich glycine (NH_2-CH_2-COOH) with FW=75.57 g/mol, and sigma Aldrich sodium nitrate ($NaNO_3$) (99.9%)) with FW = 4.99 g/mol. A stoichiometric mixture of glycine and sodium nitrate in equimolar ratio was dissolved in 100 ml of water, distillated with stirrer magnetic in a thermoplate. In order to modify the charge of GSN molecules, seven samples different pH (1.0, 3.0, 4.0, 7.0, 9.0, 10.0 and 11.0) were prepared (Fuchs 2006). In this sense, we have obtained three electric glycine configurations (Zwitterionic, Cationic, and Anionic). The pH was adjusted with nitric acid concentrate HNO_3 and ammonium hydroxide (NH_4OH). Following the steps, the crystals which were retired from the solution were washed with distilled water and immediately dried 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 ($NaNO_3$) in molar ratio 1:1 with a starting pH of 6.4, and then changing the pH of the solution at 1.0, 3.0, 4.0, 7.0, 9.0, 10.0 and 11.0. 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, to narrow down the warming effects in the sample (Rodriguez, 2004). The RAMAN spectra can be identified as roto-vibrational spectra, this is 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 determine the modes that change the polarization in the molecule, this characteristic is the main reason why RAMAN is useful in the analysis of GSN (Hernandez-Paredes et al., 2009).

In the present work, the RAMAN spectra were carried out at room temperature in frequency range to 400 to 4000 cm^{-1} with X'plora RAMAN microscope HORIBA system. Figure 1 and 2 shows the symmetry and asymmetry of the functional group NH_3^+ and the stretching vibrations found in 3244 and 2884 cm^{-1} frequency.
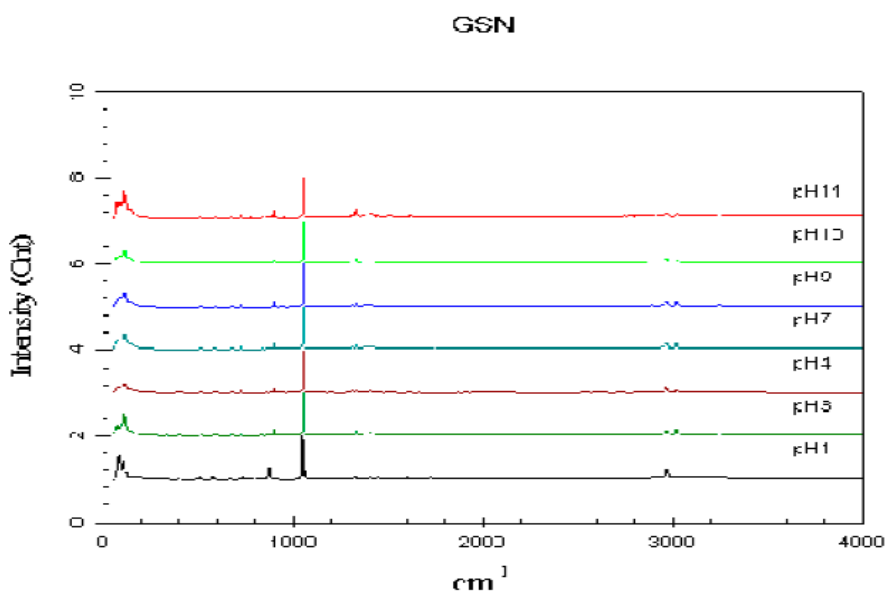

Figure 2. The RAMAN spectra of GSN to different pH.

Furthermore, the position and broadness of this mode, NH_3^+ asymmetric stretching frequency, indicate the formation of both, intra- and inter-molecular 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 these bonds was found at lower frequencies 2884 cm^{-1} (Hernandez-Paredes et al., 2008; Vijayakumar et al., 2008). The crystal structure of GSN showed 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 high polar 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 is 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 NH_3 rocking modes. The band around 178 cm^{-1} is indicative of torsion of Na. The wavelength was observed and the proposed allocation of spectrum is shown in Table 1.

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 and 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 A°, b = 5.261 A°, c = 9.115 A°, β = 119.07° and unit cell volume of 600.45 A^3. Figure 3 shows 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 like γ-glycine and sodium nitrate to pH 1.

Table 1. Frequencies of RAMAN spectra.

| Frequency (RAMAN/cm^{-1})	Assignment
3243	NH_3^+ asymmetry stretch
3024	CH_2 asymmetry stretch
3000	Υ-glycine
2976	CH_2 symmetry stretch
2884	N-H...O symmetry stretch
2725	Overtones
2616	Overtones
1659	Overtones
1614	NH_3^+ asymmetry bend
1508	NH_3^+ symmetry bend
1448	CH_2 scissoring
1397	NO_3^- asymmetry stretch
1329	CH_2 wagging
1309	CH_2 wagging
1143	CH_2 twisting
1114	NH_3^+ rocking
1052	NO_3^- symmetry stretch
939	CH_2 rocking
895	C-C stretch
723	COO^- deform
677	NO_3^- inplane deform
588	COO^- deform
508	COO^- rocking
398	NH_3^+ torsion
330	CCN bending
178	Na^+ translation
138	COO^- torsion
109	N...O vibrations
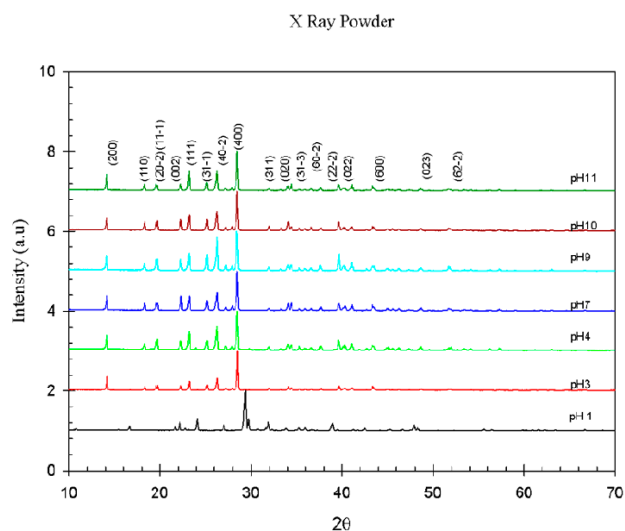
Figure 3. Efficiency of the SHG signal of GSN to different pH taken at different power of the Nd:YAG laser.

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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 (ω, $\omega_1 \rightarrow 2\ \omega_1$.) A typical setup for power SHG measurements is made from modified Kurtz- Perry method. Also, a low energy laser pulsed or continuous, is needed (Singer, 1987; Ok et al., 2006; Foerier et al., 2007). 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 GSN samples that showed high efficiency were pH1 and pH11 as shown in Figure 4. These were above pKa1 = 2.35 and pKa2 = 9.75; however, the sample pH1 in acid medium turned out to be γ-glycine in combination with sodium nitrate. The explanation of this fact is based on the total charge of the glycine molecule that, when found in an acid medium, acquires a positive charge. This prevents the coordination between glycine and sodium ion, which allows the glycine recrystallize in the form of γ-glycine and sodium ion in the salt form of sodium nitrate. Furthermore, the glycine in basic medium of pH11 is negatively charged, thus facilitating coordination between the molecule of glycine and sodium ion for GSN structure as shown in X-ray measurement. We have determined the efficiency for each one sample to different pH from 1 to11, this was performed by fitting an equation of the form $y = aX + bX^2$ where b is related to the intensity of SHG. Figure 5 shows that the samples, pH1 and pH 11, were the most efficient. Therefore, the sample of pH 1 is the most efficient, but do not contain the GSN structure justγ-glycine and sodium nitrate.
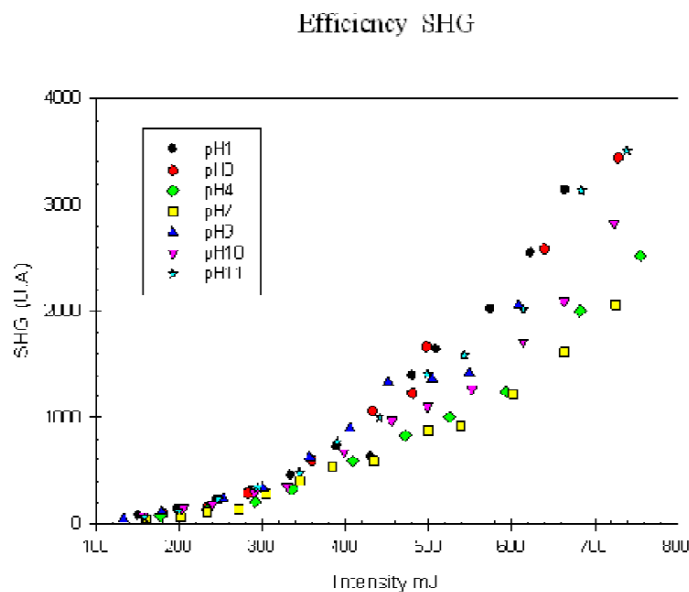
Efficiency SHG

Figure 4. The x- ray diffraction pattern of glycine sodium nitrate (GSN) to different pH.
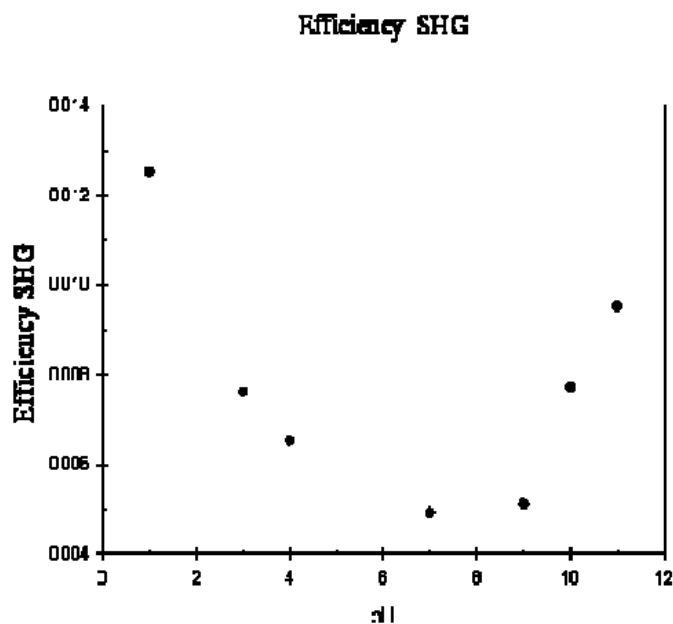
Efficiency SHG

Figure 5. Efficiency of the second-harmonic generation (SHG) signal of glycine sodium nitrate (GSN) according to b factor growth of quadratic behavior.

Conclusion

The transparent glycine sodium nitrate crystals (GSN crystals) were successfully

obtained using slow evaporation technique at room temperature and were characterized

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by various techniques. The presence of fundamental groups like donator and acceptor electrons, were verified by a RAMAN microscope. The GSN structure was characterized using XRD powder. The Xray pattern showed that the samples of GSN to basic pH contained the GSN phase and the more acid pH is observed that is obtained by glycine and sodium nitrate salt, the SHG studies shows that the more efficient sample is to pH. However, this sample does not contain the GSN structure just γ-glycine.

Acknowledgements

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