Evidence of the Second Harmonic Generation on Semi-Organic Glycine-Erbium Nitrate

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Abstract

Organic crystals have nonlinear optical effects (NLO) that make them attractive for applications in frequency conversion and optical processing. Among these we find the amino acids. Glycine is the simplest of all amino acids in the crystalline form, has three different polymorphs α , β , y γ in which the molecules exist in the dipolar form (NH³⁺ CH₂COO⁻). In this work we obtained glycine crystals doped with erbium growth by slow evaporation at room temperature. The chemical composition of the crystal was determined by Raman spectroscopy and was conducted for glycine with different concentrations of erbium. The optical absorption spectrum recorded in the wavelength range of UV-vis revealed that the crystal has good optical transparency in the range of 350-1100 nm. The second harmonic generation efficiency of the crystal measured by using the Kurtz Perry modified method.

Keywords: glycine, erbium, NLO, SHG.

Introduction

Non-linear optics (NLO) materials for second harmonic generation (SHG) have received constant attention due to the practical application in the field of optoelectronics and photonics. Thus, the opto-electronics has stimulated the search for highly optical nonlinear organic crystals for better efficient signal processing. [1, 3]



An optical material can be defined as a solid that presents events when interacts with light in the range of wavelengths of 200 nm (ultraviolet) to 3 μ m (near infrared). They are a wide group of materials that can be classified into the following types: luminescent, lasers, pigments and optical fiber. In preparing these the rare earth elements are responsible for the properties they represent, and in most cases were added as dopants to constitute only a small percentage by weight of the overall composition of optical materials [3].

Rare earth complexes have distinct properties such as optical, electrical and magnetic and are closely related to their electronic configurations and are a new type of functional materials and have potential use in the fields of photo-luminescence, electro-luminescence, laser, etc. [4].

The chemical compounds often show the ability to crystallize in more than one structural form. And the different forms are known as polymorphs and these may exhibit different mechanical, thermal and physical properties such as solubility, melting point, compressibility. Glycine the simplest of all amino-acids has three known polymorphs: α , β y γ glycine. The importance of amino acids in NLO applications is in the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in a non-centrosymmetric space group. In solid state, amino acids containing one de-protonated carboxyl group (COO-) and a protonated amino group (NH⁺³). This dipolar nature exhibits peculiar physical and chemical properties of amino acids making them ideal candidates for use in NLO [5]. This paper report the crystal growth Glycine doped with



erbium nitrate penta-hydrate, followed by characterization by UV-Vis, FTIR, Raman, analysis of X-ray diffraction (XRD) and second harmonic generation (SHG) efficiency. **Experimental details**

The crystals of Gly-[ErNO₃]5H₂O were obtained from and aqueous solution of Glycine and [ErNO₃]5H₂O at different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5%) into 50 ml of distilled water. The starting reagents were glycine JT-Baker 98.8% pure and erbium (III) nitrate pentahydrate Aldrich 99.9% metals basis. The solution was heated on a hotplate and was stirred two minutes for dissolution, then was evaporated slowly at room temperature during a month, which yielded crystals of several millimeters in size (method of slow evaporation used by several authors) [6, 7, 14]. The samples were analyzed in a Perkin Elmer Lambda 10 spectrometer in the range 200–1100 nm, to know the optical transmission. Raman technique was used to find the molecule vibrations, the equipment used is LabRAM HR-RAMAN Microscope. In order to find the SHG, the crystals were ground according to the Kurtz and Perry technique [9, 10] into powder (about 70 μ m) and densely packed between two transparent microscope glass slides [9].

Results and discussion

Uv-vis spectroscopy: (Ultra-violet wavelength) where a wide band completely transparent in all the visible range is observed (Infraredwavelengths). Its means that this material presents a good non-absorbance band in the visible range for expected applications. A little protuberance around the 300 nm is observed. This little peak is still outside the visible zone (UV zone) and it could present some absorbance if the crystal



were to be excited with 600 nm (red color) trying to obtain a second harmonic of 300 nm (UV color). Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 400–1100 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG. Due to this property this material have potential uses for SHG using an Nd: YAG laser (1064 nm) to emit a second harmonic signal within the green region (532 nm) of the electromagnetic spectra. Applications becomes promising due to the use of laser.



Figure 1. UV spectrum of glycine: erbium crystals.

Raman spectroscopy: Figure 2 displays the Raman spectra of glycine-erbium. The bands found in the IR spectrum are similar to the Raman spectrum (Table 1). In the assignment of the bands were used in the literature assignments for the glycine



molecule with similar groups. According to literature in saturated amines, the asymmetric and symmetric NH₂ group stretching are usually expected in the region 3380– 3350 cm⁻¹ and 3310–3280 cm⁻¹, respectively. However, the protonation of NH₂ group can shift in band position towards the range 3300–3100 cm⁻¹ and 3100–2600 cm⁻¹ for asymmetric and symmetric stretching modes, respectively. In Raman spectra of glycine: erbium, the asymmetric and symmetric NH₂ group stretches are at 3017 and 2974 cm⁻¹ respectively. The NH⁺³ vibrations at 3145cm⁻¹ correspond to the weak link of the H bound to O (N-H ... O), this value is related to the α -glycine [12, 13]. The presence of strong band N-H^{...}O is evident from the presence of intra- and intermolecular hydrogen bonding at frequencies to 2890 cm¹ in the spectrum. The symmetric and asymmetric deformation vibrations of the NH⁺³ groups appear in the region between 1680–1470 cm⁻¹ [11], in the spectrum glycine: erbium we find them 1670 cm⁻¹. The peak at 1443cm⁻¹ is a deformation of CH₂ group, at 1322 cm⁻¹ is attributed to the CH₂ wagging.



Figure 2. FT Raman spectrum of glycine doped with erbium.



glycine:Er	
RAMAN (cm ⁻¹)	Assignment
3145	[N–H…O]
3017	CH ₂ asymm
2975	CH ₂ symm
2890	NH ⁺³ symm
2713	Overtones/combinations
2621	NH ⁺³
1670	NH ⁺³ asym bend
2138	Combinations
1570	COO ⁻ asymm stretch
1500	CH ₂ bend + OH bend
-	Symmetric bending NH ₃
1443	Scissoring CH ₂
1422	CH ₂
-	CH ₂ scissoring
1322	CH ₂ wagging
1103	NH ⁺³ rocking
1046	C-N stretch + C-C vibration
-	CH ₂ rock
889	NH2 twist + CH2 twist
705	COO ⁻ deformation
-	COO ⁻
613	COO ⁻ wagging
500	COO bend + CH2 bend
358	CCN bend
167	COO ⁻ torsion
116	Vibrations NO

TABLE 1. Frequencies of absorption observed in Raman spectra of glycine:Er

Second Harmonic meassurement: Once the samples were placed into the glass slides, a Nd:YAG Quanta ray INDI series laser with wavelength of 1064 nm which generated an 8 ns pulse and was operated at 6 mJ/pulse and at rate of 10 Hz was shot at the proper angle and distance in order to see the SHG in green (532 nm); the expected half wavelength signal. The experimental setup consisted of a slightly modified Kurtz Perry setup. A Nd:YAG pulsed laser source was the reference and excitation beam. The beam was divided in to 2 beams consisting of a reference beam and an excitation beam. The reference beam was measured with a photomultiplier in order to detect beam energy. The other was used to excite the sample and was



mounted between two glass holders. The signal was then recorded in an oscilloscope in order obtain SHG intensity.

Fig. 3 shows the data collected from the detector and the SHG signal vs. the beam energy plot. This was done in order to measure the damage threshold. In this case, a tendency to increase the SHG intensity and beam energy is shown. Er Concentrations of 1 and 5% have good signal placed in 532 nm. For some reason in these cases the Er may take a selective place in the lattice in order to form a non-centrosymetric structure. Figure 4 we see for concentrations 0.1 and 0.5% erbium the predominant phase □-glycine, for concentrations 0.2 - 0.4% the □-glycine, which crystallizes in centrosymmetric space group; this may explain not having second harmonic emission.



Conclusions



Optical absorbance spectrum to 500–600 nm confirms that this crystal is suitable for NLO applications. The vibrational spectral analysis is performed based on the characteristic vibrations of the glycine molecule. Only at 0.1 and 0.5% of erbium was obtained second harmonic efficiency, due that the crystallization was unstable on the other concentrations and few time later they began a hydrolization phenomenon.

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References

[1] Bhat MN, Dharmaprakash S (2002). Growth of nonlinear optical □-glycine crystals. J.Crystal Growth 236: 376-380.

[2] Bhat MN, Dharmaprakash S (2002). Effect of solvents on the growth morphology and physical characteristics of nonlinear optica g-glycine crystals. J. Crystal Growth 242: 245-252.

[3] Tapati M, Tanusree K (2005). Growth and characterization of nonlinear optical Larginine dihydrate single crystals. J. Crystal Growth. 285: 178-182.

[4] Yan C, Guo C, Lu P, Qiu G (2007). Synthesis and Characterization of Rare Earth Complexes. J. Rare Earths. 25: 117-121.

[5] Sáenz PR, Cascales C, Porcher P, Maestro P (2000). Rare earth. Advanced materials. Annals Spanish Royal Soc. Chem. 4:11-26.



[6] Baran J, Ratajczak H (2005). Polarised IR and Raman spectra of the □-glicine single crystal. Spec. Act Part A 61:1611-1626.

[7] Silva-Molina RA, Duarte-Moller A, Orrantia-Borunda E, Parra- Berumen, Regalado

LE, Álvarez-Ramos ME (2011). The role of pH on the second harmonic response of glycine sodium nitrate (GSN). J. Phys. Sci. 6(4): 885-890.

[8] Vijayakumar T., Hubert JI, Reghunadhan NC, Jayakumar VS (2008). Non-bonded interactions and its contribution to the NLO activity of Glycine Sodium Nitrate – A vibrational approach. J. Molec. Struct. 877: 20–35.

[9] Silverstein, R. M.; Webster F. X. (1998) Spectrometric Identification of Organic

Compounds; 6th ed., John Wiley. Eastern & Sons Inc.: Canada.

[10] Kurtz S.K., Perry T.T., (1968) J. Appl. Phys. 39 3798–3813.

[11] Baran J, Ratajczak H. (2006). Polarised vibrational studies of the -glycine single crystal. Part I. Polarised Raman spectra—the Problem of effective local Raman tensors for the glycine zwitterions. Vib. Spectrochem. 43:125–139.

[12] Murli C, Sharma S, Karmakar S, Sikka SK (2003). □-Hlycine under high pressues: a Raman scattering study. Phys. B 339: 23-30.

[13] Murli C, Thomas S, Venkateswaran S, Sharma SM (2005). Raman spectroscopic investigation of a-glycine at different temperatures. Phys. B 364: 233-238.

[14] Gallegos-Loya E, Álvarez Ramos E, Regalado E, Orrantia Borunda. E, Duarte-Moller A (2010). Evidence of second harmonic signals in poly [μ2- L alanine-μ3-nitratosodium (I)] crystals. Inter. J. Phys Sci. Vol. 5 (13), pp. 2052-2056.

