

A study of the optical properties of semi-organic crystals doped with erbium

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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 and γ in which the molecules exist in the dipolar form ($\text{NH}_3^+ \text{CH}_2\text{COO}^-$). 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 Fourier transform infrared (FTIR), and 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 to 1100 nm. The crystalline phase was determined by X-ray diffraction and the second harmonic generation efficiency of the crystal measured by using the Kurtz Perry modified method.

Key words: Glycine, erbium, nonlinear, optical effects (NLO), second harmonic generation (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 (Bhat and Dharmaprakash, 2002; Tapati and Tanusree, 2005).

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 μm (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 (Bhat and Dharmaprakash, 2002).

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. (Yan et al., 2007).

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 , 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^+). This dipolar nature exhibits peculiar physical and chemical properties of amino acids making them ideal candidates for use in NLO (Saenz et al. 2000). This paper report the crystal growth glycine doped with erbium nitrate penta-hydrate, followed by characterization by

Ultraviolet-visible (UV-Vis) (UV-Vis), Fourier transform infrared (FTIR), Raman, analysis of X-ray diffraction (XRD) and second harmonic generation (SHG) efficiency.

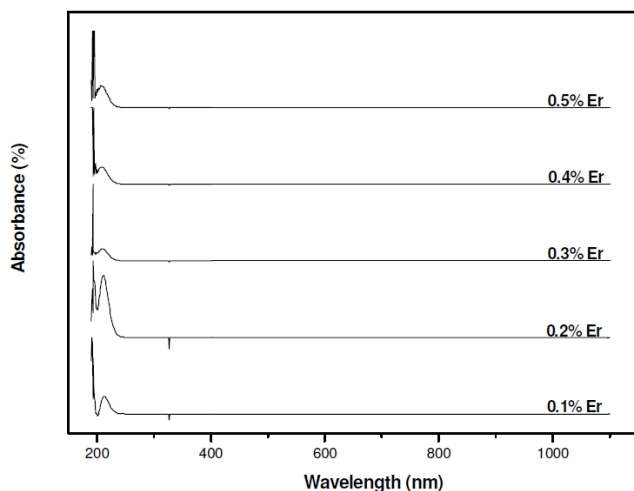


Figure 1. UV spectrum of glycine: erbium crystals.

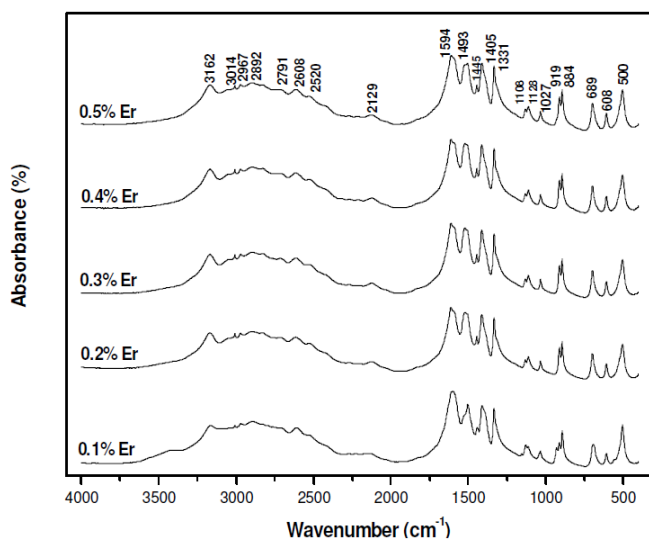


Figure 2. FTIR of glycine: erbium crystals.

Experimental details

The crystals of Gly-[ErNO₃]5H₂O were obtained from an aqueous solution of Glycine and [ErNO₃]5H₂O at different concentrations 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 stirred for two minutes for dissolution, after which it was evaporated slowly at room temperature within a month, which yielded crystals of several millimeters in size (the method of slow evaporation was used by Baran and Ratajczak (2005); Silva-Molina et al. (2011) and Vijayakumar et al. (2008)). The samples were analyzed in a Perkin Elmer Lambda 10 spectrometer in the range 200 to 1100 nm, to know the optical transmission.

The infrared spectra were obtained on a 750 Series II MAGNO NICOLET spectrometer within the range 400 to 4000 cm^{-1} . Raman technique was used to find the molecule vibrations, the equipment used is X'plora RAMAN Microscope. To obtain the XRD spectrum, an X-PERT diffractometer Phillips was used. The equipment used for thermal analysis was STD 2960 Simultaneous DTA-TGA, TA Instruments brand; samples were run from 0 to 600°C with ramp of 5°C / min in static air. In order to find the SHG, the crystals were ground according to the Kurtz and Perry technique (Kurtz and Perry, 1968) into powder (about 70 μm) and densely packed between two transparent microscope glass slides (Silverstein, 1998).

Results and discussion

UV spectroscopy

Optical transmission spectra of glycine with erbium as shown have a good transparency in between 350 and 1100 nm (Figure 1). Also it can be used for second harmonic generation for Nd-YAG laser.

IR spectroscopy

The absorptions in Figure 2 correspond to the combination of the main functional groups that form the glycine molecule: Carboxylic acid (COOH), amino group (NH₂) and CH₂ group. Their assignment frequency of the glycine crystals are given in Table 1. The band observed to 3162cm⁻¹ corresponds to the group NH⁺³ of α-glycine (Vijayakumar et al., 2008; Baran and Ratajczak, 2006). Asymmetric and symmetric vibration of CH₂ group was found to 3014 and 2967cm⁻¹ edge, respectively (Vijayakumar et al., 2008; Baran and Ratajczak, 2005). The peak at 1449 cm⁻¹ is assigned to CH₂ scissoring (Vijayakumar et al., 2008; Baran and Ratajczak, 2005, 2006). The NH⁺³ symmetric stretching frequency to 2892 cm⁻¹ is attributed of strong N-H...O intra- and intermolecular hydrogen bonding; CH₂ wagging are observed at 1331 cm⁻¹, at 1594 cm⁻¹ correspond to COO⁻ asymmetric stretch, at 935 cm⁻¹ CH₂ rocking, C-C stretch 890 cm⁻¹, 676 cm⁻¹ NO³ in-plane deform (Vijayakumar et al., 2008; Baran and Ratajczak, 2005).

Raman study

Figure 3 display 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 is usually expected in the region 3380 to 3350 cm⁻¹ and 3310 and 3280 cm⁻¹, respectively. However, the protonation of NH₂ group can shift in band position towards the range 3300 to 3100 cm⁻¹ and 3100 to 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 (Murli et al., 2003, 2005; Baran and Ratajczak, 2005, 2006). The presence of strong band $\text{NH}\cdots\text{O}$ is evident from the presence of intra- and intermolecular hydrogen bonding at frequencies to 2890 cm^{-1} in the spectrum. The symmetric and asymmetric deformation vibrations of the NH^{+3} groups appear in the region between 1680 and 1470 cm^{-1} (Baran and Ratajczak, 2006), in the spectrum glycine: erbium, we find them in 1670 cm^{-1} . The peak at 1443 cm^{-1} is a deformation of CH_2 group, at 1322 cm^{-1} is attributed to the CH_2 wagging.

Table 1. Frequencies of absorption observed in IR and Raman spectrum of glycine.

IR (cm^{-1})	RAMAN (cm^{-1})	Assignment
3162	3145	[N-H...O]
3014	3017	CH_2 asymmetric
2967	2975	CH_2 symmetric
2892	2890	NH^{+3} symmetric
2791	2713	Overtones/combinations
2608	2621	NH^{+3}
-	1670	NH^{+3} asymmetric bend
2129	2138	Combinations
1594	1570	COO^- asymmetric stretch
-	1500	CH_2 bend + OH bend
1493	-	Symmetric bending NH_2
1445	1443	Scissoring CH_2
-	1422	CH_2
1405	-	CH_2 scissoring
1331	1322	CH_2 wagging
1108	1103	NH^{+3} rocking
1027	1046	C-N stretch + C-C vibration
919	-	CH_2 rock
884	889	NH_2 twist + CH_2 twist
-	705	COO^- deformation
689	-	COO^-
608	613	COO^- wagging
500	500	COO^- bend + CH_2 bend
-	358	CCN bend
-	167	COO^- torsion
-	116	Vibrations N...O

X-ray diffraction

Figure 4 shows the XRD patterns for the glycine with different concentrations of erbium; the main phases are α and γ -glycine, dominating the first one in the crystals with concentrations of 0.1 to 0.4% of erbium. In the sample of 0.5% of erbium, the phase β -glycine predominates.

Thermal analysis

In TGA, Figure 5 shows that the sample is stable above 224°C, then it begins to degrade with a 5% loss of water in the crystals, after which a weight loss of 42% was observed in 300°C. This was due to the combustion of organic matter such as CO and NO₃, thus the decomposition of the remaining molecules continued to 600°C. For DTA, we observed stability to 200°C, then start an irreversible endothermic transition which corresponds to phase change up to 243.7°C, which approaches the melting point of pure glycine. TGA losses are similar in different samples; the temperatures of DTA melting points are decreasing with increasing erbium concentration, may be because the amount of erbium (as nitrate pentahydrate) is small compared with glycine.

Second harmonic generation (SHG)

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.

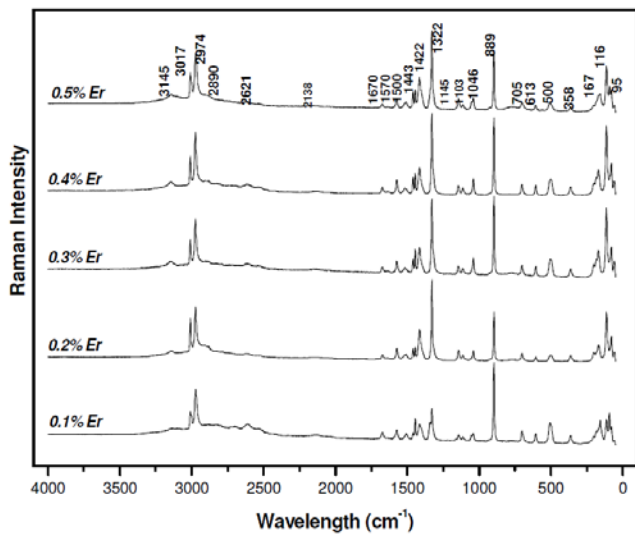


Figure 3. FT Raman spectrum of glycine doped with erbium.

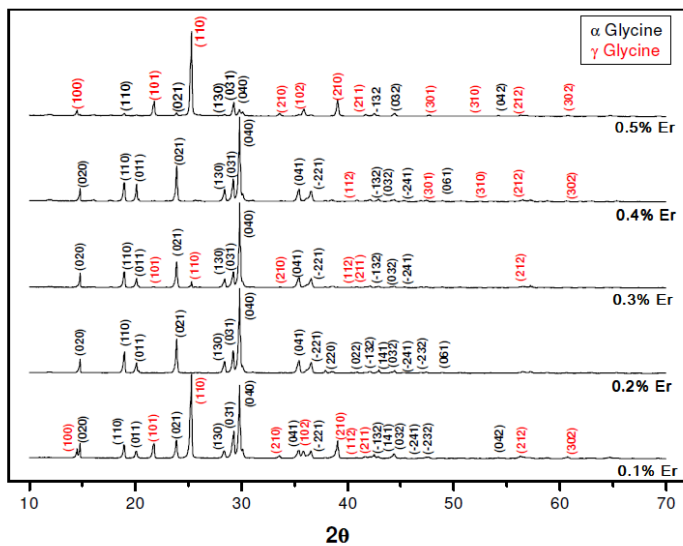


Figure 4. XRD of glycine:erbium crystals.

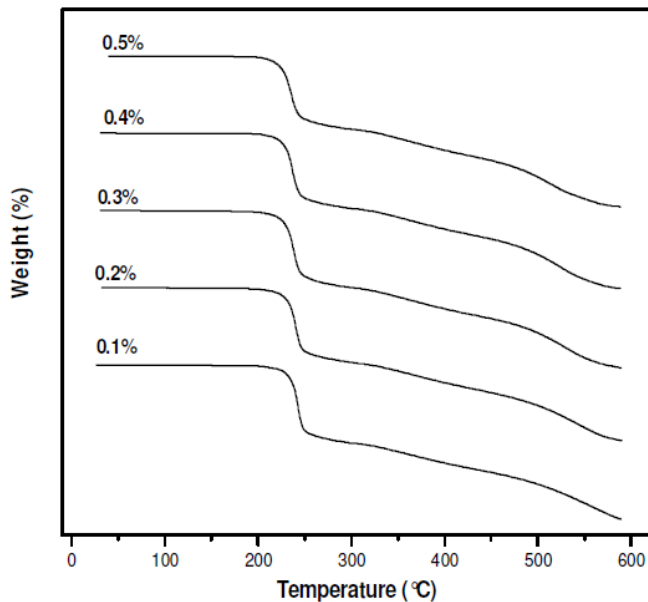


Figure 5. TGA curves of crystals glycine: Erbium.

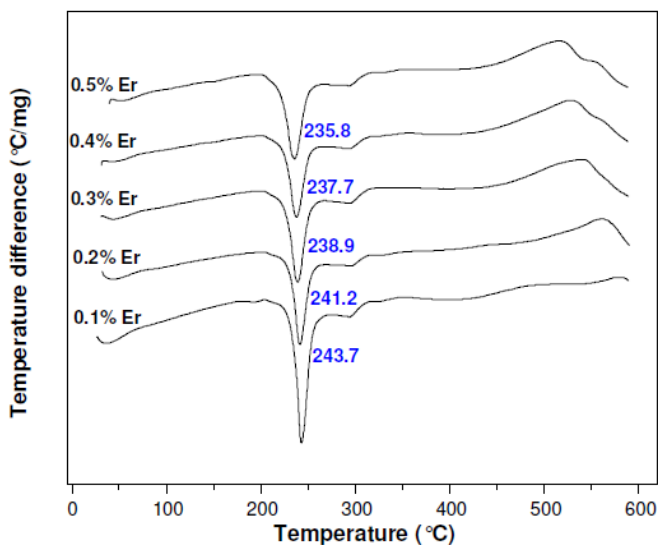


Figure 6. DTA curves of crystals glycine: Erbium.

Figure 7 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-centrosymmetric structure. From Figure 4, we see that for concentrations 0.1 and 0.5% erbium, the predominant phase is γ -glycine, for concentrations 0.2 to 0.4%, the predominant phase is α -glycine, which crystallizes in centrosymmetric space group; this may explain not having second harmonic emission.

Conclusion

Optical absorbance spectrum of 500 to 600 nm confirms that this crystal is suitable for NLO applications. The vibrational spectral analysis IR is performed based on the characteristic vibrations of the glycine molecule. The phase of the grown crystal was confirmed by powder XRD, α and γ phase glycine occurred in most of the crystals except glycine: 0.2% erbium, where there is only a phase. Only at 0.1 and 0.5% of erbium, second harmonic efficiency was obtained, but the efficiency is higher in pure glycine than erbium-doped.

References

Bhat MN, Dharmaprakash S (2002). Growth of nonlinear optical γ - glycine crystals. J. Crystal Growth 236: 376–380.

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

Baran J, Ratajczak H (2005). Polarised IR and Raman spectra of the γ -glycine single crystal. Spec. Act Part A 61: 1611-1626.

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

Changhao Y, Chunfang G, Ping L, Guanming Q (2008). Crystallization of metastable β glycine from gas phase via the sublimation of α or γ form in vacuum. *Biophys. Chem.* 132: 18-22.

Murli C, Sharma S, Karmakar S, Sikka SK (2003). α -Glycine under high pressures: a Raman scattering study. *Phys. B* 339: 23-30.

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

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

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.

Tapati M, Tanusree K (2005). Growth and characterization of nonlinear optical L-arginine dihydrate single crystals. *J. Crystal Growth.* 285: 178-182.

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.

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