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Study of SHG emission of L- Histidine HCl-[ErNO$_3$]5H$_2$O crystals

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Abstract: Mixed crystals like L-histidine and L-histidine HCl. These compounds have nonlinear optical properties in some of their polymorphs. However, their thermal stability is low. It has demonstrated that some mixed crystals of amino acids with some nitrates improve properties like thermal stability and second harmonic emission. In this work, we synthesize L- histidine- HCl crystals doped with pentha-hydrated erbium nitrate by slow evaporation at room temperature. The optical absorption results in the wavelength range of UV-vis revealed that the crystal has excellent optical transparency in the range of 350 to 1100 nm. The crystalline phase obtained by using X-ray diffraction shows the expected structure and the second harmonic signal of the crystal measured by using the Kurtz Perry modified method shown an excellent intensity taken as reference the Urea SHG emission. Results obtained in this research shown that of L- Histidine HCl-[ErNO$_3$]5H$_2$O with a 0.3% of Er (III) has a 0.65% SHG emission respect the Urea.

Keywords: NLO, SHG, L-Histidine-HCl, Low Temperature

I. INTRODUCTION

Amino acids have interest applications on Non- Linear Optics (NLO) because they are materials of second order polarizability. A non-linear optical material has some characteristic properties like they have not-centrosymmetric structure, wide transparency range (200-700 nm), and they are highly polarizable. Crystalline amino acid salts and their derivate are one of the directions in the search for new materials of second order in NLO [1-10].

The Histidine amino acid is considered a non-essential amino acid for adults, however, histidine sources in the diet (meat, fish and dairy products) probably represent the majority of the total found in the body. Histidine is used by the body to make proteins and also as a precursor of histamine neurotransmitter that is released by the body during allergic reactions. Histidine is involved in the regulation and use of several essential minerals in the body, including zinc, copper, manganese, and iron. On the other hand, crystals doped with Er (III) show unusual luminescent properties. Research from the 1970s shown a broad characterization of alkali halides like KCl: Er, KBr: Er, etc. [11-15]. The primary objective is to know the influence of Er (III) in the SHG emission of L-Histidine HCl.

II. MATERIALS AND METHODS

Crystals of L- Histidine HCl-[ErNO3]5H2O, were obtained from an aqueous solution of L- Histidine HCl and [ErNO3]5H2O varying its concentrations from 0.1% up to 0.5 % into 50 ml of distilled water. The starting reagents were L- Histidine HCl JT-Baker 98.8% pure and erbium (III) as nitrate pentahydrate Aldrich 99.9% metals basis. The solution was heated on a hot plate and stirred for ten minutes for dissolution, after which it was evaporated slowly at room temperature within a month, which yielded crystals of several millimeters in size.

UV-Vis experiments were carried out 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 measurements were carried out in an HR Lab-Ram RAMAN Horiba- JY equipment. It was used to find the characteristic molecule vibrations of the samples. To obtain the XRD spectrum, an X-PERT diffractometer Phillips was used. The instrument used for thermal analysis was STD 2960 Simultaneous DTA-TGA, TA Instruments brand; samples were run from 0 to 600°C with a ramp of 5°C / min in static air. To detect the SHG signal of the crystals, they were ground according to the Kurtz and Perry technique into powder (about 70 µm) and densely packed between two transparent microscope glass slides.

III. RESULTS AND DISCUSSION

Optical transmission spectra of L- Histidine HCl with erbium (III) shown have an excellent transparency in between 350 and 1100 nm (Figure 1). This property is mandatory to be used as frequency multiplier and as the firm candidate for second harmonic generation. The absorptions in Figure 2 correspond to the combination of the primary functional Groups that form the L- Histidine HCl molecule: Carboxylic acid (COOH), an amino group (NH_2) and CH~~2~~ group.

Their assignment frequency of the L- Histidine HCl crystals are given in Table 1. The band observed to 3411 cm^{-1} corresponds to the O–H symmetrical stretching of water. Asymmetric and symmetric vibration of NH group were found to 3157 and 3105 cm^{-1} edges, respectively. Afterward the respective asymmetric and symmetric CH^2 groups appear located at 3075 and 2995 cm^{-1}. Some characteristic frequencies are those that correspond to bond deformation placed at 1432 and 824 cm^{-1} may be due to the tension exerted by the Er (III) atom. The rest of the frequencies listed in Table 1 represents all the possible vibrations. The C–H and N–H bending vibrations can be appreciable at 1490 cm^{-1} as a sharp peak

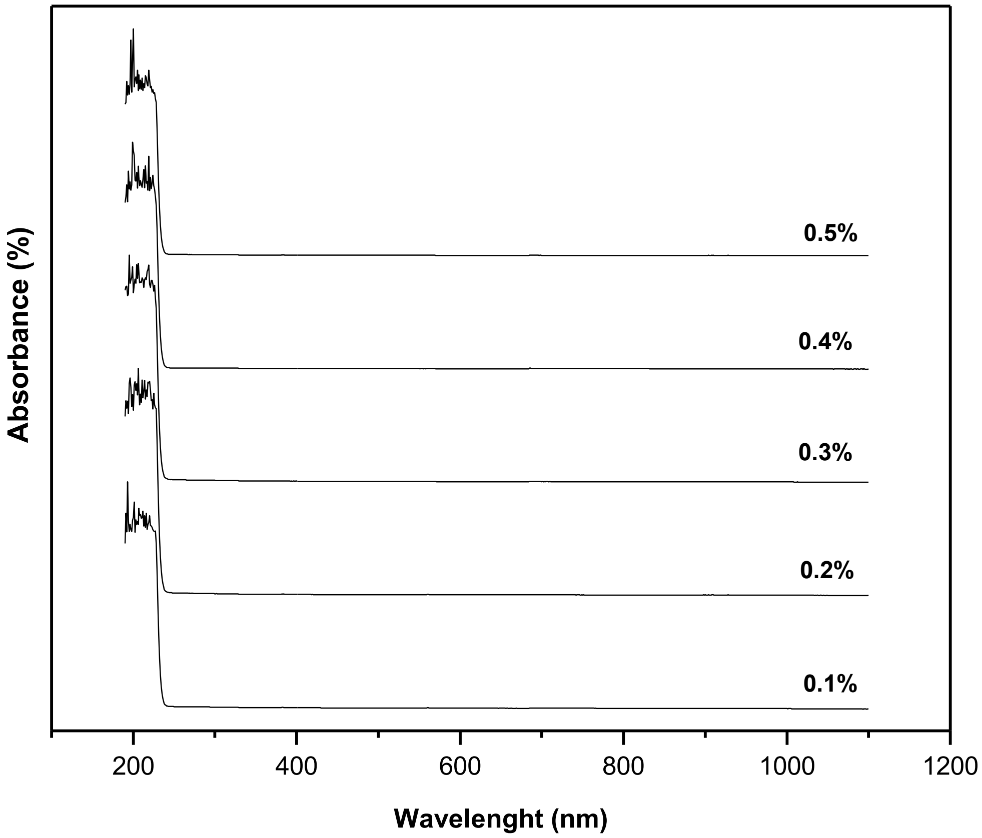

Figure 1. UV- Vis spectrum of L-Histidine HCl-[$ErNO_3$]$5H_2O$ with different Er (III) concentrations. A full transparent window appears around 200 up to 1100 nm.

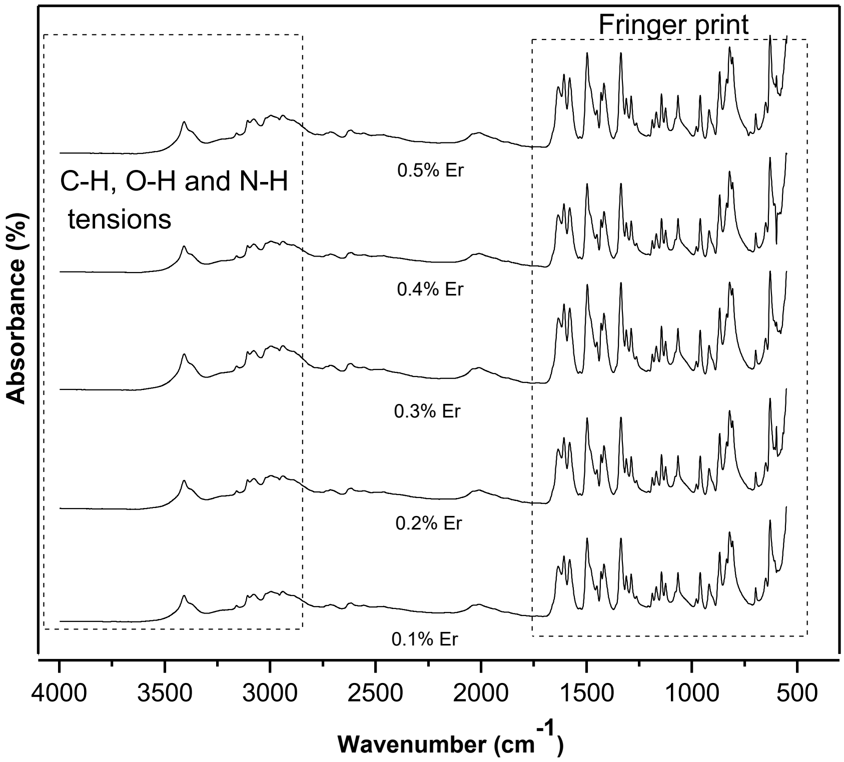

Figure 2. FTIR spectrum of L- Histidine HCl-[$ErNO_3$]$5H_2O$ with different Er (III) concentrations.

In figure 3 appears the Raman spectra of L- Histidine HCl-[$ErNO_3$]$5H_2O$. Usually, Raman spectroscopy is a complementary technique to FTIR characterization. The bands found in the FTIR spectrum are some similar to the Raman spectrum, which appears in Table 1. The bands of saturated amines, the asymmetric and symmetric NH_2 group stretching expected in the region 2600 to 2500 cm^{-1} is noticeable. The asymmetric CH3 bending at 1430 cm^{-1} and O–H bending is around 1100 cm^{-1} [15-17]. The study of symmetry was stretching and stretching vibration of a CH_2 group observed in 2955, 3000 and 3154 cm^{-1}. The band around 1200 and 900 cm^{-1} is also indicative of the NH_3 rocking modes. The peak at 138 cm^{-1} is a deformation of a CH_2 group, at 1248 cm^{-1} is attributed to the CH_2 wagging.

Table 1. Frequencies assignment of L- Histidine HCl-[ErNO3]5H2O.

Frequency (cm^{-1})	***Assignment***	***Frequency (cm^{-1})***	***Assignment***
3411	O–H sym. stretching of water	1337	CH_2 deformation
3157	N–H asym. stretching	1314	C–N stretching
3105	N–H sym. stretching	1185	C–H in plane bend & C–C stretch
3075	CH_2 asym. stretching	1141	C–H in plane bending
2995	CH_2 sym. stretching	1126	N–H bending
1635	C =O stretching	1064	C–H in plane bending
1605	H_2O deformation	964	N–H bending
1573	NH_{3+} stretching	920	C–H out of plane bending
1495	C–N stretching	824	Ring deformation
1432	Ring deformation	699	C =O deformation
1410	N–H bending	629	Ring deformation

The XRD patterns for the L- Histidine HCl with different concentrations of erbium appears in Fig 4; The L- Histidine HCl-[$ErNO_3$]$5H_2O$ crystallizes as orthorhombic 2/m, 2/m, 2/m system with structural parameters: a= 0.8944 nm, b=1.5303 nm, c=0.6838 nm and $\alpha=\beta=\gamma= 90^o$. Figure 5 illustrate the crystalline habit of the mentioned structure.

Figure 5 displays a zoom of the lowest peak intensities. There the L-Histidine HCl peaks are indexed and also a region beyond $2\theta = 26.5^o$ is the $ErNaNO_3$-$5H_2O$ contribution. Is noticeable an increment in the peaks intensities.

The crystalline habit of the orthorhombic structure appears in Figure 6. This habit is some similar to that illustrated in figure 7 where to appear the optical micrographs of the doped crystals.

Figure 8a shows that the sample is stable above 170°C, then it begins to degrade with a 10.3% loss of water in the crystals, after which a weight loss of 46% observed in 300°C. This 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 an endothermic peak at 170°C; which can be due to the crystal impurities then start an irreversible endothermic transition which corresponds to phase change up to 240°C, which corresponds to the phase shift up to 262.4 °C. TGA, figure 8b, losses are similar in different samples; the temperatures of DTA melting points are decreasing with increasing erbium concentration, may be because of the amount of erbium (as nitrate pentahydrate) is small compared with L- Histidine HCl.

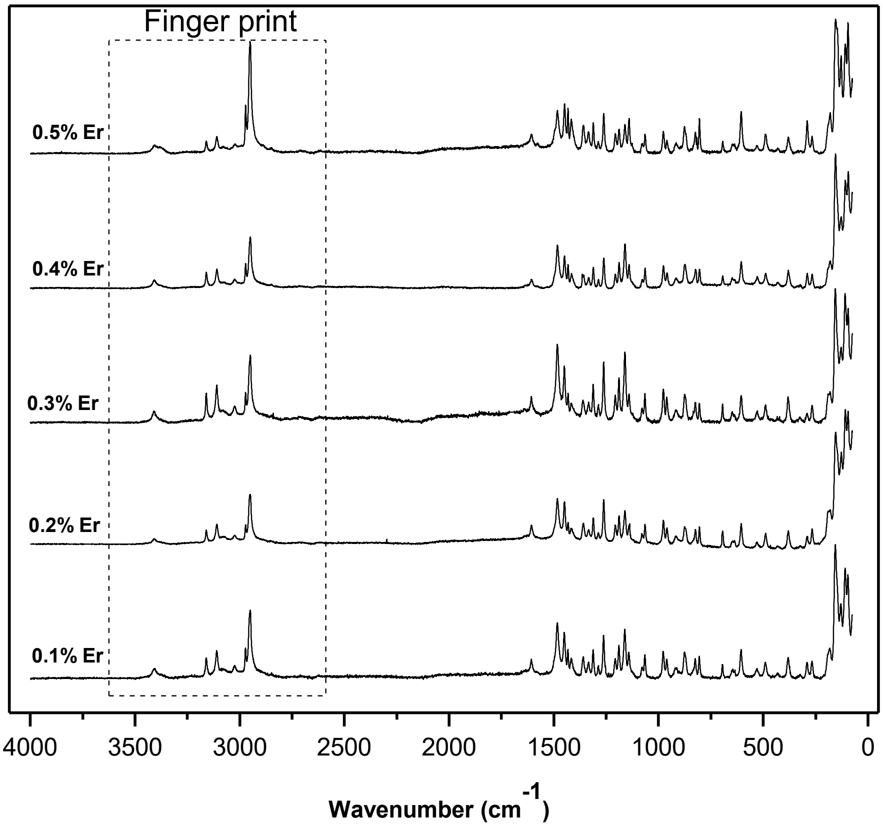

Figure 3. Raman spectrum of L- Histidine HCl-[ErNO$_3$]5H$_2$O with different Er (III) concentrations

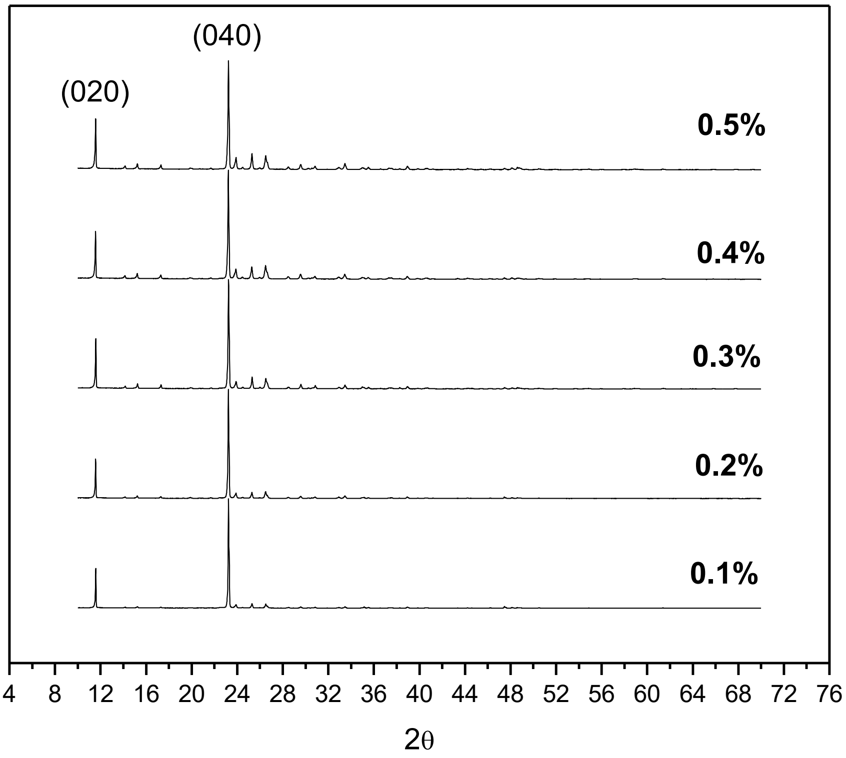

Figure 4. XRD diffraction pattern of L- Histidine HCl-[ErNO$_3$]5H$_2$O with different Er (III) concentrations. As we can see, no substantial effects of the Er (III) are appreciable.

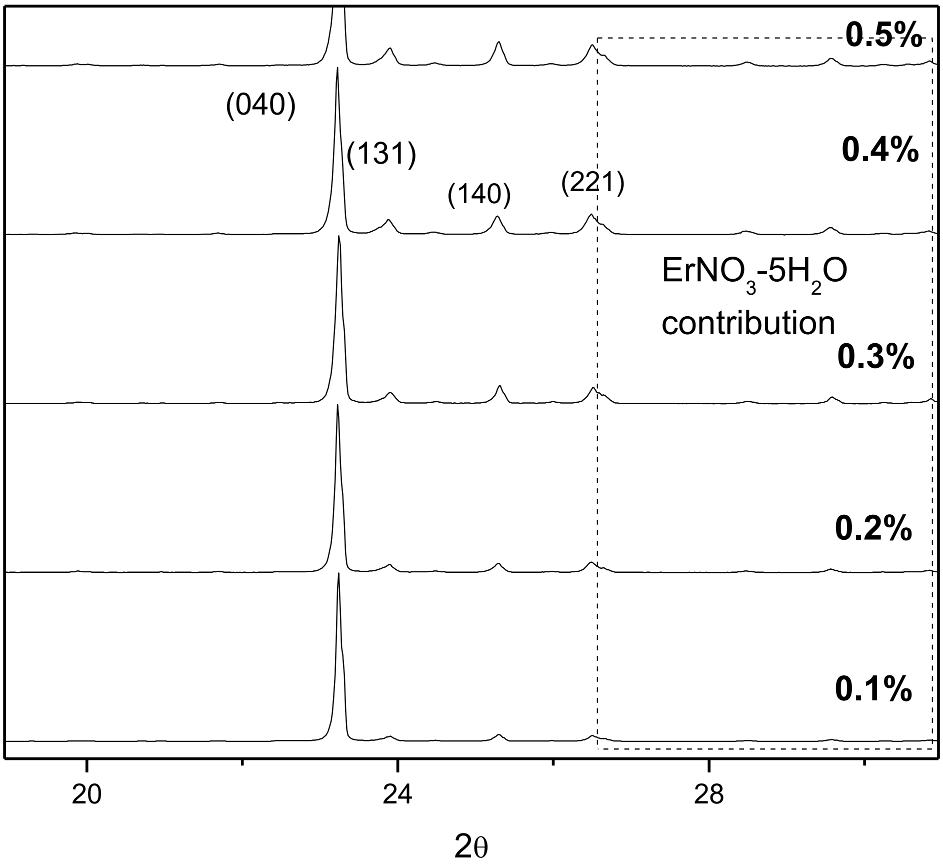

Figure 5. Zoom of the XRD pattern from figure 4 showing the Miller indexes of small diffractions peaks.

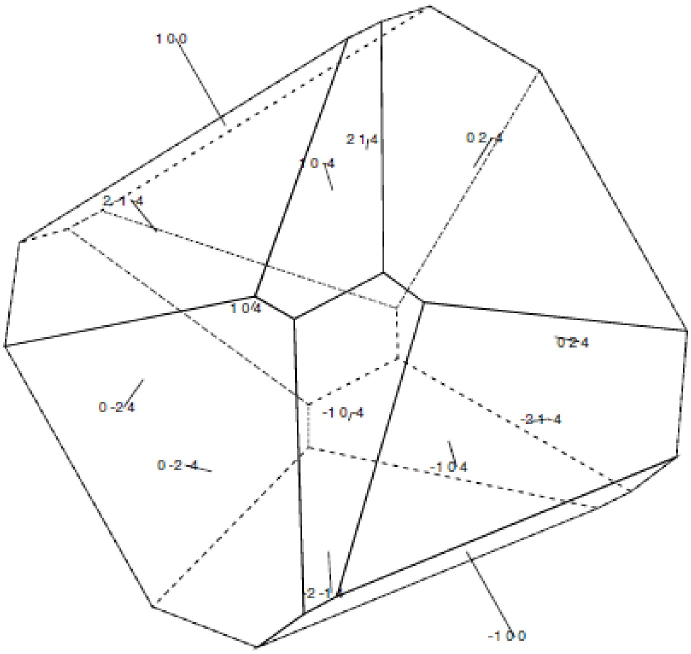

Figure 6. Crystalline habit of the orthorhombic 2/m2/m2/m structure

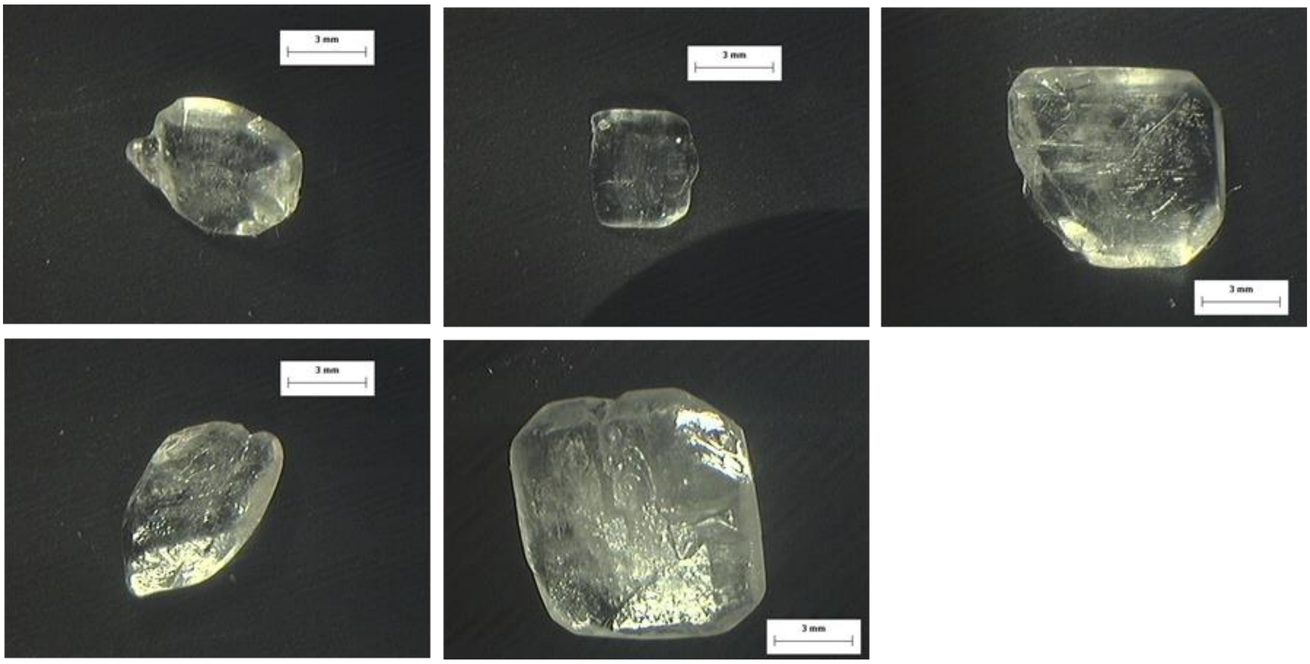

Figure 7. Optical micrographs of all samples.

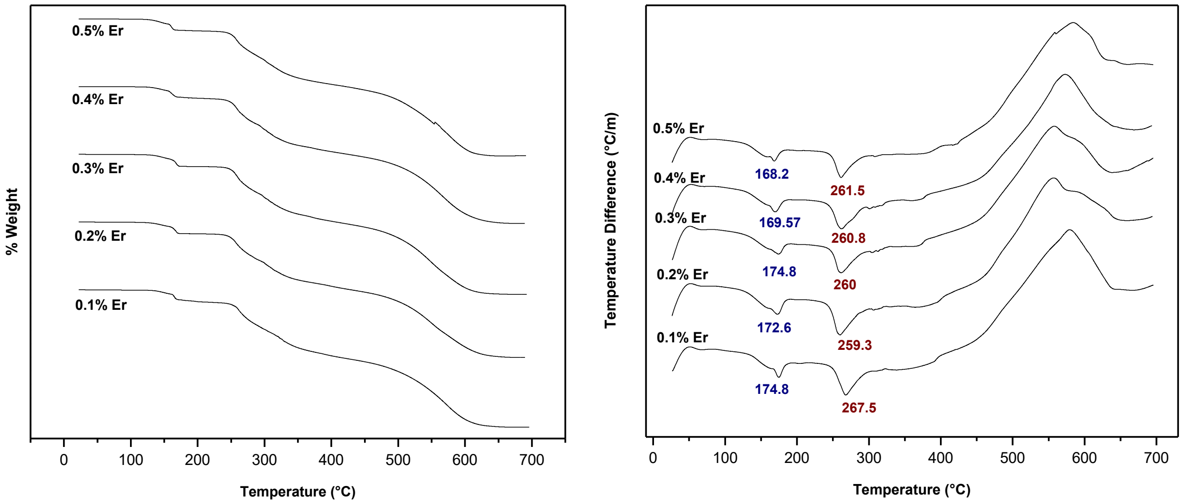

Figure 8. DTA/TGA spectrum of L- Histidine HCl-[$ErNO_3$]$5H_2O$

Samples were exposed on Nd: YAG Quanta Ray INDI series laser, operating at a wavelength of 1200 nm with a pulse of 8 ns, an energy of 4mJ/pulse and a rate of 10 Hz. The experimental setup consisted of a slightly modified Kurtz Perry setup by using Urea as the reference signal. SHG signal was collected each 60 cycles in reflection mode at an angle of 45^o. The signal was then recorded in an oscilloscope in order obtain SHG intensity. Figure 6 shows the SHG intensity of the L- Histidine HCl-[$ErNO_3$]$5H_2O$ compared with the Urea SHG signal. As we can appreciate in Figure 9, the sample doped with Er concentration of 0.3% had good signal placed in 600 nm, about 65% respect to that of Urea. For some reason, in this case, the Er may take a particular place in the lattice to form a not-centrosymmetric structure, property needed to be a candidate for SHG generation. From Figure 4, we see that for concentrations 0.5% erbium, the predominant phase is L- Histidine HCl, and the rest the dominant phase is a-L- Histidine HCl, which crystallizes in centrosymmetric space group; this may explain not having a good second harmonic emission.

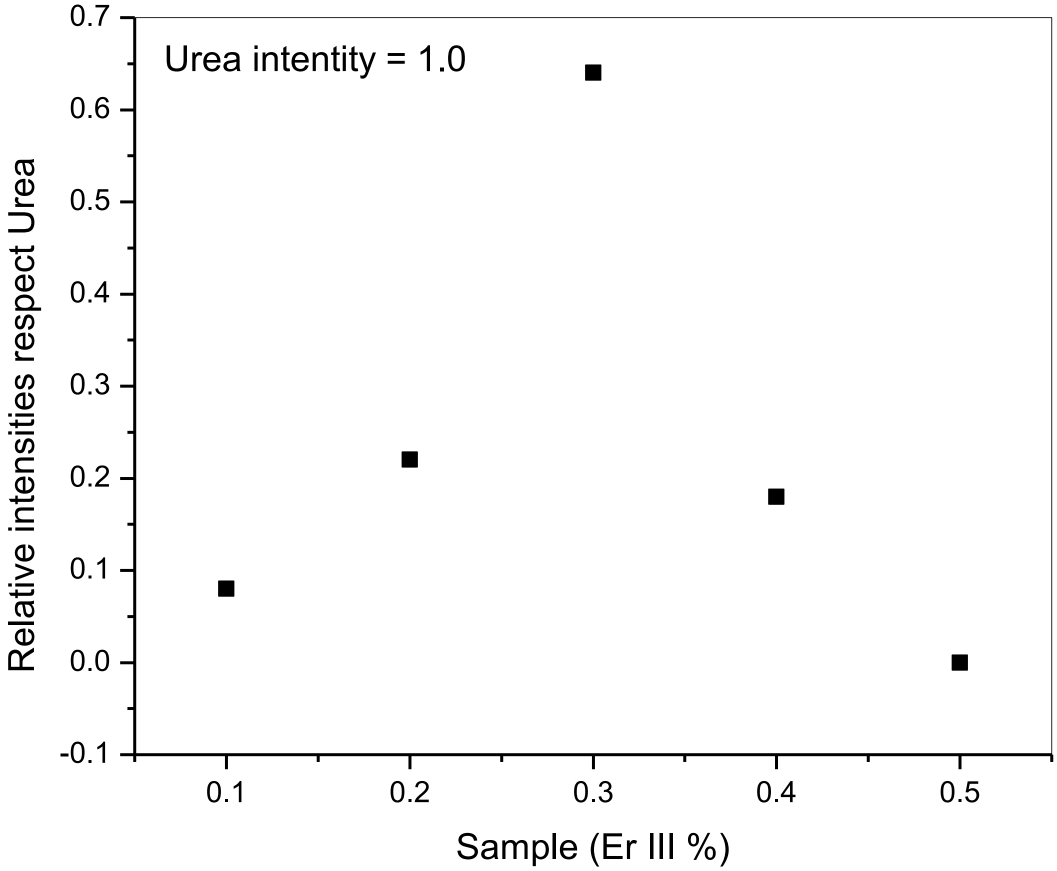

Figure 9. SHG intensities measured for L- Histidine HCl-[$ErNO_3$]$5H_2O$ at different Er concentrations.

IV. CONCLUSIONS

The slow evaporation method was used to obtain crystals of L - histidine-HCl doped with Er (III) concentrations of 0.1 to 0.5% wt. The absorption spectrum confirms the transparency of crystals in a wide range, a necessary property of an NLO crystal. The IR and Raman spectra are proving the existence of molecules which correspond to the main functional groups existing in the crystal. The L-Histidine HCl-[$ErNO_3$]$5H_2O$ crystallizes as orthorhombic 2/m, 2/m, 2/m system with structural parameters: a= 0.8944 nm, b=1.5303 nm, c=0.6838 nm and $\alpha=\beta=\gamma= 90^o$. The SHG emission shows a strong dependence of the Er concentration. The SHG intensity increase from 0.08 (0.1 %) up to 0.64 (0.3%) and decrease to 0.0 when the Er concentration increase to 0.5 %. It can be due that secreted Er atoms are present as compounds and the high polarizability vanishes.

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Conflict of Interest: The authors declare that they have no conflict of interest.

Ethical Statement: The authors declare that they have followed ethical responsibilities.

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