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SYNTHESIS OF L-PROLINE-KCl AND CHARACTERIZATION OF ITS NON-LINEAR OPTICAL PROPERTIES

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A new semiorganic material, L-Proline-KCl, was synthesized for the first time. Its solubility an metastable zone width in double distilled water were estimated. Employing a temperature reduction method, a crystal of size 16 x 6 x 5 mm^3 was grown from aqueous solution. The cell dimensions obtained by single crystal X-ray diffraction studies reveal that the crystal belongs to the monoclinic system. UV-vis-NIR studies show that the crystal is transparent in the wavelength range of 300-1100nm. Second harmonic generation conversion efficiency found using the Kurtz an Perry method is about 0.2 times that of KDP. The thermal stability of the compound was determined by TG-DTA analyses of the specimen. The experimental results show that the crystal of L-proline-KCl is a good candidate for nonlinear optical applications, optical and thermal properties.

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1. Introduction

With the laser invention on the 60’s the idea of controlling light for its application on different fields was strengthened. This originated research studies on faster and more efficient methods on generation, transmission, manipulation and detection of light on diverse intervals of wavelengths. One of the most favored areas with the development of the laser is non-linear optics, which studies the phenomena that occur when a material interacts with intense electromagnetic radiation. The non-linear processes allow the properties of the intense light that is propagated in an environment to be altered, enabling the possibility of mixing and converting frequencies of light waves through a non-linear environment. These processes aid in simplifying opto-electronic systems and developing light sources that emit at different wavelengths. This has applications on areas such as telecommunications, medicine, spectroscopy, atmospheric monitoring, generating ultra-short pulses, etc. [1].

The literature reports that several amino acids offer a variety of options to synthesize new semi-organic materials that expose improved NLO properties [2]. L-Proline is an amino acid rich in collagen and is the only one in which the amine group is part of a pyrrolidine ring. Thus, it has a rigid structure and is directional in biological systems. L-Proline has been exploited for the formation of salts with different organic and inorganic acids [3,4].

In this study, we performed the synthesis of the L-Proline ($C_5H_9NO_2$) and Potassium Chloride (KCl). Afterwards, we characterized the synthesized materials through different

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techniques. Optical microscopy was used to observe the morphology and the size of the crystals. X-ray diffraction was employed to determine the different phases and structures that are present in the samples. Optical properties were characterized with optical absorption in the UV-Vis-NIR region followed by a thermal analysis with Thermogravimetric Analysis (TGA) and with Differential Thermal Analysis (DTA). A Second Harmonic Generation (SHG) was performed to obtain the efficiency of the material.

2. Experimental procedure

2.1 Synthesis of the crystals

The crystals were grown using the slow evaporation methodology of an aqueous solution [5]. A solution was prepared by adding the mixture of the precursors, L-Proline ($C_5H_9NO_2$) and Potassium Chloride (KCl) in 100 mL of bidistilled water; at a (1:1) molar ratio, 11.5 g of L-Proline and 7.5 g of KCl. Then, the system undergoes a constant stirring until the mixture dissolves completely obtaining a homogeneous mixture. This is followed by rest at room temperature. The solution tends to an equilibrium state that favors the adherence of embryos with new molecules or constructive units. Their volume increases and the crystals precipitate. The crystal obtained after 3 weeks is shown on Fig. 1.

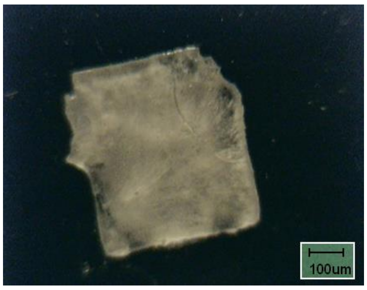

FIG. 1. Crystal of L- Proline-KCL, obtained after 3 weeks through the slow evaporation method

2.2 X-Ray Diffraction

The X-ray diffraction is very useful for the structural characterization of the materials, since it supplies information on the structures, the phases, the preferred orientation and the degree of crystallinity [5,6]. The incident monochromatic radiation over the sample corresponds to the Kσ of Cu that has a wavelength value of λ=1.540598 Å, the angular scanning step was of 0.02˚ with a 2θ value of 3-80˚. Figure 2 shows the diffractogram obtained.

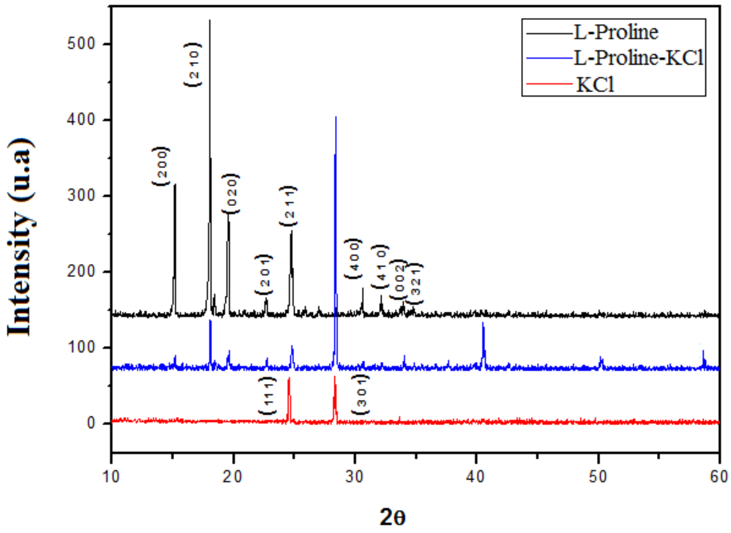

Fig. 2. In this diffractogram the peaks that correspond to L-Prolina-KCl; KCl y L-Prolina are shown. KCl has a face-centered cubic structure with lattice parameters a=b=c= 6.2917 Å. L-Proline is orthorhombic with lattice parameters a = 11.646 Å, b = 9.037 Å y c = 5.26 Å.

2.3 UV-Vis-NIR Spectroscopy

The characterization of the optical properties of the crystals was perfomed with the optical absorption in the UV-Vis-NIR region. A double beam Perkin-Elmer spectrophotometer Lambda-19 UV/VIS/NIR was used. Figure 4 shows the absorption spectrum for the L-Proline-KCl crystal.

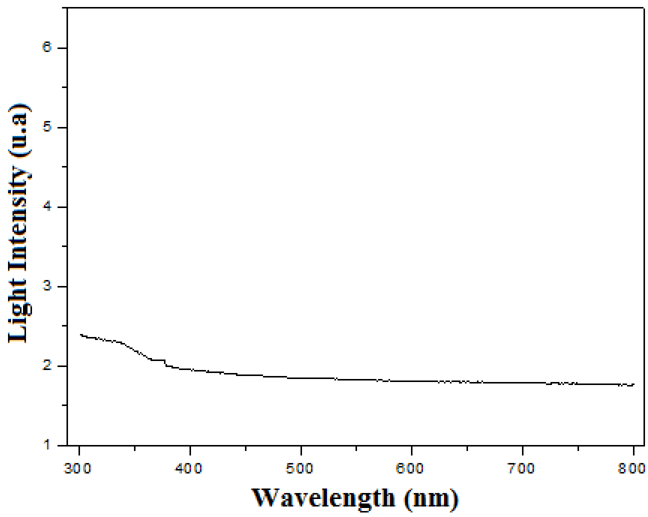

Fig. 3. Absorption spectrum of the L-Proline-KCl crystal.

2.4 TGA /DTA Analysis

The thermal analysis was perfomed with the TGA and DTA analysis proofs. A SDT 2960 Simultaneous TGA-DTA TA Instruments was used with a alumina α crucible as reference, 50 cm^3 of air and a slope of 10°C/min up to 400°C. For the analysis, the molten sample of 7mg of the L-Proline-KCl crystal was placed. Figure 4 shows the TGA-DTA curves obtained.

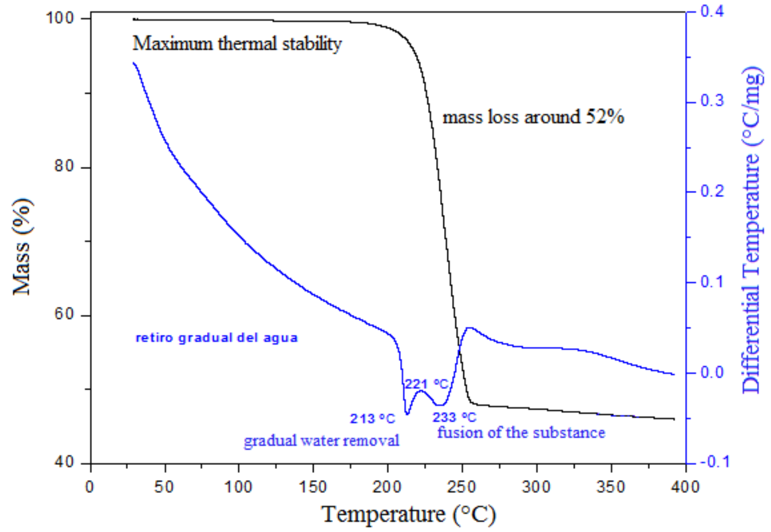

Fig. 4. TGA-DTA curves for the L-Proline-KCl sample

2.5 Second Harmonic Generation (SHG)

The SHG signal was generated exposing the sample to electromagnetic radiation of 1064 nm for 10 ns and a frequency of 10 Hz from a Nd: YAG Quanta Ray INDI series pulsed laser. The second harmonic signal was collected through a Ocean Optics optical fiber of a 10 microns diameter coupled to a Jobin Ybon TRIAX 550 monochromator and was processed by an intensified detector ICCD Spectrum Two Jobin Yvon.

Figure 5 shows the spot of the Second Harmonics Generator of the L-Proline-KCl crystal (1:1) molar ratio upon exposure to electromagnetic radiation with a wavelength of 1064 nm. Figure 6 shows its spectral characteristics.

Fig. 5. Signal spot of the SHG for L-Proline-KCl.

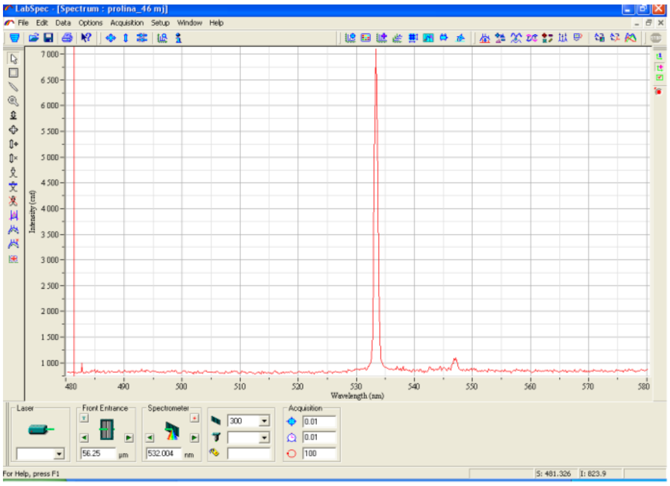

Fig. 6. Spectral characteristics of the second harmonic signal.

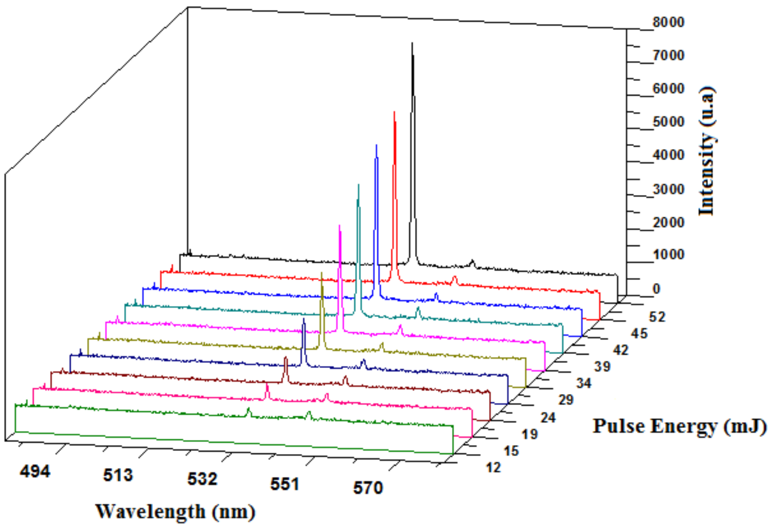

Fig. 7. Spectral behavior as a function of the 1064 nm pulse intensity of the second harmonics signal.

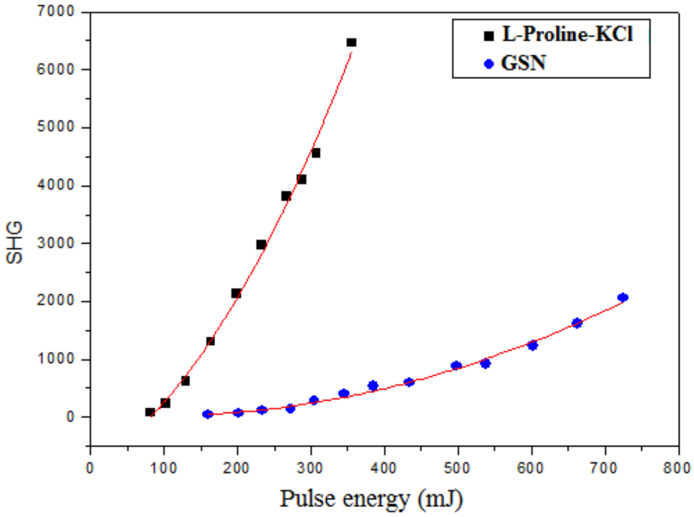

Fig. 8. Quadratic adjustment of the efficiency of the laser built from the second harmonics generation for the L-Proline-KCl and GSN.

To study the efficiency of the second harmonics generation of the L-Proline-KCl, we compared the results with Glycine Sodium Nitrate (GSN). Figure 8 shows the adjustments of the behavior of the intensity of the second harmonic with respect to the intensity of the 1064 nm of L-Proline-KCl and GSN.

Table I. Results of the quadratic adjustment of the efficiency of the laser built from the second harmonics generator for L-Proline-KCl and GSN.

Adjustment equation y = A +L-Proline-KCl	B*x + C*x^2GSN
A=-844.72	A=64.24
B=7.42	B=-0.867
C=0.03575	C=0.00486

3. Conclusions

In this work we describe the synthesis, characterization and the optical properties of the semi-organic non-linear crystals of L-Proline-KCl. Crystals of L-Proline-KCl were synthesized with the saturation technique of slow evaporation. This method was efficient for the growth of the crystals. A transparent colorless crystal of 16 x 6 x 5 mm^3 was obtained. The systematic study of the size and morphology of the crystals of L-Proline-KCl was performed. X-Ray Diffraction for the crystals shows the presence of a new material which corresponds to the monoclinic crystallographic system. The analysis of the optical properties of the studied systems does not present intrinsic absorptions in the region of the electromagnetic spectrum for the effects of frequency folding, at 532 nm. The thermal stability results show that in general the sample is stable below the 200°C, conserving its crystalline structure. As for the frequency folding, its SHG efficiency is better compared to that of GSN. Therefore, the results show that the L-Proline-KCl crystal is a good candidate for non-linear optical and thermal applications.

It is expected to find other materrials with the improved efficiency for the second harmonics generation. This is stimulating for further research on this field, with other amino acids or varying the metallic ions.

Acknowlegements

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