Effect of pH on the Second Harmonic Emission in Crystals of L-Threonine: KCl and L-Threonine: $NaNO_3$

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Abstract

Crystals of L-Threonine-Potassium Chloride and L-Threonine-Sodium Nitrate were synthesized from evaporation of aqueous solutions at room temperature. Crystals were characterized by diffraction of X-rays, whose results indicate they crystallize on Orthorhombic system. Infrared Spectroscopy results show crystals are transparent on 400-700nm range, thus making them a feasible candidate for applications of Harmonic Second on the visible region. In Raman, an important contribution of L-Threonine is observed with greater intensity on high pH, mainly at pH 11. From the second harmonic generation chart you can observe that the samples which presented a greater emission of second harmonic were those of Tre-$NaNO_3$ at pH 3, 4 and 10.

Keywords: second harmonic generation, non-linear optics, L-Threonine, pH, sodium nitrate, potassium chloride.

Introduction

Materials with second order of non-linear optics have greatly attracted due to their possible applications in new technologies of optoelectronics [1,2,12]. Organic materials have been of particular interest, since non-linear optical responses on these materials are of microscopic origin, thus offering an opportunity to utilize theoretical models along with synthesis flexibility to design and produce new materials [1, 2, 9, 12, 16, and 18].

Aminoacids have interest applications on Non-Linear Optics (NLO) because they are materials of second order. One of their properties is that they are non-volatile crystalline solids, melting at relatively high temperatures; they are insoluble in non-polar solvents and they are soluble in water, so their aqueous solutions behave like solutions with elevated bi-polar momentum. Crystalline aminoacid salts and their derivates are one of the directions in the search for new materials of second order in NLO [1, 2, 9, 11, 12, 16-18].

L-Threonine presented very good results in the formation of crystals, because, as you will observe in images obtained, after several days of drying, you obtain optically transparent and homogeneous crystals. Factors favoring the formation of crystals are, number one, aminoacid and number two, pH, because at high pH crystal is formed more efficiently and the drying process is faster [3].

This work presents the methodology for obtaining monocrystals of L-Threonine-Potassium Chloride and L-Threonine-Sodium Nitrate, as well as their structural and optical characterization.

Materials and methods

Preparation of solutions: Reactive used for the synthesis of crystals were L-Threonine ($C_4H_9NO_3$) Sigma Aldrich 98% purity PM=119, sodium nitrate ($NaNO_3$) Faga Lab 99% purity PM=84.99 and potassium chloride (KCl) Sigma Aldrich 99% purity PM=74.55. Synthesis takes place because of the reaction between Potassium Chloride-

L-Threonine and Sodium Nitrate-L-Threonine taken in an equimolar relation. The calculated amount of Potassium Chloride and Sodium Nitrate primarily dissolves in distilled water, since this was the best solvent for crystallization of L-Threonine in simple crystals. L-Threonine is slowly added to the solution and stirs well with the help of a magnetic shaker with temperature regulation to produce a homogeneous mixture of the solution. It is important to point that a slight increase of temperature was necessary for total dissolution of L-Threonine. Later, the solution was allowed to dry at room temperature, obtaining crystalline salt. A series of L-Threonine-KCl and L-Threonine-$NaNO_3$ at different pH, since literature indicates pH has a great influence on kinetics of growth, the quality of the crystal and optical properties [3].

Characterization: A UV-Vis analysis was performed in order to measure wavelength of maximum absorption and the intensity of this absorption in a sample, as well as XRD, since this gives us information on structures, phases, preferential orientation and other parameters, such as average size of crystalline grains, the degree of crystallinity, tensions present on the sample and crystalline defects, photos were taken of the crystals and finally the measurement of harmonic second was prepared [1,14,16,17].

Efficiency of Harmonic Second was evaluated using Kurtz-Perry dusts technique whose principle is shown on figure 1. [1, 16, 17]

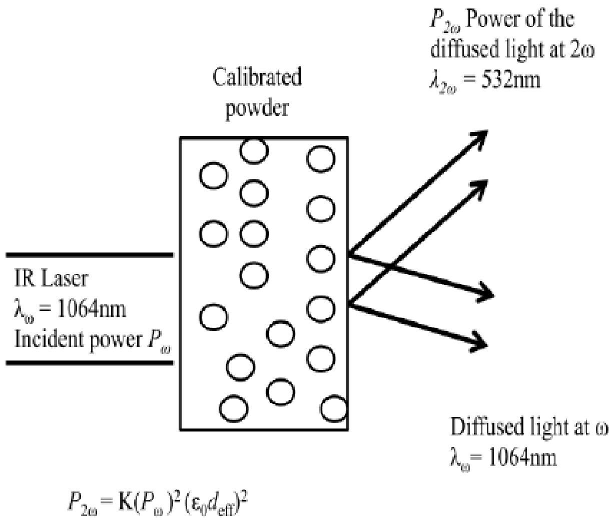

Fig 1. Kurtz and Perry powder test: SHG by calibrated crystals irradiated by nanosecond pulses at the wavelength λ_ω= 1064nm. [17].

First, crystals were ground and then dusts were placed between two glass substrates; they were pressed until a thickness of 2.0mm was achieved. Measurement of SHG on the sample was performed per instrumental arrangement shown on figure 2. [1, 16, 17]

Harmonic Second signal was generated by irradiating dusts with a pulsating laser of Nd:YAG emitting a wavelength of 1200 nm, with a duration of 8 ns per pulse, a frequency of 10 Hz and energy of 10 mJ [1,16,17]. For every analyzed sample, an average was calculated from 60 pulses readings performed on different random spots within the sample and it was compared with that obtained by the sample of urea [1,16-18].

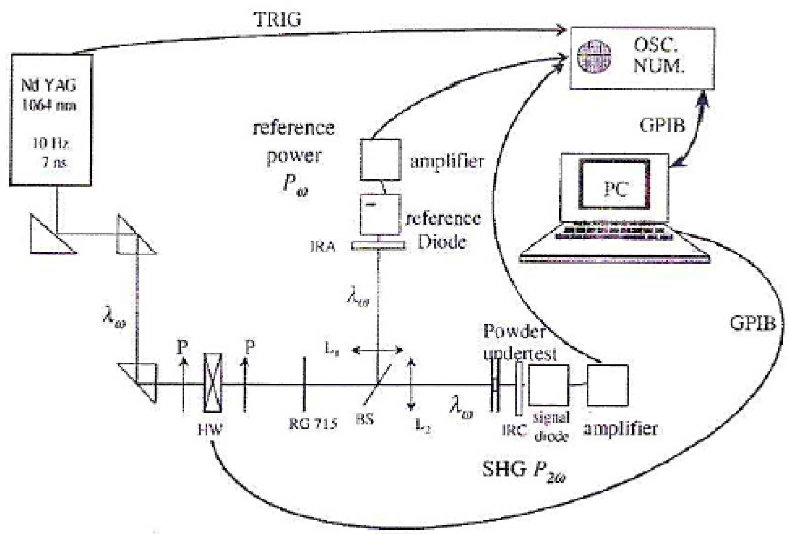

Fig 2. Experimental arrangement of Kurtz-Perry for obtaining efficiency of Second Harmonic [17].

Results and discussion

Figure 3 presents diffraction patterns for crystals at different pH of L-Threonine-$NaNO_3$, which show that recorded planes for pH 4 and 10 have a great similarity with L-Threonine characteristic structure, and for pH 8, 9 and 10, characteristic diffraction pattern of $NaNO_3$. L-Threonine characteristic peaks show an Orthorhombic crystalline system and cell parameters are: a = 13.611 Å b = 7.738 Å and c = 5.144 Å, α=β=γ=90° [1].

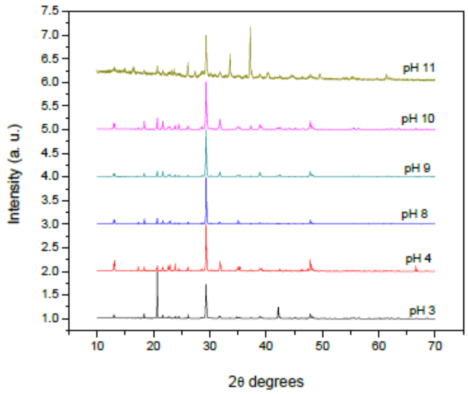

Fig 3. Xray diffraction pattern for L-Threonine $NaNO_3$ at different pH values.

On figure 4 spectrum an important contribution is observed of L-Threonine with greater intensity on high pH, especially at pH 11 [4,13-15]. Stretchings C-N (nitroalyphatic group) are observed at 750 $cm^{-1,}$ on the same region stretching C-N appears at 990 cm^{-1}. You can also observe flexion O-H at 1250 cm^{-1}, a flexion on N-H plane and symmetric stretching CH3 of 2812 to 3100 cm^{-1} [4,14].

Stretchings region is observed on 4000-2500 cm^{-1} range.

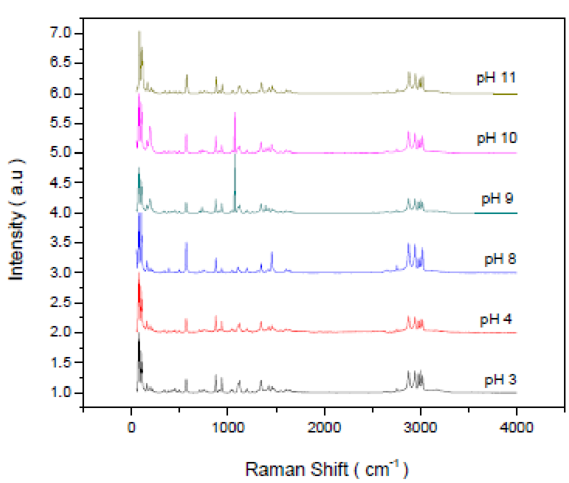

Fig 4. Raman spectrum of Thre-$NaNO_3$ at different pH values.

Fig 5. Photograph of Thre-$NaNO_3$ at pH 11.

Figure 5 shows a digital photo of a crystal of Thre-NaNO3 where we can observe high homogeneity and transparency.

Figure 6 presents diffraction patterns for crystals at different pH of L-Threonine-KCl, which show that recorded planes for pH 10.02 and 11 belong to LThreonine characteristic structure, and for pH 9.02 it shows KCl characteristic pattern [4-8].

The figure also shows that at basic pH you obtain most KCl-L-Threonine phase in comparison with acid pH. This is because formation of ionic salt of potassium is favored [8,9].

On Figure 7 spectrum, an important contribution is observed of L-Threonine on high pH, especially pH 11, although with less intensity than reference spectrum. On the other hand, almost no contribution is observed of KCl.

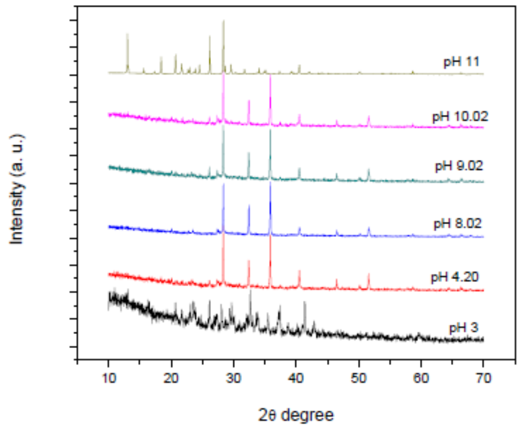

Fig 6. Xray diffraction pattern for Thre-KCl at different values of pH.

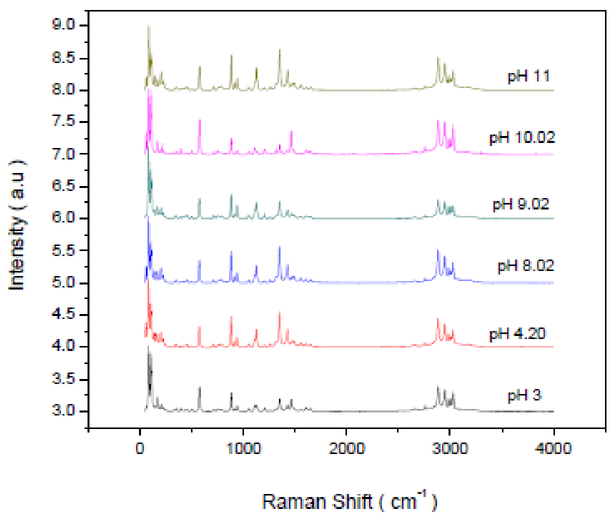

Fig 7. Raman spectrum of Thre-KCl for different pH values.

Figure 8 shows a photo of a crystal of Thre-KCl where you can observe high homogeneity and transparency [1,2,14,16,18].

Fig 8. Photograph of Thre-KCl at pH 11.

Measurement of Second Harmonic: The following table indicates the type of sample and material.

Table 1. Label of different samples

Sample	Label
1	Tre-NaNO3 pH 9
2	Tre-NaNO3 pH 10
3	Tre-NaN03 pH 11
4	Tre-NaNO3 pH 3
5	Tre-NaNO3 pH 4
6	Tre-KCl pH 11
7	Tre-KCl pH 10.02
8	Tre-KCl pH 9.02
9	Tre-KCl pH 8.02
10	Tre-KCl pH 4.2
11	Tre-KCl pH 3
12	Tre-NaNO3 pH 8

Figure 9 indicates the different types of samples and percentage of emission of second harmonic, based on measurements referring to Urea [1,16-18].

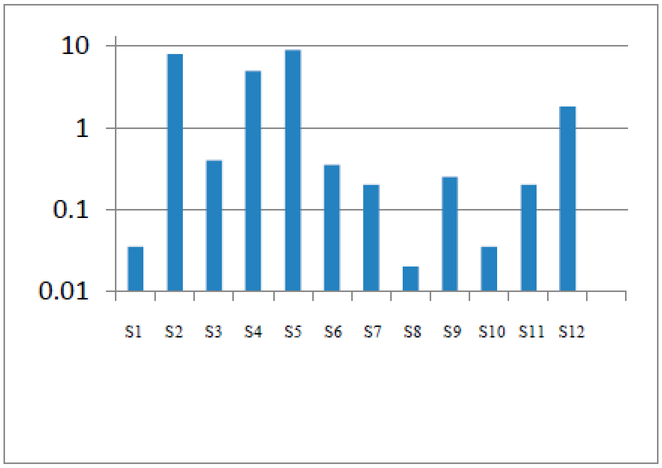

Fig. 9. Intensity of second harmonic signal of samples using urea as reference.

On figure 9 you can observe that samples presenting a better emission of second harmonic were those of Thre-$NaNO_3$ at pH 3, 4 and 10.

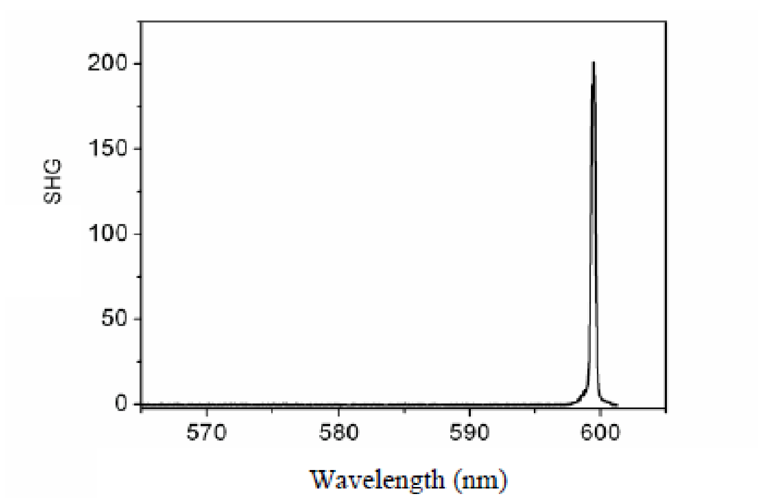

Fig. 10. SHG signal of the best sample Tre-NaNO3 pH 4

There is strong emission observed here at 595 nm (5 nm less than 600 nm mainly due to a little calibration problem in CCD), which confirms that L-Threonine is the right candidate for applications of second harmonic [1,2,9,11,16-18].

Conclusions

Optically transparent and homogeneous crystals were obtained using the process of evaporation at room temperature. Raman analysis confirmed the presence of precursors in the molecule.

At extreme values of pH samples containing $NaNO_3$ shown a better second harmonic emission. In the case of samples containing KCl we can also observe a similar effect at pH3 and pH11. By other hand the best crystal growth was at pH11 in both cases.

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References

[1] Growth and Physiochemical Properties of Second-Order Nonlinear Optical L-L-Threonine Single Crystals. G. Ramesh Kumar and S. Gokul Raj. Advances in Materials Science and Engineering Volume 2009 (2009), Article ID 704294, 40 pages.

[2] Synthesis, Crystal Growth and Characterization of L- Proline Lithium Chloride Monohydrate: A new Semiorganic Nonlinear Optical Material. T. Uma Devi, N. Lawrence, R. Ramesh Babu, S. Selvanayagan, Helen Stoeckli-Evans, and K. Ramamurthi. Crystal Growth and Design 2009 Vol. 9, No.3, 1370-1374.

[3] Efect of pH on non-linear properties of Glycine-Sodium Nitrate crystals (GSN) Q.B. Ramon Antonio Silva Molina. Master Thesis.

https://cimav.repositorioinstitucional.mx/jspui/

[4] Fundamentals of Raman spectroscopy. Laser Focus World. Editorial Digest. PennWell.

[5] Luminescent and thermo-optical properties of germanate glasses. A Iñiguez P, JD Tapia-Takaki, RP Duarte-Zamorano, JA Duarte-Moller, E Alvarez R. Optical Materials, North-Holland, Volume 30, No. 12, 2008/8/31, Pages 1796-1799.

[6] Absorption and emission properties of erbium calcium oxyborate crystals. Hai-Rui Xia, Huai-Dong Jiang, Ming Guo, Ji-Yang Wang, Jing-Qian Wei, Xiao-Bo Hu, Yao-Gang Liu. Department of Physics, National Laboratory of Crystal Materials, Shandong University. Optics Communications 188 (2001) 233-238. Elsevier Science.

[7] Effective Auger excitation of erbium luminescence by hot electrons in silicon. M.S Bresler, T. Gregorkiewiez, O.B Gusev, P.E. Pak, I.N. Yassievich. A.F Ioffe Physico-Technical Institute, Politekhnicheskaya 26, St.Petersburg, Russia, University of Amsterdam, Department of Theoretical Physics, Lund University.

[8] Optical bistability derived from the negative nonlinear absorption effect in erbium doped materials. Yoshinobu Maeda. Department of Information and control Engineering, Toyota Technological Institute. Materials Science and Engineering B81 (2001) 174-175. Elsevier Science.

[9] Viscosity studies of (L-alanine, L-proline, L-valine, L-leucine + aqueous KCl/KNO_3) solutions at different temperatures. Riyazuddeen, Imran Khan. Department of Chemistry, Aligarh Muslim University, Aligarh 202002, UP, India. The Journal of Chemical Thermodynamics. Volume 40, Issue 11, November 2008, Pages 1549-1551.

[10] Thesis of Physics Bachelor Elizabeth Tellez Flores. University of Sonora, Mexico.

https://cimav.repositorioinstitucional.mx/jspui/

[11] Narayan Bhat N. and Dharmaprakash S.M 2002 New nonlinear optical material: glycine sodium nitrate, J of Crystal Growth, 235:511-516.

[12] Non-linear Optics. Allister Ferguson. http://phys.strath.ac.uk/12- 370/sld003.htm.

[13] Encyclopedia of Laser Physics and Technology. Erbium-doped gain media, glasses. RP Photonics Encyclopedia. http://www.rpphotonics.com.

[14] Erbium-doped silicon nanocrystals in silicon/ silicon nitride superlattice structures: Light emission and energy transfer. J. Warga, R.Li, S.N Basu, L. Dal Negro. Elsevier. (2009).

[15] http://wwwchem.csustan.edu/Tutorials/INFRARED.HTM.

[16] Synthesis and characterization of nanomonocrystals of Glycine- Sodium Nitrate, GSN, with non-linear optical properties. Javier Hernandez Paredes, Santos Jesus Castillo, Hilda Esperanza Esparza Ponce, Elizabeth Tellez Flores and Jose Alberto Duarte Moller. Tecnura, vol. 9, num. 18, 2006, pp. 4-9.

[17] Novel nonlinear optical crystals of noncentrosymmetric structure based on hydrogen bonds interactions between organic and inorganic molecules. S. Debrus, H. Ratajczak, J. Venturini, N. Pincon, J. Baran, J. Barycki, T. Glowiak, A. Pietraszko. Synthetic Metals 127 (2002) 99-104. Elsevier Science.

[18] Growth and characterization of organic crystals for electrooptical and photonic applications. Alcala Salas Martha Isabel, Ramos Ortiz G., Rodriguez Rivera M. Optics Research Center A.C. Department of Photonics, Leon Guanajuato. Meeting of Research in Electrical Engineering. Zacatecas, Zac, March 25-26, 2010.