Polyhedron 91 (2015) 84–88

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

L-Proline–sodium nitrate obtained from solvent drop grinding

Javier Hernández-Paredes [a,*], Francisco Javier Carrillo-Pesqueira [a], Hilda E. Esparza-Ponce [b], Ofelia Hernández-Negrete [a], Mario E. Alvarez-Ramos [a]

[a] Departamento de Física, Universidad de Sonora (UNISON), Edificio 3R (Planta Alta) Blvd. Luis Encinas J y Rosales S/N Col. Centro, Hermosillo, Sonora C.P. 83000, Mexico
[b] Centro de Investigación en Materiales Avanzados S. C. (CIMAV), Miguel de Cervantes 120, Chihuahua, Chihuahua C.P. 31109, Mexico

ARTICLE INFO

Article history:
Received 15 December 2014
Accepted 23 February 2015
Available online 4 March 2015

Keywords:
X-ray diffraction
Crystal structure
L-Proline
SHG
Rietveld refinement

ABSTRACT

L-Proline sodium nitrate was obtained by the solvent drop grinding (SDG) technique. The compound was characterized by X-ray powder diffraction (XRPD), infrared spectroscopy (FTIR) and thermal analysis (DSC/TGA). Additionally, the material was tested for second harmonic generation (SHG). XRPD confirmed the presence of a new phase with a 1:1 stoichiometry and its crystal structure was determined. The FTIR spectroscopy depicted accurately the molecular characteristics of the compound and the thermal analysis showed that the compound is stable below 160 °C. Surprisingly, the compound displayed modest NLO properties which were strongly affected by its crystal packing features.

1. Introduction

Currently there is an increasing interest in developing compounds with large non-linear optical susceptibilities. Some organic compounds are the target to develop such materials due to their highly polarizable electronic clouds and the strong impact of changes of the molecular structure on their NLO properties [1–3]. Among these materials, amino acids have been widely studied and there is a number of research papers reporting NLO compounds synthesized by a combination of an amino acid with an inorganic salt [4–9].

Crystal growth from evaporation of solutions is widely used to produce these materials [10–12]. The technique consists of dissolving a specific amino acid/inorganic salt molar ratio in a solvent such as water. The solution is left to evaporate until the crystals precipitate. Although, it is possible to modify several parameters such as temperature, solvents, evaporation rate, etc; the technique does not always produce good quality crystals for single crystal diffraction experiments or fails to produce a new multi-component molecular solid for a particular system.

Solvent drop grinding (SDG) is an alternative method to produce new molecular materials. The technique is considered easy and environmentally friendly [13–15] that makes possible to produce materials with a minimum use of solvents, and even in some cases the use of solvents is unnecessary (solvent-free) [16]. Another advantage is that the outcome can be directly tested by the Kurtz–Perry powder technique in the search of second harmonic generation (SHG) signal [17].

Glycine and L-alanine have produced semi-organic compounds by combination with sodium nitrate [18,19]. Glycine-sodium nitrate (GSN) has been widely studied because of its potential use as NLO compound [20–23] and ferroelectric properties [24]. What is more, it was reported to have SHG efficiency 2 times more than KDP [20].

In the search for potential NLO compounds, we decided to perform screening experiments of the amino acid L-proline by combination of sodium nitrate at different molar ratios. The samples were prepared by the SDG technique and characterized initially by X-ray powder diffraction (XRPD) to look for new phases. L-Proline–sodium nitrate 1:1 M (LPSN) was found and fully characterized by XRPD, infrared (FTIR) spectroscopy, TGA/DSC thermal analysis and SHG experiment. Although, the material displayed relatively good thermal stability, its SHG efficiency was quite modest compared to that found for GSN.

2. Materials and methods

2.1. Synthesis

L-Proline (⩾99% pure) and sodium nitrate (⩾99% pure) were obtained from Sigma–Aldrich and used without further recrystallization. Three samples were prepared: (1) L-proline (0.5756 g, 5 mmol) and sodium nitrate (0.425 g, 5 mmol) in a 1:1 M ratio;

* Corresponding author. Tel.: +52 (662) 259 2108.
E-mail addresses: jahernandezparedes@gmail.com (J. Hernández-Paredes), enrique.alvarez@fisica.uson.mx (M.E. Alvarez-Ramos).

http://dx.doi.org/10.1016/j.poly.2015.02.034
0277-5387/

(2) L-proline (1.1513 g, 10 mmol) and sodium nitrate (0.425 g, 5 mmol) in a 2:1 M ratio; and (3) L-proline (0.5756 g, 5 mmol) and sodium nitrate (0.850 g, 10 mmol) in a 1:2 M ratio. The samples were placed in a mortar adding three drops of double-distilled water to assist the mechanical grinding.

2.2. Characterization

The X-ray powder diffraction experiments were carried out on a Panalytical X-Pert PRO diffractometer equipped with an X'Celerator detector, using Ni-filtered Cu Kα radiation. The equipment was operated at 40 kV and 30 mA and, generally, the XRPD patterns were acquired from 5° to 80° 2θ with a step size of 0.017°.

The crystal structure determination was carried out using the direct space approach [25] implemented in the TOPAS software package [26]. The space group was determined using the algorithm based on the iterative use of least squares refinements [27] followed by Pawley [28] refinements to obtain accurate lattice parameters. Non-hydrogen atoms were defined using rigid bodies (RBs) with the *z*-matrix notation and the simulated annealing search routine was performed allowing bonds and torsions angles to move freely. For the best solution, hydrogen atoms were placed geometrically at a reasonable X–H distance and a Rietveld [29] refinement was performed using GSAS [30] and the EXPGUI [31] interface. The L-proline molecules in the unit cell were defined as RBs for the Rietveld refinement. A constrain was applied for the isotropic displacement parameter for non-hydrogen atoms (U_{iso} global). The crystal structure analysis was performed using PLATON [32] and MERCURY 3.1 software [33].

The IR spectrum was recorded using a PerkinElmer UATR Spectrum Two in the range of 3500–550 cm^{-1}.

Thermal analysis was carried out on a TA Instruments STD Q600 using simultaneous differential thermal and thermo-gravimetric analysis (DTA–TGA) mode. Approximately 4 mg of sample was used and analyzed in the temperature range of 30–800 °C at a heating rate of 20 °C/min using an air flow rate of 50 mL/min.

The SHG experiment was performed by the Kurtz–Perry technique [17]. The sample was packed between two transparent glass slides. The SHG signal was obtained by irradiating the sample with a Quanta ray INDI series pulsed laser beam of Nd:YAG (1064 nm). The length of the pulses were 8 ns at 56 mJ/pulse and 10 Hz. The SHG output signal was analyzed with a Jobin–Yvon monochromator Triax320 and detected with a Hamamatsu R928 photomultiplier tube. Then, an EGG/PAR 165 boxcar average and readout processed it on a strip-chart recorder.

3. Results

3.1. X-ray powder diffraction

From the three solid-state grinding experiments, apparently only the mixture with a stoichiometric ratio 1:1 yield a pure phase as was observed in the XRPD patterns (see Fig. 1). The XRPD patterns of the mixtures with stoichiometric ratios 2:1 and 1:2 presented an excess of either L-proline or sodium nitrate. The latest suggested that a new compound was formed with a 1:1 stoichiometry.

The 1:1 M sample was used for the crystal structure determination. Then, a Rietveld refinement was performed (Fig. 2). Table 1 displays the crystallographic information of L-proline–sodium nitrate (LPSN) and relevant final Rietveld parameters. Table 2 shows relevant hydrogen bond connectivity and relevant bonds, angles and torsion angles are displayed in the Supplementary material (see Tables S1–S3).

LPSN crystallizes in the orthorhombic system within the $P2_12_12_1$ space group. Its lattice parameters are: a = 17.059(4),

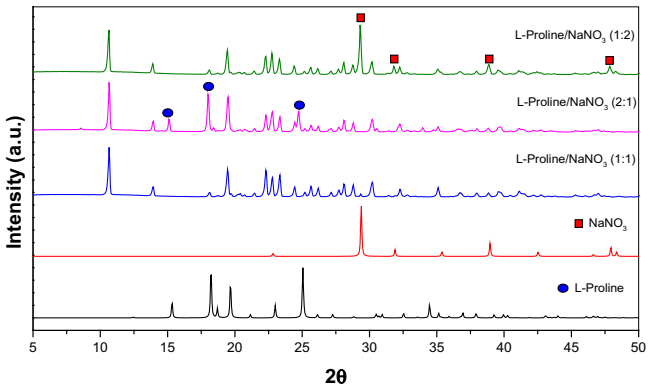

Fig. 1. Experimental X-ray powder diffraction (XRPD) patterns of the samples along with the simulated from single crystal for L-proline and sodium nitrate.

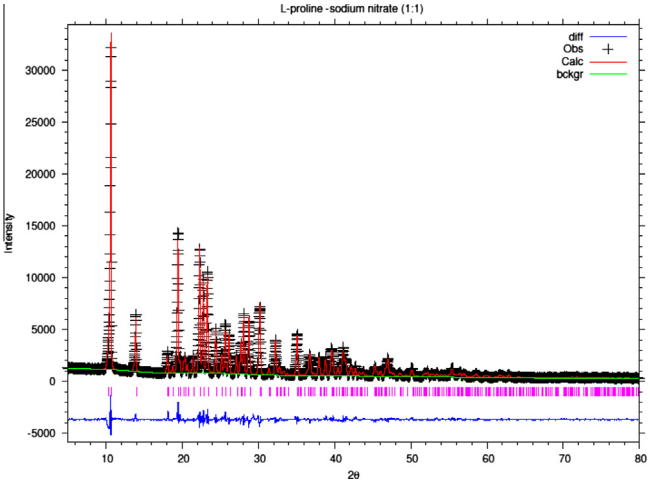

Fig. 2. Rietveld plot for LPSN. Experimental (black marks), calculated (red line) and difference (blue line). The pink bars symbolise the positions of the diffraction peaks. (Color online.)

b = 9.411(2), c = 5.0911(12) Å and V = 817.4(3) $Å^3$. The coordination geometry of the sodium atom is different from that found in GSN and LASN (see Fig. 3) [18,19]. In this case, the sodium is six-coordinated to two L-proline through Na13–O1 and Na13–O2 distances of 2.322(5) and 2.277(6) Å respectively and two nitrate groups through Na–O distances ranging from 2.36(1) to 2.37(1) Å.

The nitrate group has bonds and angles of reasonable values. N–O distances range from 1.314(16) to 1.336(11) Å and O–N–O angles are close to 120°: O3–N2–O4 equal to 119.40° (12), O3–N2–O5 equal to 121.7° (8) and O4–N2–O5 equal to 118.90° (11). The L-proline molecule is in the zwitterionic form. The molecules of L-proline are connected through N–H···O hydrogen bonds of 2.800(4) Å forming infinite chains along the *c* crystallographic axis (see Table 2).

In Fig. 4, the crystal packing features of GSN, LASN and LPSN are displayed for comparison. As we can see, GSN and LASN have similar crystal packing features, which consist of alternate layers of the amino acid and the sodium nitrate. In both cases, the nitrate ions coordinate to the sodium atom to form a 2D layered network. However, differences can be found between both structures in the amino acid layers. In GSN, the glycine molecules are bound one each other through N–H···O hydrogen bonds to form infinite chains which are linked to other neighbouring glycine chains through N–H···O hydrogen bonds to produce an infinite 2D network. Meanwhile, in LASN the L-alanine molecules are bound to