

Full Length Research Paper

Evidence of second harmonic signals in poly[μ_2 -L-alanine- μ_3 -nitrate-sodium (I)] crystals

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Poly[μ_2 L- alanine- μ_3 - nitrate- sodium (I)] crystals have been grown by the slow evaporation at room temperature technique. The nominal size of the crystals obtained by the method was of 500 nm. The UV-vis spectrum shows a wide range where absorption is lacking around 532 nm, which is required in order to have incident radiation at a 1064 nm. This guarantees the possible use of the crystal in visible light applications. The transparent nature of the crystal in the visible and infrared regions within the transmission spectrum confirms the nonlinear optical properties of the crystal. Additionally, Fourier transform infrared spectroscopy displays its functional groups which correspond to the Poly[μ_2 -L-alanine- μ_3 -nitrate-sodium(I)], where the presence of nitrates in the lattice generally can be identified by their characteristic signature within the 1660-1625, 1300-1255, 870-833 and 763-690 cm^{-1} range. Single crystal diffraction was carried out in order to determine atomic structure and lattice parameter. The results showed that: $a = 5.388(9)$ Å, $b = 9.315(15)$ Å, $c = 13.63(2)$ Å, The structure of Poly[μ_2 -L-alanine- μ_3 -nitrate-sodium(I)] shown by single crystal diffraction shows an asymmetric unit consisting of one sodium and one nitrate ion and one L-alanine molecule. The coordination geometry around the sodium atom was trigonal bipyramidal, with three bidentate nitrate anions coordinating through their oxygen atoms and two L- alanine molecules, each coordinating through one carboxyl oxygen atom.

Key words: L- alanine, second harmonic generation, nonlinear optical properties.

INTRODUCTION

Recently, the growing of single crystals has helped advance modern technology. Nonlinear optical (NLO) materials have been studied extensively for their possible applications and are expected to play a major role in photonic technology such as telecommunication, optical computing, optical data storage and optical information processing (Vijayan et al., 2006; Lydia et al., 2009).

The generation of coherent blue light through second harmonic generation (SHG) from near infrared (NIR) laser sources is an important technological feat that has

attracted much attention in the last few years (Lydia et al., 2009). Coherent blue and green light are important for many applications such as display screens, high-resolution printing and signal processing (Martin and Natarajan, 2008).

Some organic compounds exhibit large NLO responses and, in many cases, orders of magnitude larger than widely known inorganic materials. They also offer molecular design flexibility and the possibility of a virtually unlimited number of crystalline structures (Vijayan et al., 2006). A number of such crystals, especially from the amino acid family, recently had been reported (Razzetti et al., 2002, Rodrigues et al., 2003; Ambujam et al., 2006; Ramesh et al., 2006). Some amino acid crystal with

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simple inorganic salts appear to be promising materials for SHG (Baran et al., 2003).

Amino acids exhibit specific features such as (1) molecular chirality, which secures acentric crystallographic structures; (2) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (3) zwitterionic nature of molecules, which favors crystal hardness. (Lydia et al, 2009); (4) Amino acids can be used as chiral auxiliaries for nitro-aromatics and other donor–acceptor molecules with large hyperpolarizabilities, and (5) as a basis for synthesizing organic and inorganic compounds (Sethuraman et al., 2008).

A series of studies on semi-organic amino acid compounds such as L-arginine phosphate, L-arginine hydrobromide, L-histidine tetrafluoroborate, (K.Sethuraman et al., 2008), L-arginine hydrochloride (Meera et al., 2004), L-alanine acetate (Mohankumar et al., 2005) and glycine sodium nitrate (Narayan and Dharmaprakash, 2002) as potential NLO crystals have been reported. L-Alanine is an amino acid, and it forms a number of complexes when reacted with inorganic acid and salts to produce an outstanding material for NLO applications. It belongs to the orthorhombic crystal system (space group $P212121$) with a molecular weight of 89.09 and a melting point of 297°C.

The compound, Poly[μ_2 -L-alanine- μ_3 -nitrate-sodium (I)] (pLASN), $[\text{Na}(\text{NO}_3)(\text{C}_3\text{H}_7\text{NO}_2)]_n$ [15] was obtained as the product of an attempted reaction of sodium nitrate and the amino acid L-alanine in aqueous solution. In the present work, single crystals were grown and characterized by single crystal X-ray diffraction. Fourier transform infrared spectroscopy (FTIR) studies, thermo gravimetric analysis (TGA/DSC), UV–Vis–NIR spectral analysis and SHG Polyoxometalates (POMs) are oligomeric aggregates of metal cations bridged by oxide anions that form by self-assembly processes (Rhule et al., 1998). There are two generic families of POMs, the isopolyoxometalates, that contain only d0 metal cations and oxide anions and the heteropolyoxometalates that contain one or more *p*-, *d*-, or *f*-block heteroatoms in addition to the other ions (Pope, 1983; Rhule et al., 1998).

The medicinal features of these compounds cover a variety of important biological activities such as the inhibition of specific enzymes plus antiviral and antitumor activity (Pope and Mueller, 1994; Rhule et al., 1998). When used in combination with β -lactam antibiotics, polyoxotungstates enhance the effectiveness of the antibiotic against otherwise resistant strains of bacteria. Heptamolybdate, $[\text{NH}_3\text{Pri}]_6[\text{Mo}_7\text{O}_{24}]\cdot 3\text{H}_2\text{O}$ has shown potent *in vivo* antitumor activity which has been explained by repeated redox cycles of $[\text{Mo}_7\text{O}_{24}]^{6-}$ in the tumour cells.

Biomedical investigations of POMs, which contain amino acids or even peptides (Yamase et al., 1999) have been focused on finding POMs with both improved activity

against cancer and clinical safety profiles.

The reported structure $\text{Na}(\text{NO}_3)\text{C}_3\text{H}_7\text{NO}_2$ was obtained unintentionally as the product of an attempted reaction of sodium molybdate in aqueous solution with the amino acid L-alanine in order to obtain a γ type octamolybdate and coordinated by L-alanine $\text{Na}_4[\text{Mo}_8\text{O}_{26}(\text{ala})_2]\cdot 18\text{H}_2\text{O}$ (Cindrić et al., 2006). This is in contrast to Cindrić et al. (2006) in which L-alanine was used instead of *D*, L-alanine.

Synthesis and Growth of Poly[μ_2 -L-alanine- μ_3 -nitrate-sodium (I)]

The title compound, $[\text{Na}(\text{NO}_3)(\text{C}_3\text{H}_7\text{NO}_2)]_n$, was unintentionally obtained by Kristof Van Hecke in 2007 as the product of an attempted reaction of sodium molybdate in aqueous solution with the amino acid L-alanine (ala) in order to obtain a γ -type octamolybdate, $\text{Na}_4[\text{Mo}_8\text{O}_{26}(\text{ala})_2]\cdot 18\text{H}_2\text{O}$, coordinated by L-alanine.

The coordination geometry around the Na atom is trigonal–bipyramidal, with three bidentate nitrate anions coordinating through their O atoms and two L-alanine molecules each coordinating through one carboxylate O atom.

The crystals obtained during the development of this work were grown by the slow evaporation technique at room temperature in an aqueous solution. Reactive commercially available L-alanine $\text{C}_3\text{H}_7\text{NO}_2$ with stoichiometry (Sigma-Aldrich 98% purity) and molecular weight of 89.09 g/mol, and sodium nitrate NaNO_3 stoichiometry (Sigma-Aldrich 99.9% purity) and molecular weight 84.99 g/mol were used. In this work, samples were prepared at a 1:1 molar ratio in distilled water and constant stirring for 35 min and at 60°C. Evaporation time of the L-alanine sodium nitrate solution at room temperature was 45 days.

RESULTS AND DISCUSSION

In order to obtain the physical properties of the p-LASN crystals, an exhaustive characterization was carried out as thus explained.

Single crystal diffraction characterization

In this experiment, a single crystal of L-alanine sodium nitrate which measured approximately 0.3 x 0.1 x 0.1 mm was mounted on a Bruker Kappa APEXII DUO diffractometer. With the crystal at 298K, a small set of 36 frames were collected in order to determine the unit cell. One hundred reflections from these 36 frames were harvested and were used to index and refine the unit cell with:

$$a = 5.388(9) \text{ \AA}, b = 9.315(15) \text{ \AA}, c = 13.63(2) \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$$

This unit cell was used to conduct a search in the Cambridge Structural Database (version 5.30 plus four updates). A positive match was found in a work by K. Van Hecke, E. Cartuyvels, T. N. Parac-Vogt, C. Gorller-

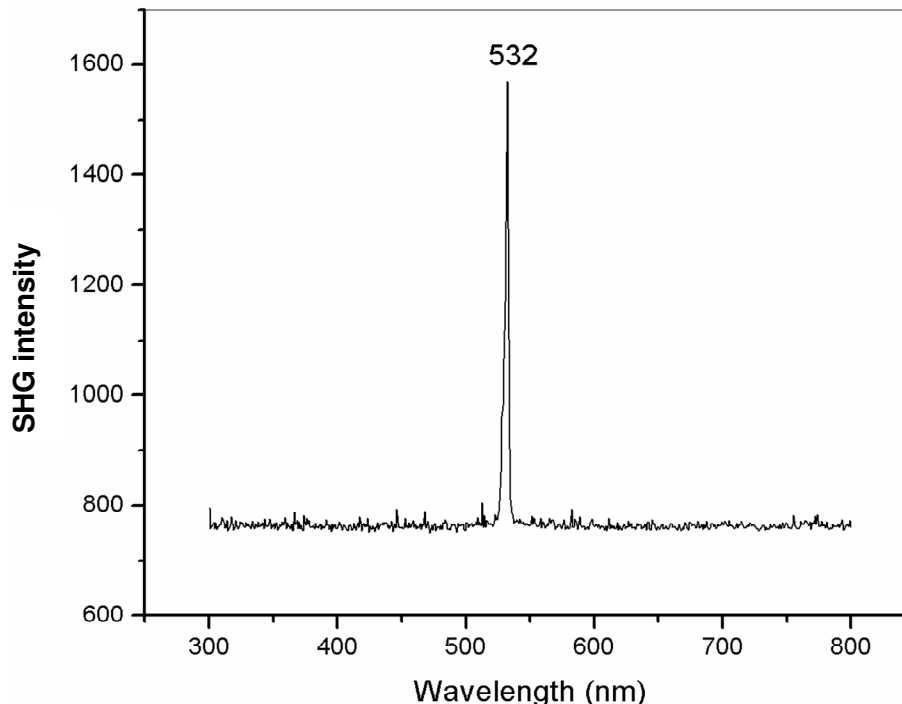


Figure 1. SHG signal obtained by using a variant of the Kurtz Perry method. Note that the main peak is placed in 532 nm, corresponding to the half wavelength of the incident radiation 1064 nm.

Walrand, and L. Van Meervelt. In this case the asymmetric unit consisted of one sodium and one nitrate ion and one *L*-alanine molecule.

The coordination geometry around the sodium atom was trigonal bipyramidal with three bidentate nitrate anions coordinating through their oxygen atoms and two *L*-alanine molecules, each coordinating through one carboxyl oxygen atom.

Three nitrate anions were bidentate coordinating to the sodium atom (2.612 (2)–2.771 (2) Å) and form one plane which is parallel to the (110) plane. The third nitrate oxygen atoms were coordinating to other symmetry equivalent sodium atoms and extend the plane formed. Almost perpendicular to this plane, two *L*-alanine molecules are coordinating to the sodium atom, each through one carboxyl oxygen atom (2.3651 (16) and 2.3891 (17) Å). The other carboxyl oxygen atoms were coordinated to sodium atoms in the upper and lower planes, respectively. Hence, an infinite amount of planes parallel to (110) are formed by nitrate anions and sodium atoms. These planes are perpendicularly linked to each other by *L*-alanine molecules.

Intermolecular hydrogen bonds are observed between N1(H1A)···O(1)[1/2 + x, -1/2 - y, 2 - z] (1.92 (4) Å), N1(H1B)···O(5)[1/2 + x, 1/2 - y, 2 - z] (2.10 (3) Å) and N1(H1C)···O(2)[1 + x, y, z] (1.87 (4) Å) and an intramolecular hydrogen bond is found for N1(H1B)···O(2) (2.44 (3) Å).

SHG signal detection

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)

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 1 shows the SHG spectrum where a main peak is located at 532 nm. Figure 2 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. As seen, good

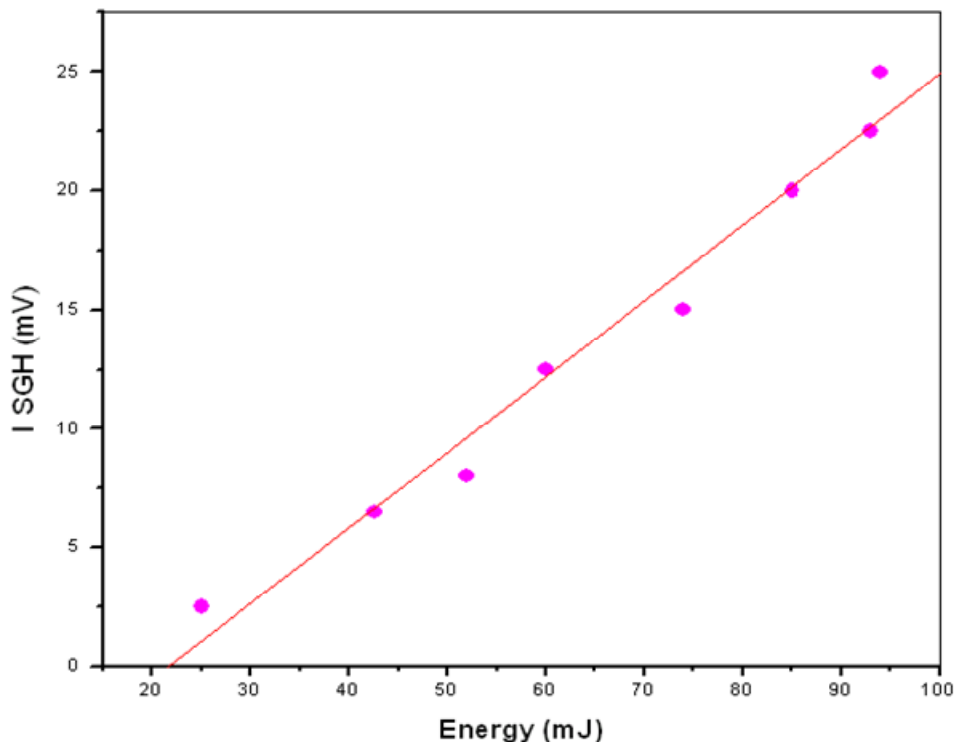


Figure 2. Efficiency of the SHG signal taken at different power of the Nd:YAG laser.

second harmonic generation was achieved in this crystal.

Conclusion

A new non-linear optical semiorganic crystal p-LASN was synthesized. Single crystals of p-LASN were grown from aqueous solution. The structure of p-LASN was confirmed by using single crystal diffraction. Its lattice parameters were found to be:

$$a = 5.388(9) \text{ \AA}, b = 9.315(15) \text{ \AA}, c = 13.63(2) \text{ \AA}, \\ \alpha = \beta = \gamma = 90^\circ$$

This unit cell was used to conduct a search in the Cambridge Structural Database (version 5.30 plus four updates). A positive match was found in a work by K. Van Hecke, E. Cartuyvels, T. N. Parac-Vogt, C. Gorller-Walrand, and L. Van Meervelt.

The coordination geometry around the Na atom was shown to be as trigonal-bipyramidal, with three bidentate nitrate anions coordinating through their O atoms and two l-alanine molecules each coordinating through one carboxylate O atom.

The SHG test is the first reported for this kind of material and an important and strong dependence on SHG intensity respect to beam energy was observed. It was impossible to detect the damage threshold due to the fact that the intensity tends to be linear with a positive

slope. This, in turn, shows that this is a promising non-linear optical material.

Lastly, good quality crystals of pLASN were obtained and the evidence of the second harmonic generation was evidenced. Thus, pLASN appears to be a new material with non-linear optical properties.

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