

Electronic structure and first hyperpolarizability of poly(μ_2 -L-alanine- μ_3 -sodium nitrate (I)) crystals

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MS received 31 July 2013; revised 6 November 2013

Abstract. Poly(μ_2 -L-alanine- μ_3 -sodium nitrate (I)), *p*-LASN, crystals have been grown by slow evaporation at room temperature. 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 the second harmonic emission, when an incident radiation of 1064 nm strikes on the crystal. 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 -sodium nitrate (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. Structural parameters were $a = 5.388(9)$ Å, $b = 9.315(15)$ Å and $c = 13.63(2)$ Å. The structure of poly(μ_2 -L-alanine- μ_3 -sodium nitrate (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. Electronic structure was obtained by using the Becke–Lee–Yang–Part and Hartree–Fock approximations with hybrid exchange–correlation three-parameter functional and G-311**G(*dp*) basis set. Theoretical and experimental results were compared and discussed as having an excellent agreement among them.

Keywords. LASN; NLO; electronic structure; DOS; hyperpolarizability; alanine.

1. 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 past few years (Razzetti *et al* 2002). Coherent blue and green lights are important for many applications such as display screens, high-resolution printing and signal processing (Vijayan *et al* 2006; Lydia *et al* 2009).

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 have been reported (Rodrigues *et al* 2003; Ambujam *et al* 2006; Ramesh *et al* 2006; Sethuraman *et al* 2008). Some amino acid crystals with simple inorganic salts appear to be promising materials for SHG (Meera *et al* 2004).

Amino acids exhibit specific features such as (i) molecular chirality, which secures acentric crystallographic structures (Mohankumar *et al* 2005); (ii) absence of strongly conjugated bonds, leading to wide transparency ranges in the visible and UV spectral regions; (iii) zwitterionic nature of molecules, which favours crystal hardness; (iv) use as chiral auxiliaries for nitro-aromatics and other donor–acceptor molecules with large hyperpolarizabilities and (v) as a basis for synthesizing organic and inorganic compounds.

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A series of studies on semi-organic amino acid compounds such as L-arginine phosphate, L-arginine hydrobromide, L-histidine tetrafluoroborate, L-arginine hydrochloride (Meera *et al* 2004), L-alanine acetate (Mohankumar *et al* 2005) and glycine sodium nitrate (Narayan Bhat 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. The compound was first crystallized by Bernl (1931) and later by Simpson and Marsh (1966). It belongs to the orthorhombic crystal system (space group P212121) with a molecular weight of 89.09 and has a melting point of 297 °C.

Polyoxometalates (POMs) are oligomeric aggregates of metal cations bridged by oxide anions that form by self-assembly processes. There are two generic families of POMs, the isopolyoxometalates, that contain only d_0 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.

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 $\text{Na}_4(\text{Mo}_8\text{O}_{26}(\text{ala})_2) \cdot 18\text{H}_2\text{O}$.

All of the NLO molecular materials show a wide transparent window in an UV-Vis spectrum and a non-centrosymmetric geometry. However, these materials need to have an absolute value of the susceptibility, $\chi^{(2)}$, which is basically associated with the non-centrosymmetric crystal structure. This property is analogous to the molecular

property called first polarizability, β . Materials, like GSN, have been shown the SHG signal when it was excited by an intense IR radiation of 1064 nm, commonly obtained from a pulsed Nd-YAG laser.

In order to quantify the β parameter, it is convenient to use *ab initio* calculations, which is highly recommended as an excellent alternative method to design NLO molecules and also predict its electronic structure. Nevertheless, the correct choice of the basis is the goal in this kind of calculations.

This work reports the DOS, band structure, the dipolar moment and the first hyperpolarizability of the p -LASN structure. Also a close comparison among the Raman, FT-IR and XRD are discussed.

2. Computational method

The p -LASN molecule appears in figure 1. This model was obtained from a single-crystal X-ray diffraction experiment at low temperature. As a structural characterization, it supports an X-ray powder diffraction which was also done and compared with that obtained by using Materials studio package. This structure is later imported to Gaussian 09 computational software in order to obtain the electronic structure. The geometry was optimized by using the B3LYP (Becke–Lee–Yang–Part), also supported by Gaussian 09 software with hybrid exchange-correlation three-parameter functional and G-311**G(dp) basis set. Total dipolar moment and the first hyperpolarizability were obtained by applying the B3LYP and HF approximation. Also the approximation to frozen core electron correlation was employed.

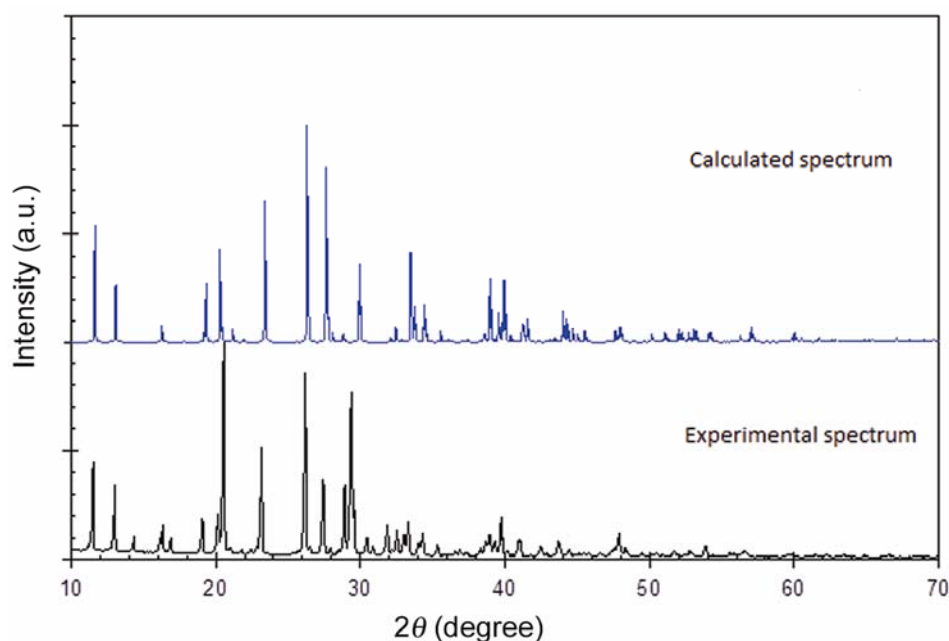


Figure 1. Experimental and calculated XRD patterns.

3. Experimental

3.1 Sample preparation

The title compound, $(\text{Na}(\text{NO}_3)(\text{C}_3\text{H}_7\text{NO}_2))$, was unintentionally obtained by Kristof *et al* (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 g-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 was used. In this work, samples were prepared at a 1:1 molar ratio in distilled water and constant stirring for 35 min at 60 °C. Evaporation time of the L-alanine sodium nitrate solution at room temperature was 45 days.

3.2 Structural characterization

In order to obtain the physical properties of the *p*-LASN crystals, an exhaustive characterization was carried out as follows: In this experiment, a single crystal of L-alanine sodium nitrate which measured approximately $0.3 \times 0.1 \times 0.1$ mm was mounted on a Bruker Kappa APEXII DUO diffractometer. With the crystal at 298 K, a small set of 36 frames was 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.

Also a Phillips Expert powder X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5428$ Å) was used for the powder X-ray diffraction pattern. The sample was scanned in the 2θ values ranging from 10 to 60 ° at the rate of 0.05°/min.

3.3 Vibrational measurements

Raman characterization were carried out at room temperature using a Micro-Raman, Horiba JY, LabRam HR, Vis 633 with a resolution of 0.3 cm^{-1} with an HeNe 632 nm laser pump. A range of 40–4000 cm^{-1} was used as sweep.

In order to obtain the presence of functional groups, FT-IR spectrum was recorded in the range of 400–4000 cm^{-1} by using a MAGNO IR 750 series II Nicolet

spectrometer. A blank of KBr was used to normalize the signal background.

4. Results and discussion

4.1 Crystal diffraction characterization

The unit cell was refined using the following parameters

$$a = 5.388(9) \text{ Å}, b = 9.315(15) \text{ Å}, c = 13.63(2) \text{ Å},$$

$$\alpha = \beta = \gamma = 90^\circ.$$

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 Kristof *et al* (2007).

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 with the sodium atom (2.612(2)–2.771(2) Å) and form one plane which is parallel to the (1 1 0) plane. The third nitrate oxygen atoms were coordinating with other symmetry equivalent to sodium atoms and extend to 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 with sodium atoms in the upper and lower planes, respectively. Hence, an infinite amount of planes parallel to (1 1 0) 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 $\text{N1(H1A)} \cdots \text{O(1)}(1/2 + x, -1/2 - y, 2 - z)$ (1.92(4) Å), $\text{N1(H1B)} \cdots \text{O(5)}(1/2 + x, 1/2 - y, 2 - z)$ (2.10(3) Å) and $\text{N1(H1C)} \cdots \text{O(2)}(1 + x, y, z)$ (1.87(4) Å) and an intramolecular hydrogen bond is found for $\text{N1(H1B)} \cdots \text{O(2)}$ (2.44(3) Å).

Figure 1 presents the comparison between the experimental and calculated XRD, the last obtained by using the structural parameters obtained by SCD. As we can appreciate, all calculated peaks appear in the experimental one. The matching between both spectra is certainly very close. This indicates that the crystal obtained is the one desired.

4.2 Electronic structure

The density of states calculation (figure 2) shows the distribution of *s* and *d* electrons in the energy bands. The overall distributions of states across the energy range of DOS

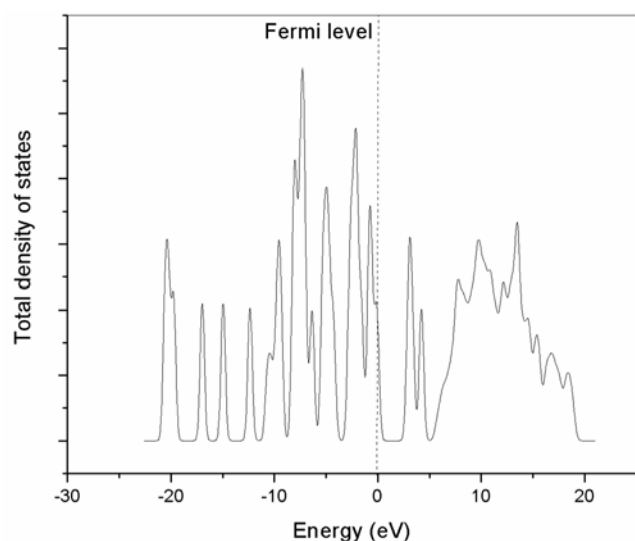


Figure 2. Calculated total DOS of *p*-LASN system.

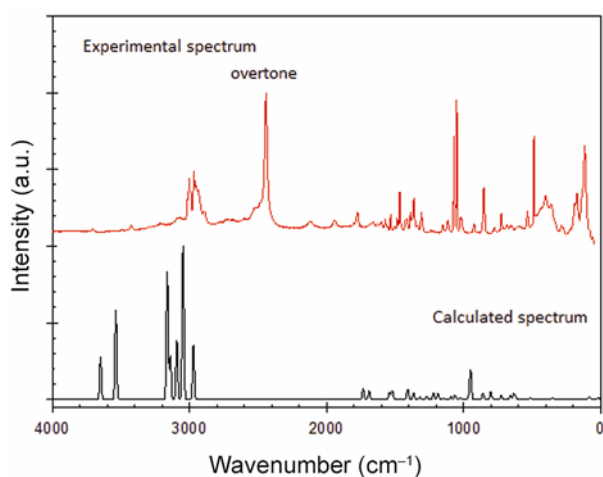


Figure 3. Comparison between the theoretical and experimental Raman frequencies.

are similar to that of GSN molecular crystals (Hernández-Paredes *et al* 2008). In that calculation, it is observed that the conduction band above the Fermi level is occupied almost 80% by *p*-type electrons associated mainly with the NO₃ ion. The unoccupied states are principally due to a mixture of *s*- and *p*-characters in the alanine molecule. An energy bandgap is observed at 2.2 eV above the Fermi level placed at 0 eV.

Figure 3 shows the comparison between the calculated Raman spectrum and its corresponding experimental measurement. An additional important component, the FT-IR spectra, appears (as comparison) in figure 4. In table 1, the labelled vibrational lines of Raman and FT-IR spectra were shown. This comparison include those results obtained theoretically by using the density functional theory (DFT) approximation. All the features of Raman and FT-IR spectra are shown in table 1.

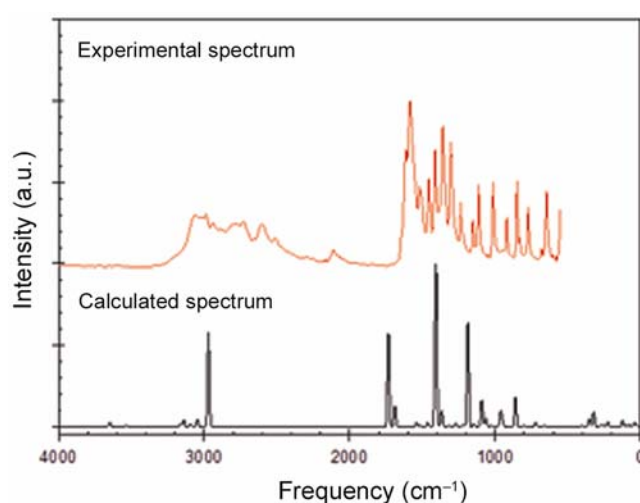


Figure 4. Comparison between the theoretical and experimental FT-IR frequencies.

In the Raman experimental spectrum, we observe an intense overtone placed at 2512 cm⁻¹. This one corresponds to the NH vibration as it appears in figure 5. This figure shows an instant capture of a Gaussian 09 simulation corresponding to the same frequency of 2512 cm⁻¹ (dashed circle).

The optical activity is well determined by the knowledge parameters, α , β and μ (Ostroverkhov *et al* 2000). At a molecular level, the response for an isolated molecule under action of an electric field is given by

$$\mu_i = \mu_i^{(0)} + \sum_j \alpha_{ij} E_j + \sum_{jk} \beta_{ijk} E_j E_k + \sum_{jkl} \gamma_{ijkl} E_j E_k E_l.$$

The correct value of the polarizability α is described by the second rank tensor, however, the average value, α_{total} can be obtained from

$$\alpha_{\text{total}} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

and the magnitude of the first hyperpolarizability can be calculated from

$$\beta_{\text{total}} = \frac{1}{5}(\beta_x + \beta_y + \beta_z),$$

where the *x*, *y* and *z* components of β have been extracted from the 3D matrix generated by Gaussian 09 software.

Finally, the results of calculation for the polarizability, α , first hyperpolarizability, β and the dipolar moment, μ appear in table 2. Unfortunately, the values for this parameters have not been reported and is not possible to do a comparison; however, the high value of the hyperpolarizability is enough to have an NLO phenomenon.

Table 1. Assignment of Raman and FT-IR *p*-LASN spectra.

| Raman line | FT-IR line | Vibration assignment |
|------------|------------|--|
| 3706 | | Overtone |
| 3426 | | Overtone |
| | | Symmetric CH ₃ stretching |
| 3000 | | Asymmetric CH ₃ stretching |
| | 2987 | Symmetric CH ₃ stretching |
| 2964 | | CH ₂ stretching and asymmetric CH ₃ stretching |
| 2948 | | Symmetric CH ₂ stretching |
| | 2941 | Symmetric NH ₃ stretching |
| 2936 | | Asymmetric CH ₂ stretching |
| 2888 | | CH ₂ stretching |
| | | Overtone |
| | 2728 | N-H...O and O-H...O stretching |
| | | Symmetric CH stretching |
| | 2599 | Symmetric CH stretching |
| 2512 | | Overtone |
| 2484 | | Overtone |
| 2444 | | Overtone |
| | 2251 | CH ₃ stretching |
| 2123 | | Overtone |
| | 2110 | Asymmetric NH ₃ stretching |
| 1939 | | Asymmetric NH ₃ deformation |
| 1775 | | Asymmetric COO stretching |
| 1659 | | Asymmetric NH ₃ deformation |
| 1630 | | Asymmetric NH ₃ deformation |
| | 1613 | NH ₃ bending |
| 1599 | | Asymmetric NH ₃ deformation |
| | 1584 | NH ₃ bending |
| 1571 | | Asymmetric COO ⁻ stretching |
| | | Overtone |
| 1531 | | Symmetric NH ₃ deformation |
| | 1518 | NH ₃ bending |
| 1503 | | CH ₃ deformation |
| | | Overtone |
| 1486 | | Asymmetric COO ⁻ deformation |
| 1466 | | C ₂ H ₂ scissors mode |
| | 1454 | Asymmetric CH ₃ bending |
| 1422 | | CH ₃ bending |
| | 1411 | Symmetric C-COO ⁻ stretching |
| 1386 | | CH ₃ puckering |
| 1363 | | Wagging CH ₂ deformation |
| | 1358 | NO ₃ stretching |
| | | CH ₂ wagging |
| 1306 | 1306 | C-H and N-H bending |
| | | Flexed position CH ₂ |
| | 1236 | NH ₃ ⁺ rocking |
| | 1218 | NH ₃ ⁺ rocking |
| 1151 | 1151 | NH ₃ ⁺ rocking and symmetric COO ⁻ stretching |
| 1113 | 1113 | NO ₃ stretching |
| 1070 | | Overtone |
| 1050 | 1048 | Symmetric CCN stretching |
| 1022 | | CH ₃ rocking |
| | 1012 | Overtone of torsional oscillation NH ₃ ⁺ |
| 926 | | NH ₃ rocking |
| | | CH ₂ rocking |
| | 918 | Overtone of torsional oscillation NH ₃ ⁺ |
| 853 | | N-C stretching |
| | 849 | NO ₃ stretching |
| | 829 | C-C stretching |
| 774 | | OH deformation |
| | 771 | NO ₃ stretching |
| 725 | | COO wagging |
| | 677 | NO ₃ ⁻ in-plane deformation |
| | 646 | COO ⁻ in-plane deformation |
| | 578 | Overtone |

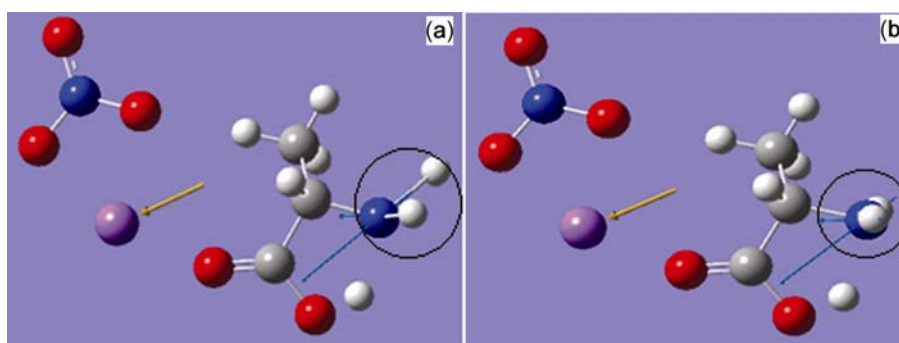


Figure 5. Instant capture of Raman vibration of *p*-LASN showing the origin of overtone at 2512 cm^{-1} . Red balls are oxygen atoms, blue balls are nitrogen atoms, grey balls are carbon atoms and white balls are hydrogen atoms.

Table 2. Calculated values for α , β and μ .

| Polarizability | Hyperpolarizability | Dipolar moment |
|-----------------------------------|----------------------------------|--------------------------------|
| $\alpha_x = 66.7560$ | $\beta_x = -180.1879$ | $\mu_x = -10.5732$ |
| $\alpha_y = 70.1644$ | $\beta_y = -73.2246$ | $\mu_y = 0.1100$ |
| $\alpha_z = 75.2966$ | $\beta_z = -201.4381$ | $\mu_z = 1.1532$ |
| $\alpha_{\text{total}} = 70.7390$ | $\beta_{\text{total}} = 56.0243$ | $\mu_{\text{total}} = 10.6364$ |

5. Conclusions

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 Van Hecke *et al* (2007).

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 use of the B3LYP (Becke–Lee–Yang–Part) supported by Gaussian 09 software with hybrid exchange-correlation three-parameter functional and G-311**G(*dp*) basis set and HF approximation were a good choice to reproduce some of the experimental results obtained from the prepared sample.

Acknowledgements

The authors thank the National Council of Science and Technology of Mexico for its financial support. Also,

they thank the National Laboratory of Nanotechnology of CIMAV, SC, Chihuahua, Mexico. The authors gratefully to acknowledge Enrique Torres Moye (X-ray laboratory), Daniel Lardizabal (thermal analysis laboratory).

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