

High-temperature Raman spectroscopy of L,L-diphenylalanine single-crystal

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ABSTRACT

The crystal structure of L,L-diphenylalanine ($C_{18}H_{20}N_2O_3 \cdot xH_2O$) is investigated by polarized Raman spectroscopy at temperatures from 303 to 443 K over the spectral range 35–3300 cm^{-1} . This dipeptide crystallizes in a tubular arrangement filled by water molecules, maintained by helical π – π stacking (phenyl...phenyl) interactions and intermolecular hydrogen bonds. We investigate the rearrangement of the diphenylalanine backbone and the role of water molecules concerning the previously reported phase transition above 413 K. To further support our vibrational results, thermal analysis and DFT calculations are also presented.

1. Introduction

Amino acids and small peptides have important regulatory functions *in vivo* and may act as hormones, neurotransmitters, antimicrobials, growth and signalling factors [1,2]. Dipeptides, in particular, are remarkably attractive for drug discovery in the pharmaceutical industry because of their low-molecular-weight, structural folding, and stability [3]. Besides that, some amino acid-based materials have drawn considerable attention in the development of technological devices due to their exceptional physical properties, such as piezoelectricity, ferroelectricity and nonlinear optical activity [4–6].

Variable-temperature and -pressure studies in amino-acid based materials have been successfully used to characterize the most important molecular interactions governing the crystalline phase of these compounds and, consequently, their physical properties [7,8]. For example, the dipeptide L,L-dileucine presents piezoelectricity at room temperature, but this property disappears when the material undergoes an irreversible phase transition at 413 K [9]. It is important to note that the crystalline behaviour of dipeptides under extreme conditions is usually different from that found in the individual crystals of the constituent amino acids. Studies with the monolayer of L-alanine, for example, do not present evidence that the material undergoes any phase transition at low temperatures (down to 10 K), while the dipeptide L-alanyl-L-alanine exhibits a slow second order phase transition at temperatures below 80 K [10,11].

The short aliphatic dipeptide L,L-diphenylalanine (see Fig.1(a)) has been identified as a major recognition motif of Alzheimer's β -amyloid polypeptide [12–14]. The majority of the studies involving this dipeptide has been focused on its self-assembly behaviour in aqueous

solution [15–18]. In this case, L,L-diphenylalanine crystallizes in a tubular arrangement, maintained by helical π – π stacking (phenyl...phenyl) interactions and intermolecular hydrogen bonds, as shown in Fig. 1(b). In addition, these tubular channels present an average diameter of 12 Å and are filled with water molecules that help to stabilize the whole structure. From the biotechnological point of view, those nanochannels are potential candidates for use as gas storage and separation materials [19,20].

Atomic force microscopy and nonlinear optical microscopy reported that L,L-diphenylalanine crystal exhibits piezoelectricity and second-harmonic generation (SHG), characterizing this material as a potential component of optical and electronic devices [21]. Studies have shown that those physical properties completely vanish when this material undergoes an irreversible phase transition above 413 K [9,22]. In this work we investigate the Raman spectra of L,L-diphenylalanine crystal at high temperatures using two different scattering geometries. By a descriptive analysis of the data, we were able to provide evidences that the phase transition of L,L-diphenylalanine crystal results from a structural change in the dipeptide backbone accompanied by the loss of water molecules from its hydrophilic nanochannels. In addition, we performed thermal analysis measurements to gain insights in the overall conformational changes occurring throughout the phase transition of the material.

2. Experimental

Single crystals of L,L-diphenylalanine, $C_{18}H_{20}N_2O_3 \cdot xH_2O$, were grown by evaporation from a saturated aqueous solution at 353 K. They were obtained as colourless needle-shaped crystals, similar to the

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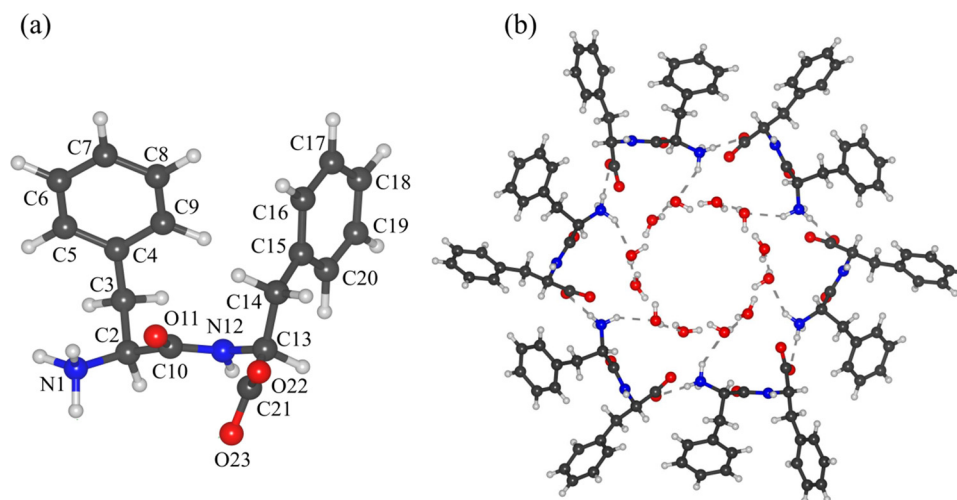


Fig. 1. (a) Schematic view of the isolated L,L-diphenylalanine molecule. (b) The cross-sectional view of the L,L-diphenylalanine nanotube partially filled by water.

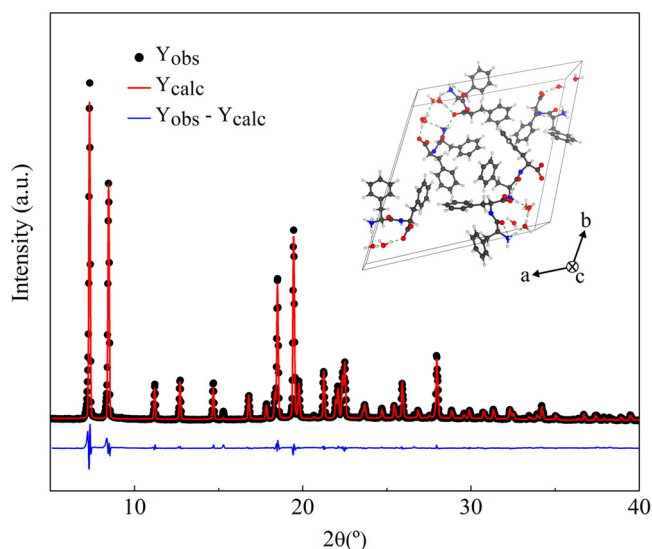


Fig. 2. Refined X-ray diffraction data of the L,L-diphenylalanine crystal. The red solid red line defines the calculated data while the closed circle line represents the observed intensities. The blue line refers to the difference between the observed and simulated profiles. The inset shows the hexagonal unit-cell of L,L-diphenylalanine viewed along the *c*-axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

growth samples in ethanol or methanol [23]. First, the powder X-ray diffraction (XRD) pattern of the L,L-diphenylalanine sample was carried out on a Bruker D8 diffractometer using $\text{CuK}\alpha$ radiation (0.15406 nm). Then, Rietveld refinement was performed with the Fullprof suite [24,25] using the patterns reported by Mason et al. [23]. The Raman spectra were obtained with a Jobin Yvon T64000 micro-Raman system equipped with an N₂-cooled charge-coupled device system. The *c*-axis of the crystal was set to be in the Z-direction and the polarized Raman spectra were measured in the backscattering configuration on the surface of the crystal that was perpendicular to the (001) plane. Porto's notation was used to describe the scattering geometry in all Raman spectra presented in this paper, e.g., Y(ZZ)Y, where the letter preceding and following the parenthesis represent the respective directions of the incident and scattered beam, whereas the directions inside the parentheses indicate the polarization of the incoming and scattered light, respectively [26]. The excitation source used was a 532 nm beam from a Verdi laser (Coherent) focused through an Olympus microscope

(objective 20x). The spectrometer slit was set for a resolution of 2 cm^{-1} . High-temperature Raman measurements were performed in a homemade heating furnace controlled by a PID temperature controller with an accuracy of 1 K. Thermogravimetric (TG) curve was recorded from ambient to 462 K at a heating rate of 5 K min^{-1} using the thermal analysis equipment (Jupiter STA 449, Netzsch). Differential Scanning Calorimetry (DSC) curve was carried out with the Netzsch Maia 200 F3 calorimeter using aluminium crucibles with about 2 mg of samples, under inert N₂ atmosphere. The temperature cycle was as follows: room temperature – 462 K – room temperature.

3. Calculations

The optimized molecular structure and vibrational spectra of the L,L-diphenylalanine were calculated by the density functional three-parameter hybrid method (DFT/B3LYP) and using the 6-31 + G(d,p) basis set [27–30]. All the quantum chemical calculations were performed using the Gaussian09 suite [31]. For computation, the initial atomic coordinates of the isolated molecule were taken from X-ray diffraction data [23]. The simulated Raman spectrum was plotted using a pure Lorentzian band shape ($\text{FWHM} = 10\text{ cm}^{-1}$). The theoretical spectrum was scaled by 0.955 (above 1800 cm^{-1}) and 0.977 (under 1800 cm^{-1}) to compensate the approximate treatment of electron correlation, basis set deficiencies and anharmonicity effects [32]. Moreover, the computed vibrational modes were interpreted by means of potential energy distribution (PED) using the VEDA 4 program [33,34], which has been used successfully in previous studies [35,36].

4. Results and discussion

To confirm the crystal structure of L,L-diphenylalanine, the Rietveld refinement based on the XRD pattern was performed and the corresponding fitting pattern is displayed in Fig. 2. The final refined lattice parameters were found to be $a = b = 24.14\text{ \AA}$ and $c = 5.45\text{ \AA}$. The reliability factors are given by the final weighted R-factor $R_{\text{wp}} = 5.94\%$ and goodness of fit indicator $S = 1.8$. By means of the Vesta software [37], the unit cell structure of the L,L-diphenylalanine was modeled, as illustrated in the inset of Fig. 2. The crystal with hexagonal symmetry and P6₁ space group, contains six crystallography independent units, each unit consisting of one L,L-diphenylalanine and two water molecules. Group factor analysis predict 732 Raman active modes distributed into irreducible representation of the C₆ factor group as $\Gamma = 146\text{ A} + 147^2\text{ E}_2 + 146^1\text{ E}_1 + 147^1\text{ E}_2 + 146^2\text{ E}_1$ (three A + ¹E₁ + ²E₁ acoustic modes are omitted) [26]. The theoretical and experimental Raman spectra (measured in Y(XX)Y and Y(ZZ)Y scattering geometries) for the spectral region $200\text{--}600\text{ cm}^{-1}$, $600\text{--}1800\text{ cm}^{-1}$ and

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