Piezoelectric Properties of Crystals of Some Protein Aminoacids and Their Related Compounds

V. V. Lemanov*, S. N. Popov*, and G. A. Pankova**

* Ioffe Physicotechnical Institute, Russian Academy of Sciences, Politekhnicheskaya ul. 26, St. Petersburg, 194021 Russia
e-mail: lemanov@pop.ioffe.rssi.ru

** Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoy pr. 31, St. Petersburg, 199034 Russia

Received December 29, 2001

Abstract—Growth of single crystals of some protein aminoacids and synthesis and growth of single crystals of their related compounds are reported. The temperature dependence of the integrated piezoelectric response of the single crystals grown was studied in the temperature range 120–320 K. The specific features in the temperature dependence are shown to be due to the enhanced damping of elastic vibrations in the crystals, which originates from the elastic vibrations being coupled to thermally activated rotation of the CH3 and NH3 molecular groups. © 2002 MAIK “Nauka/Interperiodica”.

1. INTRODUCTION

Crystals of protein aminoacids of L and D modifications, as well as of many related compounds, belong to symmetry groups which lack inversion symmetry and, in most cases, to polar symmetry groups [1]. These crystals possess properties whose symmetry is described by odd-rank tensors, such as the pyroelectric effect and spontaneous electrical polarization, piezoelectric effect [2], and optical second harmonic generation [3]. Crystals belonging to the 11 enantiomorphic point groups (lacking mirror reflection planes) also exhibit natural optical gyrotropy (optical activity) described by an axial gyration tensor. Crystals of protein aminoacids of the L and D modifications are, by definition, enantiomorphic and possess optical activity [4, 5]. The role played by all of the above properties (which are characteristic of low-symmetry systems) in the functioning of living organisms remains unclear; however, investigation of these properties is of profound interest not only in the physics of crystals but also in biophysics (see reviews [6, 7] and references therein).

The present communication reports on measurements of the temperature dependence of the integrated piezoelectric response of single crystals of a number of pure protein aminoacids and of their related compounds.

2. EXPERIMENTAL TECHNIQUES AND RESULTS

Crystals of pure aminoacids and their related compounds were grown under slow cooling of their saturated aqueous solutions. The aminoacids were dissolved in distilled water heated to 40°C (heating L aminoacids above 40°C is undesirable, because it may result in racemization, i.e., formation of the DL modification).

The temperature variation rates were typically about 1°C/day, and the growth continued, as a rule, for approximately a month. The crystals were seed-pulled.

When synthesizing and growing aminoacid-based compounds, a corresponding amount of inorganic substances was added to the solution. When the solution pH was to be changed, acetic acid or an aqueous solution of ammonia was added; these substances do not react with aminoacids and, therefore, are not involved in crystal formation. This was followed by cooling of the solutions to room temperature, filtering, and placing them in a thermostat. In some cases, for instance, when mixing L alanine and DL alanine with sulfuric, phosphoric, and phosphorous acids, the solubility of the complexes increased considerably. In this case, one first carried out slow evaporation at room temperature until a small amount of nuclei formed. Next, the solution was filtered and cooled slowly.

Tables 1 and 2 list the aminoacids and their related compounds from which single crystals were grown in the present study. Also given are the point symmetry groups of the crystals.

While no attempt was made to attain any particular optimization of the crystal growth conditions (choosing the cooling rate and pH of the solvent), we can point out, on the whole, the following features in the growth of crystals of pure aminoacids and their compounds. Large bulk crystals (about 1 cm3) of α glycine (α-Gly) and L alanine (L-Ala) were fairly easy to obtain. DL-Ala crystals could be prepared only in the form of thin needles. Asparagine monohydrate (L-Asn.H2O) and DL-methionine (DL-Met) were produced as small bulk crystals (3–5 mm in linear dimensions), L-valine (L-Val) and L-methionine (L-Met) formed thin scales,

1063-7834/02/4410-1929$22.00 © 2002 MAIK “Nauka/Interperiodica”
Table 1. Protein aminoacids, their radicals R, and crystal symmetry at T = 295 K

<table>
<thead>
<tr>
<th>Aminoacid</th>
<th>Abbreviation</th>
<th>Radical R</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-glycine</td>
<td>α-Gly</td>
<td>H</td>
<td>C_{2h}</td>
</tr>
<tr>
<td>γ-glycine</td>
<td>γ-Gly</td>
<td>H</td>
<td>C_{3}</td>
</tr>
<tr>
<td>L-alanine</td>
<td>L-Ala</td>
<td>CH_{3}</td>
<td>D_{2v}</td>
</tr>
<tr>
<td>DL-alanine</td>
<td>DL-Ala</td>
<td>CH_{3}</td>
<td>C_{2v}</td>
</tr>
<tr>
<td>L-valine</td>
<td>L-Val</td>
<td>CH(CH_{2})_{2}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-isoleucine</td>
<td>L-Ile</td>
<td>CHCH_{2}CH_{3}H_{1}</td>
<td>C_{2}, D_{2}</td>
</tr>
<tr>
<td>L-serine</td>
<td>L-Ser</td>
<td>CH_{2}OH</td>
<td>D_{2}</td>
</tr>
<tr>
<td>L-glutamic acid</td>
<td>L-Glu</td>
<td>(CH_{3})_{2}COOH</td>
<td>C_{2}, D_{2}</td>
</tr>
<tr>
<td>L-asparagine</td>
<td>L-Asn</td>
<td>CH_{2}CONH_{2}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-lysine</td>
<td>L-Lys</td>
<td>(CH_{2})<em>{3}NH</em>{3}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-arginine</td>
<td>L-Arg</td>
<td>(CH_{3})<em>{2}NH(NH</em>{2})_{2}</td>
<td>C_{2}, D_{2}</td>
</tr>
<tr>
<td>L-methionine</td>
<td>L-Met</td>
<td>(CH_{2})<em>{2}SC</em>{6}H_{5}</td>
<td>C_{2}</td>
</tr>
</tbody>
</table>

Table 2. Compounds related to protein aminoacids and their symmetry at T = 295 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gly · H_{3}PO_{3}</td>
<td>C_{2h}, C_{2} (≤225 K)</td>
</tr>
<tr>
<td>Gly · H_{3}PO_{4}</td>
<td>C_{2h}</td>
</tr>
<tr>
<td>L-Ala_{2} · H_{3}PO_{3} · H_{2}O</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-Ala · H_{3}PO_{4}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>DL-Ala_{2} · H_{2}SO_{4}</td>
<td>C_{2h} (?)</td>
</tr>
<tr>
<td>L-Val · H_{3}PO_{3}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-Val_{2} · H_{3}PO_{4}</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-Ser_{2} · H_{3}PO_{4} · H_{2}O</td>
<td>C_{2h} or C_{2}</td>
</tr>
<tr>
<td>DL-Ser_{2} · H_{2}SO_{4} · H_{2}O</td>
<td>D_{2}</td>
</tr>
<tr>
<td>L-Glu · Na</td>
<td>D_{2}</td>
</tr>
<tr>
<td>L-Lys · HCl</td>
<td>C_{2}</td>
</tr>
<tr>
<td>L-Arg · H_{3}PO_{4} · H_{2}O</td>
<td>C_{2}</td>
</tr>
</tbody>
</table>

and L- and DL-isoleucine (L- and DL-Ile) were produced in the form of thin platelets and needles, respectively. Crystals of L-serine (L-Ser) grew to form fairly thick plates (8 × 5 × 2 mm), which were transparent in solution but rapidly turned murky when exposed to air.

We grew single crystals of a number of protein aminoacid compounds (with their composition determined by elemental analysis). Large bulk crystals (about 1 cm³) of protein aminoacid compounds were obtained for glycine phosphate (Gly · H_{3}PO_{3}), glycine phosphate (Gly · H_{3}PO_{4}), and DL-diserine sulfate monohydrate (DL-Ser_{2} · H_{3}SO_{4} · H_{2}O). Smaller bulk crystals were prepared for L-Ala_{2} · H_{3}PO_{3} · H_{2}O, L-Ala · H_{3}PO_{4}, DL-Ala_{2} · H_{2}SO_{4}, L-Lys · HCl, and L-Ser_{2} · H_{3}PO_{4} · H_{2}O. Crystals of L-valine with H_{3}PO_{3} as an impurity and of L-Val · H_{3}PO_{4} formed scales and needles. Large bulk crystals were obtained for L-Arg · H_{3}PO_{4} · H_{2}O compound [8].

We made an attempt at synthesizing L-Ala · CaCl_{2} and L-Ala · H_{2}SO_{4}; the crystals obtained were large, but elemental analysis showed them to be pure alanine with a slight addition (about 5 mol %) of CaCl_{2} and H_{2}SO_{4}, respectively.

The piezoelectric response of the crystals was studied using an IS-2 NQR setup. The sample in the form of a crystal or a set of small crystallites was placed in the capacitor of a circuit to which 4-μs-long voltage pulses with a 10-MHz carrier were applied at a pulse repetition frequency of 12 Hz. The maximum voltage amplitude at the circuit was about 4 kV. The piezoelectric response signals were measured with an AI-1024 multichannel analyzer. Radio-frequency pulses excite elastic vibrations of piezoelectric crystals through the inverse piezoelectric effect. After termination of the pulse, elastic vibrations persist for a time on the order of Δt (μs) ≈ 10/α (dB/μs), where α is the elastic wave damping. This sample ringing is detected by the pickup through the direct piezoelectric effect. In crystals of soft materials such as protein aminoacids and their compounds, the elastic wave damping is typically on the order of α ≈ 10^{-1} dB/μs at room temperature and a frequency of 10 MHz. This means that the sample ringing time is Δt = 100 μs. By measuring this time, one can estimate the damping. The magnitude of the piezoelectric signal at the instant Δt = 0 is determined by the electromechanical coupling constant; i.e., it depends on the piezoelectric coefficients, elastic moduli, and dielectric permittivities. However, sample ringing in experiments of such type, particularly when using fine powders, has the pattern of random echo signals, where a signal may turn out to be stronger than that preceding it; therefore, the damping of elastic vibrations is determined in this case with a very large error. For this reason, in measurements of the temperature dependence of the piezoelectric response, we recorded the response as integrated over the total ringing time, which depends on both the electromechanical coupling coefficient and the damping of elastic vibrations. We note that the setup used by us possessed a high sensitivity and permitted detection of piezoelectric response signals with an amplitude of about 5 × 10^{-5} of the piezoelectric response of quartz crystals.

The measured temperature dependences of the integrated piezoelectric response in crystals of protein aminoacids and their related compounds are summed up in Figs. 1–7. The piezoelectric response is given in arbitrary units; nevertheless, the amplitudes of the response of different crystals in each figure are qualitatively matched. At the same time, to make the pattern more revealing, the quantitative relations in the figures are quite frequently distorted. This is manifested most strongly in Fig. 6, where the piezoelectric response signals in DL-diserine sulfate monohydrate and in trigly-