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Pyroelectricity

Water-Induced Pyroelectricity from Nonpolar Crystals of Amino Acids**

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Pyroelectricity, a property of certain crystalline materials, is the creation of a temporary surface charge upon temperature change, resulting in an external electric current. Thermal movement of the molecules alters their average positions leading to changes in the crystal dipole moments. The Greek philosopher Theophrastus discovered this property in the mineral tourmaline already in 314 BC. Since then, this phenomenon has led to a plethora of applications, such as night vision devices, burglar alarms, and portable high-voltage generators.[1] The ability of pyroelectric crystals to develop two oppositely charged faces proves that they have spontaneous polarization, and therefore only crystals belonging to the ten polar crystallographic classes out of the 32 were considered to be pyroelectric. However, this assumes bulk polarization only and ignores the role of surfaces. Although all crystals including the nonpolar ones are delineated by 2D polar surfaces,[2] no pyroelectric current in an external circuit was previously reported from such surfaces since the number of molecules residing at these sites is too small to create sufficiently thick polar layers, to allow the accumulation of neutralizing depolarization charge. Accordingly, the pyroelectric properties of crystals were only correlated with the polarity of their mathematical lattices.

As part of our studies on the conversion of nonpolar host crystals by stereospecific doping with guest molecules into polar pyroelectric mixed crystals, we discovered, surprisingly, that even the pure centrosymmetric crystals of α-glycine exhibit surface pyroelectricity from their {010} faces.

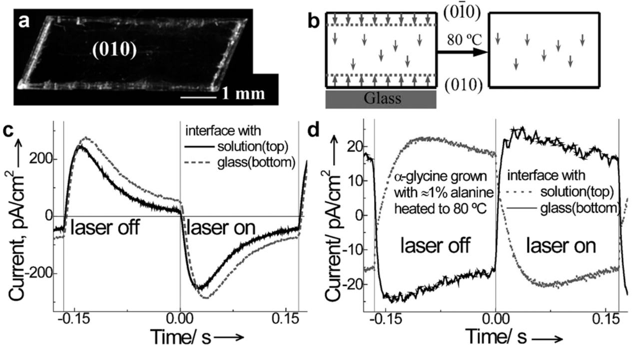

Figure 1. α-Glycine crystals grown with about 1.1 % of alanine: a) morphology; b) scheme of enantioselective incorporation of guest L-alanine (arrows pointing downwards) into the centrosymmetric crystal of α-glycine. Arrows pointing upwards represent ordered water molecules at the surface of the as-grown crystal, which are removed upon heating above 80 °C. c) Pyroelectric current generated in response to a periodic heating by a modulated laser (see the Supporting Information) of an as-grown 1.5 mm thick alanine-doped α-glycine crystal measured on {010} face. d) Pyroelectric response of a 1.8 mm thick alanine-doped α-glycine crystal after annealing at 80 °C.

When centrosymmetric α-glycine crystals, space group $P2_{1/n}$, are grown in pure water in the presence of L-alanine (Figure 1 a), the molecules of the latter are occluded enantioselectively ($\approx 1\,\%$) through the $(0\bar{1}0)$ face and induce {010}-plate-like crystals (Figure 1 b).[3,4] Consequently, weak bulk pyroelectricity is anticipated from such crystals. Surprisingly, upon step-like heating with a modulated laser (see the Supporting Information), both {010} faces of these 0.8–2 mm thick crystals generate substantial negative pyroelectric current corresponding to a $4\text{–}12\times10^{-11}\,\mathrm{C\,cm^{-2}\,K^{-1}}$ pyroelectric coefficient (Figure 1 c, Table 1). This pyroelectric coefficient is only ten times smaller than those measured for common polar pyroelectric materials, such as tourmaline or the well-studied lithium perchlorate trihydrate.[5] However, the direction of the pyroelectric current generated at the $(0\bar{1}0)$ and (010) faces upon heating is the same. This outcome and the rapid decay of the pyroelectric current after switching the laser on, are definitely inconsistent with a bulk pyroelectric effect that might arise from the entire crystal.[6] Other explanations attributable to the photo- or to the thermoelectric (Seebeck) effect, trapped charges, secondary pyroelectricity or the flexoelectric effect are inconsistent with the formation of this current (see the Supporting Information for detailed analysis). Upon heating, the current–time dependence perfectly follows the $1/\sqrt{t}$ rule (t is time) proving that the current originates in a thin polar layer near the surface[6] (see the Supporting Information for the $1/\sqrt{t}$ plot). The thickness of this layer must be less than $\approx \sqrt{Dt}/100 \approx 1\,\mu\mathrm{m}$, where $\tau =$ 5–20 ms is the time above which the dependence $1/\sqrt{t}$ is observed and $D = 0.006\,\mathrm{cm^2\,s^{-1}}$[7] is the thermal diffusion

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Table 1: Equivalent pyroelectric coefficient, *p*, of α-glycine and L-alanine (90% confidence).

Morphology and face	p [10^{-11} C cm^{-2} K^{-1}]
α-glycine doped with L-alanine	
plate (010) top and bottom	4–12
plate (010) top and bottom, cleaved or heated > 80 °C	0.1–0.3
α-glycine pure	
pyramid, (010) crystal–glass interface	2–7
truncated pyramid, (010) crystal–glass and crystal–solution interfaces	2–7
tilted pyramid (010)	1–2
pyramid (010) cleaved or heated > 80 °C	< 0.05
pyramid (011) and (110)	< 0.05
L-alanine	
rhombus, top (120)	0.6–1.2
rhombus, bottom (120)	1.5–2.9
rhombus, sides (120)	0.2–0.8
rhombus, top and bottom (120) heated above 110 °C	< 0.2
pyramid, {120}	0.5–1.8
rhombus, sides (011)	0.6–2.8
prism, top and bottom (011)	0.8–1.6

coefficient of glycine. Heating these crystals in an oven above 80 °C for about 6 h causes three effects: 1) the pyroelectric constant decreases by an order of magnitude (5×10^{-12} C cm^{-2}K^{-1}), 2) most importantly, the pyroelectric current at the ($0\bar{1}0$) and (010) faces assumes opposite directions: the current on the ($0\bar{1}0$) face reversed its direction (Figure 1c, Figure 1d), that is, the quadrupole-type outline of the current was replaced by a characteristic bulk pyroelectricity dipole type. 3) The current–time dependence changes into the one typical for bulk pyroelectricity (Figure 1d).[6] Thus the as-grown α-glycine doped with L-alanine guests has two contributions to the pyroelectric effect: 1) a strong surface component at the two {010} faces, exhibiting a quadruple-like behavior, with a negative current upon heating at the two opposite faces, and 2) a weaker, alanine-induced bulk contribution with the pyroelectric vector along the *b*-direction of the crystal. Moreover, upon heating, the surface pyroelectric effect vanishes making the bulk contribution visible. Consequently, the origin of the surface pyroelectric current might be induced, either somehow, by the presence of the L-alanine guest, or unpredictably, in variance to the currently accepted principles, the centrosymmetric crystals of α-glycine display pyroelectricity. This quandary is analyzed below.

Crystals of pure α-glycine from three different morphologies were obtained: pyramids, truncated pyramids, and tilted pyramids (Figure 2a). The most abundant morphology of the crystals comprised the pyramids and truncated pyramids where one of the {010} faces (Figure 2a,b) in both morphologies resides at the glass/water interface, and well-expressed pairs of {011} and {110} delineate the faces of the pyramid. In the truncated pyramid the {010} face pointing towards the aqueous solution was expressed as well.

Surprisingly, the {010} faces of the base pyramid of both morphologies formed at the glass/water interface produce a pyroelectric current of 50–100 pA cm^{-2} (negative upon heating and corresponding to $1\text{–}7\times10^{-11}$ C cm^{-2}K^{-1} at 27 °C; Figure 3a). The {010} faces of the truncated and the tilted pyramids that grew towards the aqueous solution–crystal interface generate pyroelectric current of the same magnitude and direction (negative upon heating). Thus any role that might have been played by the glass interface is excluded. The quadruple-like mode of the current together with the observed rapid pyroelectric current decay with time (Figure 3a), completely excludes the existence of pyroelectricity from the entire crystal. Instead, these features clearly identify the pyroelectric current as being generated in the top layer of the crystal surface. Detailed neutron diffraction analysis of α-glycine from 280 to 425 K by Langan et al.[8] searched but had not found any traces of possible disorder or traces of the pyroelectric β- and γ-polymorphs as physical contaminants, which might be suspected to be the origin of the pyroelectric current.[8,9] The enantioselective occlusion of L-alanine also excludes crystal twinning (Figure 1b).[3]

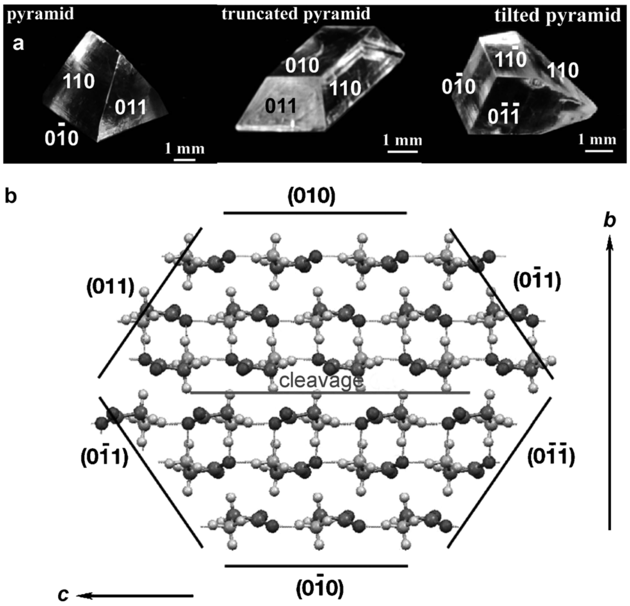

Figure 2. α-Glycine crystals. a) Three morphologies of α-glycine crystals. b) Structure of α-glycine illustrating functional groups exposed at the {010} {011} crystallographic faces.

The pyroelectric current obtained from the {010} faces decreases by about 30% upon cooling the crystals, from 50 to 16 °C, with cold N_2 (Figure 3b). However, the current reappears fully reversibly upon warming the crystal back up to 50 °C (Figure 3b). The process was repeated more than five times for six different crystals, which indicates that the entity responsible for the current generation is completely stable within this temperature range. However, upon heating above

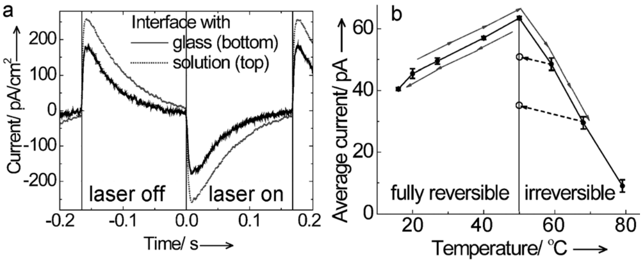

Figure 3. α-Glycine crystals. a) pyroelectric current generated in a 1 mm thick α-glycine crystal upon periodic heating and cooling measured on the {010} face. The rapid decay of the current indicates that the polarization is confined to the surface layer, while the crystal interior is not polar (see the Supporting Information). b) Average pyroelectric current, measured on {010} face at 3 Hz as a function of temperature. Below 50 °C, changes incurred by heating and cooling are fully reversible. However, above that temperature heating results in the irreversible loss of the pyroelectric signal.

50 °C the pyroelectric current decays irreversibly and permanently disappears above 80 °C (Figure 3 b, Table 1). Furthermore, the atomically smooth {010} surfaces of a cleaved crystal either do not exhibit or show barely detectable pyroelectric effect (Table 1). This finding is in keeping with the anticipation that pristine surfaces of nonpolar crystals should not display pyroelectricity, since their surfaces cannot accumulate sufficient depolarization charge to generate an external electric current. However, if these surfaces adsorb and align external molecules in a polar configuration, the formation of sufficiently thick polar pyroelectric layers is expected. Water molecules are inevitably present at the surfaces of crystals composed from polar molecules such as the zwitterionic amino acids.[10] As a result, when water molecules are aligned in a polar configuration they were shown to enhance pyroelectricity, to a magnitude, which levels that of the best pyroelectric materials, like Pb(Zr, Ti)O_3 (≈× 10^{-8} C cm^{-2} K^{-1}).[11] Therefore, we hypothesized that the origin of the observed pyroelectricity is due to hydrated polar layers, which delineate certain faces of the crystals of the amino acids. Indeed after dipping the cleaved {010} surfaces of glycine in water for a few seconds their surface pyroelectricity reappears (see Table 1).

Although the minute amount of water, after drying the crystals at room temperature, could not be detected by thermal gravimetric measurements, its presence, however, is supported by the impedance spectroscopy data, which show after heating above 80 °C, a large increase of the low-frequency impedance of the crystals (Figure 4 a). This result is consistent with the removal of water that supplies protons that induce surface and bulk conductivity. The presence of water on smooth surfaces of crystals by surface X-ray reflectivity was previously reported.[12] In addition comparative morphological studies of glycine crystals grown by sublimation (theoretical form) and those grown in aqueous solution show that water is most firmly attached at the {011} and {110} hydrophilic faces, where the negatively charged oxygen atoms of the carboxy groups and the hydrogen atoms of the positively charged ammonium groups, respectively, emerge, as seen in Figure 2 b and Figure S1.[13] Furthermore, it has been suggested from measurements of crystal growth of glycine, as well as on theoretical grounds, that the glycine crystals grow from screw dislocations creating polar spirals along the growth direction.[14] The steps and kinks that delineate these spirals are the {011}/{010} and {110}/{010} facets, whereas the {011} and {110} facets constitute the walls of the steps and {010} the base (Figure 4 b). The water molecules can hydrate the glycine molecules residing at these steps such that they can form a thin polar film, along the *b*-axis. Such films should not be polar along the *a*- and *c*-axes, as a result of the two-fold screw axis along the *b*-axis of the monoclinic crystal. This assumption suggests that either very weak or no pyroelectric current will be created at the {011} and {110} faces. Indeed, no detectable pyroelectric current (< 1 pA cm^{-2}) was produced at the {011} faces and a very weak pyroelectric current (< 5 pA cm^{-2}) was registered from the {110} faces of the pyramid (Table 1). In addition, one can also envisage that other polar hydrated films might be formed near macroscopic imperfections and crevices present in the crystals.

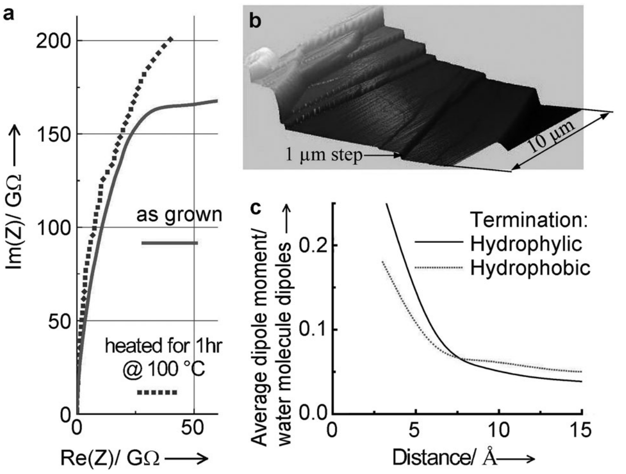

Figure 4. α-Glycine crystals. a) Impedance spectroscopy spectra (0.1 Hz–1 MHz, oscillation voltage of 50 mV) of as-prepared and annealed crystal of α-glycine measured on the {010} face. Increase in the low-frequency impedance after annealing indicates proton conductivity that is removed by annealing. b) AFM image of steps on the {010} face of an α-glycine crystal. c) Molecular dynamics simulation of the dipole moment associated with water molecules aligned in the vicinity of {010} face of α-glycine. The net dipole moment is predicted for hydrophilic and hydrophobic termination alike.

Our preliminary molecular dynamics simulations suggest that the {010} faces of the α-glycine crystals (Figure 4 c) indeed align water molecules into a polar five-layer thick multilayer. We note, that both hydrophilic terminated surfaces where the zwitterionic groups of the amino acids emerge, and the surfaces where the C–H group emerge, induce formation of a net-dipole in the vicinity of the surface. The mechanism of surface pyroelectricity has been extended to other nonpolar crystals of the amino acids including glycylglycine, D,L-aspartic acid, D,L-serine, and D,L-valine but is described below for the nonpolar enantiomorph crystals of L- and D-alanine.

The crystals of L- and D-alanine appear in the orthorhombic nonpolar space group $P2_12_12_1$.[15] Three different morphologies, rhombus, pyramid, and prism, were obtained without detectable twinning (Figure 5a). The current direction was measured at well expressed {120} and {011} opposite faces of the crystals, those pointing to the aqueous solution and those laying on the glass surface, and found to be of the same direction (Figure 5c). Repetitive cooling, by cold N_2, below room temperature (15–25 °C) does not change the pyroelectric coefficient. However, after heating in an oven above 100 °C, the pyroelectric effect disappears irreversibly. These results are similar to those observed in α-glycine and are in keeping with the formation of thin hydrated polar layers at the faces displaying pyroelectricity.

In summary, pyroelectricity should not be confined only to the ten mathematically polar crystalline lattices as considered so far. Crystals are considered as physical entities, which contain also surfaces, defects, and different imperfections, which are not considered by the crystallographic lattices. Therefore, symmetry-imposed limitations on macroscopic properties are not absolute.[16] Charged molecules, which reside at the surfaces of the crystals, interact with molecules of the environment to create thin layers that decorate the crystals and are not detectable by diffraction techniques. When these hydrate films assume a polar configuration, they are detectable even when they are very thin. The formation of such hybrid polar layers provides a rational explanation to the previously unexplained optical and electrical properties of α-glycine.[8,17] Finally, the present results suggest that pyroelectricity might become an analytical method that can probe rough polar surfaces interacting with molecules of the environment, especially with water.[18] They can also shed light on processes related to the understanding of the role of solvent on, for example, crystal growth and crystal polymorphism. Studies along these lines are currently in progress.

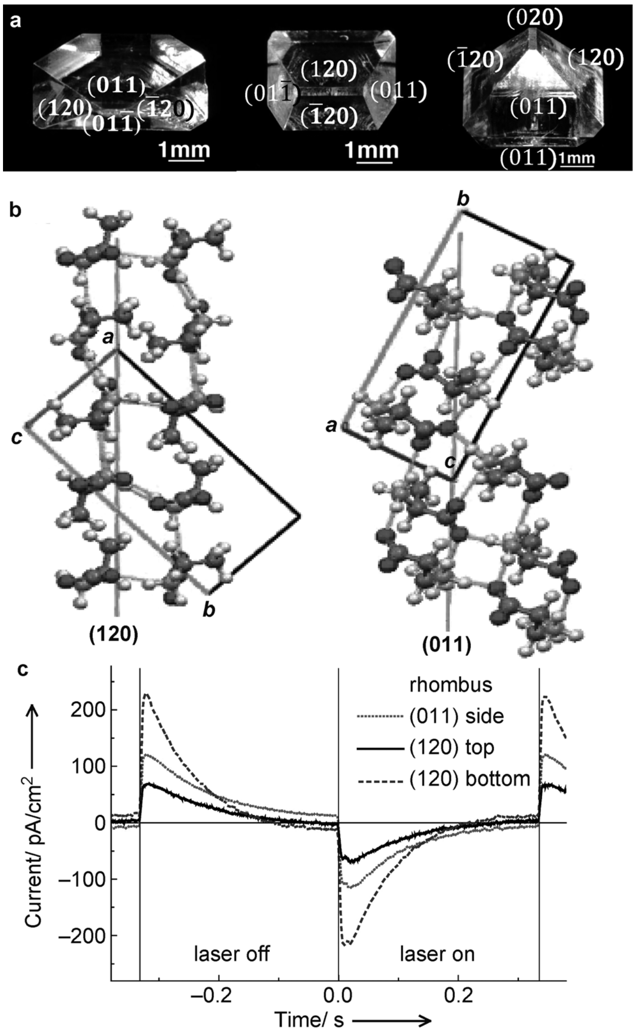

Figure 5. Alanine crystals. a) Three morphologies of alanine crystals (pyramid, rhombus, and prism). b) Structure of alanine illustrating functional groups exposed at different crystallographic faces. c) Pyroelectric current generated in a 1.5 mm thick alanine crystal. The rapid decay of the current indicates that the polarization is confined to the surface layer, while the crystal interior is not polar.

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