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# Local piezo- and ferroelectric properties of $\gamma$ -glycine single crystal observed via piezoresponse force microscopy

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## Abstract

In this work, we demonstrate an approach of local mechanical polishing processing to modify the type of intrinsic piezoelectric activity of  $\gamma$ -glycine polymorph grown in a form of a single crystal. By using the piezoresponse force microscopy, the increase in intensity for both out-of-plane (3 times) and in-plane (5 times) piezoelectric tensor components is demonstrated. Application of local switching spectroscopy reveals the piezoelectric behavior of non-polished and the ferroelectric behavior of polished areas being related to the local mechanical polishing-assistant rearrangement of  $NH_3^+$  tails of zwitterions in polymorph molecular chain of  $\gamma$ -glycine. These rearrangements were demonstrated to facilitate the switching behavior of the local dipole moment at the applied electric field surpassing the internal coercive field of about  $E_c \sim 3 \text{ G V/m}$ .

## Introduction

Glycine is a frequent material in biology and organic chemistry. The polymorphism of glycine structure in crystalline amino acids has been studied since it was discovered in 1900 by Fischer *et al* [1] and developed in 1939 by Albrecht and Corey [2]. The principal function of glycine is to serve as a building block for proteins and as an inhibitory transmitter in the central nervous system [3]. Glycine has three main polymorphs:  $\alpha$ ,  $\beta$ , and  $\gamma$  which are described in detail elsewhere [4–9]. The dielectric  $\alpha$ -phase glycine is stable without appearing polar properties [6–9]. The  $\beta$ -phase is a ferroelectric polymorph that was previously predicted theoretically [9] and then measured experimentally [10–12]. The  $\beta$ -phase has promising polar properties but the absence of stability at room temperature and high humidity to decay with time in  $\alpha$ - or  $\gamma$ - phase [13]. The only way to stabilize this phase at ambient conditions was confirmed in work [14] by using the Pt substrate. The most stable  $\gamma$ -glycine polymorph was discovered first time by Iitaka in 1954 [15]. This phase was accepted as the best compromise due to excellent stability at broad temperature and humidity ranges and the ability to form large single crystals with a non-centrosymmetric structure (space groups  $P2_1$  and  $P3_1$ ) suitable for biocompatible nanoelectronic applications [16–19]. The  $\gamma$ -glycine polymorph phase reveals strong piezoelectric properties predicted with a spontaneous polarization of about  $70.9 \mu\text{C}/\text{cm}^2$  at 300 K [20] and with a longitudinal piezoelectric coefficient ( $d_{33}$ ) measured at  $7.37 \text{ pC/N}$  [16]. An uncertain polar behavior between piezo- and ferroelectricity in  $\gamma$ -glycine polymorph is still under discussion and some theoretical [9] and experimental [11–14, 16, 17] works confirmed only the switching behavior at the nanoscale level in as-grown microcrystals. In work [18] the molecular dynamics simulation of the polarization switching dynamics in  $\gamma$ -glycine molecular cluster predicts the possible switching of the cylindrical domain at the coercive electrical field being in the vicinity of breakdown voltage ( $E_c \sim 4\text{--}8 \text{ GV m}^{-1}$ ). In work [20], the Curie temperature of  $\gamma$ -glycine was predicted to be at 630 K, with a required coercive field to switch its polarization states of about  $1 \text{ V nm}^{-1}$ . Some works rely on the cocrystallization of  $\gamma$ -

glycine and sulfamic acid to increase the piezoelectric activity of the final compound [21]. The piezoelectric tensor of the cocrystal mapped using density functional theory (DFT) was predicted for the single-crystal longitudinal response of about 2 pC/N and was verified using second-harmonic generation (SHG) and piezoresponse force microscopy (PFM) techniques [21, 22].

The employment of the local Atomic Force Microscopy (AFM) technique implemented in Piezoresponse Force mode (PFM), is a powerful tool here for studying piezo- and ferroelectric phenomena at the micro- and nanometers. This method allows for avoiding damage to the sample while applying a significantly high electric field ( $\sim 10 \text{ GV m}^{-1}$ ) at the local scale [23–25]. In this method, a sharp conductive tip in contact with the surface is periodically biased, and bias-induced surface displacements are translated into the mechanical motion of the tip. Both out-of-plane and in-plane displacements can be monitored [24].

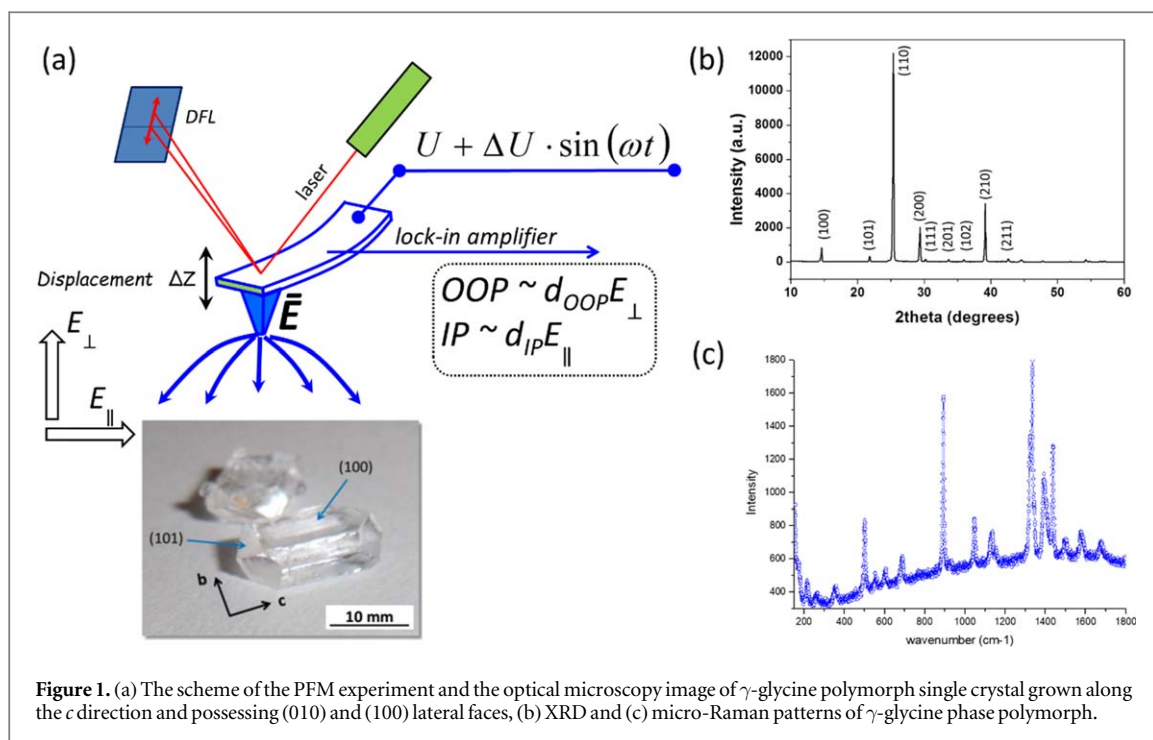
In this work, the local piezo- and ferroelectric properties of  $\gamma$ -phase glycine polymorph synthesized in a form of a single crystal were confirmed via the PFM method. An approach to stimulate the surface electromechanical activity, namely a nano-polishing method developed for organic and soft materials [26] was applied to the facet (100) of the synthesized  $\gamma$ -glycine crystal. This method was developed for the molecular and soft materials polishing procedure where the usual polishing methods such as electrolytic polishing, chemical mechanical polishing, photocatalytic chemical mechanical polishing, plasma-assisted polishing, electrochemical mechanical polishing, and catalyst-referred etching do not work properly because of molecular materials high-level dissolubility in liquid media and low stability at harsh conditions including high voltage and elevated temperature [26–28]. The obtained results open the way towards a more deep understanding of the nature of piezo- and ferroelectricity and surface electrochemistry of  $\gamma$ -glycine polymorph at the macro-, micro-, and nanoscale levels. This knowledge allows for promoting excellent chemical stability coupled with polar properties of  $\gamma$ -glycine single crystal materials for biocompatible nanoelectronic applications.

## Experimental

Single crystals of  $\gamma$ -glycine were grown from an aqueous solution by a slow evaporation method in the presence of lithium nitrate that suppressed the formation of  $\alpha$ -glycine (more details can be found in [29]). Lithium cations do not enter the crystal structure and remain in the solution as free ions. The aqueous solution of glycine (Sigma-Aldrich, 99%) and lithium nitrate (Sigma-Aldrich, 99.5%) in a 2:1 mole ratio was prepared in deionized water at room temperature. The prepared solution was stirred for four hours to dissolve fully and then filtered with a Whatman filter paper. The solution was stored in a beaker, closed with perforated paper, and allowed to evaporate slowly at ambient temperature. A few days after solvent evaporation, the solution becomes supersaturated and tiny crystals appeared, which were grown for 5 weeks to obtain the millimeter-scale crystals with hexagonal prismatic structure (figure 1(a)). After the samples were free from the solvent, they stay at ambient conditions (air environment, humidity of about 45%, temperature of about  $21^\circ$ ) prior to the macro- and microscopic measurements. No special conditions or procedures were applied to the samples to prepare them for the structural, optical, and local measurements.

The obtained  $\gamma$ -glycine single crystals were studied by x-ray diffraction (Siemens D500 diffractometer with secondary monochromator CuK $\alpha$  radiation in the  $10\text{--}60^\circ$  range with steps of  $0.05^\circ$ , the time for collecting x-rays being 100 s for each measuring point at 40 mA and 45 kV) and Micro-Raman (WiTec alpha 300 AR confocal Raman microscope with an objective (10X, NA = 0.55) focused the exciting light (solid-state laser,  $\lambda = 488 \text{ nm}$ ) onto the sample with the spot diameter of about 260 nm, and a diffraction grating of 600 dashes/mm with a spectral resolution of  $3.19 \text{ cm}^{-1}$  at  $\lambda = 488 \text{ nm}$  used for light decomposition).

The polishing of the (100) plane of  $\gamma$ -glycine single crystal was done via a local nano-polishing method developed especially for organic and soft materials polishing on a molecular scale. For the first time, this method was introduced by Hiroshi Nanjo *et al* for the nano-polishing procedure for molecular-scale flattening at (001) and (00–1) parallel surfaces of 4-dimethylamino-N-methyl-4-stilbazolium tosylate crystal [26] and then used frequently for nano-polishing procedures in different materials [30–32]. This nano-polishing method is based on scanning the sample surface by the tip of an atomic force microscope at a local scale with an appropriate load depending on the surface condition. For this and the measurements of local topography, piezo-, and ferroelectric properties a conventional AFM microscope (Ntegra, NTMDT) additionally implemented in PFM mode operating at a frequency of 50 kHz and amplitude of 10 Volts (figure 1(a)) was used. To analyze the polarization switching behavior, the PFM switching spectroscopy was used when the tip was fixed at a predefined location on the sample surface and a strong stepwise bias voltage ( $\pm 50 \text{ Volts}$ ) was applied. The Pt/Cr coated conductive silicon cantilevers ElectriMulti75-G (BudgetSensor) were used (Resonance Frequency at 75 kHz, Force Constant at  $3 \text{ N m}^{-1}$ ). All the measurements were done at ambient conditions (room temperature, humidity  $\sim 30\%$ ).

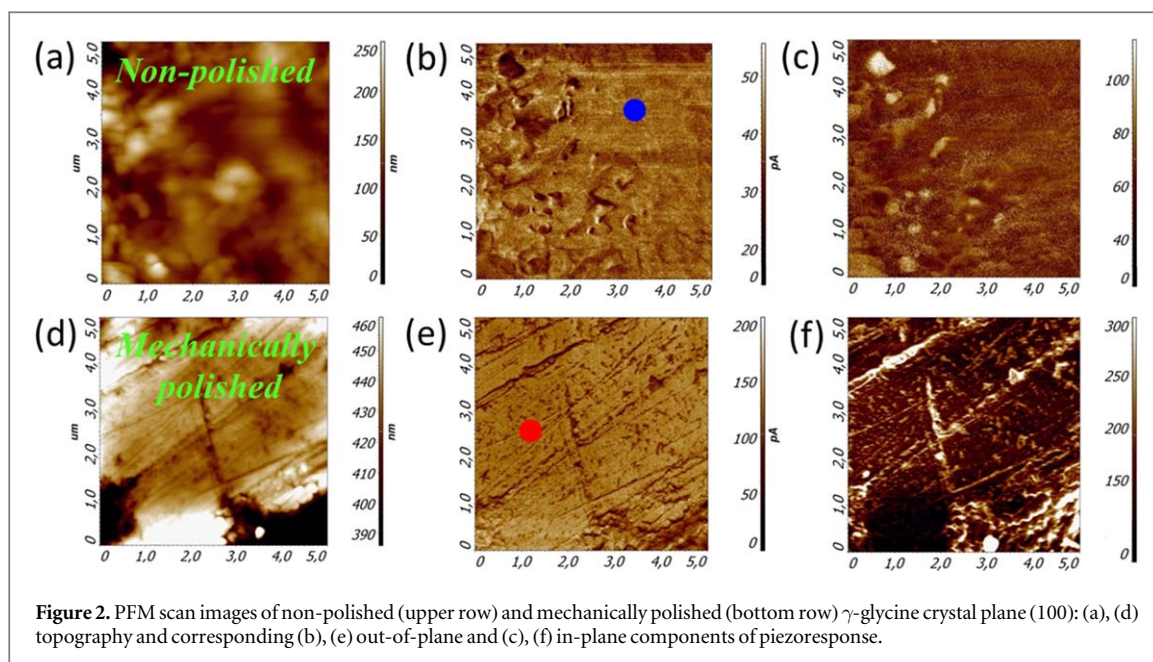


## Results and discussion

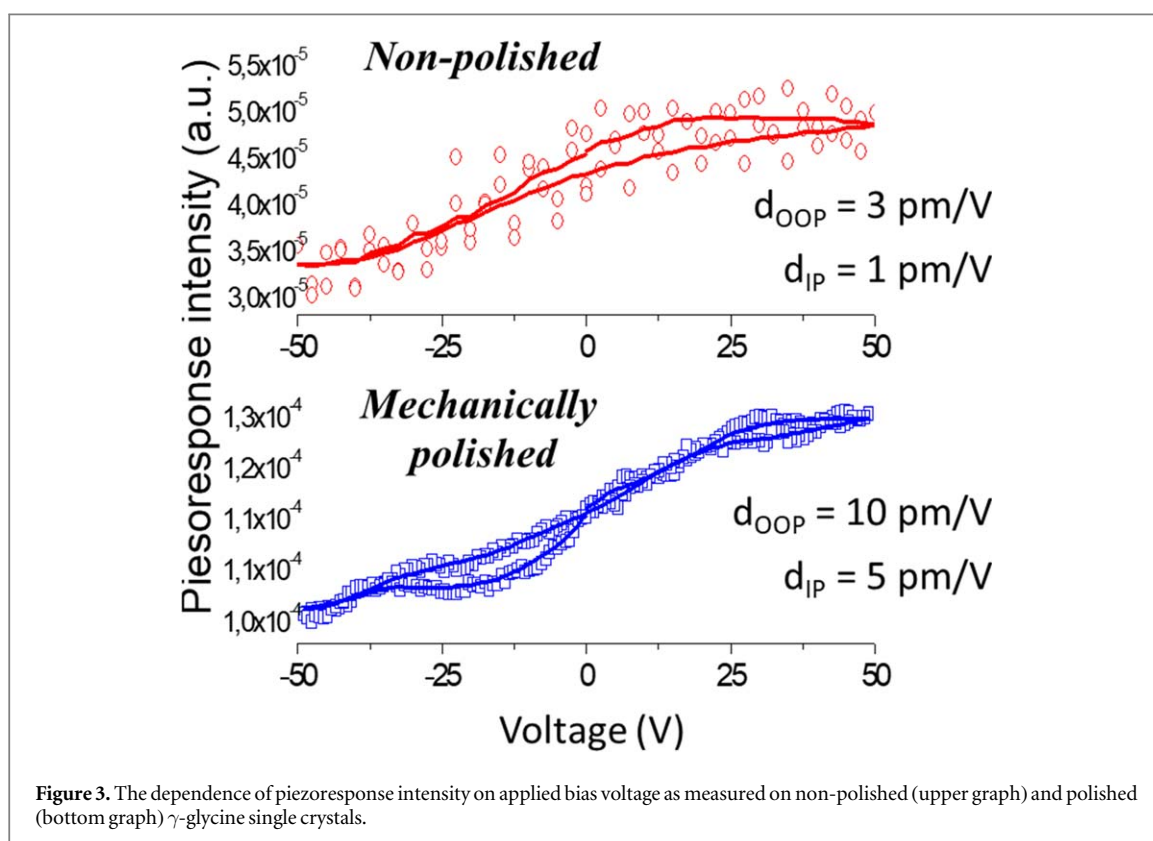
The results of single crystal XRD and micro-Raman spectroscopy confirm the formation of  $\gamma$ -glycine phase polymorph (figures 1(b), (c)). The positions of the XRD peaks in figure 1(b) correspond to the  $\gamma$ -glycine (JCPDS database (00-006-0230)). The calculated cell parameters are  $a = b = 7.038 \text{ \AA}$ ,  $c = 5.48 \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$  to be in full agreement with the literature [15]. In micro-Raman spectroscopy the two particular characteristic spectral regions: at  $100\text{--}600 \text{ cm}^{-1}$  and  $1200\text{--}1600 \text{ cm}^{-1}$  exhibit the peaks only related to  $\gamma$ -phase glycine polymorph (PF) [15].

The PFM measurements on  $\gamma$ -glycine crystal were done with two steps on non-polished and mechanically polished (100) crystal planes. In agreement with the theoretical predictions the maximum piezoresponse has to correspond to the polar axis [001] possessing the coercive field of about  $E_c \sim 3 \text{ GV/m}$  [9, 15]. The result of AFM and PFM shows distinct differences in morphology between locally polished and non-polished samples (figures 2(a), (d)), while XRD and micro-Raman spectroscopy have not revealed any distinction between both samples (not presented). Figure 2 represents the comparison of out-of-plane and in-plane components of the PFM signal for non-polished and polished areas where a significant signal increase was observed for the polished surface. This fact can be associated with the mechanical polishing-assistant depolarization of the upper layer at the surface of the sample (an effect similar to electrical high voltage dc corona polishing) and the corresponding modification of the piezo- and ferroelectric domain structure [25]. These results are going in line with the theoretical work [20], where a change of improper dihedral angle between the N atom on the  $\text{NH}_3^+$  group and the plane formed by the carboxyl acid group ( $\text{COO}^-$ ) affects the magnitude of the final polarization thus resulting the  $\text{NH}_3^+$  group undergoes a transition from the paraelectric structure to the ferroelectric one. Hence, local polishing stimulates local stress-assisted rearrangement of  $\text{NH}_3^+$  tails of zwitterions in the polymorph molecular chain of  $\gamma$ -glycine to enhance the local polar activity in the crystal. The PFM signal intensity is in agreement with the theoretical prediction to confirm the strongest signal acquired for the in-plane component of the polarization which is proportional to the effective shear piezoelectric coefficient ( $d_{15}$ ) along the [001] axis (figures 2(c), (f)) as compared to the out-of-plane component of the polarization which is proportional to the effective longitudinal piezoelectric coefficient ( $d_{33}$ ) along the [100] axis (figures 2(b), (e)).

PFM switching spectroscopy (SS-PFM) was applied to non-polished and polished samples at the area marked by red and blue spots, respectively (figures 2(b), (e)). During the SS-PFM the bias voltage (BV) was applied at  $\pm 50 \text{ V}$ , thus reaching the electric field of about  $E_{BV} \sim 3 \text{ GV/m}$  being in the range of the predicted coercive field in  $\gamma$ -glycine. The out-of-plane and in-plane components of piezoresponse on voltage dependence demonstrate the switching to show the piezoelectric behavior in  $\gamma$ -glycine (figure 3). The piezoresponse intensity was observed higher in magnitude on the polished sample for both components, thus reaffirming the effectiveness of the mechanical polishing method to enhance the local piezoelectric activity in  $\gamma$ -glycine single crystal. It is important to note that in the dependence of piezoresponse on BV for the non-polished sample, there

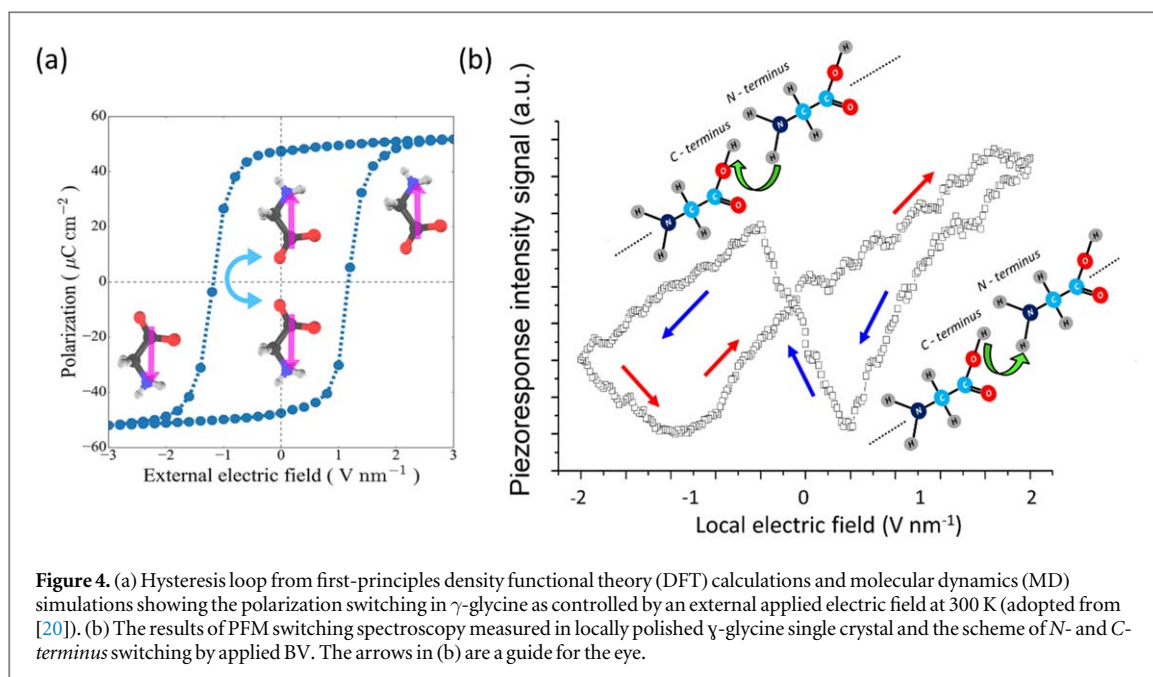


**Figure 2.** PFM scan images of non-polished (upper row) and mechanically polished (bottom row)  $\gamma$ -glycine crystal plane (100): (a), (d) topography and corresponding (b), (e) out-of-plane and (c), (f) in-plane components of piezoresponse.



**Figure 3.** The dependence of piezoresponse intensity on applied bias voltage as measured on non-polished (upper graph) and polished (bottom graph)  $\gamma$ -glycine single crystals.

is a hysteresis loop-like behavior observed for the positive part of the bias voltage. This result points out on nonequilibrium condition between polar groups coexisting on top of the surface in an as-grown non-polished  $\gamma$ -glycine single crystal. Mechanical polishing diminishes or fully neglects this imbalance (the depolarization of the upper layer) and makes the surface to be equipotential which is in agreement with [25]. The calculated out-of-plane and in-plane piezoelectric coefficients are shown in figure 3 and the highest one was obtained for the out-of-plane component in the polished sample at  $10 \text{ pm V}^{-1}$  to be close to those reported in experimental works [14, 16] ( $d_{33} \sim 7.37 \text{ pC/N}$ ) and theoretical works [7] ( $d_{33} \sim 5.8\text{--}11.6 \text{ pC/N}$ ), [20] ( $d_{33} = 8.1 \text{ pm/V}$ ). Mechanical polishing processing allows the enhancement of the  $d_{OOP}$  (three times) and  $d_{IP}$  (five times) piezoelectric tensor components in the  $\gamma$ -glycine single crystal.



Strong enhancement of PFM response observed in the polished area arose from the task on the polar group organization and distribution in modified  $\gamma$ -glycine polymorph. Nanoscale SS-PFM measurements were acquired at the maximum intensity within the locally polished area in  $\gamma$ -glycine single crystal (figure 2(f)). The dependence of piezoresponse intensity on applied BV demonstrates the hysteresis loop behavior with strong polarization switching at positive bias voltage and partly switching at negative bias voltage (figure 4). Similar behavior was predicted in work [33] where the calculations of enthalpy, entropy, and Gibbs energy for all three polymorphs of glycine showed that their thermodynamic properties (and thus macroscopic physical properties) are affected by the arrangement of  $\text{NH}_3^+$  tails of zwitterions rather than by the crystal structure. Thus the electromechanical activity at the surface of the  $\gamma$ -glycine crystal is realized through the rearrangement of  $\text{NH}_3^+$  tails of zwitterions in polymorph molecular (figure 4). The asymmetrical hysteresis behavior is appearing owing to differences for  $\text{COO}^-$  and  $\text{NH}_3^+$  groups in surface energy and chemical activity with the oxygen and non-compensated / trapped charges that are normally coexisting on the surface.

The obtained experimental results of local switching behavior fully coincide with the results reported in [34] where it was demonstrated that the polarization reversal in  $\gamma$ -glycine requires the rotation of glycine molecules by  $180^\circ$  around an axis perpendicular to the polar  $c$ -axis.

## Conclusion

The approach of the mechanical polishing procedure is demonstrated to significantly increase the piezoelectric activity of  $\gamma$ -phase glycine polymorph synthesized and grown in the form of a single crystal. The PFM method demonstrated the increase in intensity for both out-of-plane and in-plane piezoelectric tensor components in the case of the locally polished  $\gamma$ -glycine single crystal. The piezoelectric coefficients are calculated to be three times higher for the out-of-plane component and five times higher for the in-plane component in the case of the polished sample. Application of local switching spectroscopy reveals the piezoelectric behavior of non-polished and the ferroelectric behavior of polished areas being related to the local mechanical polishing-assisted rearrangement of  $\text{NH}_3^+$  tails of zwitterions in polymorph molecular chain of  $\gamma$ -glycine. These rearrangements were demonstrated to facilitate the switching behavior of the local dipole moment at the applied electric field surpassing the internal coercive field of about  $E_c \sim 3 \text{ GV/m}$ .

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## Data availability statement

The data cannot be made publicly available upon publication because they are not available in a format that is sufficiently accessible or reusable by other researchers. The data that support the findings of this study are available upon reasonable request from the authors.

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