Ferroelectrics as Smart Mechanical Materials

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The mechanical properties of materials are insensitive to space inversion, even when they are crystallographically asymmetric. In practice, this means that turning a piezoelectric crystal upside down or switching the polarization of a ferroelectric should not change its mechanical response. Strain gradients, however, introduce an additional source of asymmetry that has mechanical consequences. Using nanoindentation and contact-resonance force microscopy, this study demonstrates that the mechanical response to indentation of a uniaxial ferroelectric (LiNbO₃) does change when its polarity is switched, and use this mechanical asymmetry both to quantify its flexoelectricity and to mechanically read the sign of its ferroelectric domains.

The mechanical properties of homogeneous materials (stiffness, hardness, toughness, and so on) are insensitive to space inversion, because all the magnitudes involved (stress, strain, and elastic constants) are described by even parity tensors. This mathematical argument is even valid for crystallographically asymmetric materials such as ferroelectrics and piezoelectrics, and physically, this means that the mechanical response of a ferroelectric material should not depend on whether its polar axis is pointing up or down. However, symmetry restrictions change when deformations are inhomogeneous. For example, flexoelectricity (coupling between polarization and strain gradient) allows switching ferroelectric polarization by mechanical means, something that would be otherwise symmetry forbidden if the strain was homogeneous. Flexoelectricity can also affect the mechanical response. Importantly, the incorporation of strain gradients (a third-rank tensor) breaks spatial inversion symmetry. In ferroelectrics, piezoelectricity also breaks inversion symmetry and may cooperate or compete with flexoelectricity resulting in different energy costs of deformation. Thus, by switching ferroelectric polarization, one can affect the total polarization, resulting in a material whose mechanical response to strain gradients can be switched with a voltage.

It is the purpose of this paper to demonstrate that the mechanical response of a ferroelectric is indeed switchable. We show that mechanical asymmetry not only affects toughness, as theoretically predicted, but also all other mechanical properties, both plastic and elastic. This discovery, in turn, enables the use of purely mechanical means to quantify flexoelectricity or to determine the sign of a ferroelectric domain (or, eventually, a ferroelectric memory bit) by just poking it. Both of these concepts are demonstrated here.

Physically, an asymmetric mechanical response can be rationalized by considering the energy cost of deforming a piezoelectric material that generates a polarization $P$ in response to the deformation. This energy cost has two contributions: an elastic one, associated with the deformation itself (Hooke’s law), and an electrostatic one, associated with the deformation-induced polarization. The electrostatic energy is $1/2 \chi^{-1} P^2$, where $\chi$ is the dielectric susceptibility. Because the polarization is squared, the electrostatic energy is insensitive to its sign, so turning a piezoelectric crystal upside down will not make it any softer or harder. However, when the deformation is inhomogeneous, there are two sources of polarization: the strain itself, via piezoelectricity, and the strain gradient, via flexoelectricity. In a ferroelectric, which is a switchable piezoelectric, these two can be parallel or antiparallel depending on the ferroelectric polarity. Thus, the same inhomogeneous deformation will generate an enhanced polarization when piezoelectricity and flexoelectricity are parallel ($P = P_{\text{piezo}} + P_{\text{flexo}}$) and a reduced polarization if they are antiparallel ($P = -P_{\text{piezo}} + P_{\text{flexo}}$). The depolarization energy still depends on the square of the total polarization ($P^2$), but the magnitude of $P$ now depends on the sign of $P_{\text{piezo}}$, so the cost of deformation becomes sensitive to polarity.

It is possible to investigate the mechanical response of ferroelectrics to inhomogeneous strain using nanoindentation, which generates flexoelectricity around a sharp indenter tip (Figure 1a). The samples studied are single crystals of lithium niobate (LiNbO₃). We have chosen this material because it is a uniaxial ferroelectric, meaning that only 180° domain switching is possible. This feature prevents any stress-induced ferroelastic reorientation of the polarization, thus simplifying the analysis; however, the arguments used here can also be applied to thin films of ferroelastic–ferroelectrics such as BaTiO₃, PbTiO₃.
or BiFeO$_3$, provided they are epitaxially constrained to have their polarization out of plane.

Depending on Li$^+$ concentration, LiNbO$_3$ can be stoichiometric or congruent. The latter has defect dipoles that can introduce an extrinsic asymmetry.\cite{12,13} Here, we have studied samples of both types: stoichiometric and congruent. The stoichiometric sample was single domain (stoichiometric lithium niobate (SLN)), so space inversion was achieved by just splitting the crystal in two and turning one half upside down. The congruent sample was periodically poled (periodically poled lithium niobate (PPLN)), so both polarities were accessible on the same side. The results between SLN and PPLN were mutually consistent, indicating that sample stoichiometry or switching method do not affect the outcome.

Indentations were first performed in the monodomain crystal, z-cut (polarization perpendicular to the surface) and split with one-half placed with polarization pointing up and the other pointing down. Both sides were equally polished to

Figure 1. a) Schematic of the strain gradient field and the associated polarizations (arrows) induced by the indenter tip on a uniaxial ferroelectric with polarization pointing up (left), and polarization pointing down (right). b) Schematic of the loading and unloading force–displacement curve performed by the nanoindenter, from which the energies (inset) and mechanical parameters are obtained. c) AFM topography image of the surface of an SLN crystal after performing 25 nanoindentations with the same indentation force. d) Asymmetry behavior of energies as a function of the maximum indentation load in SLN single crystals, showing that both plastic and elastic mechanical responses are asymmetric.
mirror-like appearance. In order to get statistically meaningful results, we performed and analyzed 50 indentations for each mechanical load (25 for each polarity) and measured applying 4 different maximum loads, i.e., a total of 200 indentations. Another set of 100 indentations (50 for each polarity) at a single load were performed on the PPLN. Further details of the nanoindentation measurements are provided in the “Experimental Section,” and the full dataset of raw results is provided in the Supporting Information.

Figure 1b is a schematic of the load-displacement (F-h) curve for a Berkovich indenter. During the loading process, the material undergoes both elastic and plastic deformation. The total energy related to this process is \( U_T = \int_0^{h_{\text{max}}} Fdh \), where \( h_{\text{max}} \) is the maximum depth reached during loading and \( F \) is the force applied by the indenter. The elastic deformation is recovered upon unloading; therefore, the elastic energy can be measured as \( U_e = \int_{h_{\text{f}}}^{h_{\text{max}}} Fdh \), where \( h_f \) is the final indentation depth after complete unloading. Subtracting the total and elastic energies results in the plastic energy \( U_p = U_T - U_e \), see the inset in Figure 1b.

We define asymmetry as \( \% \text{Asym} = 100 \frac{\langle M' \rangle - \langle M'' \rangle}{\langle M \rangle} \), where \( \langle M' \rangle - \langle M'' \rangle \) is the difference between the mean mechanical indentation energies of the up-polarized and down-polarized states, while \( \langle M \rangle \) is the average for all polarities. Positive (negative) asymmetry indicates a larger value for the upward (downward) polarization. Figure 1d shows the asymmetry of the elastic, plastic, and total indentation energies as a function of the maximum indentation load. The total energy (elastic + plastic) is symmetric, reflecting that the mechanical energy provided by the indenter is independent of sample polarity, as it should. By contrast, asymmetry is observed for the plastic energy and thus also by the plasticity index (Figure S1, Supporting Information), which is the dimensionless parameter indicating the ratio of plastic energy to total energy, \( U_p / U_T \). Since fracture toughness is proportional to plasticity index,\(^{[14,15]} \) crack propagation can be sensitive to the sign of polarization.\(^{[9,10]} \) The elastic energy (Figure 1d) is also asymmetric, and this implies that not only plastic but also elastic responses must be polarity dependent. Using the Oliver–Pharr method,\(^{[16,17]} \) we have quantified one plastic and one elastic response: (a) hardness, as a measure of resistance to plastic deformation, and (b) contact stiffness, as a measure of the elastic response of the material. Both are found to depend on polarity (see Figure S1, Supporting Information).

Having demonstrated that flexoelectricity induces mechanical asymmetry, we can use this asymmetry to quantify the flexoelectric coefficient of ferroelectrics. We do this for two reasons: (i) to validate quantitatively the flexoelectric origin of the mechanical asymmetry and (ii) to demonstrate that flexocoupling coefficients can be measured by mechanical means. In piezoelectrics, finding a new and reliable way to measure flexoelectricity is particularly important because the conventional methods (electromechanical rather than mechanical) yield unrealistically high results\(^{[18]} \) due to piezoelectric contributions.\(^{[18,19]} \) We have derived a simplified analytical expression (see the Supporting Information) relating the flexocoupling coefficient to the difference in free energy (\( \Delta G \)) between the up and down polarized states:

\[
f = \frac{1}{6} \frac{\overline{E} \Delta G}{P_0 F}
\]

where \( P_0 \) is the ferroelectric spontaneous polarization (0.8 C m\(^{-2} \) for LiNbO\(_3\)),\(^{[12]} \) \( F \) is the maximum indentation load, and \( \overline{E} \) is the average of the elastic modulus measured for the up- and down-polarized states. Experimentally, the energy difference \( \Delta G \) can be obtained by subtracting the measured elastic energy (area under the unloading curve in Figure 1b) of the upward and downward polar states, i.e., \( \Delta G = U'_+ - U'_- \). Using the values obtained experimentally at 7 nN and Equation (1), the resulting flexocoupling coefficient \( f \) of SLN is 54 ± 4 V and for PPLN, it is 40 ± 5 V.

The obtained flexocoupling coefficients are still somewhat larger than the Kogan–Tagantsev expectation value, \( f < 10 \text{ V} \),\(^{[1–3]} \) but the order-of-magnitude agreement is nevertheless remarkable considering the simplifications made in order to obtain the analytical expression in Equation (1) (see the Supporting Information). The accuracy also represents an enormous improvement compared to beam-bending experiments, which, for ferroelectrics, always yield flexocoupling coefficients that are many orders of magnitude large.\(^{[3]} \)

Another notable consequence of these results is that they allow determining the polarity of a ferroelectric just by indenting its surface. This is demonstrated by contact stiffness measurements performed on PPLN (Figure 2), which show that downward-polarized material is stiffer while the upward-oriented one is more flexible.

Nanoindentation is, by definition, a destructive method, but since stiffness is an elastic property, it is not necessary to punch holes in order to read polarity. To prove this point, we use contact resonance force microscopy (CRFM)\(^{[20]} \) (see the “Experimental Section”); with this technique, we deliver an oscillatory force by vibrating the cantilever of an atomic force microscopy (AFM) in hard contact with the surface of the ferroelectric. The vibration amplitude peaks when the vibration frequency delivered by the cantilever coincides with the mechanical resonance frequency of the tip–sample contact.

Since contact resonance frequency depends on the tip–sample mechanical coupling, it is sensitive to the material’s stiffness, with higher resonance frequency corresponding to higher stiffness. The sensitivity has been used in the past to evidence contrast in Young’s modulus between domains of different ferroelastic orientations,\(^{[21,22]} \) but the technique was thought to be blind with respect to polarization sign. Our results, however, show that there is a measurable difference between the contact resonance frequencies of oppositely polarized domains (Figure 3), with downpolarized domains resonating at higher frequencies (stiffer) than up-polarized ones, in agreement with the nanoindentation results. This result is explained by the same arguments as in the indentation experiment: inhomogeneous deformation under the AFM tip induces a flexoelastic polarization that either adds to or subtracts from the piezoelectricity of the domains depending on their ferroelectric sign, resulting in asymmetric energy costs of deformation and thus different stiffness and contact resonance frequency. These results thus evidence the importance of tip-induced gradient effects for the tip–sample coupling in AFM, and demonstrate that such gradient effects can be exploited to mechanically read polarity.
To summarize, the results indicate that the mechanical responses (plastic and elastic) of a ferroelectric to inhomogeneous deformation are asymmetric and switchable. This switchable asymmetry was used both to quantify the flexoelectric coefficient itself and to determine the polar sign of a ferroelectric domain by purely mechanical means. This demonstration opens up new device possibilities such as reading a ferroelectric memory without electrodes or making coatings whose mechanical response to localized deformations (e.g., scratching) can be modified with a voltage. Nowadays, ferroelectrics are already considered as smart multifunctional materials on account of their switchable polarization and electromechanical response. Our results show that they should also be considered as smart mechanical materials.

Experimental Section

Sample Preparation and Characterization: Depending on the growth process, single crystals can be “stoichiometric,” with a ratio of 1:1:3 for Li⁺:Nb⁵⁺:O⁻², or (the most common) “congruent” which exhibit Li⁺ deficiency. Such lithium vacancies can result in defect dipoles that may be either parallel or antiparallel to the ferroelectric polarization, thus introducing an additional and extrinsic source of asymmetry[12,13] that can complicate the analysis of the results. To guarantee that any evidence of asymmetry originates from flexoelectricity, SLN single crystals, purchased from MTI Corporation, was used. These are single domain, so the SLN z-cut single crystal was cut in two equal pieces and was turned one upside down in order to study two areas with opposite polarization. Both crystals were chemical cleaned. They were sonicated for 15 min in acetone, isopropanol, and MilliQ water sequentially. Finally, both were glued in a metallic disc with silver paste, one with the

Figure 2. a) 3D plot of topography with the superimposed PFM phase image of a few indents performed in PPLN at 7 mN. Yellow means that the polarization is pointing up, whereas purple means that it is pointing down. b) Contact Stiffness measured as a function of the number of indent in part (a), showing that the relative stiffness is a direct indicator of a polar state, and therefore it is possible to “read” the polarization of a ferroelectric from its mechanical response.
polarization pointing upward and the other downward. A PPLN crystal, provided by Asylum Research, Santa Barbara, CA, USA was also studied and chemically cleaned like the SLN. These crystals were congruent; there were no commercially available stoichiometric crystals of PPLN. The polarization of the samples was checked by piezoresponse force microscopy (PFM) using an MFP-3D AFM from Asylum Research, Santa Barbara, CA.

**Nanoindentation:** Experiments were carried out in the load-control mode, using a UMIS instrument from Fischer-Cripps Laboratories equipped with a Berkovich pyramidal-shaped diamond tip. The thermal drift was always kept below $\pm 0.05 \text{ nm s}^{-1}$. Four different loads (7, 10, 15, and 20 mN) were applied. To ensure statistical robustness and accuracy of the results, a total of 50 indents per load (25 in each polar state, see Figure 1c) were performed in the SLN single crystal, and a total of 100 indents per load in the PPLN single crystal. Indents were spaced 15 µm apart (see Figure 1c), ensuring a sufficient independence of the indents in all cases.

**PFM Images on PPLN:** To correlate the direction of the polarization with each indentation, PFM experiments were carried out, using an MFP-3D AFM, and OMCL–AC240TM–R3 cantilevers, with $k \approx 2 \text{ N m}^{-1}$. PFM was mainly operated in Dual Amplitude Resonance Tracking (DART) mode to benefit from resonance signal enhancement; in PFM, an electrical ac signal was applied to the tip, used as top electrode, that excited the sample and mechanical response due to inverse piezoelectric effect was monitored.

**CRFM Images on PPLN:** Experiments were carried out using an MFP-3D AFM, in a controlled ambient with $\text{N}_2$. In CRFM, a mechanical ac excitation signal was applied to the cantilever in contact with the surface, and the resonance frequency was monitored, in this case also operating in DART mode. The mechanical resonance of the cantilever in contact with the surface strongly depends on the coupling with the mechanical properties of the surface. Nanosensors NCL Pt-coated tips, with $k \approx 48 \text{ N m}^{-1}$, were used. The contact force between the cantilever and the sample was about 25 µN.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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