Photovoltage from ferroelectric domain walls in BiFeO₃

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We calculate the component of the photovoltage in bismuth ferrite that is generated by ferroelectric domain walls, using first-principles methods, in order to compare its magnitude to the experimentally measured photovoltage. We find that excitons at the ferroelectric domain walls form an electric dipole layer resulting in a domain-wall driven photovoltage. This is of the same order of magnitude as the experimentally measured one, but only if the carrier lifetimes and diffusion lengths are larger than previously assumed.

Keywords: Domain walls, Excitons, Ferroelectric domains, Photovoltaic effect, Ferroelectrics, Oxides, Perovskite, DFT+U, Density functional calculations, First-principles calculations

**Introduction**

It has long been debated if and to what extent ferroelectric domain walls contribute to the photovoltaic effect (PVE) in ferroelectric oxides like BaTiO₃ and BiFeO₃. One possible origin of the PVE in BiFeO₃ is the so-called bulk photovoltaic effect (BPVE) [1–6]. The BPVE is a phenomenological term describing any photovoltaic effect that takes place in the homogeneous interior of the material, as opposed to interface effects. The BPVE in ferroelectrics such as BiFeO₃ and BaTiO₃ has been ascribed to noncentrosymmetric scattering or relaxation of electrons and holes after photoexcitation in noncentrosymmetric crystals, resulting in a net shift of charge carriers (“shift current”) [2, 3, 5, 6]. The BPVE depends on the polarization direction of the incoming light [4]. This dependence was indeed observed in the case of BiFeO₃, and it was hence concluded that the BPVE is at the origin of the photovoltaic effect in BiFeO₃ [7, 8].

Alternatively a domain-wall driven PVE (DW-PVE) has been proposed [9–11]. The argument in favor of the DW-PVE is a variation in the ferroelectric polarization of the atomic lattice at the domain walls. It has been suggested that this polarization variation gives rise to internal electrostatic fields at the domain walls. If true, this would mean that ferroelectric domain walls could separate photogenerated charge carriers in the same way as p–n junctions, without the need for p- and n-type doping, and it would be possible to align arbitrarily many such junctions in series and add up the individual voltages created by each single junction. However, the DW-PVE theory needs to postulate a local ferroelectric polarization not only of the spatially discrete atomic lattice, but also for the continuum of the valence electrons. But is it possible to define and determine the electric polarization of an arbitrary section of a crystal? Only then can this local polarization induce an electric field. Such approach was adopted in previous first-principles studies of voltage steps/drops at ferroelectric domain walls in PbTiO₃ [12] and BiFeO₃ [9] and yielded electrostatic potential drops (electronic potential steps) ranging from 0.02 to 0.2 V per domain wall for the dark state (without illumination). We will demonstrate below that this polarization-based approach does not yield the correct sign of the potential step/drop and the photoinduced charge density at domain walls in BiFeO₃. In contrast to the BPVE, the DW-PVE is independent of the polarization direction of the incoming light.

Some studies [6, 13] take the middle ground by assuming that the BPVE and the DW-PVE may exist simultaneously and can be cooperative or antagonistic depending on the system geometry. The argumentation here is that, besides the characteristic angular dependence of the BPVE with respect to the polarization of the incoming light, there is a polarization-independent offset in the photocurrent, which might be ascribed to a DW-PVE originating in an electrostatic field at the ferroelectric domain walls [6], and/or in a locally modified BPVE, caused by the local crystal-structure modifications at the domain walls [13].

Whereas the atomic structure of ferroelectric domain walls in BiFeO₃ is accurately known thanks to electron microscopy [14], experimental spectroscopy of photoelectrons at ferroelectric domain walls with atomic resolution is to our knowledge not possible today, but is perfectly within reach of first-principles calculations based on density-functional theory (DFT). In fact, optical excitations and the spatial distributions of the photoexcited charge carriers in molecules and solids are nowadays routinely investigated by means of many-body perturbation theory [15–18], such as the Bethe-Salpeter equation, or time-dependent density-functional theory. In the case of ferroelectric domain walls such studies would be hard to undertake because of the large system size needed to model a domain wall. However, there are approximate methods with a favorable balance between accuracy and computational cost, such as the excitonic ∆-self-consistent-field (ΔSCF) method, which yields more than qualitative agreement with highly accurate many-body methods [19], but can be performed at the same computational cost as a DFT ground-state calculation. The excitonic ΔSCF approach has been applied to study excitons in various systems, including organic dyes [20], polymers [19, 21], and surfaces [22]. Here we use it to directly determine the magnitude of the domain-wall driven photovoltaic effect in BiFeO₃, as given by the electronic potential induced by excitons localized at the domain walls.

**Methods**

We focus on the 71° and the 109° domain wall, for which the direction of the ferroelectric polarization in adjacent domains differs by about 71° and 109°, respectively. In rhombohedral perovskites like BiFeO₃ there exists also a 180° domain wall; however, due to its symmetry it should be photovoltaically inactive, and hence we do not consider it here. The DFT calculations were performed with the VASP code [24], using the projector-augmented wave (PAW)
FIG. 1. (Color online) 71° domain wall: (a) 280-atom supercell with two domain walls, (b) all three components of the ferroelectric polarization $P$, (c) polarization component $P_s$ perpendicular to the domain wall, and (d) polarization-based electronic potential energy $V_{pb}$ and electronic potential energy $V_e$ directly obtained from DFT (thick black lines), shifted to zero and smoothened [23]. The dashed lines in (d) denote open-circuit conditions.

FIG. 2. (Color online) The same as Fig. 1 for the 109° domain wall.

method and pseudopotentials with 5 (Bi), 16 (Fe), and 6 (O) valence electrons, respectively. We employed the local-spin-density approximation, and corrected the 3d states of Fe with a Hubbard-$U$ of 5.3 eV following Dudarev’s scheme [25]. The $U$ value for Fe was taken from the “materials project” database [26] and it is optimized for oxide formation energies, but it also yields an optical band gap of 2.54 eV close to the experimental one of $\approx 2.7–2.8$ eV [27–32]. This computational setup yields structural properties of BiFeO$_3$ in reasonable agreement with experiment [23, 33–37]. The reciprocal space was sampled with $2 \times 5 \times 3$ k-points for the 71° wall and with $2 \times 5 \times 5$ k-points for the 109° wall. Plane-wave basis functions with energies up to 520 eV were used. We employed a supercell approach with periodic boundary conditions, such that each supercell contained 120–280 atoms and two domain walls. Both the atomic positions and cell parameters were allowed to relax until the energy difference between subsequent ionic relaxation steps fell below 0.1 meV. Our calculated structural properties of the domain walls are similar to those in previous theoretical [14, 38–40] as well as experimental [14] works [23]. Excitons were modeled with the excitonic $\Delta$SCF method [20], namely by occupying the valence states with altogether ($N - N_X$) electrons and the conduction states with $N_X$ electrons, where $N$ and $N_X$ are the total number of electrons and excitons in the supercell, respectively. This was done in every iteration step of the electronic self-consistency cycle, using the same density functional for minimizing the energy as in a ground-state calculation. The geometries of the systems in the presence of an exciton were optimized when considering excitonic polaron states. Supercells containing 120 atoms were used in this case. The excitonic $\Delta$SCF method is suitable for exploring low-lying excited states only, whereas access to higher-lying excited states such as Rydberg states can be obtained using constrained DFT [41] or by maximizing the similarity of the excited-state orbitals to reference orbitals [42, 43]. In order to obtain the photovoltage per domain wall, $V_{photo}^{DW}$, we first determine the photovoltage profile, $V_{photo}$, which is given by the difference in electronic potential between the excited state, $V_e^X$, and the ground state, $V_e^{GS}$:

$$V_{photo}(s) = \left| V_e^X(s) - V_e^{GS}(s) \right|/(-|e|),$$

where $s$ is the coordinate perpendicular to the domain wall. The domain-wall contribution $V_{photo}^{DW}$ is then equal to the amplitude of the spatial variation of the photovoltage profile at
Polarization-based approaches [23] are positionally flexible with respect to the domain wall boundary conditions. By doing so, the electronic screening is already included. We still need to consider the screening by the lattice, which we calculate ab initio [23]. Note that, since we are working with DFT, $V_e$ is the Kohn-Sham potential. Furthermore, the use of periodic boundary conditions implies that we are calculating the short-circuit potential. The open-circuit potential is then obtained from the short-circuit potential by adding a constant gradient that compensates the potential slope in the domain interior [12]. The photovoltages are extrapolated [23, 44] to avoid finite-size effects.

**Results and discussion**

We begin the discussion with the electronic potential at the ferroelectric domain walls in the ground state (without excitons). Figure 1 depicts the ferroelectric polarization, the electronic potential energy per electron, $V_e$, and the polarization-based potential energy per electron, $V_{eb}^p$, as calculated from the polarization variation at the wall including screening [23]. If the polarization-based approach was valid, $V_{eb}^p$ should yield the same potential step/drop at the wall as $V_e$. $V_e$ has a potential minimum on the right-hand side of the wall. Accordingly, we expect excess electrons to accumulate on the right-hand side of the wall. The magnitude of the electronic potential drop (the electrostatic potential step) at the wall is 0.13 eV (extrapolated [23]).

$V_{eb}^p$ exhibits an electronic potential step at the wall instead of a potential drop, and the magnitude of the potential variation, 45 meV, is too small. For the 109° domain wall (Fig. 2) the potential has a pronounced minimum inside the domain wall, and a very small slope in the domain interior corresponding to an electronic potential drop of about 17 meV [23]. $V_{eb}^p$ lacks the minimum inside the wall, and exhibits an electronic potential step instead of a potential drop, and the magnitude of the potential variation, 56 meV, is too large. We conclude that the polarization-based approach fails to provide the correct sign and magnitude of potential steps/drops at domain walls in BiFeO$_3$. 

**FIG. 3.** (Color online) Smoothened densities of excess electrons and holes for excitons (X) at the 71° domain wall before (“instantaneous”) and after (“relaxed”) polaron formation: (a) for an X density of 0.1 X per 120-atom supercell (a planar X density of $\approx 2.3 \times 10^{13} \text{X/cm}^2$) a large polaron forms, (b) for an X density of 1 X per 120-atom supercell ($\approx 2.3 \times 10^{14} \text{X/cm}^2$) a small polaron forms. The magnitude of the electronic potential drop (the electronic potential variation, 56 meV , is too small. For the 109° domain wall (Fig. 2) the potential has a pronounced minimum inside the domain wall, and a very small slope in the domain interior corresponding to an electronic potential drop of about 17 meV [23]. $V_{eb}^p$ lacks the minimum inside the wall, and exhibits an electronic potential step instead of a potential drop, and the magnitude of the potential variation, 56 meV, is too large. We conclude that the polarization-based approach fails to provide the correct sign and magnitude of potential steps/drops at domain walls in BiFeO$_3$. 

**FIG. 4.** (Color online) Smoothened densities of excess electrons and holes for exciton (X) densities in the coexistence region of the large (dashed line) and the small (solid line) X polaron in a 120-atom supercell (SC) with 71° domain walls. (a) For a planar X density $n_{X}^{DW}$ of $\approx 1.2 \times 10^{14} \text{X/cm}^2$ the small X polaron is stable and the large X polaron is metastable. (b) For a planar X density of $\approx 2.3 \times 10^{14} \text{X/cm}^2$ the large X polaron is stable and the small X polaron is metastable. (c) Formation energies of the small (small filled circles) and the large (large empty circles) X polaron. The large X polaron is stable for X densities below $n_{X}^{crit}$ and between $n_{X}^{crit}$ and $n_{X}^{met}$ it is metastable.
Next, we will add an electron-hole pair (an exciton) to our supercell. Depending on the exciton density, two different types of exciton polarons form, as depicted in Fig. 3. For low exciton densities, a large exciton forms with photoelectrons and holes localized on opposite sides of the domain wall resulting in an excitonic dipole moment. A small exciton is metastable. Since only the large exciton configuration will lead to a sizable photovoltage, we determine next under which experimental conditions the large exciton forms.

In Ref. 46 it was found that the photocurrent in BiFeO$_3$ follows a rate equation, $n = g - n/\tau$, where $n$ is the photocarrier density, $g$ is the photocarrier generation rate, and $\tau = 75 \mu s$ is the photocarrier lifetime. Here we adopt the same rate equation for the exciton density $n_X$, which in the steady state is given by

$$n_X = g\tau = \frac{I_{\text{light}}(1 - R)/\tau}{E_{\text{photon}} d_{\text{film}}}, \quad (3)$$

where $I_{\text{light}}$ is the intensity of the light in W/cm$^2$, $d_{\text{film}}$=100 nm is the thickness of the experimentally studied films in Refs. 7 and 11, $E_{\text{photon}}$=3.06 eV is the photon energy of the laser used in the experiment in Ref. 7, and $R = 0.27$ is the reflectivity calculated at this photon energy from first principles. In the following we assume that 100% of the penetrating light is absorbed [23], in line with experiment [47]. We assume further that all photocarriers within a distance $l_{\text{diff}}$ (the diffusion length) from the domain wall reach the domain wall. Figure 4(b) shows that the critical exciton density from the supercell calculation is $n_X^{\text{cell}} \approx 0.22 X$ per supercell, corresponding to a planar exciton density of $\approx 5.2 \times 10^{13}/\text{cm}^2$. This is equal to a photoelectron density of $3.7 \times 10^{18}/\text{cm}^3$ if one assumes a diffusion length of 140 nm. From Eq. (3) we obtain the critical light intensity for the transition between large and small exciton polarons [23], which is depicted in Fig. 5. In the case of natural sunlight and a diffusion length near typical domain-wall spacings of a few hundred nanometers, the large exciton forms, which should give rise to a photovoltage, whereas in the case of a thousandfold concentrated sunlight, such as in a concentrator solar-cell setup, the small exciton polaron forms, which should contribute less to the photovoltage, if at all. The small exciton polaron might be detectable with photoluminescence spectroscopy as a state inside the band gap, or as a drop in the photovoltage at illumination intensities of...
the order of 0.1–1 W/cm² or higher, depending on the carrier diffusion length.

In the following we consider moderate light intensities, at which the large exciton forms. The domain-wall photovoltage is the spatial potential variation induced by the large exciton at the domain wall, depicted in Fig. 6. The potential generated by the excitons (partially) compensates the electronic potential drop (the electrostatic potential step) at the domain wall. The relation between exciton density and light intensity is the same as before, now we use the parameters of the experimental photovoltage measurement from Ref. 11 in Eq. (3) \( E_{\text{photon}} = 3.31 \text{ eV}, R = 0.25 \), domain-wall spacing \( d_{\text{DW}} = 140 \text{ nm} \) [23]. We also consider an estimated lower limit of \( l_{\text{diff}} = 10 \text{ nm} \) similar to that assumed in Ref. 11, and a shorter carrier lifetime of 1 ns, similar to that reported in Ref. 48. The resulting open-circuit photovoltage contribution per domain wall, together with the experimental results from Ref. 11, are depicted in Fig. 7 and extrapolated to lower light intensities using a power law [23]. In the case of the 109° domain wall we can only give a possible range (shaded area) [23]. The experimental photovoltage is the total photovoltage of a film with 71° domain walls, consisting of all photovoltaic effects (bulk and domain-wall effects), divided by the number of domains. The experimental conditions are well inside the range in which the large exciton forms (marked by the vertical solid line), for which our approach should be valid. The calculated domain-wall photovoltage matches the experimentally measured one only in the most optimistic scenario [Fig. 7(a)], in which we assume a photocarrier density of \( 10^{16} \text{ cm}^{-3} \) to \( 10^{19} \text{ cm}^{-3} \), a carrier lifetime of 75 µs, and a carrier diffusion length of 140 nm. For comparison, in Ref. 11 a carrier density of about \( 10^{12} \text{ cm}^{-3} \) to \( 10^{13} \text{ cm}^{-3} \), a carrier diffusion length of 8 nm, and a lifetime of 35 ps were assumed, and in Ref. 48 a lifetime of 1 ns. If we assume such conditions [Figs. 7(b) and 7(c)], the DW-PVE is orders of magnitude too small to account for the major part of the measured photovoltage in BiFeO₃. The domain-wall photovoltage may be further reduced through screening by free charge carriers and/or point defects that accumulate at the domain walls.

**Conclusion** We have analyzed the contribution of ferroelectric domain walls to the photovoltage in BiFeO₃ using first principles methods. In general we find that the ferroelectric polarization profile does not allow one to determine the correct sign and magnitude of the electrostatic potential at the domain walls. Instead the electronic potential should be directly determined from \textit{ab initio} calculations. The domain-wall driven photovoltages can be as large as the experimentally measured total photovoltages (up to \( \approx 10 \text{ mV per domain wall} \)), and may therefore be responsible for a large portion of the photovoltaic effect in BiFeO₃. This, however, is true only if the carrier lifetimes and carrier diffusion lengths are of the order of \( \approx 100 \mu \text{s} \) and \( \approx 100 \text{ nm} \), respectively, which is orders of magnitude larger than previously assumed. Otherwise, the domain-wall photovoltage is orders of magnitude smaller, and then the major fraction of the photovoltage should originate from other effects, for example bulk effects. Furthermore, there is a transition from a large to a small exciton polaron at high illumination intensities of the order of 0.1–1 W/cm² or higher, which might be experimentally detected as a drop in the photovoltage at high light intensities, or as a state inside the band gap in photoluminescence spectroscopy.
ACKNOWLEDGEMENT

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Photovoltage from ferroelectric domain walls in BiFeO₃:
Supplemental Material

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Table I contains our calculated structural parameters of BiFeO₃ in the R₃c phase in comparison with experimental data. Lattice parameters deviate from experiment by about 2%, typical for LDA calculations. Ferroelectric displacements of atoms from the ideal perovskite structure deviate by up to 20%. Ferroelectric distortions of the unit cell (c/a ratio and rhombohedral cell angle) are severely underestimated by ≈ 80%, nevertheless the ferroelectric polarization is in good agreement with experiment, indicating that ferroelectric properties are well captured by our computational setup.

### Calculated ground-state properties of BiFeO₃

<table>
<thead>
<tr>
<th></th>
<th>Expt</th>
<th>ideal perovskite</th>
<th>this work</th>
<th>relative error</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.57330(5); 5.57882(5); 5.5876(3); 5.58132(5)</td>
<td>5.506</td>
<td>(-1.3%)</td>
<td></td>
</tr>
<tr>
<td>c (Å)</td>
<td>13.84238(16); 13.867(1); 13.86932(16); 13.87689(15)</td>
<td>13.507</td>
<td>(-2.4%)</td>
<td></td>
</tr>
<tr>
<td>c/a</td>
<td>2.4817⁷; 2.48370⁷; 2.48607⁰; 2.48633⁰</td>
<td>√6</td>
<td>2.4556</td>
<td>(-81%)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>372.36⁷; 373.06⁷; 373.83⁷; 374.37⁷; 374.94⁷; 375.05⁰</td>
<td>342.75</td>
<td>(-8%)</td>
<td></td>
</tr>
<tr>
<td>zₚₑ</td>
<td>0.22021(09); 0.22046(8); 0.22067(8); 0.2209(5); 0.2209(6); 0.2212(15)</td>
<td>0.25</td>
<td>0.227</td>
<td>(-20%)</td>
</tr>
<tr>
<td>x₀</td>
<td>0.443(2); 0.44506(22); 0.4453(3); 0.44582(22); 0.4460(8); 0.44694(28)</td>
<td>0.5</td>
<td>0.436</td>
<td>(+12%)</td>
</tr>
<tr>
<td>y₀</td>
<td>0.0124⁷; 0.01700(28); 0.0173(12); 0.01789(28); 0.01814(35); 0.0185(13)</td>
<td>0.0</td>
<td>0.018</td>
<td>(+0%)</td>
</tr>
<tr>
<td>z₀</td>
<td>0.9511(5); 0.9513(5); 0.9515(11); 0.95183(14); 0.95183(11); 0.9543(20)</td>
<td>0.0</td>
<td>0.961</td>
<td>(-15%)</td>
</tr>
<tr>
<td>α (°)</td>
<td>59.34°; 59.35°; 59.35°; 59.39°; 59.39°; 59.42°</td>
<td>60</td>
<td>59.89</td>
<td>(-81%)</td>
</tr>
<tr>
<td>ω (°)</td>
<td>12.2°; 12.3°; 12.4°; 12.5°; 12.5°; 12.6°</td>
<td>0</td>
<td>14.4</td>
<td>(+14%)</td>
</tr>
<tr>
<td>P</td>
<td>≈ 100; 94</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Moreau et al. [1]. Single crystal X-Ray and neutron powder diffraction at room temperature.
* Palewicz et al. [2]. Neutron powder diffraction at 298 K.
* Palewicz et al. [3]. Neutron powder diffraction at 298 K.
* Palewicz et al. [3]. Neutron powder diffraction at 5 K.
* Fischer et al. [4]. Neutron powder diffraction at 293 K.
* Fischer et al. [4]. Neutron powder diffraction at 4.2 K.
* Lebeugle et al. [5]. Single crystals, R₃c phase, room temperature.

In Table II we compare our calculated DW formation energies and widths for different supercell sizes with those available in the literature. For historical reasons, we include the 180° wall, although we do not consider it in the main article. Note that Ref. 6 found close agreement between domain-wall structures seen in electron microscopy and those calculated from first principles. This is true in particular for the domain-wall widths, which are as narrow as about one atomic layer in the case of the 109° domain wall and two atomic layers in the case of the 180° domain wall, both according to experiment and to first-principles calculations (see Fig. 1 and 2 in Ref. 6). The 71° domain wall is slightly broader and extends over about three atomic planes. We fitted the polarization and tilt profiles P and A with a tangent hyperbolic to extract the DW width ξₚ.

\[
P_r(s) = P^\infty_r \tanh[(s - s_0)/\xi_P],
\]

where \( P \) is the rotating component of the polarization, \( P^\infty \) is its asymptotic value far away from the domain wall, \( s \) is the coordinate perpendicular to the domain wall, and \( s_0 \) is the position of the domain wall. In this section, different from below and the main article, polarization profiles are calculated from ionic positions and formal ionic charges (Bi³⁺, Fe³⁺, and O²⁻). Tests indicated that applying the more sophisticated Born effective charges changed the resulting polarization essentially only by a prefactor. The DW energies are close to those of Diéguez [7] and do not change very strongly with supercell size. Polarization and tilt profiles (Fig. 2) are also converged with respect to supercell size.

Figure 1 shows the layer-resolved ionic sublattice displacements compared to a paraelectric reference structure without octahedral tilts. The displacement profiles are atomically sharp.
Electron potential step at the domain wall

Figure 3 depicts the magnitude of the electrostatic open-circuit potential step at the domain wall in the ground state (without excitons). These data are also listed in Table III. The potential converges to a positive number for both walls, so that it has the opposite sign compared to the polarization-based potential. We obtain the limit $\Delta V_{DW}^{\text{pol}}(\infty)$ of the potential step for large domain-wall distances $d_{DW}$ by fitting with a power law:

$$\Delta V_{DW}^{\text{pol}}(d_{DW}) = \Delta V_{DW}^{\text{pol}}(\infty) + c \cdot d_{DW}^p,$$

where $\Delta V_{DW}^{\text{pol}}(\infty)$, $c$, and $p$ are fit parameters. The resulting exponents are $p_{71° \text{ DW}} = -2.00$ and $p_{109° \text{ DW}} = -2.07$.

### Table II. DW energies $E$ and DW widths ($\xi_p$: polarization, $\xi_A$: tilt wall width) as function of the number of atoms $n_{\text{atoms}}$ contained in the supercell. Errors are standard errors of the fit.

<table>
<thead>
<tr>
<th>$\Phi_{\text{mJ/m}^2}$</th>
<th>$\xi_p$ (Å)</th>
<th>$\xi_A$ (Å)</th>
</tr>
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<tbody>
<tr>
<td>71°</td>
<td>2.94±0.01</td>
<td>3.4±0.7</td>
</tr>
<tr>
<td>71°</td>
<td>2.94±0.05</td>
<td>2.4±0.4</td>
</tr>
<tr>
<td>71°</td>
<td>2.94±0.04</td>
<td>2.6±0.3</td>
</tr>
</tbody>
</table>

### Table III. Electrostatic open-circuit potential step $-\Delta V_{DW}^{\text{pol}}$ of the 71° and 109° domain walls without excitons as a function of the domain-wall distance $d_{DW}$ (the number of atoms in the supercell, $n_{\text{atoms}}$), as depicted in Fig. 3.

<table>
<thead>
<tr>
<th>$n_{\text{atoms}}$</th>
<th>$-\Delta V_{DW}^{\text{pol}}$ (mV)</th>
<th>$d_{DW}$ (Å)</th>
</tr>
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<tbody>
<tr>
<td>160</td>
<td>71°</td>
<td>31.2</td>
</tr>
<tr>
<td>200</td>
<td>109°</td>
<td>39.0</td>
</tr>
<tr>
<td>240</td>
<td>109°</td>
<td>46.8</td>
</tr>
<tr>
<td>280</td>
<td>71°</td>
<td>54.6</td>
</tr>
<tr>
<td>$\infty$</td>
<td>133</td>
<td>$\infty$</td>
</tr>
</tbody>
</table>

The ferroelectric polarization was calculated from ionic displacements from ideal perovskite positions using direction-averaged Born effective charges $Z^*$ of the R3c phase ($Z_{\text{Bi}}^* = 4.865, Z_{\text{Fe}}^* = 3.886, Z_{\text{O}}^* = -2.917$). First a smooth curve was fitted to the polarization profile perpendicular to the domain.
FIG. 2. Polarization $P$ profiles for different supercell sizes (a) for the 71°, (b) for the 109° domain wall, and (c) for the 180° wall. Components that do not change sign at the domain wall are drawn transparent. Dashed transparent lines are the bulk reference. The profiles were fit according to Eq. (1). $s_0$ is the position of the domain wall.

The screening (the real part of the static dielectric constant $\varepsilon$) is calculated ab initio using the primitive rhombohedral cell and a $k$-point mesh of $10 \times 10 \times 10$ points. $\varepsilon$ is diagonal in the coordinate system spanned by the hexagonal lattice vectors (the pseudocubic [111], [110], and [11̅2] directions, parallel and perpendicular to the ferroelectric polarization). The electronic contribution $\varepsilon^e$ has the eigenvalues 7.4, 8.1, and 8.1, the lattice (ionic) contribution has the eigenvalues 21, 37, and 37. In order to obtain the screening in the direction perpendicular to a domain wall, one needs to rotate $\varepsilon$ and obtains $\varepsilon^e_{ss} = 7.6$, $\varepsilon^{\text{ion}}_{ss} = 26$, and $\varepsilon^{\text{total}}_{ss} = 34$ for the 71° domain wall and $\varepsilon^e_{ss} = 7.9$, $\varepsilon^{\text{ion}}_{ss} = 32$, and $\varepsilon^{\text{total}}_{ss} = 40$ for the 109° domain wall. Both in the case of the polarization-based potential in the ground state and in the case of the photovoltage, screening is included a posteriori. For $P_s(s)$ we used the fitted curve from Eq. (3).

Electronic and lattice screening

where $s^-$ is a position in the domain interior on the left hand side of the domain wall, and $\varepsilon_{ss}$ is the calculated electronic dielectric constant for an electric field perpendicular to the domain-wall plane (see below). For $P_s(s)$ we used the fitted curve from Eq. (3).
The penetration depth calculated from our first-principles absorption coefficient (which is similar to the one measured in Ref. 11) is about 33 nm at the photon energy of 3.06 eV that was used in experiment, such that about 95% of the penetrating light is absorbed in a 100 nm thick film. In Ref. 12 the penetration depth was extrapolated to the limit of infinitely large domain-wall distances. In the case of the 71° domain wall the extrapolated voltages (numbers in boldface in Tab. IV) are depicted in Fig. 7 in the main article. In the case of the 109° domain wall it is not possible to perform such an extrapolation because there is no strongly confining potential slope. Instead we depict the range of photovoltages between that of the largest supercell (280 atoms), and the largest photovoltage as a function of supercell size (numbers in boldface in Tab. IV).

Excitonic densities

Figure 4 shows the densities of excess electron and hole for an exciton at the 109° domain wall. Similar to the case of the 71° wall (see Fig. 3 in the main article), a large or small exciton polaron forms depending on the exciton density.

\[ \varepsilon_{\text{eff}} = \varepsilon_{\text{on}} + \varepsilon_{\text{ss}}. \]

The effective dielectric constant is \( \varepsilon_{\text{eff}} = 4.4 \) for the 71° DW and \( \varepsilon_{\text{eff}} = 5.0 \) for the 109° DW.

Photovoltage

Figures 5 and 6 show all calculated photovoltage profiles for the 71° and the 109° domain wall in the 280-atom supercell.

The open-circuit (OC) voltage profiles were obtained from the short-circuit (SC) voltage profiles by adding a constant gradient such that in the domain interior the resulting OC voltage slope vanishes, as depicted in Fig. 7.

Table IV contains the calculated short-circuit and open-circuit domain-wall photovoltages obtained with different supercell sizes (different domain-wall distances), and those extrapolated to the limit of infinitely large domain-wall distances. In the case of the 71° domain wall the extrapolated voltages (numbers in boldface in Tab. IV) are depicted in Fig. 7 in the main article. In the case of the 109° domain wall it is not possible to perform such an extrapolation because there is no strongly confining potential slope. Instead we depict the range of photovoltages between that of the largest supercell (280 atoms), and the largest photovoltage as a function of supercell size (numbers in boldface in Tab. IV).

Parameters used in the rate equation

Light penetration depth in a BiFeO₃ film

The penetration depth calculated from our first-principles absorption coefficient (which is similar to the one measured in Ref. 11) is about 33 nm at the photon energy of 3.06 eV that was used in experiment, such that about 95% of the penetrating light is absorbed in a 100 nm thick film. In Ref. 12 the penetration depth was estimated to be 50 nm, which would result in 86% of the penetrating light being absorbed.


**FIG. 7.** Short-circuit (SC) photovoltage profile (thin solid line), open-circuit (OC) photovoltage profile (dashed line) for a 280-atom supercell with 71° domain walls, and the interval $I_{av}$ (thick solid line) in which the average voltage slope was compensated by a constant gradient.

**Carrier diffusion length** It is difficult to accurately estimate the photocarrier diffusion length $l_{diff}$, therefore two different numbers are considered in the main article. An upper boundary should be the length of a ferroelectric domain.

**Exciton density at the domain wall** The planar exciton density $n_X^{DW}$ is given by the number of excitons $N_X$ and the domain-wall area $A_{DW}$ contained in the supercell, $n_X^{DW} = N_X/(2A_{DW})$. The domain-wall area is $A_{DW} \approx 42.7 \text{Å}^2$ for the 71° domain wall and $A_{DW} \approx 30.2 \text{Å}^2$ for the 109° domain wall. Assuming that all photocarriers within $l_{diff}$ reach the domain walls, the exciton density can be expressed as $n_X = n_X^{DW}/l_{diff}$, where $n_X^{DW}$ is the planar exciton density at the domain wall. Then Eq. (3) in the main article becomes

$$I_{light} = \frac{n_X^{DW}E_{photon}d_{film}}{l_{diff}(1-R)\tau}. \quad (6)$$

**Extrapolation of domain-wall photovoltages to large domain-wall distances**

Figure 8 shows the open-circuit photovoltage as a function of the distance between two 71° domain walls $d_{DW}$. The photovoltage does not yet converge for our employed $d_{DW}$ (supercells with up to 280 atoms), therefore we extrapolate it to the limit of large $d_{DW}$ by means of a fit function:

$$V_{photo}^{DW}(d_{DW}) = V_{photo}^{DW}(\infty) - \Delta V_{photo}^{DW}e^{-\frac{d_{DW}^2}{l_{diff}^2}}, \quad (7)$$

where $V_{photo}^{DW}(\infty)$, $\Delta V_{photo}^{DW}$, and $b$ are fit parameters. $V_{photo}^{DW}(\infty)$ is the extrapolated domain-wall photovoltage that is used in the main article. The fit function was chosen based on the exponential decay of the wave function of a particle in a linear potential (Airy function [13]). The data for the largest considered $X$ density of 1 $X$ per supercell could not be extrapolated to large $d_{DW}$ and were therefore left out of the analysis. In the case of the 109° domain wall, see Fig. 9, the domain-wall photovoltage increases, then decreases with increasing domain-wall distance. Here we cannot easily extrapolate to large domain-wall distances, instead we consider the maximum photovoltage as a function of supercell size as an upper limit. As a lower limit we take the photovoltage of the largest considered domain-wall distance.

**TABLE IV.** Calculated short-circuit (SC) and open-circuit (OC) domain-wall photovoltages $V_{photo}^{DW}$ for different domain-wall distances $d_{DW}$ (different numbers of atoms $n_{atoms}$ in the supercell) and extrapolations to infinitely large domain-wall distances as a function of the number of excitons $n_X$ per supercell for the 71° and the 109° domain walls. Unscremed voltages are marked by the subscript “us”, such as SCus. The photovoltages printed in **boldface** are the ones drawn in Fig. 7 in the main article.
FIG. 8. Open-circuit photovoltage of the 71° domain wall as a function of the number of atoms \( n_{\text{atoms}} \) in the supercell and of the distance between domain walls, \( d_{\text{DW}} \) (data points from Table IV). Solid lines are fits with Eq. (7), dotted lines are a guide to the eye.

Extrapolation of domain-wall photovoltages to low light intensities

The photovoltages shown in Fig. 7 in the main article were extrapolated to low exciton densities (low light intensities \( I \)) with a power law of the form

\[
V_{\text{DW, photo}}^{\text{IV}}(I) = V_{\text{DW, photo}}^{\text{IV}}(I_0) \left( \frac{I}{I_0} \right)^p
\]

that was optimized using the three data points corresponding to the lowest light intensities. In the case of the 71° domain wall \( p \approx 1.14 \). The photovoltage data of the 109° DW exhibit too much noise to safely extrapolate them to low light intensities.

Smoothening of charge densities and potential

The rapid and strong oscillations of charge densities and electronic potential at atomic nuclei, which obscure variations on a larger scale, were smoothened in the following way: First the charge density or potential was averaged in a plane parallel to the domain-wall plane [in the \( r-t \) plane, compare Figs. 1(a) and 2(a) in the main article], then a sliding-window average over an \( s \) interval of one atomic plane spacing, like in Ref. [10], was applied to the excess charge carrier densities.

In order to smoothen the potential a low-pass filter was applied that removed wavelengths up to one atomic plane spacing. The two smoothening methods should be roughly equivalent, and it is only for historical reasons that one was used for the densities and the other for the potential.

[6] Yi Wang, Chris Nelson, Alexander Melville, Benjamin Winchester, Shunli Shang, Zi-Kui Liu, Darrell G Schlom, Xiaoqing Pan, and Long-Qing Chen, “BiFeO\(_3\) domain wall energies and


