Ab initio study of ferroelectricity in edged PbTiO3 nanowires under axial tension

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Ab initio study of ferroelectricity in edged PbTiO₃ nanowires under axial tension

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The atomicistic and electronic structures of PbTiO₃ nanowires with characteristic edges consisting of (100) and (010) surfaces and the crucial role of axial tensile strain on ferroelectricity have been investigated by means of ab initio density-functional theory calculations. Ferroelectricity is enhanced at the edge of the PbO-terminated nanowire because the Pb-O covalent bond that predominates ferroelectric distortions is locally strengthened. On the other hand, a considerable suppression is found in the TiO₂-terminated nanowire, caused by the charge transfer from the Pb-O site to the Ti-O site. Surprisingly, the smallest PbO-terminated nanowire with a cross section of only one-unit cell can possess ferroelectricity while ferroelectricity disappears in the TiO₂-terminated nanowires with a cross section smaller than four-by-four cells (diameter of about 17 Å). However, ferroelectricity is recovered by axial tension, where smaller nanowires require larger critical strains.

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I. INTRODUCTION

Ferroelectric (FE) nanowires have drawn much attention as one-dimensional multifunctional materials for technological applications, e.g., ferroelectric random access memories (FeRAMs).

In recent years, single-crystalline PbTiO₃ and BaTiO₃ nanowires with a diameter of 5–12 nm have been manufactured, and smaller nanowires with several lattice spacings are anticipated in the near future. Nanowires fabricated on a substrate have an atomically sharp edge structure consisting of (100) and (010) perovskite surfaces. Moreover, the edge structure is commonly observed in nanostructured materials as well as the mechanical deformation. Since the coordination number rapidly decreases at the edge in nanowires, the balance of both interactions differs considerably from that in the bulk. Hence, the edge structure can strongly affect ferroelectricity, especially in a thin nanowire where the ratio of the edge with respect to the entire volume is quite high. In addition, nanowires are normally subjected to axial tension or compression, which sometimes recovers or destabilizes the ferroelectric distortions. Thus, ferroelectricity in the edged nanowire and its response to the axial strain are fundamental issues and worth investigating.

Geneste et al. studied the finite-size effects in BaTiO₃ nanowires with an edge structure using ab initio (first-principles) calculations based on the density-functional theory (DFT) and revealed a critical diameter for ferroelectricity.

However, the situation may differ in the case of PbTiO₃ where the ferroelectric instability is quite different from that in BaTiO₃. Moreover, the termination layer of the PbTiO₃ (001) surface has immense influence on ferroelectricity while a moderate effect is found in the case of BaTiO₃ surface. Thus, it is also necessary to investigate how ferroelectricity in the PbTiO₃ nanowire is affected by terminations making up the edge structure.

In this paper, we study PbTiO₃ nanowires with atomically sharp edges consisting of (100) and (010) surfaces by means of ab initio density-functional theory calculations in order to elucidate the intrinsic effects of edges on ferroelectricity. In addition, the finite-size dependence and the crucial role of the axial tensile strain are investigated. This paper is organized as follows. In Sec. II, we describe the details of the simulation procedure. In Sec. III, the relaxed atomic configuration and electronic structure of the PbTiO₃ nanowires are presented, and the site-by-site ferroelectric distortions are discussed by focusing on the edge. We also investigate the effect of wire size on ferroelectricity. Furthermore, we discuss the ferroelectric behavior under axial tension and present the critical strain. Finally, the results are summarized in Sec. IV.

II. COMPUTATIONAL DETAILS

A. Simulation method

Ab initio calculations based on the density-functional theory and revealed a critical diameter for ferroelectricity. However, the situation may differ in the case of PbTiO₃ where the ferroelectric instability is quite different from that in BaTiO₃. Moreover, the termination layer of the PbTiO₃ (001) surface has immense influence on ferroelectricity while a moderate effect is found in the case of BaTiO₃ surface. Thus, it is also necessary to investigate how ferroelectricity in the PbTiO₃ nanowire is affected by terminations making up the edge structure.

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II. COMPUTATIONAL DETAILS

A. Simulation method

Ab initio calculations based on the density-functional theory are conducted using the Vienna Ab initio Simulation Package (VASP). The electronic wave functions are expanded in-plane waves up to a cutoff energy of 500 eV. The pseudopotentials based on the projector augmented wave (PAW) method explicitly include the O 2s and 2p, the Ti 3s, 3p, 3d, and 4s, and the Pb 5d, 6s, and 6p electrons in the valence states. The local-density approximation (LDA) of the Ceperley-Alder form is employed to evaluate the exchange-correlation energy.

B. Simulation models and procedure

We study PbTiO₃ nanowires with edges consisting of (100) and (010) surfaces, where there are two possible terminations of the PbO and TiO₂ atomic layers. Figures 1(a) and 1(b) show the simulation models of the PbO-terminated and TiO₂-terminated nanowires, respectively. Each nanowire has a cross section in which four perovskite unit cells are arranged in the x and y directions, which is denoted as the...
cross section of 4 × 4 unit cells below. Spontaneous polarization aligns along the z direction (the axial direction in the nanowire). Since a three-dimensional periodic boundary condition is applied in the calculations, a vacuum region of \( l_v = 12 \text{ Å} \) thickness is introduced in both the x and y directions so that undesirable interaction between the neighboring nanowires is sufficiently avoided. The simulation cell dimensions in the x, y, and z directions are initially set to \( 4a + l_v, 4a + l_v \), and c, respectively, where the theoretical lattice constants of the tetragonal bulk, \( a = 3.867 \text{ Å} \) and \( c = 4.034 \text{ Å} \) \((c/a = 1.043)\), are used. The Brillouin-zone (BZ) integration is carried out with a \( 2 \times 2 \times 6 \) k-point mesh generated by the Monkhorst-Pack scheme.\(^\text{29}\)

The unit cells at an edge, on a surface, and inside the nanowire are referred to as “edge cell,” “surface cell,” and “inside cell,” respectively (see Fig. 1). The terms “edge bond,” “surface bond,” and “inside bond” denote the Pb-O covalent bonds in the corresponding cells for descriptive purpose.

To obtain an equilibrium structure, atomic positions and a cell size in the z direction are fully relaxed using the conjugate gradient method until all the Hellmann-Feynman forces and the stress component \( \sigma_{zz} \) are less than \( 1.0 \times 10^{-3} \text{ eV/Å} \) and \( 1.0 \times 10^{-2} \text{ GPa} \), respectively.

Smaller nanowires with cross sections of 1 × 1, 2 × 2, and 3 × 3 unit cells are investigated in the same manner in order to elucidate the effects of nanowire size and axial strain on ferroelectricity. For tensile simulations, a small axial strain, \( \Delta \varepsilon_{zz} \), is applied to the simulation cell step by step. At each strain, internal atoms are fully relaxed under the fixed cell dimensions.

III. RESULTS AND DISCUSSION

A. Ferroelectricity in unstrained nanowires

We introduce a local polarization in two fictitious Pb-edged and Ti-edged “unit cells” as illustrated in Fig. 2 for PbO-terminated and TiO\(_2\)-terminated nanowires, respectively. The local polarization in the cell, \( \mathbf{P} \), is evaluated by

\[
\mathbf{P} = \mathbf{P}_{\text{cell}} - \mathbf{P}_{\text{edge}} - \mathbf{P}_{\text{surface}} - \mathbf{P}_{\text{inside}}
\]

where \( \mathbf{P}_{\text{cell}} \) is the total polarization of the cell, and \( \mathbf{P}_{\text{edge}}, \mathbf{P}_{\text{surface}}, \mathbf{P}_{\text{inside}} \) are the contributions from the edge, surface, and inside cells, respectively.

We have calculated the polarization \( \mathbf{P} \) for PbO-terminated and TiO\(_2\)-terminated nanowires, and found that the polarization is strongly dependent on the nanowire size and axial strain.
The local polarization evaluated via Eq. (1), $P$, is second highest, is nearly equal to that of the film. Polarization in the inside cell is also comparable to that of the bulk. On the other hand, little polarization is found in the TiO$_2$-terminated nanowire. More specifically, the inner cell in the nanowire exhibits higher polarization, which is the opposite of the trend found in the PbO-terminated nanowire. Thus, ferroelectricity in the vicinity of the edge is enhanced in the PbO-terminated nanowire while it is considerably suppressed in the TiO$_2$-terminated nanowire. Note that the TiO$_2$-terminated nanowire shrinks in the $c$ (axial) direction at equilibrium, resulting in considerable suppression of tetragonality, $c/a=0.973$ ($c/a=1.043$ for bulk), where $a$ denotes the averaged lateral lattice parameter of the wire. It was reported that ferroelectricity in PbTiO$_3$ is suppressed as uniaxial compression is applied along the $c$ axis, meaning the decrease in tetragonality. Hence, the tiny magnitude of polarization of the TiO$_2$ termination even in the inside cell is due to not only the effect of TiO$_2$-terminated surface but also the highly reduced tetragonality.

It was both theoretically and experimentally revealed that the prominent ferroelectricity and large lattice tetragonality in PbTiO$_3$ stem from the formation of the strong covalent Pb-O bond through the hybridization of the Pb 6$s$ and O 2$p$ orbitals, unlike BaTiO$_3$ where the Ba-O interaction is almost ionic. In addition, the Pb-O bond often plays a significant role in determining characteristic structures, such as a complex $c(2 \times 2)$ surface reconstruction and an atomically sharp 90° domain-wall structure. Thus, the Pb-O bond characterizes ferroelectric instability in PbTiO$_3$. Table II lists the bond length $d$ and minimum charge density $\rho_{\text{min}}$ of the edge, surface, and inside Pb-O bonds in both the PbO- and TiO$_2$-terminated nanowires.
terminated and TiO$_2$-terminated nanowires (see Fig. 1). The minimum charge density is calculated on a line between the bonded Pb and O atoms. For comparison, we also show those of the bonds in the bulk and in the film as mentioned above, whose sites correspond to the surface and inside bonds in the nanowire. In the PbO-terminated nanowire, the bond-length order is $d_{\text{edge}} > d_{\text{surface}} > d_{\text{inside}}$, and the minimum charge-density order is $(\rho_{\text{min}})_{\text{edge}} > (\rho_{\text{min}})_{\text{surface}} > (\rho_{\text{min}})_{\text{inside}}$. These findings indicate that a highly strengthened covalent bond is formed at the edge. On the other hand, $d$ and $\rho_{\text{min}}$ are longer and lower than those of the bulk in the TiO$_2$-terminated nanowire, suggesting that the Pb-O bond is weakened. Therefore, the large (small) ferroelectric distortion in the edge cell arises from the strengthened (weakened) covalent Pb-O bond in the PbO-(TiO$_2$)-terminated nanowire.

Figure 3 depicts the difference in site-by-site minimum charge density between the corresponding site of the bulk and those in the PbO-terminated and TiO$_2$-terminated nanowires. In the PbO-terminated nanowire, the charge density at the edge and surface Pb-O bonds increases while that of the Ti-O bond decreases. This indicates that the electrons transfer from the Ti-O site to the Pb-O site. Because the coordination number of the Pb atom at the edge is smaller than that of the bulk, the number of electrons contributing to the bond increases in the PbO-terminated nanowire. In fact, the Pb atoms associated with the edge, surface, and inside bonds form two, three, and four Pb-O bonds, respectively, which correspond well to the minimum charge density although the relationship is not simply linear (see Table II). Thus, the electron concentration on the edge bond due to the reduced coordination number results in locally enhanced ferroelectricity. On the other hand, charge density increases at the Ti-O bond, especially at the edge in the TiO$_2$-terminated nanowire, while it decreases at the Pb-O bond. The enhancement of the Ti-O bond can be explained in the same manner as that of the Pb-O bond in the PbO-terminated nanowire. As a result of the charge redistribution from the Pb-O site to Ti-O site in the nanowire, the covalent Pb-O bond is relatively weakened, leading to strong suppression of ferroelectricity. Thus, ferroelectricity in the PbTiO$_3$ nanowire depends significantly on the terminations. Such termination dependence is different in the BaTiO$_3$ nanowires, where ferroelectricity is suppressed in the BaO termination while it is enhanced in the TiO$_2$ termination$^{17}$ because the Ba-O interaction is not covalent but almost ionic.$^{34,35}$

### B. Effect of size on ferroelectricity

Table III lists the averaged lateral and the axial lattice parameters, $a$ and $c$, and the averaged polarization $\bar{P}$ in both the PbO-terminated and TiO$_2$-terminated nanowires as a function of cross-sectional size. As the size of the PbO-terminated nanowire decreases, both the lateral and axial lattice parameters shrink. However, the tetragonality of lattice, $c/a$, which plays an important role in stabilizing ferroelectric distortion, increases in the smaller nanowire. Surprisingly, even the smallest PbO-terminated nanowire with a $1 \times 1$ unit-cell size exhibits spontaneous polarization, which has the highest magnitude among the nanowires and bulk. This is because the ratio of the edge structure that enhances ferroelectricity with respect to the entire wire volume becomes more dominant with decreasing nanowire size. The magnitude of polarization approaches that of the bulk as the size increases. On the other hand, the lattice parameters of the smaller TiO$_2$-terminated nanowire also shrink but the tetragonality decreases because the axial lattice parameter is highly suppressed. Moreover, nanowires smaller than $4 \times 4$ cells in cross section, which corresponds to a diameter of about 17 Å, do not exhibit spontaneous polarization, indicat-
ing that there is critical size for ferroelectricity. Such disappearance of ferroelectricity is also found in the stoichiometric BaTiO$_3$ nanowire surrounded by two BaO-terminated and two TiO$_2$-terminated surfaces, and its critical size was calculated by Geneste et al.\textsuperscript{17} to be $3\times11003/3$ cells in cross section, which corresponds to a diameter of about 12 Å. They also demonstrated that the fully BaO-terminated/TiO$_2$-terminated BaTiO$_3$ nanowire requires the slightly larger (smaller) critical diameter. These indicate that critical size for ferroelectricity in perovskite nanowires is much sensitive to surface terminations, and the PbTiO$_3$ nanowire possesses relatively stronger dependence on surface terminations than the BaTiO$_3$ nanowire.

C. Influence of axial tensile strain

Figure 4 plots the averaged polarization $\bar{P}$ in the PbO-terminated and TiO$_2$-terminated nanowires as a function of the tensile strain $\varepsilon_{zz}$. Averaged polarization increases almost linearly with respect to tensile strain for all the PbO-terminated nanowires. This suggests that the axial tensile strain enhances the ferroelectricity. For the TiO$_2$-terminated nanowires which are initially paraelectric (PE), ferroelectricity appears under axial tension. The critical tensile strain to recover ferroelectricity is listed in Table IV. Smaller nanowires require larger critical strain because the TiO$_2$-terminated edge structure, which suppresses ferroelectricity, strongly affects thinner nanowires. After the critical strain, averaged polarization increases smoothly with tensile strain.

Figure 5 shows the change in atomistic and electronic configurations on the PbO (010) planes in the PbO-terminated and TiO$_2$-terminated nanowires with a cross section of $3\times3$ unit cells under axial tension. At equilibrium in the PbO-terminated nanowire, O atoms are displaced in the $-z$ direction from their ideal lattice sites and the covalent Pb-O bonds emphasized by white lines are formed, indicating ferroelectric distortion. During axial tension, all the Pb-O covalent bonds are sustained and the charge density at these sites increases. On the other hand, the upper and lower Pb-O bonds are equivalent to each other and there is no ferroelectric distortion in the unstrained TiO$_2$-terminated nanowire. After the critical strain of $\varepsilon_{zz}=0.04$, the upper bond is strengthened while the lower one is weakened for all the PbO planes accompanying the upward displacement of the

<table>
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<th>Nanowire size</th>
<th>1×1</th>
<th>2×2</th>
<th>3×3</th>
<th>4×4</th>
<th>Bulk</th>
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<tbody>
<tr>
<td>$\bar{a}$</td>
<td>3.60</td>
<td>3.64</td>
<td>3.70</td>
<td>3.73</td>
<td>3.87</td>
</tr>
<tr>
<td>$c$</td>
<td>3.92</td>
<td>3.97</td>
<td>3.99</td>
<td>4.01</td>
<td>4.03</td>
</tr>
<tr>
<td>$c/\bar{a}$</td>
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<td>1.090</td>
<td>1.081</td>
<td>1.074</td>
<td>1.043</td>
</tr>
<tr>
<td>$\bar{P}$</td>
<td>103.7</td>
<td>99.9</td>
<td>95.7</td>
<td>94.3</td>
<td>85.8</td>
</tr>
<tr>
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<td>3.81</td>
<td>3.84</td>
<td>3.85</td>
<td>3.87</td>
</tr>
<tr>
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<td>3.57</td>
<td>3.67</td>
<td>3.74</td>
<td>4.03</td>
</tr>
<tr>
<td>$c/\bar{a}$</td>
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<td>0.935</td>
<td>0.956</td>
<td>0.973</td>
<td>1.043</td>
</tr>
<tr>
<td>$\bar{P}$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.89</td>
<td>85.8</td>
</tr>
</tbody>
</table>

![FIG. 4. Averaged polarization $\bar{P}$ in (a) PbO-terminated and (b) TiO$_2$-terminated nanowires with a cross section of the 1×1, 2×2, and 3×3 cells as a function of tensile strain $\varepsilon_{zz}$.](attachment:fig4.png)
Pb atom. As a result, the nanowire undergoes a paraelectric-to-ferroelectric phase transition.

For more detailed discussion, we define the “edge,” “surface,” and “inside” bonds in the 3 × 3 nanowire (see Fig. 5) in the same manner as in the 4 × 4 nanowire. Figure 6 plots the minimum charge density, \( \rho_{\text{min}} \), at the edge, surface, and inside bonds in the PbO-terminated and TiO2-terminated nanowires with a cross section of 3 × 3 cells as a function of axial tensile strain \( \varepsilon_{zz} \). The minimum charge density at each bond increases monotonically with respect to the tensile strain in the PbO-terminated nanowire. This corresponds well to the linear increase in the averaged polarization. Under high axial tension, the edge bond keeps the highest charge density of the three. In the TiO2-terminated nanowire, the minimum charge density decreases before the critical strain. This indicates that the equivalent bonds at the upper and lower sites of the PbO plane are uniformly stretched because the structure is paraelectric (symmetric in the z direction). At the critical strain, the trend for all the bonds concurrently changes from decreasing to increasing. This indicates that ferroelectricity appears in all the sites of the nanowire at the same strain, whereas the ferroelectric distortions in the BaTiO3 nanowire do not emerge for the same tension at the different site. After that, all the upper bonds are partially strengthened. Note that the charge density increase in the edge bond is somewhat moderate, which leads to the suppression of ferroelectricity at the edge relative to the other sites.

<table>
<thead>
<tr>
<th>Nanowire size</th>
<th>( \varepsilon_{zz} )</th>
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<tbody>
<tr>
<td>1 × 1</td>
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<tr>
<td>2 × 2</td>
<td>0.08</td>
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<tr>
<td>3 × 3</td>
<td>0.04</td>
</tr>
</tbody>
</table>

### Table IV. Critical tensile strain to recover ferroelectricity \( \varepsilon_{zz} \) as a function of the TiO2-terminated nanowire size.

![FIG. 5.](image) Change in atomic structures and charge-density distributions on the PbO (010) planes in (a) PbO-terminated and (b) TiO2-terminated nanowires with a cross section of 3 × 3 unit cells under axial tensile strain \( \varepsilon_{zz} \). The gray (dark gray) and blue (black) spheres indicate Pb and O atoms, respectively. The covalent Pb-O bonds are shown by white lines.

![FIG. 6.](image) Minimum charge density \( \rho_{\text{min}} \) at the edge, surface, and inside bonds (see Fig. 5) in (a) PbO-terminated and (b) TiO2-terminated nanowires with a 3 × 3-cell cross section as a function of axial tensile strain \( \varepsilon_{zz} \). The dashed line indicates the critical strain of the PE–FE phase transition.

![Image](image)
AB INITIO STUDY OF FERROELECTRICITY IN PbTiO3 Nanowires

Ab initio density-functional theory calculations within the local-density approximation have been carried out in order to investigate the atomistic and electronic structures of PbTiO3 nanowires with atomically sharp edges composed of (100) and (010) surfaces, and the fundamental effects of axial tensile strain on ferroelectricity. Ferroelectric distortions at the edge of the PbO-terminated nanowire are enhanced while they are entirely suppressed in the TiO2-terminated nanowire. On the other hand, an opposite trend of termination dependence is observed for the BaTiO3 nanowire.17

However, the trend is different from that of the PbTiO3 nanowires, and this remains as challenging future work. We believe that our results are helpful as a criterion in discussing the basic influence of the reconstruction of the (001) surface.22,23 there are possibilities of existence of the reconstruction even in the PbTiO3 nanowires, and this remains as challenging future work. We believe that our results are helpful as a criterion in discussing the basic influence of the c(2×2) reconstruction if it exists in the nanowires.

**ACKNOWLEDGMENT**

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