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Kyoto University
Coexistence of rectilinear and vortex polarizations at twist boundaries in ferroelectric PbTiO$_3$ from first principles

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Atomic and electronic structures as well as ferroelectricity at $\Sigma 5(001)$ twist boundaries in ferroelectric PbTiO$_3$ have been investigated using first-principles (ab initio) density-functional theory calculations within the local-density approximation. The twist-boundary structure with the coincidence site lattice of O-Pb and O-O is found to be energetically favorable. At the twist boundary, rectilinear spontaneous polarization along the normal direction to the boundary is highly enhanced because of the locally strengthened covalent Pb-O bond, which predominates ferroelectricity in PbTiO$_3$. Interestingly, we found vortex or toroidal polarization in the twist-boundary plane coexisting with the rectilinear polarization. The vortex polarization arises from rotational in-plane displacement induced by the twisted misorientation of lattices. An applied tensile strain tends to increase the rectilinear polarization, especially at the twist boundary. On the other hand, the vortex polarization is suppressed upon application of a tensile strain and finally disappears at a critical strain in the TiO$_2$ layer of the boundary, whereas the PbO layer exhibits the opposite tendency.

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I. INTRODUCTION

Ferroelectric perovskite oxides, e.g., PbTiO$_3$ and BaTiO$_3$, are electroceramic materials that exhibit not only ferroelectricity but also a variety of useful electrical properties, including a high dielectric constant as well as piezoelectricity. Because of their multiple functionalities, perovskite oxides have drawn significant attention for technological applications, such as nonvolatile random access memories (FeRAMs), transducers, and electromechanical devices.$^{1,2}$

Since perovskite oxide ceramics are usually polycrystalline materials, grain boundaries (GBs) are one of the most important planar defects within the material. It is well known that the grain boundaries considerably affect electronic properties. For example, grain boundaries induce nonlinear current-voltage ($I$-$V$) characteristics and a positive temperature coefficient of resistivity (PTCR).$^{3−6}$ It has been reported that these properties are highly dependent on crystallographic misorientation and defect segregation at grain boundaries.$^{7−9}$ Thus the atomic and electronic structures of grain boundaries in perovskite oxides play a central role in determining the properties, and have been studied both experimentally and theoretically. For instance, tilt grain boundaries in perovskite oxides, including $\Sigma 3(111), \Sigma 3(112), \Sigma 5(210), \Sigma 5(310), \Sigma 13, \Sigma 17$, and random grain boundaries, have been actively investigated by means of atomic-resolution transmission electron microscopy (TEM) and scanning TEM (STEM).$^{10−33}$ Here, $\Sigma$ value means the degree of match between the structures of the two grains described by the reciprocal of the ratio of coincidence sites to the total number of sites on the following boundary plane. Some studies have employed ab initio (first-principles) density-functional theory (DFT) calculations, and these theoretical calculations have revealed detailed atomic structures, grain-boundary energies, and electronic properties of these materials. On the other hand, the properties of twist boundaries are poorly understood at present because very few investigations have been conducted thus far on tilt grain boundaries. Only limited reports exist so far: Nomura et al. studied a $\Sigma 5(001)$ twist boundary in SrTiO$_3$ by TEM observations, and showed that the twist boundary is atomically sharp and possesses a coincidence site lattice (CSL) structure.$^{34}$ Astala and Bristowe elucidated on the stability of the CSL structure and electronic properties of the twist boundary.$^{35}$ However, to the best of the authors’ knowledge, ferroelectricity at twist boundaries has never been studied so far in spite of great scientific interest in microstructural properties as well as the technological importance of this aspect for reliability of devices. Only a first-principles study of the interplay between symmetrical tilt grain boundaries and domain walls (DWs) in ferroelectric PbTiO$_3$ has been reported very recently.$^{36}$

Since ferroelectricity originates from the delicate balance between short-range covalent interactions and long-range Coulombic interactions,$^{37,38}$ spontaneous polarization is expected to be significantly affected at a twist boundary in which the heterogeneous atomic arrangement should break this balance. For a deeper understanding of ferroelectric properties at twist boundaries, it is essential to elucidate the detailed atomic and electronic structures of these boundaries.

In this study, we investigated ferroelectricity at the $\Sigma 5(001)$ twist boundaries in a typical ferroelectric perovskite, PbTiO$_3$, from both atomistic as well as electronic points of view using ab initio density-functional theory calculations, which previously have successfully yielded microscopic descriptions of grain boundaries.$^{27,32,39,40}$ Additionally, we have investigated the fundamental effects of strain, which is often strongly coupled with ferroelectricity.$^{41−43}$

II. COMPUTATIONAL DETAILS

A. Simulation method

Ab initio (first-principles) calculations based on density-functional theory$^{44,45}$ (DFT) were conducted using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code.$^{46−48}$ The local-density approximation (LDA) parametrized by Perdew and Zunger$^{49}$ from Ceperley-Alder

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The electron-ion interaction is described by norm-conserving Troullier-Martins pseudopotentials, which explicitly include the Pb 5d, 6s, and 6p, the Ti 3s, 3p, 3d, and 4s, and the O 2s and 2p electrons in the valence states. The Pb and Ti pseudopotentials are generated scalar relativistically. The reference configurations and cut-off radii used for pseudopotential generation are listed in Table I.

The electronic wave functions were expanded in a basis set of strictly localized numerical atomic orbitals (NAOs) implemented in the VASP code and a mixed-basis (MB) set with norm-conserving pseudopotentials (NCPP) implemented in the MBPP code. Overall, the structural, elastic, and electronic properties calculated in this study agree well with the previous results using different methodologies. In particular, the tetragonality of lattice $c/a$ and the internal atomic coordinates $u_z$, which are closely related to ferroelectricity, are in very good agreement. These clearly indicate the reliability of the present calculations. It should be noted that the small underestimate in the lattice constants and band-gap energies from the experimental values is not a problem of our pseudopotentials but a well-known issue concerning to the LDA functional and the DFT framework themselves, respectively.

**B. Simulation models and procedure**

Figures 1(b) and 1(c) show the schematic illustration of the modeling of the Σ5 twist-boundary structure and the simulation model of the Σ5 (001) twist boundary in ferroelectric PbTiO$_3$. The Σ5 (001) twist boundary can be constructed by rotating one upper grain by $\tan^{-1}(1/3) = 18.4^\circ$ and the other lower grain by $-18.4^\circ$ around the [001] axis [the misorientation angle is $2\tan^{-1}(1/3) = 36.9^\circ$]. Hence the crystal orientations in the x and y directions are [210] and [120], respectively, for the upper grain, and [210] and [120], respectively, for the lower grain. This grain boundary has one
TABLE I. Reference configurations and cutoff radii (in bohrs) of norm-conserving Troullier-Martins pseudopotentials for PbTiO$_3$. The Pb and Ti pseudopotentials are generated scalar relativistically for their ionic configuration (ionic charge of +2), explicitly including their semicore states in the valence.

<table>
<thead>
<tr>
<th>Reference configuration</th>
<th>Pb 6$s^2$, 6$p^6$, 5$d^{10}$, 5$f^0$</th>
<th>Ti 3$s^2$, 3$p^6$, 3$d^2$, 4$f^0$</th>
<th>O 2$s^2$, 2$p^4$, 3$d^0$, 4$f^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core radius (bohr)</td>
<td>$s$ 2.20</td>
<td>1.30</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>$p$ 2.60</td>
<td>1.30</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>$d$ 2.00</td>
<td>1.30</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>$f$ 2.50</td>
<td>2.00</td>
<td>1.50</td>
</tr>
</tbody>
</table>

matched lattice point [see the red circle in Fig. 1(b)] per five square lattices on the (001) boundary plane (see the squares in the same figure), indicating the Σ5 grain-boundary structure. Since the three-dimensional periodic boundary condition is applied in the present calculations, the simulation cell contains two equivalent twist boundaries indicated as “GB” at the edge and the center of the cell. The simulation cell consists of 16 (001) atomic layers, altering the PbO and TiO$_2$ planes along the $z$ direction. Thus the total number of atoms in the cell is 200. For descriptive purposes, we assign layer numbers 1 to 8 for the upper grain and −1 to −8 for the lower grain. The spontaneous polarization $P$ lies along the $z$ direction. The initial simulation cell dimensions in the $x$, $y$, and $z$ directions are set to $\sqrt{3}a$, $\sqrt{5}a$, and $8c$, respectively, where $a$ and $c$ are the theoretical lattice constants of the bulk, $a = 3.849\,\text{Å}$ and $c = 4.031\,\text{Å}$ ($c/a = 1.047$). The Brillouin zone (BZ) integrations were carried out using a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh. The electronic density, Hartree, and exchange-correlation potentials were calculated in a uniform real-space grid with an equivalent plane-wave cutoff of 200 Ry.

In this study, we mainly considered a symmetrical coincidence site lattice (CSL) structure for this interfacial alignment of both grains, since it has already been shown both experimentally and theoretically that the Σ5 twist boundary in the perovskite oxides is atomically sharp and possesses the CSL structures. Figure 1(d) shows the three possible CSL twist-boundary structures that were employed in this study. These models have different CSL atomic sites; the O-Pb and O-O sites for the CSL-1 structure, the Ti-O site for CSL-2, and the Ti-Pb site for CSL-3 [see the arrows in Fig. 1(d)]. Additionally, we took into account the structural degrees of freedom of the rigid-body translation of one grain with respect to the other to confirm that the CSL twist boundary is the stable structure. The rigid-body translation vector $t$ consists of two components representing the shift in the $x$ and $y$ directions. For each shift, two grains in the simulation cell are displaced rigidly along the grain-boundary plane with respect to each other. The initial position $t = (0, 0)$ is set to the CSL-3 structure. The atomic relaxation was conducted using the conjugate-gradient (CG) method until the Hellmann-Feynman forces and the normal stress component of $\sigma_{zz}$ were less than $5.0 \times 10^{-3}$ eV/Å and $5.0 \times 10^{-2}$ GPa, respectively.

For tensile simulations, a small incremental strain $\Delta \varepsilon_{zz}$ was applied step by step in the $z$ direction to the simulation cell. At each strain, the internal atomic positions were relaxed using the CG method.

TABLE II. Lattice constants, internal atomic coordinates, elastic constants, and band-gap energies $E_{gap}$ of the ferroelectric-tetragonal PbTiO$_3$ bulk calculated by different computational methodologies. $a$ and $c$ are the lattice constants of the tetragonal lattice. $u_i$ denotes the internal atomic coordinate in the $z$ direction, normalized by the lattice constant $c$. The atoms shown in Fig. 1(a) are included within parentheses. The subscript of the elastic constant $c_{ij}$ follows the Voigt notation. Experimental values are also shown for comparison.

<table>
<thead>
<tr>
<th>Methodology code</th>
<th>LCAO + NCPP (This work)</th>
<th>PW + PAW$^{53}$</th>
<th>MB + NCPP$^{52,59}$</th>
<th>Experiment$^{60-62}$</th>
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<td>SIESTA</td>
<td>VASP</td>
<td>MBPP</td>
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<tr>
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<td>3.853</td>
<td>3.905</td>
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<tr>
<td>$c$ (Å)</td>
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<td>4.042</td>
<td>4.045</td>
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<tr>
<td>$c/a$</td>
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<td>1.064</td>
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<tr>
<td>$u_i[\text{Pb}]$</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>$u_i[\text{Ti}]$</td>
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<td>0.534</td>
<td>0.531</td>
<td>0.539</td>
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<tr>
<td>$u_i[\text{O1}]$</td>
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<td>0.090</td>
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<td>$u_i[\text{O2}]$</td>
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<td>0.606</td>
<td>0.601</td>
<td>0.617</td>
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<tr>
<td>$c_{11}$ (GPa)</td>
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<td>284.3</td>
<td>293</td>
<td>235</td>
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<td>$c_{12}$ (GPa)</td>
<td>122.5</td>
<td>114.6</td>
<td>129</td>
<td>101</td>
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<tr>
<td>$c_{13}$ (GPa)</td>
<td>99.6</td>
<td>91.6</td>
<td>99.2</td>
<td>98.8</td>
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<tr>
<td>$c_{33}$ (GPa)</td>
<td>105.9</td>
<td>98.7</td>
<td>92.5</td>
<td>105</td>
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<tr>
<td>$c_{44}$ (GPa)</td>
<td>67.3</td>
<td>61.0</td>
<td>67.2</td>
<td>69</td>
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<tr>
<td>$c_{36}$ (GPa)</td>
<td>110.3</td>
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<tr>
<td>$E_{gap}$ (eV)</td>
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<td>1.65</td>
<td>1.62</td>
<td>3.5</td>
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</table>

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III. RESULTS AND DISCUSSION

A. Grain-boundary energy

The grain-boundary energy $\gamma$ was evaluated using

$$\gamma = \frac{E_{\text{model}} - E_{\text{bulk}}N}{2S_{\text{GB}}},$$  

(1)

where $E_{\text{model}}$, $E_{\text{bulk}}$, $N$, and $S_{\text{GB}}$ denote the total energy of the relaxed simulation model of the twist boundary, the total energy per unit cell of the bulk, the number of unit cells in the simulation model, and the cross-sectional area of the twist boundary, respectively. Figure 2 shows the $\gamma$ surface of $\Sigma5$ twist boundary with $x$ and $y$ rigid-body translations. From the structural symmetry, we can find three different local minima on the $\gamma$ surface, which correspond to three CSL structures shown in Fig. 1(d). This result agrees with the fact that the $\Sigma5$ twist boundary with the CSL structure was observed experimentally. The grain-boundary energies $\gamma$ of the three CSL twist boundaries are listed in Table III. The twist boundary with the CSL-1 structure is energetically the most favorable because it has the lowest grain-boundary energy. The CSL-1 structure was also found to be the most stable of the SrTiO$_3$ $\Sigma5$ twist boundaries. The grain-boundary energy of $\gamma = 1.499 \text{ J/m}^2$ for PbTiO$_3$ is close to that of SrTiO$_3$, $\gamma = 1.2 \text{ J/m}^2$. In comparison, a smaller grain-boundary energy was reported for a tilt grain boundary in the perovskite oxides: 0.375 J/m$^2$ for $\Sigma3(111)$, 0.686 J/m$^2$ for $\Sigma3(112)$, from 0.948 to 1.114 J/m$^2$ for $\Sigma5(210)$ for different GB-DW arrangements in ferroelectric PbTiO$_3$, 0.52 J/m$^2$ for $\Sigma3(111)[110]$, 1.02 J/m$^2$ for $\Sigma5(310)[001]$ in SrTiO$_3$, and 1.02 J/m$^2$ for $\Sigma5(310)[001]$ in BaTiO$_3$.

Dasher et al. have experimentally shown that the grain-boundary population in the perovskite oxides is correlated to the sum of energies of the surfaces comprising the boundary and grain-boundary energies. According to this relationship, the grain-boundary population in ferroelectrics can be estimated by calculating a series of surface and grain-boundary energies.

![FIG. 2. (Color online) $\gamma$ surface of the $\Sigma5$ twist boundary as a function of the rigid-body translations. The white dashed lines indicate the structural periodicity to the rigid-body translations. The origin $O$ is set to the CLS-3 structure.](image)

B. Atomic and electronic structures at twist boundary

Structural relaxation leads to local volume expansion at the twist boundaries: The interlayer distance between the $-1$ and $1$ layers of 2.452, 2.409, and 2.395 Å in the CSL-1, CSL-2, and CSL-3 structures, respectively, is almost 30% larger than that of 1.874 Å in the bulk. On the other hand, a slight change in the interlayer distance (less than 3%) is found between the adjacent $-1$ and $-2$, and 1 and 2 layers, indicating that volume expansion is highly confined at the twist boundary. Nomura et al. experimentally observed such a local volume expansion in a SrTiO$_3$ $\Sigma5$ twist boundary using TEM. They reported that the twist-boundary structure is atomically sharp and the layer interval at the twist boundary is 1.3 times larger than that of a SrTiO$_3$ single crystal, which corresponds to our result for PbTiO$_3$.

Figure 3 shows the atomic displacement and the relaxed atomic structure at the three different CSL twist boundaries. Although each CSL structure shows a different and complicated displacement pattern, some common trends can be discerned: From the cross-sectional views, all in-plane displacement is centrosymmetric. The displacement vector shows that the Pb and Ti atoms separate from each other, whereas the Pb and O atoms and the Ti and O atoms approach each other. Such a displacement pattern should result from repulsive ionic interaction between the cations Pb and Ti, and attractive interaction between the anion O and the cations. In contrast, no in-plane displacement could be observed in a single crystal, wherein the repulsive and attractive interactions are in fine balance because of the regular atomic arrangement.

Another important feature is that the displacement of Pb atoms is much more active than that of the others. Remarkably, some Pb atoms (e.g., Pb1 in the CSL-1 structure) represent a dominant displacement in the $z$ direction of the polar axis (see the side views).

Pb atoms play an important role in determining ferroelectricity in PbTiO$_3$ because they form a strong covalent Pb-O bond through the hybridization of the Pb 6$s$ and O 2$p$ orbitals, which leads to large displacement and lattice tetragonality. In fact, the covalent Pb-O bond often characterizes ferroelectric nanostructures, e.g., surfaces, edges in nanowires and surface steps, and an atomically sharp 90$^\circ$ domain-wall structure. Here, we further investigate the covalent Pb-O bonding character at the twist boundary. Figure 4 shows the distribution of minimum charge density $\rho_{\text{min}}$ along Pb-O in the most stable CSL-1 twist-boundary structure. The minimum charge density $\rho_{\text{min}}$ is calculated on a line between the Pb and O atoms, which should be one of the parameters representing the covalent Pb-O bond strength.

Around the Pb1 atom that shows remarkable displacement, we find the minimum charge density higher than that in the bulk along the corresponding Pb1 and three neighboring O atoms. This suggests that the Pb1 atom forms three strong covalent

### TABLE III. Calculated grain-boundary energies $\gamma$ (in J/m$^2$) for three different CSL $\Sigma5$ twist-boundary structures.

<table>
<thead>
<tr>
<th></th>
<th>CSL-1</th>
<th>CSL-2</th>
<th>CSL-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$ (J/m$^2$)</td>
<td>1.499</td>
<td>1.518</td>
<td>1.551</td>
</tr>
</tbody>
</table>

...
bonds with the neighboring O atoms. On the other hand, only a single covalent bond is formed on the Pb2 and Pb3 atoms, in which a small displacement is found [see also Fig. 3(a)]. Thus the dominant displacement of the Pb1 atom is driven by the formation of three strengthened covalent Pb1-O bonds, while only a single bond on the Pb2 and Pb3 atoms results in their relatively small displacement. It should be noted that a similar bonding character and relationship between the bond strength and displacement can be found in the CSL-2 and CSL-3 structures as well.
and \( \text{TiO}_2 \) layers, respectively. For comparison, ferroelectric distortions in the bulk along the polar axis where \( \bar{\delta} \) the bulk is reference, the minimum charge density of the covalent Pb-O bond in the polar axis along the \( z \) of the bulk, \( \rho_{\text{int}} \) introduced a ferroelectric distortion of the \( z \) was found on layer 1 of the TiO\(_2\) plane. Thus ferroelectricity is PbO plane, while a relatively moderate increase of about 25% decrease on the adjacent walls.\(^{63,81}\) Below, we separately discuss the ferroelectricity at twist boundary (i) in the polar axis of the \( z \) (ii) in the in-plane (\( x \) and \( y \) directions).

Figure 5 shows the layer-by-layer ferroelectric distortion in the polar axis along the \( z \) direction for the three different CSL models. Here, the ferroelectric distortion is normalized by that of the bulk, \( \delta_z^* = \delta_z/\delta_z^{\text{bulk}} \), where the bulk value \( \delta_z^{\text{bulk}} \) is 0.335 and 0.282 \( \text{Å} \) for the PbO and TiO\(_2\) layers, respectively. For all the CSL structures, a remarkable increase in \( \delta_z \) was found at the twist boundary on the layers \( -1 \) and \( 1 \): \( \delta_z \) increased by 35%–50% with respect to the bulk value on the \( -1 \) layer of the PbO plane, while a relatively moderate increase of about 25% was found on layer 1 of the TiO\(_2\) plane. Thus ferroelectricity is enhanced just at the twist boundary, although there is a slight decrease on the adjacent \( -2 \) and 2 layers. Considering that remarkable ferroelectricity and large lattice tetragonality in PbTiO\(_3\) arises from a formation of the strong covalent Pb-O bond,\(^{76,77}\) this strong enhancement of ferroelectric distortions must be driven by the partially strengthened Pb-O bond at the twist boundary shown in the previous section. Since the influence of the twist boundary is confined to almost three atomic layers on the upper and lower side grains, the effective thickness of the \( \Sigma 5 \) twist boundary for ferroelectricity is estimated to be about 13 \( \text{Å} \). It is to be noted that, in the middle of the grains, the ferroelectric distortions are almost same as the bulk value, which suggests that the present models should have a sufficient size of the grains to neglect undesirable interactions from neighboring twist boundaries.

Figure 6 shows the vector field of in-plane (in the \( x \) and \( y \) directions) ferroelectric distortions just at the twist boundary on the \( -1 \) (PbO) and 1 (TiO\(_2\)) layers for the three different CSL structures. Here, the ferroelectric distortions are calculated via Eq. (2) for each unit plane shown by the dashed squares in Fig. 6. Nontrivial in-plane ferroelectric distortions, the magnitudes of which are almost equal to or more than that of the bulk in the polar direction, were found on the \( -1 \) layer of the PbO plane. In addition, the ferroelectric distortion vector represents a vortex or toroidal pattern around the center of the cell \( O \). A similar vortex pattern was also found on layer 1 of the TiO\(_2\) plane. However, the magnitude of the ferroelectric distortion vectors on the TiO\(_2\) plane is much smaller than that on the PbO plane. It should be noted that this in-plane ferroelectric distortion must be induced by the twist-boundary structure because in the PbTiO\(_3\) single

### Table IV. Radial and azimuthal components of in-plane ferroelectric distortions, \( \delta_r \) and \( \delta_\theta \), and toroidal moment \( \tau_z \), at the twist boundary on the \( -1 \) (PbO) and 1 (TiO\(_2\)) layers in three different CSL structures. Two values in the CSL-1 structure correspond to sites \( A \) and \( B \), respectively [see Fig. 6(a)]. For comparison, ferroelectric distortions in the bulk along the polar axis \( \delta_z^{\text{bulk}} \) are 0.335 and 0.282 \( \text{Å} \) for the PbO and TiO\(_2\) layers, respectively.

<table>
<thead>
<tr>
<th>Layer number (-1) (PbO)</th>
<th>Layer number 1 (TiO(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_r ) (( \text{Å} ))</td>
<td>( \delta_\theta ) (( \text{Å} ))</td>
</tr>
<tr>
<td>CSL-1</td>
<td>0.148, -0.223</td>
</tr>
<tr>
<td>CSL-2</td>
<td>0.179</td>
</tr>
<tr>
<td>CSL-3</td>
<td>0.561</td>
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</table>
The coexistence of rectilinear and vortex ferroelectric distortions on the twist boundary of the CSL structures was studied. The in-plane ferroelectric distortions were decomposed into radial and azimuthal components with respect to the vortex center $O$.

The radial and azimuthal components of the in-plane ferroelectric distortions were calculated as follows:

$$\delta r = \delta \rho \cos \theta, \quad \delta \theta = \delta \rho \sin \theta.$$

A nonzero and nontrivial toroidal moment was found in all the CSL structures, which clearly signifies the existence of a vortex polarization at the twist boundary. The vortex polarization direction is anticlockwise for the CSL-1 and CSL-2 structures, and is clockwise for the CSL-3 structure, because of the positive and negative $\tau_z$, respectively. A larger toroidal moment is induced on the $-1$ layer of the PbO plane, while the moment is almost an order of magnitude smaller on layer 1 of the TiO$_2$. This toroidal moment arises from a rotational in-plane displacement of cations and anions with respect to the center of the cell as discussed in the previous section. In fact, the magnitude of displacement on the PbO and TiO$_2$ plane corresponds to the toroidal moments.

Such an unusual polarization with vortices is also formed in various ferroelectric nanostructures, for instance, ultrathin films, nanowires, and nanoparticles. However, the formation mechanism of vortex polarizations in these nanostructures should be different from the case of the twist boundary. In the ferroelectric nanostructures, the termination...
of polarization at their surface gives rise to surface charges, which create a depolarizing field that destabilizes the ferroelectric state. To minimize the depolarizing field, the system could adopt a vortex state in which surface charges are compensated for due to the closed polarization loops aligned parallel to the surfaces. The resulting vortex polarization state is thus a natural consequence of energy minimization under geometrical and electrical boundary conditions in the presence of polarization fields. On the other hand, no surface charge appears at the twist boundary because of the absence of free surfaces, however, vortex polarization could be induced by a complex atomic relaxation at the twist boundary. This will be discussed later from the atomistic and electronic points of view.

D. Effect of strain on ferroelectricity at twist boundary

We next briefly report how a tensile strain $\varepsilon_{zz}$ applied in the normal direction to the twist boundary affects both rectilinear and vortex polarization. Figure 7 shows the ferroelectric distortion $\delta z$ and toroidal moment $\tau z$ of the most stable CSL-1 twist-boundary model as a function of the tensile strain $\varepsilon_{zz}$. The ferroelectric distortions near the twist boundary increase smoothly with respect to the tensile strain on both the PbO and TiO$_2$ layers. In particular, $\delta z$ at the twist boundary (layer $-1$) exhibits a higher increasing rate than the other layers owing to strain concentration at the twist boundary. This indicates that spontaneous polarization at the twist boundary is enhanced by the tensile strain.

The toroidal moment on the PbO layer also increases with increasing strain, whereas that on the TiO$_2$ layer decreases and finally disappears at a strain of $\varepsilon_{zz} = 0.10$. The same tendency was reported for BaTiO$_3$ nanowires with vortices wherein the applied axial strain suppressed transverse vortex polarization on the TiO$_2$ plane of the wires.  

IV. CONCLUSION

In this study, ab initio (first-principles) density-functional theory calculations were carried out in order to investigate ferroelectricity at the $\Sigma 5$ (001) twist boundary in PbTiO$_3$ from atomistic and electronic points of view and the fundamental effects of tensile strain on ferroelectricity at the twist boundary. The coincidence site lattice (CSL) structure of O-Pb and O-O was found to be energetically favorable, and the grain-boundary energy was calculated to be $E_{GB} = 1.499 \text{ J/m}^2$. We found the coexistence of both rectilinear spontaneous polarization in the normal direction to the twist boundary and vortex or toroidal in-plane polarization. The rectilinear polarization was highly enhanced at the twist boundary because of the locally strengthened covalent Pb-O bond, which predominates ferroelectricity in PbTiO$_3$ and characterizes the ferroelectric nanostructures. Vortex polarization at the twist boundary was induced by rotational in-plane displacement resulting from the twisted misorientation of lattices. A tensile strain applied to the twist boundary in the normal direction tends to increase the rectilinear polarization. On the other hand, vortex polarization was suppressed and finally disappeared at a critical strain on the TiO$_2$ layer of the boundary, while the PbO layer exhibits the opposite tendency.

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