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Effect of intrinsic point defects on ferroelectric polarization behavior of SrTiO₃

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(Received 9 August 2016; revised manuscript received 23 November 2016; published 4 January 2017)

The effect of a variety of intrinsic defects and defect clusters in bulk and thin films of SrTiO₃ on ferroelectric polarization and switching mechanisms is investigated by means of density-functional-theory based calculations and the Berry phase approach. Our results show that both the titanium Ti_{Sr}^{••} and strontium Sr_{Ti}^{''} antisite defects induce ferroelectric polarization in SrTiO₃, with the Ti_{Sr}^{••} defect causing a more pronounced spontaneous polarization and higher activation barriers of polarization reversal than Sr_{Ti}^{''}. The presence of oxygen vacancies bound to the antisite defects can either enhance or diminish polarization depending on the configuration of the defect pair, but it always leads to larger activation barriers of polarization switching as compared to the antisite defects with no oxygen vacancies. We also show that the magnitude of spontaneous polarization in SrTiO₃ can be tuned by controlling the degree of Sr/Ti nonstoichiometry. Other intrinsic point defects such as Frenkel defect pairs and electron small polarons also contribute to the emergence of ferroelectric polarization in SrTiO₃.

DOI: [10.1103/PhysRevB.95.035301](https://doi.org/10.1103/PhysRevB.95.035301)**I. INTRODUCTION**

Switchable polarization in ferroelectric materials due to the orientation of dipoles by an external electric field is central to various energy and information storage technologies including sensors and actuators [1], electro-optic devices [2–4], and ferroelectric field-effect transistors for nonvolatile memories [5,6]. In past years it has been revealed that ferroelectric polarization is not exclusive to polar materials and can be induced throughout the nonferroelectric layer of the heterostructure by combining a nonferroelectric oxide such as SrTiO₃ with a ferroelectric oxide, e.g., BaTiO₃ [7], or even with another nonferroelectric oxide, e.g., LaCrO₃ [8]. Moreover, the emergence of net ferroelectric polarization was recently demonstrated for nanometer-thick films of SrTiO₃ [9] where this effect was attributed to electrically induced alignment of polar nanoregions that can naturally form because of the presence of intrinsic defects in SrTiO₃ crystals. It was previously demonstrated that intrinsic defects such as the antisite Ti defects can form in the bulk phase of Ti-rich SrTiO₃, generate local polarization around the antisite Ti center due to an off-center displacement of the defect, and might contribute to the appearance of polar nanoregions [9,10] in a manner similar to extrinsic defects [11].

Native point defects in perovskite-structured SrTiO₃ were studied extensively in the past both experimentally and theoretically with the largest emphasis being placed on the oxygen vacancy as the most prominent point defect in SrTiO₃ that affects a wide range of material properties including electronic and optical behavior [12–18]. SrTiO₃ point defect chemistry, thermodynamics, and kinetics of defect formation and diffusion were also investigated in great detail [19–23]. For example, oxygen vacancies serve as a source of *n*-type conductivity that can vary with oxygen partial pressure and

are responsible for insulator-to-metal transition [18]. Oxygen vacancies are also known to play a key role in the resistive switching process under applied electric field due to their low activation energies of diffusion [12,24–26]. Also, it is well established that point defects including oxygen vacancies play a critical role in mediating polarization switching in ferroelectrics by controlling the local polarization stability, acting as pinning sites for domain-wall motion and ultimately defining the mechanism and kinetics of polarization switching [27,28].

The impact of intrinsic point defects including oxygen vacancies on the polarization switching phenomenon in SrTiO₃ is much less understood. In this study we carry out a systematic investigation of the effect of native defects in bulk and thin-film SrTiO₃ on ferroelectric polarization and polarization reversal at a single defect level by means of first-principles electronic structure calculations.

II. COMPUTATIONAL METHOD

First-principles calculations are performed within the density functional theory (DFT) formalism using the projector augmented wave (PAW) potentials [29] as implemented in the Vienna *Ab initio* Simulation Package (VASP) [30]. The PAW potentials for Sr, Ti, O, and Ru contain 10, 12, 6, and 14 valence electrons, respectively, that is, Sr: $4s^2 4p^6 5s^2$, Ti: $3s^2 3p^6 4s^2 3d^2$, O: $2s^2 2p^4$, and Ru: $4p^6 5s^1 4d^7$. The generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [31] is employed in the modified form for solids PBEsol [32] along with a plane wave cutoff energy of 400 eV. The rotationally invariant PBEsol + *U* approach is adopted with $U_{\text{eff}} = 4.36$ eV on the Ti 3*d* orbitals that was shown to provide a good description of the electronic structure properties of SrTiO₃ with and without defects [10,23,33]. The ions are relaxed by applying a conjugate-gradient algorithm until the Hellmann-Feynman forces are less than 20 meV/Å with an optimized lattice

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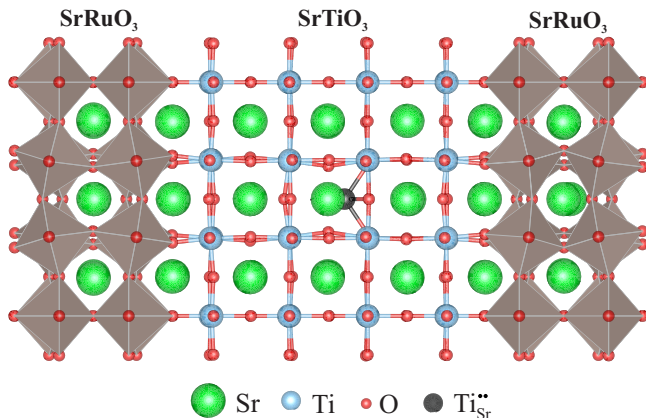


FIG. 1. The atomic structure of SrTiO₃/SrRuO₃ thin films with the antisite Ti_{Sr}^{••} defect in the middle of the supercell which induces polarization along the [100] direction.

constant of 3.903 Å. The $3 \times 3 \times 3$ Monkhorst-Pack k mesh is used for the Brillouin zone integration for a $3 \times 3 \times 3$ supercell, while the mesh was adjusted for other supercells to provide a similar k -point density in each direction.

To investigate the influence of intrinsic defects and defect clusters on the polarization properties of SrTiO₃, we construct a $3 \times 3 \times 3$ supercell consisting of 135 atoms for the bulk calculations and a $3 \times 3 \times 7$ multilayered structure comprised of four SrTiO₃ and three SrRuO₃ layers for the thin-film calculations (see Fig. 1). To optimize the geometry, we first constrained the in-plane structure of each bulk material component of the SrRuO₃/SrTiO₃ heterostructure to the optimized lattice constant of SrTiO₃ and performed full relaxation of internal coordinates and c/a ratio. For SrRuO₃ we find $c/a = 1.017$, while SrTiO₃ remains cubic with $c/a = 1$. The structure of the SrRuO₃/SrTiO₃ supercell was constructed by stacking SrRuO₃/SrTiO₃ cells along the [100] direction and performing full atom relaxation. In all bulk calculations the lattice constant was fixed and only atom relaxation was allowed.

The Berry-phase approach [34] within the modern theory of polarization is employed to calculate polarization properties. According to this approach the spontaneous polarization is defined as the difference in polarization between the polar and nonpolar (centrosymmetric) reference states [35]. To estimate polarization switching barriers we calculate the migration energy profile E_m along the minimum energy path between two polarization states (P_- and P_+) using the climbing image nudged elastic band method [36]. To denote the SrTiO₃ point defects we adopt the Kröger-Vink nomenclature [20,37].

III. RESULTS AND DISCUSSION

A. Ti_{Sr}^{••} antisite defect

We start by considering the titanium-strontium Ti_{Sr}^{••} antisite defect where the Ti⁴⁺ ion occupies a site on the Sr²⁺ sublattice. This defect was predicted to be the dominant defect in SrTiO₃ along with the oxygen vacancy V_O under Ti-rich conditions [10,23]. To find the most stable atomic configuration for Ti_{Sr}^{••} we examine the atomic structures with the Ti atom shifted

TABLE I. Quantities calculated for a $3 \times 3 \times 3$ SrTiO₃ supercell with different defects: defect off-centering d along the corresponding directions, Born charge associated with the off-centered cation, average spontaneous polarization P , and activation barrier for polarization switching E_m . Calculated Born charges for pristine SrTiO₃ are 2.56, 6.57, -5.23 , and -1.93 for Sr, Ti, O_{||}, and O_⊥, correspondingly.

Defect	d (Å)	Born charge	P ($\mu\text{C}/\text{cm}^2$)	E_m (eV)
Ti _{Sr} ^{••}	0.78 [100]	1.72	16.8	0.13
Ti _{Sr} ^{••} -V _O [×]	0.82 [011]			
Ti _{Sr} ^{••} -V _O ^{••}	0.79 [011]	2.48	22.6	0.23
Sr _{Ti} ^{''}	0.26 [011]	3.11	7.6	0.05
Sr _{Ti} ^{''} -V _O [×]	0.81 [100]	3.59	15.7	0.76
Sr _{Ti} ^{''} -V _O ^{••}	0.81 [100]			
V _{Ti} ^{'''} -O _i [×]	0.61 [110]	2.2	20.3	0.54
V _{Sr} ^{''} -O _i [×]	1.24 [100]	0.15	7.2	0.61
Ti _{Ti} [•] -V _O [×]	0.08 [100]	5.1	5.0	

along the [100], [110], and [111] crystallographic directions. A large Ti_{Sr}^{••} off-centering of 0.78 Å along the [100] direction is found to be the most energetically favorable with an energy gain of 0.48 eV with respect to the nonshifted configuration, in agreement with previous estimates [9,10]. The displaced Ti atom forms four Ti-O bonds of length 2.20 Å that are much closer to the Ti-O bond distances in pristine SrTiO₃ (1.95 Å). We attribute this displacement primarily to the covalency effect due to an effective hybridization between $3d$ states of the antisite and $2p$ states of the neighboring O ions as seen from the analysis of the partial density of states. The atomic configuration with the shifted Ti_{Sr}^{••} can thus be considered as an electric dipole comprised of a negatively charged Sr vacancy and a positively charged Ti interstitial which induces the electric polarization.

Using the Berry phase method we estimate the average polarization of the supercell $P^{100}(\text{Ti}_{\text{Sr}}^{\bullet\bullet})$ to be 16.8 $\mu\text{C}/\text{cm}^2$. In full agreement with previous calculations [9], we find that despite the large off-centering of Ti_{Sr}^{••}, its local dipole moment is relatively small due to a small Born effective charge of 1.72 (see Table I). Consequently, the overall dipole moment is dominated by the induced dipole moments in the surrounding cells rather than by the dipole moment of the antisite Ti atom which accounts for about 8.1% of the total dipole moment of the supercell. Thus, the electric dipole moment induced by a large off-centering of the defect atom is accompanied by geometrical distortions polarizing the region surrounding the defect.

We also estimate the migration energy barriers for [100] \rightarrow $[\bar{1}00]$ polarization switching and find that the barrier for the direct switching between these two polarization states is rather large (0.48 eV), while the two-step migration via the intermediate state [110] is characterized by the barrier of only 0.13 eV (see Fig. 2). For this metastable state the average supercell polarization $P^{110}(\text{Ti}_{\text{Sr}}^{\bullet\bullet}) = 15.1 \mu\text{C}/\text{cm}^2$.

The influence of oxygen vacancies on SrTiO₃ polarization properties is not well understood at the *ab initio* level despite the predominant role of this defect in SrTiO₃ defect

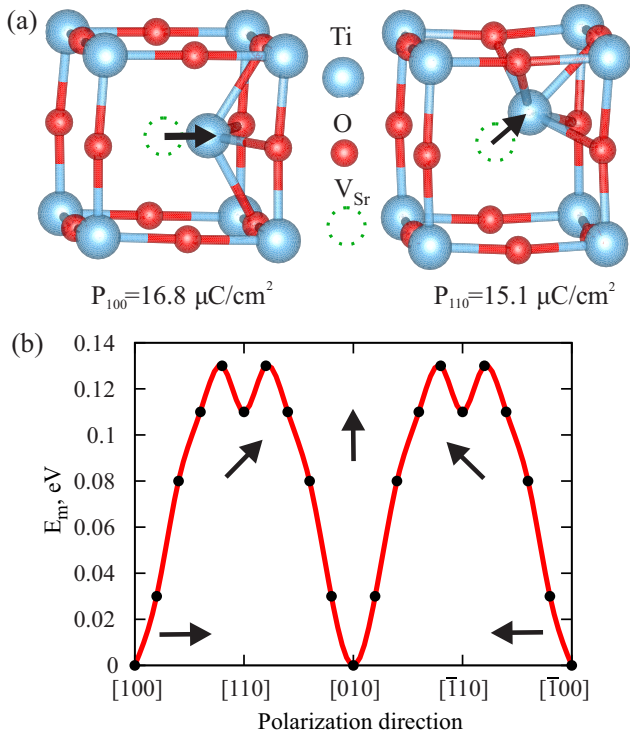


FIG. 2. (a) Atomic structures of SrTiO₃ with the antisite Ti_{Sr}²⁺ defect for two polarization states with Ti_{Sr}²⁺ shifted along the [100] and [110] directions. (b) Migration energy profile between polarization states caused by the Ti_{Sr}²⁺ defect. Polarization reversal from [100] to [1-10] is achieved via the metastable polarization states with the [110] and [1-10] directions.

chemistry. Previous theoretical studies suggested that Ti_{Sr}²⁺ and V_O together with V_{Sr}²⁺ should be the most thermodynamically stable defects in SrTiO₃ under Ti-rich conditions [10,17,23], while the Ti-rich environment is predicted to be energetically more favorable than excess SrO in SrTiO₃ [23]. Calculated formation energies as a function of Fermi level indicate that the doubly charged V_O²⁺ should be more stable than the singly charged V_O[•] and neutral V_O[×] even in *n*-type SrTiO₃ in which the Fermi level is close to the bottom of the conduction band [10,17]. It is expected that the presence of the positively charged oxygen vacancies in the vicinity of the Ti_{Sr}²⁺ defect may change the dipole moment induced by Ti_{Sr}²⁺.

First, our calculations reveal a negative binding energy of about -0.4 eV between V_O²⁺ and Ti_{Sr}²⁺ indicating that the formation of the defect complex is energetically favored over the isolated defects. To examine different atomic arrangements between these defects, we displace Ti_{Sr}²⁺ with respect to V_O²⁺ as shown in Fig. 3. We find that the most stable configuration is nonmagnetic and characterized by a Ti_{Sr}²⁺ off-centering of 0.79 Å along the [110] direction towards the vacancy exhibiting polarization $P^{110}(\text{Ti}_{\text{Sr}}^{2+}-\text{V}_{\text{O}}^{2+}) = 22.6 \mu\text{C}/\text{cm}^2$ which is enhanced with respect to the Ti_{Sr}²⁺ case with no oxygen vacancy. We also find that a slightly less favorable (by 0.02 eV) spin-polarized configuration with a magnetic moment of $2\mu_B$ has a much lower polarization $P^{110}(\text{Ti}_{\text{Sr}}^{2+}-\text{V}_{\text{O}}^{2+}) = 5.61 \mu\text{C}/\text{cm}^2$ caused by a much less pronounced off-centering of 0.43 Å.

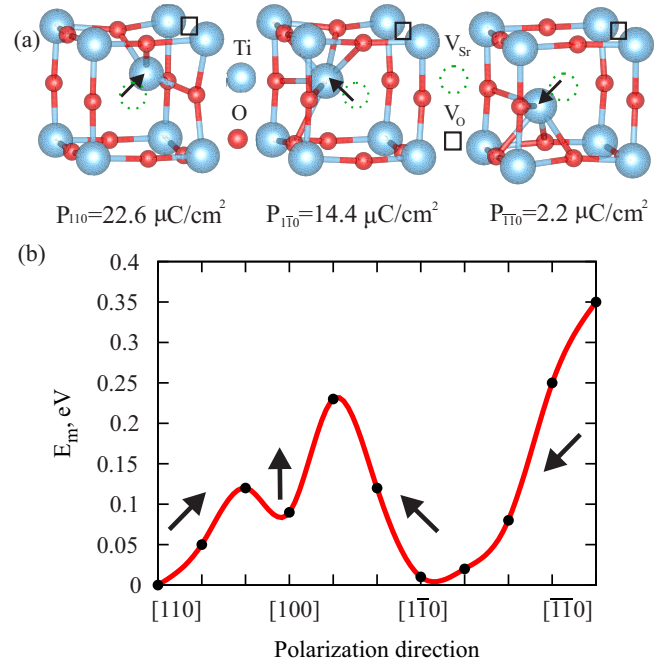


FIG. 3. (a) Atomic structures of SrTiO₃ with Ti_{Sr}²⁺ and V_O²⁺ for polarization states with Ti_{Sr}²⁺ shifted along the [110], [1-10], and [1-1-0] directions. (b) Migration energy profiles between polarization states caused by the Ti_{Sr}²⁺ and V_O²⁺ defects. Polarization switching from [110] to [1-10] can be achieved via the metastable polarization state with the [100] direction.

The nonsymmetrical state P_- is characterized by a reduced polarization $P^{1-10}(\text{Ti}_{\text{Sr}}^{2+}-\text{V}_{\text{O}}^{2+}) = 14.4 \mu\text{C}/\text{cm}^2$ caused by a 0.81 Å off-centering. Such a decrease relative to the most stable P^{110} state could be explained by the opposite directions of dipoles formed by V_{Sr}²⁺-Ti_{Sr}²⁺ and V_{Sr}²⁺-V_O²⁺. The switching barrier between these two polarization states is computed to be 0.24 eV, which is twice higher than for Ti_{Sr}²⁺ with no oxygen vacancy. A displacement along the [1-1-0] direction leads to a substantially diminished polarization $P^{1-1-0}(\text{Ti}_{\text{Sr}}^{2+}-\text{V}_{\text{O}}^{2+}) = 2.2 \mu\text{C}/\text{cm}^2$ and a greater switching barrier.

We next analyze the Ti_{Sr}²⁺-V_O[×] defect complex since neutral V_O[×] may have the formation energy only slightly higher than those of the positive charge states in the *n*-type region [17]. We find that the complex is stable with an estimated binding energy of about -0.35 eV, but is characterized by the metallic behavior and no polarization can be given. In this case one electron of the antisite defect moves to the conduction band forming a metallic state near the Fermi level while the second electron forms a localized in-gap state (Fig. 4). In relation to polarization properties this suggests that the formation of the Ti_{Sr}²⁺-V_O[×] defect complexes may also contribute to the resistive switching in Ti-rich SrTiO₃; however, the interplay between polarization and metallic conductivity being in the focus of many recent studies of perovskite oxides [38,39] deserves a separate detailed investigation.

We should note here that antiferroelectricity in perovskite oxides is a well recognized phenomena that leads to the competition between ferroelectric and antiferroelectric phases depending on the interplay between different factors such as

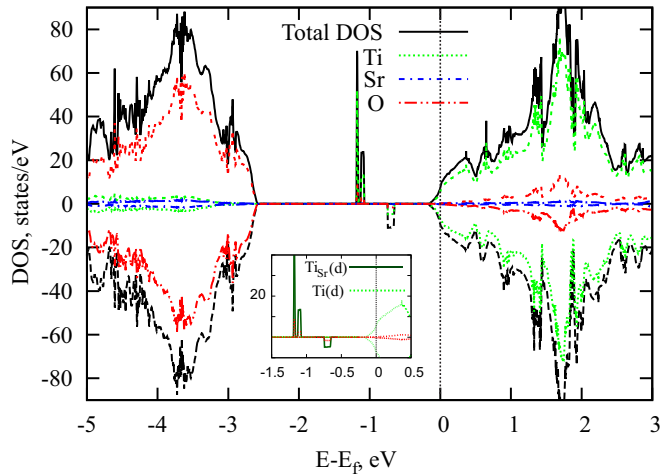


FIG. 4. Density of electronic states calculated for the $\text{Ti}_{\text{Sr}}^{2+}\text{-V}_{\text{O}}^{\times}$ defect complex. The Fermi level corresponds to zero.

chemical composition, strain, size effects, and reconstruction at surfaces [40–42]. Although we have not investigated in detail how various intrinsic defects producing ferroelectric polarization in SrTiO_3 interact with each other, to obtain some insight into the possibility of antiferroelectric ordering, we compared the energetics of both ferroelectric and antiferroelectric configurations of two $\text{Ti}_{\text{Sr}}^{2+}$ antisite defects placed in a model $3 \times 3 \times 3$ supercell. We found that the antiferroelectric configuration is less favorable than the ferroelectric configuration by 0.13 eV.

B. $\text{Sr}_{\text{Ti}}^{\prime\prime}$ antisite defect

Similarly to $\text{Ti}_{\text{Sr}}^{2+}$, the formation of the antisite $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect in which a Sr ion substitutes one Ti ion is expected in Sr-rich SrTiO_3 (Fig. 5) [23]. This configuration can be regarded as an electric dipole composed of a strontium interstitial and a titanium vacancy. In this structure the Sr ion is coordinated by six O atoms with the Sr-O distances being considerably shorter (2.22–2.26 Å) than those in pristine SrTiO_3 (2.76 Å) where Sr is coordinated by 12 oxygens. Our calculations reveal that the most energetically favorable configuration of $\text{Sr}_{\text{Ti}}^{\prime\prime}$ has an off-centering of 0.26 Å along the [110] direction (Fig. 5). We do not observe any significant overlap between the Sr and O states in partial density of states and attribute this displacement mainly to the electrostatic effect. Also, since the ionic size of Sr^{2+} is much larger than that of Ti^{4+} , there is little space for the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ antisite to displace and the off-centering is much smaller than we observe for the $\text{Ti}_{\text{Sr}}^{2+}$ antisite defect.

The calculated electric polarization $P^{110}(\text{Sr}_{\text{Ti}}^{\prime\prime})$ equals to $7.6 \mu\text{C}/\text{cm}^2$ which is about twice smaller than in the $\text{Ti}_{\text{Sr}}^{2+}$ case. The energy barrier calculated for polarization switching is only 0.05 eV rendering a low coercive voltage (Fig. 5). The contribution of the antisite Sr atom to the total dipole moment of the supercell is found to be about 10.6%, being comparable with the $\text{Ti}_{\text{Sr}}^{2+}$ case. This spin-polarized structure of $\text{Sr}_{\text{Ti}}^{\prime\prime}$ induces magnetic moments on the nearest to $\text{Sr}_{\text{Ti}}^{\prime\prime}$ oxygen atoms and is more energetically favorable than the nonmagnetic structure by about 0.17 eV exhibiting a much higher polarization switching barrier of ~ 0.3 eV. We also estimate polarization

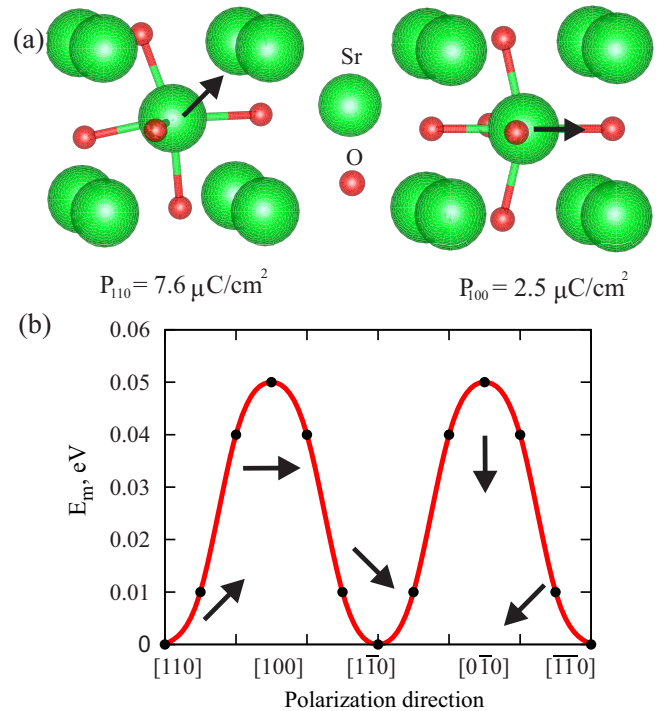


FIG. 5. (a) Atomic structures of SrTiO_3 with the antisite $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect corresponding to two different polarization states with the defect shifted along the [110] and [100] directions. (b) Migration energy profile between polarization states caused by the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect. Polarization switching from the [110] to the $[\bar{1}\bar{1}0]$ direction can be achieved via the polarization states with the [100] and $[0\bar{1}0]$ directions.

$P^{100}(\text{Sr}_{\text{Ti}}^{\prime\prime})$ induced by the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ displacement along the [100] direction, which is the direction of film growth to be as low as $2.5 \mu\text{C}/\text{cm}^2$.

The addition of oxygen vacancies is also found to have a significant impact on ferroelectric polarization induced by the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect. Recently, the formation of $\text{Sr}_{\text{Ti}}^{\prime\prime}\text{-V}_{\text{O}}^{\bullet\bullet}$ defect complexes was observed experimentally during the electroforming and resistive switching of SrTiO_3 [43]. These complexes were previously calculated to have low formation enthalpies under Sr-rich conditions [23] and we estimate that the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect has very large binding energies of -1.76 and -1.85 eV with doubly charged $\text{V}_{\text{O}}^{\bullet\bullet}$ and neutral $\text{V}_{\text{O}}^{\times}$ vacancies, correspondingly.

Our calculations show that the positively charged oxygen vacancy causes a metallic state near the Fermi level and therefore no polarization can be provided for the $\text{Sr}_{\text{Ti}}^{\prime\prime}\text{-V}_{\text{O}}^{\bullet\bullet}$ defect pair. On the other hand, neutral $\text{V}_{\text{O}}^{\times}$ leads to semiconducting behavior and the most stable structure is characterized by a large off-centering (0.81 Å) of the antisite defect along the [100] direction as shown in Fig. 6. In this case the antisite $\text{Sr}_{\text{Ti}}^{\prime\prime}$ forms four short bonds of 2.23 Å and one much longer bond of 2.72 Å with the neighboring oxygen atoms. The average polarization of the supercell is estimated as $15.7 \mu\text{C}/\text{cm}^2$. The energy profile of $\text{Sr}_{\text{Ti}}^{\prime\prime}$ diffusion associated with polarization switching in the presence of $\text{V}_{\text{O}}^{\times}$ becomes nonsymmetrical with a very high switching barrier of 0.76 eV and a flat minimum for the P_- state (Fig. 6). This state induces a small polarization of

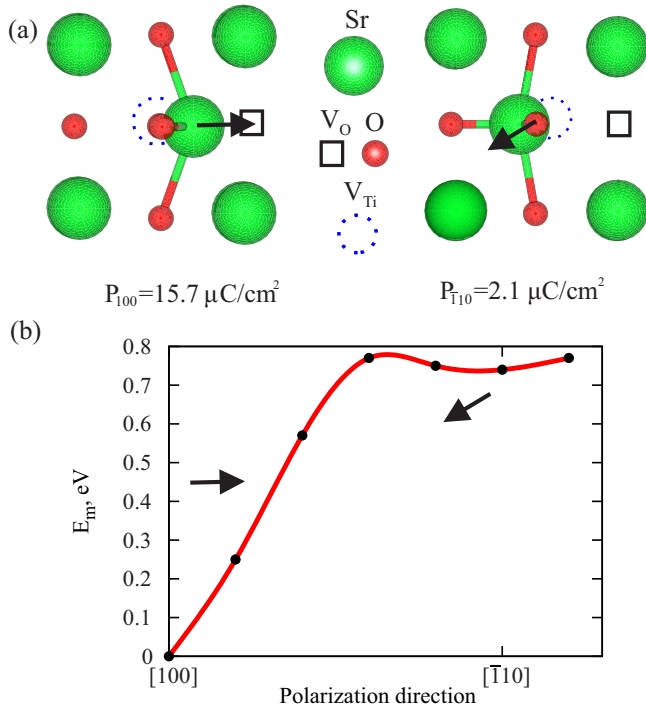


FIG. 6. (a) Atomic structures of SrTiO₃ with the Sr²⁺ defect and neutral V_O^x corresponding to two different polarization states with the antisite defect shifted along the [100] and [110] directions. (b) Energy profile between two polarization states caused by Sr²⁺ and V_O^x. The polarization state for the [110] direction has a very flat minimum suggesting that the state with Sr²⁺ shifted along the [100] direction acts as a trap.

2.1 μC/cm² and should be unstable with respect to polarization switching. The switching via diffusion of oxygen vacancies, however, is expected to have large barriers (~0.6–1.0 eV) [44].

In general, the results obtained for spontaneous polarization induced by the antisite Ti_{Sr}^{••} and Sr_{Ti}²⁺ defects are in qualitative agreement with experimental findings showing that although the excess of Sr can lead to ferroelectricity in polycrystalline SrTiO₃ at low temperatures, the observed polarization is considerably lower than for Ti-rich samples [45].

C. Frenkel defects and small polarons

The deficiency of cation atoms and excess of oxygen atoms leads to the formation of Frenkel defect pairs. In the case of the titanium vacancy V_{Ti}^{'''} and oxygen interstitial O_i^x pair we find that the most stable position for O_i^x is to be shifted from the V_{Ti}^{'''} site along the [110] direction by 0.61 Å as depicted in Fig. 7. The distance between O_i^x and two adjacent lattice oxygen atoms is 1.35 Å, while the corresponding angle between three oxygen atoms is about 110°. The electric dipole formed by this Frenkel pair causes a large average polarization P¹¹⁰(V_{Ti}^{'''}-O_i^x) of about 20.3 μC/cm², but with a high switching barrier of 0.54 eV.

Calculations of the other Frenkel defect pair composed of a Sr vacancy and an oxygen interstitial reveal that it is energetically preferable for O_i^x to be shifted along the [100] direction with the 1.24 Å off-centering from the initial Sr

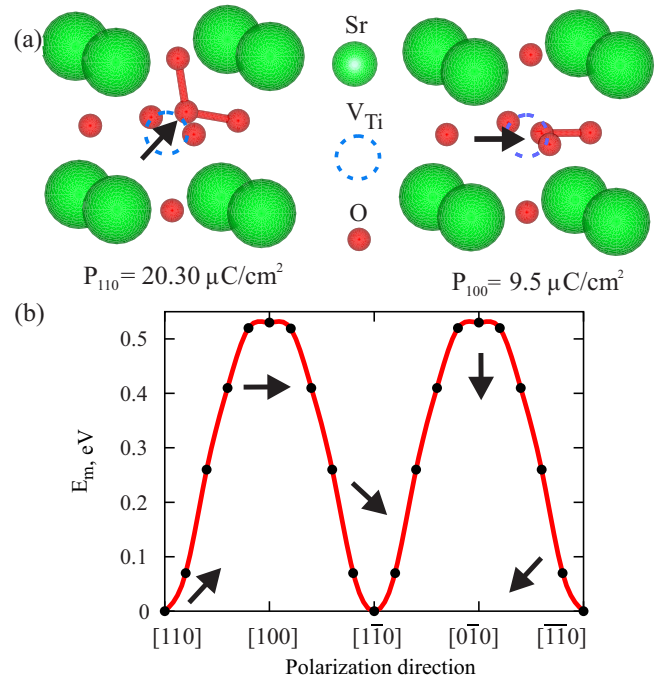


FIG. 7. (a) Atomic structures of SrTiO₃ with the Frenkel defect pair V_{Ti}^{'''}-O_i^x corresponding to two different polarization states with O_i^x shifted along the [110] and [100] directions. (b) Migration energy profile between polarization states caused by V_{Ti}^{'''}-O_i^x.

position (Fig. 8). However, such a significant off-centering does not induce a large local dipole moment because of the very small Born charge of 0.15 on the O interstitial (see Table I). The overall polarization of the supercell in this case is computed

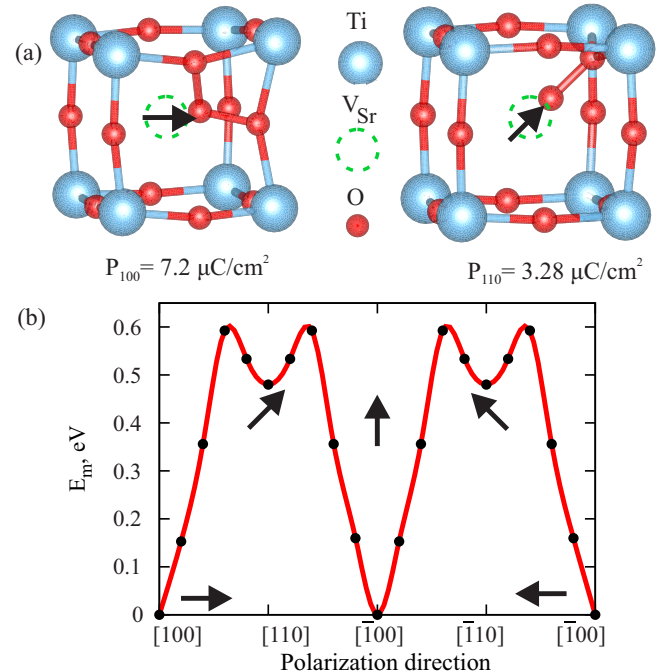


FIG. 8. (a) Atomic structures of SrTiO₃ with the Frenkel defect pair V_{Sr}^{''}-O_i^x corresponding to two different polarization states with O_i^x shifted along the [100] and [110] directions. (b) Migration energy profile between polarization states caused by V_{Sr}^{''}-O_i^x.

to be around $7.2 \mu\text{C}/\text{cm}^2$ with the high diffusion barrier for polarization switching of 0.61 eV .

It was previously shown that excess electrons in the bulk SrTiO_3 do not become localized in the form of small polarons on Ti atoms, but can be stabilized in the presence of oxygen vacancies [46]. It turned out that in n -type SrTiO_3 the most stable configuration corresponds to the case when each oxygen vacancy traps one small polaron remaining in a $+1$ charge state and providing one electron to the conduction band. We find that the dipole moment produced by such a defect pair causes a moderately large polarization of $5.0 \mu\text{C}/\text{cm}^2$.

D. The impact of defect concentration and the $\text{SrTiO}_3/\text{SrRuO}_3$ interface

In this section we aim to examine how the defect concentration and the presence of the interface with SrRuO_3 can impact polarization properties of SrTiO_3 . To simulate different concentrations of the antisite $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ and $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defects we consider one defect in $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$ supercells corresponding to a Sr/Ti ratio of 0.78, 0.93, 0.97, 1.03, 1.07, and 1.28, respectively. In addition, we examine two $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ (or $\text{Sr}_{\text{Ti}}^{\prime\prime}$) defects in a $3 \times 3 \times 3$ supercell with the largest defect separation attainable in this cell which corresponds to the Sr/Ti ratio of 0.86 and 1.16. As seen from Fig. 9, an increase of the $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ defect concentration causes noticeably enhanced polarization, but as the defect concentration increases polarization gets diminished partly due to a much smaller displacement of $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ being 0.45 \AA for Sr/Ti = 0.78 as compared to 0.78 \AA for Sr/Ti = 0.93. A similar trend is observed for the $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defect and we also find that the high concentration of antisite $\text{Sr}_{\text{Ti}}^{\prime\prime}$ (Sr/Ti = 1.29) leads to a metallic electronic structure. This is consistent with experimental observations showing the absence of ferroelectricity in Sr-rich SrTiO_3 (001) thin films [47] as well as the

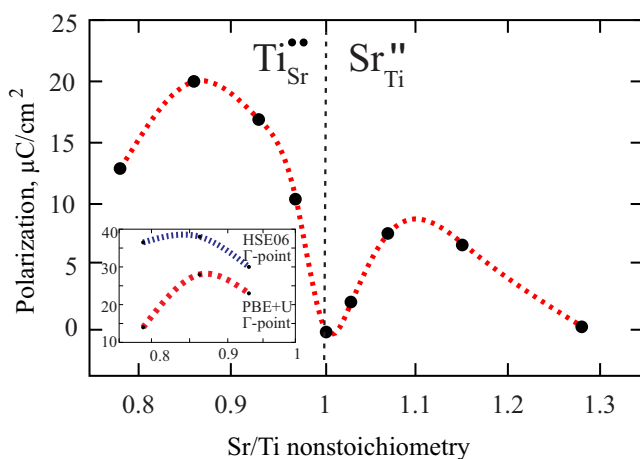


FIG. 9. Average spontaneous polarization as a function of defect concentration. Sr-rich condition Sr/Ti > 1 corresponds to the larger concentration of $\text{Sr}_{\text{Ti}}^{\prime\prime}$ and Sr/Ti < 1 corresponds to the larger concentration of $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$. The inset is a comparison between the results obtained using PBEsol+ U and the hybrid HSE06 functional for three different concentrations of the $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ defect computed only at the Γ point.

presence of ferroelectricity in polycrystalline SrTiO_3 at low stoichiometry of Sr/Ti = 1.04–1.10 [45].

Importantly, for a Sr/Ti ratio of 1.16 the system with two neighboring $\text{Sr}_{\text{Ti}}^{\prime\prime}$ defects becomes more stable if the defects are displaced along the different directions ([110] and $[1\bar{1}0]$) giving rise to a decrease of the total polarization, the effect that is not observed for $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$. Overall, we predict the same trend for spontaneous polarization as a function of Sr/Ti nonstoichiometry as previously measured for Ti- and Sr-rich SrTiO_3 samples [45], with the antisite $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ defect causing a more pronounced polarization than $\text{Sr}_{\text{Ti}}^{\prime\prime}$ for the same defect concentration.

To obtain some insights into the impact of a thin-film interface on polarization properties, we focus on the antisite $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ defect that exhibits the most pronounced and easily switchable polarization in the bulk phase. It was previously demonstrated that the creation of this defect in the $\text{SrTiO}_3/\text{SrRuO}_3$ thin films is more probable than in the bulk SrTiO_3 due to its lower formation energy [9]. Since no polarization was experimentally detected in the SrRuO_3 region of the heterostructure [9], we assume that all the dipole moments are induced by the four SrTiO_3 layers.

In order to directly compare spontaneous polarization of the $\text{SrTiO}_3/\text{SrRuO}_3$ interfacial structure with the case of bulk SrTiO_3 , we also estimate polarization for a $3 \times 3 \times 4$ supercell of the bulk SrTiO_3 that corresponds to the same number of SrTiO_3 layers as in the heterostructure. Our calculations predict that the presence of the interface with metallic SrRuO_3 has very little influence on the average atomic displacements that are a little decreased at the interface, and therefore should not have a considerable impact on the total polarization. Based on the obtained results and the fact that the formation energy of $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ becomes significantly reduced in thin films [9], we conclude that the enhancement of polarization in thin films is not due to the influence of the $\text{SrTiO}_3/\text{SrRuO}_3$ interface.

E. The effect of the functional and k -point sampling

We should note here that it is known that SrTiO_3 exhibits both antiferrodistortive and ferroelectric instabilities in the cubic phase [48]. However, it was found that polar instability in SrTiO_3 is very weak leading to an energy gain of only 0.8 meV per formula unit (at 0 antiferrodistortive angle) reaching around 0.1 meV at the theoretical equilibrium antiferrodistortive angle of 5.7 when using the PBEsol functional, which is consistent with our estimates. We observe that the Ti-O displacement in SrTiO_3 becomes even smaller when using PBEsol+ U as compared to the plain PBEsol functional. In any case, these instabilities should be captured in our models as we consider intrinsic defects in large supercells imposing no symmetry constraints.

To assess the effect of U on polarization properties of SrTiO_3 , we perform additional calculations for the U values in the 4 – 4.5 eV range previously used in the literature for SrTiO_3 . As expected, we find that increasing the U value leads to a stronger electron localization on Ti atoms, while the total polarization is decreased. Similarly, decreasing the U value results in a more pronounced electron delocalization that increases the total polarization. However, the results obtained for the antisite $\text{Ti}_{\text{Sr}}^{\bullet\bullet}$ defect show that variation of the U value

in the 4–4.5 eV range affects ferroelectric polarization only within 10%.

In order to evaluate the effect of the functional on the polarization properties of SrTiO₃, we also employ the HSE06 functional [49] to compute polarization on the example of the antisite Ti_{Sr}^{••} defect as a function of the defect concentration to be compared with the PBEsol+*U* approach (*U*_{eff} = 4.36 eV). Since hybrid calculations for supercell sizes used in our study in combination with dense *k*-point meshes are very time consuming, we only carry out Γ -point calculations. We find that both the *k*-point sampling and the functional have an influence on the calculated polarization (see Fig. 9). For example, polarization for the Sr/Ti = 0.93 nonstoichiometry level estimated using PBE+*U* at the Γ point is found to be 23 $\mu\text{C}/\text{cm}^2$, whereas it is 16.8 $\mu\text{C}/\text{cm}^2$ for a $3 \times 3 \times 3$ *k*-point mesh. The same effect of *k*-point sampling is expected for the HSE06 functional and thus polarization values in the hybrid approach should be lower than we find in calculations using only the Γ point. Overall, however, both hybrid and PBE+*U* approaches show the same trend in polarization as a function of the antisite concentration with the hybrid method showing more pronounced polarization.

IV. CONCLUSIONS

In summary, we have explored the impact of a range of native point defects on ferroelectric polarization and the mechanisms of polarization reversal in bulk and thin films of

SrTiO₃ by employing DFT calculations in combination with the Berry phase approach. We have shown that the antisite Ti_{Sr}^{••} defect should result in the pronounced spontaneous polarization; however, the presence of oxygen vacancies may substantially reduce the polarization, make polarization switching barriers much higher, and even cause noninsulating behavior. The presence of antisite Sr_{Ti}^{''} induces smaller polarization with lower barriers of polarization switching than those for Ti_{Sr}^{••}, in quantitative agreement with previously measured polarization for Sr- and Ti-rich SrTiO₃ samples. We have also found that the increase in spontaneous polarization in SrTiO₃/SrRuO₃ thin films can be achieved by tailoring the degree of Sr/Ti nonstoichiometry and is not due to the presence of SrTiO₃/SrRuO₃ interfaces. Some other intrinsic point defects such as Frenkel defect pairs and electron small polarons have been also found to give sizable contributions to spontaneous polarization of SrTiO₃.

ACKNOWLEDGMENTS

We would like to thank Alexei Gruverman for fruitful discussions and comments on this study. The Holland Computing Center at the University of Nebraska–Lincoln is acknowledged for computational support. This work was supported by the National Science Foundation (NSF) through the Nebraska Materials Research Science and Engineering Center (MRSEC) (Grant No. DMR-1420645). V.A. gratefully acknowledges support from the startup package.

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