Role of Ti Antisitelike Defects in SrTiO$_3$

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Through first-principles calculations, the role of Ti antisitelike defects in the electrical and optical properties of SrTiO$_3$ is proposed. Significant Ti off-centering from the Sr site toward the [100] or [110] direction leads to switchable polar states, and attractive interactions with the O vacancy drive them to form defect pairs. In these defect configurations, localized electronic states are introduced below the conduction band minimum. Our findings on Ti antisitelike defects suggest that they are responsible for the ferroelectricity and blue light emission in nonstoichiometric SrTiO$_3$.

In recent years, SrTiO$_3$ has been greatly focused on because of its variety of outstanding physical properties: (i) an insulator-metal transition and superconductivity at low temperatures by electron doping [1,2], (ii) the formation of a two-dimensional electron gas at interfaces between SrTiO$_3$ and other oxides [3], (iii) blue light emission in Ar$^+$-irradiated, electron-doped, and O-deficient SrTiO$_3$ [4], and (iv) ferroelectricity without any intentional doping [5]. At present, it is considered that the O vacancy (V$_O$) is intimately related to these phenomena. The formation of V$_O$ clusters has been suggested through scanning transmission electron microscopy observation [6]. A recent density functional study [7] showed that linear clustering is more stable than isolated V$_O$ and is accompanied by strong electron localization at the neighboring Ti 3$d$ states, which can correspond to a blue light emission level inside the band gap. On the other hand, several experimental studies have revealed the presence of a Sr vacancy (V$_{Sr}$) and its complexes [8,9]. In spite of the fact that defects other than V$_O$ can also contribute to the above issues, such effects have not yet been discussed in depth.

In this Letter, we provide new insight into nonstoichiometric SrTiO$_3$ through a systematic first-principles study of Ti antisitelike defects. Our results demonstrate that off-centered Ti from the Sr site (Ti$_{O/C}$), regarded as a polar defect pair composed of a Ti interstitial (Ti$_i$) and V$_{Sr}$, has a low formation energy comparable to that of V$_O$. Ti$_{O/C}$ is switchable between its different configurations, and forms a defect pair with V$_O$ (Ti$_{O/C}$ + V$_O$) as a result of attractive interactions. Such features can explain the observation of ferroelectricity in undoped SrTiO$_3$ [5] as well as the formation of V$_{Sr}$-related defect species [8,9]. Besides, these defects introduce deep electronic states in the band gap, which can contribute to blue light emission [4] and optical absorption involving two in-gap levels [10,11].

The calculations were performed using the projector augmented-wave (PAW) method [12] and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) [13] as implemented in the VASP code [14]. PAW data sets with radial cutoffs of 1.3, 1.3, and 0.8 Å were used for Sr, Ti, and O, respectively. The electronic wave functions were described using a plane wave basis set with an energy cutoff of 400 eV. To correct the on-site Coulomb interaction of the Ti 3$d$ orbitals, a rotationally invariant + $U$ method [15] was applied with $U = 5.0$ eV and $J = 0.64$ eV [7,16]. A $3 \times 3 \times 3$ supercell containing 135 atoms and $k$ points sampled using a $2 \times 2 \times 2$ mesh were used. The atomic coordinates were relaxed until the Hellmann-Feynman force acting on each atom was reduced to less than 0.02 eV/Å.

The defect formation energies are evaluated as

$$E_f (D^q) = E_F (D^q) - E_F (H) - \sum_n \mu_n + q (E_V + E_F),$$

(1)

where $E_F (D^q)$ is the total energy of a supercell with a defect $D$ in charge state $q$, and $E_F (H)$ is the total energy of a perfect SrTiO$_3$ supercell. $n_i$ is the number of type $i$ atoms added to ($n_i > 0$) and/or removed from ($n_i < 0$) the perfect supercell, and $\mu_i$ is the atomic chemical potential.

Two different O-poor conditions, i.e., the Sr- and Ti-rich limit ($\mu_{Sr} = \mu_{Sr(bulk)}$, $\mu_{Ti} = \mu_{Ti(bulk)}$, and $\mu_{Sr} + 3 \mu_{O} = \mu_{SrTiO_3(bulk)}$) and the Ti-rich limit ($\mu_{Ti} = \mu_{Ti(bulk)}$, $\mu_{Ti} + \mu_{O} = \mu_{TiO(bulk)}$, and $\mu_{Sr} + 3 \mu_{O} = \mu_{SrTiO_3(bulk)}$), were considered to address defect energetics in reduced SrTiO$_3$. $E_V$ and $E_F$ are the valence band maximum (VBM) and the Fermi level measured from the VBM, respectively.

To correct errors associated with an insufficient description of the band structure by the GGA + $U$ and the use of finite-sized supercells, a few postprocesses were carried out [17–19]: (i) VBM alignment was applied to charged systems using average potentials. (ii) Band-gap corrections were performed on the basis of defect-induced electronic states. The formation energies of V$_O$, whose one-electron states follow the upward shift of the conduction band due to the $U$ correction, were extrapolated to an experimental...
band gap ($E_{g}^{\exp}$) of 3.3 eV by adding $m\Delta E_g$, where $m$ and $\Delta E_g$ are the number of electrons occupying the defect states and the band-gap difference, equal to $E_{g}^{\exp} - E_{g}^{GGA+U}$, respectively ($E_{g}^{GGA+U} = 2.34$ eV). In the case of TiOC and TiOC + V$_O$, whose states become deeper from the conduction band minimum (CBM) with increasing $U$ and lie at $\sim 1$ eV below the CBM for $U = 5.0$ eV and $J = 0.64$ eV, the formation energies were obtained using the same scheme as for the case of V$_O$. The validity of this extrapolation scheme for TiOC and TiOC + V$_O$ was assessed using the HSE06 hybrid functional [20]. It yields a band gap of 3.25 eV, which is much closer to $E_{g}^{\exp}$ than the GGA + $U$ value. However, the one-electron defect states are located at $\sim 1$ eV below the CBM, similar to the case of using GGA + $U$. This means that the defect states observed in the GGA + $U$ calculations follow the shift of the CBM, and hence our correction scheme for TiOC and TiOC + V$_O$ is justified. (iii) The cell-size dependence was examined using supercells containing 40–625 atoms. It is known that the formation energies of V$_{Sr}$ in SrTiO$_3$ decrease as the cell size increases owing to atomic relaxation associated with electron delocalization [21]. We found such trends for TiOC and V$_O$ when the GGA was used. In the GGA + $U$ case, however, the formation energies of TiOC and neutral V$_O$ are almost independent of the cell size (they vary within a few tenths of eV). The formation energies of charged V$_O$ decrease as the cell size increases, and the trends with and without the $U$ correction appear to be identical. An extrapolation to the dilute limit, i.e., infinite cell size, indicated that their formation energies can be lowered by $\sim 1$ eV from the values for the 135-atom cell that are shown later in Fig. 3. However, this does not alter our discussion and conclusions.

Figure 1 shows the atomic configurations of TiOC. The Sr site in SrTiO$_3$ is surrounded by 12 symmetrically equivalent O atoms. The antisite Ti atom at this site is unstable, and thereby large Ti off-centering of $\sim 0.8$ Å occurs toward one of the six equivalent positions along the [100] direction (TiOC:100) and one of 12 equivalent positions along the [110] direction (TiOC:110) (Fig. 1 and Table I). TiOC:100 forms four Ti–O bonds of length 2.25 Å, and TiOC:110 has one Ti–O bond of length 2.19 Å and four bonds of length 2.33 Å. Such off-centering can be understood in terms of the large difference in ionic radius between Ti$^{2+}$ (0.86 Å) and Sr$^{2+}$ (1.44 Å) [22], similar to the Li off-centering in K$_3$Li$_3$NbO$_9$ [23]. The distance between the Ti atoms in the TiOC:100 and TiOC:110 configurations is 0.59 Å, and the energy barriers are 0.23 eV for TiOC:100 → TiOC:110 and 0.14 eV for TiOC:100 → TiOC:100. These values are much smaller than the reported migration energies of 0.6 eV for V$_O$ [7] and 1.2 eV for the linear V$_O$-cluster [7]. The switching of TiOC:100 ↔ TiOC:110 is thus very likely. Owing to the large Ti displacements, each TiOC can also be regarded as a polar defect pair, i.e., Ti$_i$ + V$_{Sr}$, having a dipole moment (+$p$) in the V$_{Sr}$ to Ti$_i$ direction. The +$p$ direction is [100] for TiOC:100 and [110] for TiOC:110. These atomic structures of TiOC:100 and TiOC:110, i.e., Ti$_i$ + V$_{Sr}$, are consistent with the experimental observations of V$_{Sr}$ and related defects [8,9].

Moving on to the electronic structure, both configurations of TiOC introduce localized states below the CBM in the majority spin component, as shown in Fig. 2 and Table I. No in-gap states are found in the minority spin component, yielding a magnetic moment of $2\mu_B$. However, TiOC does not have a strong effect on the host conduction and valence bands. In the case of TiOC:100, two deep localized states are located at 0.96 and 1.29 eV below the CBM and have orbital characteristics of $d_{yz}$ and $(d_{yz}-d_{zx})$, respectively. TiOC:110 behaves similarly. Its induced states lie 1.02 eV with $(d_{yz}$ and $d_{zx})$

![FIG. 1 (color online). Local atomic configurations of off-centered Ti antisitelike defects: TiOC:100 and TiOC:110. O$_{\text{p}}$, O$_{\text{p}}$, and O$_{\text{p}}$, respectively (only one of symmetrically equivalent atoms is indicated for each species).](Image)

| TABLE I. Properties of off-centered Ti antisitelike defects (TiOC) and pairs of TiOC with V$_O$ (TiOC + V$_O$). $d$ denotes the atomic distance from Ti to V$_{Sr}$ in TiOC and from Ti to V$_O$ in TiOC + V$_O$. $\epsilon$ is the energy of the defect-induced one-electron state measured from the CBM. $E_b$ is the binding energy between TiOC and V$_O$. |
|---|---|---|---|---|
| TiOC | $d$ (Å) | TiOC + V$_O$ [+P] | $d$ (Å) | TiOC + V$_O$ [-P] |
| TiOC:100 | 0.77 | 0.96 | 1.29 | 0.18 | 1.10 | 3.10 | 0.01 | 0.31 | 2.12 |
| TiOC:110 | 0.76 | 1.02 | 1.12 | 2.25 | 0.28 | 1.15 | 3.61 | -0.10 | 0.92 | 1.11 |

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characteristics and 1.12 eV with \( (d_{3z^2-r^2} \text{ and } d_{xy}) \) characteristics below the CBM. Thermodynamical transition levels, \( \epsilon(2+/+) \) and \( \epsilon(+/0) \), occur at 1.54 and 0.31 eV below the CBM for TiOC:100 and 1.17 and 0.24 eV for TiOC:110, respectively [Fig. 3]. Therefore, neither TiOC:100 nor TiOC:110 release their electrons into the conduction band at room temperature; i.e., they are deep donors. Owing to the high formation energies, the concentrations of both defects should be low in the \( n \)-type region, i.e., when \( E_F \) is close to the CBM, under Sr- and Ti-rich conditions. At the Ti-rich limit, the formation energies of these defects are lowered by \( \sim 2 \) eV, and are comparable to that of \( V_O \) in the \( n \)-type region. Thus, TiOC:100 and TiOC:110 can be dominant defects in Ti-rich SrTiO\(_3\) as well as \( V_O \). It is noteworthy that their formation energies are much higher under Sr-poor, Ti-rich, and O-rich conditions; for example, at the limit given as \( \mu_{\text{Ti}} + 2\mu_{O} = \mu_{\text{TiO}_2(\text{bulk})}, \mu_{O} = \frac{1}{2}\mu_{\text{O}_2(\text{molecule})}, \mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_{O} = \mu_{\text{SrTiO}_3(\text{bulk})} \), they are 4.88 eV higher than the values at the Ti-rich limit. Therefore, TiOC is unlikely to form under the O-rich conditions.

Another finding for TiOC defects is that they favor coupling with \( V_O \). In the \( n \)-type region, where the neutral and 2+ charge states are energetically the most favorable for TiOC and \( V_O \), respectively, the binding energy \( E^b \) is obtained as

\[
E^b = E^f((\text{TiOC} + V_O)^{2+}) - E^f(\text{TiOC}^0) - E^f(V_O^+) \tag{2}
\]

A negative \( E^b \) indicates that TiOC and \( V_O \) are preferentially located close to each other (exothermic), whereas a positive value means that they repel each other (endothermic). By taking into account the two types of \( V_O \) locations using an idea in Ref. [24] as an analogy, the stability of the defect pairs is monitored: one binds with the nearest-neighbor \( V_O \) lying in (nearly) the same direction as the +p direction, and the other binds with the closest \( V_O \) located in (nearly) the opposite direction. The former and latter defect pairs are denoted as \([+P]\) and \([-P]\), and the corresponding O atoms are indicated as \( O_{+p} \) and \( O_{-p} \) in Fig. 1, respectively. Because of the positive charge of \( V_O \), it is expected that \([+P]\) enhances the \(+p\) of isolated TiOC but \([-P]\) makes it weaker. We found that \([+P]\) is exothermic for both TiOC:100 and TiOC:110 and more stable than \([-P]\) by \( \sim 0.2 \) eV [Table I]. Accordingly, we can conjecture that as the \( V_O \) concentration increases, the attractive interactions facilitate the formation of TiOC + \( V_O \) \([+P]\). TiOC:100 + \( V_O \) \([+P]\) and TiOC:110 + \( V_O \) \([+P]\) also yield deep localized one-electron states at nearly 1.1 eV from the CBM in both spin components (zero \( \mu_B \)) [Fig. 2 and Table I]. Spin-polarized configurations with a magnetic moment of \( 2\mu_B \) are found to be less stable by 0.04 eV for both TiOC + \( V_O \) [25].

On the basis of our results, we now explain two interesting phenomena observed in various experiments, for which the mechanisms are not yet clear. First, how TiOC and its pair are related to the blue light emission [4] and the two in-gap optical absorption levels [10,11] is clarified. According to the Franck-Condon principle, vertical transition energies have been evaluated as the differences of total energies after the band-gap corrections. The emission energy in the recombination process of an electron (\( e^- \)) at the deep donor states of TiOC with a hole (\( h^+ \)) at the VB, i.e., TiOC + \( h^+ \to \text{TiOC}^+ \), is computed to be \( \sim 2.3 \) eV for both TiOC:100 and TiOC:110. The \([+P]\) pairs provide similar energies of \( \sim 2.4 \) eV by \( (\text{TiOC} + V_O)^{2+} + h^+ \to (\text{TiOC} + V_O)^{3+} \). These values are close to the blue light emission energy of \( \sim 2.8 \) eV [4]. For the absorption, when the electrons at the deep states of TiOC:100 and TiOC:110 are photoexcited to the CBM, they produce absorption ener-
gies of 1.0–1.1 eV for $\text{Ti}^{4+}_{\text{OC}} \rightarrow \text{Ti}^{3+}_{\text{OC}} + e^-$. Likewise, the $[+P]$ pairs provide energies of $\sim 1.0$ eV for $(\text{TiO}_6 + V_O)^{2+} \rightarrow (\text{TiO}_6 + V_O)^{3+} + e^-$ and 2.2–2.3 eV for $(\text{TiO}_6 + V_O)^{3+} \rightarrow (\text{TiO}_6 + V_O)^{4+} + e^-$. These transitions are consistent with measurement of the two broad peaks centered at approximately 1.3–1.4 and 2.4–2.5 eV in the absorption spectra [10,11].

Next, the ferroelectricity in the reduced SrTiO$_3$ samples [5] can be explained by $\text{TiO}_6$ and $\text{TiO}_6 + V_O$. There are two scenarios considered: (i) Similar to typical displacive-type ferroelectrics, $\text{TiO}_6$ has switchable dipole moments, i.e., $\text{TiO}_6:100 \rightarrow \text{TiO}_6:100$ (e.g., via $\text{TiO}_6:110$, $\text{TiO}_6:010$, and $\text{TiO}_6:110$) or $\text{TiO}_6:110 \rightarrow \text{TiO}_6:110$ (e.g., via $\text{TiO}_6:010$, $\text{TiO}_6:110$, and $\text{TiO}_6:100$) over the low energy barriers of $\sim 0.2$ eV as described above. The switching energy is comparable to the double-well barriers of $\sim 0.1$ eV in ferroelectric PbTiO$_3$ [26] and $\sim 0.15$ eV in K$_{0.5}$Li$_{0.5}$NbO$_3$ [23]. With increasing $\text{TiO}_6$ concentrations, i.e., decreasing distances between the $\text{TiO}_6$, the long-range dipole-dipole interaction may become stronger and yield a net polarization by the alignment of $+\nu$ dipole moments. (ii) Recently, ferroelectricity in Ti-site-doped SrTiO$_3$ has been suggested to be closely connected to the formation of polar nano-regions (PNRs) [27,28], which are known to play a crucial role in ferroelectric relaxor behavior [29]. In Ca- and Pr-doped systems, the PNRs are created around the A-site dopants. By the analogy with the extrinsic A-site dopants, it is natural to consider $\text{TiO}_6$ as an intrinsic A-site dopant. $\text{TiO}_6$ and $\text{TiO}_6 + V_O$ in reduced SrTiO$_3$ are expected to create the PNRs around themselves.

The larger experimental net polarization observed in reduced SrTiO$_3$ [5] than that in Ca-doped SrTiO$_3$ is probably due to the large Ti off-centering ($\sim 0.8$ Å) from the Sr site in the $\text{TiO}_6$ configurations, which may induce a larger local dipole moment and/or create stronger PNRs compared with those developed by relatively weak Ca off-centering ($\sim 0.1–0.3$ Å) [30].

In conclusion, the crucial roles of the Ti off-centering defects in reduced SrTiO$_3$ are illustrated thorough first-principles calculations. The Ti off-centering exhibits two stable configurations, switching between them, and coupling with the O vacancy. These defects can lead to the ferroelectric state without intentional doping. Both Ti off-centering configurations and their pairs with the O vacancy produce in-gap energy states, which elucidates the blue light emission and the optical absorption involving two deep levels.

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