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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$_3$.

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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 V$_O$ 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 a possibility has 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$_{iOC}$), 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$_{iOC}$ is switchable between its different configurations, and forms a defect pair with V$_O$ (Ti$_{iOC}$ + 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

$$E^f(D^q) = E_T(D^q) - E_T(H) - \sum_i n_i \mu_i + q(E_V + E_F),$$

(1)

where $E_T(D^q)$ is the total energy of a supercell with a defect $D$ in charge state $q$, and $E_T(H)$ 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
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 Ti$_{OC}$. 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 (Ti$_{OC:100}$) and one of 12 equivalent positions along the [110] direction (Ti$_{OC:110}$) (Fig. 1 and Table I). Ti$_{OC:100}$ forms four Ti–O bonds of length 2.25 Å, and Ti$_{OC:110}$ 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$_5$Li$_3$NbO$_9$ [23]. The distance between the Ti atoms in the Ti$_{OC:100}$ and Ti$_{OC:110}$ configurations is 0.59 Å, and the energy barriers are 0.23 eV for Ti$_{OC:100} \rightarrow$ Ti$_{OC:110}$ and 0.14 eV for Ti$_{OC:100} \leftarrow$ Ti$_{OC:110}$. 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 Ti$_{OC:100} \rightarrow$ Ti$_{OC:110}$ is thus very likely. Owing to the large Ti displacements, each Ti$_{OC}$ 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 Ti$_{OC:100}$ and [110] for Ti$_{OC:110}$. These atomic structures of Ti$_{OC:100}$ and Ti$_{OC:110}$, 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 Ti$_{OC}$ 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, Ti$_{OC}$ does not have a strong effect on the host conduction and valence bands. In the case of Ti$_{OC:100}$, two deep localized states are located at 0.96 and 1.29 eV below the CBM and have orbital characteristics of $d_{xz}$ and ($d_{x^2-y^2}$ and $d_{z^2}$), respectively. Ti$_{OC:110}$ behaves similarly. Its induced states lie 1.02 eV with ($d_{xz}$ and $d_{xt}$)
characteristics and 1.12 eV with \((d_{3z^2-r^2} \text{ and } d_{xy})\) characteristics below the CBM. Thermodynamical transition levels, \(E(2^+)/E\) and \(E(+0)/E\), 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 \(-2\) eV, and are comparable to that of VO in the \(n\)-type region. Thus, TiOC:100 and TiOC:110 can be dominant defects in Ti-rich SrTiO\(_3\) as well as VO. 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 \(\mu_{\text{Ti}} + 2\mu_O = \mu_{\text{TiO}_2(\text{bulk})}, \mu_O = \frac{1}{2} \mu_{\text{O}_2(\text{molecule})}\) and \(\mu_{\text{Sr}} + \mu_{\text{Ti}} + 3\mu_O = \mu_{\text{SrO}_2(\text{bulk})}\), 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 VO. In the \(n\)-type region, where the neutral and 2+ charge states are energetically the most favorable for TiOC and VO, respectively, the binding energy \(E^b\) is obtained as

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

A negative \(E^b\) indicates that TiOC and VO 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 VO locations using an idea in Ref. [24] as an analogy, the stability of the defect pairs is monitored: one binds with the nearest-neighbor VO lying in (nearly) the same direction as the \(+p\) direction, and the other binds with the closest VO 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 VO, 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 \(-0.2\) eV [Table I]. Accordingly, we can conjecture that as the VO concentration increases, the attractive interactions facilitate the formation of TiOC + VO \([+P]\). TiOC:100 + VO \([+P]\) and TiOC:110 + VO \([+P]\) 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 + VO [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 VBM, i.e., TiOC \(+ h^+ \rightarrow TiOC^+\) is computed to be \(-2.3\) eV for both TiOC:100 and TiOC:110. The \([+P]\) pairs provide similar energies of \(-2.4\) eV by \((\text{TiOC} + V_O)^{2+} + h^+ \rightarrow (\text{TiOC} + V_O)^{3+}\). These values are close to the blue light emission energy of \(-2.8\) 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 TiO$^+$ → TiO$^{2+}$ + e$^-$ and 1.8–2.1 eV for TiO$_2$ → TiO$^{3+}$ + e$^-$. Likewise, the [+P] pairs provide energies of ~1.0 eV for (TiO$_2$ + V$_O$)$^{2+}$ → (TiO$^+$ + V$_O$)$^{3+}$ + e$^-$ and 2.2–2.3 eV for (TiO$_2$ + V$_O$)$^{3+}$ → (TiO$^+$ + 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 TiO$_2$ and TiO$_2$ + V$_O$. There are two scenarios considered: (i) Similar to typical displacive-type ferroelectrics, TiO$_2$ has switchable dipole moments, i.e., TiO$_{101}^{100}$ → TiO$_{110}^{110}$ (e.g., via TiO$_{110}$, TiO$_{301}$, and TiO$_{110}^{110}$) or TiO$_{110}$ → TiO$_{1110}$ (e.g., via TiO$_{110}$, TiO$_{110}$, and TiO$_{110}^{110}$), over the low energy barriers of ~0.2 eV as described above. The switching energy is comparable to the double-well barriers of ~0.1 eV in ferroelectric PbTiO$_3$ [26] and ~0.15 eV in K$_{0.5}$Li$_{0.5}$NbO$_3$ [23]. With increasing TiO$_2$ concentrations, i.e., decreasing distances between the TiO$_2$, the long-range dipole-dipole interaction may become stronger and yield a net polarization by the alignment of +p dipole moments. (ii) Recently, ferroelectricity in A-site-doped SrTiO$_3$ has been suggested to be closely connected to the formation of polar nanostructures (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 TiO$_2$ as an intrinsic A-site dopant. TiO$_2$ and TiO$_2$ + V$_O$ in reduced SrTiO$_3$ are expected to create the PNRs among 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 (~0.8 Å) from the Sr site in the TiO$_2$ configurations, which may induce a larger local dipole moment and/or create stronger PNRs compared with those developed by relatively weak Ca off-centering (~0.1–0.3 Å) [30].

In conclusion, the crucial roles of the Ti off-centering defects in reduced SrTiO$_3$ are illustrated through 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 elucidate the blue light emission and the optical absorption involving two deep levels.

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[25] We found that the stability of TiO$_{101}^{100}$ + V$_O$ sensitively depends on spin configurations and applied U values. In the non-spin-polarized case, [+P] is the most stable among TiO$_{101}^{100}$ + V$_O$ involving V$_O$ at various O sites [Fig. 1], while the spin-polarized configuration of TiO$_{101}^{100}$ + V$_O$ has a 0.08 eV lower energy than [+P]. In contrast, another $U - J$ value of 2.3 eV [7] predicts that [+P] is the most favorable irrespective of the spin configurations. Although these results imply an uncertainty in the most stable configuration and hence the direction of the dipole moment for TiO$_{101}^{100}$ + V$_O$, we focus on the [+P] and [-P] configurations for concise discussion.