Composition dependent intrinsic defect structures in SrTiO$_3$

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Intrinsic point defect complexes in SrTiO$_3$ under different chemical conditions are studied using density functional theory. The Schottky defect complex consisting of nominally charged Sr, Ti and O vacancies is predicted to be the most stable defect structure in stoichiometric SrTiO$_3$, with a relatively low formation energy of 1.64 eV per defect. In addition, the mechanisms of defect complex formation in nonstoichiometric SrTiO$_3$ are investigated. Excess SrO leads to the formation of oxygen vacancies and a strontium–titanium antisite defect, while a strontium vacancy together with an oxygen vacancy and a titanium–strontium antisite defect are produced in an excess TiO$_2$ environment. Since point defects, such as oxygen vacancies and cation antisite defects, are intimately related to the functionality of SrTiO$_3$, these results provide guidelines for controlling the formation of intrinsic point defects and optimizing the functionality of SrTiO$_3$ by controlling nonstoichiometric chemical compositions of SrO and TiO$_2$ in experiments.

1 Introduction

Ceramics with the perovskite-type structure (general formula ABO$_3$) consist of a network of corner-sharing BO$_6$ octahedra enclosing large cavities, which form higher-coordination sites for the A-cations in a roughly cubic array. This structure can accommodate a wide variety of chemical compositions and atomic defects, which have been identified as the origin of the rich variety of phenomena observed in perovskite oxides. As a prototypical perovskite, strontium titanate (SrTiO$_3$) is an ideal model system, due to both its simple cubic symmetry and its wide applications, such as insulating layers in dynamic random-access memories, ferroelectric thin-film structures, wide applications, such as insulating layers in dynamic random-access memories. It has also been elucidated. Here, grain boundaries have been found to be intrinsically nonstoichiometric. Such nonstoichiometry is dominated by various types of point defects at different grain boundaries. These defects play a key role in the stability of grain boundaries; leading to structural distortions and significant changes in material properties.

The stability of various types of point defects is a focus of a number of theoretical studies. Theoretical investigations using empirical interatomic potentials have evaluated the energetics of intrinsic point defects in undoped and doped SrTiO$_3$. These studies predicted that the Schottky defect complex, V$_{Sr}^{2-}$ + V$_{Ti}^{4+}$ + 3V$_{O}^{2-}$, has a much smaller formation energy than Sr, Ti and O Frenkel defect complexes. For dopants, it has been shown that all mono- and divalent cations prefer to substitute at strontium sites, but the substitution sites for trivalent and tetravalent cations are more complex. On the other hand, theoretical investigations of SrTiO$_3$ using first principles calculations have also been performed, but to our knowledge these studies have focused primarily on isolated point defects. Tanaka et al. studied the energetics of Sr (V$_{Sr}$), Ti (V$_{Ti}$) and O (V$_{O}$) vacancies, and they found that the relative stability of the defect species is dependent upon the atomic chemical potential. Choi et al. investigated the energetics of the Ti$_{Sr}$ cation antisite defect and predicted that the Ti$_{Sr}$ antisite defect could be the dominant defect in Ti-rich SrTiO$_3$, as well as V$_{O}$. In Nb-doped SrTiO$_3$, with very modest modifications in the Sr/Ti ratio, the conductivity can be tuned by several orders of magnitude, producing either a dark or light colored insulator. Furthermore, through a combination of transmission electron microscopy and first principles calculations, the effect of intrinsic point defects on the grain boundary of SrTiO$_3$ has also been elucidated. Here, grain boundaries have been found to be intrinsically nonstoichiometric. Such nonstoichiometry is dominated by various types of point defects at different grain boundaries. These defects play a key role in the stability of grain boundaries; leading to structural distortions and significant changes in material properties.

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While a great number of experimental and theoretical investigations have been performed, the types and concentrations of possible defect complexes in stoichiometric and nonstoichiometric SrTiO3 remain unverified. In this study, we aim to provide: (1) fundamental and comprehensive insight into the energetics and stability of charged point defect complexes in SrTiO3; and (2) guidelines for the experimental fabrication and optimization of the properties of SrTiO3 through the control of point defect types. This paper is structured as follows: first, we calculate the energetics of isolated defects in different charged states, in which the chemical potential environments resulting from SrTiO3 stability limits are considered. Subsequently, the types and concentrations of predominant defect complexes under stoichiometric and nonstoichiometric SrTiO3 are quantitatively analyzed. We predict that the Schottky defect complex consisting of nominally charged Sr, Ti and O vacancies is the most stable defect structure. Furthermore, we predict that specific defect complexes can be obtained by controlling the relative chemical compositions of SrO and TiO2 during the experimental growth process.

2 Computational details

2.1 DFT calculation details

The VASP (Vienna Ab Initio Simulation Package) code using the projector augmented wave method is used in the present density functional theory (DFT) calculations.20 The generalized gradient approximation (GGA) with the exchange correlation potential of Perdew–Burke–Ernzerhof (PBE) is selected.20 To correct for the on-site Coulomb interaction of the 3d orbitals, the rotationally invariant +U method21 is applied with U = 5.0 eV and J = 0.64 eV.20 All computations are based on a 3 × 3 × 3 supercell consisting of 135 atoms with a 2 × 2 × 2 k-point grid22 and a cutoff energy of 400 eV for the plane wave basis set. The crystal structures were relaxed until the forces on individual atoms were smaller than 5 × 10−3 eV Å−1. Spin polarization was taken into account in all calculations. The calculated lattice constant for bulk SrTiO3 was determined to be 3.93 Å, in typical DFT agreement with the experimental value of a₀ = 3.89 Å.24

2.2 Point defect formation energy

The defect formation energies, $E_f$, are evaluated as:

$$ E_f = E_d - E_p + \sum n_i \mu_i + q(\Delta E_F + E_{VBM}) $$

where $E_d$ and $E_p$ are the total energies of the defective and defect free supercells, respectively, $q$ is the charge state of the defect, $n_i$ is the number of atoms being removed or added, and $\mu_i$ is the corresponding chemical potential. $E_{VBM}$ and $\Delta E_F$ are the energy levels corresponding to the valance band maximum (VBM) and the Fermi energy measured from the VBM, respectively. The Fermi energy, $\Delta E_F$, changes its position within the band gap, $E_g$, which is represented by the energy difference between the valance band maximum and the conduction-band minimum (CBM) as $E_g = E_{VBM}(-1) + E_{CBM}(+1) - 2E_F(0)$, where −1,+1 and 0 are the charge states. The calculated $E_g$ is 2.68 eV is smaller than the experimental value of 3.25 eV,25 but is typical of DFT calculations. In our calculations, however, this difference $(\Delta E_F = 0.57 eV)$ can considerably affect the computed point defect formation energies.26 Previous studies have shown that the error in defect formation energies due to the underestimated DFT band gap can be corrected by adding a constant energy shift (in this case 0.57 eV) to the conduction states in order to match the experimental gap.26 For an isolated defect, it can be assumed that the energy levels of the acceptor-like and the deep donor-like defects follow the VBM and are thus unchanged. On the other hand, shallow donor-like defect levels follow the CBM and are thus shifted upward by the same amount as the band gap.26 Defect formation energies are corrected accordingly, i.e., no correction is added to the formation energies of the oxygen interstitials, but $m\Delta E_F$ ($m$ is the number of electrons occupying the defect states) is added to the formation energies of the oxygen vacancies.26 Here, whether a donor level is deep or shallow is determined by checking the one electron energy level in the band gap of the corresponding defect.20

The thermodynamic transition level of a defect between charge states $q$ and $q'$, $\varepsilon(q/q')$, corresponds to the Fermi energy at which the formation energies for charge states $q$ and $q'$ are equal. When measured from the VBM, the thermodynamic transition level is given as:

$$ \varepsilon(q/q') = E_{\text{VBM}}^q - E_{\text{VBM}}^q q - q $$

where $E_{\text{VBM}}^q$ denotes the defect formation energy for charge state $q$ when the Fermi energy is located at the VBM. The position of the thermodynamic transition level given in eqn (2) is the ionization energy of a defect, i.e., the acceptor or donor energy.27

2.3 Formalism for chemical potential in ternary oxides

As shown in eqn (1), the formation energy of a defect depends on the chemical potential of the ions added or removed from the perfect crystal to form the defect. A thermodynamically consistent process for determining the experimentally relevant range of chemical potentials is outlined below. This approach was originally developed in the context of binary oxides28,29 and then extended to ternary oxides, such as $\text{Y}_2\text{SiO}_5$,30,31 $\text{LiNbO}_3$32 and $\text{Y}_3\text{Al}_5\text{O}_{12}$.33

The total energy of a stoichiometric unit of SrTiO3 can be expressed as:

$$ \mu_{\text{Sr}} + 3\mu_{\text{Ti}} + 6\mu_{\text{O}} = \mu_{\text{SrTiO}_3} $$

The stability of the system against decomposition into its constituent elements places upper limits on the chemical potential of each element in SrTiO3. The reference substances are pure solids of Sr and Ti, as well as molecular oxygen (O2). Therefore, additional restrictions are set by:

$$ \mu_{\text{Sr}} \leq \mu_{\text{Sr}}^{\text{bulk}} $$

(4.1)
$$ \mu_{\text{Ti}} \leq \mu_{\text{Ti}}^{\text{bulk}} $$

(4.2)
$$ \mu_{\text{O}} \leq \mu_{\text{O}_2} $$

(4.3)
Since neither SrO nor TiO$_2$ precipitates from bulk SrTiO$_3$, the following restrictions are also included:

\[
\mu_{\text{Sr}} + \mu_{\text{O}} \leq \mu_{\text{SrO}} \quad (5.1)
\]
\[
\mu_{\text{Ti}} + 2\mu_{\text{O}} \leq \mu_{\text{TiO}_2} \quad (5.2)
\]

The above set of equations defines the range of chemical potentials consistent with the stability of SrTiO$_3$ against decomposition into binary oxides or into its elemental components. Given the boundary for the chemical potential of each element, a valid range for the formation energies of the point defects can be examined.

### 3 Results and discussion

An initial step in studying the energetics of defects is to determine the preferred position of an isolated point defect. As a consequence of the SrTiO$_3$ Pm3m symmetry, the structures of atomic vacancies (V$_O$, V$_{Sr}$, and V$_{Ti}$) and cation antisite defects (Sr$_{Ti}$ and Ti$_{Sr}$) are straightforward since there is only one crystallographically inequivalent site for each atom. In contrast, the structures of the interstitial configurations (O$_i$, Sr$_i$, and Ti$_i$; here, subscript i means interstitial) are more complex. Our recent \textit{ab initio} molecular dynamics simulation showed that oxygen favors a split-interstitial configuration along the \{100\} direction (Fig. 1a), with two atoms sharing a single lattice site. Similarly, Sr forms a split-interstitial but along the \{111\} direction (Fig. 1b). The titanium interstitial (Fig. 1c), however, occupies a bridge site between two Sr atoms along a channel and in-plane with four nearest neighboring Ti and/or O atoms. In the present study, these configurations for O$_i$, Sr$_i$, and Ti$_i$ are, therefore, investigated.

After comprehensively considering the abovementioned chemical potential restrictions, a well-defined ternary phase diagram of SrTiO$_3$ is determined and shown in Fig. 2. This figure depicts a narrow region of stability for SrTiO$_3$, defined by the quadrangle ABCD and restricted by the Ti, O$_2$, SrO and TiO$_2$ precipitation lines. The corner points, A, B, C, and D, correspond to Ti- & TiO$_2$-rich, O- & TiO$_2$-rich, O- & SrO-rich and Ti- & SrO-rich precipitate phase boundaries, respectively. The values of the chemical potentials for Sr, Ti and O at the corner points are given in Table 1.

#### 3.1 Formation energies of isolated point defects

The formation energies of all isolated point defect types with different charge states in SrTiO$_3$ are calculated using eqn (1). Since the defect formation energies depend on the electron Fermi energy, the influence of the Fermi energy on the stability of each individual defect is considered. The reference zero for the Fermi energy is assigned to be the VBM. For any point inside the ABCD quadrangle in Fig. 2, the defect formation energy is located between the maximum and minimum values for each defect species at points A, B, C, and D. The electron Fermi energy dependent defect formation energies at points A, B, C and D are shown in Fig. 3.

The nominally charged states, $2^-$, $4^-$ and $2^0$, are preferred for V$_{Sr}$, V$_{Ti}$ and V$_{SrTi}$, respectively. Conversely, the charge states of the other defects significantly depend on the Fermi energy. The thermodynamic transition levels for V$_O$, O$_i$, Sr$_i$, Ti$_i$ and Ti$_{Sr}$ are shown in Fig. 4 (here, all thermodynamic transition energies are measured from the VBM). The V$_O$ shows two transitions, which are ($2^+$/1$^+$/2$^-$) at 2.68 eV and (1$^+$/0) at 2.83 eV. Both O$_i$ and Sr$_i$ exhibit a “negative-U” behavior, indicating that their acceptor level is below its donor level and the singly charged defect is unstable at all Fermi levels. The thermodynamic transition energy for O$_i$ from 0 to $2^-$ is at 1.11 eV, and that of Sr$_i$ from $2^-$ to 0 at 2.60 eV. In the case of Ti$_i$, four transitions are observed. They are (4$^+$/3$^+$/2$^+$) at 0.39 eV, (3$^+$/2$^+$$/1^+$) at 2.67 eV, (2$^+$/1$^+$) at 2.74 eV and (1$^+$/0) at 3.00 eV. For Ti$_{Sr}$, the (2$^+$/1$^+$) and (1$^+$/0) transitions occur at 0.17 eV and 0.29 eV, respectively. Furthermore, the formation energy of each point defect also depends on the chemical potential, as shown in Fig. 3.

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**Fig. 1** Interstitial configurations in SrTiO$_3$ viewed along (010): (a) an oxygen split-interstitial along \{100\} (in red), (b) a strontium split-interstitial along \{111\} (in blue) and (c) a titanium interstitial occupying a bridge position between two Sr sites (in green).

**Fig. 2** Chemical potential diagram of Sr–Ti–O, where SrTiO$_3$ is stable in the quadrangle ABCD area.

**Table 1** Chemical potentials ($-\mu_{\text{Sr}}$, $-\mu_{\text{Ti}}$, $-\mu_{\text{O}}$) of Sr, Ti and O at the corner points, A, B, C and D in Fig. 2.

<table>
<thead>
<tr>
<th>Point</th>
<th>$-\mu_{\text{Sr}}$</th>
<th>$-\mu_{\text{Ti}}$</th>
<th>$-\mu_{\text{O}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.86</td>
<td>0</td>
<td>4.75</td>
</tr>
<tr>
<td>B</td>
<td>6.61</td>
<td>9.50</td>
<td>0</td>
</tr>
<tr>
<td>C</td>
<td>5.49</td>
<td>10.62</td>
<td>0</td>
</tr>
<tr>
<td>D</td>
<td>0.18</td>
<td>0</td>
<td>5.31</td>
</tr>
</tbody>
</table>
Antisite Sr Sr
O Frenkel O O
Ti Frenkel Ti Ti
Sr Frenkel Sr Sr

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3.2 Formation energies of native defect complexes

Although isolated point defects may exist in charged states, the overall crystal must be neutral. The charge compensation between acceptors and donors is an important mechanism for maintaining the overall crystal neutrality and thus requires the consideration of a series of different defect complexes. According to classical models, native defect complexes are described by Frenkel, Schottky and cation antisite defect mechanisms. All native defect complex formation energies are computed using neutral (denoted as N-defect complexes) and/or nominally charged (denoted as C-defect complexes) isolated point defect calculations. In other words, the defect complex formation energy is defined as the sum of the formation energies of all of the corresponding isolated defects. Such study does provide the simplification of not having to consider the effect of the Fermi energy.

The calculated formation energies of the native defect complexes are listed in Table 2. From Table 2, it can be seen that the relative stability of each defect complex depends on the charge states of the isolated defects within the complex. For N-defect complexes, the magnitudes of the formation energies have the following sequence: O Frenkel < Schottky < Cation Antisite < Sr Frenkel < Ti Frenkel. In the case of C-defect complexes, the sequence of formation energies is: Schottky < O Frenkel < Sr Frenkel < Ti Frenkel < Cation Antisite. Furthermore, the formation energies of the native defect complexes consisting of nominally charged isolated defects are lower than those consisting of neutral or partially charged (not included in Table 2) isolated defects. Therefore, the defect complexes comprised of nominally charged isolated defects will dominate, with the Schottky defect complex consisting of $V_{\text{Sr}}^{2-} + V_{\text{Ti}}^{4+} + 3V_{\text{O}}^{2-}$ being the most stable defect structure.

We now compare our results to a previous semi-empirical interatomic potential (SIP) study. In this previous study, all isolated point defects were nominally charged, and thus comparable to our C-defect complexes, as shown in Table 2. Both the present DFT study and the previous SIP study predict that the Schottky and O Frenkel defects have the lowest and the second lowest formation energies, respectively. The formation energies of defect complexes obtained from the DFT and SIP methods show a similar trend, although the SIP results for the Sr and Ti Frenkel pairs agree only qualitatively with our DFT results. Compared to our DFT results, the previous SIP results underestimated the formation energy of the Sr Frenkel defect by 1.21 eV per defect and overestimated that of the Ti Frenkel pair by 1.44 eV per defect. For the cation antisite defect, a comparison is not possible due to the absence of similar results in the SIP study.

From the calculated formation energies (Table 2), the concentration of each native defect complex can be determined according to the Arrhenius formula as follows:

$$C_d = N_{\text{site}}N_{\text{config}}\exp(-E_d/k_BT)$$  \hspace{1cm} (6)

<table>
<thead>
<tr>
<th>N-defect complex</th>
<th>$E_d$</th>
<th>C-defect complex</th>
<th>$E_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>0 $\leftrightarrow$ $V_{\text{Sr}}^0 + V_{\text{Ti}}^{2-} + 3V_{\text{O}}^{2-} + \text{SrTiO}_3$</td>
<td>5.73</td>
<td>0 $\leftrightarrow$ $V_{\text{Sr}}^{2-} + V_{\text{Ti}}^{4+} + 3V_{\text{O}}^{2-} + \text{SrTiO}_3$</td>
</tr>
<tr>
<td>Sr Frenkel</td>
<td>$\text{Sr}<em>{\text{Sr}}^0 + V</em>{\text{Ti}}^{2-} + \text{Sr}_{\text{Ti}}^{2+}</td>
<td>8.31</td>
<td>$\text{Sr}<em>{\text{Sr}}^0 + V</em>{\text{Sr}}^{2-} + \text{Sr}_{\text{Ti}}^{2+}</td>
</tr>
<tr>
<td>Ti Frenkel</td>
<td>$\text{Ti}<em>{\text{Sr}}^{2+} + V</em>{\text{Sr}}^{2-} + V_{\text{Ti}}^{4+}</td>
<td>11.20</td>
<td>$\text{Ti}<em>{\text{Sr}}^{2+} + V</em>{\text{Sr}}^{2-} + V_{\text{Ti}}^{4+}</td>
</tr>
<tr>
<td>O Frenkel</td>
<td>$O_{\text{Sr}}^0 + \text{SrTi}^{2+}</td>
<td>4.43</td>
<td>$O_{\text{Sr}}^0 + V_{\text{Sr}}^{2-} + O_{\text{Ti}}^{2-}</td>
</tr>
<tr>
<td>Antisite</td>
<td>$\text{Sr}<em>{\text{Sr}}^0 + \text{Ti}</em>{\text{Ti}}^{2+}</td>
<td>6.43</td>
<td>$\text{Sr}<em>{\text{Sr}}^0 + \text{Ti}</em>{\text{Ti}}^{2+} + \text{Sr}_{\text{Sr}}^{2-}</td>
</tr>
</tbody>
</table>

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possible defect formation reactions, the reaction enthalpies of (R7) and (R10) are also relatively low, indicating the possibility of $O^{2-}$ and $Ti^{4+}$ defects. The reaction (R6) is unlikely, since its reaction enthalpy is high (up to 15.16 eV). The temperature dependent concentrations of the final defects in each reaction are provided in Fig. 6(a) and (b) for a quantitative description.

In nonstoichiometric SrTiO$_3$ with excess SrO or TiO$_2$, the possible defect reactions play a key role in determining the type and concentrations of point defects created during the synthesis process. This is especially important for oxygen vacancies, as they are known to be intimately related to desirable functionalities in SrTiO$_3$. As indicated by (R2) and (R9), both excess SrO and TiO$_2$ growth conditions induce additional oxygen vacancies. Our calculations suggest that nonstoichiometric chemical compositions, with either excess SrO or TiO$_2$, could be used to fabricate SrTiO$_3$ in order to maximize oxygen vacancies. Another point that should be considered is the fact that cation antisite defects are energetically unfavorable in stoichiometric SrTiO$_3$ but form readily in nonstoichiometric SrTiO$_3$, i.e. Sr$_{2-}^{2+}$ and Ti$_{2+}^{4+}$ environments, respectively. Accordingly, the type and concentration of cation antisite defect could also be controlled by adjusting the amount of excess SrO or TiO$_2$. Meanwhile, a small concentration of $O^{2-}$ and $Ti^{4+}$ defects together with $Sr^{2-}$ and $V^{2+}$ as the most probable defects. The reaction enthalpies of (R7) and (R10) are also relatively low, indicating the possibility of $O^{2-}$ and $Ti^{4+}$ defects. The reaction (R6) is unlikely, since its reaction enthalpy is high (up to 15.16 eV). The temperature dependent concentrations of the final defects in each reaction are provided in Fig. 6(a) and (b) for a quantitative description.

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here are expected to provide insights for understanding the discrepancies in defect types/concentrations and hence the related performance of SrTiO$_3$ synthesized under various conditions. Based on the present theoretical results, the control of defect structures in SrTiO$_3$ could be achieved by tuning the processing conditions; thereby providing a route by which the functionality and performance of SrTiO$_3$ can be optimized.

4 Conclusions

The energetics of point defects in stoichiometric and nonstoichiometric SrTiO$_3$ have been comprehensively investigated using DFT calculations. The formation energies of isolated intrinsic point defects depend on both the electron Fermi energy and the element chemical potentials. It is found that the charge states of V$_O$ (2+/1+/0), O$_i$ (0/2+/C0), Ti$_i$ (4+/3+/2+/1+/0) and Ti$_{Sr}$ (2+/1+) change as a function of electron Fermi energy, while V$_{Sr}$, V$_{Ti}$ and SrTi prefer their nominal charge states (2+/C0, 4+/C0 and 2+/C0, respectively) across the entire band gap.

The formation energies of native defect complexes are found to be related to the charge states of their corresponding intrinsic point defects. The defect complexes comprised of nominally charged defects have lower formation energies than those consisting neutral and partially charged defects. Among the nominally charged-defect complexes, the Schottky defect complex (V$_{Sr}$ 2− + V$_{Ti}$ 4+ + 3V$_O$ 2−), which has the lowest formation energy, is found to be the most stable defect structure, while the O Frenkel defect complex may also occur as a result of its relatively low formation energy.

Nonstoichiometry, such as excess SrO or TiO$_2$ in SrTiO$_3$, results in different point defect complexes. For excess SrO, the formation of V$_O$ 2+ and Sr Ti$_{Sr}$ 2+ is energetically favorable, while the V$_{Sr}$ 2− together with Ti$_{Sr}$ 2+ and V$_O$ 2+ are the predominant defects found in excess TiO$_2$ environments. An excess of both SrO and TiO$_2$ leads to an increase in the concentration of oxygen vacancies. Similarly, SrTi$_{2+}$ and Ti$_{Sr}$ 2+ antisite defects will appear under SrO-rich and TiO$_2$-rich conditions, respectively. It is expected that these results will provide guidelines for controlling processing conditions in order to optimize functionalities based on specific defects.

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References