Oxygen vacancy diffusion in bulk SrTiO$_3$ from density functional theory calculations

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Abstract

Point defects and their diffusion contribute significantly to the properties of perovskite materials. However, even for the prototypical case of oxygen vacancies in SrTiO$_3$ (STO), the predictions of oxygen vacancy activity vary widely. Here we present a comprehensive and systematic study of the diffusion barriers in bulk STO. Using density functional theory (DFT), we assess the role of different supercell sizes, density functionals, and charge states. Our results show that vacancy-induced octahedral rotations, which are limited by the boundary conditions of the supercell, can significantly affect the computed oxygen vacancy diffusion energy barrier. In addition, we find that the diffusion energy barrier of a charged oxygen vacancy is lower than that of a neutral one. This difference is magnified in small supercells. This work provides important insights and guidance that should be considered for investigations of point defect diffusion in perovskite materials and in oxide superlattices.

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1. Introduction

Ceramics with a perovskite-type structure (general formula $ABO_3$) consist of a network of corner-sharing $BO_6$ octahedra, which form higher-coordination sites for the $A$-cations in a roughly cubic array. The wide variety of chemical compositions and atomic defects that can be accommodated in this structure give rise to the rich variety of phenomena observed in perovskite oxides. As a prototypical perovskite, SrTiO$_3$ (STO) attracts considerable attention due to its good insulating properties, excellent optical transparency, and high dielectric constants [1,2]. It has also been demonstrated that STO shows potential capacitive [3] and resistive switching properties [4-7]. In addition, STO has been extensively used as a substrate for superlattices and is the parent oxide that leads to two-dimensional electron gases (2DEGs) [8,9] in many oxide heterointerfaces.

Oxygen vacancies ($V_O$) are representative intrinsic defects that, in many cases, play an important role in the physical properties of STO. An $V_O$ is generally produced during crystal growth or film deposition processes with nonstoichiometric reactants, as a result of oxygen gas release accompanying heat treatment, and in doped STO serving as a charge compensation mechanism. They form readily within STO and have been indicated to be the driving force behind STO-associated blue and green light emission [10,11] and high $n$-type conductivity [12-15]. Therefore, fully understanding the stability and diffusion of $V_O$ is critical for tailoring the physical properties of STO for future applications. However, while the energetics and stability of oxygen vacancies and their effects on the properties of STO are understood, less is known about the energetics of $V_O$ diffusion.

Numerous efforts have sought to study the diffusion of $V_O$ in STO, producing values of $V_O$ migration energy barriers (MEBs) that vary significantly. For instance, the activation energy of $V_O$ diffusion was estimated to be 0.60–0.98 eV based on different experimental measurements [16-18]. Even different density functional theory (DFT) calculations exhibit significant deviations between the calculated values of the oxygen vacancy diffusion barrier. The DFT estimations of the energy barrier range from 0.35 to 0.9 eV [19-26]. The deviations in DFT results are considerable and the
underlying cause for such deviations is unclear, as different simulation setups and parameters have been employed in the previous calculations. Carrasco et al. [22] calculated neutral $V_0$ migration energy barriers in different STO supercells containing 40–180 atoms with different shapes, predicting a range of values from 0.35 to 0.7 eV, depending on the size and shape of the supercell. Evaarestov et al. [26] performed similar work using the VASP code. They found that the migration energy barrier mainly decreases with increasing supercell size. However, due to computational limitations, the largest STO supercell they studied contained 270 atom. Al-Hamadany et al. [23] explored charged and neutral oxygen vacancy migration in STO using spin-polarized DFT with the local density approximation (LDA). They employed STO supercells containing up to 320 atoms. The energy barriers in the largest cells, containing 320 atoms, were 0.81 and 0.77 eV for the neutral and charged (2+) oxygen vacancy, respectively. Lontsi-Fomena et al. [24] investigated oxygen vacancy diffusion in supercells of 40 atoms using the Perdew–Burke–Ernzerhof (PBE) functional, finding the migration energy barrier for a charged (2+) oxygen vacancy to be 0.58 eV. In order to consider the localization of and vacancy charge states to systematically examine their effects with increasing supercell size. However due to computational limitations number of unit cells, DFT exchange–correlation functionals, calculation setups and parameters have been employed in the previous simulation for solids, PBEsol [30], are chosen as the exchange–correlation functionals. Although different values could be tested, these values predicted a larger band gap, which was closer to the experimental value of 3.2 eV for bulk STO [34]. The $V_0$ position and diffusion path are depicted in Fig. 1. Because of the symmetry of the cubic structure, there is just one unique diffusion path (Fig. 1(b) depicts the diffusion path in a representative 3 × 3 × 3 supercell). The diffusion paths for neutral and charged vacancy in these supercells are indistinguishable.

The oxygen vacancy formation energy is defined as:
\[
E_f(V_0) = E_{tot}(V_0) - E_{tot}(\text{Bulk}) - \sum_{i} n_i \mu_i + q_i (E_F + E_{F} + \Delta V)
\]

where $E_f(V_0)$ is the total energy derived from a supercell calculation with one oxygen vacancy in charge state: $q$, $E_{tot}$ (Bulk) is the total energy for the reference perfect bulk supercell; $n_i$ indicates the number of atoms of type $i$ that have been added to ($n_i > 0$) or removed from ($n_i < 0$) the supercell when the defect is formed; and $\mu_i$ is the corresponding chemical potential of each species. $E_F$ is the Fermi level, referenced to the valence-band maximum $E_v$ in the bulk. $\Delta V$ is a correction term, to align the reference potential in our defect supercell with that in the bulk [35]. In this work, the formation energy of a neutral $V_0$ and charged $V_0^\pm$ were calculated. The chemical potential of oxygen is chosen to be $\nu E_0$ (equilibrium gas state), when the PBEsol +$U$ functional were applied, the value of $\Delta V$ in $2 \times 2 \times 2, 3 \times 3 \times 3, 4 \times 4 \times 4$ and $5 \times 5 \times 5$ are calculated as 0.16 eV, 0.06 eV, 0.02 eV and 0.03 eV, respectively.

The migration barriers of the neutral and charged oxygen vacancy were both computed by the climbing-image nudged elastic band (CI-NEB) method [36]. We first tested up to 5 images in a $2 \times 2 \times 2$ STO supercell and found that the calculated migration energy barrier is not sensitive to the number of images, which is attributed to the simple chemical environment along the diffusion path and success of the climbing image algorithm. For the $3 \times 3 \times 3$ and $4 \times 4 \times 4$ supercells we used 3 images, and 1 image for the most computationally costly $5 \times 5 \times 5$ supercell.

3. Results and discussion

3.1. Lattice constant

Prior to the defect study, the geometry of STO was optimized using different exchange–correlation functionals. In all calculations, no distortions were found in the perfect optimized STO supercells. The calculated lattice constants are summarized in Table 1. These values are comparable with other simulations [37,34] and experimental results (3.905 Å [38]). Among these functionals, PBEsol [30] predicts a lattice constant, which is the closest to the experimental value. PBEsol + $U$, PBE, and PBE +$U$ functionals overestimate the lattice parameter (~1%). These lattice constants are used for subsequent calculations of the energetics of oxygen vacancy formation and diffusion barriers.

3.2. Defect formation energy (DFE)

It is known that the $V_0$ formation energy depends on the oxygen chemical potential and electronic Fermi level [39]. Here, the oxy-
gen chemical potential was chosen as $\frac{4.338}{4.338}$ eV, which is half of the chemical potential of the $O_2$ molecule. We applied the method of reference [39] to calculate the Fermi level energy, assuming the Fermi level is at the conduction band minimum. In addition, the interaction from periodic images was estimated based on the formulism in [40] and this interaction is found to be rather small (<1.2% in the $2 \times 2 \times 2$ STO supercell). Therefore, this correction term [40] was not included in our calculations of formation energies. The oxygen vacancy formation energies of neutral and charged (2+) states in different supercells are listed in Table 2. The relative formation energies versus supercell size obtained with the PBEsol + $U$ functional are plotted in Fig. 2. The oxygen vacancy formation energy in a $2 \times 2 \times 2$ supercell is used as a reference and is set to 0. It is observed that the DFEs decrease with increasing system size; when the supercell is larger than $4 \times 4 \times 4$, the DFEs is approaching to convergence, which is consistent with other studies on defect stabilities [35]. The DFEs drop by $\frac{0.3}{0.3}$ eV (PBEsol + $U$) for the neutral oxygen vacancy when the supercell is enlarged from $2 \times 2 \times 2$ to $4 \times 4 \times 4$. For the charged oxygen vacancy, DFEs decrease by $\sim 1.6$ eV using PBEsol + $U$. These decreases in DFEs are attributed to the long-ranged relaxation of atoms caused by $V_{O5}$ in the supercell. The effect of electron localization in the $V_{O}$ site may be more accurately described using the PBEsol + $U$, because the charge density is strongly localized on the two Ti atoms adjacent to the oxygen vacancy. Buban et al. [35] found that the DFEs of neutral and charged (1+, 2+) $V_{O5}$ dropped by roughly 1.1–1.38 eV when going from a 40- to a 320-atom supercell, which is comparable with our value of 1.6 eV calculated with the PBEsol + $U$ functional on a charged oxygen vacancy. The results of PBE with spin polarization, PBEsol, and PBE + $U$ show similar trends as described above.

### 3.3. Migration energy barrier

#### 3.3.1. Effect of supercell size on oxygen vacancy migration energy barrier

Fig. 3 shows the migration energy barriers of a neutral vacancy obtained using different supercell sizes. Similar to DFEs, the MEBs decrease as the supercell size increases. The MEB determined using a $2 \times 2 \times 2$ supercell deviates considerably from those of larger supercells, indicating that this supercell size is too small to predict the MEB accurately. When the system size reaches to $5 \times 5 \times 5$, the spread of DFT values is significantly reduced. For a single oxygen vacancy in STO, the relaxations, which appear as a long-ranged inward relaxation, extend far from the oxygen vacancy site ($\sim 16$ Å) [35]. As the boundaries of the larger STO supercells are approached, the relaxation of these atoms far from the vacancy is very small. When the STO supercell size increases to $5 \times 5 \times 5$, Fig. 1. (a) Isolated $V_{O}$ in a $3 \times 3 \times 3$ STO supercell; (b) the oxygen vacancy diffuses to the adjacent oxygen position; (c) $V_{O}$ diffusion path in a $3 \times 3 \times 3$ STO supercell. The green, red, and blue balls represent Sr, O, and Ti atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### Table 1

<table>
<thead>
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<th>DFT functional</th>
<th>PBEsol</th>
<th>PBEsol + $U$</th>
<th>PBE</th>
<th>PBE + $U$</th>
<th>PBE</th>
<th>PW</th>
<th>B3LYP</th>
<th>LDA</th>
<th>Exp.</th>
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</table>

### Table 2

<table>
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<th>Charge state</th>
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<th>$3 \times 3 \times 3$</th>
<th>$4 \times 4 \times 4$</th>
<th>$5 \times 5 \times 5$</th>
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</thead>
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<td>$V_{O}$ (0)</td>
<td>6.491</td>
<td>6.576</td>
<td>6.177</td>
<td>6.095</td>
</tr>
<tr>
<td>$V_{O}$ (2+)</td>
<td>8.296</td>
<td>6.943</td>
<td>6.634</td>
<td>6.219</td>
</tr>
</tbody>
</table>
the MEBs of an oxygen vacancy approaches convergence, as Fig. 3 illustrates. The range of converged values, 0.39–0.49 eV, underestimates the MEB of an isolated oxygen vacancy derived from experiments and some other computations of ~0.60 eV [18,24,25]. The underestimation relative to other simulations primarily comes from STO supercell size effects. Previously, it was shown that increased interactions between oxygen vacancies result in an enhancement in the oxygen migration energy barriers [25]. In our largest supercell (5 × 5 × 5, containing 625 atoms), the interaction between two adjacent oxygen vacancies is significantly lower than in the smaller supercells (up to 320 atoms) previously studied [23–25]. As such, the migration energy barriers for the 5 × 5 × 5 supercell are expected to be lower than earlier simulations which employed much smaller supercells. The reason for the underestimate when comparing with the experimental result of ~0.6 eV may be due to limitations of the standard DFT method we employed in our calculations or the interactions of a single oxygen vacancy with complex defects in the experimental sample. Hybrid functionals such as the B3PW xc-functional have been demonstrated to predict a more accurate optical gap (3.65 eV) for bulk STO [41]. However, it is still a huge challenge of computational cost to use such approaches to predict the vacancy migration energy barrier in very large STO supercells in which the vacancy concentration can reach a value comparable to experiment.

For PBEsol or PBEsol + U, the energy barriers calculated in 3 × 3 × 3 STO supercells are lower than that of the 4 × 4 × 4 supercell. We found that this comes from the difference of the distortion model of the local atomic environment around the oxygen diffusion path in 3 × 3 × 3 and 4 × 4 × 4 supercells. Due to the absence of one oxygen atom in STO bulk, oxygen octahedral rotations are introduced into the system [11]. This local configuration change is limited by the boundary condition of the supercell, leading to the two different situations observed in the 3 × 3 × 3 and 4 × 4 × 4 supercells. One situation makes the distances between the diffusing oxygen atom and its nearest oxygen neighbor longer, while the other shortens it, resulting in substantially different MEBs.

The initial and transition point configurations of the 3 × 3 × 3 and 4 × 4 × 4 STO supercells are shown in Fig. 4. An oxygen octahedral rotation (a b c0) pattern (following Glazer pattern [42]) is found when an oxygen vacancy is introduced into the system (shown as Fig. 4(a), in a 4 × 4 × 4 supercell). Here, we use the bond angle of O6–Ti1–O3, which is near the oxygen vacancy (shown as Fig. 4(c) and (e)) to characterize the oxygen octahedral rotation magnitude in different sizes of STO supercells. The magnitudes of this angle in the initial state (IS) and transition state (TS) are shown in Fig. 4(b), where it is evident that boundary conditions control the rotational characteristics. For the initial states, when the number of unit cells in a particular direction is even, bond angles of O6–Ti1–O3 are smaller with values of 86.46°, 87.42° in 2 × 2 × 2 and 4 × 4 × 4, respectively. On the other hand, for an odd number of unit cells, these bond angles are larger with values of 88.24°, 88.08° in 3 × 3 × 3 and 5 × 5 × 5, respectively. Similar observa-
tions are found for the transition states, where the O₈–Ti₁–O₉ bond angles are again smaller with values of 88.15°, 93.43° in even-numbered supercells (2, 4, respectively) and larger, i.e., 95.76°, 96.47°, in odd-numbered supercells (3, 5, respectively). In the $2\times 2$ supercell, this angle is much lower than those in other supercells, because the corresponding oxygen rotations are pinned by periodic boundary conditions.

The distances between the diffusing oxygen atom A and its first nearest oxygen atom B or C at the transition state are shown in Fig. 4(d) and (f). These distances are smaller in even-number-size supercells (2.84 Å in $2\times 2$ and 2.89 Å in $4\times 4$), and larger in odd-number-size supercells (2.94 Å in $3\times 3$ and 2.95 Å in $5\times 5$). Therefore, one can infer that the repulsive Coulomb interaction between the diffusing oxygen atom and its nearest oxygen atom in a $3\times 3$ supercell is lower than that in a $4\times 4$ supercell. As such, this weaker repulsive interaction would enhance the oxygen diffusion rates by lowering diffusion barriers. This difference in the local atomistic environment in different supercells, due to the artificial boundary conditions, is considered to be the cause of the observed anomaly and explains why the MEB in a $3\times 3$ supercell is lower than that in the $4\times 4$ supercell.

3.3.2. The effect of charge states of the oxygen vacancy

We further examine the effect of charge states of the oxygen vacancy on the MEB. Results using PBEsol are shown in Fig. 5. The MEB of a neutral oxygen vacancy is found to be higher than that of a charged vacancy, which is consistent with the previous study carried out by Al-Hamadany et al. [23]. The MEB difference between the neutral and charged vacancies is substantial (as high as 0.35 eV) in small supercells ($2\times 2$). However, this energy difference decreases quickly to less than 0.05 eV upon increasing supercell size.

To further elucidate the effects of charge states on oxygen vacancies, the charge density differences of the saddle point configurations between charged and neutral states are analyzed, as shown in Fig. 6. For consistency, charge density difference calculations using the atomic positions of the relaxed neutral configurations as a reference structure were employed to obtain induced charge density distributions for both the neutral and charged vacancy. We observe that with increasing supercell size, the excess charge (2e⁻) becomes more delocalized, reducing the total charge density on titanium and oxygen atoms, thereby diminishing the effect of the extra charge on MEBs. This is indeed more pronounced in larger supercells ($n\times n\times n$, $n > 3$) where there is a relatively smaller difference in the MEBs for neutral and charged vacancies.

3.3.3. The effect of +U

As mentioned above, the charge density should be strongly localized around the Ti atoms adjacent to the oxygen vacancy. The GGA + U method adds a Hubbard-type term to the density functional that penalizes partial occupancies in correlated orbitals and subsequently increases electron localization. Fig. 7 shows the migration energy barrier of (a) a neutral oxygen vacancy and (b) a charged oxygen vacancy calculated using either the PBEsol or PBEsol + U functional. In general, we find the inclusion of a Hubbard-U type term results in higher MEBs for neutral vacancies (the exception being the $2\times 2$ case). For a charged oxygen vacancy in the large $5\times 5$ supercell, we obtain a MEB of 0.40 eV, 0.48 eV, 0.33 eV, and 0.27 eV using PBEsol + U, PBE + U, PBEsol, and PBE, respectively (see Table 3).
that the charge density difference is localized to regions surrounding STO supercells containing a neutral oxygen vacancy. We observe that PBEsol + U calculations significantly affect the charge density distribution of the STO supercells. Diffusion energy barriers of an isolated oxygen vacancy in STO supercells calculated with different DFT methods. Table 3 Diffusion energy barriers of an isolated oxygen vacancy in STO supercells calculated with different DFT methods.

Applying Hubbard-type terms in DFT calculations can significantly affect the charge density distribution of the STO supercells. Fig. S1 (supplementary material) shows the charge density difference between PBEsol + U and PBEsol for saddle points in different STO supercells containing a neutral oxygen vacancy. We observe that the charge density difference is localized to regions surrounding the Ti atoms due to the Hubbard-type term in DFT making the electronic Ti d-orbitals more localized. Because of the charge interaction effect between titanium and its neighboring oxygen atoms, the orbitals of the neighboring oxygen atoms also become localized. An oxygen vacancy in an STO supercell significantly changes the electronic states of atoms near the vacancy site. It is well established that localized states can be more adequately described with the application of a Hubbard-U term, thus implying that DFT + U calculations may be more reliable for predicting MEBs for an oxygen vacancy in STO supercells. In addition, density of states (DOS) for the 3 × 3 × 3 supercell were calculated using the PBEsol + U and PBEsol functionals. The valence band maximum (VBM) and conduction band minimum (CBM) gap calculated by PBEsol + U is closer to the experimental value, seeing supplementary material. This also indicates that adding a Hubbard-type term can more accurately describe the electronic states of STO supercell and further predict a more reliable vacancy migration energy barriers.

4. Conclusion

The migration energy barrier of an isolated oxygen vacancy was systematically examined using DFT. Our results indicate that artificial boundary conditions, which are limited by finite supercell size, are important causes of deviations in the calculations—typically resulting in dramatic overestimations of migration energy barriers in small supercells. Increasing the size of the supercell employed in the simulations leads to decreased values of the energy barrier. When a sufficiently large supercell is employed, different simulation approaches result in similar values, between 0.39 and 0.49 eV. Limited by supercell boundary conditions, the octahedral rotation induced by oxygen vacancy generates two different results. One outcome makes the distance between diffusing oxygen atom and its nearest oxygen longer (3 × 3 × 3 or 5 × 5 × 5 supercells) and the other makes it shorter (2 × 2 × 2 or 4 × 4 × 4 supercells), which affect the oxygen vacancy migration energy barrier in different size supercells. On the other hand, the computed MEBs of neutral and charged oxygen vacancy indicate that a charged vacancy has a lower MEB than the neutral vacancy and that the effects of different DFT functionals and vacancy charge states are substantial in small 2 × 2 × 2 supercells and diminishing as supercell size increases. Finally, a comparison of the energy barriers and induced charge density distributions calculated with and without the addition of a Hubbard–U term suggests that PBEsol + U and PBE + U methods can more accurately describe the electronic state of STO supercells and thus would be preferable for studying vacancy migration within this material. We note that our predicted values lie below the experimental value of ~0.60 eV, probably due to the limitation of DFT functional chosen and the complex defect interactions in experimental samples. However, our work provides a deep analysis of DFT simulations of oxygen vacancy MEBs in STO supercells. These results provide fundamental insights on oxygen vacancy diffusion in STO, which can be extended to all perovskite structure materials.

Author contributions

LZ and HX directed the study, analyzed results and wrote the manuscript. BL and PK did part of the calculations, analyzed the results. HZ, VRC, PG analyzed the results. All authors made contributions to write the manuscript.

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Appendix A. Supplementary material

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