Trends in Surface Oxygen Formation Energy in Perovskite Oxides

Yoyo Hinuma,* Shinya Mine, Takashi Toyao, and Ken-ichi Shimizu

ABSTRACT: Perovskite oxides comprise an important class of materials, and some of their applications depend on the surface reactivity characteristics. We calculated, using density functional theory, the surface O vacancy formation energy ($E_{O\text{vac}}$) for perovskite-structure oxides, with a transition metal (Ti–Fe) as the B-site cation, to estimate the catalytic reactivity of perovskite oxides. The $E_{O\text{vac}}$ value correlated well with the band gap and bulk formation energy, which is a trend also found in other oxides. A low $E_{O\text{vac}}$ value, which is expected to result in higher catalytic activity via the Mars–van Krevelen mechanism, was found in metallic perovskites such as CaCoO$_3$, BaFeO$_3$, and SrFeO$_3$. On the other hand, titanates had high $E_{O\text{vac}}$ values, typically exceeding 4 eV/atom, suggesting that these materials are less reactive when O vacancy formation is involved in the reaction mechanism.

1. INTRODUCTION

Defects can significantly influence the properties of metal oxides. The most representative defect is the O vacancy, which can strongly affect the electrical, optical, magnetic, mechanical, and catalytic properties on intentional or unintentional introduction into the metal oxide structure. O vacancies on the surface of metal oxide catalysts often act as reaction sites for heterogeneous catalysis; thus, the formation energy of an O vacancy at the surface (denoted as $E_{O\text{vac}}$ in this paper) is often used as a descriptor of the catalytic activity of metal oxides.

Experimental investigations of O vacancies are difficult, although research on O vacancies in the field of catalysis is obviously important. Surface O vacancies also play an important role in polaron formation and stabilization in oxides such as CeO$_2$ and TiO$_2$. Determination of the $E_{O\text{vac}}$ value requires highly sophisticated techniques, and its evaluation is not always possible. On the other hand, there are recent theoretical studies on the formation of O vacancies in metal oxides, but still the number of investigated surfaces remains limited. Therefore, studies on the physical principles determining $E_{O\text{vac}}$ and the development of guidelines to estimate $E_{O\text{vac}}$ using other properties that are much easier to obtain are highly desirable.

Perovskite structure oxides make up an important class of materials. Applications to catalysis include ethane dehydrogenation by La$_{0.8}$Ba$_{0.2}$MnO$_3$, NO adsorption/oxidation, deoxygenation of coal bed methane on LaCoO$_3$, liquid-phase organic reactions, and CaTiO$_3$ nanosheets for photocatalytic hydrogen evolution. While there have been extensive computational studies of O vacancy formation energies in the bulk, recent studies of surface $E_{O\text{vac}}$ are quite limited but have been increasing recently.

The band gap, bulk formation energy, and electron affinity were reported to correlate well with $E_{O\text{vac}}$ in d$^0$ and d$^{10}$ binary oxides. Removal of neutral O results in two electrons being left behind. These electrons are excited from the valence band to the conduction band but typically relax and occupy defect states that may be lower than the conduction band minimum. Removal of O results in severing metal–O bonds, and the bulk formation energy provides a measure of the bond strength. This paper reports calculated $E_{O\text{vac}}$ values for known perovskite structure oxides terminated by the (001) orientation. Relations between $E_{O\text{vac}}$ and the band gap or bulk formation energy is discussed together with strategies to reduce $E_{O\text{vac}}$ to obtain more reactive support materials.

2. METHODOLOGY

First-principles calculations were conducted using the projector augmented-wave method and approximations as implemented in the VASP code. The strongly constrained and appropriately normed (SCAN) meta generalized gradient approximation (meta-GGA) was considered together with Dudarev’s formulation for the Hubbard $U$ correction. The effective U value, $U - J$, which is hereafter denoted as $U_{\text{eff}}$, was set at 2.7 eV on the valence d states of transition metals, including lanthanides. This $U_{\text{eff}}$ value is based on a study on...
perovskite structure oxides by Wexler et al.\textsuperscript{15} Spin-polarized calculations were conducted such that spins of an element all point in the same direction. When two cation species have nonzero spin, calculations were conducted where the spins of the two elements are parallel and antiparallel, respectively, and the lower energy spin configuration was adopted. The rationale for the selection of compounds discussed in this study is given in Supporting Information.

The surface of calculated slab models has a (001) orientation in the cubic setting. Calculations of defects, namely O vacancies, were conducted using a slab with $2\sqrt{2} \times 2\sqrt{2} \times S$ (=40) perovskite units separated by 15 Å vacuum (the in-plane area of the slab (blue parallelograms in Figure 1; the coefficient 2 accounts for both sides of the slab), and $E_{\text{bulk}}$ is obtained from a bulk calculation. The surface energy of one surface is not available because a strictly nonpolar slab that is stoichiometric and where all A-cation and B-cation layers are intact cannot be obtained. The nonexistence of a nonpolar slab means that the vacuum level is ill-defined, and thus the ionization potential, work function, and electron affinity cannot be calculated. The O vacancy formation energy $E_{\text{Ovac}}$ is defined as

$$E_{\text{Ovac}} = E_{\text{removed}} - E_{\text{slab}} + E(O_2)/2$$

where $E_{\text{removed}}$ and $E(O_2)$ are the energy of the slab after removal of an O atom from one side of the slab (A-site or B-site cation terminated layer, hereafter A-cation and B-cation layer, respectively) and the energy of an O$_2$ gas molecule at 0 K, respectively.

### 3. RESULTS AND DISCUSSION

Tables 1 and 2 summarize the results of first-principles calculations in this study. The space group number is provided in parentheses. Table S2 in the Supporting Information shows the space group symbol and number side by side. The bulk properties shown (Table 1) are the volume per atom ($v$), minimum band gap (BG), bulk formation energy with respect to elementary metals and O$_2$ gas ($E_{\text{form}}$), and net spin per five atoms in the bulk ($n_{\text{spin}}$). Systems are identified where the Jahn–Teller effect is expected for transition metals in an octahedral coordination environment. Slab properties in Table 2, obtained for slab-and-vacuum model cells with 40 perovskite units, are $E_{\text{cleave}}$, the net spin of a slab ($n_{\text{spin slab}}$), $E_{\text{Ovac}}$, and difference in net spin ($\Delta n_{\text{spin}}$) for O desorption from the A- and B-cation layers (denoted by A and B, respectively). Calculations where spin states far from the defect have changed significantly are removed from the table and not considered further. For example, the spin of the B-site cation on the surface without defects flipped after removal of O from the B-cation layer of BaMnO$_3$ (221) and LaFeO$_3$ (62).

Figure 2 plots the minimum $E_{\text{Ovac}}$ value for O removal from the A-cation layer against the B-cation layer. There is a modest positive correlation with a coefficient of determination ($R^2$) of 0.64 for all shown points. The points can be categorized into three groups: Ti-containing compounds, which are clustered at the top right (high $E_{\text{Ovac}}$) metals at the bottom left (low $E_{\text{Ovac}}$), and other nonmetals. Among the “other nonmetals”, O removal from the A-cation layer has lower energy when the B-site cation has fewer d electrons (V), while removal from the B-cation layer is favored in B-site cations with more d electrons (Co and Fe).

Figures S2–S4 show the partial electronic density of states (DOS) for bulk perovskites. The conduction band (CB) bottom is the B-site cation 3d states in all cases, which means that the defect state arising from electrons left in the slab after neutral O removal consists of mostly B-site cation 3d states. The nominal charge of Ti in titanates is 4+, with no 3d electrons. Notable charge states are the intermediate spin of Ti in titanates or the high-spin d$^5$ in Fe$^{3+}$ (LaFeO$_3$), and low (no)-spin d$^6$ in ScCoO$_3$. Removal of O from the A-cation layer results in severing of one O⋯O (“B-cation” bond from a 6-fold coordinated B-cation, and removal from the B-cation layer causes severing of two O⋯O (“B-cation” bonds from two 5-fold-coordinated B-cations. O removal causes changes in the number of d electrons in B-cation(s), which is accompanied by a change in the bonding environment, especially a change in the distribution of bond lengths. Removal of O from the B-cation...
Table 1. Bulk Properties of Systems Considered for Defect Calculations\(^a\)

| system          | \(v\) (Å\(^3\)) | BG (eV) | \(E_{\text{form}}\) (eV/atom) | \(n_{\text{spin}}\) (elementary charge/5 atoms) |
|-----------------|------------------|--------|-----------------------------|-----------------------------------------------|
| BaFeO\(_3\) (221) | 12.50            | 0.02   | −2.31                       | 4.19                                          |
| BaFeO\(_3\) (123) | 12.50            | 0.02   | −2.31                       | 4.19                                          |
| BaMnO\(_3\) (221) | 12.27            | 0.00   | −5.84                       | 3.25                                          |
| BaTiO\(_3\) (221) | 12.97            | 2.46   | −3.58                       | 0.00                                          |
| BaTiO\(_3\) (123) | 12.97            | 2.46   | −3.58                       | 0.00                                          |
| BaTiO\(_3\) (99)  | 12.98            | 2.46   | −3.58                       | 0.00                                          |
| BaVO\(_3\) (221) | 12.42            | 0.01   | −3.02                       | 1.00                                          |
| BiMnO\(_3\) (62)  | 12.09            | 0.65   | −5.11                       | 4.00                                          |
| BiMnO\(_3\) (15)  | 12.42            | 0.57   | −5.11                       | 4.00                                          |
| CaCoO\(_3\) (62)  | 10.58            | 0.01   | −2.09                       | 3.00                                          |
| CaTiO\(_3\) (62)  | 11.30            | 3.24   | −3.65                       | 0.00                                          |
| CaTiO\(_3\) (62)  | 11.08            | 3.06   | −2.75                       | 0.00                                          |
| CaTiO\(_3\) (33)  | 11.07            | 3.06   | −2.75                       | 0.00                                          |
| CdVO\(_3\) (62)  | 10.74            | 1.04   | −2.28                       | 1.00                                          |
| ScCoO\(_3\) (62)  | 9.43             | 2.41   | −2.72                       | 0.00                                          |
| LaFeO\(_3\) (62)  | 12.25            | 1.07   | −3.09                       | 5.00                                          |
| SrFeO\(_3\) (221) | 11.34            | 0.01   | −2.42                       | 4.01                                          |
| SrFeO\(_3\) (123) | 11.34            | 0.01   | −2.42                       | 4.01                                          |
| MnTiO\(_3\) (62)  | 10.46            | 2.13   | −6.52                       | 5.00                                          |
| MnVO\(_3\) (62)  | 10.11            | 0.38   | −6.06                       | 6.00                                          |
| PbTiO\(_3\) (99)  | 12.56            | 2.37   | −2.68                       | 0.00                                          |
| SrTiO\(_3\) (221) | 12.10            | 2.62   | −3.65                       | 0.00                                          |
| SrTiO\(_3\) (140) | 12.08            | 2.69   | −3.65                       | 0.00                                          |
| SrVO\(_3\) (221) | 11.49            | 0.02   | −3.11                       | 1.00                                          |
| YTiO\(_3\) (62)  | 12.00            | 1.85   | −3.79                       | 1.00                                          |

\(^a\)The parentheses following the compound name indicate the space group number.

Table 2. Bulk Properties of Systems Considered for Defect Calculations\(^a\)

| system          | \(E_{\text{diam}}\) (eV/Å\(^3\)) | \(n_{\text{spin, slab}}\) (elementary charge/200 atoms) | \(E_{\text{Ovac}}\) (A, eV) | \(E_{\text{Ovac}}\) (B, eV) | \(\Delta n_{\text{spin}}\) (A, elementary charge/defect) | \(\Delta n_{\text{spin}}\) (B, elementary charge/defect) |
|-----------------|-----------------------------------|----------------------------------------------------------|-----------------------------|-----------------------------|----------------------------------------------------------|----------------------------------------------------------|
| BaFeO\(_3\) (221) | 47.99                             | 170.42                                                   | 0.92                        | −0.40                       | 7.75                                                     | 6.22                                                     |
| BaFeO\(_3\) (123) | 49.80                             | 170.64                                                   | 0.60                        | −1.14                       | 7.85                                                     | 3.53                                                     |
| BaMnO\(_3\) (62)  | 41.60                             | 78.35                                                    |                             |                             |                                                          |                                                          |
| BaTiO\(_3\) (221) | 60.19                             | 0.00                                                     | 5.53                        | 4.72                        | 0.90                                                     | 1.18                                                     |
| BaTiO\(_3\) (123) | 60.27                             | 0.00                                                     | 5.54                        | 4.61                        | 0.89                                                     | 2.00                                                     |
| BaTiO\(_3\) (99)  | 61.39                             | 0.00                                                     | 5.53                        | 4.30                        | 0.45                                                     | 1.01                                                     |
| BaTiO\(_3\) (38)  | 60.64                             | 0.00                                                     | 5.53                        | 4.39                        | 1.55                                                     | 1.00                                                     |
| BaVO\(_3\) (221) | 20.69                             | 40.00                                                    |                             |                             |                                                          |                                                          |
| BiMnO\(_3\) (62)  | 22.85                             | 160.00                                                   | 1.94                        | 2.12                        | 2.02                                                     | 2.02                                                     |
| BiMnO\(_3\) (15)  | 35.05                             | 159.97                                                   | 3.08                        | 2.50                        | 0.00                                                     | 2.00                                                     |
| CaCoO\(_3\) (62)  | 52.35                             | 100.01                                                   | 0.02                        |                             |                                                          |                                                          |
| CaTiO\(_3\) (62)  | 73.56                             | 0.00                                                     | 5.78                        | 5.74                        | 0.00                                                     | 1.02                                                     |
| CdTiO\(_3\) (62)  | 72.81                             | 0.00                                                     | 3.17                        | 4.56                        | 0.00                                                     | 0.72                                                     |
| CdTiO\(_3\) (33)  | 72.77                             | 0.00                                                     | 3.17                        | 4.25                        | 0.00                                                     | 2.00                                                     |
| CdVO\(_3\) (62)  | 68.32                             | 40.00                                                    | 0.88                        | 2.39                        | 2.00                                                     | 2.00                                                     |
| ScCoO\(_3\) (62)  | 105.40                            | 3.63                                                     | 3.70                        | 0.79                        | 3.63                                                     | 1.63                                                     |
| LaFeO\(_3\) (62)  | 88.68                             | 197.53                                                   | 5.01                        |                             |                                                          |                                                          |
| SrFeO\(_3\) (221) | 59.89                             | 164.68                                                   | 1.19                        | 0.10                        | 2.27                                                     | 0.64                                                     |
| SrFeO\(_3\) (123) | 60.24                             | 164.56                                                   | 0.95                        | −0.22                       | 1.98                                                     | 0.67                                                     |
| MnTiO\(_3\) (62)  | 75.31                             | 200.00                                                   | 4.48                        | 5.70                        | 0.00                                                     | 0.24                                                     |
| MnVO\(_3\) (62)   | 69.58                             | 240.00                                                   | 1.35                        | 2.50                        | 2.00                                                     | 2.00                                                     |
| PtTiO\(_3\) (99)  | 47.01                             | 0.00                                                     | 4.31                        | 4.40                        | 0.00                                                     | 2.00                                                     |
| SrTiO\(_3\) (221) | 69.63                             | 0.00                                                     | 5.58                        | 4.81                        | 1.20                                                     | 2.00                                                     |
| SrTiO\(_3\) (140) | 69.38                             | 0.00                                                     | 5.62                        | 5.27                        | 1.28                                                     | 1.02                                                     |
| SrVO\(_3\) (221)  | 43.23                             | 40.00                                                    |                             |                             |                                                          |                                                          |
| YTiO\(_3\) (62)  | 100.95                            | 40.00                                                    | 4.98                        | 4.64                        | 0.00                                                     | 2.00                                                     |

\(^a\)The parentheses following the compound name indicate the space group number. A and B represent O removal from the A-cation and B-cation layer, respectively.
layer results in a higher flexibility because a bond is severed from B-cations with already missing bonds. This could be the reason for the smaller spread in $E_{\text{Ovac}}$ values for O removal from the B-cation layer in comparison to the A-cation layer for “other nonmetals” in Figure 2. In particular, Fe–O and Co–O bond lengths in LaFeO$_3$ (62) and ScCoO$_3$ (62) are almost all the same. Adding extra electrons from O removal from the A-cation layer forces Jahn–Teller distortion to the Fe or Co that bonded to the removed O, which would force large local changes in bond lengths and/or unfavorable electronic states in Fe or Co. The lack of mitigating mechanisms could lead to the high $E_{\text{Ovac}}$ values for O removal from the A-cation layer in LaFeO$_3$ (62) and ScCoO$_3$ (62).

Figure 3 gives a plot of BG versus minimum $E_{\text{Ovac}}$. The space group number is shown together with the chemical formula.

There is a positive correlation trend in both the A- and B-site terminated layers, with the lowest $E_{\text{Ovac}}$ value being found in metallic systems. This trend was also found in binary carbide, nitride,$^{24}$ and $d^0$ and $d^{10}$ binary oxide systems,$^{23}$ as well as the (100) and (110) surfaces of Zn-containing normal spinels.$^{25}$ $E_{\text{Ovac}}$ from the B-cation layer of ScCoO$_3$ (62) appears to be an extreme layer for the BG plot (Figure 3b) but is not in the $E_{\text{form}}$ plot (Figure 4b). The high $E_{\text{Ovac}}$ in titanates comes from the electronic structure; all titanates have BG values exceeding 1.5 eV, and all nontitanates except for ScCoO$_3$ have BG values below 1.5 eV (Figure 4).

Figure 5 shows the DOS of the bulk, slab, and slab with O removed from the A- and B-cation layers of CaTiO$_3$ (33) and ScCoO$_3$ (62). The formation of surfaces results in the formation of surface states within the band gap. The formation of O vacancies results in additional defect states. In CdTiO$_3$ (33) (Figure 5a,c,e,f), the defect state is closer to the valence band in O removal from the A-cation layer in comparison to that from the B-cation layer, and this is reflected in the lower $E_{\text{Ovac}}$ in the former. On the other hand, the Fermi level after O removal is at the top of the valence band in ScCoO$_3$ (62) (Figure 5b,d,f,h). Variations in the defect state position among various compounds was also observed in $d^0$ and $d^{10}$ binary oxides.$^{23}$

4. SUMMARY

We calculated the $E_{\text{Ovac}}$ values for perovskite-structure oxides with a transition metal (Ti–Fe) as the B-site cation. The $E_{\text{Ovac}}$ correlates well with the band gap and bulk formation energy, which is a trend also found in other oxides. A low $E_{\text{Ovac}}$ value, which is expected to result in higher catalytic activity, is found in metallic perovskites such as CaCoO$_3$, BaFeO$_3$, and SrFeO$_3$. On the other hand, titanates had high $E_{\text{Ovac}}$ values, typically exceeding 4 eV/atom.
Justification of the selection of perovskite compounds considered in this study and electronic DOS of select bulk states (PDF)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00702.

**AUTHOR INFORMATION**

**Corresponding Author**

Yoyo Hinuma — Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda 563-8577, Japan; orcid.org/0000-0003-2272-1178; Email: y.hinuma@aist.go.jp

**Authors**

Shinya Mine — Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan; orcid.org/0000-0002-8339-0301

Takashi Toyao — Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan; Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto 615-8520, Japan; orcid.org/0000-0002-6062-5622

Ken-ichi Shimizu — Institute for Catalysis, Hokkaido University, Sapporo 001-0021, Japan; Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto 615-8520, Japan; orcid.org/0000-0003-0501-0294

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c00702

**Notes**

The authors declare no competing financial interest.

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