Comparative Ab Initio Calculations of ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) Surfaces

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Abstract: We performed, for the first time, ab initio calculations for the ReO₃-terminated ReO₃ (001) surface and analyzed systematic trends in the ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surfaces using first-principles calculations. According to the ab initio calculation results, all ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surface upper-layer atoms relax inwards towards the crystal bulk, all second-layer atoms relax upwards and all third-layer atoms, again, relax inwards. The ReO₃-terminated ReO₃ and ZrO₂-terminated SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surface band gaps at the Γ–Γ point are always reduced in comparison to their bulk band gap values. The Zr–O chemical bond populations in the SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ perovskite bulk are always smaller than those near the ZrO₂-terminated (001) surfaces. In contrast, the Re–O chemical bond population in the ReO₃ bulk (0.212e) is larger than that near the ReO₂-terminated ReO₃ (001) surface (0.170e). Nevertheless, the Re–O chemical bond population between the Re atom located on the ReO₂-terminated ReO₃ (001) surface upper layer and the O atom located on the ReO₂-terminated ReO₃ (001) surface second layer (0.262e) is the largest.

Keywords: ab initio methods; ABO₃ perovskites; ReO₃; (001) surface; B3PW; B3LYP

1. Introduction

Forefront (001) surfaces as well as (001) interface phenomena—which occur in the ABO₃ perovskite oxides and ReO₃—are hot topics in modern solid state physics due to their desirable atomic and electronic processes [1–9]. During the last quarter century, due to their great technological importance, as well as a comprehensive fundamental interest, the SrZrO₃, BaZrO₃, CaZrO₃ and PbZrO₃ (001) surfaces have been extensively investigated both theoretically and experimentally [10–22]. SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ matrices are so-called ABO₃ perovskites, where A = Sr; Ba; Pb; or Ca and B = Zr. ABO₃ perovskites have a large number of industrially important applications, for example, as actuators, capacitors and charge storage devices, etc. [23–27]. For many of those ABO₃ perovskite applications, surface quality and structure play important roles. For example, recent studies have shown that the catalytic properties of ABO₃ perovskite oxides are largely related to oxygen vacancies, which alter their electronic and crystal structures as well as surface chemistry [28–32].

Rhenium trioxide, ReO₃, is often referred to as a covalent metal since it has very high electrical conductivity [33]. The electrical conductivity of ReO₃ is similar to that of silver or copper [33]. Despite the great technological interest, there have been very few ab initio calculations and experimental studies performed on ReO₃ polar (001) surfaces [34–37]. It is worth noting that there have been no ab initio studies performed, to the best of our knowledge, on the atomic relaxation of the ReO₂-terminated polar ReO₃ (001) surface. ReO₃ related materials, such as LiReO₃ and Li₂ReO₅, are prospective battery materials.
The predictive power of first-principle calculations allows for the theoretical design of new materials for advanced technology applications. An excellent example is the theoretical prediction of the average voltages for a four-volt battery cathodes from first-principles calculations by Ceder and his coworkers [39,40]. Moreover, recently, based on first-principles calculations, it was shown that a five-volt battery was possible using Li$_2$CoMn$_2$O$_8$ as the cathode material [41,42].

In the classical cubic unit cells of SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskites, which contain five atoms, the A type atom is located at the cube-corner position with the coordinates (0, 0, 0). The B type atom is located at the body-center position with the coordinates (1/2, 1/2, 1/2). Finally, the three O atoms are located at face-centered positions equal to (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2). The ABO$_3$ perovskite’s A atom is always considerably larger than its B atom. All cubic ABO$_3$ perovskites belong to the Pm3m space group, for which the space group number is 221. ReO$_3$ forms the crystallizes in the cubic ABO$_3$ perovskite structure—Pm3m space group and space group number 221—with the only difference being the unoccupied A-cation site [37].

The goal of the work reported in this paper is to perform, for the first time, ab initio calculations for polar ReO$_2$-terminated ReO$_3$ (001) surfaces. The ab initio calculation results for the polar ReO$_2$-terminated ReO$_3$ (001) surface were compared with the calculation results for neutral ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surfaces. The calculation results for all five materials were carefully analyzed and systematic trends common for all ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surfaces were elucidated and are reported herein.

2. Computational Method

We performed ab initio calculations for the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$bulk and ReO$_2$ or ZrO$_2$-terminated (001) surfaces, respectively, using the hybrid exchange–correlation functionals B3PW [43] or B3LYP [44] as well as the widely recognized CRYSTAL computer code [45]. The SrTiO$_3$ [46], CaF$_2$ [47] and MgF$_2$ [48] bulk Γ–Γ band gaps that were calculated using different exchange–correlation functionals are provided in Table 1. The experimentally measured SrTiO$_3$ [49], CaF$_2$ [50] and MgF$_2$ [51,52] bulk band gaps at the Γ-point are listed in Table 1 for the purpose of comparison. It is well known that the local-density approximations (LDA) and generalized-gradient approximations (GGA) used in density functional theory (DFT) systematically underestimate the band gap in complex oxide materials, such as ABO$_3$ perovskites and insulators by a factor of almost two (Table 1). In contrast, it is well known that the Hartree–Fock (HF) method systematically overestimates the band gap of solids. With the aim of generating a reliable basis for further ABO$_3$ perovskites and ReO$_3$ bulk and (001) surface calculations, which require a precise description of the Γ–Γ band gap, we performed the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk and (001) surface calculations by means of the hybrid exchange–correlation functionals B3PW or B3LYP, which utilize 20% of the HF method and 80% of the DFT Hamiltonian method when implemented in the CRYSTAL computer package [45].

<table>
<thead>
<tr>
<th>Method</th>
<th>SrTiO$_3$ [46]</th>
<th>CaF$_2$ [47]</th>
<th>MgF$_2$ [48]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>3.75 [49]</td>
<td>12.1 [50]</td>
<td>12.4 [51]; 13.0 [52]</td>
</tr>
<tr>
<td>B3PW</td>
<td>3.96</td>
<td>10.96</td>
<td>9.48</td>
</tr>
<tr>
<td>B3LYP</td>
<td>3.89</td>
<td>10.85</td>
<td>9.42</td>
</tr>
<tr>
<td>HF</td>
<td>12.33</td>
<td>20.77</td>
<td>19.65</td>
</tr>
<tr>
<td>PWE</td>
<td>2.31</td>
<td>8.51</td>
<td>6.94</td>
</tr>
<tr>
<td>PBE</td>
<td>2.35</td>
<td>8.45</td>
<td>6.91</td>
</tr>
</tbody>
</table>

For example, as can be seen from Table 1, the ab initio HF calculations strongly overestimate the experimental SrTiO$_3$ bulk band gap at the Γ-point—by 3.29 times. In contrast, the DFT-based
PWGGA and PBE exchange–correlation functionals considerably underestimate the experimental SrTiO$_3$ band gap at the $\Gamma$-point—by 1.62 and 1.60 times, respectively. Finally, the B3PW and B3LYP hybrid-exchange correlation functionals only slightly overestimate the experimental SrTiO$_3$ band gap at the $\Gamma$-point—by 1.06 and 1.04 times, respectively. For predominantly this reason, the B3PW and B3LYP hybrid exchange–correlation functionals were used in all subsequent ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk and (001) surface ab initio calculations performed by means of the CRYSTAL computer code [45].

The key power of the CRYSTAL computer code, which is important for the study of neutral SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ as well as polar ReO$_3$ (001) surfaces, is its use of the 2D isolated slab model, without artificial repetition along the $z$-axis. The reciprocal space integration, in the ab initio calculations, were performed by sampling the Brillouin zone with an $8 \times 8 \times 1$ times extended Pack–Monkhorst mesh for the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surfaces and $8 \times 8 \times 8$ mesh for the bulk of those materials. In order to achieve highly accurate calculations, large enough tolerances of 7, 8, 7, 7 and 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, first-exchange pseudo-overlap and second-exchange pseudo-overlap, respectively [45].

In order to calculate the neutral BO$_2$-terminated ABO$_3$ perovskite (001) surfaces (Figure 1), we used symmetrical slabs consisting of nine, neutral, alternating BO$_2$ or AO layers perpendicular to the [001] crystal direction [11,14,16,41]. The slabs were rotated to make them perpendicular to the Oz axis. The CRYSTAL computer package [45] made it possible to avoid artificial periodicity along the Oz direction and to perform calculations for stand-alone 2D slabs. Taking into account the classical ionic charges for A$(+2e)$, for B$(+4e)$ and for O$(-2e)$, both the AO and BO$_2$ layers have a formal ionic charge equal to zero. The nine-layer slab, used in ABO$_3$ perovskite (001) surface calculations, was terminated on both sides by BO$_2$ planes and thereby consisted of a 23-atom supercell (Figure 1). The calculated BO$_2$-terminated ABO$_3$ perovskite (001) slabs were non-stoichiometric, with an empirical unit cell of $A_4B_5O_{14}$ [11,14,16,41].

![Figure 1. Side-view of the nine-layer BO$_2$-terminated ABO$_3$ perovskite (001) surface.](image-url)
In contrast to neutral ABO$_3$ perovskite (001) surfaces, it is much more difficult to calculate polar, ReO$_2$-terminated ReO$_3$ (001) surfaces, which consist of charged ReO$_2$ and O layers, taking into account the classical ionic charges of Re(+6e) and O(−2e) (Figure 2). Furthermore, for the ReO$_2$-terminated polar ReO$_3$ (001) surface calculations, we used symmetrical nine-layer slabs, which consisted of polar, alternating ReO$_2$ and O layers and contained 19 atoms, with an empirical unit cell of B$_5$O$_{14}$. The nine-layer ReO$_2$-terminated ReO$_3$ surface, taking into account formal ionic charges (ReO$_2$(+2e)−O(−2e)−ReO$_2$(+2e)−O(−2e)−ReO$_2$(+2e)−O(−2e)−ReO$_2$(+2e)−O(−2e)−ReO$_2$(+2e)), has a positive charge equal to +2e. In all calculations performed by CRYSTAL computer code, the unit cell should be neutral. In order to make the calculations feasible, for polar ReO$_2$-terminated ReO$_3$ (001) surfaces, instead of ionic basis sets—as in case of ABO$_3$ perovskites—the basis sets for neutral Re and O atoms were used. For example, for the O atom, the basis sets developed by Piskunov et al. [46] were used, and two electrons were removed from the O$^{2−}$ ion to obtain the basis set for the neutral O atom [5,53,54]. For the Re atom, we used the basis set developed by Cora [45]. Using the atomic basis sets for Re and O atoms, we obtained the polar ReO$_2$-terminated ReO$_3$ (001) surface with a formal charge equal to 0, and thereby, such calculations are feasible with the CRYSTAL computer code. As we know from previous studies, for example, with polar CaTiO$_3$ and SrTiO$_3$ (111) surfaces [55–59], a very strong electron redistribution is observed, which deletes the polarity effects. It is evident that it is impossible to calculate the asymmetric slabs with different terminations, such as ReO$_2$−O−ReO$_2$−O−ReO$_2$−O, since, in the case for the asymmetric slab, it has a large dipole moment perpendicular to the ReO$_2$-terminated ReO$_3$ crystal (001) surface.

![Figure 2. Side-view of the nine-layer ReO$_2$-terminated ReO$_3$ polar (001) surface.](image)

To correctly describe the chemical bonding as well as covalency effects for both ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$, CaZrO$_3$ bulk and their (001) surfaces, we used a standard Mulliken population analysis as it is implemented in the CRYSTAL computer code [45]. Namely, the Mulliken population analysis was used for the chemical bond populations $P$, effective atomic charges $q$, as well as another local properties of the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ electronic structure, such as the bond orders, atomic covalences and full valences [60–62].
3. Numeric Results of ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$, CaZrO$_3$ Bulk and (001) Surface Calculations

3.1. Ab Initio Calculations of ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ Bulk Properties

In order to begin the calculations, by means of the B3LYP or B3PW functional, the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk lattice constants were calculated and compared with actual experimental data (Table 2). As shown in Table 2, the B3LYP calculated ReO$_3$ bulk lattice constant (3.758 Å) is only overestimated by 0.29% with respect to the experimental value of 3.747 Å [63]. The, by means of hybrid exchange–correlation functionals, calculated SrZrO$_3$, BaZrO$_3$ and PbZrO$_3$ bulk lattice constants are overestimated with respect to the experimentally measured bulk lattice constants by 0.99%, 0.83% and 1.41%, respectively [64–66]. The theoretical ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ [67] bulk lattice constants were used in all subsequent (001) surface calculations.

Table 2. B3LYP or B3PW calculated ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk lattice constants (in Å). The experimental bulk lattice constants are listed for the purpose of comparison.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Functional</th>
<th>Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO$_3$</td>
<td>B3LYP</td>
<td>3.758</td>
<td>3.747 [63]</td>
</tr>
<tr>
<td>SrZrO$_3$</td>
<td>B3LYP</td>
<td>4.195</td>
<td>4.154 [64]</td>
</tr>
<tr>
<td>BaZrO$_3$</td>
<td>B3PW</td>
<td>4.234</td>
<td>4.199 [65]</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>B3LYP</td>
<td>4.220</td>
<td>4.1614 [66]</td>
</tr>
<tr>
<td>CaZrO$_3$</td>
<td>B3LYP</td>
<td>4.157</td>
<td>No data for cubic phase</td>
</tr>
</tbody>
</table>

The calculated effective charge is +2.382e for the Re atom in the ReO$_3$ bulk matrix (Table 3). The calculated Zr effective charges in the SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskites (+2.174e, +2.134e, +2.111e and +2.144e, respectively) are similar to each other and strongly different from the Zr formal ionic charge (+4e). The calculated O effective charge in the ReO$_3$ bulk is equal to −0.794e. Ab initio calculated O effective charges in the SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskites are equal to −1.351e, −1.316e, −1.160e and −1.310e, respectively. Therefore, the SrZrO$_3$, BaZrO$_3$ and CaZrO$_3$ O effective charges are similar, but the O effective charge in the PbZrO$_3$ crystal is considerably smaller, only −1.160e (Table 3). The chemical bond population between Re and O atoms in ReO$_3$ is equal to +0.212e. The chemical bond population between Zr and O atoms in SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ matrices are equal to +0.092e, 0.108e, 0.106e, 0.086e, respectively. Large chemical bond population values between B and O atoms in ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ crystals indicate that the chemical bonding in these materials is covalent.

Table 3. By means of the hybrid exchange–correlation functionals B3LYP or B3PW calculated effective atomic charges Q and bond populations P in ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$.

<table>
<thead>
<tr>
<th>Material, Bulk</th>
<th>Ion</th>
<th>Property</th>
<th>ReO$_3$ B3LYP</th>
<th>SrZrO$_3$ B3LYP</th>
<th>BaZrO$_3$ B3PW</th>
<th>PbZrO$_3$ B3LYP</th>
<th>CaZrO$_3$ B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Q</td>
<td>+1.880</td>
<td>+1.815</td>
<td>+1.368</td>
<td>+1.787</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>+0.002</td>
<td>−0.012</td>
<td>+0.030</td>
<td>+0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>Q</td>
<td>−0.794</td>
<td>−1.351</td>
<td>−1.316</td>
<td>−1.160</td>
<td>−1.310</td>
<td></td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>+0.212</td>
<td>+0.092</td>
<td>+0.108</td>
<td>+0.106</td>
<td>+0.086</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Q</td>
<td>+2.382</td>
<td>+2.174</td>
<td>+2.134</td>
<td>+2.111</td>
<td>+2.144</td>
<td></td>
</tr>
</tbody>
</table>

By means of the B3LYP or B3PW hybrid exchange–correlation functionals, the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk band gaps at the Γ–Γ point were calculated for the cubic phase of these crystals. It is worth mentioning that the hybrid exchange–correlation functionals, such as B3LYP or B3PW are in excellent agreement with the experimentally obtained band gaps of related...
ABO$_3$ perovskites and their (001) surfaces [5,16,47,48,68], whereas the density functional theory, consistently underestimates the band gap of complex oxide materials. From another side, it is well known that the Hartree–Fock method considerably overestimates the band gap of complex oxide materials. The B3LYP-calculated bulk band gap for ReO$_3$ at the Γ-point is equal to 5.76 eV (Table 4). To the best of our knowledge, there are no reported experimental data for the ReO$_3$ bulk band gap at the Γ-point. The calculated optical band gap for BaZrO$_3$ at the Γ-point (4.93 eV) is only underestimated by 6.98% regarding the experimental value of 5.3 eV [69]. The ab initio calculated optical band gaps at the Γ-point for SrZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite cubic phases are 5.31, 5.63 and 5.40 eV, respectively. Unfortunately, it is not possible to compare the ab initio calculation results for the band gaps at the Γ-point for SrZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskites with experimental results, since there are, currently, no reports of the band gaps of SrZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite cubic phases in the literature.

Table 4. B3LYP or B3PW calculated ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk band gaps at the Γ–Γ point for the cubic phase. The ab initio calculation results are compared with the available experimental data.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Optical Band Gap at Γ–Γ Point</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ab initio Data</td>
</tr>
<tr>
<td>ReO$_3$</td>
<td>B3LYP</td>
<td>5.76</td>
</tr>
<tr>
<td>SrZrO$_3$</td>
<td>B3LYP</td>
<td>5.31</td>
</tr>
<tr>
<td>BaZrO$_3$</td>
<td>B3PW</td>
<td>4.93</td>
</tr>
<tr>
<td>PbZrO$_3$</td>
<td>B3LYP</td>
<td>5.63</td>
</tr>
<tr>
<td>CaZrO$_3$</td>
<td>B3LYP</td>
<td>5.40</td>
</tr>
</tbody>
</table>

3.2. Ab Initio Calculations of ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) Surfaces

B3LYP or B3PW ab initio calculations for the upper three-layer atom relaxation for the neutral ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ as well as polar ReO$_2$-terminated ReO$_3$ (001) surfaces (Table 5) were performed. It is worth noting that the ReO$_3$ material has the cubic ABO$_3$ perovskite structure and symmetry with the space group number 221, but with the only difference being the A atom vacancy (Figure 2). For the cases of SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite ZrO$_2$-terminated as well as ReO$_3$ crystal ReO$_2$-terminated (001) surfaces, according to the ab initio calculations, all upper-layer atoms relax towards the bulk (Table 5). The ReO$_2$-terminated ReO$_3$ (001) surface upper-layer Re atom displacement magnitude (3.19% of $a_0$) is slightly larger than the ab initio calculated ABO$_3$ perovskite ZrO$_2$-terminated (001) surface Zr atom relaxation magnitudes, which are in the range of 1.30% of $a_0$ for the CaZrO$_3$ to 2.37% of $a_0$ for the PbZrO$_3$ perovskite (Table 5). In contrast, all SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite second-layer ZrO$_2$-terminated (001) surface atoms relax in the outward direction. The only exception to this systematic trend is the second-layer ReO$_2$-terminated ReO$_3$ (001) surface O atom inward relaxation towards the bulk; however, this has a small relaxation magnitude, equal to ~0.32% of $a_0$. All the ab initio calculated third-layer atoms for the ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ as well as ReO$_2$-terminated ReO$_3$ (001) surfaces, again, as in the case of the upper-layer atoms, relax inwards, towards the crystal bulk (Table 5). Nevertheless, the relaxation magnitudes of all first-layer atoms for the ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite as well as ReO$_2$-terminated ReO$_3$ (001) surfaces are much larger than the relevant relaxation magnitudes of the respective third-layer atoms (Table 5).

To compare ab initio calculation results for ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surfaces with the available experimental results, the calculated surface rumplings $s$ (the relative displacement of oxygen with respect to the metal in the upper surface layer) as well as the changes in interlayer distances, $\Delta d_{12}$ and $\Delta d_{23}$, are shown in Table 6. The calculations of the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surface interlayer distances rely on the positions of the metal ions (Figure 1), which are well known to be much stronger electron scatterers than oxygen ions [70]. As can be seen
from Table 6, all the calculated ZrO₂-terminated SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surfaces show the reduction of the interlayer distance Δ₁₂ and expansion of Δ₂₃. For all ZrO₂-terminated SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surfaces, the reduction in the interlayer distance, Δ₁₂, is larger than the expansion of the respective interlayer distance, Δ₂₃. The ab initio calculated surface rumpling, s, is positive and largest between all calculated surface rumplings (+2.02) for the ReO₂-terminated ReO₃ (001) surface. The calculated surface rumplings, s, for the ZrO₂-terminated BaZrO₃ and PbZrO₃ (001) surfaces (+0.09 and +0.38, respectively) are also positive, but much smaller than for the ReO₂-terminated ReO₃ (001) surface (+2.02). In contrast, the calculated surface rumplings, s, for the ZrO₂-terminated SrZrO₃ and CaZrO₃ (001) surfaces are negative (−0.72 and −1.01, respectively).

**Table 5.** ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ upper three-layer atom relaxation (in percent of the crystal bulk lattice constant) for the BO₂-terminated (001) surfaces calculated by the B3LYP exchange–correlation functional for ReO₃, SrZrO₃, PbZrO₃ and CaZrO₃ perovskites as well as by the B3PW method for BaZrO₃.

<table>
<thead>
<tr>
<th>Surfaces, (001)</th>
<th>ReO₃</th>
<th>SrZrO₃</th>
<th>BaZrO₃</th>
<th>PbZrO₃</th>
<th>CaZrO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer</td>
<td>Ion</td>
<td>ReO₂-t.</td>
<td>ZrO₂-t.</td>
<td>ZrO₂-t.</td>
<td>ZrO₂-t.</td>
</tr>
<tr>
<td>1</td>
<td>B</td>
<td>−3.19</td>
<td>−1.38</td>
<td>−1.79</td>
<td>−2.37</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>−1.17</td>
<td>−2.10</td>
<td>−1.70</td>
<td>−1.99</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>Absent</td>
<td>+2.81</td>
<td>+1.94</td>
<td>+4.36</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>−0.32</td>
<td>+0.91</td>
<td>+0.85</td>
<td>+1.04</td>
</tr>
<tr>
<td>3</td>
<td>B</td>
<td>−0.17</td>
<td>−0.04</td>
<td>−0.03</td>
<td>−0.47</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>−0.11</td>
<td>−0.05</td>
<td>0.00</td>
<td>−0.28</td>
</tr>
</tbody>
</table>

**Table 6.** B3PW and B3LYP calculated surface rumplings, s, as well as relative displacements, Δdᵢⱼ, between the 3 near-surface planes for the BO₂-terminated ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surfaces as a percent of the bulk crystal lattice constant.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>BO₂-Terminated (001) Surface</th>
<th>s</th>
<th>Δd₁₂</th>
<th>Δd₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ReO₃</td>
<td>B3LYP</td>
<td>+2.02</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>SrZrO₃</td>
<td>B3LYP</td>
<td>−0.72</td>
<td>−4.19</td>
<td>+2.85</td>
<td></td>
</tr>
<tr>
<td>BaZrO₃</td>
<td>B3PW</td>
<td>+0.09</td>
<td>−3.73</td>
<td>+1.97</td>
<td></td>
</tr>
<tr>
<td>PbZrO₃</td>
<td>B3LYP</td>
<td>+0.38</td>
<td>−6.73</td>
<td>+4.83</td>
<td></td>
</tr>
<tr>
<td>CaZrO₃</td>
<td>B3LYP</td>
<td>−1.01</td>
<td>−5.53</td>
<td>+4.28</td>
<td></td>
</tr>
</tbody>
</table>

Unfortunately, to the best of our knowledge, there are no experimental data available for the ReO₃, SrZrO₃, BaZrO₃, PbZrO₃ and CaZrO₃ (001) surface rumpling, s, as well as interlayer distances, Δ₁₂ and Δ₂₃. However, such experimental data exist for the related ABO₃ perovskite, SrTiO₃ (Table 7). To compare the calculated and experimental SrTiO₃ (001) surface structures, the calculated surface rumpling, s, as well as the changes in interlayer distances, Δdᵢⱼ, are detailed in Table 7. From Table 7, it can be seen that the agreement is fairly good for all theoretical calculation methods, which all give the same sign for the surface rumpling, s, as well as the changes in the interlayer distances, Δdᵢⱼ. For example, the calculated surface rumpling, s, for the SrO-terminated surface is much larger than for the TiO₂-terminated SrTiO₃ (001) surface for all theoretical methods [25,71–75]. From Table 7, it can be seen that both the calculated SrO and TiO₂-terminated SrTiO₃ (001) surfaces always exhibit a reduction in the interlayer distance, Δ₁₂ and an expansion of Δ₂₃. The theoretically calculated surface rumpling amplitudes, s, for both SrTiO₃ (001) surface terminations are in fair agreement with the LEED [70], RHEED [76], MEIS [77] and SXRD [78] experiments (Table 7). Nevertheless, the calculated changes in interlayer distances disagree with the LEED experiments [70] for the TiO₂-terminated SrTiO₃ (001) surface, which show an increase in Δ₁₂ and reduction in Δ₂₃ (Table 7). In contrast, all ab initio as well as classical shell model calculations show a reduction in the interlayer distance, Δ₁₂ and an expansion
of $\Delta d_{23}$ (Table 7). Nevertheless, as can be seen from Table 7, unfortunately, the different experiments contradict each other with respect to the sign of $\Delta d_{12}$ and $\Delta d_{23}$ for the SrO-terminated SrTiO$_3$ (001) surface and for the sign of $\Delta d_{23}$ for the TiO$_2$-terminated SrTiO$_3$ (001) surface (Table 7).

Table 7. Calculated and experimental surface rumpling $s$ and relative displacements $\Delta d_{ij}$ (in percent of the bulk lattice constant) for the upper-three surface layers of SrO and TiO$_2$-terminated SrTiO$_3$ (001) slabs.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s$</td>
<td>$\Delta d_{12}$</td>
</tr>
<tr>
<td>Ab initio [25,71]</td>
<td>5.66</td>
<td>$-6.58$</td>
</tr>
<tr>
<td>Shell model [72]</td>
<td>8.2</td>
<td>$-8.6$</td>
</tr>
<tr>
<td>HF-LYP [73]</td>
<td>3.8</td>
<td>$-4.3$</td>
</tr>
<tr>
<td>Ab initio [74]</td>
<td>5.8</td>
<td>$-6.9$</td>
</tr>
<tr>
<td>Ab initio [75]</td>
<td>7.7</td>
<td>$-8.6$</td>
</tr>
<tr>
<td>LEED exp. [70]</td>
<td>4.1 $\pm$ 2</td>
<td>$-5 \pm 1$</td>
</tr>
<tr>
<td>RHEED exp. [76]</td>
<td>4.1</td>
<td>2.6</td>
</tr>
<tr>
<td>MEIS exp. [77]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SXRD exp. [78]</td>
<td>1.3 $\pm$ 12.1</td>
<td>$-0.3 \pm 3.6$</td>
</tr>
</tbody>
</table>

The ab initio calculated atomic charges, the Mulliken static charges as well as bond populations between nearest atoms are reported in Table 8. The most important effect, as can be seen from Table 8, is strengthening of the Zr–O chemical bond near the ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surface in comparison to the bulk [79–82]. In contrast, for the ReO$_2$-terminated ReO$_3$ (001) surface, the chemical bond population between the Re and O atoms in the upper surface layer 0.170$e$ (Table 8) is slightly smaller than the Re–O chemical bond population in the ReO$_3$ bulk (0.212e). Nevertheless, the chemical bond population between the upper-layer Re atom and the second-layer O atom (0.262$e$) for the ReO$_2$-terminated ReO$_3$ (001) surface is considerably larger than the Re–O chemical bond population in the ReO$_3$ crystal bulk (0.212e). It is worth noticing, that the Re and O effective charges in the ReO$_3$ crystal bulk (+2.382e for Re and $-0.794e$ for O) are much smaller than those expected in the ionic model (+6e for Re and $-2e$ for O). Moreover, the Re–O chemical bond in the ReO$_3$ bulk is considerably populated (+0.212e). It is interesting to note that the Re–O chemical bond population for the ReO$_2$-terminated ReO$_3$ (001) surface third layer (+0.208e) (Table 8) is already highly similar to the Re–O chemical bond population in the ReO$_3$ bulk matrix (0.212e). The Re effective charge in the ReO$_2$-terminated ReO$_3$ (001) surface third layer (+2.341e) is almost as high as the Re effective charge value (+2.382e) in the ReO$_3$ bulk crystal. In contrast, the Re effective charge on the ReO$_2$-terminated ReO$_3$ (001) surface upper layer, where the surface effect is strong, (+2.258e) is much smaller than the Re effective charge in the ReO$_3$ crystal bulk (+2.382e).

As can be seen from the ab initio calculation results, detailed in Table 9, the Zr–O chemical bond populations for all four calculated perovskites SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ are larger near their ZrO$_2$-terminated (001) surfaces than in the bulk. However, the opposite is true for the ReO$_3$ crystal. The Re–O chemical bond population in the ReO$_3$ bulk (0.212e) is larger than it is near the ReO$_2$-terminated ReO$_3$ (001) surface (0.170e). However, it is worth noting that the Re–O chemical bond population between the ReO$_2$-terminated (001) surface upper-layer Re atom and the second-layer O atom (0.262e) is considerably larger than the Re–O chemical bond population in the ReO$_3$ crystal bulk (0.212e).

The, by means of the hybrid exchange–correlation functionals, calculated bulk band gaps at the $\Gamma$–$\Gamma$ point for ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ crystals are equal to 5.76, 5.31, 4.93, 5.63 and 5.40 eV, respectively (Table 10). In most cases, there are no experimental data available for the ReO$_3$, SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk band gaps in the cubic phase. However, the calculated BaZrO$_3$ band gap at the $\Gamma$–$\Gamma$ point (4.93 eV) is in fair agreement with the experimental data (5.3 eV) [69]. According to the performed ab initio calculations, the systematic trend is reduction of the ReO$_3$, SrZrO$_3$, Crystals 2020, 10, 745
Table 8. Ab initio calculated absolute magnitudes of atomic shifts $D$ (in Å), the effective atomic charges $Q$ (in $e$) and nearest atom $\text{Me–O}$ bond populations $P$ (in $e$) for the $\text{ReO}_2$ and $\text{ZrO}_2$-terminated $\text{ReO}_3$, $\text{SrZrO}_3$, $\text{BaZrO}_3$, $\text{PbZrO}_3$ and $\text{CaZrO}_3$ (001) surfaces.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Property Ion</th>
<th>$\text{ReO}_3$</th>
<th>$\text{SZO}$</th>
<th>$\text{BZO}$</th>
<th>$\text{PZO}$</th>
<th>$\text{CZO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$D$ B</td>
<td>−0.120</td>
<td>−0.058</td>
<td>−0.076</td>
<td>−0.100</td>
<td>−0.054</td>
</tr>
<tr>
<td></td>
<td>$Q$</td>
<td>+2.258</td>
<td>+2.196</td>
<td>+2.173</td>
<td>+2.165</td>
<td>+2.172</td>
</tr>
<tr>
<td></td>
<td>$P$</td>
<td>+0.170</td>
<td>+0.114</td>
<td>+0.132</td>
<td>+0.116</td>
<td>+0.102</td>
</tr>
<tr>
<td>2</td>
<td>$D$ A</td>
<td>−0.012</td>
<td>−0.002</td>
<td>−0.018</td>
<td>+0.046</td>
<td>+0.018</td>
</tr>
<tr>
<td></td>
<td>$Q$</td>
<td>+0.118</td>
<td>+0.082</td>
<td>+0.184</td>
<td>+0.176</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$P$</td>
<td>+1.869</td>
<td>+1.797</td>
<td>+1.357</td>
<td>+1.772</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$D$ B</td>
<td>−0.006</td>
<td>−0.002</td>
<td>−0.001</td>
<td>−0.020</td>
<td>−0.002</td>
</tr>
<tr>
<td></td>
<td>$Q$</td>
<td>+0.214</td>
<td>+0.094</td>
<td>+0.106</td>
<td>+0.098</td>
<td>+0.090</td>
</tr>
<tr>
<td></td>
<td>$P$</td>
<td>+0.092</td>
<td>+0.114</td>
<td>+0.124</td>
<td>+0.098</td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Ab initio calculated $\text{B–O}$ chemical bond populations for $\text{ReO}_3$, $\text{SrZrO}_3$, $\text{BaZrO}_3$, $\text{PbZrO}_3$ and $\text{CaZrO}_3$ bulk as well as for $\text{BO}_2$-terminated (001) surfaces (in $e$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>$\text{B–O}$ Chemical Bond Populations</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ReO}_3$</td>
<td>B3LYP</td>
<td>0.212 0.170</td>
</tr>
<tr>
<td>$\text{SrZrO}_3$</td>
<td>B3LYP</td>
<td>0.092 0.114</td>
</tr>
<tr>
<td>$\text{BaZrO}_3$</td>
<td>B3PW</td>
<td>0.108 0.132</td>
</tr>
<tr>
<td>$\text{PbZrO}_3$</td>
<td>BLYP</td>
<td>0.106 0.116</td>
</tr>
<tr>
<td>$\text{CaZrO}_3$</td>
<td>B3LYP</td>
<td>0.086 0.102</td>
</tr>
</tbody>
</table>

Table 10. Ab initio calculated optical band gaps at the $\Gamma$–$\Gamma$ point for $\text{ReO}_3$, $\text{SrZrO}_3$, $\text{BaZrO}_3$, $\text{PbZrO}_3$ and $\text{CaZrO}_3$ bulk as well as their $\text{ReO}_2$ or $\text{ZrO}_2$-terminated (001) surfaces.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>Band Gap at $\Gamma$–$\Gamma$ Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{ReO}_3$</td>
<td>B3LYP</td>
<td>5.76 0.22</td>
</tr>
<tr>
<td>$\text{SrZrO}_3$</td>
<td>B3LYP</td>
<td>5.31 4.91</td>
</tr>
<tr>
<td>$\text{BaZrO}_3$</td>
<td>B3PW</td>
<td>4.93 4.48</td>
</tr>
<tr>
<td>$\text{PbZrO}_3$</td>
<td>B3LYP</td>
<td>5.63 4.60</td>
</tr>
<tr>
<td>$\text{CaZrO}_3$</td>
<td>B3LYP</td>
<td>5.40 5.22</td>
</tr>
</tbody>
</table>

BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ bulk band gaps near their ReO$_2$ or ZrO$_2$-terminated (001) surfaces, respectively. Namely, the calculated band gap values at the $\Gamma$–$\Gamma$ point for ReO$_2$-terminated ReO$_3$ and ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ terminated (001) surfaces of 0.22, 4.91, 4.48, 4.60 and 5.22 eV, respectively, were always smaller with respect to the bulk band gap value (Table 10).
4. Conclusions

For the ab initio calculated ReO$_2$-terminated ReO$_3$ as well as ZrO$_2$-terminated SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ (001) surfaces, the systematic trend was that all upper-layer surface atoms relaxed inwards, towards the bulk, all second-layer surface atoms relaxed upwards, and again, all third-layer surface atoms relaxed inwards. As a result of the performed relaxation, all five material surfaces exhibited a reduction in the interlayer distance, $\Delta d_{12}$ and expansion of $\Delta d_{23}$.

For all the ab initio calculated materials, the changes in the interlayer distances between the first and second layer were larger than the respective changes in the interlayer distances between the second and third layer.

According to the performed ab initio calculations, the SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite BO$_2$-terminated as well as ReO$_2$-terminated ReO$_3$ (001) surface band gaps were always smaller with respect to their bulk band gap values.

The Zr–O chemical bond population in SrZrO$_3$, BaZrO$_3$, PbZrO$_3$ and CaZrO$_3$ perovskite bulk was always smaller than that near the ZrO$_2$-terminated (001) surface. In contrast, the Re–O chemical bond population in the ReO$_3$ bulk (0.212e) was larger than that near the ReO$_2$-terminated ReO$_3$ (001) surface (0.170e). The Re–O chemical bond population between the Re atom located on the ReO$_2$-terminated ReO$_3$ (001) surface upper layer as well as the O atom located on the ReO$_2$-terminated ReO$_3$ (001) surface second layer was the largest (0.262e).

Author Contributions: All authors equally contributed to the performed ab initio calculations as well as to the preparation of the manuscript. Namely, mostly R.I.E. and A.I.P. wrote the Introduction. Mostly J.P., J.G. and R.J. wrote the section Computational Method. All authors equally wrote the sections Numeric Results and Conclusions. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interests.

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