Surface reconstruction and band alignment of nonmetallic $A(II)B(IV)O_3$ perovskites

Ha-Jun Sung⁰,^{1,*} Yasuhide Mochizuki⁰,¹ and Fumiyasu Oba^{1,2,†}

¹Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology, Yokohama 226-8503, Japan ²Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated Systems, National Institute for Materials Science, Tsukuba 305-0047, Japan

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Understanding the band alignment at oxide surfaces is of great importance for designing oxide-surface-based electronic, catalytic, and photocatalytic applications. We systematically investigate the band alignment of (001) surfaces of $A(II)B(IV)O_3$ perovskites (A = Ca, Sr, Ba, Pb; B = Ti, Zr, Hf, Ge, Sn) through first-principles calculations using semilocal and hybrid functionals. The results are discussed with an emphasis on the effects of surface reconstruction on the band alignment. Reconstructed stoichiometric surfaces are generated by an evolutionary algorithm with surface energy minimization for various surface periodicity units by taking the orthorhombic phase of CaTiO₃, the tetragonal phase of SrTiO₃, and the cubic phases of SrTiO₃ and BaSnO₃ as representatives. Two types of reconstruction patterns are obtained as energetically favorable configurations common to these phases, which are composed of half-AO and -BO₂ topmost layers, respectively. These reconstructed stoichiometric surfaces have energies comparable to those of nonstoichiometric surfaces, with full AO or BO₂ termination under specific chemical potential conditions in CaTiO₃ and SrTiO₃. We systematically calculate the positions of the valence-band maxima and the conduction-band minima with respect to the vacuum level, namely, the ionization potentials and the electron affinities, for the reconstructed stoichiometric and the nonstoichiometric surfaces of $A(II)B(IV)O_3$ perovskites. The ionization potentials and electron affinities at the reconstructed surfaces well describe the termination-plane dependencies of experimentally reported values. The surface band positions are found to show an approximately linear trend against the Goldschmidt tolerance factor, with the sign of slopes opposite to each other for the two types of reconstruction patterns. This tendency is explained by the tolerance-factor dependency of surface rumpling that significantly modifies the surface dipole, although the band positions of A = Pb systems exhibit a larger deviation from an expected trend due to Pb lone-pair states.

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I. INTRODUCTION

Perovskite oxides with a formula ABO_3 have attracted much attention owing to their intriguing physical and chemical properties for a broad range of technological applications such as catalysis, photocatalysis, electronics, and fuel cells [1–10]. Their flexibility in doping and epitaxial strain modulation is advantageous in realizing the target applications [11–15]. Especially, energy band alignment plays an essential role for designing surfaces and heterointerfaces in electronic and electrochemical applications [16,17]. The relative bandedge positions between perovskite oxides and other solids or molecules can be optimized for target device performance by controlling the chemical composition of the *A*- and *B*-site cations in ABO_3 , as well as applying appropriate surface and interface treatments [18–20].

The band alignment of surfaces, namely, the lineup of their ionization potentials (IPs) and electron affinities (EAs), is known to depend on the surface dipole, which is affected by the details of the structure, stoichiometry, and environmental conditions [21-23]. For instance, by engineering the band

alignment in ZnO/PbS quantum-dot solar cells through the different ligand treatments, power conversion efficiency is enhanced [24]. The atomic geometry of surfaces can be very different from that of bulk owing to atomic miscoordination, relaxation, and reconstruction, and presents large variety, even within the same crystallographic orientation. In GaAs, even for the clean (100) surface, the experimental studies indicate a substantial variation of its work function and IP with surface geometry up to about 0.82 eV [25]. Since the surface stoichiometry, reconstruction, and crystallographic orientation are not independent variables for determining surface dipoles, the interplay between these parameters makes the dependency of the band alignment on the surface geometry a rather complex problem which remains largely unexplored by both theory and experiment. For instance, SrTiO₃, which is one of the representatives of perovskite oxides, has a large number of reconstruction patterns, even on the low-index (001) surface with $p(2 \times 1)$, $p(2 \times 2)$, $p(6 \times 2)$, $c(4 \times 2)$, $c(6 \times 2)$ 2), $c(4 \times 4)$, $(\sqrt{5} \times \sqrt{5})R26.6^{\circ}$, and $(\sqrt{13} \times \sqrt{13})R33.7^{\circ}$, some of which remain uncharacterized on an atomic scale [26–30]. Some details for the TiO₂-rich $p(2 \times 1)$ and $c(4 \times 2)$ reconstructions are now understood as consisting of TiO₂ double layers [31,32]. A buffered hydrofluoric acid (BHF) etches the SrO layer and thereby makes the surfaces TiO₂ terminated [33]. A number of reconstruction patterns arise

^{*}sung@msl.titech.ac.jp

[†]oba@msl.titech.ac.jp

from annealing BHF-etched surfaces under ultrahigh-vacuum conditions [26–28], and the size of the lateral periodicity units of reconstructed surfaces strongly depends on the initial surface treatments before annealing process [34]. It is known that such nonstoichiometric reconstructed surfaces have specific effects on the surface dipole [20] and thereby band positions. Meanwhile, stoichiometric reconstructed surfaces for perovskite oxides have not often been considered in other studies, even though they can be environmentally driven.

Perovskite oxides contain alternating AO and BO₂ planes along the (100) directions. According to the formal valence states of the A and B cations, nonmetallic perovskite oxides can be classified as polar and nonpolar ones. Nonpolar perovskite oxides consist of formally neutral $[A^{2+}O^{2-}]^{0}$ and $[B^{4+}O_2^{2-}]^0$ layers as in SrTiO₃, while polar perovskite oxides contain charged $[A^+O^{2-}]^-$ and $[B^{5+}O^{2-}_2]^+$ or $[A^{3+}O^{2-}]^+$ and $[B^{3+}O_2^{2-}]^{-}$ layers as in KTaO₃ and LaAlO₃, respectively. The $\{100\}$ AO and BO₂ surfaces of the nonpolar perovskite oxides are therefore neutral from the viewpoint of the formal valence states, but actual surfaces are charged owing to the deviation from the formal valence states. The {110} and {111} surfaces are necessarily charged with the dipole moments perpendicular to the surfaces, regardless of the valence states of the cations. Such polar surfaces are generally unstable because of the large electrostatic contribution to the surface energy [35]. The polar instability should be suppressed in various ways, for example, charge compensation by adsorption, structural reconstructions, composition changes, and/or carrier accumulation [36–38]. Since these compensation mechanisms strongly depend not only on the systems but also on the environmental conditions, it is hard to investigate the nonpolar and polar surfaces in the same manner. The band positions at nonpolar surfaces have been investigated using first-principles calculations for a variety of materials, including perovskite oxides [19], as well as other prototypical semiconductors and insulators [39–46]. However, systematic knowledge of the surface reconstruction effect on the band positions is lacking for perovskite oxides with diverse chemical compositions.

In this work, we focus on the (001) nonpolar stoichiometric and nonstoichiometric surfaces of perovskite oxides and perform first-principles calculations to investigate their relative surface energies and band positions. Based on the hybrid functional approach, we evaluate the IPs and EAs of 20 nonmetallic $A(II)B(IV)O_3$ perovskites (A = Ca, Sr, Ba, Pb; B = Ti, Zr, Hf, Ge, Sn) using slab models for prototypical reconstructed stoichiometric and cleaved nonstoichiometric surfaces. In the next section, we address the calculation methods for the band positions in our slab models and the reconstructed patterns with low surface energies using an evolutionary structure search method. Then we discuss stability of the reconstructed stoichiometric and cleaved nonstoichiometric surfaces for three representative systems—CaTiO₃, SrTiO₃, and BaSnO₃—as a function of chemical potentials. Finally, we systematically investigate the effects of bulk chemical composition and surface atomic structure on the band alignment.



FIG. 1. Schematic side view of atomic configurations for reconstructed (001) surface geometry optimization. The atoms on the topmost half-monolayer (red region) are rearranged by global optimization, while the atoms in the blue and black regions are relaxed and fixed during the geometry optimization, respectively.

II. METHODOLOGY

The first-principles calculations were performed using the Perdew-Burke-Ernzerhof semilocal functional tuned for solids (PBEsol) [47] and the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [48-50] for the exchangecorrelation energy and potential, and the projector augmentedwave method [51], as implemented in the VASP code [52,53]. The PBEsol functional was used for bulk and surface geometry optimization, which has been shown to reproduce lattice parameters well for a number of metal oxides [54]. The HSE06 functional with a Fock-exchange mixing parameter of 0.25 and a screening parameter of 0.207 \AA^{-1} [48–50] was used to obtain more reliable band gaps and band-edge positions within the geometries determined using PBEsol. For bulk geometry optimization including both lattice parameters and internal coordinates, the wave functions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. A k-point set was generated for cubic phases by the $6 \times 6 \times 6$ Γ -centered mesh for Brillouin zone integration, and nearly the same k-point density was considered for the orthorhombic and tetragonal phases. For surface calculations, the slab structure (>23 Å thick) was modeled by including a vacuum region (>20 Å thick) in the supercell geometry using an algorithm reported in Refs. [45,55]. The internal coordinates were optimized with supercell dimensions fixed, until the residual forces were less than $0.02 \text{ eV}/\text{\AA}$.

We explored reconstructed *ABO*₃ (001) surfaces with low surface energies by using an *ab initio* evolutionary structure search method, as implemented in the AMADEUS code [56]. In this method, the conformational space annealing (CSA) algorithm [57] for global optimization is combined with firstprinciples calculations. The efficiency of this approach has been demonstrated by the prediction of carbon and silicon allotropes with direct band gaps and the two-dimensional B₉ Kagome lattice on the Ag(111) surface [58–61]. To model stoichiometric surfaces for cubic phases, we considered halfmonolayer coverages of the topmost atoms for five types of *ABO*₃ (001) surface supercells with different lateral periodicity units, $p(2 \times 1)$, $p(2 \times 2)$, $c(2 \times 2)$, $c(4 \times 2)$, and $c(4 \times 4)$ (Fig. 1). We use the same notation for describing surface structures of tetragonal and orthorhombic phases based on a pseudocubic periodicity unit so that the correspondence of reconstructed surface structures between cubic and noncubic systems is clear. In principle, some of the surfaces with smaller periodicities [e.g., $p(2 \times 1)$] are naturally included in larger ones [e.g., $p(2 \times 2)$]. Nevertheless, we complementally consider the smaller surface units because the larger degrees of freedom in the larger surface units make the ground-state structure searches more difficult within realistic computational time. In our slab model, the topmost layer is rearranged by a global optimization method, and the middle two and lower three layers were relaxed and held fixed, respectively (Fig. 1); additional calculations for cubic $SrTiO_3$ surfaces where the topmost two layers are rearranged yielded nearly identical results, as will be mentioned later. The number of configurations was set to 30 in the population size of the CSA, and the surface energy was used to express the objective function. We consider the slab geometry with only six sublayers (about 10 Å) to reduce the computational cost for a reconstructed surface search, and the optimized topmost layer (red region in Fig. 1) is then placed at both sides of the nonpolar 13 subunit layers in slab models for subsequent surface energy and band-position calculations. For each surface configuration, the surface energies were minimized through atomic relaxation using the PBEsol functional. For Brillouin zone integration, k-point sets were generated by $3 \times 6 \times 1$, $3 \times 3 \times 1$, $4 \times 4 \times 1$, $2 \times 4 \times 1$, and $2 \times 2 \times 1$ meshes for the $p(2 \times 1)$, $p(2 \times 2)$, $c(2 \times 2)$, $c(4 \times 2)$, and $c(4 \times 4)$ supercells, respectively.

The relative band-edge positions of arbitrary semiconductors and insulators can be determined by the IP and EA of each system, which are defined as the valence-band maximum (VBM) and conduction-band minimum (CBM) with respect to the vacuum level, respectively. The IPs and EAs were calculated based on the bulk-based definition, which excludes the explicit effects of surface states [62,63]. The IP (I) and EA (A) can be evaluated as the sum of two contributions as

$$I = \Delta V - \varepsilon_{\rm VBM-Ref}^{\rm bulk},\tag{1}$$

$$A = \Delta V - \varepsilon_{\rm CBM-Ref}^{\rm bulk},\tag{2}$$

where $\varepsilon_{\text{VBM-Ref}}^{\text{bulk}}$ and $\varepsilon_{\text{CBM-Ref}}^{\text{bulk}}$ are the VBM and CBM with respect to a reference level in a bulk system, respectively, and ΔV is the potential energy difference between the vacuum and reference levels in a slab model. We define the reference level as macroscopically averaged electrostatic potential in the bulk models and the middle of the slab models that is assumed to be bulklike. While $\varepsilon_{\text{VBM-Ref}}^{\text{bulk}}$ and $\varepsilon_{\text{CBM-Ref}}^{\text{bulk}}$ are independent of surface structure and composition, ΔV includes the surface-dependent dipole contribution, leading to the surface dependence of the IPs and EAs.

III. RESULTS AND DISCUSSION

A. Relative stability of perovskite polymorphs

Perovskite oxides possess various octahedra-distorted structures, the representatives of which can be written as $a^0a^0a^0$, $a^-a^-a^+$, $a^0a^0c^-$, $a^-a^-c^0$, $a^-a^-a^-$, $a^0a^0a^+$, and

 $a^+a^+a^+$ in the Glazer notation, and their corresponding space groups are $Pm\bar{3}m$, Pbnm, I4/mcm, Ibmm, $R\bar{3}c$, P4/mbm, and $Im\bar{3}$, respectively [64,65]. Table I enumerates the experimental and calculated lattice parameters for the stable and metastable structures at room temperature (RT) [66–80]. Among the $A(II)B(IV)O_3$ perovskites, the structures for CaTiO_3, CaZrO_3, CaHfO_3, CaGeO_3, CaSnO_3, SrZrO_3, SrHfO_3, and SrSnO_3 have been experimentally reported as orthorhombic *Pbnm* at RT, while SrTiO_3, SrGeO_3, BaZrO_3, BaHfO_3, and BaSnO_3 have been reported to possess the cubic $Pm\bar{3}m$ structure (hereafter, we refer to them as *Pbnm-ABO_3* and $Pm\bar{3}m$ -*ABO_3*, respectively). In general, the lattice parameters are well reproduced by our calculations using the PBEsol functional.

Figure 2 shows the relative energies between seven polymorphs of 20 $A(II)B(IV)O_3$ perovskites (A = Ca, Sr, Ba, Pb; B = Ti, Zr, Hf, Ge, Sn), which were obtained using the PBEsol functional. The reported phases are well reproduced by the calculation results. Although the lowest energy phases of SrTiO₃ and SrGeO₃ are calculated to be the tetragonal I4/mcm phase (" $a^0a^0c^-$ " in the Glazer notation), the energy difference from the cubic $Pm\bar{3}m$ structure is only about 10 meV/f.u. The *Pbnm*-CaGeO₃ and *Pm* $\bar{3}m$ -SrGeO₃ are metastable at ambient pressure and start to amorphize at a temperature higher than 900 and 323 K, respectively [73,81]. Moreover, for BaTiO₃, PbTiO₃, PbZrO₃, and PbHfO₃, the stable phases are the rhombohedral R3m, tetragonal P4mm, and orthorhombic *Pbam* structures (inset in Fig. 2), which are polar and antipolar distorted structures with off-centering displacement of the B-site ions. In these compounds, since the surface energies depend on the cation displacement direction to the pseudocubic (001) surface [82], the calculated lowest energy structures among nonpolar distorted polymorphs, namely, Pm3m-BaTiO₃, Pbnm-PbTiO₃, Pbnm-PbZrO₃, and Pbnm-PbHfO₃, are considered in the present surface modeling. Recent experimental reports indicate that BaTiO₃ shows an order-disorder-type phase transition, and even the cubic phase involves local off-centering of Ti atoms toward one of the $\langle 111 \rangle$ directions [83,84]. We did not consider such off-centering, although it affects the band structure to be similar to that of the low-temperature rhombohedral phase [85]. For SrTiO₃, the low-temperature phase (under 105 K) with tetragonal *I4/mcm* symmetry [86] was additionally considered to investigate the effects of the octahedral rotations on surface reconstruction.

B. Nonpolar stoichiometric surfaces with atomic reconstruction

The band alignment calculations were performed mainly for reconstructed stoichiometric and cleaved nonstoichiometric slab models. It is known that the (001) surfaces of cubic $A(II)B(IV)O_3$ perovskite oxides, which are classified as Tasker type 3, are weakly polar when their actual charges are considered because the compounds are not fully ionic by quantum description [87], as mentioned above. Hinuma *et al.* proposed that the Tasker type-3 surfaces can be divided into nonpolar type-C and polar surfaces, while nonpolar type A and B in their definition correspond to Tasker type 1 and 2, respectively [55]. For nonpolar type-C surfaces, the terminating planes of the surfaces must lie on atomic layers, TABLE I. Experimental and calculated lattice parameters for reported stable and metastable perovskite phases at room temperature. Experimental data are taken from Refs. [66–80].

	Experiment					Calculation		
Chemical formula	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
CaTiO ₃	Pbnm ^a	5.394	5.423	7.633	5.344	5.463	7.612	
CaZrO ₃	<i>Pbnm</i> ^b	5.591	5.761	8.017	5.555	5.748	7.975	
CaHfO ₃	<i>Pbnm</i> ^c	5.576	5.733	7.987	5.524	5.707	7.916	
CaGeO ₃	Pbnm ^d	5.261	5.269	7.445	5.275	5.337	7.483	
CaSnO ₃	<i>Pbnm</i> ^c	5.532	5.681	7.906	5.512	5.689	7.896	
SrTiO ₃	Pm3m ^e	3.905	_	_	3.908	_	_	
SrZrO ₃	Pbnm ^f	5.785	5.815	8.196	5.766	5.820	8.169	
SrHfO ₃	Pbnm ^g	5.752	5.765	8.134	5.739	5.772	8.117	
SrGeO ₃	Pm3m ^h	3.797	_	_	3.825	_	_	
SrSnO ₃	Pbnm ⁱ	5.708	5.712	8.071	5.721	5.746	8.089	
BaTiO ₃	P4mm ^j	3.999	_	4.018	3.981	_	4.032	
BaZrO ₃	Pm3m ^b	4.191	_	_	4.190	_	_	
BaHfO ₃	Pm3m ^k	4.171	_	_	4.158	_	_	
BaGeO ₃		Not available						
BaSnO ₃	$Pm\bar{3}m^{1}$	4.116	_	_	4.136	_	_	
PbTiO ₃	P4mm ^m	3.904	_	4.144	3.882	_	4.167	
PbZrO ₃	<i>Pbam</i> ⁿ	5.875	11.774	8.207	5.870	11.763	8.167	
PbHfO ₃	<i>Pbam</i> ^o	5.845	11.709	8.195	5.807	11.655	8.127	
PbGeO ₃		Not available						
PbSnO ₃			Ne	ot available				

^aReference [66]; ^bReference [67]; ^cReference [68]; ^dReference [69]; ^eReference [70]; ^fReference [71]; ^gReference [72]; ^hReference [73]; ⁱReference [74]; ^jReference [75]; ^kReference [76]; ^lReference [77]; ^mReference [78]; ⁿReference [79]; ^oReference [80].

and removing half of the atoms on the topmost layer yields nonpolar, stoichiometric surfaces.

For $A(II)B(IV)O_3$ perovskite (001) surfaces which are defined as nonpolar type C, we consider two kinds of stoichiometric surfaces in each of the $p(2 \times 1)$, $p(2 \times 2)$, $c(2 \times 2)$, $c(4 \times 2)$, and $c(4 \times 4)$ supercells, where the topmost layers consist of half-monolayer coverages of atoms, referred to as

half-AO and half- BO_2 surfaces (Fig. 1). We explored energetically favorable surface reconstruction of the topmost layers using an *ab initio* evolutionary structure search. We performed the structure search for (001) surfaces with various lateral periodicity units for SrTiO₃ and BaSnO₃ as representative cubic perovskite oxides. The resultant SrTiO₃ and BaSnO₃ (001) surfaces exhibit the same reconstruction patterns in



FIG. 2. Relative energies of seven polymorphs for 20 perovskite oxides (in eV/f.u.). The energy zero is set to be the total energy of the lowest energy nonpolar polymorph for each perovskite oxide. The results for BaTiO₃, PbTiO₃, PbZrO₃, and PbHfO₃ are enlarged in the inset, where the energies of reported polar and antipolar structures are additionally included.



FIG. 3. Top view of cubic SrTiO₃ (001) surfaces with $p(2 \times 1)$, $p(2 \times 2)$, $c(2 \times 2)$, and $c(4 \times 2)$ reconstructions. The green, blue, and red spheres represent Sr (*A*-site), Ti (*B*-site), and O atoms, respectively. The energy with respect to the lowest energy h- $AO^{c(4\times4)}$ or h- $BO_2^{c(4\times4)}$ surface (see Fig. 4) is indicated below each panel.

their supercells except for $p(2 \times 2)$ reconstruction (Fig. 3 and Fig. S1 in the Supplemental Material [88]). Among the considered supercells, we found the most stable surface reconstruction patterns in the $c(4 \times 4)$ supercells as half-AO and half- BO_2 surface models, which are denoted as h- $AO^{c(4\times4)}$ and $h-BO_2^{c(4\times4)}$, respectively [Fig. 4(a)]. In order to investigate the band positions, we chose these $h-AO^{c(4\times4)}$ and $h-BO_2^{c(4\times4)}$ surfaces as prototypical reconstructed structures with low surface energies. The h- $AO^{c(4\times4)}$ surface shows a stripe pattern with AO terraces, whereas the $h-BO_2^{c(4\times 4)}$ surface has ordered BO_2 islands with a brickwork pattern. In an experimental report for SrTiO₃, STM images for the $c(4 \times 4)$ reconstruction also show brickwork patterns [27]. We also confirmed that surface-structure searches involving both the topmost layers and sublayers give the same results as Fig. 4(a). However, Deacon-Smith et al. have found interlayer cation exchange as a surface-stabilization mechanism for a polar KTaO₃ (001) surface using a global structure optimization method based on the interatomic potentials [89]. We attribute this discrepancy to the cation valence states: the (001) planes of $A(I)B(V)O_3$ perovskites including KTaO₃ are largely charged and therefore prone to be rearranged, in contrast to those of $A(II)B(IV)O_3$, including SrTiO₃.

For more realistic modeling, we consider the tilting and rotation of the BO_6 octahedra. Investigating this effect is important not only for simulating the surfaces of octahedradistorted perovskites such as the *Pbnm* phases, but also for understanding the effects of excessive atomic relaxation to lower the symmetry in computationally metastable phases at 0 K, an example of which includes $Pm\bar{3}m$ -SrTiO₃ [90]. We discuss *Pbnm*-CaTiO₃ and *I4/mcm*-SrTiO₃ as two representatives here. Interestingly, on both the *Pbnm*-CaTiO₃ and *I4/mcm*-SrTiO₃ and *I4/mcm*-SrTiO₃ (001) surfaces, the stripe type of half-AO and the island type with brickwork patterns of half-BO₂ are again obtained as energetically favorable pseudo $c(4 \times 4)$ reconstructed surfaces which have atomic structures of the topmost



FIG. 4. (a) Top and side views of atomic configurations for $h-AO^{c(4\times4)}$ (left panel) and $h-BO_2^{c(4\times4)}$ (right panel) reconstructed (001) surfaces of cubic SrTiO₃. The green, blue, and red spheres represent Sr (*A*-site), Ti (*B*-site), and O atoms, respectively. (b) Surface energies of $h-AO^{c(4\times4)}$ and $h-BO_2^{c(4\times4)}$ for 17 perovskite oxides, which are denoted as orange and green circles, respectively. The cubic and orthorhombic phases listed in Table I are considered with the exceptions of $Pm\bar{3}m$ -BaTiO₃, *Pbnm*-PbTiO₃, *Pbnm*-PbZrO₃, and *Pbnm*-PbHfO₃. The notation for the $c(4 \times 4)$ reconstruction pattern is based on the pseudocubic unit cell for noncubic systems.

layers similar to those of the corresponding cubic models (Figs. S2 and S3 in the Supplemental Material [88]). We therefore expect that the proposed $c(4 \times 4)$ reconstructions are reasonable in many of the considered perovskite oxides, regardless of octahedral tilting and rotation.

Figure 4(b) shows the surface energies of two prototypical reconstructed surfaces based on the bulk structures experimentally reported at RT, except for BaTiO₃, PbTiO₃, PbZrO₃, and PbHfO₃ (see Table II), which were obtained using the PBEsol functional. The surface energy E_{surf} , with surface area *S* is given by

$$E_{\rm surf} = \frac{1}{2S} \left(E_{\rm slab} - 56 E_{ABO_3} \right),\tag{3}$$

where E_{slab} and E_{ABO_3} are the total energies of the slab model and bulk ABO_3 , respectively, and the factors of 2 and 56 indicate the numbers of surfaces and formula units contained in the slab models. In most cases, h- $AO^{c(4\times4)}$ has lower surface energy than h- $BO_2^{c(4\times4)}$, where the exceptions are BaTiO₃, CaGeO₃, and SrGeO₃. In particular, h- $BO_2^{c(4\times4)}$ are clearly more stable than h- $AO^{c(4\times4)}$ in CaGeO₃ and SrGeO₃. These Ge-based perovskite oxides are known to be metastable at ambient pressure [73,81]. The h- $BO_2^{c(4\times4)}$ surfaces with the reduced coordination number of surface Ge atoms appear to be energetically favorable.

C. Surface energy

To discuss the relative stability of the predicted reconstructed stoichiometric surfaces with respect to cleaved nonstoichiometric surfaces, we evaluate thermodynamic grand potentials as a function of chemical potentials in a pseudobinary representation. The surface energy for surface area S can be calculated more generally than the case of Eq. (3) as [91]

$$E_{\text{surf}} = \frac{1}{2S} \left[E_{\text{slab}} - N_{AO}(E_{AO} + \Delta \mu_{AO}) - N_{BO_2} (E_{BO_2} + \Delta \mu_{BO_2}) \right], \tag{4}$$

where N_{AO} and N_{BO_2} are the numbers of AO and BO_2 subunits to form the slab. $\Delta \mu_{AO}$ and $\Delta \mu_{BO_2}$ are the chemical potentials of AO and BO₂ with respect to the total energies of bulk AO and BO₂ (E_{AO} and E_{BO_2}), respectively. The equilibrium condition for the bulk ABO_3 is given by

$$\Delta \mu_{AO} + \Delta \mu_{BO_2} = E_f \left(= E_{ABO_3} - E_{AO} - E_{BO_2} \right), \quad (5)$$

where $E_{\rm f}$ is its formation energy from bulk AO and BO₂. Following Eq. (5), the two chemical potentials are not independent, and we choose to eliminate $\Delta \mu_{AO}$ when presenting out results. Equations (3) and (4) provide the same results when N_{AO} equals N_{BO_2} . Accordingly, $\Delta \mu_{BO_2}$ is allowed to vary over the range

$$E_{\rm f} \leqslant \Delta \mu_{BO_2} \leqslant 0.$$
 (6)

The lower and upper limits correspond to the conditions that the system is in equilibrium with AO and BO₂, respectively; in some AO-BO₂ systems where Ruddlesden-Popper phases A_2BO_4 are stable, the lower limit of $\Delta \mu_{BO_2}$ is determined by A_2BO_4 , instead of AO.

Figure 5 shows the relative surface energies of cleaved nonstoichiometric surfaces (AO- and BO2-terminated surfaces) with atomic relaxation and the reconstructed stoichiometric surfaces for Pbnm-CaTiO₃, Pm3m-SrTiO₃, and $Pm\bar{3}m$ -BaSnO₃, which were obtained using the PBEsol functional. The AO and BO₂-terminated surfaces have a comparable range of thermodynamic stability in CaTiO₃, while the AO-terminated surface is more stable for SrTiO₃ under most chemical potential conditions. The AO-terminated surface is energetically favorable in the whole given chemical potential range for BaSnO₃. The reconstructed surfaces do not change their surface energy against the chemical potential due to the stoichiometric nature $(N_{AO} = N_{BO_2})$. Here, we note that the surface energies of the AO- and BO2-terminated surfaces have crossing points at $\Delta \mu_{\text{TiO}_2} = -0.26$ and -0.15 eV for CaTiO₃ and SrTiO₃, respectively. At these chemical potential values, the reconstructed h- $AO^{c(4 \times 4)}$ surfaces are energetically comparable to the AO- and BO₂-terminated surfaces.

While we considered the $c(4 \times 4)$ supercells in surfacestructure search, the derived primitive cell of $h-AO^{c(4\times4)}$ is $p(2\sqrt{2} \times \sqrt{2})$ [red dashed line in Fig. 4(a)]. On the other hand, that of h-BO₂^{c(4×4)} is $p(2\sqrt{2} \times 2\sqrt{2})$. Here, we can expand the terrace width (N = 1, 2, 3, 4...) of h-AO^{c(4×4)} by using larger $p(N\sqrt{2} \times \sqrt{2})$ supercells. The terrace formation with $p(N\sqrt{2} \times \sqrt{2})$ reconstructions was experimentally observed in $Pm\bar{3}m$ -KTaO₃ by sample cleaving [38]. The (001) surfaces of such $A(I)B(V)O_3$ perovskites have polar instability and therefore need some surface-stabilization mechanism [38,89]. On the other hand, the weakly polar (001) surfaces in $A(II)B(IV)O_3$ perovskites would not have to make strong modifications of the electronic properties such as metallization of the surface [92,93]. On the h- $AO^{c(4\times4)}$ surfaces, the in-plane atomic positions of the topmost layer are quite similar to those of the bulk region, but with reduced bond lengths and rumpling by charge redistribution near the surfaces. While the surface energy of h- $AO^{c(4\times4)}$ for CaTiO₃ is slightly above the crossing point in Fig. 5, we found that the surface energy of $p(N\sqrt{2} \times \sqrt{2})$ with $N \ge 3$ is lower than those of the cleaved nonstoichiometric AO and BO2-terminated surfaces at the crossing point. The proposed stoichiometric surfaces are stable in a limited range of the chemical potential conditions. However, the experimentally reported TiO₂-double layer surfaces for SrTiO₃ are also metastable even under the TiO₂-rich condition (Fig. 5) [30–32]. Under various surface conditions such as annealing temperature, oxygen partial pressure, and initial surface treatments, a large number of reconstruction patterns for $SrTiO_3$ (001) surfaces are reproducible [26–32]. This means that each reconstructed surface maintains their surface structure after cooling down the temperature due to kinetic energy barrier. In a recent experiment, Lei et al. have produced high-quality SrTiO₃ film with no evidence of O vacancies by controlling the stoichiometry for both the cations and oxide ions [94]. By alternately ablating the targets of SrO and TiO₂, a SrTiO₃ film can be grown one atomic layer at a time by combining the strengths of reactive molecularbeam epitaxy and pulsed-laser deposition. Using such growth techniques, the surface stoichiometry can be also controlled. For example, the surface structure becomes stoichiometric when 0.5 monolayer AO (BO_2) is deposited on top of the fully BO₂ (AO)-terminated surfaces.

TABLE II. Calculated and experimental values of band gaps (E_g), ionization potentials (IP), and electron affinities (EA) for 17 $A(II)B(IV)O_3$ perovskites. The cubic and orthorhombic phases listed in Table I are considered with the exceptions of $Pm\bar{3}m$ -BaTiO₃, *Pbnm*-PbTiO₃, *Pbnm*-PbZrO₃, and *Pbnm*-PbHfO₃. The calculated IPs and EAs are shown for h- $AO^{c(4\times4)}$ and h- $BO_2^{c(4\times4)}$ reconstructed (001) surfaces; the notation for the $c(4 \times 4)$ reconstruction pattern is based on the pseudocubic unit cell for the orthorhombic phases. Experimental data are taken from Refs. [5,95–103,105–108]. The experimental IPs and EAs have been estimated from electrochemical measurement for BaTiO₃, PbTiO₃, BaSnO₃ (at pH = 0), and CaTiO₃ (at pH = 5.6) [106–108] and Kelvin prove measurement on SrTiO₃/LaAlO₃ and CaTiO₃/TiO₂ interfaces [5,105]. The asterisked values (*) are estimated by combining reported IPs or EAs and E_g .

	Band gap		h- $AO^{c(4\times4)}$ (calc.)		h- $BO_2^{c(4\times 4)}$ (calc.)		Experiment	
Chemical formula	Calc.	Expt.	IP	EA	IP	EA	IP	EA
CaTiO ₃	3.59	3.58 ^a	6.28	2.69	7.60	4.01	6.44, ¹ 7.48*	2.86*, 3.90 ⁿ
CaZrO ₃	5.69	5.70 ^b	6.55	0.86	7.23	1.54		
CaHfO ₃	6.11	6.40 ^b	6.62	0.51	7.22	1.11		
CaGeO ₃	3.79	_	6.55	2.76	8.34	4.55		
CaSnO ₃	4.11	4.40 ^c	6.81	2.70	7.53	3.42		
SrTiO ₃	3.09	3.25 ^d	5.27	2.18	7.24	4.15	5.75*, 7.45*	$2.50^{\rm m}, 4.20^{\rm m}$
SrZrO ₃	5.39	5.60 ^e	6.02	0.63	6.87	1.48		
SrHfO ₃	5.78	6.07 ^f	6.04	0.26	6.99	1.21		
SrGeO ₃	1.73	_	5.38	3.65	7.65	5.92		
SrSnO ₃	3.45	3.93 ^g	6.16	2.71	7.28	3.83		
BaTiO ₃	2.94	3.20 ^h	4.72	1.78	7.57	4.63	7.74*	4.54 ^h
BaZrO ₃	4.70	5.30 ⁱ	5.28	0.58	6.73	2.03		
BaHfO ₃	5.05	5.54 ^j	5.32	0.27	6.92	1.87		
BaSnO ₃	2.34	3.10 ^k	5.44	3.10	7.21	4.87	7.79*	4.69 ^k
PbTiO ₃	2.31	2.75 ^h	5.65	3.34	7.15	4.84	7.19*	4.44 ^h
PbZrO ₃	3.75	_	5.46	1.71	6.87	3.12		
PbHfO ₃	3.81	_	5.59	1.78	6.85	3.04		

^aReference [95]; ^bReference [96]; ^cReference [97]; ^dReference [98]; ^eReference [99]; ^fReference [100]; ^gReference [101]; ^hReference [108]; ⁱReference [102]; ^jReference [103]; ^kReference [107]; ^hReference [106]; ⁿReference [105]; ^mReference [5].

D. Band alignment at surfaces

As a summary of surface band alignment, Fig. 6 shows the calculated VBM and CBM with respect to the vacuum level (the negatives of the IP and EA, respectively) for experimentally accessible $A(II)B(IV)O_3$ perovskite phases at RT with some exceptions (see Tables I and II). For comparison, we include available experimental band position and band-gap data [5,95–108], as well as the theoretical values for the cleaved nonstoichiometric surfaces, for which the same slab

thickness as the reconstructed models is used. These theoretical and experimental IPs and EAs are enumerated in Tables II and III, along with the band gaps. Stevanović *et al.* reported the theoretical IP values of 4.41 and 6.71 eV for SrO- and TiO₂-terminated SrTiO₃ (001) surfaces, respectively, based on the *GW* approximation with empirical V_d potential acting on the Ti *d* orbitals [39,109]. These IP values are close to our HSE06 results, within only ~0.3 eV differences (see Table III).



FIG. 5. Surface energies as a function of chemical potential $\Delta \mu_{BO_2}$ for reconstructed stoichiometric and fully AO- or BO₂-terminated nonstoichiometric (001) surfaces of *Pbnm*-CaTiO₃, *Pm*3*m*-SrTiO₃, and *Pm*3*m*-BaSnO₃. The vertical dash-double dotted lines denote the lower limits of the chemical potentials determined by Ruddlesden-Popper phases A_2BO_4 . The notation for the $c(4 \times 4)$ reconstruction pattern is based on the pseudocubic unit cell for the orthorhombic CaTiO₃ phase. In the middle panel, the surface energies for the reported $c(6 \times 2)$, $c(4 \times 2)$, and $p(2 \times 1)$ reconstruction patterns with TiO₂ double layers are included [30–32].



FIG. 6. Band alignment based on the positions of the VBM and CBM relative to the vacuum level (the negatives of the IPs and EAs) for 17 perovskite oxides. The values for h- $AO^{c(4\times4)}$ and h- $BO_2^{c(4\times4)}$ reconstructed stoichiometric (001) surfaces (closed color bar) and nonstoichiometric (001) surfaces with full AO and BO₂ terminations (open bar) are shown for each phase and enumerated in Tables II and III, respectively. The cubic and orthorhombic phases listed in Table I are considered with the exceptions of $Pm\bar{3}m$ -BaTiO₃, *Pbnm*-PbTiO₃, *Pbnm*-PbZrO₃, and *Pbnm*-PbHfO₃. The notation for the $c(4 \times 4)$ reconstruction pattern is based on the pseudocubic unit cell for the orthorhombic phases. The red solid and dashed lines represent accessible experimental IP and EA values, respectively, which are also provided in Table II.

The band edges of reconstructed surfaces are related to those of AO- and BO_2 -terminated surfaces. In most cases of the h- $AO^{c(4\times4)}$ surfaces, the VBM positions are close to the average values of two cleaved surfaces. This behavior is understandable in view of the coexistence of AO and BO_2 ter-

TABLE III. Ionization potentials (IPs) and electron affinities (EAs) calculated for fully AO- and BO_2 -terminated nonstoichiometric (001) surfaces of 17 $A(II)B(IV)O_3$ perovskites. The cubic and orthorhombic phases listed in Table I are considered with the exceptions of $Pm\bar{3}m$ -BaTiO₃, *Pbnm*-PbTiO₃, *Pbnm*-PbZrO₃, and *Pbnm*-PbHfO₃.

	AO-te	erminated	BO ₂ -terminated	
Chemical formula	IP	EA	IP	EA
CaTiO ₃	5.24	1.64	7.71	4.13
CaZrO ₃	5.84	0.15	7.08	1.39
CaHfO ₃	5.77	-0.34	7.14	1.03
CaGeO ₃	5.41	1.62	8.09	4.31
CaSnO ₃	6.13	2.02	7.44	3.33
SrTiO ₃	4.72	1.63	7.04	3.95
SrZrO ₃	5.16	-0.24	6.71	1.31
SrHfO ₃	5.19	-0.60	6.83	1.03
SrGeO ₃	4.61	2.89	7.50	5.78
SrSnO ₃	5.34	1.88	7.01	3.56
BaTiO ₃	3.77	0.82	7.80	4.85
BaZrO ₃	4.80	0.10	6.35	1.65
BaHfO ₃	4.88	-0.17	6.58	1.54
BaSnO ₃	4.97	2.63	6.53	4.19
PbTiO ₃	5.19	2.88	6.25	3.94
PbZrO ₃	5.31	1.56	5.75	2.00
PbHfO ₃	5.51	1.70	5.80	1.99

mination in their topmost and subsurface layers, respectively. On the other hand, the VBM positions of $h-BO_2^{c(4\times4)}$ surfaces are similar to those of the BO_2 -terminated surfaces or even lower than them. This is mainly due to the geometric effect at the surface. The oxygen ions at the $h-BO_2^{c(4\times4)}$ surfaces are closer to the vacuum at the topmost layers than that of the BO_2 -terminated surface (on average, 0.2 Å further from the center), which leads to the negative potential drop through the surface layers. Thus $h-AO^{c(4\times4)}$ and $h-BO_2^{c(4\times4)}$ slabs show largely different band positions, even though both of them have the same stoichiometry as the corresponding bulk. The surface terminations and structures were not reported in Refs. [104–108] on photoemission and electrochemical measurements for experimental band positions. However, interestingly, the proposed surface reconstruction gives band positions closer to the experimental results than the cleaved nonstoichiometric surfaces, as detailed below.

The experimental IPs and EAs reported for Pbnm-CaTiO₃ and Pm3m-SrTiO₃ show a large spread, depending on the experimental conditions [5,104–107]. The preferred termination is determined by the annealing and chemical treatment conditions: for SrTiO₃ surfaces, annealing in ambient condition or oxygen overpressures yields Sr-rich surfaces, while annealing at moderate temperatures in reducing atmospheres results in Ti-rich surfaces [34,110]. As shown in Fig. 6 and Table II, each of the experimental values is close to the theoretical value for $h-BO_2^{c(4\times 4)}$ or $h-AO^{c(4\times 4)}$. The difference between the experimental and theoretical IP values is 0.5 eV at h-SrO^{$c(4\times4)$}. The measured IP of 7.4 eV for SrTiO₃ by photoemission experiments is also in good agreement with calculated IP for the h-TiO₂^{$c(4\times4)$} surface [104]. Similarly, measured work-function values strongly depend on the surface termination for perovskite oxides. For example, in a $SrTiO_3$ (001) surface, the work function of a TiO2-terminated surface is 4.2 eV while that of a SrO-terminated surface is 2.5 eV by in situ Kelvin probe measurement [5]. Given that $SrTiO_3$ is intrinsically or extrinsically doped into *n*-type readily, the work function would be close to the EA. Intriguingly, these reported work-function values of SrO- and TiO2-terminated surfaces are well matched with our EA values of h-SrO^{$c(4\times4)$} and h-TiO₂^{$c(4\times4)$}, respectively. Furthermore, the band positions of CaTiO₃ are estimated by both a Kelvin prove technique for a CaTiO₃/TiO₂ interface and an electrochemical measurement, which are in good agreement with the calculated results for h-CaO^{c(4×4)} and h-TiO₂^{c(4×4)}, respectively [105,106]. For BaSnO₃, the h-BaO^{$c(4\times4)$} surface is calculated to be more stable than the h-SnO₂^{c(4×4)} surface [see Fig. 4(b)]. However, the CBM position is well reproduced by the calculation for the h-SnO₂^{c(4 \times 4)} surface. Even in the same chemical composition, we cannot find the correlation between surface energies and the band positions (see Fig. S4 in the Supplemental Material [88]). Meanwhile, the VBM position of BaSnO₃ has a difference of about 0.6 eV from an experimental value [107]. This discrepancy is partly attributed to the band-gap difference of 0.66 eV between the experiment and HSE06 calculation (Table II). For BaTiO₃ and PbTiO₃, although we consider the cubic $Pm\bar{3}m$ and orthorhombic *Pbnm* structures, respectively, the calculated band positions for the h- $BO_2^{c(4\times4)}$ surfaces are in reasonable agreement with the measured values [108].

E. Trends in the band alignment

In this section, we discuss the chemical tendency of the surface band positions. To focus on the effects of chemical composition, we have performed systematic slab calculations for the reconstructed surfaces of $Pm\bar{3}m-ABO_3$ without octahedral tilting and rotation. In Fig. 7, we classify the family of $A(II)B(IV)O_3$ perovskites into those with B = Ti, Zr, Hf, Ge, and Sn and show correlations with the Goldschmidt tolerance factor [111], $t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$, a geometric descriptor that is frequently used to discuss the stability of ABX_3 perovskites, where r_A , r_B , and r_X are Shannon's ionic radii of the A-, B-, and X-site ions, respectively.

For the h- $AO^{c(4\times4)}$ surfaces, the VBM positions relative to the vacuum level (the negatives of the IPs) move upward as the size of the A-site ions increases in the order Ca, Sr, and Ba [Fig. 7(a)]. Thus, the VBM positions have a positive correlation with the tolerance factor. On the other hand, the VBM positions of the $h-BO_2^{c(4\times4)}$ surfaces show a negative correlation with the tolerance factor [Fig. 7(b)]. These opposite trends are also found for reconstructed $p(2 \times 1)$, $p(2 \times 1)$ 2), $c(2 \times 2)$, and $c(4 \times 2)$ surfaces, within the averaged VBM (or IP) differences at each material of about 0.78 eV when using PBEsol (see Fig. S5 in the Supplemental Material [88]). The A = Pb systems show lower VBM (larger IP) values than an expected trend. On one hand, the hybridization of lone-pair states of Pb^{2+} ions with O-2*p* states are expected to increase the VBM compared with other systems where the VBM is more largely dominated by O-2p states [45]. On the other, the lone-pair states at the surface would enhance the surface dipole to lower the VBM. The latter contribution seems to excel in the A = Pb systems.

In contrast to the VBM positions or IPs, the CBM positions or EAs have a less correlation with the tolerance factor at



FIG. 7. Positions of the VBM (upper panel) and CBM (below panel) relative to the vacuum level (the negatives of the IPs and EAs, respectively) as a function of the Goldschmidt tolerance factor for (a) $h-AO^{c(4\times4)}$ and (b) $h-BO_2^{c(4\times4)}$ reconstructed (001) surfaces of 20 cubic perovskite oxides. The dashed lines are linear fits to all the points. Root-mean-square errors (RMSEs) for the VBM vs the vacuum level are 0.37 and 0.29 eV for fitted lines in (a) and (b), respectively.

first sight. This presumably originates from the fact that the conduction-band orbital characteristics are formed mainly by various *d* or *s* states of the *B*-site ions, while the valence bands are mainly composed of the common O 2p states except for the A = Pb systems. For instance, in the case of Sr-based transition metal perovskite oxides, Sr BO_3 (B = Ti, Zr, Hf), their CBM positions are mainly derived from the Ti 3*d*, Zr 4*d*, and Hf 5*d* states, respectively, and increase in this order. We can also expect this tendency from the band-gap values of Sr BO_3 , which increase as the *B*-site ion goes down in the periodic table (see Table II). A similar trend is found for the CBM positions and band gaps of Ca BO_3 and Ba BO_3 with B = Ti, Zr, Hf. Within the same *B*-site cation family, the correlation of the EAs with the tolerance factor is actually similar to that for the IPs: positive and negative correlations for the h- $AO_2^{c(4\times4)}$ and h- $BO_2^{c(4\times4)}$ surfaces, respectively.

To explore the origin of the opposite tolerance-factor dependencies at the h- $AO^{c(4\times4)}$ and h- $BO_2^{c(4\times4)}$ surfaces, we estimated the surface rumpling, which leads to the creation of a dipole moment near the surface. Figure 8(a) shows the amount of surface rumpling on the topmost and subsurface layer, s_{top} and s_{sub} , respectively, as a function of the tolerance factor. Here, the *z* positions of ions are approximated as averaged values of relevant ionic species located on the same layers [Fig. 8(b)]. Although the trend of s_{sub} is opposite to that of s_{top} [compare the solid and broken lines in Fig. 8(a)], the absolute value for s_{sub} is about ten times smaller than s_{top} . It is noteworthy that the magnitude of s_{top} is affected by not only the cation size of the topmost layer (r_{top}) but also that of the subsurface layer (r_{sub}). A larger s_{top} is induced by smaller r_{top}



FIG. 8. (a) Surface rumpling on the topmost and subsurface layers for $h-AO^{c(4\times4)}$ and $h-BO_2^{c(4\times4)}$ reconstructed (001) surfaces of 20 cubic perovskite oxides as a function of the Goldschmidt tolerance factor. The solid and dashed lines are linear fits to the points of s_{top} and s_{sub} , respectively. RMSEs are 0.07 (0.01) and 0.07 (0.02) Å for fitted black and red solid (dashed) lines, respectively. The surface rumpling (s_{top} and s_{sub}) is defined in (b) using a schematic side view of $h-AO^{c(4\times4)}$. A larger positive value of the surface rumpling indicates that the O ions are closer to vacuum than the cations on the topmost and subsurface layers. (c) The VBM relative to the vacuum level vs the total surface rumpling on the topmost and subsurface layers ($s_{top} + s_{sub}$).

and larger r_{sub} values (see Fig. S6 in the Supplemental Material [88]), and therefore by small (large) tolerance factors for h- $AO^{c(4\times4)}$ (h- $BO_2^{c(4\times4)}$). Thus, the rumpling at the h- $AO^{c(4\times4)}$ and h- $BO_2^{c(4\times4)}$ surfaces shows the opposite dependencies on the tolerance factor, leading to the opposite band-position trends in Fig. 7. As we mentioned above, the band positions of Pb BO_3 systems consistently exhibit larger deviations than the other systems due to the lone-pair states of the Pb²⁺ ions. However, since they still follow the correlation of the VBM with the tolerance factor, we expect that the surface dipole induced by surface rumpling dominates the band positions even for the A = Pb systems.

Figure 8(c) shows the tendency of the VBM positions (the negatives of the IPs) as a function of surface rumpling. A larger positive value of the surface rumpling indicates that the O ions are closer to vacuum than the cations on the topmost and subsurface layers. Based on the simple charged parallel plates model, the surface dipole with outward direction can be generated by positive surface rumpling [23,45]. Notice that the surface rumpling values for the $h-BO_2^{c(4\times 4)}$ surfaces are indeed distributed on a relatively right side compared with those for the h-AO^{c(4×4)}, and the VBM positions of h-BO^{c(4×4)}₂ are mostly lower than those of h-AO^{$c(4\times4)$} in Fig. 8(c). We performed a surface charge redistribution analysis for the $c(4 \times 4)$ reconstructed SrTiO₃ and BaTiO₃ surfaces (see Fig. S7 in the Supplemental Material [88]). On the h-BO₂^{c(4×4)} surface, charge transfer from the subsurface to the topmost layer is larger than on the h- $AO^{c(4\times4)}$ layer. It is probable that more negative potential drops across the topmost layer of the h- $BO_2^{c(4\times4)}$ surfaces result from greater charge transfer. For each perovskite oxide, the VBM (IP) differences between the h-AO^{c(4×4)} and h-BO^{c(4×4)} surfaces decrease as the radii of the A- and B-site ions are similar, varying from 2.84 eV for BaGeO₃ (t = 1.10) to 0.07 eV for CaZrO₃ (t = 0.91) (see Fig. 7), because the discrepancy of the surface dipole is reduced between the two reconstructed surfaces. It has been reported for divalent metal oxides that, although the effects of surface relaxation and orientation on the VBM positions (or IPs) amount to \sim 1.7 eV, their nonpolar stoichiometric surfaces show almost linear trends between the VBM positions and the cube root of volume per atom, which well follows the tendency in the Madelung potential on the O site [45,46]. In addition, surface rumpling acts to enhance this dependency of the VBM [45,46]. Meanwhile, we did not find such a tendency for the reconstructed surfaces of perovskite oxides considered here. Furthermore, Jacobs et al. [19] reported that the work function of perovskite oxides can be described by the position of the O-2p band center and the O-bond ionicity based on the Bader charge [112–115]. However, whereas these possible descriptors strongly depend on the oxidation state of the B-site cation [19], there is no clear physical trend with them in the band positions of $A(II)B(IV)O_3$ perovskites (see Fig. S8 in the Supplemental Material [88]). The rumpling-induced surface dipole appears to dominate, and the tolerance factor is a better descriptor for the surface dipole and therefore the band positions.

IV. CONCLUSIONS

We have systematically investigated the band positions at reconstructed stoichiometric and cleaved nonstoichiometric (001) surfaces of 20 $A(II)B(IV)O_3$ perovskites using first-

principles calculations in combination with an evolutionary structure search. Two types of $c(4 \times 4)$ reconstructed surfaces are selected as prototypical configurations in which the topmost layer consists of a half subunit, half-AO or half-BO₂. These reconstructed stoichiometric surfaces are energetically comparable to the cleaved nonstoichiometric surfaces in a specific chemical potential range for CaTiO₃ and SrTiO₃. Even though these two types of reconstructed surfaces have an identical crystallographic orientation and similar energies, the band positions are quite different from each other. In particular, the experimentally reported termination dependence of SrTiO₃ surface band positions is well reproduced by the calculated values for the reconstructed surfaces. As a compositional trend of perovskite oxides, we found that the IPs have an approximately linear trend against the Goldschmidt tolerance factor overall, while the EAs follow the same trend within the common B-site-cation systems. The smaller and larger cation size on the topmost and subsurface layers, respectively, induces larger surface rumpling, which generates larger surface dipole. Consequently, the band positions of the half-AO and half-BO₂ reconstructed surfaces exhibit the opposite

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trend against the tolerance factor. These results allow a better understanding of the band alignment of perovskite oxides with the effects of surface termination and reconstruction.

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