Ab initio Calculations of $YAlO_3$ and ABO_3 Perovskite (001), (011) and (111) Surfaces, Interfaces and Defects

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Abstract—**We performed first-principles calculations for technologically most important ABO_3 perovskites, such as, $CaTiO_3$, $SrTiO_3$, $PbTiO_3$, $BaTiO_3$, $SrZrO_3$ and $PbZrO_3$ (001), (011) and (111) surfaces, interfaces and bulk *F*-centers. For ABO_3 perovskite neutral (001) surfaces, in most cases, all upper surface layer atoms relax inward, whereas the all second surface layer atoms relax outward, and again, all third surface layer atoms relax inward. The relaxation pattern for $YAlO_3$ charged (001) surfaces is quite different from ABO_3 perovskite neutral (001) surfaces. The ABO_3 perovskite (001) surface energies are almost equal for both AO and BO_2-terminations, and always considerably smaller than the (011) and especially (111) surface energies. Systematic trends in $BaTiO_3$, $SrTiO_3$, $SrZrO_3$ and $PbZrO_3$ bulk *F*-center calculations are analyzed.**

Index Terms—**$YAlO_3$; ABO_3 perovskites; B3LYP; B3PW; surfaces**

I. INTRODUCTION

Surface and interface phenomena, taking place in the ABO_3 perovskites as well as their nanostructures, the complex nature of their surface and interface states, the novel mechanisms of surface electronic processes are the key topics in nowadays solid state physics [1-7]. $CaTiO_3$ (CTO), $SrTiO_3$ (STO), $PbTiO_3$ (PTO), $BaTiO_3$ (BTO), $SrZrO_3$ (SZO) and $PbZrO_3$ (PZO) materials are so-called ABO_3 perovskites, and they have a large amount of technologically important applications, such as, for example, capacitors, actuators, and charge storage devices, and many others [8], for which the surface quality and structure are essential. This is the main reason, why in the last twenty-five years ABO_3 perovskite (001) surfaces were worldwide intensively explored both experimentally and theoretically [9-21]. At the *ab initio* level, it is much more difficult to calculate the ABO_3 perovskite very complex, charged and polar (011) [11-13, 21-26] and (111) surfaces [27-31], than the neutral (001) surfaces [9-21].

Logical next step, after the ABO_3 perovskite (001), (011) and (111) surface theoretical investigations, is to calculate interfaces between the two ABO_3 perovskites. The further development of ABO_3 perovskite (001) interfaces is a highly promising research direction due to potential nanoscale device applications. Taking into account the enormous technological potential of ABO_3 perovskites as well as numerous first principles calculations of their (001) surfaces [11-21], it is difficult to understand why only a small amount of experimental and *ab initio* studies exist dealing with $BaTiO_3/SrTiO_3$, $SrZrO_3/PbZrO_3$ and $PbTiO_3/SrTiO_3$ (001) interfaces [32-36].

It is worth to notice, that all properties of the industrially important ABO_3 perovskites are affected by the defects, for example, by oxygen vacancies. Oxygen vacancy (V_0) (so-called neutral *F*-center) in ABO_3 perovskites traps two electrons. Experimental and theoretical investigations of *F*-centres in complex ABO_3 matrixes are a very important topic, since the *F*-center is the best known classical point defect, which strongly affects all material properties [37-44].

II. COMPUTATIONAL METHOD

We performed our *ab initio* calculations for ABO_3 perovskite and $YAlO_3$ (YAO) surfaces using the hybrid exchange-correlation functionals B3PW [45] or B3LYP [46] as well as the world well known CRYSTAL computer code [47]. The strong side of the CRYSTAL computer code is possibility to perform *ab initio* calculations for isolated two-dimensional slabs perpendicular to the ABO_3 perovskite surface, without any artificial periodicity in the z direction.

For example, for calculations of ABO_3 perovskite and $YAlO_3$ (001) surfaces, we used symmetrical slabs consisting of nine alternating neutral AO and BO_2 (in case of ABO_3 perovskites), or charged YO and AlO_2 (in case of $YAlO_3$) layers. In case of ABO_3 perovskites, our first slab was terminated by AO planes from both slab sides and consisted of a supercell which contained 22 atoms. The second slab, in case of ABO_3 perovskites, was terminated from both sides by BO_2-planes and consisted from a supercell containing 23 atoms. Both AO and BO_2-terminated slabs were non-stoichiometric, with their unit cell equations $A_5B_4O_{13}$ and $A_4B_5O_{14}$. Since supercell in our calculations should be neutral, we used a basis sets for neutral Y, Al and O atoms [47] in our $YAlO_3$ (001) surface calculations. Calculation details for ABO_3 perovskite polar (011) and (111) surfaces are described by us in references [11-13, 21-31].

We have used the same model for modelling of $BaTiO_3/SrTiO_3$, $SrZrO_3/PbZrO_3$ and $PbTiO_3/SrTiO_3$ (001) interfaces [34-36]. For example, calculations of the $BaTiO_3/SrTiO_3$ (001) interfaces were carried out using the symmetrically terminated slab model. The $SrTiO_3$ substrate contained 11 atomic monolayers and was terminated by the TiO_2 monolayer from both substrate sides. Next, monolayer by monolayer epitaxial growth was modelled by adding a pair of $BaTiO_3$ (001) monolayers symmetrically to both sides of a $SrTiO_3$ substrate slab [34-36]. Finally, the ABO_3 perovskite, or for example, the $BaTiO_3$ bulk *F*-center calculations were carried out using 3 x 3 x 3 times extended supercell model. Such a supercell in our calculations contains 134 atoms as well as one isolated *F*-center defect [38,40,43].

III. First-Principles calculations of surfaces

As a first step of our calculations, we calculated the ABO_3 perovskite and YAO bulk lattice constants [2]. Using the B3PW hybrid exchange-correlation functional, we calculated the STO (3.904Å), BTO (4.008Å), PTO (3.936Å), and CTO (3.851Å) as well as using the hybrid B3LYP exchange-correlation functional the SZO (4.195Å), PZO (4.220Å), and YAO (3.712Å) cubic bulk lattice constants. We used calculated cubic bulk lattice constants in all our future calculations.

TABLE I. Our calculated relaxation of atoms (in percent of bulk lattice constant) for CTO, BTO, SZO, PZO perovskites as well as YAO.

Crystal		CTO	BTO	SZO	PZO	YAO
(001)-termin.		CaO	BaO	SrO	PbO	YO
Layer	Ion	B3PW	B3PW	B3LYP	B3LYP	B3LYP
1	A	-8.31	-1.99	-7.63	-5.69	-9.16
	O	-0.42	-0.63	-0.86	-2.37	1.89
2	B	1.12	1.74	0.86	0.57	-0.32
	O	0.01	1.40	-0.05	0.09	-0.20
3	A	-	-	-1.53	-0.47	-3.34
	O	-	-	-0.45	-0.47	-0.03
(001)-termin.		TiO_2	TiO_2	ZrO_2	ZrO_2	AlO_2
1	B	-1.71	-3.08	-1.38	-2.37	-0.23
	O	-0.10	-0.35	-2.10	-1.99	-0.55
2	A	2.75	2.51	2.81	4.36	0.48
	O	1.05	0.38	0.91	1.04	0.10
3	B	-	-	-0.04	-0.47	0.00
	O	-	-	-0.05	-0.28	-0.01

As a next step of our calculations, we performed upper three layer atom relaxation for neutral AO and BO_2-terminated ABO_3 perovskite (001) surfaces as well as charged YO and AlO_2-terminated $YAlO_3$ (001) surfaces (Table I). In the case of ABO_3 perovskites, all upper layer atoms for both terminations relax inwards, all second layer atoms, with the single exception of second layer O atom for SrO-terminated SZO (001) surface, outwards, and all third layer atoms for both terminations, again, relax inwards [2]. The relaxation pattern for charged YO and AlO_2-terminated $YAlO_3$ (001) surfaces is quite different from neutral ABO_3 perovskite (001) surface relaxation pattern.

TABLE II. Our calculated surface energies (in eV per surface cell).

Crystal	CTO	BTO	SZO	PZO
Termination	Surface energies for (001) surfaces			
AO	0.94	1.19	1.13	1.00
BO_2	1.13	1.07	1.24	0.93
	Surface energies for (011) surfaces			
BO	3.13	2.04	3.61	1.89
A	1.91	3.24	2.21	1.74
O	1.86	1.72	2.23	1.85
	Surface energies for (111) surfaces			
AO_3	5.86	8.40	9.45	8.21
B	4.18	7.28	7.98	6.93

As we can see from Table II, our calculated ABO_3 perovskite neutral (001) surface energies for both AO and BO_2-terminations are almost equal, whereas polar (011) and (111) surface energies for different surface terminations are quite different. It is worth to notice, that the polar (111) surface energies, independently from termination, always are considerably larger than the polar (011) surface energies, but polar (011) surface energies are always larger than the (001) surface energies.

IV. First-Principles calculations of interfaces

We performed *ab initio* studies dealing with $BaTiO_3/SrTiO_3$, $SrZrO_3/PbZrO_3$ and $PbTiO_3/SrTiO_3$ (001) interfaces [34-36]. As example we will analyze $BaTiO_3/SrTiO_3$ (001) interface. We used as a substrate 11 layer thick symmetrical $SrTiO_3$ (001) slab from both sides terminated with TiO_2 (001) surfaces and augmented to both sides of this substrate BaO-terminated $BaTiO_3$ slab. The band gap of this our 13-layers containing system is equal to 3.47 eV. If we add to the $SrTiO_3$ (001) substrate from both sides 3, 5, 7 or 9 BaO-terminated layers, the band gap of our system is equal to 3.29, 3.25, 3.24 and 3.22 eV. So, the $BaTiO_3/SrTiO_3$ interface band gap rather slowly decrease with the number of layers from 3.47 eV (1 augmented BaO-terminated layer from both sides) till 3.22 eV (9 augmented BaO-terminated $BaTiO_3$ layers augmented from both sides on $SrTiO_3$ substrate). If we augment on $SrTiO_3$ (001) slab from both sides 2, 4, 6, 8 or 10 TiO_2-terminated $BaTiO_3$ (001) layers, the interface band gap is equal to 2.33, 2.16, 2.10, 2.06 and 2.06 eV.

V. FIRST-PRINCIPLES CALCULATIONS OF DEFECTS

Our B3PW calculated nearest atom displacements surrounding the *F*-center in ABO_3 perovskites are collected in Table III and compared with related results obtained for other ABO_3 perovskites [38-41, 43].

TABLE III. CALCULATED BULK *F*-CENTER MAIN CHARACTERISTICS.

Bulk *F*-center	BTO	STO	SZO	PZO
F-center charge, e	-1.103	-1.1	-1.25	-0.68
F under CB, eV	0.23	0.69	1.12	1.72
Form. energy, eV	10.3	7.1	7.55	7.25
B relax., % of a_0	1.06	7.76	3.68	0.48
O relax., % of a_0	-0.71	-7.79	-2.63	-
A relax., % of a_0	-0.08	3.94	0.46	-5.99

As we can see from Table III, the two nearest to the *F*-center Ti atoms are by 1.06% of a_0 repulsed in the $BaTiO_3$ from the oxygen vacancy. Also in another ABO_3 perovskites, such as $SrTiO_3$, $SrZrO_3$ and $PbZrO_3$, B atoms are repulsed from the oxygen vacancy by 7.76, 3.68 and 0.48 % of a_0. In contrast, the second nearest O atoms in the ABO_3 perovskites always are attracted towards the *F*-center by 0.71, 7.79 and 2.63 % of a_0 in the $BaTiO_3$, $SrTiO_3$ and $SrZrO_3$.

Inside the oxygen vacancy in $BaTiO_3$, $SrTiO_3$, $SrZrO_3$ and $PbZrO_3$ are located -1.103*e*, -1.1*e*, -1.25*e* and -0.68*e* of additional charge. The *F*-center formation energy for ABO_3 perovskites are in the range between 7 and 10 eV. For example, the calculated $BaTiO_3$, $SrTiO_3$, $SrZrO_3$ and $PbZrO_3$ formation energies are equal to 10.3, 7.1, 7.55 and 7.25 eV. The *F*-center defect induced levels in the band gap of ABO_3 perovskites are located more close to the conduction band bottom, than the valence band top. For example, the *F*-center defect induced levels are located 0.23, 0.69, 1.12 and 1.72 eV below the conduction band bottom in the $BaTiO_3$, $SrTiO_3$, $SrZrO_3$ and $PbZrO_3$ perovskites.

CONCLUSIONS

ABO_3 perovskite neutral (001) surface upper layer atoms, with a few exceptions, relax inwards, second layer atoms upwards, and third layer atoms, again, inwards. Relaxation pattern for $YAlO_3$ charged (001) surfaces is quite different from ABO_3 perovskite neutral (001) surfaces. The ABO_3 perovskite (001) surface energies for both possible terminations AO and BO_2 are almost similar. The ABO_3 perovskite polar (111) surface energies are considerably larger than the polar (011) surface energies. The neutral ABO_3 perovskite (001) surface energies always are smaller than the polar (011) and especially (111) surface energies. The $BaTiO_3/SrTiO_3$, $SrZrO_3/PbZrO_3$ and $PbTiO_3/SrTiO_3$ (001) interface band gap depends much more strongly from the termination of the upper augmented layer (AO or BO_2) than from the number of augmented layers. Results of our calculations for the classical point defect *F*-center in ABO_3 perovskites are presented, and systematic trends, common for *F*-center defects in ABO_3 perovskites are analyzed.

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