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Ab initio hybrid DFT calculations of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces

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ABSTRACT

The results of *ab initio* calculations for polar BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces using the CRYSTAL code are presented. By means of the hybrid B3LYP approach, the surface relaxation has been calculated for two possible B (B = Ti or Zr) or AO₃ (A = Ba, Pb or Sr) BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface terminations. According to performed B3LYP calculations, all atoms of the first surface layer, for both terminations, relax inwards. The only exception is a small outward relaxation of the PbO₃-terminated PbTiO₃ (111) surface upper layer Pb atom. B3LYP calculated surface energies for BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces are considerably larger than the surface energies for Ti (Zr)-terminated (111) surfaces. Performed B3LYP calculations indicate a considerable increase of Ti–O (Zr–O) chemical bond covalency near the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface relative to the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ bulk. Calculated band gaps at the Γ -point near the PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces are reduced, but near BaTiO₃ (111) surfaces increased, with respect to the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ bulk band gap at the Γ -point values.

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1. Introduction

ABO₃ perovskite thin films are important in numerous material research and high technology applications, such as, for example, fuel and hydrogen sensors, non-volatile random access memory devices, as well as microelectronics industry [1,2]. Complementary, the polar BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces are also of fundamental interest. For example, in (001) oriented ABO₃ perovskite films, atoms are stacked simply by neutral BO₂ and AO planes. Just opposite, in polar (111) oriented ABO₃ perovskite thin films, atoms are situated by charged B and AO₃ planes, with drastically different physical and chemical interactions [3].

Motivated by rapidly growing number of high technology applications, a large number of theoretical *ab initio* simulations have been performed for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (001) and (011) surfaces [4–24]. It is surprising, that despite the high technological potential, only some small number of contributions were reported up to now dealing with BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surface *ab initio* calculations [25–28].

From the experimental point of view, antiferroelectric PbZrO₃ thin films were grown on Pt/Ti/SiO₂/Si substrates applying predominant (111) orientation with a sol–gel process. The Pt/PbZrO₃/Pt

film capacitor exhibited well-saturated hysteresis loops at an applied voltage of 5 V [29]. Sa et al. [30] produced Pr-doped PbZrO₃ antiferroelectric thin films on Pt/Ti/SiO₂/Si substrates by a chemical solution deposition method. The PbZrO₃ thin films with different Pr doping contents crystallized in perovskite phase with strong (111) preferred orientation. Alkoy et al. [31] produced PbZrO₃ thin films on Pt(111)/Ti/SiO₂/Si substrates by sol–gel spin coating. Increasing molarity and thickness led to crystallization and grain growth in the films. Double polarization vs electric field hysteresis loops were obtained due to fully [111] pseudo-cubic orientation. Sa et al. [32] proposed a method to improve charge and energy storage performance of PbZrO₃ thin films by α -Fe₂O₃ nanoparticles doping. The PbZrO₃ thin films were deposited on Pt(111)/Ti/SiO₂/Si substrates. Sa et al. [33] reported the W-doping induced antiferroelectric to ferroelectric phase transition in PbZrO₃ thin films prepared on Pt/Ti/SiO₂/Si substrates. With increasing W-doping content, the orientation of the thin films changed from preferred (111)_{Cubic} to complete (100)_{Cubic}, due to W-doping induced lattice distortion.

Taking into account the high technological potential of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ surfaces, in this study predictive first-principles calculations of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surface structures were performed. The paper is organized as follows. In Section 2 computational details are presented. The results of simulations for surface structures, charge distributions, energies, and bond populations are reported in Section 3.

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Finally, the results are analyzed and conclusions are presented in Section 4.

2. Computational details

First-principles DFT-B3LYP simulations for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surfaces were performed using the CRYSTAL computer code [34]. The main advantage of the CRYSTAL code, important for the study of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces, is implementation of the isolated 2D slab model. In order to use in calculations the linear combination of atomic orbitals (LCAO)-GTF method, it is desirable to have optimized basis sets (BS). The development of new BSs for SrTiO₃, BaTiO₃ and PbTiO₃ crystals were performed by Piskunov et al. [35]. In presented calculations, this new BS for O atoms, which differs from the early performed calculations [36,37] by inclusion of polarizable *d*-orbitals on O ions, was used. For the Zr atom, in SrZrO₃ and PbZrO₃ perovskites, the same BS as in Refs. [11,26,38] was used. With aim to perform (111) surface calculations for neutral supercells, 2 electrons have been added to Ba²⁺, Pb²⁺ and Sr²⁺ ions, 4 electrons to Ba⁴⁺ and Zr⁴⁺ ion, and 2 electrons were removed from the O²⁻ ion. Subsequently, all BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surface calculations were performed using neutral slabs containing 9 layers and 21 or 24 atoms for B and AO₃-terminations, respectively. Numerical calculations were performed using the hybrid exchange-correlation B3LYP functional including a hybrid of nonlocal Fock exact exchange, LDA exchange and Becke's gradient corrected exchange functional [39], in combination with the nonlocal gradient corrected correlation potential by Lee–Yang–Parr [40]. The reciprocal space integration was performed by sampling the Brillouin zone using the 5 × 5 × 1 extended Pack-Monkhorst net [41].

All SrZrO₃, PbZrO₃, BaTiO₃ and PbTiO₃ (111) surfaces have the same symmetry group, and were modeled with two-dimensional slabs, containing nine planes perpendicular to the [111] crystal direction. In order to calculate, for example, polar SrZrO₃ (111) surfaces, symmetrical slabs consisting of nine alternating Zr and SrO₃ layers were used (see Fig. 1). One of these slabs is terminated by Zr planes (so called Zr-terminated SrZrO₃ (111) surface) and consists of a supercell containing 21 atoms (Zr–SrO₃–Zr–SrO₃–Zr–SrO₃–Zr–SrO₃–Zr) (see Fig. 2a). The second slab is terminated by SrO₃ planes (so called SrO₃-terminated SrZrO₃ (111) surface) and consists of a supercell containing 24 atoms (SrO₃–Zr–SrO₃–Zr–SrO₃–Zr–SrO₃–Zr–SrO₃) (see Fig. 2b). These slabs are non-stoichiometric, and they have unit cell formulas Sr₄Zr₅O₁₂ and Sr₅Zr₄O₁₅, respectively. As it is known from previous computational studies dealing with polar SrTiO₃, BaTiO₃, CaTiO₃, BaZrO₃ and SrZrO₃ (111) surfaces [25,42–47], a huge

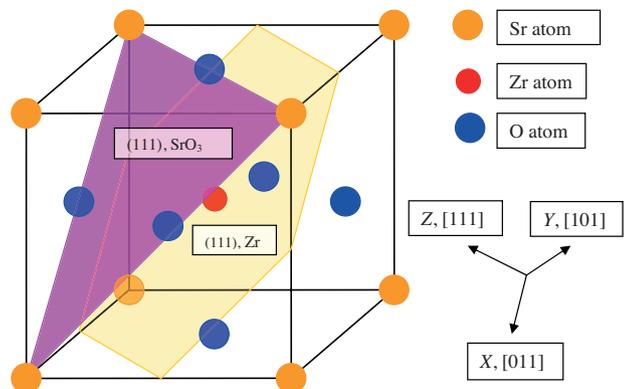


Fig. 1. Sketch of the cubic SrZrO₃ perovskite structure showing two possible (111) surface terminations: SrO₃ and Zr.

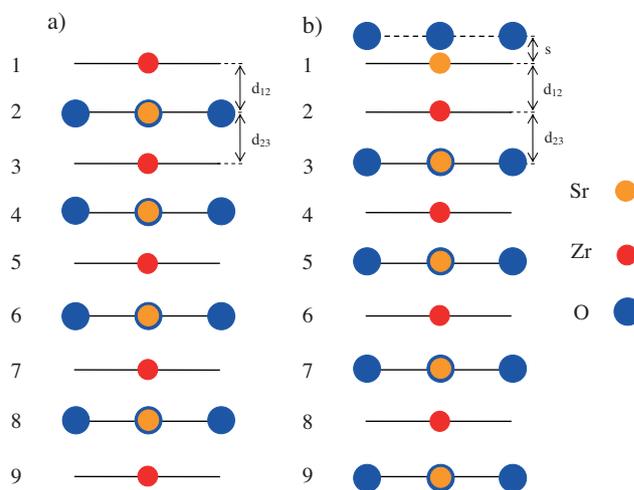


Fig. 2. Sketch of the side views of slab geometries used to study SrZrO₃ (111) surfaces. (a) Non-stoichiometric nine-layer slab with Zr-terminated surfaces. (b) Non-stoichiometric nine-layer slab with SrO₃-terminated surfaces with definitions of surface rumpling *s* and the near-surface interplanar separations Δd_{12} and Δd_{23} .

electron redistribution takes place for such terminations in order to cancel the polarity, but the Zr or SrO₃-terminated SrZrO₃ (111) surface keeps its insulating character, and therefore such calculations are feasible. Similar model for related SrZrO₃ (110) polar surfaces recently was used also by Chen et al. [20]. Their calculation results demonstrated that the charge neutralization and polarity compensation could be achieved by charge redistributions of surface atoms. Of course, it is not feasible to perform calculations for asymmetric stoichiometric slabs with different terminations, for example, Zr–SrO₃–Zr–SrO₃–Zr–SrO₃–Zr–SrO₃, since this would lead to a large dipole moment for an asymmetric slab (see Fig. 3).

Next, the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ cleavage and surface energies were calculated. It is obvious, that SrZrO₃ perovskite Zr and SrO₃-terminated (111) surfaces are mutually complementary. (Henceforth, SrZrO₃ will be used for presentation purposes, but everything that is said will apply equally also to the BaTiO₃, PbTiO₃ and PbZrO₃ (111) surface energy calculations.) Surfaces with both terminations arise simultaneously under cleavage of the crystal and therefore the relevant cleavage energy is distributed equally between created surfaces. Consequently, the cleavage energy is the same for both terminations. The cleavage energy of

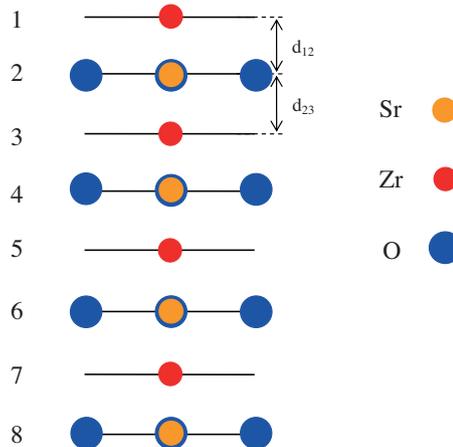


Fig. 3. Sketch of the stoichiometric eight-layer slab with Zr and SrO₃-terminated (111) surfaces with definitions of the near-surface interplanar separations Δd_{12} and Δd_{23} .

Table 1

By means of the hybrid B3LYP method calculated bulk lattice constants (in Å), effective charges Q and bond populations P (in e) of atoms in BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ crystals. The experimental bulk lattice constants [48–51] are listed for comparison purposes.

Crystal	BaTiO ₃	PbTiO ₃	SrZrO ₃	PbZrO ₃
B3LYP calculated lattice const.	4.021	3.963	4.195	4.220
Experimental lattice constant	4.00 [48]	3.97 [49]	4.109 [50]	4.161 [51]
Ion or bond	Property	Value	Value	Value
A	Q	+1.797	+1.392	+1.880
B	Q	+2.365	+2.345	+2.174
O	Q	−1.387	−1.246	−1.351
A—O	P	−0.032	+0.014	+0.002
B—O	P	+0.100	+0.100	+0.092
O—O	P	−0.038	−0.048	−0.008

the complementary SrZrO₃ surface $E_{cl}(SrO_3 + Zr)$ can be obtained via the following equation:

$$E_{cl}(SrO_3 + Zr) = (1/4)[E_{slab}^{unrel}(Zr) + E_{slab}^{unrel}(SrO_3) - 9E_{bulk}] \quad (1)$$

where $E_{slab}^{unrel}(Zr)$ is the total energy of unrelaxed 21-atom Zr-terminated SrZrO₃ slab (see Fig. 2a). $E_{slab}^{unrel}(SrO_3)$ is the total energy of unrelaxed 24-atom SrO₃-terminated SrZrO₃ (111) slab (see Fig. 2b). E_{bulk} is the bulk energy per formula unit containing 5 atoms in the cubic SrZrO₃ structure. Factor 9 in Eq. (1) before the E_{bulk} arises from the fact that 21-atom Zr-terminated and 24-atom SrO₃-terminated SrZrO₃ (111) slabs together contain nine 5-atom SrZrO₃ bulk unit cells. Factor 1/4 means that totally four surfaces are created upon the crystal cleavage.

When both sides of the slab are allowed to relax, the relaxation energies for each of the surfaces can be obtained from the equation:

$$E_{rel}(\chi) = \frac{1}{2}[E_{slab}^{rel}(\chi) - E_{slab}^{unrel}(\chi)] \quad (2)$$

where $\chi = Zr$ or SrO₃ specifies the actual SrZrO₃ (111) termination. $E_{slab}^{rel}(\chi)$ is the Zr or SrO₃-terminated SrZrO₃ (111) slab energy after relaxation. $E_{slab}^{unrel}(\chi)$ is the Zr or SrO₃-terminated SrZrO₃ (111) slab total energy without the geometry relaxation. Factor 1/2 means that two surfaces are created upon the crystal cleavage. Finally, the SrZrO₃ (111) surface energy is a sum of the cleavage and relaxation energies:

$$E_{surf}(\chi) = E_{cl}(SrO_3 + Zr) + E_{rel}(\chi) \quad (3)$$

3. Numerical results of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface calculations

By means of the hybrid B3LYP method the BaTiO₃ (4.021 Å), PbTiO₃ (3.963 Å), SrZrO₃ (4.195 Å) and PbZrO₃ (4.220 Å) theoretical bulk lattice constants were calculated. For BaTiO₃, SrZrO₃ and PbZrO₃ they are by 0.53%, 2.09% and 1.42% larger than the corresponding experimental values of 4.00 Å, 4.109 Å and 4.161 Å. In contrast, the B3LYP calculated PbTiO₃ bulk lattice constant (3.963 Å) is only by 0.18% smaller than the experimentally detected value of 3.97 Å [48–51] (see Table 1). Thereby, the computational method used in the present calculations is suitable for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surface atomic and electronic structure investigations. The theoretical bulk lattice constants were used in the all following (111) surface investigations.

In order to describe the chemical bonding between different atoms and covalency effects, a classical Mulliken population analysis [52] for the chemical bond populations P and effective charges on atoms Q was used. By means of the hybrid B3LYP functional calculated effective charges for the BaTiO₃ crystal bulk are (+2.365 e) for the Ti atom, (+1.797 e) for the Ba atom, and finally (−1.387 e) for the O atom. The bond population value of the chemical bonding between Ti and O atoms in the BaTiO₃ crystal is equal to (+0.100 e) (see Table 1). The negative chemical bond population

Table 2

By means of the B3LYP hybrid functional calculated and experimentally measured BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ bulk, as well as B and AO₃-terminated (111) surface band gaps at the Γ -point (in electron volts).

Crystal	B3LYP, bulk gap	Exp. bulk gap	B3LYP, B-term.	B3LYP, AO ₃ -term.
BaTiO ₃	3.49	3.3 [53]	4.14	3.60
PbTiO ₃	4.15	3.4 [28]	3.93	3.78
SrZrO ₃	5.31	5.6 [54]	4.57	4.75
PbZrO ₃	5.63		3.68	3.95

value between O and O atoms in the BaTiO₃ crystal (−0.038 e) indicates repulsion between them. The calculated effective charges for the PbTiO₃ bulk are (+2.345 e) for the Ti atom, (+1.392 e) for the Pb atom, and (−1.246 e) for the O atom. The chemical bond population between Ti and O atoms in PbTiO₃ is equal to (+0.100 e). Finally, the bond population in the PbTiO₃ bulk between O and O atoms is negative (−0.048 e), namely there are repulsion between O and O atoms.

B3LYP calculated effective Mulliken charges for the Sr atom (+1.880 e) are by 6% smaller than the classical ionic charges of (+2 e). B3LYP calculated effective charges for the Zr atom (+2.174 e) and for the O atom (−1.351 e) in the SrZrO₃ matrix are obviously smaller than the standard ionic charges of (+4 e and −2 e) pointing to a large amount of covalency in the chemical bonding between Zr and O atoms. The considerable degree of covalency in the chemical bonding between Zr and O atoms in the SrZrO₃ is confirmed also by the large bond population value between Zr and O atoms (+0.092 e). The Pb (+1.368 e), O (−1.160 e) and Zr (+2.111 e) effective charges in the PbZrO₃ matrix are slightly smaller than in SrZrO₃, and consequently the bond population value between Zr and O atoms in the PbZrO₃ crystal (+0.106 e) is larger than in SrZrO₃. The Pb—O bond population (+0.030 e) value in the PbZrO₃ crystal is exactly 15 times larger than the Sr—O bond population value (+0.002 e) in the SrZrO₃ matrix.

The calculated by means of the hybrid B3LYP functional bulk band gaps at the Γ -point of four BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ perovskites are summarized in Table 2. In the framework of the current paper calculated ABO₃ perovskite bulk band gap is the energy difference (in electron volts) between the top of the valence band and the bottom of the conduction band at the Γ -point. As we can see from Table 2, the BaTiO₃ experimentally measured optical band gap is equal to 3.3 eV [53]. The calculated bulk band gap at the Γ -point for the BaTiO₃ perovskite 3.49 eV, using the B3LYP functional, is in an excellent agreement with the experimental value. It is worth to notice, that by Sanna et al. [53] by means of the DFT calculated band gap for the BaTiO₃ bulk is 1.63 eV, but the DFT + GW band gap amount to 3.68 eV, namely very close to the experimental value and current B3LYP calculation result. The band gap at the Γ -point calculated for PbTiO₃ crystal by means of the hybrid B3LYP functional 4.15 eV, is in a satisfactory agreement with the experiment (see Table 2). The discrepancy between the experimental and calculated value is only 22%. This agreement is reasonable, if we take

Table 3
B3LYP calculated relaxation of Ti or Zr, as well as BaO₃, PbO₃ and SrO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface upper three layer atoms (as a percentage of the bulk crystal lattice constant $a_0 = 4.021, 3.963, 4.195, 4.220 \text{ \AA}$, respectively). Positive (negative) values refer to displacements in the direction outwards (inwards) of the surface.

Layer	Ion	BaTiO ₃ Displ. (Δz) Ti-term. (111)	PbTiO ₃ Displ. (Δz) Ti-term. (111)	SrZrO ₃ Displ. (Δz) Zr-term. (111)	PbZrO ₃ Displ. (Δz) Zr-term. (111)
1	B	-11.19	-7.57	-5.72	-9.24
2	A	-6.22	-10.09	-11.92	+5.92
	O	+2.74	-0.13	+0.79	+2.61
3	B	-0.25	+0.53	+1.53	-2.73

Layer	Ion	BaTiO ₃ Displ. (Δz) BaO ₃ -term. (111)	PbTiO ₃ Displ. (Δz) PbO ₃ -term. (111)	SrZrO ₃ Displ. (Δz) SrO ₃ -term. (111)	PbZrO ₃ Displ. (Δz) PbO ₃ -term. (111)
1	A	-1.24	+1.01	-0.74	-0.05
	O	-3.98	-2.52	-0.52	-1.26
2	B	+2.49	+0.02	+0.74	+1.18
3	A	+1.49	+1.26	-0.02	-0.02
	O	-0.25	+1.26	-0.18	-0.02

Table 4
B3LYP calculated surface rumpling s and relative displacements Δd_{ij} between the three near-surface planes, for the B-, and AO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces. Units are per cent of the bulk lattice constant.

Material	Termination	s	Δd_{12}	Δd_{23}	Termination	Δd_{12}	Δd_{23}
BaTiO ₃	BaO ₃	-2.74	-3.73	+1.00	Ti	-4.97	-5.97
PbTiO ₃	PbO ₃	-3.53	+0.99	-1.24	Ti	+2.52	-10.62
SrZrO ₃	SrO ₃	+0.22	-1.48	+0.76	Zr	+6.20	-13.45
PbZrO ₃	PbO ₃	-1.21	-1.23	+1.20	Zr	-15.16	+8.65

into account the experimental problems in determining the band gap, including the optical absorption edge tails which extend up to several tenths of eV [28]. By means of hybrid B3LYP method calculated band gap at the Γ -point for SrZrO₃ bulk (5.31 eV) is in an outstanding agreement with the experimental value of 5.6 eV [54]. Finally, B3LYP calculated band gap at the Γ -point for the PbZrO₃ crystal is equal to 5.63 eV (see Table 2).

As follows from the performed hybrid B3LYP calculations for Ti-terminated BaTiO₃ (111) surface (see Table 3), the upper layer Ti atom very strongly (by 11.19% of a bulk lattice constant a_0) moves inward. The second layer Ba atom also considerably relaxes inward (by 6.22% of a_0), but just opposite the second layer O atom moves outward by 2.74% of a_0 . Finally, inward relaxation of the third layer Ti atom is very small, only 0.25% of a_0 . For Ti-terminated PbTiO₃ (111) surface all first and second layer atoms moves inward. The strongest relaxation between them exhibit second layer O atom, which moves inward by 10.09% of a_0 . The third layer Ti atom relaxes slightly outwards, by 0.53% of a_0 . According to the numerical results of performed *ab initio* calculations, the upper layer Zr atoms for Zr-terminated SrZrO₃ and PbZrO₃ (111) surfaces very strongly (by 5.72% and 9.24% of bulk lattice constant a_0) moves inwards in direction toward the bulk (see Table 3). The second layer Sr and Pb atoms for Zr-terminated SrZrO₃ and PbZrO₃ (111) surfaces also strongly relaxes, but just in opposite directions by (11.92% of a_0) inwards and by (5.92% of a_0) outwards. The second layer O atoms for both materials relaxes outwards by much smaller displacements than the metal atoms (0.79% and 2.61% of a_0), respectively. Outward and inward relaxation of the third layer metal atoms are smaller than for the first and second layer metal atoms. According to the performed B3LYP calculations, we can see, that the common feature for all four calculated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ perovskites, is rather strong inward relaxation of the upper layer metal atoms (see Table 3).

According to the performed B3LYP calculation results for BaO₃-terminated BaTiO₃ (111) surface, both upper layer atoms relax inwards. The upper layer metal atom relaxes inward by 1.24% of a_0 , but O atom moves inward even more strongly by 3.98% of a_0 (see

Table 5
B3LYP calculated cleavage, relaxation, and surface energies for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces (in electron volts per surface cell).

Surface	Termination	E_{cl}	E_{rel}	E_{surf}
BaTiO ₃ (111)	Ti-terminated	9.22	-1.94	7.28
	BaO ₃ -terminated	9.22	-0.82	8.40
PbTiO ₃ (111)	Ti-terminated	8.31	-2.17	6.14
	PbO ₃ -terminated	8.31	-0.20	8.11
SrZrO ₃ (111)	Zr-terminated	9.55	-1.57	7.98
	SrO ₃ -terminated	9.55	-0.10	9.45
PbZrO ₃ (111)	Zr-terminated	8.34	-1.41	6.93
	PbO ₃ -terminated	8.34	-0.13	8.21

Table 3). The second layer Ti atom outward relaxation (2.49% of a_0) is approximately two times larger than the upper layer Ba atom inward relaxation. Finally, the third layer Ba atom rather strongly relaxes outward by 1.49% of a_0 , but the same layer O atom relaxes inward by a small magnitude (0.25% of a_0). Just opposite to BaTiO₃, SrZrO₃ and PbZrO₃ perovskites, the PbO₃-terminated PbTiO₃ (111) surface upper layer Pb atom slightly relaxes outwards by 1.01% of a_0 , while another three perovskite upper layer metal atoms relaxes inwards (see Table 3). For both SrO₃ and PbO₃-terminated SrZrO₃ and PbZrO₃ polar (111) surfaces all upper layer metal and oxygen atoms moves inwards in direction toward the bulk by relatively small displacement magnitudes ranging from 0.05% of a_0 for the Pb atom on the PbO₃-terminated PbZrO₃ (111) surface till 1.26% of a_0 for the O atom on the same surface (see Table 3). The second layer Zr atom outward relaxation magnitude (0.74% of a_0) on the SrO₃-terminated SrZrO₃ (111) surface exactly coincides with the first layer Sr atom inward relaxation magnitude (0.74% of a_0). Third layer O atom on the SrO₃-terminated SrZrO₃ (111) surface relax inwards by 0.18% of a_0 . All another third layer atoms on SrO₃ and PbO₃-terminated SrZrO₃ and PbZrO₃ (111) surfaces moves inwards by negligibly small displacement, only 0.02% of the lattice constant a_0 . According to the performed B3LYP calculations, the common behavior for all four BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ perovskites

Table 6

The A–B bond populations P (in e) and the relevant interatomic distances R (in Å) for two different (111) terminations in BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃. Symbols I–III denote the number of each plane enumerated from the surface. The nearest-neighbor Ti–O distance in the unrelaxed BaTiO₃ bulk lattice is 2.0105 Å, in the unrelaxed PbTiO₃ bulk is 1.9815 Å, in the unrelaxed SrZrO₃ bulk the nearest Zr–O distance is 2.0975 Å, and finally, in the unrelaxed PbZrO₃ bulk the nearest Zr–O distance is equal to 2.11 Å.

Atom A	Atom B	BaTiO ₃		PbTiO ₃		SrZrO ₃		PbZrO ₃	
		P	R	P	R	P	R	P	R
		BaO ₃ -terminated		PbO ₃ -terminated		SrO ₃ -terminated		PbO ₃ -terminated	
A(I)	O(I)	−0.022	2.845	+0.050	2.806	+0.004	2.966	+0.050	2.984
B(II)	O(I)	+0.118	1.872	+0.116	1.925	+0.098	2.067	+0.114	2.052
	O(III)	+0.054	2.075	+0.068	2.011	+0.080	2.120	+0.092	2.140
A(III)	B(II)	−0.002	3.496	+0.002	3.416	0.000	3.644	+0.006	3.672
	O(III)	−0.032	2.844	+0.018	2.804	+0.002	2.966	+0.032	2.984
Atom A	Atom B	BaTiO ₃		PbTiO ₃		SrZrO ₃		PbZrO ₃	
		P	R	P	R	P	R	P	R
		Ti-terminated		Ti-terminated		Zr-terminated		Zr-terminated	
B(I)	A(II)	0.000	3.421	+0.004	3.467	+0.002	3.728	+0.014	3.494
	O(II)	+0.014	1.748	+0.098	1.827	−0.008	1.953	+0.028	1.867
A(II)	O(II)	−0.022	2.866	+0.018	2.830	+0.006	3.014	+0.054	2.987
B(III)	A(II)	0.000	3.410	+0.004	3.316	0.000	3.486	+0.010	3.792
	O(II)	+0.066	2.082	+0.086	1.967	+0.096	2.080	+0.074	2.247

is inward relaxation of all upper layer oxygen atoms, and outward relaxation of the second layer metal atoms (see Table 3).

Experimentally relatively easy measurable properties are the surface rumpling s (the displacement of oxygen with respect to the metal in the upper surface layer) and changes in interlayer distances Δd_{12} and Δd_{23} (1, 2, and 3 are the number of surface layers). My *ab initio* calculation results for this properties are presented in Table 4. The calculations of the interlayer distances are based on the positions of relaxed metal ions. It is possible to see from Table 4, that the BaO₃-terminated BaTiO₃ (111) surface shows the reduction of interlayer distance Δd_{12} and expansion of Δd_{23} , whereas, in contrast, the PbO₃-terminated PbTiO₃ (111) surface exhibit the expansion of interlayer distance Δd_{12} and reduction of Δd_{23} . In the case of Ti-terminated BaTiO₃ and PbTiO₃ (111) surfaces, both surfaces exhibit reduction of interlayer distance Δd_{23} . At the same time Ti-terminated BaTiO₃ (111) surface shows strong reduction of interlayer distance Δd_{12} , but the Ti-terminated PbTiO₃ (111) surface exhibit approximately two time smaller expansion of interlayer distance Δd_{12} . Turning now to SrZrO₃ and PbZrO₃ perovskites, it is possible to see from Table 4 that both the SrO₃ and PbO₃-terminated SrZrO₃ and PbZrO₃ (111) polar surfaces exhibits the decrease of interlayer distance Δd_{12} and expansion of Δd_{23} . The Zr-terminated PbZrO₃ (111) surface shows the reduction of interlayer distance Δd_{12} and expansion of Δd_{23} , but, just opposite, the Zr-terminated SrZrO₃ (111) surface, demonstrate the expansion of the interlayer distance Δd_{12} and reduction of Δd_{23} . My calculated surface rumpling for the PbO₃-terminated PbZrO₃ (111) surface is exactly 5.5 times larger than the surface rumpling for the SrO₃-terminated SrZrO₃ (111) surface. To the best of my knowledge, there are no experimental measurements for SrZrO₃ and PbZrO₃ polar (111) surfaces with which I can compare my *ab initio* calculated values of s , Δd_{12} and Δd_{23} .

In the case of (111) surface band gap calculations, the surface states splits off from the top of the valence band and the bottom of the conduction band [55]. The band gap at the Γ -point, namely the energy range with no electronic states between the highest occupied surface state, which split off from the top of the valence band, and lowest unoccupied surface state, which split off from the bottom of the conduction band, were calculated for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces. The B3LYP calculated band gaps at the Γ -point for the PbO₃ (3.78 eV) and Ti-terminated (3.93 eV) PbTiO₃, SrO₃ (4.75 eV) and Zr-terminated (4.57 eV) SrZrO₃, as well as for PbO₃ (3.95 eV) and Zr-terminated (3.68 eV) PbZrO₃ (111) surfaces, becomes smaller with respect to the calculated bulk band gap

at the Γ -point of 4.15 eV for PbTiO₃, 5.31 eV for SrZrO₃, and 5.63 eV for PbZrO₃ (see Table 2). In contrast, the B3LYP calculated band gaps at the Γ -point for the BaO₃ (3.60 eV) and Ti-terminated (4.14 eV) BaTiO₃ (111) surfaces are slightly larger than the calculated BaTiO₃ bulk band gap at the Γ -point of 3.49 eV. By means of hybrid B3LYP method calculated band gap at the Γ -point for SrZrO₃ bulk (5.31 eV) is in an outstanding agreement with the experimental value of 5.6 eV [54]. The narrowest band gap at the Γ -point between all BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces, according to performed B3LYP simulations, is for the BaO₃-terminated BaTiO₃ (111) surface (3.60 eV) (see Table 2).

The surface energies for the relaxed BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surfaces were calculated using Eqs. (1)–(3). The B3LYP calculated surface relaxation energy for Ti-terminated BaTiO₃ (111) surface (−1.94 eV) (see Table 5) is more than two times larger than the corresponding surface relaxation energy for BaO₃-terminated BaTiO₃ (111) surface (−0.82 eV). Consequently, the calculated surface energy for Ti-terminated BaTiO₃ (111) surface is equal to 7.28 eV, and is 8.40 eV for BaO₃-terminated BaTiO₃ (111) surface. The B3LYP calculated Ti-terminated PbTiO₃ (111) surface relaxation energy (−2.17 eV) is the largest surface relaxation energy between all calculated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ perovskite (111) surface relaxation energies, and almost eleven times larger than the PbO₃-terminated PbTiO₃ (111) surface energy (−0.20 eV) (see Table 5). Consequently, for the PbTiO₃ perovskite, there are the largest (111) surface energy difference (1.97 eV) between the Ti-terminated (6.14 eV) and PbO₃-terminated (8.11 eV) (111) surfaces among all four calculated perovskites. My calculated surface energies for SrO₃ and PbO₃-terminated SrZrO₃ and PbZrO₃ (111) surfaces (9.45 and 8.21 eV, respectively) are much larger than the surface energies for Zr-terminated SrZrO₃ and PbZrO₃ (111) surfaces (7.98 and 6.93 eV) (see Table 5). The relaxation energies for Zr-terminated SrZrO₃ and PbZrO₃ polar (111) surfaces are more than fifteen times and more than ten times, respectively, larger than the relaxation energies for SrO₃ and PbO₃-terminated SrZrO₃ and PbZrO₃ (111) surfaces.

As follows from the chemical bond covalency analysis, for all four calculated BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ perovskites, the main effect for the BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surfaces is the strengthening of the Ti–O (Zr–O) chemical bond covalency near the BaO₃ (+0.118 e), PbO₃ (+0.116 e), SrO₃ (+0.098 e), and PbO₃-terminated (+0.114 e) BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ (111) surfaces (see Table 6).

Table 7
B3LYP calculated Mulliken atomic charges Q (in e) and changes in atomic charges ΔQ with respect to the bulk charges (in e) for the two BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface terminations. The calculated Mulliken charges in the BaTiO₃ bulk are: +2.365 e (Ti), –1.387 e (O), and +1.797 e (Ba). For the PbTiO₃ bulk charges are: +2.345 e (Ti), –1.246 e (O), and +1.392 e (Pb). For the SrZrO₃ bulk charges are: +2.174 e (Zr), –1.351 e (O), and +1.880 e (Sr). Finally, for the PbZrO₃ bulk charges are: +2.111 e (Zr), –1.160 e (O), and +1.368 e (Pb).

Atom, layer	BaTiO ₃		PbTiO ₃		SrZrO ₃		PbZrO ₃	
	Q BaO ₃ -terminated	ΔQ	Q PbO ₃ -terminated	ΔQ	Q SrO ₃ -terminated	ΔQ	Q PbO ₃ -terminated	ΔQ
A(I)	+1.792	–0.005	+1.387	–0.005	+1.891	+0.011	+1.400	+0.032
O(I)	–1.054	+0.333	–0.895	+0.351	–1.014	+0.337	–0.848	+0.312
B(II)	+2.313	–0.052	+2.32	–0.025	+2.213	+0.039	+2.157	+0.046
A(III)	+1.784	–0.013	+1.385	–0.007	+1.874	–0.006	+1.324	–0.044
O(III)	–1.326	+0.061	–1.215	+0.031	–1.348	+0.003	–1.139	+0.021

Atom, layer	BaTiO ₃		PbTiO ₃		SrZrO ₃		PbZrO ₃	
	Q Ti-terminated	ΔQ	Q Ti-terminated	ΔQ	Q Zr-terminated	ΔQ	Q Zr-terminated	ΔQ
B(I)	+1.814	–0.551	+1.771	–0.574	+1.391	–0.783	+1.858	–0.253
A(II)	+1.713	–0.084	+1.171	–0.221	+1.819	–0.061	+0.464	–0.904
O(II)	–1.403	–0.016	–1.258	–0.012	–1.314	+0.037	–1.120	+0.040
B(III)	+2.167	–0.198	+2.200	–0.145	+2.033	–0.141	+2.131	+0.020

This effect, the strong Ti–O (Zr–O) chemical bond covalency, was already well pronounced for BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ crystals in the bulk (+0.100 e , +0.100 e , +0.092 e , and +0.106 e , respectively). According to performed B3LYP calculations, there are no increase in the Ti–O (Zr–O) chemical bond population value near the Ti (Zr)-terminated BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ polar (111) surfaces.

The B3LYP calculated Mulliken effective charges Q , and their changes ΔQ with respect to the bulk values, near the BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ (111) surface are presented in Table 7. According to performed B3LYP calculations, the charge of the first layer surface Ti (Zr) atom in the Ti (Zr)-terminated BaTiO₃, PbTiO₃, SrZrO₃, and PbZrO₃ polar (111) surfaces is reduced extremely strongly by 0.551 e , 0.574 e , 0.783 e and 0.253 e , respectively. Ti (Zr) atoms in the third layer lose much less charge (0.198 e , 0.145 e and 0.141 e) for BaTiO₃, PbTiO₃ and SrZrO₃ perovskites, and even gain a very small amount of charge (0.02 e) for PbZrO₃ crystal Zr atom. The second layer Ba, Pb and Sr atom charge was reduced by rather small amount of 0.084 e , 0.221 e and 0.061 e , respectively, whereas the second layer Pb charge on PbZrO₃ crystal was reduced by a very huge amount of 0.904 e . The largest, and almost equal four all four calculated perovskites, charge change on the BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces is observed for the upper layer O atoms (0.333 e , 0.351 e , 0.337 e and 0.312 e , respectively). This gives a large positive change of 0.994 e , 1.048 e , 1.022 e and 0.968 e in the charge for each of the BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface upper layers. The charge change in the BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surface third layer is negligible in comparison with the upper layer, only 0.17 e , 0.086 e , 0.003 e and 0.019 e , respectively.

4. Conclusions

Predictive B3LYP calculations, in order to investigate the polar (111) surface atomic and electronic structure of BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ perovskites, were performed. The surface relaxation has been calculated for two possible B (B=Ti or Zr) or AO₃ (A=Ba, Pb or Sr) BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface terminations. According to performed B3LYP calculations, all atoms of the first surface layer, for both surface terminations and all four investigated perovskites, relax inwards. The only exception is a small outward relaxation of the PbO₃-terminated PbTiO₃ (111)

surface upper layer Pb atom by 1.01% of the bulk lattice constant a_0 . All Ti or Zr-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface upper layer atom relaxations are considerably larger than the BaO₃, PbO₃, SrO₃ and PbO₃-terminated (111) surface upper layer atom relaxations. Performed *ab initio* calculation results are in a good agreement with simple chemical bonding theories in assessing surface structure stability [56]. B3LYP calculated bulk band gap at the Γ -point for BaTiO₃, PbTiO₃ and SrZrO₃ perovskites (3.49, 4.15 and 5.31 eV, respectively) is in a good agreement with the experimental values of (3.2, 3.4 and 5.6 eV, respectively). Calculated band gap at the Γ -point for the PbO₃ and SrO₃, as well as Ti and Zr-terminated PbTiO₃, SrZrO₃ and PbZrO₃ polar (111) surfaces, becomes smaller with respect to the bulk band at the Γ -point gap. In contrast, the B3LYP calculated band gap at the Γ -point for BaO₃ and Ti-terminated BaTiO₃ polar (111) surface is wider than the BaTiO₃ bulk band gap at the Γ -point. B3LYP calculated surface energies for BaO₃, PbO₃, SrO₃ and PbO₃-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces are considerably larger than the corresponding surface energies for Ti (Zr)-terminated BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surfaces. According to performed *ab initio* calculations, the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface energy, for both terminations, is always considerably larger than the earlier calculated respective (011) and (001) surface energy [6,11]. Performed B3LYP calculations indicate a considerable increase of Ti–O (Zr–O) chemical bond covalency near the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ (111) surface (0.118 e , 0.116 e , 0.098 e and 0.114 e , respectively) relative to the BaTiO₃, PbTiO₃, SrZrO₃ and PbZrO₃ bulk (0.100 e , 0.100 e , 0.092 e and 0.106 e , respectively).

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