



# Ab initio calculations of CaZrO<sub>3</sub> (011) surfaces: systematic trends in polar (011) surface calculations of ABO<sub>3</sub> perovskites

Roberts I. Eglitis<sup>1,\*</sup> , J. Kleperis<sup>1</sup>, J. Purans<sup>1</sup>, A. I. Popov<sup>1</sup>, and Ran Jia<sup>1,2</sup>

<sup>1</sup>Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga 1063, Latvia

<sup>2</sup>Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, People's Republic of China

Received: 7 May 2019

Accepted: 10 September 2019

Published online:  
23 September 2019

© Springer Science+Business  
Media, LLC, part of Springer  
Nature 2019

## ABSTRACT

By means of the CRYSTAL computer program package, first-principles calculations of polar ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces were performed. Our calculation results for polar CaZrO<sub>3</sub> (011) surfaces are compared with the previous ab initio calculation results for ABO<sub>3</sub> perovskite (011) and (001) surfaces. From the results of our hybrid B3LYP calculations, all upper-layer atoms on the ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces relax inwards. The only exception from this systematic trend is outward relaxation of the oxygen atom on the ZrO-terminated CaZrO<sub>3</sub> (011) surface. Different ZrO, Ca and O terminations of the CaZrO<sub>3</sub> (011) surface lead to a quite different surface energies of 3.46, 1.49, and 2.08 eV. Our calculations predict a considerable increase in the Zr–O chemical bond covalency near the CaZrO<sub>3</sub> (011) surface, both in the directions perpendicular to the surface (0.240*e*) as well as in the plane (0.138*e*), as compared to the CaZrO<sub>3</sub> (001) surface (0.102*e*) and to the bulk (0.086*e*). Such increase in the B–O chemical bond population from the bulk towards the (001) and especially (011) surfaces is a systematic trend in all our eight calculated ABO<sub>3</sub> perovskites.

## Introduction

Surface and interface phenomena, taking place in the ABO<sub>3</sub> perovskites and their nanostructures, as well as mechanisms of various (001) and (011) surface electronic processes, are the key topics in theoretical solid-state physics [1–27]. CaTiO<sub>3</sub>, SrTiO<sub>3</sub>, PbTiO<sub>3</sub>, BaTiO<sub>3</sub>, CaZrO<sub>3</sub>, SrZrO<sub>3</sub>, PbZrO<sub>3</sub> and BaZrO<sub>3</sub>

perovskites all have a general chemical formula ABO<sub>3</sub>, where (A = Ca, Sr, Pb or Ba and B = Ti or Zr). The A cation size as a rule is much larger than the relevant B cation size. The ABO<sub>3</sub> perovskite cubic-symmetry structure has the B atom in sixfold oxygen coordination, surrounded by an octahedron of O atoms as well as the A atom in 12-fold oxygen cuboctahedral coordination. As temperature

Address correspondence to E-mail: rieglitis@gmail.com

decreases, some of  $ABO_3$  perovskites, like  $SrTiO_3$  and  $BaZrO_3$ , stay in its high-temperature cubic phase, while other  $ABO_3$  perovskites, such as  $CaTiO_3$ ,  $PbTiO_3$ ,  $BaTiO_3$ ,  $CaZrO_3$ ,  $SrZrO_3$  and  $PbZrO_3$ , exhibit different phase transitions. The neutral (001) as well as polar and charged (011) surfaces of the  $ABO_3$  perovskites are both of fundamental interest for basic research, and also very important for practical applications, for example, numerous microelectronic, catalytic, and other high-technology applications as well as they are frequently used as substrates for growth of other materials such as cuprate superconductors [28–34].

The predictive power of *ab initio* calculations caused by both the explosive development of new computational codes and powerful increase in computer speed allows for us to design a new material for high technology purposes on the paper. Very good example is prediction of the average battery voltage for a large amount of 4 V battery cathodes from *ab initio* calculations by Ceder et al. [35, 36]. Moreover, on the basis of our *ab initio* calculations performed by Eglitis and Borstel [37, 38], it was demonstrated that the cubic spinel structure  $Li_2CoMn_3O_8$  battery cathode material will lead to the novel high-voltage lithium-ion battery working at the 5 V range [37, 38].

A great variety of metal ions can occupy the A and B sites in the technologically important  $ABO_3$  perovskite structure, and such versatility of this class of materials makes them a perfect choice for a large number of catalytic applications, including electrocatalytic operations. An SOEC cathode should have high electronic and ionic conductivities. An  $ABO_3$  perovskite oxide can possess both of these conductivities. Thereby, very novel and forefront research direction is perovskite material cathodes. Due to the problems such as Ni reoxidation and requirement of using a reducing agent in the feed stream, coke deposition at lower temperatures, and further reduction of CO to carbon at high cathodic potentials, the focus of research on  $CO_2$  electrolysis has shifted from improvement of metal-cermet electrodes to developing of alternative materials. Oxide-based mixed ionic and electrical conductors (MIECs), specifically perovskite-type MIEC oxides, have attracted attention due to their easily tunable ionic and electrical conductivity, high stability at high temperatures as well as resistance to coke formation.

Therefore, it is self-evident that in last 25 years  $CaTiO_3$ ,  $SrTiO_3$ ,  $PbTiO_3$ ,  $BaTiO_3$ ,  $CaZrO_3$ ,  $SrZrO_3$ ,  $PbZrO_3$  and  $BaZrO_3$  perovskite neutral (001) surfaces were world wide extensively explored both theoretically and experimentally [39–54]. Recently, systematic trends in *ab initio* calculations for eight technologically most important  $ABO_3$  perovskite neutral (001) surfaces were summarized by Eglitis et al. [55, 56]. For example, it was pointed out that relaxation of  $ABO_3$  perovskite (001) surface metal atoms for upper two surface layers, as a rule, is larger than that of oxygen atoms. For  $ABO_3$  perovskite (001) surfaces, in most cases, all atoms of the first surface layer relax inwards, towards the bulk, all atoms of the second surface layer relax outwards, and, again, all atoms of the third surface layer relax inwards [55, 56]. It is worth to notice that for both AO and  $BO_2$  terminations, the  $ABO_3$  perovskite (001) surface energies are almost equivalent. According to our *ab initio* calculations [55, 56], the  $ABO_3$  perovskite (001) surface band gaps are always reduced regarding to their respective bulk band gap values. Finally, in  $ABO_3$  perovskite bulk, the B–O chemical bond population is always smaller than near the (001) surface [55, 56].

In contrast to neutral (001) surfaces, the  $ABO_3$  perovskite polar (011) surfaces are much more complicated, since they consist of charged and polar planes, and thereby also of course less studied, both theoretically and experimentally. To the best of our knowledge, first *ab initio* study of the atomic and electronic structure of the polar  $CaTiO_3$  (011) surface was performed by Zhang et al. [57]. The calculation results by Zhang et al. indicated that the energetically most favourable  $CaTiO_3$  surfaces are the CaO-terminated (001) (0.824 eV), the A-type O-terminated (011) (0.837 eV), and the  $TiO_2$ -terminated (001) (1.021 eV) surfaces. This result by Zhang et al. [57] sharply contrasted with all another calculation results dealing with  $ABO_3$  perovskite (001) and (011) surfaces [58–69], where the  $ABO_3$  perovskite (001) surface energies are always smaller than (011) surface energies. One year later, Eglitis and Vanderbilt [11] performed very comprehensive first-principles calculations for three possible  $CaTiO_3$  (011) surface terminations. Just opposite to Zhang et al. [57], Eglitis and Vanderbilt [11] found that CaO (0.94 eV)- and  $TiO_2$  (1.13 eV)-terminated (001) surface energies are considerably smaller than the O-terminated (1.86 eV)  $CaTiO_3$  (011) surface energy, in a line with all other

previous ab initio studies for  $ABO_3$  perovskite polar (011) surfaces [58–69].

The first ab initio calculations for polar  $SrTiO_3$  (011) surfaces were carried out by Bottin et al. [59]. One year later, Heifets and his co-workers [60] performed ab initio Hartree–Fock (HF) calculations for  $SrTiO_3$  (011) surfaces. Around 10 years ago Eglitis and Vanderbilt [10] performed first-principles calculations for O-, Sr- and TiO-terminated  $SrTiO_3$  (011) surfaces using a hybrid description of exchange and correlation. Finally, Enterkin et al. [61] reported a comprehensive research on the  $3 \times 1$  polar  $SrTiO_3$  (110) surface structure obtained through transmission electron diffraction and direct methods and confirmed through density functional theory calculations and scanning tunnelling microscopy images and simulations.

First in the world ab initio calculations for  $PbTiO_3$  and  $BaTiO_3$  (011) surfaces were performed by Eglitis and Vanderbilt [9]. Eglitis and Vanderbilt presented and discussed the results of calculations of surface relaxations and rumplings for the polar (011) surfaces of  $PbTiO_3$  and  $BaTiO_3$  by means of the hybrid B3PW description of exchange and correlation [9]. They considered three types of polar  $PbTiO_3$  and  $BaTiO_3$  (011) surfaces, terminated on a TiO layer, a Pb or Ba layer as well as O layer. They found that the relaxation energies for TiO-terminated  $PbTiO_3$  and  $BaTiO_3$  polar (011) surfaces are much larger than for the Pb- or Ba-terminated (011) surfaces. Two years later Zhang et al. [62] performed ab initio calculations of the atomic and electronic structure as well as stability of the polar  $PbTiO_3$  (011) surfaces. At the same time independently Zhang et al. [63] by means of the GGA exchange–correlation functional performed first-principles calculations for the surface energy, cleavage energy, surface grand potential as well as surface relaxation for five different terminations of polar  $PbTiO_3$  (011) surface. Simultaneously with Eglitis and Vanderbilt [9] in 2007, Xie et al. [64] investigated the electronic and atomic structures of the polar  $BaTiO_3$  (011) surfaces by means of ab initio DFT calculations using the slab model. Finally, Wang et al. [65] explored the thermodynamic surface stability for polar  $BaTiO_3$  (011) surface five terminations, namely  $BaTiO$ ,  $TiO$ ,  $Ba$ ,  $O_2$  and  $O$ .

To the best of our knowledge no ab initio studies exist dealing with polar  $CaZrO_3$  (011) surfaces, and thereby in this paper we performed first in the world predictive theoretical calculations for  $CaZrO_3$  (011)

surfaces. Eglitis and Rohlifing [66] performed first ab initio calculations of surface relaxations, energetics, rumplings, optical band gaps as well as charge distribution for three different terminations of polar  $SrZrO_3$  and  $PbZrO_3$  (011) surfaces. It is worth to notice, that 4 years latter Chen et al. [67] also at ab initio level investigated the stabilities and electronic properties of five possible terminations for  $SrZrO_3$  (011) polar surfaces.

First ab initio calculations for  $BaZrO_3$  (011) surfaces were simultaneously performed 10 years ago by Eglitis [68] as well as by Heifets et al. [69]. Eglitis [68] performed polar  $BaZrO_3$  (011) surface relaxation as well as calculated the surface energies and rumplings for three different terminations, namely Ba, ZrO and O. Heifets et al. [69] by means of the density functional theory calculations studied the atomic and electronic structure as well as charge redistribution of polar  $BaZrO_3$  (011) surfaces.

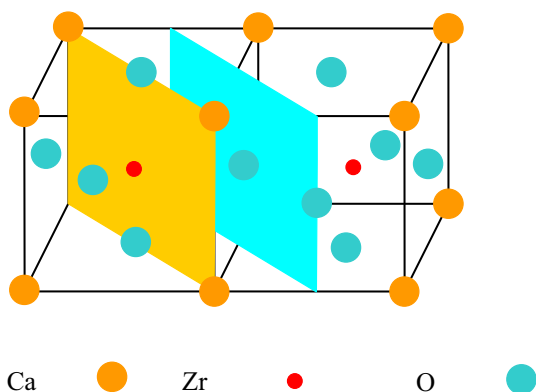
Along with theoretical ab initio investigations of  $ABO_3$  perovskite (011) surfaces, their polar (011) surfaces are world wide extensively studied also experimentally. For example, Crosby et al. [70] resolved the surface structure of (110) faceted strontium titanate nanoparticles synthesized via solvothermal method using high-resolution microscopy. The authors demonstrate that the surface is a titania-rich structure containing tetrahedrally coordinated  $TiO_4$  units similar to the family of  $(n \times 1)$  reconstructions observed on (110) surfaces of bulk crystalline  $SrTiO_3$  [70]. As an another example of brilliant experimental work, 8 years ago Enterkin et al. [61] reported a solution to the  $3 \times 1$   $SrTiO_3$  (110) surface structure obtained through transmission electron diffraction and direct methods and confirmed through scanning tunnelling microscopy and simulations [61].

The aim of this research paper was to carry out first in the world ab initio calculations for  $CaZrO_3$  polar (011) surfaces in order to complete our more than 10 year long work dealing with first-principles calculations of polar and charged  $ABO_3$  perovskite (011) surfaces [9–11, 59, 60, 66, 68]. For our  $CaZrO_3$  (011) surface calculations, we chose the high symmetry cubic phase because it is most extensively studied for  $CaTiO_3$ ,  $SrTiO_3$ ,  $PbTiO_3$ ,  $BaTiO_3$ ,  $SrZrO_3$ ,  $PbZrO_3$  and  $BaZrO_3$  perovskites. The (011) surface studies for other  $CaZrO_3$  low symmetry phases remain a challenging problem for our future calculations. After we completed first-principles calculations for  $CaZrO_3$

(011) surfaces, we analysed results for all eight  $ABO_3$  perovskites, and detected systematic trends common for  $CaTiO_3$ ,  $SrTiO_3$ ,  $PbTiO_3$ ,  $BaTiO_3$ ,  $CaZrO_3$ ,  $SrZrO_3$ ,  $PbZrO_3$  and  $BaZrO_3$  perovskite polar (011) surfaces in a form interesting for a large audience of readers.

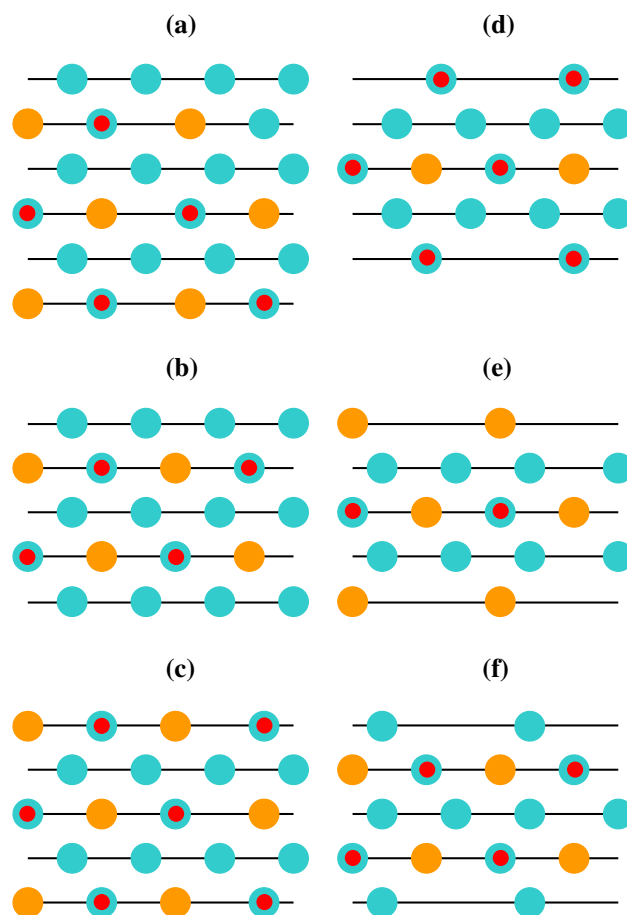
### Computational method as well as polar $CaZrO_3$ (011) surface models and energies

In this paper, we performed ab initio calculations for polar  $CaZrO_3$  (011) surfaces, using the hybrid exchange–correlation functional B3LYP [71] as well as the world well-known CRYSTAL [72] computer code. Our previous calculation results for  $CaTiO_3$ ,  $SrTiO_3$ ,  $PbTiO_3$ ,  $BaTiO_3$ ,  $SrZrO_3$ ,  $PbZrO_3$  and  $BaZrO_3$  (011) surfaces performed by B3LYP [71] or B3PW [73] functional are listed for comparison purpose with aim to detect systematic trends in polar (011) surface calculations for all eight technologically most important  $ABO_3$  perovskites. For  $CaZrO_3$  bulk, we performed the reciprocal-space integration by sampling the Brillouin zone with an  $8 \times 8 \times 8$  times, whereas for (011) surfaces with  $8 \times 8 \times 1$  times extended Pack–Monkhorst net [74]. In this paper, for Ca, Zr and O atoms, we used exactly the same basis sets as in our previous work dealing with ab initio calculations of neutral  $CaZrO_3$  (001) surfaces [75]. The polar  $CaZrO_3$  (011) surfaces were modelled with two-dimensional (2D) slabs, which contained nine planes perpendicular to the [011] crystal direction (Fig. 1). The main difficulty in modelling the  $CaZrO_3$  (011) polar surface is that it consists of charged planes, O–O or  $CaZrO_3$ . If we assume fixed ionic



**Figure 1** Schematic picture of the cubic  $CaZrO_3$  perovskite structure containing two (011) cleavage planes which create charged  $O_2$  and  $CaZrO$  (011) surfaces.

charges  $Ca^{2+}$ ,  $Zr^{4+}$  and  $O^{2-}$  in the  $CaZrO_3$  perovskite, then calculating the polar  $CaZrO_3$  (011) surface precisely as would be acquired from a  $CaZrO_3$  crystal cleavage leads to either an endless macroscopic dipole moment in the direction perpendicular to the (011) surface, when the slab is terminated by different planes— $O_2$  and  $CaZrO$  (Fig. 2a), or an excess of charge, when both sides of the slab are terminated by the same crystalline planes ( $O_2$ – $O_2$ ) (Fig. 2b) or ( $CaZrO$ – $CaZrO$ ) (Fig. 2c). It is well known that these two kinds of crystal terminations make the polar  $CaZrO_3$  (011) surface unstable [1, 60, 76]. In ab initio calculations for a slab terminated by the different kind of planes the charge redistribution near the surface, in principle, can



**Figure 2**  $CaZrO_3$  (011) surface slab models (a–f) used in our calculations.  $CaZrO_3$  slabs obtained by crystal cleaving yields mixed  $O_2^-$  and  $CaZrO$ -terminated polar surfaces (a),  $O_2^-$ -terminated (b) as well as  $CaZrO$ -terminated (c) charged surfaces. Our modified nonpolar and neutral  $TiO$ -terminated  $CaZrO_3$  (011) surfaces (d), Ca-terminated (e) and O-terminated (f) surfaces.

compensate the macroscopic dipole moment. From another side, in the *ab initio* calculations of slabs terminated by the same planes the charge neutrality may be easily retained by setting in the computer input files an appropriate number of electrons or the zero net charge of the unit cell. Nevertheless, careful calculations [1, 59, 77] demonstrate that these two options for  $ABO_3$  perovskite surfaces are energetically expensive with respect to the dipole moment elimination via introduction of vacancies.

For these two reasons, in order to get as good as possible results, we used for our  $\text{CaZrO}_3$  (011) surface calculations nonpolar  $\text{CaZrO}$ -terminated surfaces and modified their upper and lower layers. Namely, we removed the Ca atom from the upper and lower layer of the nine-layer symmetric  $\text{CaZrO}$ -terminated slab (Fig. 2d). We get a neutral 21-atom containing  $\text{ZrO}$ -terminated  $\text{CaZrO}_3$  (011) slab as illustrated in Fig. 2d. If we simultaneously remove both the Zr and O atoms from the upper and lower layers of the symmetric 9-layer  $\text{CaZrO}$ -terminated  $\text{CaZrO}_3$  (011) slab, we get a neutral Ca-terminated  $\text{CaZrO}_3$  (011) 9-layer slab which contains 19 atoms (Fig. 2e). Lastly, if we remove the O atom again from the upper and lower layers of the nine-layer symmetric O–O-terminated  $\text{CaZrO}_3$  (011) slab, we get the neutral and symmetric 20-atom containing nine-layer supercell with O-terminated  $\text{CaZrO}_3$  (011) surfaces (Fig. 2f).

With aim to calculate the  $\text{CaZrO}_3$  (011) surface energies, we started with the cleavage energy calculations for unrelaxed Ca- and  $\text{ZrO}$ -terminated (011) surfaces. Surfaces with Ca and  $\text{ZrO}$  terminations simultaneously arise under (011) cleavage of the  $\text{CaZrO}_3$  crystal. We assume that the cleavage energy is equally distributed between the created Ca- and  $\text{ZrO}$ -terminated (011) surfaces. In our  $\text{CaZrO}_3$  (011) surface calculations, the nine-layer Ca-terminated (011) slab with 19 atoms and the  $\text{ZrO}$ -terminated (011) slab with 21 atoms together contain 40 atoms, or in another words eight bulk unit cells (40 atoms), thereby:

$$E_{\text{surf}}^{\text{unr}}(\Psi) = 1/4 [E_{\text{slab}}^{\text{unr}}(\text{Ca}) + E_{\text{slab}}^{\text{unr}}(\text{ZrO}) - 8E_{\text{bulk}}], \quad (1)$$

where  $\Psi$  means Ca or  $\text{ZrO}$  termination of  $\text{CaZrO}_3$  (011) surface,  $E_{\text{slab}}^{\text{unr}}(\Psi)$  are the total energies of the unrelaxed Ca- or  $\text{ZrO}$ -terminated  $\text{CaZrO}_3$  (011) slabs,  $E_{\text{bulk}}$  is the total energy per bulk unit cell, and the coefficient of  $1/4$  comes from the event that we create four surfaces due the cleavage procedure. As a next step, we will calculate the relaxation energies for each

of Ca- and  $\text{ZrO}$ -terminated  $\text{CaZrO}_3$  (011) slabs, when both sides of the slabs relax, by means of the following equation:

$$E_{\text{rel}}(\Psi) = 1/2 [E_{\text{slab}}^{\text{rel}}(\Psi) - E_{\text{slab}}^{\text{unr}}(\Psi)], \quad (2)$$

where  $E_{\text{slab}}^{\text{rel}}(\Psi)$  is the slab energy after the geometry relaxation ( $\Psi = \text{Ca}$  or  $\text{ZrO}$ ). The  $\text{CaZrO}_3$  (011) surface energy is equal to a sum of the cleavage and relaxation energies:

$$E_{\text{surf}}(\Psi) = E_{\text{surf}}^{\text{unr}}(\Psi) + E_{\text{rel}}(\Psi), \quad (3)$$

Finally, in case when we cleave the  $\text{CaZrO}_3$  crystal in another way, we got two equal O-terminated  $\text{CaZrO}_3$  (011) surface slabs. Each of them contains 20 atoms. Thereby, we can simplify our calculations, since the unit cell of the nine-plane O-terminated  $\text{CaZrO}_3$  (011) slab contains four bulk unit cells. The surface energy for O-terminated (011) surface is equal to:

$$E_{\text{surf}}(\text{O}) = 1/2 [E_{\text{slab}}^{\text{rel}}(\text{O}) - 4E_{\text{bulk}}], \quad (4)$$

where  $E_{\text{surf}}(\text{O})$  and  $E_{\text{slab}}^{\text{rel}}(\text{O})$  are the O-terminated  $\text{CaZrO}_3$  (011) surface energy and the relaxed O-terminated  $\text{CaZrO}_3$  (011) slab total energy.

### Calculation results for polar $\text{CaZrO}_3$ (011) surfaces

As a first step of our calculations, we calculated, by means of the hybrid B3LYP functional, the  $\text{CaZrO}_3$  bulk lattice constant and found it equal to 4.157 Å. In order to characterize the covalency effects and chemical bonding, we used a classical Mulliken population description for the effective atomic charges  $Q$  and other local properties of  $\text{CaZrO}_3$  electronic structure as defined in Refs. [78, 79]. By means of B3LYP hybrid exchange–correlation functional, our calculated  $\text{CaZrO}_3$  effective bulk atomic charges are equal to (+ 1.787 $e$ ) for the Ca atom, (+ 2.144 $e$ ) for the Zr atom, and (– 1.310 $e$ ) for the O atom. Our calculated  $\text{CaZrO}_3$  bulk bond population of the chemical bonding is largest between Zr and O atoms (+ 0.086 $e$ ). The bond population between Ca and O atoms is more than six times smaller (+ 0.014 $e$ ) than between Zr and O atoms. Finally, the bond population between O and O atoms is even negative (– 0.010 $e$ ), which indicates a small repulsion between O and O atoms in the  $\text{CaZrO}_3$  bulk matrix.

As we explained in “Computational method as well as polar  $\text{CaZrO}_3$  (011) surface models and

energies" section, nonpolar and neutral ZrO-, Ca- and O-terminated (011) surfaces for the CaZrO<sub>3</sub> perovskite can be constructed by us as shown in Fig. 2d–f, respectively. Our calculated atomic displacements obtained by B3LYP hybrid exchange–correlation functional for ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces are shown in Table 1.

**Table 1** Our B3LYP calculated atomic relaxations for the CaZrO<sub>3</sub> (011) surfaces (in per cent of the bulk lattice constant  $a_0$ ) for the three surface terminations ZrO, Ca and O

Layer	Ion	$\Delta z$	$\Delta y$
ZrO-terminated CaZrO <sub>3</sub> (011) surface			
1	Zr	− 6.06	
1	O	+ 4.96	
2	O	− 0.38	
3	Ca	− 3.61	
3	O	− 7.94	
3	Zr	− 0.41	
Ca-terminated CaZrO <sub>3</sub> (011) surface			
1	Ca	− 18.67	
2	O	+ 1.25	
3	Zr	+ 0.25	
3	O	− 0.63	
3	Ca	− 0.14	
O-terminated CaZrO <sub>3</sub> (011) surface			
1	O	− 5.97	− 5.05
2	Zr	+ 0.75	− 2.17
2	Ca	+ 1.78	13.95
2	O	+ 0.67	1.32
3	O	+ 0.51	1.23

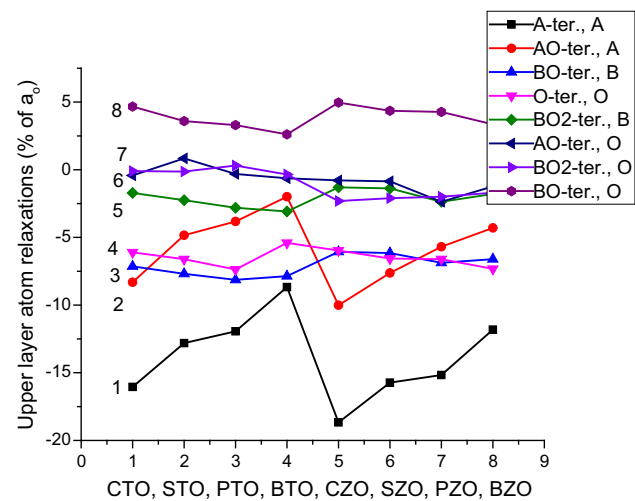
Positive signs correspond to outwards atomic displacements

**Table 2** Our calculated upper-layer atom relaxations for all eight ABO<sub>3</sub> perovskite AO-, A- and O-terminated (011) as well as AO- and BO<sub>2</sub>-terminated (001) surfaces

Term	Atom	CTO	STO	PTO	BTO	CZO	SZO	PZO	BZO
BO (011)	B	− 7.14	− 7.69	− 8.13	− 7.86	− 6.06	− 6.16	− 6.87	− 6.61
	O	+ 4.67	+ 3.59	+ 3.30	+ 2.61	+ 4.96	+ 4.36	+ 4.27	+ 3.35
A (011)	A	− 16.05	− 12.81	− 11.94	− 8.67	− 18.67	− 15.73	− 15.17	− 11.81
O (011)	O	− 6.10	− 6.61	− 7.37	− 5.40	− 5.97	− 6.56	− 6.61	− 7.32
BO <sub>2</sub> (001)	B	− 1.71	− 2.25	− 2.81	− 3.08	− 1.30	− 1.38	− 2.37	− 1.79
	O	− 0.10	− 0.13	+ 0.31	− 0.35	− 2.31	− 2.10	− 1.99	− 1.70
AO (001)	A	− 8.31	− 4.84	− 3.82	− 1.99	− 10.01	− 7.63	− 5.69	− 4.30
	O	− 0.42	+ 0.84	− 0.31	− 0.63	− 0.79	− 0.86	− 2.37	− 1.23

Positive signs correspond to outwards atomic displacements

From the results of our calculations (Table 1), all atoms of the upper CaZrO<sub>3</sub> (011) surface layer relax inward, namely towards the bulk, for all three ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces. The only exception is outward relaxation of ZrO-terminated CaZrO<sub>3</sub> (011) surface upper-layer O atom by 4.96% of the bulk lattice constant  $a_0$ . As we can see from Table 2 and Fig. 3, also for all another our calculated ABO<sub>3</sub> perovskites systematic trend is that all upper-layer atoms for all three (011) terminations relax inward with the exception of BO-terminated



**Figure 3** Our calculated upper-layer atom relaxations for all eight ABO<sub>3</sub> perovskite BO-, A- and O-terminated (011) as well as AO- and BO<sub>2</sub>-terminated (001) surfaces. A-terminated (011) surface A atom relaxation (line 1). AO-terminated (001) surface A (line 2) and O (line 6) atom relaxations. BO-terminated (011) surface B atom (line 3) and O atom (line 8) atom relaxations. O-terminated (011) surface O atom relaxation (line 4). BO<sub>2</sub>-terminated (001) surface B atom (line 5) and O atom (line 7) atom relaxations.

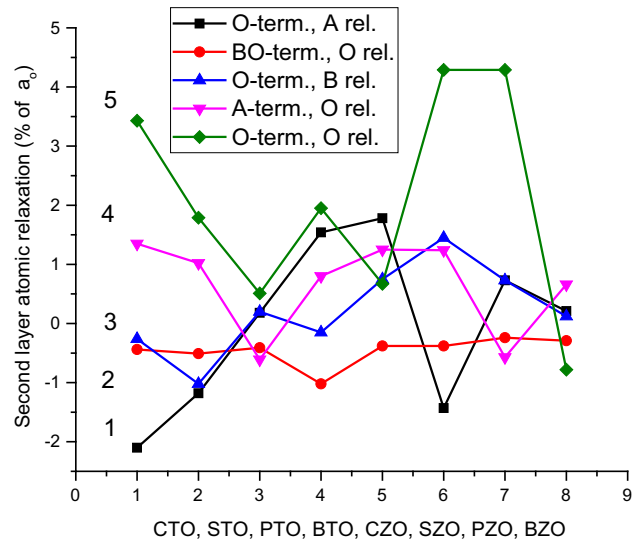
(011) surface upper-layer O atoms. The largest relaxation magnitude between all upper-layer  $\text{CaZrO}_3$  (011) surface atoms exhibits the Ca-terminated (011) surface Ca atom by 18.67% of  $a_0$ . This our calculated Ca atom displacement magnitude (18.67% of  $a_0$ ) is approximately three times larger than the relevant displacement magnitudes for Zr atom (6.06% of  $a_0$ ) on the ZrO-terminated and O atom (5.97% of  $a_0$ ) on the O-terminated  $\text{CaZrO}_3$  polar (011) surfaces. Also for all another  $\text{ABO}_3$  perovskites, the A atom inward relaxation magnitude on A-terminated (011) surface always is larger than the B atom and O atom relaxation magnitudes on BO- and O-terminated  $\text{ABO}_3$  perovskite (011) surfaces (Table 2 and Fig. 3). However it is worth to notice that for the  $\text{BaTiO}_3$  perovskite, the Ba atom inward relaxation (8.67% of  $a_0$ ) on the Ba-terminated  $\text{BaTiO}_3$  (011) surface is only slightly larger than the Ti atom inward relaxation (7.86% of  $a_0$ ) on the TiO-terminated  $\text{BaTiO}_3$  (011) surface (Table 2 and Fig. 3). As we can see from Table 2 and Fig. 3, systematic trend is that the  $\text{ABO}_3$  perovskite (011) surface upper-layer atom relaxation almost always is larger than the (001) surface upper-layer atom relaxation. For  $\text{ABO}_3$  perovskite (011) and (001) terminated surfaces, in most cases the metal atom relaxation magnitudes are larger than the oxygen atom relaxation magnitudes.

All second-layer ZrO-, Ca- and O-terminated  $\text{CaZrO}_3$  (011) surface atoms relax upwards, with the sole exception for O atom on the ZrO-terminated (011) surface (Table 1). Such systematic tendency, mostly upward relaxation of second-layer atoms on BO-, A- and O-terminated (011) surfaces, is common for all eight  $\text{ABO}_3$  perovskites (Table 3 and Fig. 4). Namely, according to our calculations, for CTO, STO, PTO, BTO, CZO, SZO, PZO and BZO perovskite second layers, upwards relax 23 atoms, whereas inwards only 17 atoms (Table 3 and Fig. 4).

Finally, all ZrO-, Ca- and O-terminated  $\text{CaZrO}_3$  (011) surface third-layer atoms relax inwards, with

the exception of Ca-terminated (011) surface third-layer Zr atom and O-terminated (011) surface O atom, which both relax upwards (Table 1). Also for all our eight calculated  $\text{ABO}_3$  perovskite BO-, A- and O-terminated (011) surface third-layer atoms, a large majority, namely 37 atoms, relax inwards, while only 16 atoms relax outwards (Table 4 and Fig. 5).

According to our B3LYP calculations, on the ZrO-terminated  $\text{CaZrO}_3$  (011) surface, the upper-layer Zr atom relax inwards by 6.06% of the  $a_0$ , but the same upper-layer O atom relax outwards by 4.96% (Table 1), creating a large surface rumpling equal to 11.02 (Table 5). On the ZrO-terminated  $\text{CaZrO}_3$  (011) surface, the displacement magnitudes of all atoms in the third layer are larger than in the second-layer and the third-layer O atom displacement magnitude



**Figure 4** Our calculated O-terminated (011) surface A atom relaxations (line 1), BO-terminated (011) surface O atom relaxations (line 2), O-terminated (011) surface B atom relaxations (line 3), A-terminated (011) surface O atom relaxations (line 4), and, finally, O-terminated (011) surface O-atom relaxations (line 5).

**Table 3** Our calculated second-layer atom relaxations for all eight  $\text{ABO}_3$  perovskite BO-, A- and O-terminated (011) surfaces

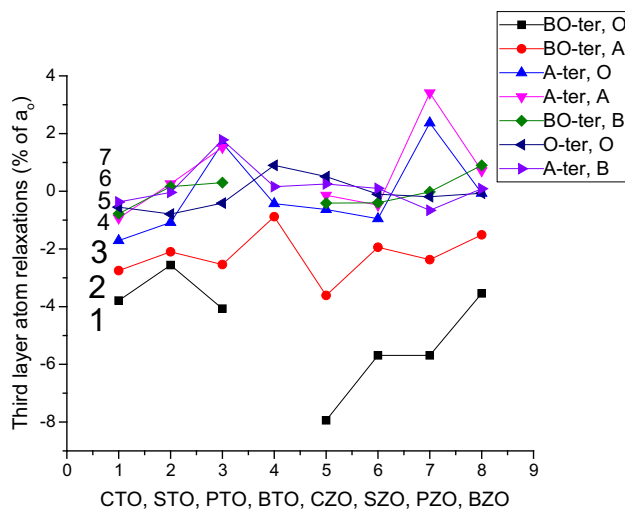
Term	Atom	CTO	STO	PTO	BTO	CZO	SZO	PZO	BZO
BO (011)	O	- 0.44	- 0.51	- 0.41	- 1.02	- 0.38	- 0.38	- 0.24	- 0.29
A (011)	O	+ 1.35	+ 1.02	- 0.61	+ 0.80	+ 1.25	+ 1.24	- 0.57	+ 0.66
O (011)	B	- 0.26	- 1.02	+ 0.20	- 0.15	+ 0.75	+ 1.45	+ 0.73	+ 0.12
	A	- 2.10	- 1.18	+ 0.18	+ 1.54	+ 1.78	- 1.43	+ 0.73	+ 0.21
	O	+ 3.43	+ 1.79	+ 0.51	+ 1.95	+ 0.67	+ 4.29	+ 4.29	- 0.78

Positive signs correspond to outwards atomic displacements

**Table 4** Our calculated third-layer atom relaxations for all eight ABO<sub>3</sub> perovskite AO-, A- and O-terminated (011) surfaces

Term	Atom	CTO	STO	PTO	BTO	CZO	SZO	PZO	BZO
BO (011)	B	- 0.78	+ 0.16	+ 0.30		- 0.41	- 0.40	- 0.02	+ 0.90
	A	- 2.75	- 2.10	- 2.54	- 0.88	- 3.61	- 1.94	- 2.37	- 1.51
	O	- 3.79	- 2.56	- 4.07		- 7.94	- 5.69	- 5.69	- 3.54
A (011)	B	- 0.37	- 0.04	+ 1.78	+ 0.16	+ 0.25	+ 0.10	- 0.66	+ 0.09
	A	- 0.93	+ 0.26	+ 1.52		- 0.14	- 0.48	+ 3.41	+ 0.71
	O	- 1.71	- 1.08	+ 1.67	- 0.43	- 0.63	- 0.95	+ 2.37	- 0.07
O (011)	O	- 0.55	- 0.79	- 0.41	+ 0.90	+ 0.51	- 0.10	- 0.19	- 0.07

Positive signs correspond to outwards atomic displacements



**Figure 5** Our calculated third-layer atom relaxations for all eight ABO<sub>3</sub> perovskite BO-, A- and O-terminated (011) surfaces. BO-terminated (011) surface O atom relaxation (line 1), A atom relaxation (line 2) and B atom relaxation (line 5). A-terminated (011) surface O atom relaxation (line 3), A atom relaxation (line 4) and B atom relaxation (line 7) as well as O-terminated (011) surface O atom relaxation (line 6).

7.94% of  $a_0$  is the largest displacement magnitude between ZrO-terminated (011) surface all three layer atoms (Table 1). Our calculated first interlayer

distance  $\Delta d_{12}$  values (Table 5) show that the reduced distance between the first and second layers for ZrO-terminated CaZrO<sub>3</sub> (011) surface is more than 189 times larger than the corresponding expansion  $\Delta d_{23}$  between the second and third layers. From Table 5, all our eight calculated ABO<sub>3</sub> perovskite BO-terminated (011) surfaces exhibit very large surface rumpling, ranging from 9.96 for BaZrO<sub>3</sub> till 11.81 for CaTiO<sub>3</sub>. For all our eight calculated ABO<sub>3</sub> perovskites, systematic trend is reduction in the interlayer distance  $\Delta d_{12}$ , ranging from 5.68 for CaZrO<sub>3</sub> till 7.72 for PbTiO<sub>3</sub>. Our calculated BO-terminated (011) surface interlayer distance  $\Delta d_{23}$  is reduced for STO, PTO, BTO, PZO and BZO perovskites, but expanded by a very small magnitude for CZO, CTO and SZO perovskites (Table 5).

The O-terminated CaZrO<sub>3</sub> (011) surface has a lower symmetry than the ZrO- and Ca-terminated CaZrO<sub>3</sub> (011) surfaces; therefore, atomic displacements occur not only in the  $z$  direction perpendicular to the surface, but also in the  $y$  direction along the surface. For example, the O atom on the O-terminated CaZrO<sub>3</sub> (011) surface moves inwards, in the  $z$  direction by 5.97% and by a comparable magnitude of 5.05% also along the surface in the  $y$  direction (Table 1). All second-layer O-terminated CaZrO<sub>3</sub> (011) surface,

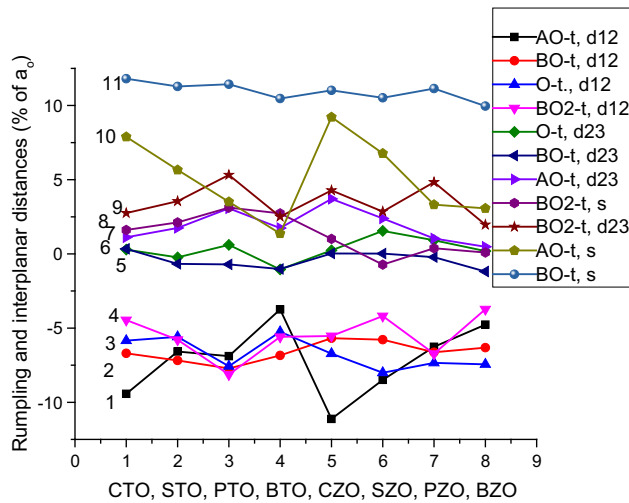
**Table 5** Our calculated surface rumpling  $s$  and relative displacements  $\Delta d_{ij}$  (in per cent of the ABO<sub>3</sub> perovskite bulk lattice constant  $a_0$ ) for the three near-surface planes on the BO- and O-terminated ABO<sub>3</sub> perovskite (011) surfaces

Material	BO-terminated (011) surface			O-terminated (011) surface	
	$s$	$\Delta d_{12}$	$\Delta d_{23}$	$\Delta d_{12}$	$\Delta d_{23}$
CaZrO <sub>3</sub> (this paper)	11.02	- 5.68	0.03	- 6.72	0.24
CaTiO <sub>3</sub> [11]	11.81	- 6.70	0.34	- 5.84	0.29
SrTiO <sub>3</sub> [10]	11.28	- 7.18	- 0.67	- 5.59	- 0.23
PbTiO <sub>3</sub> [9]	11.43	- 7.72	- 0.71	- 7.57	0.61
BaTiO <sub>3</sub> [9]	10.47	- 6.84	- 1.02	- 5.25	- 1.05
SrZrO <sub>3</sub> [62]	10.52	- 5.78	0.02	- 8.01	1.55
PbZrO <sub>3</sub> [62]	11.14	- 6.63	- 0.22	- 7.34	0.92
BaZrO <sub>3</sub> [64]	9.96	- 6.32	- 1.19	- 7.44	0.19



atoms relax outwards in the *z* direction by 0.75% for Zr atom, 1.78% for Ca atom and 0.67% for O atom. It is worth to notice that the second-layer Ca atom exhibits the largest displacement magnitude among all our calculated CaZrO<sub>3</sub> atoms along the surface in the *y* direction by 13.95%. The third-layer O atom, same as all three second-layer atoms, also moves outward in the *z* direction, but by a small displacement magnitude of 0.51%. From Table 5, for the O-terminated CaZrO<sub>3</sub> (011) surface there is a substantial contraction of the interlayer distance  $\Delta d_{12}$  on the *z* direction by 6.72% and only a very small expansion of  $\Delta d_{23}$  by 0.24%. Also for all other our calculated ABO<sub>3</sub> perovskites a large contraction of the interlayer distance  $\Delta d_{12}$  for O-terminated (011) surface occurs ranging from 5.25% for BTO till 8.01% for SZO. For most of ABO<sub>3</sub> perovskite O-terminated

(011) surfaces, like CZO, CTO, PTO, SZO, PZO and BZO, there are a small expansion of the interlayer distance  $\Delta d_{23}$  observed from our calculations, whereas for STO and BTO perovskites the interlayer distance  $\Delta d_{23}$  contracts. Comparison of surface rumpling *s* and interlayer distances  $\Delta d_{ij}$  for ABO<sub>3</sub> perovskite (011) and (001) surfaces is depicted in Fig. 6. As we can see from Fig. 6, surface rumplings *s* for ABO<sub>3</sub> perovskite BO-terminated (011) surfaces are always larger than the relevant surface rumplings for AO and especially BO<sub>2</sub>-terminated ABO<sub>3</sub> perovskite (001) surfaces. ABO<sub>3</sub> perovskite interlayer distances  $\Delta d_{12}$  are always reduced for their BO-terminated (011) as well as BO<sub>2</sub> and especially AO-terminated (001) surfaces (Fig. 6). In contrast, the interlayer distances  $\Delta d_{23}$  are always expanded for ABO<sub>3</sub> perovskite (001) surfaces, but they may be either expanded or reduced for BO- and O-terminated (011) surfaces (Fig. 6).



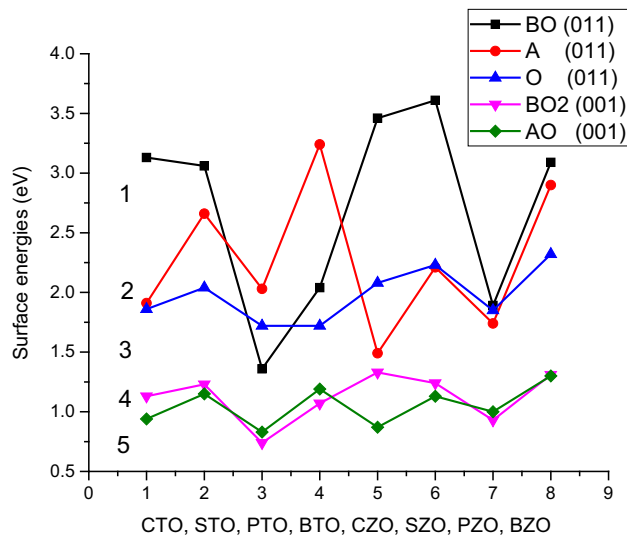
**Figure 6** Our calculated surface rumplings *s* and interplanar distances  $\Delta d_{12}$  and  $\Delta d_{23}$  for BO (lines 2, 6, 11)- and O (lines 3, 5)-terminated ABO<sub>3</sub> perovskite polar (011) surfaces as well as for BO<sub>2</sub> (lines 4, 8, 9)- and AO (lines 1, 7, 10)-terminated neutral (001) surfaces.

Our calculated surface energies of the relaxed ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces are presented in Table 6 and plotted in Fig. 7 together with another ABO<sub>3</sub> perovskite (011) as well as for comparison purpose also BO<sub>2</sub>- and AO-terminated ABO<sub>3</sub> perovskite (001) surface energies [55]. The CaZrO<sub>3</sub> (011) surface energies were computed by us using Eqs. (1)–(4). Unlike the ABO<sub>3</sub> perovskite (001) surfaces [55], from Table 6 we can see that different terminations of the ABO<sub>3</sub> perovskite (011) surface, as a rule, lead to considerable difference in the surface energies. For example, the our calculated surface energy difference between ZrO (3.46 eV)- and Ca (1.49 eV)-terminated CaZrO<sub>3</sub> (011) surfaces is really huge and equal to 1.97 eV, which is more than any of ZrO<sub>2</sub> (1.33 eV)- or CaO (0.87 eV)-terminated CaZrO<sub>3</sub> (001) surface energies. Among all three of our B3LYP calculated CaZrO<sub>3</sub> (011) surfaces, the Ca-terminated CaZrO<sub>3</sub> (011) surface has the lowest surface energy

**Table 6** Our calculated surface energies for CaZrO<sub>3</sub>, CaTiO<sub>3</sub> [11], SrTiO<sub>3</sub> [10], PbTiO<sub>3</sub> [9], BaTiO<sub>3</sub> [9], SrZrO<sub>3</sub> [66], PbZrO<sub>3</sub> [66] and BaZrO<sub>3</sub> [68] (011) surfaces (in electron volt per surface cell). Our

earlier calculated ABO<sub>3</sub> perovskite (001) surface energies are listed for comparison purpose [9–11, 66, 68, 75]

Term	$E_{surf}$	CTO	STO	PTO	BTO	CZO	SZO	PZO	BZO
BO	(011)	3.13	3.06	1.36	2.04	3.46	3.61	1.89	3.09
A	(011)	1.91	2.66	2.03	3.24	1.49	2.21	1.74	2.90
O	(011)	1.86	2.04	1.72	1.72	2.08	2.23	1.85	2.32
BO <sub>2</sub>	(001)	1.13	1.23	0.74	1.07	1.33	1.24	0.93	1.31
AO	(001)	0.94	1.15	0.83	1.19	0.87	1.13	1.00	1.30



**Figure 7** Our calculated  $ABO_3$  perovskite surface energies for polar BO (line 1)-, A (line 2)- and O (line 3)-terminated (011) as well as neutral  $BO_2$  (line 4)- and AO (line 5)-terminated (001) surfaces.

equal to 1.49 eV, which only slightly by 0.16 eV exceeds the surface energy for  $ZrO_2$ -terminated  $CaZrO_3$  (001) surface [75]. The surface energy for the Ca-terminated  $CaZrO_3$  (011) surface 1.49 eV is more than two times smaller than the  $ZrO$ -terminated  $CaZrO_3$  (011) surface energy 3.46 eV (Table 6). The O-terminated  $CaZrO_3$  (011) surface energy 2.08 eV is very close to the sum of  $ZrO_2$  (1.33 eV)- and CaO (0.87 eV)-terminated  $CaZrO_3$  (001) surface energies equal to 2.20 eV.

In Table 7, we collected our B3LYP calculated interatomic distances  $R$  as well as chemical bond populations  $P$  for the  $ZrO$ , Ca and O terminations of the  $CaZrO_3$  (011) surface. The most important effect observed here is a strong increase in the  $Zr-O$  chemical bonding covalency near the  $ZrO$ - and O-terminated  $CaZrO_3$  (011) surface as compared to both the  $CaZrO_3$  bulk (0.086 $e$ ) and even to the  $ZrO_2$ -terminated  $CaZrO_3$  (001) surface 0.102 $e$ . For the O-terminated  $CaZrO_3$  (011) surface, the O(I)- $Zr$ (II) chemical bond population is equal to 0.130 $e$ , which is by 0.044 $e$  larger than the  $CaZrO_3$  bulk  $Zr-O$  bond population as well as by 0.028 $e$  larger than the relevant  $ZrO_2$ -terminated  $CaZrO_3$  (001) surface chemical bond population. For our calculated  $ZrO$ -terminated  $CaZrO_3$  (011) surface, the  $Zr-O$  chemical bond population is larger in the direction perpendicular to the  $ZrO$ -terminated (011) surface 0.240 $e$  than in the plane 0.138 $e$  (Table 7). As we can see from Table 8 and

**Table 7** Our calculated A–B chemical bond populations  $P$  (in  $e$ ) as well as interatomic distances  $R$  (in Å) on  $CaZrO_3$  (011) surfaces

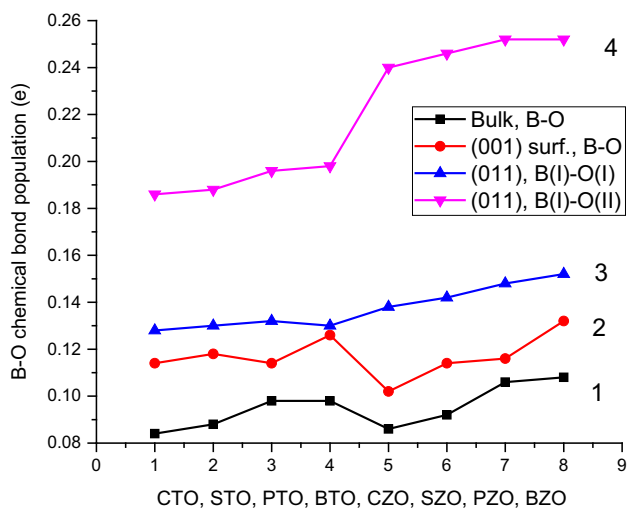
CaZrO <sub>3</sub> (011) surface			
Atom A	Atom B	$P$	$R$
ZrO-terminated CaZrO <sub>3</sub> (011) surface			
Zr(I)	O(I)	0.138	2.128
	O(II)	0.240	1.919
O(II)	Zr(III)	0.114	2.079
	Ca(III)	0.018	3.009
Zr(III)	O(III)	0.012	3.108
	Ca(III)	0.002	3.603
	O(III)	0.114	2.102
	O(IV)	0.082	2.067
Ca(III)	O(III)	0.016	2.945
	O(IV)	0.016	2.867
O(III)	O(IV)	– 0.052	2.789
Ca-terminated CaZrO <sub>3</sub> (011) surface			
Ca(I)	O(II)	0.028	2.625
O(II)	Ca(III)	0.022	2.969
	Zr(III)	0.078	2.108
Ca(III)	O(III)	– 0.010	2.979
	O(III)	0.012	2.94
Zr(III)	O(IV)	0.014	2.936
	O(III)	0.052	2.079
O(III)	Ca(III)	0.002	3.600
	O(IV)	0.112	2.086
O(III)	O(IV)	– 0.012	2.927
O-terminated CaZrO <sub>3</sub> (011) surface			
O(I)	Ca(II)	0.022	2.470
	Zr(II)	0.130	1.986
Ca(II)	O(II)	– 0.010	2.959
	O(II)	– 0.012	2.415
Zr(II)	Zr(II)	– 0.002	3.078
	O(III)	0.186	1.989
O(II)	O(III)	– 0.002	2.945
Ca(II)	O(III)	0.006	2.743
O(III)	O(IV)	– 0.014	2.939
	Zr(IV)	0.066	2.130
	Ca(IV)	0.012	2.925

Symbols I–IV denote the number of each plane enumerated from the surface. The nearest-neighbour  $Zr-O$  distance is 2.0785 Å in  $CaZrO_3$  bulk

Fig. 8, systematic trend is that the B–O chemical bond population in all our eight calculated  $ABO_3$  perovskite bulk as a rule are smaller than near their (001) as well as especially (011) surfaces. It is worth to notice that for all eight  $ABO_3$  perovskites (Table 8 and Fig. 8), the BO-terminated (011) surface B–O

**Table 8** Our calculated eight ABO<sub>3</sub> perovskite bulk, BO<sub>2</sub>-terminated (001) surface as well as BO-terminated (011) surface B–O chemical bond populations in the plane (B(I)–O(I)) and in the direction perpendicular to the (011) surface (B(I)–O(II))

	CZO	CTO	STO	PTO	BTO	SZO	PZO	BZO
Bulk (B–O)	0.086	0.084	0.088	0.098	0.098	0.092	0.106	0.108
(001) (B–O)	0.102	0.114	0.118	0.114	0.126	0.114	0.116	0.132
(011) (B(I)–O(I))	0.138	0.128	0.130	0.132	0.130	0.142	0.148	0.152
(011) (B(I)–O(II))	0.240	0.186	0.188	0.196	0.198	0.246	0.252	0.252



**Figure 8** Our calculated B–O chemical bond populations for ABO<sub>3</sub> perovskite bulk (line 1), BO<sub>2</sub>-terminated (001) surfaces (line 2) as well as B(I)–O(I) (line 3) and B(I)–O(II) (line 4) chemical bond populations for the BO-terminated ABO<sub>3</sub> perovskite (011) surfaces.

chemical bond population is larger in the direction perpendicular to the BO-terminated (011) surface than in the plane.

In Table 9 we listed our calculated CaZrO<sub>3</sub> effective Mulliken charges *Q* as well as their changes  $\Delta Q$  in comparison with the respective bulk values for near the surface atoms for the ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces. Firstly, on the ZrO-terminated CaZrO<sub>3</sub> (011) surface, the effective Mulliken charge on the first surface layer Zr atom (+ 2.178*e*) is slightly increased by + 0.034*e* in comparison with the relevant bulk value. The third-layer metal atom Ca loses – 0.033*e* charge, while the other third-layer metal atom Zr gains almost the same amount of charge, namely 0.039*e*. It is interesting to notice that the O atoms in the first, second, third and fourth surface layers have reduced charges making them less negative. The largest O atom charge change equal to (0.178*e*) is observed for the CaZrO<sub>3</sub> subsurface O atoms, thereby giving a large positive charge

**Table 9** Our B3LYP calculated Mulliken atomic charges *Q* (in *e*) and changes in atomic charges  $\Delta Q$  with respect to the CaZrO<sub>3</sub> bulk charges (in *e*) on the ZrO-, Ca- and O-terminated CaZrO<sub>3</sub> (011) surfaces

CaZrO <sub>3</sub> (011) surface		
Atom	<i>Q</i>	$\Delta Q$
ZrO-terminated CaZrO <sub>3</sub> (011) surface		
Zr(I)	+ 2.178	+ 0.034
O(I)	– 1.263	+ 0.047
O(II)	– 1.132	+ 0.178
Ca(III)	+ 1.754	– 0.033
Zr(III)	+ 2.183	+ 0.039
O(III)	– 1.283	+ 0.027
O(IV)	– 1.300	+ 0.01
Ca-terminated CaZrO <sub>3</sub> (011) surface		
Ca(I)	+ 1.686	– 0.101
O(II)	– 1.467	– 0.157
Ca(III)	+ 1.778	– 0.009
Zr(III)	+ 2.177	+ 0.033
O(III)	– 1.394	– 0.084
O(IV)	– 1.312	– 0.002
O-terminated CaZrO <sub>3</sub> (011) surface		
O(I)	– 1.314	– 0.004
Ca(II)	+ 1.734	– 0.053
Zr(II)	+ 2.173	+ 0.029
O(II)	– 1.327	– 0.017
O(III)	– 1.297	+ 0.013
Ca(IV)	+ 1.775	– 0.012
Zr(IV)	+ 2.153	+ 0.009
O(IV)	– 1.291	+ 0.019

The CaZrO<sub>3</sub> bulk Mulliken charges are equal to 1.787*e* for Ca, 2.144*e* for Zr, and – 1.310*e* for O

change of 0.356*e* for the whole subsurface layer (Table 9).

On the CaZrO<sub>3</sub> Ca-terminated (011) surface, the only positive charge change is observed for the third-layer Zr atom, where the Zr atom charge increases by 0.033*e* from the bulk value 2.144*e* till 2.177*e*. The largest charge changes are for the subsurface O ion (0.157*e*) as well as surface Ca ion (0.101*e*). Thereby,

our calculated largest overall charge change occurs in the Ca-terminated  $\text{CaZrO}_3$  (011) surface subsurface layer ( $0.314e$ ). On the O-terminated  $\text{CaZrO}_3$  (011) surface, the largest charge change between all atoms is observed for the subsurface Ca atom equal to  $0.053e$ , whereas the total charge density change in the fourth layer is almost negligible and equal to only  $0.016e$ .

## Summary and conclusions

Based on our current ab initio B3LYP calculations for polar  $\text{CaZrO}_3$  (011) surfaces as well as for comparison purposes listed previous B3PW and B3LYP calculations [9–11, 66, 68, 75] for CTO, STO, PTO, BTO, SZO, PZO and BZO (011) surfaces, the following systematic trends for  $\text{ABO}_3$  perovskite polar (011) surfaces were detected:

1. For  $\text{ABO}_3$  perovskite polar (011) surfaces, systematic trend is that most of upper-layer atoms relax inwards, with only exception of all eight  $\text{ABO}_3$  perovskite BO-terminated (011) surface O atoms. Twenty three of BO-, A- and O-terminated  $\text{ABO}_3$  perovskite (011) surface second-layer atoms relax outwards, whereas 17 second-layer atoms inwards. Finally, a large majority of (011) surface third-layer atoms, namely 37 atoms, relax inwards, while only 16 remaining atoms relax outwards. It is worth to notice, that inward relaxation of upper-layer atoms, upwards relaxation of second-layer atoms and, again, inwards relaxation of third-layer atoms were even more strongly pronounced effect for the  $\text{ABO}_3$  perovskite (001) surfaces [55].
2. The strongest relaxation magnitude between all BO-, A-, and O-terminated  $\text{ABO}_3$  perovskite (011) surfaces always exhibit the A-terminated (011) surface upper-layer A atoms. The BO-terminated  $\text{ABO}_3$  perovskite (011) surface third-layer atoms, in most cases, exhibit larger relaxation magnitude than the second-layer atoms.
3. The BO-terminated  $\text{ABO}_3$  perovskite (011) surface upper layer rather large metal atom inwards relaxation as well as the same upper-layer oxygen atom outwards relaxation leads to a considerable rumpling of the outermost plane ranging from 9.96 for BZO till 11.81 for CTO. For all our eight calculated  $\text{ABO}_3$  perovskite BO and O-terminated (011) surfaces, a systematic trend is a strong contraction of the interlayer distance  $\Delta d_{12}$ , ranging from 5.68 (CZO) till 7.72 (PTO) for BO-terminated (011) surface as well as from 5.25 (BTO) till 8.01 (SZO) for O-terminated  $\text{CaZrO}_3$  (011) surface. For all eight  $\text{ABO}_3$  perovskites and for both BO and O terminations, the interlayer distance  $\Delta d_{23}$  exhibits either very small expansion for ZrO-terminated (011) surface for CZO, CTO, SZO perovskites ranging from 0.03 (CZO) till 0.34 (CTO) and for O-terminated (011) surfaces small expansion is observed for CZO, CTO, PTO, SZO, PZO and BZO ranging from 0.19 BZO till 1.55 (CZO), or a small contraction for remaining of eight  $\text{ABO}_3$  perovskites.
4. Unlike the  $\text{ABO}_3$  perovskite (001) surfaces [55] different BO, A and O terminations of the  $\text{ABO}_3$  perovskite (011) surface, as a rule, usually, lead to a considerable difference in the surface energies. Our calculated eight  $\text{ABO}_3$  perovskite (011) surface energies are always larger than the (001) surface energies. Although in some cases, the  $\text{ABO}_3$  perovskite (011) and (001) surface energies are really close, as for example the  $\text{CaZrO}_3$  perovskite Ca-terminated  $\text{CaZrO}_3$  (011) surface energy (1.49 eV) only by 0.16 eV exceeds the ZrO<sub>2</sub>-terminated  $\text{CaZrO}_3$  (001) surface energy equal to 1.33 eV.
5. The B–O chemical bond population in  $\text{ABO}_3$  perovskites increase in direction from the bulk, ranging from  $0.084e$  (CTO) till  $0.108e$  (BZO) towards the BO<sub>2</sub>-terminated (001) surface, ranging from  $0.102e$  (CZO) till  $0.132e$  (BZO) and reach its maximum for BO-terminated  $\text{ABO}_3$  perovskite (011) surface. Our calculated BO-terminated (011) surface B(I)–O(I) in plane chemical bond population is in the range from  $0.128e$  (CTO) till  $0.152e$  (BZO). Finally, the maximal chemical bond population value is for the direction perpendicular to the BO-terminated  $\text{ABO}_3$  perovskite (011) surface, where B(I)–O(II) values are in the range from  $0.186e$  (CTO) till  $0.252e$  (PZO, BZO).

## Acknowledgements

Financial support via Latvian-Ukrainian Joint Research Project No. LV-UA/2018/2 for A. I. Popov,

Latvian Council of Science Project No. 2018/2-0083 “Theoretical prediction of hybrid nanostructured photocatalytic materials for efficient water splitting” for R. I. Eglitis and J. Kleperis as well as ERAF project No. 1.1.1.1/18/A/073 for R. I. Eglitis and J. Purans is greatly acknowledged.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

## References

- [1] Noguera C (2000) Polar oxide surfaces. *J Phys Condens Matter* 12:R367–R410
- [2] Goniakowski J, Finocchi F, Noguera C (2008) Polarity of oxide surfaces and nanostructures. *Rep Prog Phys* 71:016501
- [3] Sanna S, Schmidt WG (2017) LiNbO<sub>3</sub> surfaces from a microscopic perspective. *J Phys Condens Matter* 29:413001
- [4] Dawber M, Rabe KM, Scott JF (2005) Physics of thin-film ferroelectric oxides. *Rev Mod Phys* 77:1083–1130
- [5] Ribeiro RAP, Andrés J, Longo E, Lazaro SR (2018) Magnetism and multiferroic properties at MnTiO<sub>3</sub> surfaces: a DFT study. *Appl Surf Sci* 452:463–472
- [6] Ribeiro RAP, Lazaro SR, Gatti C (2016) The role of exchange–correlation functional on the description of multiferroic properties using density functional theory: the ATiO<sub>3</sub> (A = Mn, Fe, Ni) case study. *RSC Adv* 6:101216–101225
- [7] Liu ZQ, Liu JH, Biegalski MD, Hu JM, Shang L, Ji Y, Wang JM, Hsu SL, Wong AT, Cordill MJ, Gludovatz B, Marker C, Yan H, Feng ZX, You L, Lin MW, Ward TZ, Liu ZK, Jiang CB, Chen LQ, Ritchie RO, Christen HM, Ramesh R (2018) Electrically reversible cracks in an intermetallic film controlled by an electric field. *Nat Commun* 9:41
- [8] Cohen RE (1992) Origin of ferroelectricity in perovskite oxides. *Nature* 358:136–138
- [9] Eglitis RI, Vanderbilt D (2007) Ab initio calculations of BaTiO<sub>3</sub> and PbTiO<sub>3</sub> (001) and (011) surface structure. *Phys Rev B* 76:155439
- [10] Eglitis RI, Vanderbilt D (2008) First-principles calculations of atomic and electronic structure of SrTiO<sub>3</sub> (001) and (011) surfaces. *Phys Rev B* 77:195408
- [11] Eglitis RI, Vanderbilt D (2008) Ab initio calculations of the atomic and electronic structure of CaTiO<sub>3</sub> (001) and (011) surfaces. *Phys Rev B* 78:155420
- [12] Yukawa R, Ozawa K, Yamamoto S, Liu RY, Matsuda I (2015) Anisotropic effective mass approximation model to calculate multiple subband structures at wide-gap semiconductor surfaces: application to accumulation layers of SrTiO<sub>3</sub> and ZnO. *Surf Sci* 641:224–230
- [13] Kronik L, Shapira Y (1999) Surface photovoltage phenomena: theory, experiment, and applications. *Surf Sci Rep* 37:1–206
- [14] Zhu Y, Salvador PA, Rohrer GS (2017) Controlling the termination and photochemical reactivity of the SrTiO<sub>3</sub> (110) surface. *Phys Chem Chem Phys* 19:7910–7918
- [15] Janesko BG, Jones SI (2017) Quantifying the delocalization of surface and bulk *F*-centers. *Surf Sci* 659:9–15
- [16] Kotomin EA, Eglitis RI, Maier J, Heifets E (2001) Calculations of the atomic and electronic structure for SrTiO<sub>3</sub> perovskite thin films. *Thin Solid Films* 400:76–80
- [17] Koirala P, Gulec A, Marks LD (2017) Surface heterogeneity in KTaO<sub>3</sub> (001). *Surf Sci* 657:15–19
- [18] Piskunov S, Eglitis RI (2015) First principles hybrid DFT calculations of BaTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) interface. *Solid State Ion* 274:29–33
- [19] Carrasco J, Illas F, Lopez N, Kotomin EA, Zhukovskii YF, Evarestov RA, Mastrokov YA, Piskunov S, Maier J (2006) First-principles calculations of the atomic and electronic structure of *F* centers in the bulk and on the (001) surface of SrTiO<sub>3</sub>. *Phys Rev B* 73:064106
- [20] Li D, Zhao MH, Garra J, Kolpak AM, Rappe AM, Bonnell DA, Vohs JM (2008) Direct in situ determination of the polarization dependence of physisorption on ferroelectric surfaces. *Nat Mater* 7:473–477
- [21] Fong DD, Kolpak AM, Eastman JA, Streiffer SK, Fuoss PH, Stephenson GB, Thompson C, Kim DM, Choi KJ, Eom CB, Grinberg I, Rappe AM (2006) Stabilization of monodomain polarization in ultrathin PbTiO<sub>3</sub> films. *Phys Rev Lett* 96:127601
- [22] Eglitis RI, Piskunov S, Zhukovskii YF (2016) Ab initio calculations of PbTiO<sub>3</sub>/SrTiO<sub>3</sub> (001) heterostructures. *Phys Status Solidi C* 13:913–920
- [23] Kolpak AM, Li D, Shao R, Rappe AM, Bonnell DA (2008) Evolution of the structure and thermodynamic stability of the BaTiO<sub>3</sub> (001) surface. *Phys Rev Lett* 101:036102
- [24] Piskunov S, Eglitis RI (2016) Comparative ab initio calculations of SrTiO<sub>3</sub>/BaTiO<sub>3</sub> and SrZrO<sub>3</sub>/PbZrO<sub>3</sub> (001) heterostructures. *Nucl Instrum Methods Phys Res Sect B Beam Interact Mater Atoms* 374:20–23
- [25] Gerhold S, Riva M, Yildiz B, Schmid M, Diebold U (2016) Adjusting island density and morphology of the SrTiO<sub>3</sub> (110)-(4 × 1) surface: pulsed laser deposition combined with scanning tunnelling microscopy. *Surf Sci* 651:76–83
- [26] Jia W, Vikhnin VS, Liu H, Kapphan S, Eglitis R, Usvyat D (1999) Critical effects in optical response due to charge transfer vibronic excitons and their structure in perovskite like systems. *J Lumin* 83–84:109–113

- [27] Farlenkov AS, Ananyev MV, Eremin VA, Porotnikova NM, Kurumchin EK, Melekh BT (2016) Oxygen isotope exchange in doped calcium and barium zirconates. *Solid State Ion* 290:108–115
- [28] Scott JF (2000) *Ferroelectric memories*. Springer, Berlin
- [29] Lines ME, Glass AM (1977) *Principles and applications of ferroelectrics and related materials*. Clarendon, Oxford
- [30] Anan'ev MV, Bershetskaya NM, Plaksin SV, Kurumchin EK (2012) Phase equilibriums, oxygen exchange kinetics and diffusion in oxides  $\text{CaZr}_{1-x}\text{Sc}_x\text{O}_{3-x/2-\delta}$ . *Russ J Electrochem* 48:879–886
- [31] Antonova EP, Ananyev MV, Porotnikova NM, Kurumchin EK (2016) Oxygen isotope exchange and electrical conductivity of  $\text{CaZr}_{1-x}\text{Sc}_x\text{O}_{3-x/2}$ . *J Solid State Electrochem* 20:1497–1500
- [32] Lyagaeva YG, Medvedev DA, Demin AK, Yaroslavtseva TV, Plaksin SV, Porotnikova NM (2014) Specific features of preparation of dense deramic based on barium zirconate. *Semiconductors* 48:1353–1358
- [33] Savchin VP, Popov AI, Aksimentyeva OI, Klym H, Horbenko YY, Serga V, Moskina A, Karbovnyk I (2016) Cathodoluminescence characterization of polystyrene- $\text{BaZrO}_3$  hybrid composites. *Low Temp Phys* 42:760–763
- [34] Aksimentyeva OI, Savchyn VP, Dyakonov VP, Piechota S, Horbenko YY, Opainych IY, Demchenko PY, Popov A, Szymczak H (2014) Modification of polymer-magnetic nanoparticles by luminescent and conducting substances. *Mol Cryst Liq Cryst* 590:35–42
- [35] Ceder G (1998) Computational materials science—predicting properties from scratch. *Science* 280:1099–1100
- [36] Ceder G, Chiang YM, Sadoway DR, Aydinol MK, Jang YI, Huang B (1998) Identification of cathode materials for lithium batteries guided by first-principles calculations. *Nature* 392:694–696
- [37] Eglitis RI, Borstel G (2005) Towards a practical rechargeable 5 V Li ion battery. *Phys Status Solidi A* 202:R13–R15
- [38] Eglitis RI (2015) Theoretical prediction of the 5 V rechargeable Li ion battery using  $\text{Li}_2\text{CoMn}_3\text{O}_8$  as a cathode. *Phys Scr* 90:094012
- [39] Arrigoni M, Kotomin EA, Maier J (2017) First-principles study of perovskite ultrathin films: stability and confinement effects. *Isr J Chem* 57:509–521
- [40] Arrigoni M, Bjørnheim TS, Kotomin EA, Maier J (2016) First principles study of confinement effects for oxygen vacancies in  $\text{BaZrO}_3$  (001) ultra-thin films. *Phys Chem Chem Phys* 18:9902–9908
- [41] Iles N, Finocchi F, Khodja KD (2010) A systematic study of ideal and double layer reconstructions of  $\text{ABO}_3$  (001) surfaces ( $A = \text{Sr}, \text{Ba}$ ;  $B = \text{Ti}, \text{Zr}$ ). *J Phys Condens Matter* 22:305001
- [42] Aballe L, Matencio S, Foerster M, Barrena E, Sanchez F, Fontcuberta J, Ocal C (2015) Instability and surface potential modulation of self-patterned (001)  $\text{SrTiO}_3$  surfaces. *Chem Mater* 27:6198–6204
- [43] Goh ES, Ong LH, Yoon TL, Chew KH (2016) Structural relaxation of  $\text{BaTiO}_3$  slab with tetragonal (100) surface: ab-initio comparison of different thickness. *Curr Appl Phys* 16:1491–1497
- [44] Eglitis RI (2015) Ab initio hybrid DFT calculations of  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{SrZrO}_3$  and  $\text{PbZrO}_3$  (111) surfaces. *Appl Surf Sci* 358:556–562
- [45] Zhuang HL, Ganesh P, Cooper VR, Xu H, Kent PRC (2014) Understanding the interactions between oxygen vacancies at  $\text{SrTiO}_3$  (001) surfaces. *Phys Rev B* 90:064106
- [46] Borstel G, Eglitis RI, Kotomin EA, Heifets E (2003) Modelling of defects and surfaces in perovskite ferroelectrics. *Phys Status Solidi B* 236:253–264
- [47] Lee YL, Morgan D (2015) Ab initio defect energetics of perovskite (001) surfaces for solid oxide fuel cells. A comparative study of  $\text{LaMnO}_3$  versus  $\text{SrTiO}_3$  and  $\text{LaAlO}_3$ . *Phys Rev B* 91:195430
- [48] Luo B, Wang X, Tian E, Li G, Li L (2015) Structural and electronic properties of cubic  $\text{KNbO}_3$  (001) surfaces: a first-principles study. *Appl Surf Sci* 351:558–564
- [49] Eglitis RI (2013) Ab initio calculations of the atomic and electronic structure of  $\text{BaZrO}_3$  (111) surfaces. *Solid State Ion* 230:43–47
- [50] Brik MG, Ma CG, Krasnenko V (2013) First-principles calculations of the structural and electronic properties of the cubic  $\text{CaZrO}_3$  (001) surfaces. *Surf Sci* 608:146–153
- [51] Pilania G, Ramprasad R (2010) Adsorption of atomic oxygen on cubic  $\text{PbTiO}_3$  and  $\text{LaMnO}_3$  (001) surfaces: a density functional theory study. *Surf Sci* 604:1889–1893
- [52] Cord B, Courths R (1985) Electronic study of  $\text{SrTiO}_3$  (001) surfaces by photoemission. *Surf Sci* 162:34–38
- [53] Dejneka A, Tyunina M, Narkilahti J, Levoska J, Chvostova D, Jastrubik L, Trepakov VA (2010) Tensile strain induced changes in the optical spectra of  $\text{SrTiO}_3$  epitaxial thin films. *Phys Solid State* 52:2082–2089
- [54] Erdman N, Poepelmeier KR, Asta M, Warschkow O, Ellis DE, Marks LD (2002) The structure and chemistry of the  $\text{TiO}_2$  rich surface of  $\text{SrTiO}_3$  (001). *Nature* 419:55–58
- [55] Eglitis RI, Popov AI (2018) Systematic trends in (001) surface ab initio calculations of  $\text{ABO}_3$  perovskites. *J Saudi Chem Soc* 22:459–468
- [56] Eglitis RI (2014) Ab initio calculations of  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{PbTiO}_3$ ,  $\text{CaTiO}_3$ ,  $\text{SrZrO}_3$ ,  $\text{PbZrO}_3$  and  $\text{BaZrO}_3$  (001), (011) and (111) surfaces as well as  $F$  centers, polarons, KTN solid solutions and Nb impurities therein. *Int J Mod Phys* 28:1430009

- [57] Zhang JM, Cui J, Xu KW, Ji V, Man ZY (2007) Ab initio modelling of  $\text{CaTiO}_3$  (110) polar surfaces. *Phys Rev B* 76:115426
- [58] Heifets E, Kotomin EA, Maier J (2000) Semiempirical simulations of surface relaxation for perovskite titanates. *Surf Sci* 462:19–35
- [59] Bottin F, Finocchi F, Noguera C (2003) Stability and electronic structure of the  $(1 \times 1)$   $\text{SrTiO}_3$  (110) polar surfaces by first-principles calculations. *Phys Rev B* 68:035418
- [60] Heifets E, Goddard WA, Kotomin EA, Eglitis RI, Borstel G (2004) Ab initio calculations of the  $\text{SrTiO}_3$  (110) polar surface. *Phys Rev B* 69:035408
- [61] Enterkin JA, Subramanian AK, Russell BC, Castell MR, Poeppelmeier KR, Marks LD (2010) A homologous series of structures on the surface of  $\text{SrTiO}_3$  (110). *Nat Mater* 9:245–248
- [62] Zhang GX, Xie Y, Yu HT, Fu HG (2009) First-principles calculations of the stability and electronic properties of the  $\text{PbTiO}_3$  (110) polar surface. *J Comput Chem* 30:1785–1798
- [63] Zhang JM, Pang Q, Xu KW, Ji V (2009) First-principles study of the (110) polar surface of cubic  $\text{PbTiO}_3$ . *Comput Mater Sci* 44:1360–1365
- [64] Xie Y, Yu HT, Zhang GH, Fu HG, Sun JZ (2007) First-principles investigation of stability and structural properties of the  $\text{BaTiO}_3$  (110) polar surface. *J Phys Chem C* 111:6343–6349
- [65] Wang J, Tang G, Wu XS (2012) Thermodynamic stability of  $\text{BaTiO}_3$  (110) surfaces. *Phys Status Solidi B* 249:796–800
- [66] Eglitis RI, Rohlfing M (2010) First-principles calculations of the atomic and electronic structure of  $\text{SrZrO}_3$  and  $\text{PbZrO}_3$  (001) and (011) surfaces. *J Phys Condens Matter* 22:415901
- [67] Chen H, Xie Y, Zhang GH, Yu HT (2014) A first-principles investigation of the stability and electronic properties of  $\text{SrZrO}_3$  (110)  $(1 \times 1)$  polar terminations. *J Phys Condens Matter* 26:395002
- [68] Eglitis RI (2007) First principles calculations of  $\text{BaZrO}_3$  (001) and (011) surfaces. *J Phys Condens Matter* 19:356004
- [69] Heifets E, Ho J, Merinov B (2007) Density functional simulation of the  $\text{BaZrO}_3$  (011) surface structure. *Phys Rev B* 75:155431
- [70] Crosby LA, Kennedy RM, Chen BR, Wen JG, Poeppelmeier KR, Bedzyk JM, Marks LD (2016) Complex surface structure of (110) terminated strontium titanate nanododecahedra. *Nanoscale* 8:16606–16611
- [71] Lee C, Yang W, Parr RG (1988) Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789
- [72] Saunders VR, Dovesi R, Roetti C, Causa N, Harrison NM, Orlando R, Zicovich-Wilson CM (2014) CRYSTAL-2009 user manual. University of Torino, Torino, Italy
- [73] Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652
- [74] Monkhorst HJ, Pack JD (1976) Special points for Brillouin-zone integrations. *Phys Rev B* 13:5188–5192
- [75] Eglitis RI (2015) Theoretical modelling of the energy surface (001) and topology of  $\text{CaZrO}_3$  perovskite. *Ferroelectrics* 483:75–85
- [76] Tasker PW (1979) The stability of ionic crystal surfaces. *J Phys C* 12:4977–4984
- [77] Pojani A, Finocchi F, Noguera C (1999) Polarity of the  $\text{SrTiO}_3$  (111) and (110) surfaces. *Surf Sci* 442:179–198
- [78] Catlow CRA, Stoneham AM (1983) Ionicity in solids. *J Phys C Solid State Phys* 16:4321–4338
- [79] Bochicchio RC, Reale HF (1993) On the nature of crystalline bonding: extension of statistical population analysis to two- and three-dimensional crystalline systems. *J Phys B At Mol Opt Phys* 26:4871–4883

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.