

First-Principles Calculations of SrZrO₃ (001) Surfaces

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The results of calculations of surface relaxations, rumplings, and charge distribution for the SrZrO₃ (001) surface using ab initio code CRYSTAL and a hybrid description of exchange and correlation are presented. Both SrO and ZrO₂ terminations of the SrZrO₃ (001) surface are considered. On the (001) surfaces all upper and third layer atoms relax inward, while outward relaxations of all atoms in the second layer are found with the sole exception of SrO-terminated SrZrO₃ (001) surface second layer O atom. Calculated surface rumpling for the SrO-terminated SrZrO₃ (001) surface 6.77% of the lattice constant is by a factor of ten larger than the surface rumpling for the ZrO₂-terminated SrZrO₃ (001) surface 0.72% of a₀. A considerable increase in the Zr-O chemical bond covalency near the SrZrO₃ (001) surface as compared to the bulk is predicted.

Keywords *Ab initio* calculations; surface structure; SrZrO₃

Introduction

Strontium zirconate SrZrO₃ is of technological interest because of applications in fuel cells, hydrogen gas sensors and steam electrolysis [1]. For all these SrZrO₃ applications, the surface structure and the related surface electronic and chemical properties are of primary importance. *Ab initio* calculations of SrZrO₃ surface characteristics are useful to understand processes in which surfaces play a crucial role, such as the chemistry of surface reactions, interface phenomena, and adsorption.

Considering high technological importance of SrZrO₃, it is surprising that during the last years only a small number of theoretical *ab initio* studies exist dealing with SrZrO₃ (001) surfaces [2–5]. First *ab initio* studies for the SrZrO₃ (001) surface was performed by Evarestov *et al.* [2]. Authors used three slab models with different surface terminations to calculate the various surface characteristics including surface energies, atomic charges and density of electronic states [2, 3]. Sambrano *et al.* [4] investigated the structural and electronic properties of SrZrO₃ selected surfaces by means of density functional theory. They analyzed the relaxation effects for two symmetric and asymmetric SrZrO₃ (001) surface terminations. They discussed the electronic and energy band properties on the basis of band structure as well as density of states calculations [4]. Wang and Arai [5] used density functional calculations to investigate the (001) surface of cubic SrZrO₃ with both SrO and ZrO₂ termination. They found that the SrO surface is similar to its counterpart in

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SrTiO₃, while there are marked differences between the ZrO₂ and TiO₂ (001) terminations in SrZrO₃ and SrTiO₃, respectively, concerning the surface relaxation and rumpling [5].

Computational Method and Surface Models

To perform the first-principles DFT-B3LYP calculations, I used the CRYSTAL computer code [6]. This code employs the Gaussian-type functions (GTF) localized at atoms as the basis for an expansion of the crystalline orbitals. Features of the CRYSTAL code, which are most important for study of perovskite surfaces, are its ability to calculate the electronic structure of materials within both HF and Kohn-Sham (KS) Hamiltonians and implementation of isolated 2D slab model without its artificial repetition along the z -axis.

My calculations were performed using the hybrid exchange-correlation B3LYP functional involving a hybrid of non-local Fock exact exchange, LDA exchange and Becke's gradient corrected exchange functionals [7], combined with the nonlocal gradient corrected correlation potential by Lee-Yang-Parr [8].

The reciprocal space integration was performed by sampling the Brillouin zone of the five-atom cubic unit cell with the $5 \times 5 \times 1$ Pack-Monkhorst net [9], that provides the balanced summation in direct and reciprocal spaces. To achieve high accuracy, large enough tolerances of 7, 8, 7, 7, 14 were chosen for the Coulomb overlap, Coulomb penetration, exchange overlap, the first exchange pseudo-overlap, and for the second exchange pseudo-overlap, respectively [6].

The SrZrO₃ (001) surfaces were modelled with two-dimensional (2D) slabs, consisting of several planes perpendicular to the [001] crystal direction. The CRYSTAL code allowed us to avoid artificial periodicity along the Oz direction and to perform simulations for stand-alone 2D slabs. To simulate SrZrO₃ (001) surfaces, we used symmetrical (with respect to the mirror plane) slabs consisting of nine alternating SrO and ZrO₂ layers. One of these slabs was terminated by SrO planes and consisted of a supercell containing 22 atoms. The second slab was terminated by ZrO₂ planes and consisted of a supercell containing 23 atoms. These slabs are with unit cell formulae Sr₅Zr₄O₁₃ and Sr₄Zr₅O₁₄, respectively. These two (SrO and ZrO₂) terminations are the only two possible flat and dense (001) surfaces in SrZrO₃ perovskite lattice structure.

Main Results

As a starting point of my calculations, I calculated the SrZrO₃ bulk lattice constant. My calculated lattice constant for SrZrO₃ bulk (4.195 Å) is slightly larger than the experimental value of 4.109 Å [10]. I used the theoretical SrZrO₃ bulk lattice constant in following (001) surface structure calculations. To characterize the chemical bonding and covalency effects, I used a standard Mulliken population analysis for the effective atomic charges Q and other local properties of electronic structure as described, for example, in [11, 12]. My calculated effective charges for the SrZrO₃ bulk are (+1.880 e) for the Sr atom, (+2.174 e) for the Zr atom, and (−1.351 e) for the O atom. The bond population of the chemical bonding between Zr and O atoms is (+0.092 e) in SrZrO₃ bulk. The bond populations between the Sr and O atoms in SrZrO₃ bulk is negligible, only (+0.002 e). Finally, the bond populations between O and O atoms in SrZrO₃ bulk (−0.008 e) is negative, which indicates repulsion between O–O atoms. Calculated effective charges for the Sr atom are exactly the same as the Sr charges obtained earlier by Evarestov and his co-workers (+1.88 e) [2] and very close to the Sr ionic charge (+2 e). Calculated effective charges for the Zr atom are by 0.054 e larger

Table 1

Atomic relaxation (in per cent of the bulk lattice constant) for the SrO- and ZrO₂-terminated SrZrO₃ (001) surfaces calculated by the hybrid B3LYP method. Positive (negative) values refer to displacements in the direction outwards from (inwards to) the surface.

Layer	SrO-terminated		ZrO ₂ -terminated	
	Ion	Displacement	Ion	Displacement
1	Sr	-7.63	Zr	-1.38
	O	-0.86	O	-2.10
2	Zr	+0.86	Sr	+2.81
	O	-0.05	O	+0.91
3	Sr	-1.53	Zr	-0.04
	O	-0.45	O	-0.05

than those calculated in Ref. [2], but charges for the O atom is by $0.021e$ smaller than the O charges calculated by Evarestov *et al.* [2]. The effective atomic charges of Zr and O ions, due to the covalency contribution in Zr-O chemical bonding, differ considerably from the ionic charges ($+4e$ and $-2e$).

My calculated atomic displacements for the SrZrO₃ (001) surface upper three layers are presented in Table 1. According to the results of my calculations all atoms of the first and third SrZrO₃ surface layer relax inwards, i. e. towards the bulk, while outward relaxations of all atoms in the second layer are found for both SrZrO₃ (001) terminations. The only exception is inward relaxation of the SrO-terminated SrZrO₃ (001) surface second layer oxygen atom by a very small magnitude of 0.05% of a_0 . The relaxation of the surface upper layer metal atom for SrO-terminated SrZrO₃ (001) surface are much larger than that of oxygen atom what leads to a considerable rumpling (see Table 2) of the outermost plane (6.77% of a_0). My calculated surface rumpling for SrO-terminated SrZrO₃ (001) surface are approximately ten times larger than the surface rumpling for the ZrO₂-terminated SrZrO₃ (001) surface (0.72% of a_0) (see Table 2). Calculated atomic displacement directions for ZrO₂-terminated SrZrO₃ (001) surface coincides with earlier calculation results performed by Evarestov *et al.* [2] and local density approximation (LDA) calculations carried out by Wang and Arai [5]. Calculated surface rumplings for SrO-terminated surface (6.77% of a_0) and for ZrO₂-terminated surface (0.72% of a_0) are in a reasonable agreement with surface rumplings for the SrO-terminated terminated SrZrO₃ (001) surface (7.8% of a_0) and for the

Table 2

Calculated surface rumpling s , and relative displacements Δd_{ij} between the three near-surface planes, for the SrO- and ZrO₂-terminated SrZrO₃ (001) surfaces. Units are percent of the bulk lattice constant.

SrO-terminated SrZrO ₃ (001) surface			ZrO ₂ -terminated SrZrO ₃ (001) surface		
s	Δd_{12}	Δd_{23}	s	Δd_{12}	Δd_{23}
6.77	-8.49	+2.39	0.72	-4.19	+2.85

ZrO₂-terminated SrZrO₃ (001) surface (0.3% of a₀) calculated earlier by Wang and Arai by means of general gradient approximation (GGA) [5].

In order to compare the calculated surface structures with experimental results, the surface rumpling s (the relative displacement of oxygen with respect to the metal in the surface layer) and the changes in interlayer distances Δd_{12} and Δd_{23} (1,2, and 3 are the numbers of near-surface layers) are presented in Table 2. My calculations of the interlayer distances are based on the positions of relaxed metal ions, which are known to be much stronger electron scatters than oxygen ions [13]. From Table 2 one can see that all SrZrO₃ (001) surfaces show the reduction of interlayer distance Δd_{12} and expansion of Δd_{23} . For all SrZrO₃ surface (001) terminations the reduction of interlayer distance Δd_{12} is considerably larger than the expansion of the interlayer distance Δd_{23} .

I begin discussion of the electronic structure of SrO and ZrO₂-terminated SrZrO₃ (001) surfaces with the analysis of charge redistribution in near surface planes. The calculated atomic displacements, effective static atomic charges (calculated using Mulliken population analysis) and bond populations between nearest metal and oxygen atoms are presented in Table 3. First of all, note that the effective static charges of Sr (+1.858 e) on the SrO-terminated SrTiO₃ (001) surface are close to the +2 e formal ionic charges. Ti and O effective static charges are much smaller than the formal ionic charges, similarly to the bulk, what results from the Ti—O covalent bonding. Comparing with the very small bulk Sr—O (+0.002 e) bond populations, I see that the Sr—O bond populations near the SrO-terminated SrZrO₃ (001) surface are four times larger than in the bulk (see Table 3). The major effect observed near the ZrO₂-terminated SrZrO₃ (001) surface is a strengthening of

Table 3

Calculated absolute magnitudes of atomic displacements D (in Å), the effective atomic charges Q (in e) and the bond populations P between nearest Me—O atoms (in e) for the ZrO₂- and SrO-terminated SrZrO₃ (001) surfaces.

Layer	Property	Ion	ZrO ₂ -term.	Ion	SrO-term.
1	D	Zr	-0.058	Sr	-0.320
	Q		+2.196		+1.858
	P		+0.114		+0.008
	D	O	-0.088	O	-0.036
	Q		-1.277		-1.524
	P		-0.002		+0.042
2	D	Sr	+0.118	Zr	+0.036
	Q		+1.869		+2.227
	P		+0.002		+0.076
	D	O	+0.038	O	-0.002
	Q		-1.287		-1.398
	P		+0.094		+0.002
3	D	Zr	-0.00166	Sr	-0.064
	Q		+2.172		+1.877
	P		+0.102		+0.002
	D	O	-0.002	O	-0.0188
	Q		-1.331		-1.361
	P		+0.002		+0.094

the Zr—O chemical bond (see Table 3). Recall that the Zr and O effective charges ($+2.174e$ and $-1.351e$) in the SrZrO₃ bulk are much smaller than expected in an ionic model and that the Zr—O bond population is ($+0.092e$). Table 3 shows that the Zr—O bond population for the ZrO₂-terminated SrZrO₃ (001) surface is considerably larger than the associated bulk value.

Conclusions

According to the results of my B3LYP calculations all SrZrO₃ (001) surface upper and third layer atoms relax inwards, while outward relaxations of all atoms in the second layer, with exception of the second layer O atom on the SrO-terminated SrZrO₃ (001) surface, are found at both kinds of (001) terminations. Inward relaxation of SrZrO₃ (001) surface first and third layer atoms and outward relaxation of second layer atoms are typical, with some exceptions, also for other technologically important ABO₃ perovskites such as, for example, SrTiO₃, BaTiO₃, PbTiO₃, CaTiO₃ and BaZrO₃ [14–17], and also are in a general agreement with previous *ab initio* calculations dealing with SrZrO₃ (001) surfaces [2–5].

My calculated surface rumpling of 6.77% of a_0 for the SrO-terminated SrZrO₃ (001) surface is almost ten times larger than that of the corresponding ZrO₂-terminated SrZrO₃ (001) surface. My calculations predict a compression of the interlayer distance between first and second planes and an expansion between second and third planes for both SrZrO₃ (001) surfaces.

My B3LYP calculations indicate a considerable increase of Zr-O chemical bond covalency near the SrZrO₃ (001) surface ($+0.114e$) relative to the SrZrO₃ bulk ($+0.092e$). This should have an impact on the electronic structure of surface defects (e. g., F centers) [18], as well as on the adsorption and surface diffusion of atoms and small molecules relevant for catalysis.

Acknowledgments

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