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Ab initio calculations for the polar (0 0 1) surfaces of $YAlO_3$

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ABSTRACT

The results of *ab initio* calculations of polar $YAlO_3$ (0 0 1) surfaces by means of a hybrid B3LYP exchange-correlation functional as it is implemented in the CRYSTAL computer code are presented. Both polar YO and AlO_2-terminations of the cubic $YAlO_3$ (0 0 1) surface were considered. We performed relaxation of atoms on the upper three layers of both YO and AlO_2-terminated $YAlO_3$ (0 0 1) surfaces using in our calculations slabs containing 22 and 23 atoms as well as 9 layers, respectively. We predict a significant increase of the Al-O chemical bond covalency on the AlO_2-terminated $YAlO_3$ (0 0 1) surface with respect to the $YAlO_3$ bulk. Our calculated YO and AlO_2-terminated $YAlO_3$ polar (0 0 1) surface energies are considerably larger than the related structure ABO_3 perovskite neutral (0 0 1) surface energies, but comparable with ABO_3 perovskite polar (0 1 1) surface energies. Our calculated optical band gap near the YO-terminated $YAlO_3$ (0 0 1) surface is decreased, but near the AlO_2-terminated (0 0 1) surface is increased with respect to the calculated $YAlO_3$ bulk optical band gap.

1. Introduction

Among perovskites, yttrium orthoaluminate single crystals $YAlO_3$, commonly denoted as YAP, is one of the three Y-Al-double oxides, together with $Y_3Al_5O_{12}$ garnet (YAG) and $Y_4Al_2O_9$ monoclinic (YAM) crystal structures. It has high refractive index, optical transparency, mechanical resistance, chemical inertness and stability, which make it suitable for many optical applications. It is already about 50 years since the advent of high quality single crystals of $YAlO_3$, employing the Czochralski technique [1]. Since then, most of the spectroscopic studies have been associated with the laser application of rare-earth ions doped YAPsingle crystals [2–3]. Besides their extensive laser applications, YAPcrystals are thoroughly studied for their use as scintillators both as doped single crystals by the Czochralski method [4–5] and, recently, as thin films prepared by liquid phase epitaxy [6]. Single crystals and ceramics of Mn-doped $YAlO_3$ have been reported to be applicable as perspective laser materials and materials for thermostimulated and optically stimulated dosimetry [7–15]. On the other side, YAP is one of the promising candidates for gate insulator in new generation of metal oxide semiconductor field-effect transistors (MOSFETs) for modern electronics [16], since it has a wide band gap energy (Eg ~ 8.5 eV) [17] and quite high relative permittivity (~16) [18]. Optical properties YAP single crystals as well point defects (F and F^+) created by particle radiation reflect its anisotropic nature [17,21–24] and somehow similar to that for Al_2O_3 and $Y_3Al_5O_{12}$ [25–29]. While $Y_3Al_5O_{12}$ crystallizes in the cubic form having a garnet structure, $YAlO_3$ compounds have two well-known modifications: orthorhombic (see Table 1) and hexagonal [30]. However, it was also possible to obtain $YAlO_3$ in a cubic structure, as was reported first by Keith and Roy [31] and then by Yamaguchi et al. [32], Liu et al [33] and Zatrub et al [34,35]. This kind of material can be obtained e.g. after annealing of the hexagonal $YAlO_3$ nanopowder at temperature of around 1000 °C [32]. Diffraction data as arising from the cubic form of $YAlO_3$ can be found in ICDD no. 38-0222. Note also, that kinetically controlled synthesis of metastable $YAlO_3$ through molecular level design has been recently discussed in ref. [35].

Surface, interface and defect phenomena taking place in the ABO_3 perovskites and materials with related cubic ABO_3 perovskite structure, like $YAlO_3$, as well as their nanostructures, the nature of surface and interface states are hot and very important topics in modern solid state physics [36–52]. It is very easy to describe the high temperature cubic $YAlO_3$ structure with a space group *Pm3m*, which consists of octahedral AlO_6 centers that describe a cube with Al vertices and Al-O-Al edges. In order to keep our calculation time realistic, we restricted all our $YAlO_3$ (0 0 1) surface calculations only to high symmetry cubic $YAlO_3$ structure.

Taking into account the high technological importance of $YAlO_3$ polar surfaces, in this paper predictive *ab initio* calculations of $YAlO_3$ (0 0 1) surface structures were performed. The paper is organized in a following way. In Section 2 details of computational method as well as employed polar surface model were presented. Next, in Section 3, the results of our calculations for $YAlO_3$ (0 0 1) polar surface structures, energies, charge distributions, and bond populations are presented.

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Table 1
Structural, optical and F-type center characteristic of $YAlO_3$ crystals in orthorhombically distorted perovskite structure.

Lattice parameters: orthorhombically distorted perovskite structure	a = 5.180 Å b = 5.330 Å c = 7.375 Å			[19]
B	192			[20]
Band gap energy, E_g	8.5			[17]
Urbach tail parameters:	< **a** > // ***E***	< **b** > // ***E***	< ***c*** > // ***E***	[21]
s_0	0.552	0.479	0.448	
$h\omega_{eff}$	33.5	32.5	35.8	
E_0	8.056	8.018	8.151	
F center:				[27]
Optical absorption bands	5.84 and 5.15			
Luminescence bands	2.95			
F^+ center:				[27]
Optical absorption bands	6.5; 5.63 and 4.3			
Luminescence bands	3.49			

Finally, our obtained results are carefully analyzed and conclusions are summarized in Section 4.

2. Computational method and (0 0 1) surface model

We performed *ab initio* calculations, using the hybrid exchange–correlation functional B3LYP [53] implemented in the CRYSTAL computer code [54], for the $YAlO_3$ material bulk and its YO and AlO_2-terminated polar (0 0 1) surfaces. In our *ab initio* calculations, the reciprocal-space integration were performed by sampling the Brillouin zone with an 8 × 8 × 8 times extended Pack-Monkhorst *k*-point mesh for $YAlO_3$ bulk as well as with 8 × 8 × 1 times extended *k*-point mesh for (0 0 1) surfaces [55]. In order to describe the chemical bonding, effective atomic charges as well as covalency effects, we employed a standard Mulliken population analysis [56,57]. Unique feature of the CRYSTAL code is possibility to calculate isolated two-dimensional perpendicular to the crystal surface, without artificial periodicity along the *z* direction.

In order to calculate $YAlO_3$ polar (0 0 1) surfaces, we used symmetrical slabs containing nine alternating YO and AlO_2 layers. First slab in our calculations was terminated from both sides by YO planes and consisted of a 22 atom supercell (Fig. 1). Second slab from both sides

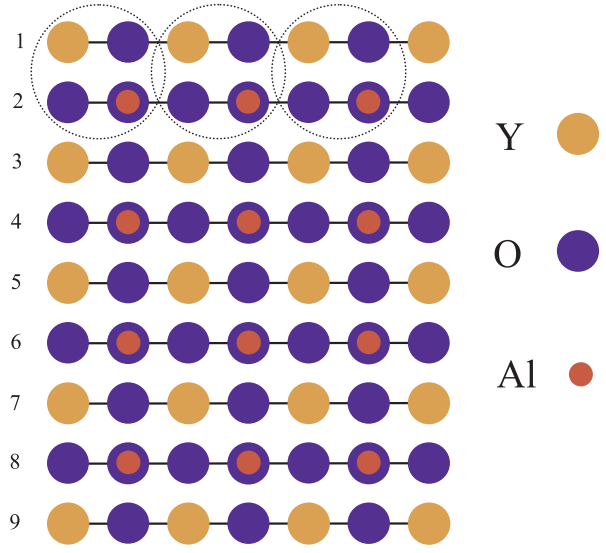

Fig. 1. Side view of the YO-terminated YAlO3 (0 0 1) surface containing nine alternating YO and AlO2 layers.

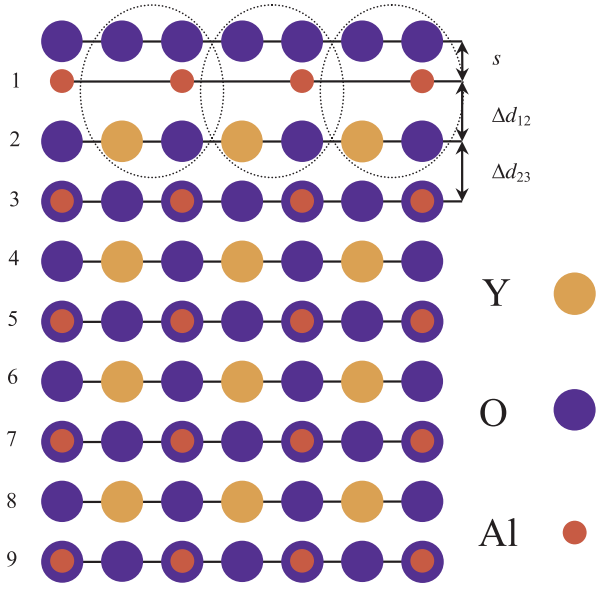

Fig. 2. Side view of the AlO2-terminated YAlO3 (0 0 1) surface containing the definitions of the surface rumpling *s* and the near-surface interplane distances Δd_{ij}.

was terminated by AlO_2 planes and thereby consisted of a 23 atoms containing supercell (Fig. 2). Both slabs, used in our calculations, were non-stoichiometric, with unit cell equations $Y_5Al_4O_{13}$ and $Y_4Al_5O_{14}$ for YO and AlO_2-terminated $YAlO_3$ (0 0 1) surfaces.

All supercells in our calculations should be neutral. Using formal ionic charges +3*e* for Y, +3*e* for Al, and -2*e* for O, our polar (0 0 1) $YAlO_3$ surfaces consists from alternating charged planes YO with formal ionic charge +1*e*, and AlO_2 with ionic charge −1*e*. For example, for 9 layer YO-terminated $YAlO_3$ (0 0 1) surface (or supercell) (YO-AlO_2-YO-AlO_2-YO-AlO_2-YO-AlO_2-YO) we will get 9 alternating charged layers ((+1*e*)-(−1*e*)-(+1*e*)-(−1*e*)-(+1*e*)-(−1*e*)-(+1*e*)-(−1*e*)-(+1*e*)) with summary charge equal to +1*e*. Such supercell is charged with charge + 1*e*, and it is well known, that it is impossible to perform calculations for charged supercells [54]. Therefore, in order to avoid charged supercells and to perform our calculations for neutral YO and AlO_2-terminated $YAlO_3$ (0 0 1) surfaces, we used basis sets (BS) for neutral Y, Al and O atoms [54]. We used exactly the same BS for neutral Y, Al and O atoms [54] in all our calculations performed for YO and AlO_2-terminated $YAlO_3$ (0 0 1) surfaces as well as for $YAlO_3$ bulk. As it is well known from previous studies dealing with polar ABO_3 perovskite surfaces [58–63], which have exactly the same cubic symmetry as $YAlO_3$, the strong electron redistribution happens for such terminations in order to cancel the polarity, but the YO and AlO_2-terminated $YAlO_3$ (0 0 1) surface keeps its insulating character, and it is possible to perform such calculations. Of course, it is impossible to carry out our calculations for asymmetric slabs with different terminations, such as for example, YO-AlO_2-YO-AlO_2-YO-AlO_2-YO-AlO_2, since this would lead to a very large dipole moment for an asymmetric slab. It is worth to notice, that asymmetric slabs are stoichiometric.

As a next step, the $YAlO_3$ (0 0 1) surface, cleavage as well as relaxation energies were calculated. First step, we calculated the cleavage energy for unrelaxed YO and AlO_2-terminated $YAlO_3$ (0 0 1) surfaces. It is obvious, that the cleavage energy is equally shared among the created $YAlO_3$ (0 0 1) surfaces, resulting from the simultaneous (0 0 1) cleavage of the crystal. In our performed B3LYP ab initio calculations, the 9 layer containing YO-terminated slab with 22 atoms and AlO_2-termianted (0 0 1) slab with 23 atoms, represent together 9 bulk unit cells, or 45 atoms:

$$E^{unr}_{surf}(\lambda) = \frac{1}{4}[E^{unr}_{slab}(YO) + E^{unr}_{slab}(AlO_2) - 9E_{bulk}], \quad (1)$$