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ORIGINAL ARTICLE

Systematic trends in (0 0 1) surface *ab initio* calculations of ABO_3 perovskites

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Abstract By means of the hybrid exchange–correlation functionals, as it is implemented in the CRYSTAL computer code, *ab initio* calculations for main ABO_3 perovskite (0 0 1) surfaces, namely $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrZrO_3$, $BaZrO_3$, $PbZrO_3$ and $CaZrO_3$, were performed. For ABO_3 perovskite (0 0 1) surfaces, with a few exceptions, all atoms of the upper surface layer relax inward, all atoms of the second surface layer relax outward, and all third layer atoms, again, inward. The relaxation of (0 0 1) surface metal atoms for ABO_3 perovskite upper two surface layers for both AO and BO_2-terminations, in most cases, are considerably larger than that of oxygen atoms, what leads to a considerable rumpling of the outermost plane. The ABO_3 perovskite (0 0 1) surface energies always are smaller than the (0 1 1) and especially (1 1 1) surface energies. The ABO_3 perovskite AO and BO_2-terminated (0 0 1) surface band gaps always are reduced with respect to the bulk values. The B–O chemical bond population in ABO_3 perovskite bulk always are smaller than near the (0 0 1) and especially (0 1 1) surfaces.

1. Introduction

Surface and interface phenomena, occurring in the complex oxide materials and their nanostructures, the nature of surface and interface states, and the mechanisms of surface electronic processes are very important topics in modern solid state physics [1–15]. $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrZrO_3$, $BaZrO_3$, $PbZrO_3$ and $CaZrO_3$ perovskites belongs to the family of ABO_3-type perovskite oxides, and possess a large number of industrially important applications, including charge storage devices, capacitors, actuators, as well as many others [16–21]. Therefore, it is obvious, that in last quarter of century $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrZrO_3$, $BaZrO_3$, $PbZrO_3$ and $CaZrO_3$ perovskites and their (0 0 1) surfaces were worldwide extensively investigated both theoretically and experimentally [18–47].

Each of these ABO_3 perovskites displays a different sequence of structural phase transitions from the cubic paraelectric phase as the temperature is lowered. At room temperature $SrTiO_3$ and $BaZrO_3$ are known to have cubic structures, whereas $CaTiO_3$, $SrZrO_3$, $PbZrO_3$ and $CaZrO_3$ are at orthorhombic structures. On the other hand, $PbTiO_3$ shows tetragonal structure, while $BaTiO_3$ has the tetragonal–orthorhombic phase transition just at temperatures close to

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room temperature. The experimental temperature of the transition from the low temperature phase to the high temperature cubic structure, the appropriate experimental lattice parameters as well as experimentally evaluated band gap energies E_g [48–68] are reviewed in Table 1. Note here that in most cases the experimental band gap energy values are obtained at room temperatures (RT) and in a few cases between 4.2 K and RT, while for most of the high temperature cubic modifications due to the technical impossibility to perform optical measurements, the appropriate experimental data are not available. It is worth to notice, that for $BaTiO_3$ perovskite no uniquely defined band gap can be detected from an exponential edge, Wemple proposes [50], using as a basis indirect arguments, that the room temperature band gaps are equal to 3.38 and 3.27 eV, respectively, for light polarized parallel and perpendicular to the ferroelectric ***c*** axis (Table 1).

Caused by explosive development of new and emerging technologies, the atomic and electronic properties as well as the structure of the ABO_3 perovskite (0 0 1) surfaces have been intensively explored experimentally during the last years. For example, the $SrTiO_3$ (0 0 1) surface structure has been experimentally analyzed by means of the atomic force microscopy [39], transmission electron microscopy (TEM) [40], low-energy electron diffraction and scanning tunneling microscopy [41], scanning probe microscopy [42] as well as high resolution X-ray photoelectron spectroscopy (XPS) [43]. Ultraviolet Photoelectron Spectroscopy (UPS) studies were performed on $BaTiO_3$ (0 0 1) surfaces [44]. Microscopic structure and electronic states on the (0 0 1) $BaTiO_3$ single-crystal surfaces annealed in ultrahigh vacuum were observed by scanning tunneling microscopy and spectroscopy (STM/S) [45]. Nevertheless, it is worth to notice, that for the SrO-terminated $SrTiO_3$ (0 0 1) surface, the low energy electron diffraction (LEED) [46] and reflection high-energy electron diffraction (RHEED) [47] experiments clearly contradict each other regarding the compression or extension of the interlayer distance Δd_{12}, probably because of differences in sample preparation or different interpretations of indirect experimental data on the atomic surface relaxations.

On the theory side, it is much more easy to calculate the ABO_3 perovskite (0 0 1) surface, which is neutral, than the very complex polar and charged (0 1 1) or (1 1 1) surfaces [69–73]. In this paper, the comprehensive *ab initio* calculations dealing with $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrZrO_3$, $BaZrO_3$, $PbZrO_3$ and $CaZrO_3$ (0 0 1) surfaces focusing on surface relaxations, chemical bond covalencies, optical band gaps and surface energies were performed and obtained systematic trends, common for all eight perovskites, were analyzed.

For example, experimentally detected Γ–Γ band gap for the $SrTiO_3$ bulk in the cubic phase is equal to 3.75 eV [49], whereas no experimental data exist for the band gap at $BaTiO_3$ cubic phase. The direct $BaTiO_3$ band gap detected in the tetragonal to orthorhombic phase transition temperature 278 K at different experimental conditions is equal to 3.27 or 3.38 eV [50]. It is well known that the Hartree–Fock (HF) method systematically overestimates the band gap of solids. Indeed, our by means of the HF method calculated Γ–Γ band gaps for $SrTiO_3$ and $BaTiO_3$ are equal to 12.33 and 11.73 eV, respectively [74]. From another side, the Density Functional Theory (DFT), as a rule, strongly underestimate the band gap of solids. For example, the LDA calculated Γ–Γ band gaps for $SrTiO_3$ and $BaTiO_3$ are equal to 2.36 and 1.98 eV, respectively [74]. In order to get a reliable basis for further ABO_3 perovskite bulk and (0 0 1) surface defect calculations, which requires a precise description of the optical band gap, we performed most of our calculations by means of the hybrid exchange–correlation functionals B3PW and B3LYP, which coinjoin 20% of the HF and 80% of the DFT Hamiltonian, as it is implemented in the CRYSTAL computer code. Logically, that the hybrid exchange–correlation functionals, since they are a combination of HF and DFT Hamiltonians, allows to achieve a fair agreement between *ab initio* calculated and experimentally measured band gaps for ABO_3 perovskite bulk as well as their (0 0 1) surfaces.

Table 1 Experimental data for ABO_3 perovskites, including band gap values (in eV) and lattice constants (in Å).

Material	Structure at RT	Band gap E_g (eV) at RT	Transition Temp. to cubic phase (K)	Expt. lattice const. (Å) in cubic phase
$SrTiO_3$	Cubic	3.75 eV (direct); 3.25 eV (indirect) .25 eV (indirect) [49]	110 K [58]	3.89845 Å–110 K [55] 3.9053 Å–293 K [51]
$BaTiO_3$	Tetragonal ↔ orthorhombic (278 K)	3.38 eV (// ***c***); 3.27 eV (⊥ ***c***) [50]	403 K [58]	4.0037 Å–474 K [48] 4.0136 Å–674 K [48] 4.0239 Å–874 K [48] 4.0415 Å–1174 K [48] 4.0539 Å–1387 K [48] 4.0658 Å–1574 K [48] 4.0701 Å–1645 K [48]
$PbTiO_3$	Tetragonal	3.4 eV [60,66]	763 K [54] 763 K [52]	3.970 Å–777 K [52]
$CaTiO_3$	Orthorhombic	∼3.5 eV [67]	1647 K [62]	3.8967 Å–777 K [62]
$SrZrO_3$	Orthorhombic	5.6 eV [68]	1433 K [63] 1360 K [59]	4.154 Å–1423 K [59]
$BaZrO_3$	Cubic	5.3 eV [60]	Cubic in all T	4.199 Å–RT [56]
$PbZrO_3$	Orthorhombic	3.7 eV [60]	501–508 K [53]	4.1614 Å–520 K [61]
$CaZrO_3$	Orthorhombic	5.7 eV [65]	2173 ± 100 K [57,64]	No data for cubic phase

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