



Hybrid HF–DFT modeling of monolayer water adsorption on (001) surface of cubic BaHfO₃ and BaZrO₃ crystals

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ABSTRACT

First-principles calculations have been used to study the atomic structure, preferred sites and adsorption energies for water adsorption at different terminations of the cubic phase of perovskite-structured BaHfO₃ and BaZrO₃. By considering different initial positions of water molecules, the possibility of water dissociation has been investigated. It is demonstrated that the site selectivity and the form of adsorbed molecule can be affected by the choice of surface unit cell. Dissociative adsorption was found to be favorable for all surfaces in consideration. Hydroxylation of ZrO₂- and HfO₂-terminated surfaces is accomplished by a noticeable reconstruction of the surface structure of cubic phase towards the orthorhombic phase. Calculated atomic charges in bare and hydroxylated surfaces show that BaHfO₃ crystal is slightly more ionic than BaZrO₃.

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1. Introduction

The ABO₃ perovskite-type crystals, where A is a divalent cation, B is a tetravalent transition-metal atom, exhibit a variety of interesting electronic, electromechanical, and conductive properties [1,2], which are the basis for many existing and potential applications [3,4].

Perovskites can exist in different phase modifications depending on the combination of cations A and B [5,6] and their properties are often symmetry dependent. In the ABO₃ perovskite structure the smaller tetravalent B cation resides in the center of corner-sharing BO₆ octahedra. The larger bivalent A cation is located in the cavities between eight octahedra with a 12-fold oxygen coordination. In barium zirconate and barium hafnate tetravalent cation fits almost perfectly on the B site: thus, the Goldschmidt [7] tolerance factor is about 1.0 [8] and the symmetry of these crystals is cubic.

Barium zirconate, BaZrO₃, is a very important ceramic material which has many technological applications. Moreover, it has attracted great attention as a high temperature proton conductor with possible applications in fuel cells and hydrogen sensors [9,10]. The properties of BaZrO₃ have been measured during the past 40 years. Nevertheless, until now, only several calculations have been reported [11–13] on the atomic and electronic structure of bulk BaZrO₃. The work of King-Smith and Vanderbilt [11] was the first where the lattice constants, elastic constants, zone-center phonon frequencies, Grüneisen parameters, and band structures were calculated for series of perovskites including BaZrO₃. Combined theoretical and experimental study of

the low-temperature properties of BaZrO₃ was made by Akbarzadeh et al. [13]. At the same time, a number of works was attended to modeling of the protonic conduction in doped zirconates [2,14]. Conduction of perovskites is controlled by the oxygen vacancies generated by doping with trivalent cations. Exposure to humid atmospheres incorporates hydroxide ions into vacancies, allowing the crystal to behave as an efficient proton conductor.

Barium hafnate, BaHfO₃, apparently, is similar to BaZrO₃ on its useful properties and it is a promising material for electronic applications. It has been well known as a high melting temperature material [15,16]. However, to the best of our knowledge, there are a few works exploring its physical properties. Recently, Maekawa and co-workers [17] have reported some thermal and mechanical properties of a polycrystalline sample of this compound. Crystal structure and microwave dielectric properties of some alkaline-earth hafnates including BaHfO₃, have been investigated by Feteira et al. [18]. The theoretical study of structural, elastic, electronic and optical properties for BaHfO₃, using plane wave method (PW), in the framework of the density functional theory (DFT) within the local density approximation (LDA) was carried in [19]. In [20] the electronic band structure and vibrational properties of the BaHfO₃, using DFT–LDA were investigated. Cohesive energies for a range of simple II–IV perovskites were calculated in [8] using generalized gradient approximation (GGA) exchange–correlation functionals [21] in PW DFT framework.

The surface effects of ceramics are important for their applications. There has been a continuous interest in the surface properties of these materials. In all mentioned applications perovskites serve as an electrolyte in contact with catalysts and electrodes. Therefore, knowledge about BaHfO₃ and BaZrO₃ surface structures would be

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very useful for understanding of chemical processes at the crystal surfaces as well as for understanding of the structure and behavior of interfaces with other materials. Nevertheless, the experimental studies of perovskite surfaces are complicated by the presence of surface defects, making it difficult to verify the surface stoichiometry. Starting by work of Padilla and Vanderbilt [22], the first-principles methods have been successfully applied to the study of the surface properties of BaTiO₃ and BaZrO₃ perovskites [23–26]. However, to our knowledge, there is no theoretical study on the surface properties of cubic BaHfO₃.

A wide range of crystalline, single, and multicomponent oxide materials can be produced by hydrothermal technology [27]. Conventional and microwave-assisted hydrothermal syntheses of perovskite-type ceramics BaZrO₃ and BaHfO₃ are carried out in temperatures varying from 80 to 260 °C, under saturated water vapor pressure. Thermogravimetric analysis shows a gradual mass loss in the temperature range of 200–800 °C attributed to physisorbed water and hydroxyl groups [28]. These data confirm the fact that perovskite surfaces are modified by adsorbed water species up to 800 °C. The presence of water is also usual in electrochemical systems. However, both experimental and theoretical investigations of water adsorption on BaZrO₃ and BaHfO₃ surface are practically absent.

Our theoretical studies based on computer modeling techniques have previously addressed to the adsorption of water molecules at the surfaces of perovskite-type strontium titanates and zirconates [29,30], and strontium hafnate [30,31]. In particular, first-principles simulations using hybrid Hartree-Fock (HF) DFT exchange-correlation functionals have been performed to estimate the water adsorption energies and investigate the factors promoting the water dissociation. This will now be extended to include the adsorption of water molecules at surfaces of the cubic phases of BaHfO₃ and BaZrO₃. Using quantum mechanical simulations within the framework of linear combination of atomic orbitals (LCAO) calculations, we have investigated the surface relaxation and the structural properties of adsorbed water species at the different surface terminations. We have also investigated how the calculated values of water adsorption energies can be affected by the choice of the surface unit cell. To this end, we have considered 1×1 and $\sqrt{2} \times \sqrt{2}$ extended 2D unit cells. We demonstrate that the use of extended unit cell is important for correct description of water adsorption at the cubic perovskite surfaces. In addition, we have analyzed the surface atomic charges and their changes upon the water adsorption.

In Section 2 we describe the computational details of our calculations. In Section 3, we consider the results obtained for bulk phases and for (001) surface relaxation of cubic SrZrO₃ and SrHfO₃. In Section 4, we analyze the results calculated for different models of water adsorption on perovskite surfaces and discuss them. Section 5 summarizes the main conclusions obtained in this study.

2. Computational details

Most of the quantum-chemical calculations of electronic structure of crystals and their surfaces are performed using two types of Hamiltonian models [32] based, respectively, on HF or DFT approximations. The HF method is originated from the variational principle and does not contain any empirical parameters. Strictly speaking, the approximate form of the exchange-correlation functionals does not allow DFT methods to be considered as completely *ab initio* approach. In spite of this, the advantage of the DFT methods is accounting for correlation effects, which cannot yet be estimated for the crystals using the post-HF methods, as it is done in the theory of molecules. Nevertheless, the incomplete compensation of electron self-interacting term in the exchange functionals may lead to incorrect description of highly localized electronic states. This fact should not be ignored in the study of surface phenomena, because the great deal of change in the electronic states occurs around the top of the valence band or

within the band gap [33]. Since the HF and DFT methods mostly give the systematic errors of opposite sign [34], the use of hybrid exchange-correlation functionals can improve the accuracy of calculations.

The second aspect which determines the type of quantum-chemical calculations is the choice of the basis set for the crystalline orbitals expansion. PW basis which has some technical advantages over LCAO approximation is used in the most of present-day simulations of periodic systems. At the same time, the periodic LCAO method also provides the good quality of calculated properties [32]. Moreover, the LCAO calculations of the surface systems do not require artificial repeating of slab along the normal to the surface direction [32], in contrast to PW calculations where it is necessary to restore 3D periodicity due to incompleteness of 2D PW basis in 3D space. Finally, it should be noted, that Mulliken population analysis is easily generalized for the periodic systems [35,36] if LCAO expansion of crystal orbitals is employed.

The calculations presented in this work were performed within the LCAO approximation, using hybrid HF–DFT Hamiltonian with the Crystal2006 code [37,38]. For our study we choose the PBE0 [39–41] exchange-correlation functional because it had been successfully applied for calculation of both perovskite bulk and surface properties [32]. The Stuttgart [42,43] small-core pseudopotentials have been used for Zr, Hf and Ba core–valence electron interactions. To exclude the basis set linear dependence in LCAO crystal calculations, the diffuse *s*-, *p*-, *d*-, and *f*-Gaussian-type orbitals with exponents less than 0.1 have been removed from the corresponding Hf and Ba basis sets. Exponents of polarizing *f*-functions for Zr and Hf atoms have been optimized in bulk crystal calculations. The polarizing *f*-function for barium atom which was included in the initial basis set has been excluded due to negligible contribution in the case of Ba²⁺ ionic state. The preliminary calculation confirmed that this function influences insignificantly on bulk crystal properties. For O atom we used all-electron 8-411G(*d*) basis set [44,45] which was adjusted for calculations of crystalline perovskites. Contracted 31G(*p*) basis set [45] has been used for hydrogen atom.

The Monkhorst–Pack [46] $8 \times 8 \times 8$ net was used in the Brillouin zone sampling in the case of bulk cubic crystals. For slab systems with primitive and extended unit cells 8×8 and 4×4 2D *k*-nets were employed, correspondingly.

3. Bulk and surface properties of cubic BaHfO₃ and BaZrO₃

The cubic perovskite crystal structure is characterized by the space group *Pm* $\bar{3}$ *m*. The lattice constant of both BaZrO₃ and BaHfO₃ was optimized and obtained values have been used in all surface simulations. Calculated lattice parameters, bulk modules, cohesion energies, and band gaps are given in Table 1. The Murnaghan [47] equation of state is used to estimate the bulk modules of the regarded crystals. For comparison, in Table 1 we also include our previous data for cubic strontium hafnate obtained in [48] using the identical approach. Calculated values agree well with the available experimental data [49–53] (see Table 1). The bulk properties of barium hafnate

Table 1
Calculated bulk properties^a of cubic BaZrO₃, BaHfO₃, and SrHfO₃ crystals.

Quantity	BaZrO ₃ This work	BaHfO ₃ This work	SrHfO ₃ Ref. [48]
Cell <i>a</i> , Å	4.19 (4.19, [49])	4.19 (4.18, [18])	4.13 (4.11, [51])
Bulk modulus <i>B</i> , GPa	172	175	180
Cohesive energy <i>E</i> _{ab} , eV	32.8 (33.5, ^b)	33.3	32.9 (34.0, ^c)
Band gap, <i>E</i> _{gap} , eV	5.4 (5.3, [50])	5.8	6.4

^a Available experimental data are given in parenthesis.

^b Calculated from standard molar enthalpies of formation [52].

^c Estimated using thermochemical data [53].

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