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Proton conduction across and along BaO– and ZrO_2–terminated (001) $BaZrO_3$ surfaces using density functional theory

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ABSTRACT

We investigated proton conduction across and along energetically favorable BaO– and ZrO_2–terminated (001) $BaZrO_3$ surfaces by using density functional theory. The proton concentration at the surfaces was evaluated from the space charge model using the proton segregation energy. The proton was segregated at the ZrO_2–terminated surface more than the BaO–terminated surface. The proton mobility across and along the surfaces was evaluated from the proton migration barrier. The proton mobility along the ZrO_2–terminated surface was highest among the four pathways. Therefore, from the product of the concentration and mobility, the proton can conduct easily along the ZrO_2–terminated (001) surface. The proton conduction along the ZrO_2–terminated (001) surface can help find a potentially easy path, such as surface grain boundaries and triple phase boundaries.

1. Introduction

Highly resistive grain boundaries of barium zirconate ($BaZrO_3$), which is a well-known solid oxide proton conductor, have been regarded as a serious problem, and widely investigated both experimentally and computationally [1–10]. Recently, several studies have reported that its surfaces showed an even higher proton resistivity than grain boundaries [11–14]. Chen et al. experimentally investigated for the first time the formation of surface space charge at Ni/10% Y-doped $BaZrO_3$ by using impedance spectroscopy, and estimated that the Schottky-barrier height at the surface was higher than that at the grain boundary by 0.35 V [11]. Ho et al. and Heifets et al. investigated $BaZrO_3$ surfaces by using density functional theory (DFT), and reported that BaO– and ZrO_2–terminated (001) surfaces were energetically favorable under the stable bulk $BaZrO_3$ condition [15,16]; these two surfaces have been mainly chosen for computational surface studies [12–14]. Polfus et al. investigated the surface space charge formation at the ZrO_2–terminated (001) surface by using DFT, and reported a high Schottky-barrier height of 0.98 V at 800 K [12]; Bjorheim et al. also reported similar results [13]. We investigated the proton conductivity across the BaO–terminated (001) surface by using DFT with further consideration of proton migration barrier, and reported that the surface impeded the proton conduction more than the grain boundary by four orders of magnitude at 900 K [14].

These earlier computational studies only considered the proton conduction across the surface and not along the surface. Shim et al. investigated oxygen incorporation at surface grain boundaries of yttria stabilized zirconia (YSZ) by using secondary ion mass spectrometry and impedance spectroscopy, and reported that the surface grain boundaries enhanced the oxygen incorporation [17]; Park et al. reported no migration barrier for oxygen incorporation into a Σ5 YSZ surface grain boundary by using DFT [18]. The oxygen incorporation requires its conduction along the surface to the surface grain boundaries. Therefore, the proton conduction along the surface should be considered because it could help find a potentially easy path, such as the surface grain boundaries (*SGBs*) and triple phase boundaries (*TPBs*) [17–19].

In this report, we investigated the proton conduction across and along the energetically favorable BaO– and ZrO_2–terminated (001) $BaZrO_3$ surfaces by using DFT. The segregation energies of proton ($OH_O^{\cdot}$ in Kroger-Vink notation) and + 2 charged oxygen vacancy ($V_O^{\cdot\cdot}$) were considered to evaluate the profiles of the electrostatic potential and the proton concentration. The proton migration barriers across and along the BaO– and ZrO_2–terminated (001) $BaZrO_3$ surfaces were calculated for proton mobilities. Based on the proton concentration and mobility, the proton conductivities across and along the BaO– and ZrO_2–terminated (001) $BaZrO_3$ surfaces were evaluated as a function of inverse temperature.

2. Calculation details

All calculations were performed using the Vienna *ab-initio* simulation package (VASP) based on DFT [20–23]. Following is a summary of

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the DFT calculation method used for the surface structure and the space charge model; further details are seen in [10,14,24,25]. Electron wave functions were described using the projector augmented wave method implemented in the VASP [26,27]. The exchange correlation energy was the generalized gradient approximation of PBE [28]. The wave functions were expanded in plane waves with a cutoff energy of 500 eV. Partial wave occupancies were calculated with the Gaussian smearing method, and the width of smearing was 0.05 eV. Electronic and geometric optimizations were converged when the total energy difference between successive calculation steps was less than 10^{-5} and 10^{-4} eV, respectively. All atoms were allowed to relax until the force on each atom was below 0.002 eV/nm. All atomic images were drawn using the VESTA software [29].

By using the computational settings, we optimized the unit cell of $BaZrO_3$ with an 8 × 8 × 8 *Monkhorst-Pack k*-points mesh [30]. The optimized lattice constant of 0.425 nm is in good agreement with the experimentally measured value of 0.419 nm [31]. Based on the optimized unit cell, 2 × 2 and 4 × 4 sized BaO– and ZrO_2–terminated (001) $BaZrO_3$ surface cells with 14 layers and 1.5 nm vacuum on top were constructed with 4 × 4 × 1 and 2 × 2 × 1 *k*-points meshes, respectively; these surface cells are denoted by BaO (001) and ZrO_2 (001), respectively. The surface cells were composed of the seven BaO and seven ZrO_2 layers. The bottom two layers were fixed, while the top 12 layers were allowed to relax. The vacuum size of 1.5 nm was enough to disregard the spurious electron interaction between the two repeating surfaces [14].

The segregation energies of $OH_O^{\cdot}$ ($E_{OH_O^{\cdot}}$,seg) and $V_O^{\cdot\cdot}$($E_{V_O^{\cdot\cdot}}$,seg) were calculated using 4 × 4 sized surface cells. We considered the effective charges of the proton ($OH_O^{\cdot}$) and O vacancy ($V_O^{\cdot\cdot}$) as +1 and +2, respectively. $E_{OH_O^{\cdot}}$,seg is calculated as $E_{OH_O^{\cdot}},seg = E_{OH_O^{\cdot}}(S) - E_{OH_O^{\cdot}}(B)$, where $E_{OH_O^{\cdot}}(S)$ is the energy of the surface cell when a $OH_O^{\cdot}$ is positioned on the surface, and $E_{OH_O^{\cdot}}(B)$ is the energy of the surface cell when a $OH_O^{\cdot}$ is positioned at bulk (*B*); the eighth layer in the surface cell is chosen to represent *B*. The same equation is used to calculate $E_{V_O^{\cdot\cdot}}$,seg. Yang et al. studied the proton-proton interaction at a Σ3 $BaZrO_3$ grain boundary; the proton-proton interaction reduced $E_{OH_O^{\cdot}}$,seg by about 25% [10]. Lei et al. studied the proton-dopant interaction at ZrO_2 (001) using DFT and its value was 0.16 eV [32]. The proton-proton and proton-dopant interactions were not considered in this paper; instead, we mainly focused on the effect of surfaces on the proton conduction.

The segregation energies were converted into the electrostatic potential and the proton concentration using the space charge model [1–14,33,34]. The Y acceptor dopant was set to 10% concentration, and its distribution was assumed to be uniform throughout the material to the surface (Mott-Schottky approximation). The hydration enthalpy and entropy were obtained from the results of Kreuer et al.; − 0.79 eV and − 0.89 meV/K, respectively [35]. The partial pressure of water and the relative dielectric constant of $BaZrO_3$ were 0.025 atm and 46, resectivley; more details of the space charge model are in [1–14,33,34].

The proton migration barrier ($\underline{E_m}$) in the 2 × 2 sized surface cell was calculated using the climbing nudged elastic band tool [36]; the proton migration was well described by the 2 × 2 sized surface cell because of its small size. E_m is calculated as $E_m = E_{TS} - E_{ini}$, where E_{TS} and E_{ini} are the energies of the transition state and initial state, respectively. The calculated E_m in BaO (001) and ZrO_2 (001) is converted into proton mobility (μ) as

$$\mu = \frac{D_0 q}{k_B T} exp\left(\frac{-E_m}{k_B T}\right) \tag{1}$$

,where D_0 is the prefactor, q is the charge state of proton, k_B is the Boltzmann constant, and T is the temperature, respectively; more details of the μ calculation are in [10,14]. D_0 is calculated as

$$D_0 = \frac{1}{6} d^2 \nu \tag{2}$$

, where *d* is the jump distance of the proton and set to 0.15 nm, and ν is the attempt frequency of the proton hoping. The ν of 26 THz was taken from the result of Gomez et al. [37]. We only considered E_m for proton transfer in each pathway due to the smaller E_m for proton rotation, and assumed that the E_m below the second layer was regarded as the bulk value (0.45 eV) of 10% Y-doped $BaZrO_3$ in BaO (001) and ZrO_2 (001); the bulk value includes the effect of proton-dopant association, as mentioned by Yamazaki et al. [38].

Table 1
Segregation energies of proton ($E_{OH_O^{\cdot}}$,seg) and oxygen vacancy ($E_{V_O^{\cdot\cdot}}$,seg) in BaO– and ZrO_2–terminated (001) surfaces (BaO (001) and ZrO_2 (001)).

Surface	$E_{OH_O^{\cdot}}$,seg (eV)	$E_{V_O^{\cdot\cdot}}$,seg (eV)	Reference
BaO (001)	− 0.96	− 0.26	This work
ZrO_2 (001)	− 1.26	− 0.92	This work
ZrO_2 (001)	− 1.35	− 1.00	12
ZrO_2 (001)	− 1.30	− 0.67	13
BaO (001)	− 0.75	–	39
ZrO_2 (001)	− 1.72	–	39

Based on proton concentration (c) and μ, the proton resistivity (ρ) is calculated as

$$\rho = \frac{1}{c \cdot q \cdot \mu} \tag{3}$$

In order to evaluate ρ across and along the surfaces, the surface cells are divided into *n* slices by a slab thickness. Each c, μ, and ρ with respect to the *i*-th slice are assigned as c^i, μ^i, and ρ^i, respectively; c^i and μ^i are assumed to be constant within each slice.

3. Results and discussion

Table 1 shows the segregation energies of $OH_O^{\cdot}$ ($E_{OH_O^{\cdot}}$,seg) and $V_O^{\cdot\cdot}$ ($E_{V_O^{\cdot\cdot}}$,seg) in BaO (001) and ZrO_2 (001). The trend of $E_{OH_O^{\cdot}}$,seg in BaO (001) and ZrO_2 (001) is consistent with results of Tauer et al. [39]. The $E_{OH_O^{\cdot}}$,seg and $E_{V_O^{\cdot\cdot}}$,seg in ZrO_2 (001) are in good agreement with results of Polfus et al. [12]. The $E_{V_O^{\cdot\cdot}}$,seg in ZrO_2 (001) of Bjorheim et al. is a bit different because of the smaller surface cell size than others [13]. The higher segregation tendency of $OH_O^{\cdot}$ and $V_O^{\cdot\cdot}$ in ZrO_2 (001) may be associated with the lower coordinated O atom on the surface ($O_{O^{\times},S}$); the coordination of the $O_{O^{\times},S}$ in the BaO (001) and ZrO_2 (001) are four and two, respectively, and the lower coordinated $O_{O^{\times},S}$ indicates its lower stability.

Fig. 1 shows the electrostatic potential difference ($\Delta\varphi(z)$) and the proton concentration (c) as a function of the distance from the surface (z) in (a) BaO (001) and (b) ZrO_2 (001) using the space charge model; z is the depth from the surface. The white, dark yellow, light yellow, and gray colors indicate the vacuum (*V*), surface core (*SC*), surface space charge (*SSC*), and bulk (*B*) regions, respectively. The position of *SC* is above the terminating surface and its width is set to 0.21 nm that corresponds to a half of the $BaZrO_3$ lattice constant. The extremely low oxygen vacancy concentration is not depicted in Fig. 1 for clarity; this data are in [12,14]. The black solid and red dotted lines indicate $\Delta\varphi(z)$ and c, respectively. $\Delta\varphi(z)$ is calculated as $\Delta\varphi(z) = \varphi(z) - \varphi(\infty)$, where $\varphi(z)$ is the electrostatic potential at z and $\varphi(\infty)$ is that at $z = \infty$ (*i.e.*, bulk); $\Delta\varphi(SC)$ is the Schottky-barrier height. Due to low $E_{OH_O^{\cdot}}$,seg, φ is generated at *SC* and exponentially decreases at *SSC* in both BaO (001) and ZrO_2 (001); $\varphi(SC)$ is set to a constant. The calculated $\Delta\varphi(SC)$ at 800 K in BaO (001) and ZrO_2 (001) are 0.66 and 0.97 V, respectively; the $\Delta\varphi(SC)$ in ZrO_2 (001) is in good agreement with the result of Polfus et al. (0.98 V at 800 K) [12]. The $c(SC)$ at 800 K in BaO (001) and ZrO_2 (001) are 0.67 and 0.86/formula unit, respectively. The higher $c(SC)$ in ZrO_2 (001) is mainly due to lager number of $O_{O^{\times},S}$ sites and lower $E_{OH_O^{\cdot}}$,seg. The $c(SSC)$ is depleted to compensate the overall charge neutrality in both BaO (001) and ZrO_2 (001). The widths of *SSC* regions in BaO (001) and ZrO_2 (001) are 1.6 and 2.0 nm, respectively.