We studied Σ3 BaZrO3 (210)[001] tilt grain boundaries using density functional theory and a space charge layer model. Formation enthalpies of BaZrO3 and competing oxides were calculated using fitted elemental-phase reference energy (FERE) correction, and a stable region of BaZrO3, as functions of Ba and O chemical potentials, was determined. Grain boundary energies were evaluated as functions of Ba and O chemical potentials within the determined stable region of BaZrO3 from the FERE correction. Among the six tested grain boundaries, an energetically favorable nonstoichiometric grain boundary was determined. Based on the nonstoichiometric grain boundary, we calculated the electrostatic potential and concentrations of proton and oxygen vacancy using a space charge layer model.

Key-words : Nonstoichiometric grain boundary, Density functional theory, Grain boundary energy, Space charge layer

1. Introduction

Acceptor-doped barium zirconate (BaZrO3) has been widely used in protonic ceramic fuel cells as an electrolyte due to its sound stability and high proton conductivity at grain interiors.1–3 Despite the latter advantage, the low conductivities at the grain boundary (GB) have been a serious problem.5,6 The space charge layer (SCL) model was introduced to understand this problem better.5–11 In the model, the electrostatic potential and charge-carrier concentrations of BaZrO3 were analyzed using a numerical calculation and density functional theory (DFT). Based on the results from DFT, the accepted origin of the low GB proton conductivities is believed to be highly segregated protons at BaZrO3 GBs.7–11

The studies about the BaZrO3 GBs have mainly focused on stoichiometric GBs and their SCL formation.7–11 Helgee et al. investigated the origin of the space charge at BaZrO3 GBs by DFT. They reported that the electrostatic potential at the GBs that was calculated using the SCL model was around 0.6 V at the temperature range of 400–600 K.7 Polfus et al. investigated the defect chemistry of a Σ3 BaZrO3 (111) GB using DFT, and reported similar results about the electrostatic potential and defect concentrations.9 Contrary to the stoichiometric GBs, nonstoichiometric BaZrO3 GBs have not been investigated yet, as far as we know. The studies of nonstoichiometric GBs have been performed on some other perovskite materials, such as BaTiO3 and SrTiO3.6,12 Choi et al. investigated cation profiles of BaTiO3 using high-resolution electron microscopy, and reported that the Ti/Ba ratio of GBs was higher than that of grain interior.12 Kim et al. investigated SrTiO3 GBs by using scanning transmission electron microscopy and DFT. They reported that the GBs were intrinsically nonstoichiometric, and provided the origin of the “double Schottky barrier”.13 Therefore, study of the nonstoichiometric BaZrO3 GBs is required in order to investigate GBs that are energetically more favorable. In addition, the effect of the Ba and O chemical potentials on GB energy should be studied to evaluate more realistic GBs developed under fabrication and/or operating conditions.

We calculated the stable region of bulk BaZrO3 as functions of Ba and O chemical potentials to determine the range of Ba and O chemical potentials for the evaluation of the GBs. Two stoichiometric, and four nonstoichiometric, GBs were evaluated under the determined range of Ba and O chemical potentials at 1000 K. We found that a nonstoichiometric GB was energetically the most stable among the tested GBs, and its SCL was evaluated using DFT.

2. Calculation details

2.1 Computational settings

All calculations were performed using the Vienna ab initio simulation package (VASP) based on DFT.14–17 Following is a summary of the DFT calculation method used for GB super cells; further details may be seen in Yang’s paper.18 Electron wave functions were described using the projector augmented wave (PAW) method ofBloch implemented in the VASP by Kresse and Joubert.19,20 The exchange correlation (XC) energy was described by the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) and PBE + U.21,22 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 differences between successive calculations steps were less than 10–13 and 10–2 eV, respectively. All atoms were allowed to relax until the force on each atom was below 0.09 eV/Å with a Monkhorst-Pack k-points mesh.23 All images were drawn using the Visualization for Electronic and Structural Analysis (VESTA) tool.24

2.2 Fitted elemental-phase reference energy

The fitted elemental-phase reference energy (FERE) correction

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developed by Stevanovic et al.\textsuperscript{25} was introduced in order to improve the accuracy of the formation enthalpies of BaZrO\textsubscript{3} and competing oxides: BaO, BaO\textsubscript{2}, ZrO\textsubscript{2}, and Zr\textsubscript{3}O. Following is the data summarized from Stevanovic’s paper.\textsuperscript{25} The effective U (U\textsubscript{eff} = U - J) values for Ba, Zr, and O were 0, 3, and 0 eV, respectively; U\textsubscript{eff} is applied to the d-orbital of the metal atoms and the p-orbital of the O atom. The FEREs are expressed as E\textsubscript{FERE} = E\textsubscript{PBE+U} + δE\textsubscript{FERE}, where E\textsubscript{PBE+U} is the PBE + U energy of the i atom (i = Ba, Zr, or O), and δE\textsubscript{FERE} is the energy shift of the i atom; δE\textsubscript{FERE}, δE\textsubscript{FERE}, and δE\textsubscript{FERE} are 0.54, 0.72, and 0.23 eV, respectively. The calculated lattice parameters of BaZrO\textsubscript{3} and the competing oxides were well matched with experimentally measured lattice parameters, as shown in Table 1. The FERE calculation does not change the lattice constants of BaO and BaO\textsubscript{2}, because the U\textsubscript{eff} of Ba and O are set to 0 eV.

### 2.3 Configuration of stoichiometric and nonstoichiometric GBs

Figure 1 shows the stoichiometric and nonstoichiometric \( \Sigma 3 \) BaZrO\textsubscript{3} (210)[001] tilt GB super cells that were optimized with a 4 \times 4 \times 1 \textit{k}-point mesh, except Fig. 1(d). This part of Fig. 1 is the structure before optimization. The structure changes too much to be amorphous after optimization. The super cells are shown along the [001] direction, and the sizes along the [210], [120], and [001] directions are \( l, m, \) and \( n \), respectively. When a unit cell of BaZrO\textsubscript{3} is cleaved with a (210) surface, BaO- and ZrO\textsubscript{2}-terminated surfaces are generated. The BaO- and ZrO\textsubscript{2}-terminated GBs are constructed by joining two BaO- and two ZrO\textsubscript{2}-terminated surfaces, respectively, and removing some overlapping cations and anions within the GB regions, as shown in Figs. 1(b), 1(c), 1(e), and 1(f). The GB super cells are shown along the [001] direction. The blue, yellow, and red circles indicate the Ba, Zr, and O atoms, respectively.

### 2.4 Space charge layer model

The space charge layer model was introduced to calculate the electrostatic potential difference at GB and the concentrations of proton and the doubly positively charged oxygen vacancy.\textsuperscript{31} The Mot-Schottky approximation was assumed

### Table 1. Lattice constants of BaZrO\textsubscript{3} and the competing oxides from the PBE, FERE, and experiment

| Compound (crystal structure) | Lattice constant (Å) | PBE | FERE | Exp. |
|-----------------------------|----------------------|-----|------|------|
| a/b/c                      |                     |     |      |      |
| BaO (cubic)                 | 5.59                 | 5.59| 5.53 |      |
| BaO\textsubscript{2} (tetragonal) | 3.86/6.97        | 3.86/6.97| 3.81/6.82 |      |
| ZrO\textsubscript{2} (cubic) | 5.14                 | 5.19| 5.11 |      |
| Zr\textsubscript{3}O (trigonal) | 5.67/31.39      | 5.76/31.88| 5.56/31.18 |      |
| BaZrO\textsubscript{3} (cubic) | 4.25                 | 4.28| 4.19 |      |

### Table 2. Cell lengths and volumes of BaZrO\textsubscript{3} GBs: BaO GB and ZrO\textsubscript{2} GB are stoichiometric, and BaO GB–Zr, BaO GB–ZrO\textsubscript{2}, ZrO\textsubscript{2} GB–Ba, and ZrO\textsubscript{2} GB–BaO are nonstoichiometric

| GB                  | Cell length (Å) | Volume (Å\textsuperscript{3}) |
|---------------------|-----------------|-------------------------------|
|                     | l   | m   | n   |     |
| (a) BaO GB          | 8.52 | 9.55| 44.28| 3602.00|
| (b) BaO GB–Zr       | 8.52 | 9.54| 41.26| 3352.10|
| (c) BaO GB–ZrO\textsubscript{2} | 8.47 | 9.61| 41.50| 3377.10|
| (d) ZrO\textsubscript{2} GB | 8.52 | 10.17| 44.91| 3893.02|
| (e) ZrO\textsubscript{2} GB–Ba | 8.55 | 9.62| 41.58| 3420.44|
| (f) ZrO\textsubscript{2} GB–BaO | 8.56 | 9.53| 41.26| 3366.79 |

Fig. 1. Stoichiometric and nonstoichiometric BaZrO\textsubscript{3} (210)[001] tilt grain boundaries (GBs): (a) and (d) are the BaO and ZrO\textsubscript{2} GBs, respectively. Based on the BaO and ZrO\textsubscript{2} GBs, (b), (c), (e), and (f) were constructed by removing cations and/or anions within the GB regions, and labelled BaO GB–Zr, BaO GB–ZrO\textsubscript{2}, ZrO\textsubscript{2} GB–Ba, and ZrO\textsubscript{2} GB–BaO, respectively. The regions are shaded in Fig. 1, where (b) and (e) were constructed by removing 4 Zr and 4 Ba atoms (labelled BaO GB–Zr, ZrO\textsubscript{2} GB–Ba), respectively. Figures 1(c) and 1(f) were constructed by removing cations and/or anions within the GB regions. The regions are shaded in Fig. 1, where (b) and (e) were constructed by removing 4 Zr and 4 Ba atoms (labelled BaO GB–Zr, ZrO\textsubscript{2} GB–Ba), respectively. Figures 1(c) and 1(f) were constructed by removing 4 Zr and 4 O atoms (labelled BaO GB–ZrO\textsubscript{2}, ZrO\textsubscript{2} GB–BaO), respectively. The GB super cell dimensions (\( l, m, n \)) and the cell volumes are shown in Table 2. The cell volumes of the BaO and ZrO\textsubscript{2} GBs are greater than those of the other four nonstoichiometric GBs, due to the initial short distances between the cations located in the GB regions. BaO GB and ZrO\textsubscript{2} GB contain short distances between Ba atoms, and Zr atoms, respectively, and those close atoms are indicated in the red-dotted ellipses in Figs. 1(a) and 1(d).
for the constant dopant concentration throughout the material to the GB. The trivalent dopant concentration was set to 10%. The partial pressure of water and the relative dielectric constant were set to 0.025 atm and 75, respectively.\(^{1,18}\) The hydration enthalpy and entropy of BaZrO\(_3\) were \(-0.79\) eV and \(-0.89\) meV/K, respectively.\(^{1,18}\) More details of the space charge layer model are explained in Yang’s paper.\(^{19}\) The numerical calculation was carried out using MATLAB.\(^ {31}\)

3. Results and discussion

In order to study the stable region of bulk BaZrO\(_3\), the formation enthalpies of BaZrO\(_3\) and the competing oxides were calculated as

\[
\Delta H_{\text{Ba,Zr,O}} = E_{\text{Ba,Zr,O}} - xE_{\text{Ba}} - yE_{\text{Zr}} - zE_{\text{O}}
\]

where \(E_{\text{Ba,Zr,O}}\) is the energy of BaZrO\(_3\), \(x\), \(y\), and \(z\) are the numbers of atoms. The calculated \(\Delta Hs\) were listed in Table 3. The stability diagram of BaZrO\(_3\) was constructed based on the \(\Delta Hs\), as shown in Fig. 2. The stable region of BaZrO\(_3\) and the borderlines between the competing oxides were calculated from the inequality conditions as

\[
x\Delta \mu_{\text{Ba}} + y\Delta \mu_{\text{Zr}} + z\Delta \mu_{\text{O}} \leq \Delta H_{\text{Ba,Zr,O}}
\]

where \(\Delta \mu_i\) is the chemical potential of the \(i\) atom (\(i = \text{Ba, Zr, and O}\)). The grey, red, and blue regions indicate the stable regions of BaZrO\(_3\) based on the PBE, FERE, and experimental \(\Delta Hs\), respectively. More details of the stability diagram may be seen in Stevanovic’s and Heifets’s papers.\(^{25,34,35}\) The \(\Delta Hs\) of the FERE agreed well with the experimental \(\Delta Hs\), while those of the PBE were not.

**Table 3. Formation enthalpies of BaZrO\(_3\) and the competing oxides from the PBE, FERE, and experiment**

| Compound      | PBE  | FERE | Exp. |
|---------------|------|------|------|
| BaO           | -5.10| -5.84| -5.72\(^ {32}\) |
| BaO\(_2\)     | -5.58| -6.52| -6.57\(^ {32}\) |
| ZrO\(_2\)     | -9.97| -11.50| -11.40\(^ {32}\) |
| Zr\(_2\)O     | -5.51| -7.88| —    |
| BaZrO\(_3\)   | -16.19| -18.28| -18.33\(^ {31}\) |

*Fig. 2. Stability diagram of BaZrO\(_3\). The black dot, red solid, and blue one-dot chain lines indicate the borderlines between BaZrO\(_3\) and the competing oxides from PBE, FERE and experimental \(\Delta Hs\), respectively. The grey, red, and blue areas indicate the stable BaZrO\(_3\) regions from the PBE, FERE, and experimental \(\Delta Hs\), respectively.*

**Fig. 3.** Grain boundary energies (\(\Omega\)) (a) as a function of \(\Delta \mu_{\text{Ba}}\) at 1000 K and 0.2 atm of \(p_{O_2}\), and as a function of \(\log(p_{O_2}/p_0)\) at 1000 K under the conditions of (b) \(\Delta \mu_{\text{Ba}} + \Delta \mu_{\text{O}} = \Delta H_{\text{BaO}}\) and (c) \(\Delta \mu_{\text{Ba}} + \Delta \mu_{\text{O}} = \Delta H_{\text{BaZrO}_3} - \Delta H_{\text{ZrO}_2}\).
its energy is out of the y-axis range in Fig. 3. The Ωs of BaZrO₃ as a function of Δμₓₒ are listed in Table 4. The Ωs of two stoichiometric GBs do not depend on Δμₓₒ, while those of the four nonstoichiometric GBs vary due to their nonstoichiometric chemical compositions. The BaO GB–ZrO₂ and BaO GB (0,1/2) were energetically favorable among the six tested GBs, as shown in Fig. 3(a). The BaO GB–ZrO₂ was the most stable under a ZrO₂ rich condition, while the BaO GB (0,1/2) was the most stable under a BaO rich condition.

We also calculated Ω as a function of log (pₒ₂/pₒ₂₀) when Δμₓₒ = ΔHₓₒ–BaO (Ba rich) and Δμₓₒ = ΔHₓₒ–ZrO₂ (Zr rich), as shown in Figs. 3(b) and 3(c), respectively. The temperature (T) was set to 1000 K, and Δμₓₒ is calculated as

$$Δμₓₒ = \frac{1}{2} \left[ H_{O₂} − TS_{O₂} + k_B T \ln \left( \frac{p_{O₂}}{p_{O₂₀}} \right) \right]$$

where Hₒ₂ and Sₒ₂ are the enthalpy and entropy of O₂, respectively; k_B is the Boltzmann constant and pₒ₂ and pₒ₂₀ are the O₂ partial pressure and standard pressure, respectively; ΔHₓₒ was obtained from the NIST-JANAF thermochemical table, and converted to the pₒ₂/pₒ₂₀. Under the Δμₓₒ = ΔHₓₒ–BaO condition, the BaO GB (0,1/2) was the most stable over the whole range of pₒ₂, while BaO GB–ZrO₂ and ZrO₂ GB–BaO were also quite stable. Under the Δμₓₒ = ΔHₓₒ–ZrO₂ condition, BaO GB–ZrO₂ was the most stable. The experimental results(37,38) about BaO evaporation from BaZrO₃ may indicate reduced Δμₓₒ at high temperatures. Therefore, we can expect that the ZrO₂ GB–BaO may be dominant during the cell fabrication temperature. This GB was used for further study on segregation energies of a proton and an oxygen vacancy.

Figures 4(a) and 4(b) show the segregation energy variation of the defect [D = proton (H) or oxygen vacancy (V)] in the ZrO₂ GB–BaO as a function of its position (z); z = 0 indicates the GB plane (the black dotted vertical line). The segregation energy of defect (E₉ₓₒ–seg) in the GB super cell was calculated as

$$E₉ₓₒ–seg = E^{GBC}_D − E^{B}_D$$

where E^{GBC}_D is the energy of the GB super cell with a D at the GB core (GBC), and E^{B}_D is the energy of the GB super cell with a D at bulk; E^{GBC}_D is calculated by averaging the energy values of the GB super cell, when the D is positioned away from the GBC. The width of the GBC typically contains 1–3 atomic planes from the GB plane; its thickness is approximately 3 Å. E^{B}_D is set to zero as reference in E₉ₓₒ–seg of Fig. 4. The black square and the red circle indicate H and V, respectively. The protons attached to the O at the GB plane, and displaced away about 0.8 Å from the plane, showed the lowest E₉ₓₒ–seg, while V located at the first nearest GB plane showed the lowest: E₉ₓₒ–seg and E₉ₓₒ–seg were −1.23 and −0.50 eV, respectively.

Figure 5 shows the profiles of electrostatic potential difference (Δφ) and concentrations of the defects (Cₓₒ) of H and V as a function of z at (a) 600, (b) 900, and (c) 1200 K, respectively. The dark-yellow, light-yellow, and white areas represent the GB core (GBC), space charge layer (SCL), and bulk (B) regions, respectively. The f.u. in Cₓₒ indicates the formula unit.

4. Conclusions

Σ3 BaZrO₃ (210)[001] tilt grain boundaries were studied using density functional theory and a space charge layer model. The stable region of BaZrO₃ was evaluated using ΔHₛ of BaZrO₃ and the competing oxides from the FERE correction. The FERE correction estimated the stable region of BaZrO₃ well. Ω was calculated with the optimized two stoichiometric and four nonstoichiometric GBs under the BaZrO₃ stable condition.

Table 4. Grain boundary energies of two stoichiometric and four nonstoichiometric BaZrO₃ GBs at 1000 K and 0.2 atm of oxygen partial pressure under BaO (Δμₓₒ = −4.67) and ZrO₂ (Δμₓₒ = −5.62) rich conditions.

| GB          | GB energy (eV/Å²) |
|-------------|-------------------|
|             | Δμₓₒ = −4.67     | Δμₓₒ = −5.62     |
| BaO GB      | 0.11             | 0.11             | 0.12             | 0.12             |
| BaO GB–Zr   | 0.10             | 0.12             | 0.10             | 0.10             |
| BaO GB–ZrO₂ | 0.07             | 0.10             | 0.07             | 0.10             |
| ZrO₂ GB     | 0.41             | 0.41             | 0.10             | 0.08             |
| ZrO₂ GB–Ba  | 0.10             | 0.12             | 0.08             | 0.05             |
| Ref. 9      | 0.07             | 0.07             | 0.07             | 0.07             |
Among the six grain boundaries, ZrO$_2$ GB–BaO was the most stable under ZrO$_2$ rich condition. Based on the ZrO$_2$ GB–BaO, $\Delta \phi$ (0) at 600, 900, and 1200 K were 1.08, 0.94, and 0.72 V, respectively.

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