A DFT-Based Descriptor to Predict the Water Vapor Corrosion Resistance of Rare-Earth Monosilicates

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Abstract: Rare-earth monosilicates are used as environmental barrier coatings (EBCs) due to their excellent water vapor corrosion resistance. However, existing experimental studies on the water vapor corrosion behavior of rare-earth monosilicates are discrepant or even contradictory. Previous theoretical investigations on water vapor corrosion resistance mainly focus on a Mulliken analysis of Si-O bonds in the monosilicates. In this study, the structural and electronic properties of rare-earth monosilicates have been studied by density functional theory (DFT) calculations, and a descriptor correlated to the corrosion resistance has been developed. The maximum isosurface value of the valence band maximum (VBM$_{\text{Fmax}}$) can be used to predict the water vapor corrosion resistance of RE$_2$SiO$_5$. The results show that RE$_2$SiO$_5$ with a smaller VBM$_{\text{Fmax}}$ may have better water vapor corrosion resistance.

Keywords: ceramics; rare-earth monosilicates; first principles; corrosion

1. Introduction

Rare-earth (RE) silicates are promising candidates for environmental barrier coatings (EBCs) due to their exceptional high-temperature durability, chemical compatibility and water vapor corrosion resistance [1]. Rare-earth monosilicates, RE$_2$SiO$_5$, have two types of monoclinic crystalline structures: RE$_2$SiO$_5$ with a space group of P2$_1$/c are called X1 phase when the ionic radius of RE elements (RE = La–Gd) is larger, while the X2 phase with a C2/c space group forms by the elements from Tb to Lu [2]. The water vapor corrosion behaviors and mechanisms may be different between the two phases.

Recently, many experimental studies have been carried out regarding the water vapor corrosion resistance of RE$_2$SiO$_5$ as EBCs. Wang et al. [3] found that X2-RE$_2$SiO$_5$ are more stable than X1-RE$_2$SiO$_5$ in high-temperature water steam. Nasiri et al. [4] investigated the water vapor corrosion resistance of RE$_2$SiO$_5$ (RE = Y, Gd, Er, Yb and Lu) in air with 90% water, and found that their water vapor resistance has the following order: Y$_2$SiO$_5$ > Er$_2$SiO$_5$ > Yb$_2$SiO$_5$ > Lu$_2$SiO$_5$ > Gd$_2$SiO$_5$. Klemm et al. [5] studied the water vapor corrosion resistance of Y$_2$SiO$_5$ and Sc$_2$SiO$_5$, indicating that Y$_2$SiO$_5$ exhibited better water vapor corrosion resistance. Unfortunately, the existing experimental studies on the water vapor corrosion behavior of rare-earth monosilicates may be discrepant or even contradictory due to the different experimental conditions [6]. It is worth pointing out that the water vapor corrosion resistance of rare-earth monosilicates can also be evaluated by theoretical calculations. For example, Han et al. [7] studied the water vapor corrosion resistance of X2-RE$_2$SiO$_5$ (RE = Lu, Yb, Tm, Er, Ho, Dy, Y and Sc) using first-principles calculations. They concluded that the water vapor corrosion resistance of X2-RE$_2$SiO$_5$ demonstrated the following order: Sc$_2$SiO$_5$ > Dy$_2$SiO$_5$ > Y$_2$SiO$_5$ > Ho$_2$SiO$_5$ > Er$_2$SiO$_5$ > Yb$_2$SiO$_5$ > Tm$_2$SiO$_5$ > Lu$_2$SiO$_5$, which...
shows some disagreement with the experimental findings [3,5,6]. Therefore, it is still a challenge to provide a precise order of the water vapor corrosion resistance of RE$_2$SiO$_5$.

In previous theoretical studies [7,8], researchers mainly focused on the Si-O bonds instead of RE-O bonds of rare-earth silicates to compare their water vapor corrosion resistances. However, the [REO$_x$] polyhedron is less rigid than the [SiO$_4$] tetrahedral, and is easier to collapse and react with water molecules. In this work, we used density functional theory (DFT) calculations to investigate the water vapor corrosion resistance of RE$_2$SiO$_5$ through RE-O bonds. By comparing the structural and electronic properties of RE$_2$SiO$_5$, we have developed a descriptor, i.e., the maximum isosurface value of the valence band maximum (VBM$_{F\text{max}}$), to predict their water vapor corrosion resistances.

2. Materials and Methods

All DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [9]. The projector augmented-wave (PAW) method and plane-wave basis sets are used [10,11]. The Perdew–Burke–Ernzerhof (PBE) potential is adopted to treat exchange–correlation interactions at the generalized gradient approximation (GGA) level [12]. The cut-off energy for the plane-wave basis was set to 520 eV throughout the present study. The k-point sampling of the Brillouin zone is based on the Monkhorst–Pack method [13]. A $3 \times 4 \times 4$ k-point grid and a $2 \times 5 \times 3$ k-point grid were used for X1-RE$_2$SiO$_5$ and X2-RE$_2$SiO$_5$, respectively. The crystal structures were completely optimized by the lattice parameters and internal atomic coordinates until the total energy difference and the forces on atoms were less than $1.0 \times 10^{-6}$ eV and 0.01 eV/Å, respectively. Visualizations of all the structures were performed using VESTA [14].

3. Results and Discussion

3.1. Crystal Structure of RE$_2$SiO$_5$

The calculated lattice parameters of RE$_2$SiO$_5$ and the experimental data are compared in Table 1, and the $1\%$ disagreement suggests that the optimized structures are reasonable. The crystal structures of X1- and X2-RE$_2$SiO$_5$ are shown in Figure 1a,b. The unit cell of RE$_2$SiO$_5$ contains 32 atoms, including two different RE sites (labeled as RE1 and RE2), one Si site and five different O sites (labeled as O1–O5). The four O positions of O1–O4 form a Si-centered tetrahedron [SiO$_4$], while O5 atoms only loosely bond with rare-earth atoms [2]. The difference between X1-RE$_2$SiO$_5$ and X2-RE$_2$SiO$_5$ lies in the coordination number of rare-earth atoms, ranging from nine to seven and seven to six [2]. Figure 1c shows the energy difference between the X1 phase and X2 phase for the same RE$_2$SiO$_5$. The increasing energy difference indicates that the structural stability of the X1 phase decreases with the increasing ionic radius of RE atoms; RE elements tend to more often form X2-RE$_2$SiO$_5$ with an increase in the ionic radius of RE atoms [15].

When exposed to water-vapor-containing environments, RE$_2$SiO$_5$ will suffer from rapid recession, eventually generating Si(OH)$_4$ and RE(OH)$_3$ gas [3,6]. Generally, the [REO$_x$] polyhedron is less rigid than the [SiO$_4$] tetrahedral, and the RE-O bonds tend to show different bonding properties for different rare-earth monosilicates. As shown in Figure 2, we found that the radial distribution functions, g(r), of Si-O bonds remained unchanged, while the distribution of RE-O bonds changed remarkably in both X1- and X2-RE$_2$SiO$_5$. Therefore, the difference in the water vapor corrosion resistance should be closely related to the changing RE-O bonds and their electronic structures.
Table 1. Experimental and calculated lattice parameters of X1- and X2-RE$_2$SiO$_5$.

| Method          | a (Å)   | b (Å)   | c (Å)   | β (°)   | Volume (Å$^3$) |
|-----------------|---------|---------|---------|---------|----------------|
|                 | Exp.    | Calc.   | Exp.    | Calc.   | Exp.           | Calc.   |
| La$_2$SiO$_5$   | 9.3320  | 9.3564  | 7.5088  | 7.0168  | 109.0060       | 109.0060 |
| Pr$_2$SiO$_5$   | 9.2530  | 9.3420  | 7.3010  | 6.8106  | 108.7720       | 108.7720 |
| Nd$_2$SiO$_5$   | 9.2295  | 9.3039  | 7.2848  | 6.7906  | 108.5470       | 108.5470 |
| Sm$_2$SiO$_5$   | 9.1610  | 9.2362  | 7.1120  | 6.7900  | 108.1510       | 108.1510 |
| Eu$_2$SiO$_5$   | 9.1420  | 9.1706  | 7.0540  | 6.7107  | 107.7030       | 107.7030 |
| Gd$_2$SiO$_5$   | 9.1200  | 9.1758  | 7.0600  | 6.7732  | 107.0230       | 107.0230 |
| Tb$_2$SiO$_5$   | 14.3660 | 14.5384 | 6.9766  | 10.5585 | 122.1380       | 122.1380 |
| Dy$_2$SiO$_5$   | 14.3800 | 14.5296 | 6.7400  | 10.5085 | 122.1140       | 122.1140 |
| Ho$_2$SiO$_5$   | 14.3500 | 14.4802 | 6.7100  | 10.4563 | 122.0950       | 122.0950 |
| Er$_2$SiO$_5$   | 14.3660 | 14.4344 | 6.6976  | 10.4101 | 122.1120       | 122.1120 |
| Tm$_2$SiO$_5$   | 14.3020 | 14.3815 | 6.6620  | 10.3130 | 122.2100       | 122.2100 |
| Lu$_2$SiO$_5$   | 14.2774 | 14.2735 | 6.6398  | 10.2465 | 122.2240       | 122.2240 |
| Y$_2$SiO$_5$    | 14.5643 | 14.5111 | 6.8354  | 10.5122 | 122.0870       | 122.0870 |
| Sc$_2$SiO$_5$   | 13.8636 | 13.7566 | 6.4838  | 10.0833 | 121.8350       | 121.8350 |

Figure 1. The crystal structure of RE$_2$SiO$_5$: (a) X1-RE$_2$SiO$_5$ and (b) X2-RE$_2$SiO$_5$. Si tetrahedra, RE polyhedra and O atoms are colored by blue, green and red, respectively. (c) The energy difference between the X1 phase and X2 phase for the same RE$_2$SiO$_5$. 
3.2. The Valence Band Maximum (VBM) of \( \text{RE}_2\text{SiO}_5 \)

Chemical reactivity can be related to the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) characteristics in molecules, while in bulk materials it can be described by the valence band maximum (VBM) and the conduction band minimum (CBM) [22]. Previously, we [23] investigated the hydration sensitivity of triclinic tricalcium silicate by a combination of DFT calculations and molecular dynamics. We found that the long-term reaction with water molecules is controlled by the proton transport of silicate, and can be intrinsically related to the valence band maximum of the bulk solid. Similarly, for the corrosion behaviors induced by water vapor, the valance band maximum (VBM) of the bulk solid could be used as a descriptor to estimate the water-related corrosion resistance.

Figure 3 shows the partial charge density at the VBM of X1-RE\(_2\)SiO\(_5\). The partial charge density at the VBM only exists at the sites of O atoms, suggesting that O atoms would experience an electrophilic attack. Interestingly, the charge densities distributions of X1-RE\(_2\)SiO\(_5\) are almost unchanged for RE = La, Pr, Nd and Sm, and are mainly located around O5 atoms. However, Gd\(_2\)SiO\(_5\) shows a completely different profile, where the charge densities are mainly located around O1–O4 atoms. O5 atoms bond with RE much more loosely when compared with the O1–O4 atoms bonding with Si atoms [2]. This may suggest that Gd\(_2\)SiO\(_5\) is much more stable when reacting with water vapor, indicating that Gd\(_2\)SiO\(_5\) has better water vapor corrosion resistance. The localization of the valence band maximum in \( \text{RE}_2\text{SiO}_5 \) can be related to the water vapor corrosion resistance, and the maximum isosurface value of the valence band maximum (VBM\(_{\text{Fmax}}\)) can be used to describe the electronic localization of \( \text{RE}_2\text{SiO}_5 \) [23]. As listed in Table 2, the VBM\(_{\text{Fmax}}\) of Gd\(_2\)SiO\(_5\) is much smaller than that of other X1-RE\(_2\)SiO\(_5\) (RE = La, Pr, Nd, Sm and Eu). More specifically, the VBM\(_{\text{Fmax}}\) of X1-RE\(_2\)SiO\(_5\) ranks as Pr\(_2\)SiO\(_5\) > La\(_2\)SiO\(_5\) > Nd\(_2\)SiO\(_5\) > Sm\(_2\)SiO\(_5\) > Eu\(_2\)SiO\(_5\) > Gd\(_2\)SiO\(_5\). Such a decreasing VBM\(_{\text{Fmax}}\) value corresponds with an increasing water vapor corrosion resistance, implying that Gd\(_2\)SiO\(_5\) has the best water vapor corrosion resistance among X1-RE\(_2\)SiO\(_5\).

Table 2. The maximum isosurface value of the valence band maximum (VBM\(_{\text{Fmax}}\)) of X1-RE\(_2\)SiO\(_5\).

|          | La\(_2\)SiO\(_5\) | Pr\(_2\)SiO\(_5\) | Nd\(_2\)SiO\(_5\) | Sm\(_2\)SiO\(_5\) | Eu\(_2\)SiO\(_5\) | Gd\(_2\)SiO\(_5\) |
|----------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| VBM\(_{\text{Fmax}}\)(e/Å\(^3\)) | 0.098             | 0.099             | 0.097             | 0.094             | 0.060             | 0.053             |

Figure 2. Radial distribution functions, \( g(r) \), of Si-O bonds and RE-O bonds in (a) X1-RE\(_2\)SiO\(_5\) and (b) X2-RE\(_2\)SiO\(_5\) compounds.
Figure 3. The valence band maximum (VBM) of X1-RE$_2$SiO$_5$. (a) X1-RE$_2$SiO$_5$ (RE = La, Pr, Nd and Sm). (b) Eu$_2$SiO$_5$. (c) Gd$_2$SiO$_5$. Si atoms (blue) and O atoms (red) are shown. RE atoms (RE = La, Pr, Nd and Sm) are presented by green, Eu is presented by fuchsia and Gd is presented by purple. The isosurface level is set at 0.005 e/Å.

For the X2-RE$_2$SiO$_5$ (RE = Tb, Dy, Ho, Er, Tm, Lu, Sc and Y) compounds, their VBM$_{\text{Fmax}}$ is also analyzed, as shown in Figure 4. It is worth pointing out that the charge densities distributions of X2-RE$_2$SiO$_5$ are almost unchanged for RE = Tb, Dy, Ho, Er, Tm, Lu and Y. However, Sc$_2$SiO$_5$ shows a slightly different profile, where the charge densities around O atoms are a little more than those of other X2-RE$_2$SiO$_5$. This could imply that Sc$_2$SiO$_5$ is less stable when reacting with water vapor, indicating that Sc$_2$SiO$_5$ has worse water vapor corrosion resistance. Both Y$_2$SiO$_5$ and Er$_2$SiO$_5$ have a smaller value of the VBM$_{\text{Fmax}}$ than that of Gd$_2$SiO$_5$, indicating that Gd$_2$SiO$_5$ has worse water vapor corrosion resistance. This is in agreement with the experimental outcomes of Wang et al. [3]. On the basis of the trend in Figure 3c, Y$_2$SiO$_5$ has better water vapor corrosion resistance than Sc$_2$SiO$_5$, which is consistent with what Klemm et al. concluded [5]. The decreasing order of RE$_2$SiO$_5$ (RE = Y, Er and Lu) in our results may also provide an explanation for the experimental results conducted by Nasiri et al. [4]. Additionally, we can conclude that the water vapor corrosion resistance of X2-RE$_2$SiO$_5$ has the following order: Tb$_2$SiO$_5$ > Dy$_2$SiO$_5$ > Y$_2$SiO$_5$ > Ho$_2$SiO$_5$ > Er$_2$SiO$_5$ > Tm$_2$SiO$_5$ > Lu$_2$SiO$_5$ > Sc$_2$SiO$_5$.

Figure 4. The valence band maximum (VBM) of X2-RE$_2$SiO$_5$. (a) X2-RE$_2$SiO$_5$ (RE = Tb, Dy, Ho, Er, Tm, Lu and Y). (b) Sc$_2$SiO$_5$. Si atoms (blue) and O atoms (red) are shown. RE atoms (RE = Tb, Dy, Ho, Er, Tm, Lu and Y) are presented by green and Sc is presented by light purple. The isosurface level is set at 0.001 e/Å. (c) The maximum isosurface value of the valence band maximum (VBM$_{\text{Fmax}}$) of X2-RE$_2$SiO$_5$ (RE = Tb, Dy, Ho, Er, Tm, Lu, Sc and Y).
4. Conclusions

The water vapor corrosion resistance of RE$_2$SiO$_5$ (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu, Sc and Y) was studied based on DFT calculations. A DFT-based descriptor, the maximum isosurface value of the valence band maximum (VBM$_{\text{max}}$), was developed to predict the corrosion resistance for both X1- and X2-RE$_2$SiO$_5$. According to the proposed descriptor, it was found that Gd$_2$SiO$_5$ had the best water vapor corrosion resistance in X1-RE$_2$SiO$_5$ and that the water vapor corrosion resistance of X2-RE$_2$SiO$_5$ has the following order: Tb$_2$SiO$_5$ > Dy$_2$SiO$_5$ > Y$_2$SiO$_5$ > Ho$_2$SiO$_5$ > Er$_2$SiO$_5$ > Tm$_2$SiO$_5$ > Lu$_2$SiO$_5$ > Sc$_2$SiO$_5$.

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