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## COMMUNICATION

# First-Principles Study on the Cubic $CaSiO_3$ (001) Surface

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**Abstract**: The geometric and electronic structure of the cubic $CaSiO_3$ (001) surfaces have been studied using first-principles density functional theory (DFT) calculations. Two different terminations, CaO- and $SiO_2$- terminated surfaces, were investigated. It has been found that Ca atom has the largest relaxation for both kinds of terminations, and the rumpling of the CaO-terminated surface is much larger than that of the $SiO_2$-terminated surface. The band gaps of the CaO- and $SiO_2$-terminated surfaces were calculated to be smaller than that of the $CaSiO_3$ bulk. It was also shown that the $SiO_2$-terminated surface has a lower energy than the CaO-terminated surface.

**AMS subject classifications:** 68U05, 68U07
**Keywords:** $CaSiO_3$, surface structure, density functional theory, electronic structure

## 1. Introduction

Composition estimates of the Earth reveal that the MgO-FeO-CaO-$SiO_2$-$Al_2O_3$ system could occupy ~ 99% of the mantle volume [1]. In the Earth's lower mantle, the Ca-bearing phase is present in the $CaSiO_3$ perovskite form [2,3], which is the third most important phase. Under ambient conditions, however, $CaSiO_3$ perovskite is not stable and it could readily convert to glass on the release of pressure. At 490-580 K and 27-72 GPa, $CaSiO_3$ perovskite undergoes

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phase transformation from tetragonal symmetry to ideal cubic structure [4].

Density functional theory (DFT) studies have been carried out on the lattice structure, sound velocity and elastic properties of bulk $CaSiO_3$ in tetragonal and orthorhombic phases as well as in low-symmetry cubic phase [5-7]. However, the structural and electronic properties of the $CaSiO_3$ surface are rarely investigated, despite the fact that the surfaces of other Ca-bearing perovskites, e.g. $CaTiO_3$ [8-10] and $CaZrO_3$ [11], have been well studied. In this work, first-principles calculations were carried out on the systematic study of the geometric and electronic properties of cubic $CaSiO_3$ (001) surface with CaO and $SiO_2$ terminations. The rumpling of the surfaces, band structures and energetic properties of the two kinds of terminations are compared to each other.

## 2. Computational details

The DFT calculations presented in this work were carried out within the generalized gradient approximation (GGA), using the projector-augmented wave (PAW) method and a plane-wave basis set, as implemented in the Vienna *ab initio* Simulation Package (VASP) [12,13]. The plane-wave energy cutoff is 600 eV for all calculations and the Brillouin zone integration is performed using the Monkhorst-Pack scheme with Ca (3s, 3p, 4s), Si (3s, 3p), and O(2s, 2p) treated as valence.

## 3. Results and discussion

### 3.1 Structural properties

We first optimized lattice constant of cubic bulk $CaSiO_3$ with the 12×12×12 *k*-point mesh. The computed lattice constant of cubic $CaSiO_3$ is 3.604 Å, which is in good agreement with the equation of state (EOS) determined lattice constant of cubic $CaSiO_3$ in previous experimental study (3.572 Å) [14] and other GGA calculated result (3.546 Å) [5]. This theoretical lattice constant was used in all surface calculations presented here. Two symmetrical repeat-slab surface models with space group P4/mmm were used for the calculations: CaO-terminated and $SiO_2$-terminated surfaces. For the CaO-terminated surface, the unit slab consists of four CaO and three $SiO_2$ layers, so that the slab is terminated with CaO layer on either surface. Similarly, for the $SiO_2$-terminated slab, there are three CaO and four $SiO_2$ layers in the unit slab, so $SiO_2$ layers are terminated on both outmost surfaces. For each unit slab, there are seven alternating CaO and $SiO_2$ layers, together with a 12 Å vacuum separation to minimize possible interactions between neighboring slab surfaces. For both slabs, the in-plane lattice constant is set to the computed cubic equilibrium value 3.604 Å, and the atomic

displacements perpendicular to the surface are fully relaxed using a 12×12×2 *k*-point mesh.

Because of the P4/mmm symmetry, there is a mirror reflection on the central layer of each slab, thus the relaxations of the atoms on top and bottom layers are of the same amplitude but along opposite directions, and so are other symmetrical layers. **Table 1** lists the atomic displacements $\delta z$ of the outmost three layers. For CaO-terminated surface, the surface layer Ca atom and O atom move toward opposite directions, i.e. the Ca atom moves inward to the central layer and the O atom relaxes outward to the vacuum region. The surface Ca atom has a large relaxation of 3.44% of the bulk lattice constant, which is the greatest relaxation of all atoms of both layers. For the $SiO_2$-terminated surface, the surface Si atom relaxes remarkably toward the central layer by 2.64 %. However, the largest relaxation is not on the surface layer atoms but on the second layer Ca atom, which relaxes outward (toward the surface) by 2.73%. It is noted that the Ca and Si atoms relax toward opposite directions with respect to the same-layer O atoms except the second layer of CaO-terminated slab. The Ca and Si atoms relax much more remarkably than O atoms in all layers. It is also found that the displacements of Ca atoms are much larger than those of Si atoms in both surface slabs, suggesting that Ca atom is much easier to relax than Si atom.

**Table 1.** Calculated atomic displacements (relative to ideal positions) $\delta z$ of the top three layers of CaO- and $SiO_2$-terminated $CaSiO_3$ surfaces. Units are in percent of theoretical $CaSiO_3$ cubic bulk lattice constant ($a$=3.604 Å). Positive values refer to displacements towards the surface.

| layer | CaO-terminated | | $SiO_2$-terminated | |
|---|---|---|---|---|
| | Atom | $\delta z$ | Atom | $\delta z$ |
| 1 | Ca | −3.44 | Si | −2.64 |
| | O | 0.79 | O | 1.35 |
| 2 | Si | 1.16 | Ca | 2.73 |
| | O | 0.03 | O | −0.09 |
| 3 | Ca | −0.45 | Si | −0.35 |
| | O | 0.14 | O | 0.20 |

In **Table 2**, we show the surface relaxation parameters. Surface rumpling parameter $s$ measures the outward displacement of the surface layer O atom with respect to the surface layer Ca or Si atom. $\Delta d_{12}$ is the change of the first interlayer spacing, as measured from the surface to the second layer Ca and Si atoms $z$-coordinate, and $\Delta d_{23}$ is similar with $\Delta d_{12}$ but between the second and the third layers. It can be seen from **Table 2** that the rumplings of CaO-terminated and $SiO_2$-terminated surfaces are very close, i.e. the rumpling of CaO-terminated surface is only slightly larger than that of $SiO_2$-terminated surface. Thus, our calculation suggests that the $CaSiO_3$ (001) surface could be almost even rough when it is terminated with either CaO or $SiO_2$ termination. Parameter $\Delta d_{12}$ is negative for both kinds of

terminations, indicating that the distance between the first and the second layers becomes smaller by comparison with its bulk value. The absolute value of $\Delta d_{12}$ for $SiO_2$-terminated surface is larger than that of CaO-terminated surface, suggesting that the distance between the surface layer and the second layer is much more reduced for $SiO_2$-terminated surface. On the contrary, $\Delta d_{23}$, the distance between the second and the third layers expands for both terminations, and the expansion is larger for $SiO_2$-terminated surface than for CaO-terminated surface.

**Table 2.** Surface relaxation parameters for CaO- and $SiO_2$-terminated $CaSiO_3$ surface. Values are in percent of theoretical $CaSiO_3$ cubic bulk lattice constant ($a$=3.604 Å)

| Surface | $s$ | $\Delta d_{12}$ | $\Delta d_{23}$ |
|---|---|---|---|
| CaO-terminated | 4.23 | −4.60 | 1.61 |
| $SiO_2$-terminated | 3.99 | −5.37 | 3.08 |

## 3.2 Band structures and partial density of states

In **Figure 1**, we show the calculated band structures of CaO- and $SiO_2$-terminated relaxed surfaces together with the band structure of bulk cubic $CaSiO_3$. The cubic bulk $CaSiO_3$ is calculated to have an indirect band gap of 3.55 eV, with the valance band maximum locating at R point and the conduction band minimum at Γ point as presented in **Figure 1(a)**. As can be seen from **Figure 1(b)**, the top valence band of CaO-terminated surface is flat between X and M points, with the calculated band gap of 2.57 eV. This gap value shows ~1 eV reduction with respect to its bulk band gap value. For the band structure of the $SiO_2$-terminated surface in **Figure 1(c)**, the calculated band gap is 1.62 eV, which is more reduced compared to its bulk value. The driving force for this relatively larger gap reduction is partially due to the tendency of the upper valence band states intruding upward near the M point. In addition, the lower conduction bands of $SiO_2$-terminated surface locate even lower than those of the CaO-terminated one, which narrows the band gap much more.

To clarify the reason of the reduced gaps of the surface slabs compared with the bulk, we then calculated the partial density of states (PDOS) of CaO- and $SiO_2$-terminated $CaSiO_3$ surfaces, as is shown in **Figure 2**. For both two surface types, O 2p states occupy the topmost valence bands, and Si 3s and 3p states contribute most to the lowest conduction bands. It is obvious that the central layer Si 3s and 3p PDOS of the CaO-termination is quite similar to the third layer Si 3s and 3p PDOS of the $SiO_2$-termination. However, the second layer Si 3s and 3p PDOS of the CaO-termination is very different to the surface layer Si 3s and 3p PDOS of the $SiO_2$-termination. The $SiO_2$-termination surface layer Si 3s and 3p has relatively large PDOS in the lowest conduction band area, ranging from 1.62 eV to ~4 eV, which suggests

that the surface Si 3s and 3p PDOS intrusion into the lower part is the main reason of the large band gap reduction of the $SiO_2$-terminated surface with respect to that of the $CaSiO_3$ bulk.

## 3.3 Surface energies

In order to compare the energetic stability of CaO-terminated and $SiO_2$-terminated surfaces, we calculated their surface energies using the standard approach of the surface energy calculation [8,11,15]. The surface energy $E_s$ is defined as the sum of the cleavage energy ($E_{cle}$) and relaxation energy ($E_{rel}$):

$$E_s(I) = E_{cle} + E_{rel}(I) \tag{1}$$

where "I" denotes CaO or $SiO_2$ terminations. Since the two terminations form simultaneously under cleavage, it is assumed that the relevant cleavage energy is the same for both terminations:

$$E_{cle} = \frac{1}{4}[E_{slab}^{unrel}(C_aO) + E_{slab}^{unrel}(SiO_2) - 7E_{bulk}] \tag{2}$$

Where $E_{slab}^{unrel}(C_aO)$ and $E_{slab}^{unrel}(SiO_2)$ are the energies for unrelaxed CaO- and $SiO_2$-terminated slabs respectively, and $E_{bulk}$ is the cubic $CaSiO_3$ bulk unit cell energy. The factor 1/4 is due to the fact that four surfaces are created during the cleavage, and the factor 7 is introduced because the two seven-layer slabs represent seven bulk unit cells. The relaxation energy is defined as the energy change after relaxation:

$$E_{rel}(I) = \frac{1}{2}[E_{slab}^{rel}(I) - E_{slab}^{unrel}(I)] \tag{3}$$

Where $E_{slab}^{rel}(I)$ is the slab energy after relaxation. Since both top and bottom surfaces of the

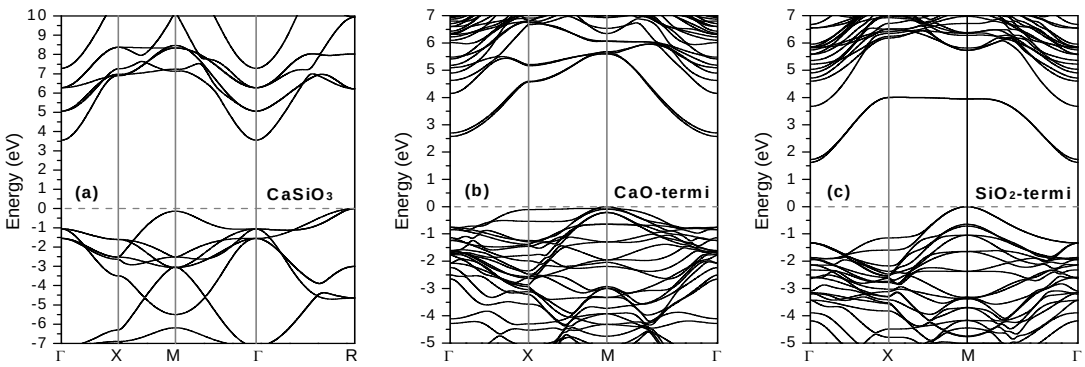


**Figure 1:** Band structures of $CaSiO_3$ cubic bulk (a), CaO-terminated surface (b) and $SiO_2$-terminated surface (c)

slab are relaxed, a factor 1/2 is introduced in Equation 3. The surface energies we obtained are $E_s(C_aO) = 0.98eV$ and $E_s(SiO_2) = 0.87eV$ , respectively, which indicates that the $SiO_2$-terminated surface is energetically favorable. In other words, there could be more $SiO_2$ terminations on $CaSiO_3$ (001) surface rather than CaO terminated ones.

# 4. Conclusion

We have found from first-principles DFT calculations that for the cubic $CaSiO_3$ (001) surface, the rumpling of CaO-terminated surface is larger than that of the $SiO_2$-terminated one. Ca atoms relax much more than Si and O atoms for both kinds of surface termination. Compared with the band gap of cubic bulk $CaSiO_3$, the band gap of $SiO_2$-terminated surface reduces much more than CaO termination, which is mainly due to the downward of the conduction band state of surface layer Si 3s and 3p states. Energy calculation reveals that the two models of surface terminations has relative close surface stabilities, with the $SiO_2$-terminiated surface more stable than the CaO-terminated one.

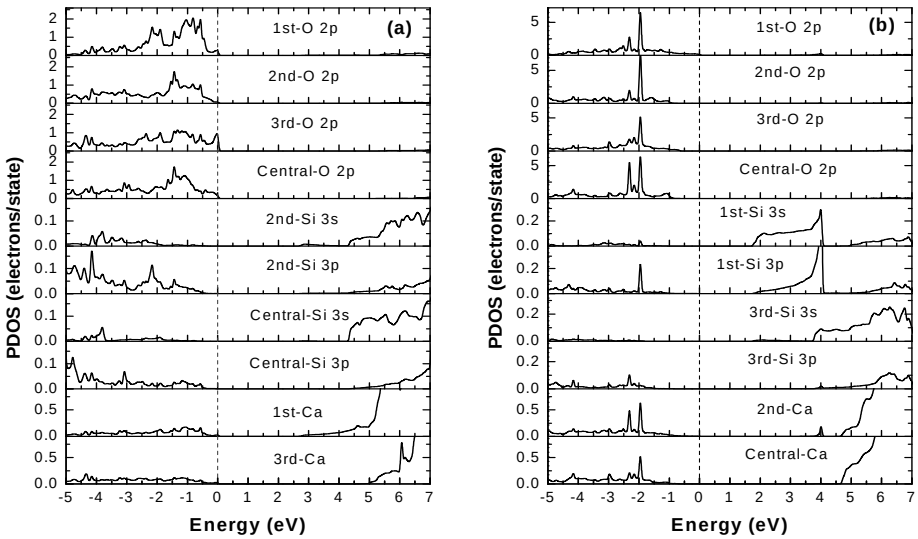


**Figure 2:** PDOS of atoms in each layer: (a) CaO-terminated surface and (b) $SiO_2$-terminated surface.

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