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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