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Structural, electronic properties with different terminations for fluorapatite (001) surface: A first-principles investigation

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ABSTRACT

The Ca-rich, Ca-middle and PO_4-rich terminations of fluorapatite (0 0 1) surface have been investigated with first-principles calculations based on density functional theory (DFT). Results show that the major displacement of the Ca atom in the Ca layer is along the *z*-axis direction, while these atoms in the $Ca_3(PO_4)_3F$ layer show more lateral movements in the (0 0 1) plane, especially for the Ca-middle and PO_4-rich terminations. The Ca-middle termination has the lowest surface energy (0.793 J/m^2), and is more similar to the bulk in charge distribution. These bonds near the surface appear to be mainly contractive, which indicates that they are strengthened after the relaxation. The Ca—O bonds are more susceptible during the redistribution of the charge in the surface. Further analysis shows that the interactions in the Ca-rich termination are not as strong as that of the Ca-middle and PO_4-rich terminations.

1. Introduction

Apatites, the important functional materials, have attracted extensive attentions due to their unique hexagonal structures. The corresponding researches encompass a series of frontiers, such as environmental remediation, nuclear waste treatment, laser materials, micro-nanometer coating materials, biomimetic and medical materials, and so on [1–11]. In addition, apatites are the most abundant phosphorus-bearing minerals, which usually contain other valuable compositions, such as rare earths and uranium [12]. Therefore, the effective separation of these elements is related to the comprehensive recovery and utilization of the apatite resources.

Recently, first-principle methods have been widely used in acquiring the micro-structural information of various minerals and practices with high accuracy. L. Calderı'n and M.J. Stott have done some studies on the electronic and crystallographic structures of different apatites [13]. The calculations showed that apatites are quite flexible regarding the presence of different anions in the *c* channel. Paul Rulis et al. have taken systematic studies on the fluorapatite and hydroxyapatite, which include the crystal structures and surfaces [14,15]. E. Menéndez-Proupin et al. have studied the elastic properties of fluorapatite [16]. The results of the above investigations have showed that fluorapatite is slightly stiffer than hydroxyapatite in the hexagonal plane and is also more compliant along the hexagonal axis.

For the crystal termination, the periodic arrangement of atoms would be interrupted suddenly and form the new surface state, which lead to a series of important changes, including the interactions among atoms, charge distribution and electronic state [17]. Meanwhile, the different terminations that contain various atoms can directly affect the properties of the surface, such as surface synthesis, surface modification and the interaction of the reagent on the minerals surface. In this paper, three different terminations of the fluorapatite (0 0 1) surface are calculated systematically. It is expected that this research is of high interest for understanding the structure and electronic properties of fluorapatite, and also providing the theoretical basis for surface interaction.

2. Computational methods and models

All calculations were carried out using the density-functional theory (DFT) with Cambridge Serial Total Energy Package (CASTEP) [18]. The ultra-soft pseudo-potential [19] was performed to describe the electron–ion interactions. The exchange correlation functional using was the generalized gradient approximation (GGA) developed by Perdew-Wang generalized-gradient approximation (PW91) [20]. The plane-wave cutoff energy of 400 eV was used throughout and the Brillouin zone was sampled with

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k-points of a 2 × 2 × 2 grid for all the structural calculations, which were found to be enough for our present system. The self-consistent calculations were considered and the convergence tolerances were set using the followings parameters: The maximum displacement, maximum force, maximum energy change, maximum stress and SCF convergence tolerance were 0.002 Å, 0.08 eV/Å, 2.0×10^{-5} eV/atom, 0.1 GPa and 2.0×10^{-6} eV/atom, respectively. Valence electron configurations considered in this study were O $2s^2 2p^4$, F $2s^2 2p^5$, P $3s^2 3p^3$, Ca $3s^2 3p^6 4s^2$.

We have firstly optimized the bulk fluorapatite model and got the following lattice parameters: a = b = 9.478 Å, c = 6.894 Å. As shown in Table 1, the results are in good agreement with the experimental values [21] with the errors are 1.09% and 0.07% respectively, which means that our method is credible for the subsequent calculations.

Table 1
The comparison between the lattice parameters of the optimized model and the experimental results of the bulk.

Parameter	a(b)/Å	c/Å
Calculated value	9.478	6.894
Experimental value	9.375	6.887
Error	1.09%	0.07%

As shown in Fig. 1, the fluorapatite bulk contains two $Ca_5(PO_4)_3$-F structures which distribute in six layers along the (0 0 1) plane, with the stacking sequence of Ca, $Ca_3(PO_4)_3F$, Ca, Ca, $Ca_3(PO_4)_3F$ and Ca. Generally, these Ca atoms can be divided into two groups: the columnar Ca_1 in the independent Ca layer and the mirror Ca_2 in the $Ca_3(PO_4)_3F$ layer [22]. In fact, the two adjacent Ca_1 (see Fig. 1, $Ca_{1\text{-}1}$ and $Ca_{1\text{-}2}$) are quite different though they have the same coordination number in bulk. The $Ca_{1\text{-}1}$ bond with more O atoms in the lower $Ca_3(PO_4)_3F$ layer and the $Ca_{1\text{-}2}$ combine with that in the upper layer. When exposed along the fluorapatite (0 0 1) plane at the same time, the $Ca_{1\text{-}1}$ and $Ca_{1\text{-}2}$ will have different coordination numbers and show individual characteristics. Therefore, the fluorapatite (0 0 1) surface consists of three types of terminations, that is, Ca-middle, PO_4-rich and Ca-rich terminations. In order to effectively study these properties, the slab models should contain enough atom layers to exhibit the bulk-like character interiors. Meanwhile the vacuum region added on each surface is 10 Å, which has been demonstrated to be enough for this study. The side views of the three (1 × 1) slabs of fluorapatite (0 0 1) surface are shown in Fig. 2. Fig. 2(a) is the Ca-rich termination that contains seventeen atomic layers, Fig. 2(b) is the Ca-middle termination that has fifteen atomic layers and Fig. 2(c) is the PO_4-rich termination that owns thirteen layers of atoms. All atoms were fully relaxed during the surface structural optimizations.

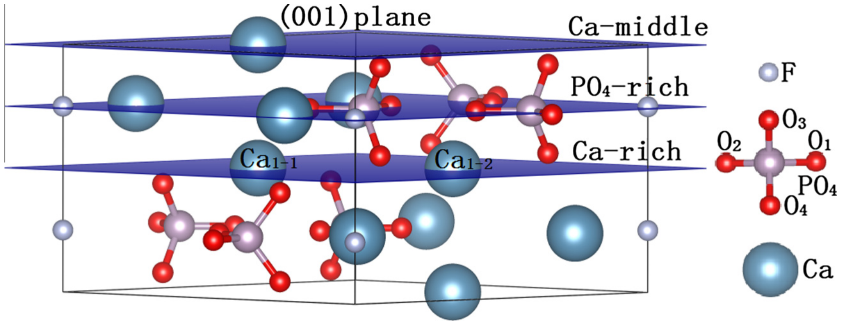

Fig. 1. Crystal structure of fluorapatite and the stacking sequence of (0 0 1) surface layers.

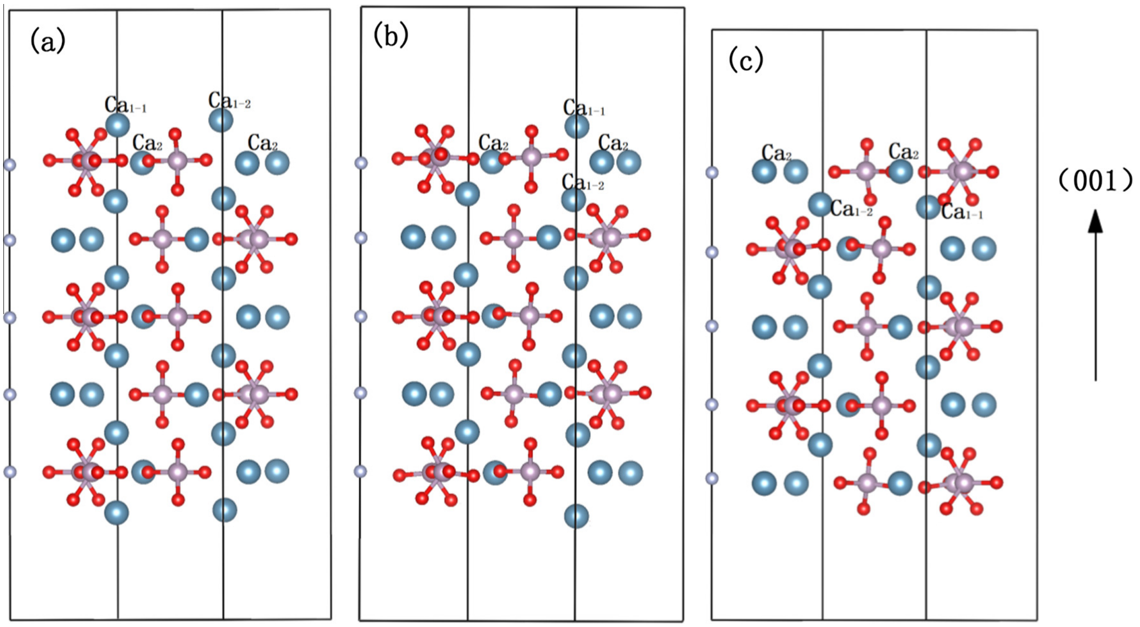

Fig. 2. Side views of the three different slab models of the fluorapatite (0 0 1) surface: (a) Ca-rich termination, (b) Ca-middle termination and (c) PO_4-rich termination.