



First-principles investigation on the geometries, stabilities and defective properties of fluoride surfaces



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ABSTRACT

From first-principles calculations, we perform a systematic study of the stoichiometric surface morphology of NaF, MgF₂ and CaF₂ and the associated stability, charge transfer and defective properties. Given the geometries of their low index surfaces, it is found that the surfaces with the lowest surface energies for NaF, MgF₂, and CaF₂ are (100), (110) and (111) surfaces, respectively. The dependence of surface energies, electrostatic potentials and effective charges on the slab thickness is discussed. Moreover, we demonstrate the broken bond model, which is based on the covalent interactions, is also suitable for ionic fluoride crystals after modification. By setting a fitting parameter k around 0.5, the estimated surface energies are close to the ones by slab modeling for all the 10 surfaces considered in this work.

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1. Introduction

Metal fluorides have attracted great attention due to their special properties and important applications in many fields such as medicine [1,2], water treatment, extractive metallurgy [3], optical material [4], and fluoride source in chemical industry [5]. Recently, the interest in metal fluorides as materials for heterogeneous catalysis is renewed by the development of their synthesis techniques, introducing higher surface-to-bulk ratios [6,7]. In these applications, the surfaces and interfaces play very important roles.

Moreover, fluoride solids are very important adsorbent in the fluoride volatility technology of spent nuclear fuel recovery, in which the adsorption and desorption technique is applied to purify the UF₆. In spent fuel recovery processes, U is fluorinated to volatile UF₆ by F₂. Thus U is separated from some other species such as Th, Pa, rare-earth, and alkaline-earth metals. However, in gaseous UF₆, there is a certain amount of other fission products, such as Nb, Ru, Sb, Mo and Te, whose fluorides have high volatility. According to the different adsorbing properties from other fission products on fluoride adsorbent surfaces, UF₆ can be purified by adsorption

and desorption process. So far, a variety of adsorbents have been investigated by experiments such as LiF, NaF, MgF₂ and CaF₂ [8–11].

While the fluoride volatility technology is advancing steadily, there is less knowledge about the detailed mechanism in the adsorption and desorption processes. Since the interactions of fluoride crystals with gaseous UF₆ and impurities are initiated at the surfaces, a thorough understanding of the surface properties is a necessary step to understand the associated surface interactions with the adsorbed gases. Namely, it is very essential to know the geometries of different fluoride surfaces, their stability and the differences between these surfaces. These properties are determined by the atomic details such as interfacial electron cloud overlap, surface atomic reconstruction and charge redistribution, calling for first-principles investigations at the atomic scale. So far, there have been few theoretical studies on fluoride surfaces reported. Moreover, the reported results are obtained by using different software, methods, and potentials [12–14], which creates difficulties in comparison between them.

In this work, we have performed a systematic study of the stoichiometric surface morphology of NaF, MgF₂ and CaF₂ and the associated stability, electronic structures and defective properties. From the atomic geometries of these surfaces, the broken bond model is used to estimate their surface energies. We find a simple rule to predict the surface stabilities of metal fluorides. Our results

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extend the understanding of the properties of fluoride surfaces using first-principles calculations, and pave the way to further investigate the fluoride volatility process at the atomic scale.

2. Calculation details

Our calculations are performed under the framework of density functional theory as implemented in the Vienna ab initio simulation package (VASP) [15,16]. The projected augmented wave method (PAW) [17] and the generalized gradient approximation (GGA) [18] are used. The exchange–correlation potential is described by the Perdew–Burke–Ernzerhof (PBE) functional [19] and the local density approximation (LDA). The wave functions are expanded in a plane-wave basis set with an energy cutoff (E_{cut}) at 600 eV. The k -points in the two dimensional Brillouin zone are sampled within the Monkhorst–Pack scheme [20] for different surfaces and bulk simulations, as listed in Table 1. A vacuum width of 1.5 nm is used for all surfaces, which ensures the interaction between repeated slabs in direction normal to the surface is negligible. The lattice constants and internal freedom of the unit cell are fully optimized until the Hellman–Feynman forces on the atoms are less than 0.01 eV/Å. The effective charge for each atom (charge difference after bonding) is calculated using Bader charge analysis [21]. All these calculations are checked using larger energy cutoffs and denser k -meshes; the results of total energy and Hellmann–Feynman forces are converged within 0.01 eV and 0.01 eV/Å, respectively.

3. Results and discussions

3.1. Bulk properties

Here, NaF, MgF₂ and CaF₂ are chosen as typical fluoride crystals for two reasons. First of all, these crystals are more popular adsorbents in the spent fuel recovery process, as mentioned above. Moreover, they have very different crystal structures, each representing a group of materials with similar atomic structures. As shown in Fig. 1, sodium fluoride (NaF) is an inorganic chemical compound with a face-centered cubic lattice B₁ structure. Similar to sodium chloride, it crystallizes in a cubic motif where both Na⁺ and F[−] occupy octahedral coordination sites as indicated by green box in Fig. 1(a). Magnesium fluoride (MgF₂) crystallizes as tetragonal crystal with a space group *P42/mnm*. The structure of MgF₂ is similar to that in rutile, featuring octahedral Mg²⁺ centers and 3-coordinate fluoride centers, as shown in Fig. 1(b). CaF₂ crystallizes in a cubic motif called a fluorite structure. Ca²⁺ ions are eight-coordinated, centered in a cubic box formed by eight F[−] anions. Each F[−] anion is surrounded by four Ca²⁺ ions, as shown in Fig. 1(c).

Here, an energy cutoff of 600 eV is applied, since using a low one yields non-smooth energy surface as shown in Fig. 2, where $E_{cut} = 400$ eV is applied, and the ground-energy values corresponding to different exchange–correlation terms are compared at different lattice constants. It can be found that by using a low E_{cut} , the obtained lattice constant of NaF with the lowest total energy deviates significantly from the experimental value [22]. Moreover, the energy minima do not present as quadratic functions, indicating a

poor prediction of the elastic parameters. Therefore, we should emphasize that a high E_{cut} value should be employed.

The calculated lattice parameters are compared to the corresponding experimental values in Table 2, for all three fluoride crystals chosen in the present study. The PBE results agree well with the experimental values, with negligible overestimate ($\Delta V < 3\%$). In contrast, the LDA results have relatively larger mismatches. Therefore, PBE functional is adopted in this work for further calculation. The calculated elasticity-relevant properties of NaF, MgF₂, and CaF₂ are listed in Table 3. These PBE results are also reasonably consistent with the experimental reported values, indicating our simulations are reliable.

3.2. Surface atomic geometries

With the calibrated E_{cut} and the chosen exchange–correlation term, the optimized surface configurations of the three chosen fluoride solids are obtained. As shown in Fig. 3, NaF (100) and NaF (110) surfaces are both non-polarized, while the (111) surface is polarized. Since the Na⁺ cations and F[−] anions alternatively stack along the (111) direction, the structure of NaF (111) has two kinds of terminals. Each surface atom on NaF (100) has five nearest-neighbor atoms surrounded, while the one on NaF (110) has four. In contrast, the surface atoms on NaF (111) has the lowest coordination number. For both Na-terminated and F-terminated NaF (111) surfaces, each surface atom has only three nearest-neighbor atoms. Fig. 4 shows all of the four surface structures, corresponding to the case of low-index MgF₂. These surfaces are all non-polarized. In the case of CaF₂, the (100) surface is polarized, which has a monolayer of Ca²⁺ cations on one surface and a monolayer of F[−] anions on the other. Both of the other two surfaces (110) and (111) are non-polarized, as shown in Fig. 5.

3.3. Surface stabilities

The surface energy is the energy required to create a surface and it correlates with the catalytic activity, adsorption and segregation. For a non-polar surface, the surface energy is calculated using slab models as:

$$E_{surf} = \frac{(E_{slab}(N) - N \cdot E_{bulk})}{2S_{surf}}, \quad (1)$$

where $E_{slab}(N)$ is the total energy of the simulated slab with two identical surfaces, N is the number of atoms in the simulation box, E_{bulk} is the total energy per atom of the bulk structure, and S_{surf} is the surface area. In the case of a polar surface, E_{surf} is difficult to determine. Building slabs with odd number of layers with identical surfaces result in a non-stoichiometric slab, which does not represent the correct surface energy when compared to the bulk case. On the other hand, building slabs with even number of layers would result in two different surfaces. In order to resolve this dilemma, in this work, E_{surf} of a polar surface is obtained by averaging over two surfaces with different terminations [31]. Here, the chemical potentials are not considered since the surfaces are all stoichiometric in this work. However, we should emphasize that for calculating the surface energies of non-stoichiometric surfaces [32] or adsorbed surfaces [33], the corresponding chemical potentials should be

Table 1
The k -points used in the calculations of bulk and surfaces for different metal fluorides.

	Bulk	(100)	(110)	(111)	(001)	(101)
NaF	10 × 10 × 10	10 × 10 × 1	10 × 6 × 1	6 × 6 × 1	–	–
MgF ₂	10 × 10 × 16	10 × 10 × 1	16 × 8 × 1	–	10 × 10 × 1	8 × 10 × 1
CaF ₂	8 × 8 × 8	8 × 8 × 1	8 × 6 × 1	6 × 6 × 1	–	–

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