First-principle study of polytype structures of 1:1 dioctahedral phyllosilicates

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ABSTRACT

The polytype structures of the three 1:1 dioctahedral phyllosilicates found in nature, kaolinite, dickite, and nacrite, have been investigated, using first-principle calculations within density functional theory. The crystal structures were calculated by being optimized with relaxation of all atomic positions. The calculated structural parameters, including the orientation of the OH groups, for the three polytypes are in good agreement with experimental data. In particular, for kaolinite and dickite, the three-inner surface OH groups were predicted to be oriented nearly perpendicular to the (001) plane. In contrast, one of the inner surface OH groups of nacrite was predicted to be nearly parallel with respect to the (001) plane. Based on a comparison of formation energies, the chiral polymorphs of kaolinite (B- or C-site vacancy) have similar formation energies as dickite and nacrite, while achiral kaolinite with A-site vacancy is only slightly less stable than the other polytypes.

INTRODUCTION

Kaolinite [Al(\text{SiO}_4)(\text{OH})_8] is a 1:1 dioctahedral phyllosilicate (layered aluminosilicate) with little, if any, isomorphous substitution (Bailey 1980). Each layer consists of a sheet of SiO\text{4}, tetrahedra forming six-membered silicate rings connected via a common apical oxygen atom to a sheet of edge-sharing AlO\text{4}, octahedra. Of the 12 possible polytypes, only three are found in nature: kaolinite, dickite, and nacrite. These minerals are stacked with different positions of octahedral vacancies in successive layers. Kaolinite is known to be the most abundant polytype, while dickite and nacrite are less common. It is not certain why only these three kaolinite polytypes exist although there are as many as 28 possible ways of layer stacking (Newnham 1961).

Since Pauling (1930) first outlined the crystal structure of kaolinite and related phyllosilicates, many studies have been conducted to clarify the details of its structure and polymorphs. The crystal structure of kaolinite (non-H atoms) was first reported by Brindley and Robinson (1946) using powder X-ray diffraction. Bailey demonstrated that both kaolinite and dickite are based on a 1\text{M} stacking sequence of layers (Bailey 1963, 1988). As a result of these studies, it has been shown that octahedral site vacancies alternate in dickite, whereas in kaolinite the location of the vacancy is the same in repeating layers. Of the many possible polytypes of 1:1 phyllosilicates, the two most common polytypes found in nature, kaolinite and dickite, are based on the 1\text{M} structure. In the 1\text{M} structure, there are three possible locations for the vacant octahedral site, denoted as A-, B-, or C-site vacancies. If the vacant site occurs in the B- or C-site, the structures are chiral; in the case of the A-vacant site, the structure is achiral. In nature, the vacant site of kaolinite occurs in the B (or C) position resulting in a chiral structure. The sequence of layers in nacrite is that of the standard 6\text{R} polytype (Bailey 1988).

Molecular dynamics simulations based on first-principles calculations have proven to be a powerful tool for obtaining microscopic insight into the atomic and electronic properties of materials. Kaolinite and its polymorphs have been the subject of recent theoretical studies using first-principle methods (Balan et al. 2001; Benco et al. 2001a, b; where predicted crystal structures and vibrational spectra have been compared to experimental data. In the papers by Benco et al. (2001a, 2001b), the orientation of the OH groups in kaolinite and dickite were reported; however, nacrite was not included in their study.

Perhaps the most useful way to test the applicability of first-principle calculations is to compare the predicted structural parameters and layer stacking with experimental values (Ligny and Navrotsky 1999; Bookin et al. 1989). In the case of the kaolinite group polymorphs, such a comparison can provide insight about why one polymorph is favored over another. In the present study, we performed first-principles calculations for kaolinite, dickite, and nacrite, the three polytypes found in nature, using density functional theory (DFT). To the best of our knowledge, this is the first reported first-principle study of the three polymorphs using the same level of approximation. At present, first-principle calculations using density functional theory provides perhaps the best-available level of approximation that provides a high level of theory within the constraints of reasonable computational time required for these large calculations.

METHOD

The calculations were performed using the plane-wave pseudo-potential software CASTEP (Segall et al. 2002). Density-functional theory (DFT) using a generalized gradient approximation (GGA) was used, where Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al. 1996) was adopted as the exchange-correlation functional.

For structural optimization, electron-core interactions were described by small-