Kaolin polytypes revisited ab initio at 10 GPa

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ABSTRACT

Based on systematic ab initio exploration, we reported last year that two new interlayer translations for kaolinite, –a/3 and (a+b)/3, allowed a new family of kaolin polytypes under moderate pressure. Both translations place each silicon atom of a kaolin layer on top of a hydroxyl group from the kaolin layer below, resulting in a triangular dipyramidal fivefold coordination to all silicon atoms. The predicted –a/3 translation has since been independently observed experimentally at ~7 GPa, as kaolinite III phase, by compression of a natural kaolinite (Keokuk, Iowa). Encouraged by that verification, we extend here to the entire kaolin system both translations we had predicted for kaolinite. Based on calculated enthalpies and cell volumes for models optimized with ab initio density functional theory (DFT) calculations under pressure, we report three main results. First, we predict the existence of a kaolinite IV phase at a pressure not higher than 60 GPa and its likely crystal structure. Second, we predict three novel high-pressure crystal-structure models for nacrite, ranked by their enthalpy value, one of which is likely to be observed at about 10 GPa. Finally, three other novel and ranked high-pressure crystal-structure models are reported for dickite. Our results from interpretation of ab initio DFT calculations should guide experimental studies and facilitate their interpretation.

Keywords: Kaolin polytypes, kaolinite, dickite, nacrite, phase transitions, high pressure, ab initio DFT calculations

INTRODUCTION

In a systematic ab initio DFT exploration, Mercier and Le Page (2008) (MLP8) rationalized low-energy phases in the kaolin system, based on an assumption of energy independence between non-neighboring layers. In the present letter, the MLP8 reference system for fractional atom coordinates is used throughout. Table 2 of MLP8 lists 72 possible low-energy phases at zero pressure, 36 of which are energy-distinguishable. The list includes all four kaolin polytypes then known: kaolinite, dickite, nacrite, and HP-dickite. A rough graph of enthalpy vs. pressure for all 36 phases (their Fig. 4) resulted from the list. All current reliable observations about synthesis, diagenesis, and phase transformations of members of the kaolin system were rationalized with this graph. In particular, the layer-slipping mechanism of Dera et al. (2003) for the reversible dickite ↔ HP-dickite transformation at ~2 GPa allowed rationalization of the observed existence of dickite at zero pressure and of the puzzling absence from the literature of reliable observations of any solid-to-solid transformation of kaolinite, dickite, or nacrite into each other under pressure.

In an extension of the work in MLP8, Mercier and Le Page (2009) (MLP9) assumed the generality of the layer-slipping mechanism for kaolin polytype transformations proposed by Dera et al. (2003). Application to a systematic search for post-kaolinite phases through an examination of 19 possible structure models has led MLP9 to the prediction of two prime candidate model phases for post-kaolinite, one with space group symmetry P1 and the other with Cm at 12 GPa, both new structures (MLP9). They result, respectively, from new interlayer translations –a/3 and (a+b)/3, which were argued to only exist at high pressure (MLP9).

Upon application of pressure in a diamond anvil cell at room temperature, Welch and Crichton (2010) have recently observed two phase transitions in kaolinite from Keokuk (Iowa). The ambient phase (kaolinite I) transforms reversibly into kaolinite II at 3.7 GPa, whereas kaolinite II transforms irreversibly into kaolinite III at 7.8 GPa. Using powder diffraction data recalculated with the models from supplementary tables in MLP8 and MLP9, Welch and Crichton identified their kaolinite II phase as MLP8’s model K5a [=MLP9 model (KT1)a] and their kaolinite III phase as the prime-candidate triclinic P1 phase for high-pressure kaolinite predicted by MLP9. This recent discovery of the kaolinite III phase has established experimentally the novel –a/3 and by extension (a+b)/3 translations, which were predicted by MLP9 to occur upon compression of kaolinite. We extend here in MLP8 fashion those interlayer translations from kaolinite to the whole system of kaolin polytypes at 10 GPa. In particular, we establish ab initio in this way the crystal structures that post-nacrite and post-HP-dickite phases are likely to adopt upon compression to about 10 GPa.

EXPERIMENTAL METHODS

Model building

Table 2 in MLP8 lists the combinations of the six possible kπ/3 (k = 0–5) rotations R of the kaolin layers with the six interlayer translations T [0; (2a+b)/3;