American Mineralogist, Volume 95, pages 1117–1120, 2010

LETTER

Kaolin polytypes revisited ab initio at 10 GPa

PATRICK H.J. MERCIER,[1,*] YVON LE PAGE,[1] AND SERGE DESGRENIERS[2]

[1]Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, Ontario K1A 0R6, Canada
[2]Laboratoire de Physique des Solides Denses, Department of Physics, University of Ottawa, 150 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada

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