Thermodynamic Behaviors of Pyrophyllite and Montmorillonite Clay Structures: A Perspective Derived from Plane-Wave DFT

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Abstract

Buffer clay materials possess the mechanical, thermal, and hydraulic properties required to sufficiently swell and fill gaps between vitrified used nuclear fuel and surrounding rock during long-term deep geological storage. However, typical clays need to be functionalized to further provide protection against the mobilization of harmful radionuclides such as iodine and technetium-99. While many functionalized clays have been synthesized and their respective performances were studied, fundamental understanding of the functionalization processes (e.g., location of functional groups, mechanical process of functionalization) is still lacking. To gain a deeper understanding, plane-wave density functional theory was used to investigate thermodynamic behaviors of two common phyllosilicate clays: pyrophyllite and montmorillonite. Benchmarked modeling approaches were established using pyrophyllite as the clay model while the effects of isomorphic substitution, that resulted in overall negative charge, was evaluated by comparing energies of edge surface structures and sodium ion adsorption onto both clays, respectively. In addition to defining a standard periodic modeling approach for functionalized clays, this work helps provide initial insight into how functionalization may impact clay structure formation and adsorption sites during metal intercalation.