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Quantum mechanical calculations of trans-vacant and cis-vacant polymorphism in dioctahedral 2:1 phyllosilicates

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ABSTRACT

Trans-vacant and cis-vacant polymorphs of smectites and illites were distinguished by studying different cation substitutions in octahedral and tetrahedral sheets and in the interlayer. The standard Kohn-Sham self-consistent density functional method was used in the generalized gradient approximation (GGA) with numerical atomic orbitals as the basis set. The calculations reproduce the differences in the lattice parameters between the cis-vacant and trans-vacant configurations as observed from experimental studies of phyllosilicates. This theoretical approach is a useful tool for predicting crystallographic properties that must be calculated for smectites and illites because they cannot be determined experimentally in these clay minerals, especially the cis-vacant and trans-vacant configurations. The effect of cation substitutions in the octahedral and tetrahedral sheets on various structural features is also presented. The calculated effects are consistent with experimental results. The energy differences between the cis-vacant and trans-vacant polymorphs for a given composition are lower than the energy changes produced by the relative cation distributions in the octahedral sheet. Nevertheless, in the most illitic samples the trans-vacant arrangement is more stable than the cis-vacant form, in accord with experimental studies.