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A first-principles study of the phase transition from Holl-I to Holl-II in the composition $KAlSi_3O_8$

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Abstract

The phase relation and structural evolution of Holl-I and Holl-II in the composition $KAlSi_3O_8$ at 0 K have been investigated by the first-principles method up to 130 GPa. Holl-I and Holl-II are polymorphs of $KAlSi_3O_8$ stable at low pressures and high pressures, respectively. The transition pressure is determined at ~23(5) GPa, in agreement with recent experimental observations. All experimentally observed major changes associated with this phase transition such as the deviation of the γ-angle from 90°, splitting of the *a*- and *b*-axes, as well as its *P*-*V* evolution, are successfully simulated. By evaluating the effect of different Al/Si substitution mechanisms on the computing cell of Holl-I, we have found: (1) different Al/Si substitution mechanisms do not result in apparent difference in the minimized cohesive energies, suggesting a possible random distribution of Al and Si; (2) different Al/Si substitution mechanisms lead to different powder X-ray diffraction features, which, compared to the experimentally observed powder X-ray diffraction data, implies that local non-random distribution of Al and Si exists to some extent in the Holl-I structure; and (3) the phase transition from Holl-I to Holl-II might be associated with a change in the distribution pattern of Al and Si in the structure. From the simulated compression data, we have derived K_0 = 174 GPa and V_0 = 244.82 Å^3 for Holl-I, and K_0 = 168 GPa and V_0 = 244.8 Å^3 for Holl-II (K'_0 fixed at 4). The larger K_0 of Holl-I is probably related to the more stable squared open tunnel delimited by the rigid tetragonal octahedral framework, which is gradually deformed by compression in Holl-II after the phase transition from Holl-I to Holl-II.

Keywords: Equation of state, first-principles simulation, Holl-I, Holl-II, phase transition