A first-principles study of the phase transition from Holl-I to Holl-II in the composition KAlSi$_3$O$_8$

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ABSTRACT

The phase relation and structural evolution of Holl-I and Holl-II in the composition KAlSi$_3$O$_8$ at 0 K have been investigated by the first-principles method up to 130 GPa. Holl-I and Holl-II are polymorphs of KAlSi$_3$O$_8$ 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 $\gamma$-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 square 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

INTRODUCTION

Feldspar is one of the dominant phases in the Earth’s upper continental crust and may be carried from the Earth’s surface down to the Earth’s interior via the subduction process (Dupre and Allegre 1983; Hofmann 1997; Bozhilov et al. 1999; Hirose et al. 1999; Liu et al. 2007; Wu et al. 2009). As demonstrated by some high-P experiments up to about 24 GPa (Irifune et al. 1994), the proportion of its high-P form, mainly KAlSi$_3$O$_8$-hollandite, could volumetrically account for one third of the phase assemblages of the subducted upper continental crust composition, so that its importance in the geodynamic process in the deep interior of the Earth cannot be overestimated. Orthoclase (Or, KAlSi$_3$O$_8$) is one of the major end-members in the feldspar family, and its high-P behavior is of great interest to many investigators (e.g., Yamada et al. 1984; Zhang et al. 1993; Urakawa et al. 1994; Yagi et al. 1994; Tutti et al. 2001; Akaogi et al. 2004; Sueda et al. 2004; Nishiyama et al. 2005; Liu 2006; Ferroir et al. 2006; Yong et al. 2006; Liu and El Goresy 2007; Hirao et al. 2008; Liu et al. 2010). First, Or (KAlSi$_3$O$_8$) breaks down to a three-phase assemblage (wadelite-type K$_2$Si$_2$O$_5$ + kyanite-type Al$_2$Si$_3$O$_9$ + SiO$_2$) at around 6 GPa and 600–1400 °C. Second, these three phases recombine to form a hollandite-type phase with the composition KAlSi$_3$O$_8$ (Holl-I hereafter) at about 9–10 GPa and 1000–1500 °C. Third, Holl-I transforms to a structurally modified hollandite-like phase (Holl-II; KAlSi$_3$O$_8$) at about 23–25 GPa and 500–1500 °C. Finally, Holl-II possibly remains thermodynamically stable up to 128 GPa. Mainly due to its unquenchable nature during decompression, Holl-II was difficult to detect within experimental products generated by traditional high-P quench methods, so that some discrepancy in the phase transition from Holl-I to Holl-II was reported (Tutti et al. 2001; Sueda et al. 2004; Nishiyama et al. 2005; Ferroir et al. 2006). Holl-I has tetragonal symmetry $I4/m$ (Ringwood et al. 1967; Yamada et al. 1984), whereas Holl-II has monoclinic symmetry...