Structure refinement of high-pressure hexagonal aluminous phases $K\textsubscript{1.00}Mg\textsubscript{2.06}Al\textsubscript{1.80}Si\textsubscript{1.15}O\textsubscript{12}$ and $Na\textsubscript{1.04}Mg\textsubscript{1.88}Al\textsubscript{4.64}Si\textsubscript{1.32}O\textsubscript{12}$

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ABSTRACT

Two hexagonal aluminous phases, which could serve as potential Na- and K-host minerals in the lower mantle, with compositions $K\textsubscript{1.00}Mg\textsubscript{2.06}Al\textsubscript{1.80}Si\textsubscript{1.15}O\textsubscript{12}$ and $Na\textsubscript{1.04}Mg\textsubscript{1.88}Al\textsubscript{4.64}Si\textsubscript{1.32}O\textsubscript{12}$ were synthesized at 22–25 GPa and 1500 °C. The K-rich hexagonal aluminous phase was synthesized for the first time. Crystal structures of both hexagonal aluminous phases were refined using the Rietveld method. Obtained interatomic distances and bond angles were compared to published data on the hexagonal aluminous phase CaMg$_2$Al$_2$O$_4$. The general chemical formula of the hexagonal aluminous phase is represented as $[\text{M3}][\text{M2}][\text{M1}]_2\text{O}_{12}$, where the small-, middle-, and large-sized cations occupy the M1, M2, and M3 sites, respectively. Changes of size and shape of M1O$_6$ octahedra by the substitution of Si$^{4+}$ for Al$^{3+}$ in the M1 site make it possible to adjust the size of the M2 and the M3 sites to accommodate Na$^+$ and Mg$^{2+}$ in the M2 sites and Na$^+$ and K$^+$ in the M3 sites, respectively. The stability of hexagonal aluminous phases in a relatively wide compositional range of 30–50 mol% in NaAlSiO$_4$ component along the NaAlSiO$_4$-MgAl$_2$O$_4$ join can be explained by possible replacement of Mg$^{2+}$ by Na$^+$ in the M2 site and by shrinkage and deformation of M1O$_6$ octahedra with the coupled substitution: $\text{M}^2\text{Mg}^{2+} + \text{M}^2\text{Al}^{3+} \rightarrow \text{M}^2\text{Na}^+ + \text{M}^2\text{Si}^{4+}$.

Keywords: Hexagonal aluminous phase, lower mantle, alkali element, Rietveld analysis, crystal structure, high pressure, MORB

INTRODUCTION

High-pressure high-temperature experiments on mid-ocean ridge basalt (MORB) indicated that some Al-rich phases coexist with Mg-perovskite, Ca-perovskite, and stishovite at conditions of the Earth’s lower mantle (HirosHi et al. 1999). A calcium ferrite phase and a hexagonal aluminous phase have been identified as host phases in subducting slabs at lower mantle conditions, the hexagonal aluminous phase could play an important role in potassium circulation in the deep mantle (Miyajima et al. 2001). The hexagonal aluminous phase is denoted as “Hex phase” hereafter.

The general chemical formula of the Hex phase is $[\text{M3}][\text{M2}][\text{M1}]_2\text{O}_{12}$. The crystal structure of the Hex phase is shown in Figure 1. The basic framework of the structure is double chain of M1O$_6$ octahedra (M1 = Al$^{3+}$, Si$^{4+}$, Mg$^{2+}$) that are connected by shared edges. This double chain framework is similar to that of the calcium ferrite-type crystal structure. In addition to the M1 site for small-sized cations, there are two different sites for middle-sized cations (M2) and relatively large cations (M3). In the calcium ferrite structure, there is only one large cation site. The M2 sites of the Hex phase are triangular tunnel-like spaces along the c-axis surrounded by three double chains of M1O$_6$ octahedra with a coordination environment of a trigonal prism with six coordinating O atoms. These sites accommodate middle-sized cations like Mg$^{2+}$. The M3 sites are in the other tunnel-like space surrounded by six double chains of M1O$_6$ octahedra and are coordinated by nine O atoms. These M3 sites accommodate Na$^+$, K$^+$, and Ca$^{2+}$, which have relatively large ionic radii. The M3 sites are filled by cations. A more detailed description of this structure is given in Makovicky and Arnskov Olsen (2008).