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Structure refinement of high-pressure hexagonal aluminous phases $K_{1.00}Mg_{2.00}Al_{4.80}Si_{1.15}O_{12}$ and $Na_{1.04}Mg_{1.88}Al_{4.64}Si_{1.32}O_{12}$

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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 $K_{1.00}Mg_{2.00}Al_{4.80}Si_{1.15}O_{12}$ and $Na_{1.04}Mg_{1.88}Al_{4.64}Si_{1.32}O_{12}$ 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 $CaMg_2Al_6O_{12}$. The general chemical formula of the hexagonal aluminous phase is represented as $[M3][M2]_2[M1]_6O_{12}$, 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 $NaAlSiO_4$-$MgAl_2O_4$ 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: $^{M2}Mg^{2+} + {}^{M1}Al^{3+} \rightarrow {}^{M2}Na^+ + {}^{M1}Si^{4+}$.

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