Crystal structure of calcium-ferrite type NaAlSiO$_4$ up to 45 GPa

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**Abstract**

Alkali-rich aluminous high-pressure phases including calcium-ferrite (CF) type NaAlSiO$_4$ are thought to constitute ~20% by volume of subducted mid-ocean ridge basalt (MORB) under lower mantle conditions. As a potentially significant host for incompatible elements in the deep mantle, knowledge of the crystal structure and physical properties of CF-type phases is therefore important to understanding the crystal chemistry of alkali storage and recycling in the Earth’s mantle. We determined the evolution of the crystal structure of pure CF-NaAlSiO$_4$ and Fe-bearing CF-NaAlSiO$_4$ at pressures up to ~45 GPa using synchrotron-based, single-crystal X-ray diffraction. Using the high-pressure lattice parameters, we also determined a third-order Birch-Murnaghan equation of state, with $V_0 = 241.6(1)$ Å$^3$, $K_0 = 220(4)$ GPa, and $K'_0 = 2.6(3)$ for Fe-free CF, and $V_0 = 244.2(2)$ Å$^3$, $K_0 = 211(6)$ GPa, and $K'_0 = 2.6(3)$ for Fe-bearing CF. The addition of Fe into CF-NaAlSiO$_4$ resulted in a 10 ± 5% decrease in the stiffest direction of linear compressibility along the c-axis, leading to stronger elastic anisotropy compared with the Fe-free CF phase. The NaO$_4$ polyhedra volume is 2.6 times larger and about 60% more compressible than the octahedral (Al,Si)O$_6$ sites, with $K_0^{NaO_4} = 127$ GPa and $K_0^{(Al,Si)O_6} = 304$ GPa. Raman spectra of the pure CF-type NaAlSiO$_4$ sample shows that the pressure coefficient of the mean vibrational mode, 1.60(7) cm$^{-1}$/GPa, is slightly higher than 1.36(6) cm$^{-1}$/GPa obtained for the Fe-bearing CF-NaAlSiO$_4$ sample. The ability of CF-type phases to contain incompatible elements such as Na beyond the stability field of jadeite requires larger and less-compressible NaO$_4$ polyhedra. Detailed high-pressure crystallographic information for the CF phases provides knowledge on how large alkali metals are hosted in alumina framework structures with stability well into the lowermost mantle.

**Keywords:** CF-type NaAlSiO$_4$, single-crystal structure refinements, incompatible Na elements, high pressures, Raman spectroscopy, lower mantle

**Introduction**

The bulk lower mantle is considered well mixed above the D" layer, yet regional heterogeneities are identified by seismology and geochemical studies (e.g., Jenkins et al. 2017; Romanowicz and Wenk 2017). Calcium-ferrite (CF) type phases and the new hexagonal aluminous phase (NAL phase) may collectively account for 10–30 vol% of subducted oceanic crust below ~2700 km and therefore likely play an important role in the observed regional-scale seismological and geochemical heterogeneities (Bina and Helffrich 2014; French and Romanowicz 2014; Fukao and Obayashi 2013; Litasov and Ohtani 2005; Wu et al. 2016, 2017). However, the high-pressure behaviors (e.g., structure, stability, and elasticity) of the alkali-rich aluminous high-pressure phases remain poorly known compared with other lower mantle minerals such as bridgmanite [(Mg,Fe)SiO$_6$], davemaoite (CaSiO$_3$), and perferroclase [(Mg,Fe)O] (Fujino et al. 2012; Ono et al. 2004; Wentzcovitch et al. 1995). Determining the structure and thermo-dynamic properties of the major alkali-rich phases will therefore improve computational models of slab dynamics as well as our understanding of the behavior of incompatible elements in the lowermost mantle.

Average mid-ocean ridge basalt contains 10–12 wt% CaO and 2–3 wt% Na$_2$O, largely in plagioclase and clinopyroxenes in the upper mantle (Sun et al. 1979). On subduction to below 50–60 km, the basalt-eclogite transition changes the mineralogy of MORB where Ca-pyroxene (diopside), Na-pyroxene (jadeite) and garnet host the majority of alkali metals and aluminum (Yoder and Tilley 1962; Ringwood and Green 1966). Below ~300 km, pyroxene and garnet form a solution of majoritic garnet but below the transition zone (410–660 km) the breakdown of majoritic garnet leads to bridgmanite, davemaoite, and stishovite, where Al, the majority of Na, and some Ca are hosted in the CF-type and/or NAL-phases (depending on depth) with complex chemical compositions (Kesson et al. 1994; Ono et al. 2001; Ricouleau et al. 2010). CF phases crystallizing in the orthorhombic system (space group Pbnm) display solid solutions with the general formula A$_2$B$_2$O$_{12}$, where A represents a large mono- or divalent cations, like Na$^+$, K$^+$, or Ca$^{2+}$, and B is a sixfold-coordinated cation site.