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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, $K_{T0} = 220(4)$ GPa, and $K'_{T0} = 2.6(3)$ for Fe-free CF, and $V_0 = 244.2(2)$ Å^3, $K_{T0} = 211(6)$ GPa, and $K'_{T0} = 2.6(3)$ for Fe-bearing CF. The addition of Fe into CF-$NaAlSiO_4$ resulted in a $10 \pm 5\%$ 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_8 polyhedra volume is 2.6 times larger and about 60% more compressible than the octahedral $(Al,Si)O_6$ sites, with $K_0^{NaO_8} = 127$ 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_8 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