Structure and compressibility of Fe-bearing Al-phase D

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ABSTRACT

Due to its large thermal stability, Al-phase D, the (Al,Fe3+)2SiO6H2 member of the dense hydrous magnesium silicate (DHMS) phase D, may survive along hot subduction geotherms or even at ambient mantle temperatures in the Earth’s transition zone and lower mantle, therefore potentially playing a major role as a water reservoir and carrier in the Earth’s interior. We have investigated the crystal structure and high-pressure behavior of Fe-bearing Al-phase D with a composition of Al1.53(2)Fe0.22(1)Si0.86(1)O6H3.33(9) by means of single-crystal X-ray diffraction. While the structure of pure Al-phase D (AlSiO6) has space group P63/mcm and consists of equally populated and half-occupied (AlSi)O6 octahedra, Fe-incorporation in Al-phase D seems to induce partial ordering of the cations over the octahedral sites, resulting in a change of the space group from P63/mcm to P62/22 and in well-resolved diffuse scattering streaks observed in X-ray images. The evolution of the unit-cell volume of Fe-bearing Al-phase D between room pressure and 38 GPa, determined by means of synchrotron X-ray diffraction in a diamond anvil cell, is well described by a third-order Birch-Murnaghan equation of state having an isothermal bulk modulus K0 = 166.3(15) GPa and first pressure derivative K′0 = 4.46(12). Above 38 GPa, a change in the compression behavior is observed, likely related to the high-to-low spin crossover of octahedrally coordinated Fe3+. The evolution of the unit-cell volume across the spin crossover was modeled using a recently proposed formalism based on crystal-field theory, which shows that the spin crossover region extends from approximately 30 to 65 GPa. Given the absence of abrupt changes in the compression mechanism of Fe-bearing Al-phase D before the spin crossover, we show that the strength of H-bonds and likely their symmetrization do not greatly affect the elastic properties of phase D solid solutions, independently of their compositions.

Keywords: DHMS, phase D, X-ray diffraction, equation of state, spin crossover

INTRODUCTION

The stability of dense hydrous magnesium silicates (DHMS) at high-pressure and high-temperature conditions has been extensively studied for more than 20 years, as these phases can potentially carry and recycle water from Earth’s surface to its deep interior (e.g., Frost 2006; Nishi et al. 2014; Ohtani et al. 2014). The crystal structure of DHMS generally consists of hexagonal closest-packed (hcp) layers of O atoms with Mg and Si occupying interstitial octahedral and tetrahedral sites, respectively. However, in phase D and phase H, which are stable under mantle transition zone and lower mantle conditions, Si displays octahedral coordination, allowing partial (Yang et al. 1997) or complete (Bindi et al. 2014) mixing with Mg to take place. Al incorporation in the crystal structures of these two phases further promotes cation mixing at octahedral sites and enhances their thermal stability, allowing Al-bearing phase D and phase H to potentially survive along hot subduction geotherms or even at ambient mantle temperatures in the transition zone and lower mantle (Ohira et al. 2014; Pamato et al. 2015).

In the end-member Mg-phase D (space group P31m), with nominal composition MgSi2O6H2, Mg and Si occupy distinct octahedral sites, named M1 and M2, respectively, located on alternated interstitial layers of the oxygen hcp sublattice (Yang et al. 1997). M2 octahedra are connected with one another through one edge and to M1 octahedra through vertices, while M1 octahedra are separated from one another and share vertices with M2 octahedra (Online Materials1 Fig. S1a). The remaining two octahedral sites, i.e., M3 and M4, share faces with M2 and M1, respectively, and are nominally vacant in Mg-phase D. Previous studies showed that the crystal structure of phase D becomes progressively disordered in the proximity of its Al-end-member (Boffa Ballaran et al. 2010; Pamato et al. 2015). As Al is incorporated in the structure of phase D via the Mg2+ + Si4+ = 2Al3+ substitution, not only this cation substitutes in both M1 and M2, but also causes a partial redistribution of the cations in the M3 and M4 sites. In an Al-rich phase D sample having Mg + Fe = 0.3 atoms per formula unit, cation disordering was observed in the form of partially occupied, but not equally populated M2 and M3 sites, while M1 showed full occupancy and M4 appeared vacant (Boffa Ballaran et al. 2010). In Mg- and Fe-free...