Compressional behavior and spin state of δ-(Al,Fe)OOH at high pressures

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ABSTRACT

Hydrogen transport from the surface to the deep interior and distribution in the mantle are important in the evolution and dynamics of the Earth. An aluminum oxy-hydroxide, δ-AlOOH, might influence hydrogen transport in the deep mantle because of its high stability extending to lower mantle conditions. The compressional behavior and spin states of δ-(AlFe3+)OOH phases were investigated with synchrotron X-ray diffraction and Mössbauer spectroscopy under high pressure and room temperature. Pressure-volume (P–V) profiles of the δ-(Al0.80Fe0.20)OOH1.15, [Fe/(Al+Fe) = 0.174(3), δ-Fe5] and the δ-(Al0.82Fe0.18)OOH1.15, [Fe/(Al+Fe) = 0.124(2), δ-Fe12] show that these hydrous phases undergo two distinct structural transitions involving changes in hydrogen bonding environments and a high- to low-spin crossover in Fe3+. A change of axial compressibility accompanied by a transition from an ordered (P21/nm) to disordered hydrogen bond (Pnnm) occurs near 10 GPa for both δ-Fe5 and δ-Fe12 samples. Through this transition, the crystallographic a and b axes become stiffer, whereas the c axis does not show such a change, as observed in pure δ-AlOOH. A volume collapse due to a transition from high- to low-spin states in the Fe3+ ions is complete below 32–40 GPa in δ-Fe5 and δ-Fe12, which is ~10 GPa lower than that reported for pure ε-FeOOH. Evaluation of the Mössbauer spectra of δ-(Al0.82Fe0.18)OOH1.15, [Fe/(Al+Fe) = 0.133(3), δ-Fe13] also indicate a spin transition between 32–45 GPa. Phases in the δ-(Al,Fe)OOH solid solution with similar iron concentrations as those studied here could cause an anomalously high ρ/νp ratio (bulk sound velocity, defined as √(K/ρ) at depths corresponding to the spin crossover region (~900 to ~1000 km depth), whereas outside the spin crossover region a low ρ/νp anomaly would be expected. These results suggest that the δ-(Al,Fe)OOH solid solution may play an important role in understanding the heterogeneous structure of the deep Earth.

Keywords: δ-AlOOH, δ-(Al,Fe)OOH, hydrous minerals, high-pressure, X-ray diffraction, Mössbauer spectroscopy, diamond-anvil cell, synchrotron, water transport in the deep mantle

INTRODUCTION

Volatile transport, in particular hydrogen in the forms of water and hydroxyl, from the surface to the deep interior and distribution in the mantle are important in understanding the evolution and dynamics of the Earth. Important hosts of hydrogen in the deep mantle are hydrous and nominally anhydrous minerals (e.g., Bell and Rossman 1992; Ohtani 2005, 2015; Smyth and Jacobsen 2006; Wirth et al. 2007; Pearson et al. 2014; Ohtani et al. 2016; Kaminsky 2017; Tschauner et al. 2018). A dense aluminum oxy-hydroxide, δ-AlOOH, could play a key role in hydrogen transport in the mantle transition zone and the lower mantle (e.g., Ohtani et al. 2016). This hydrous phase is a high-pressure polymorph of diaspore (α-AlOOH) and Boehmite (γ-AlOOH), and was first synthesized by Suzuki et al. (2000) at 21 GPa and 1273 K in a multi-anvil apparatus. High-pressure and high-temperature experiments using a multi-anvil apparatus and a laser-heated diamond-anvil cell (DAC) combined with in situ X-ray diffraction (XRD) have demonstrated the stability of δ-AlOOH at 21–142 GPa and 973–2410 K, corresponding to the conditions of the regions deeper than the lower transition zone (Sano et al. 2004, 2008; Pamatto et al. 2015; Fukuyama et al. 2017; Abe et al. 2018; Duan et al. 2018). This high stability implies that δ-AlOOH has the potential to transport hydrogen to the core-mantle boundary (CMB) region.

The structure and physical properties of δ-AlOOH at ambient- and high-pressure conditions have also been investigated. At ambient conditions, δ-AlOOH has a distorted rutile-type structure.