Spectroscopic evidence for the Fe$^{3+}$ spin transition in iron-bearing δ-AlOOH at high pressure

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Abstract

δ-AlOOH has emerged as a promising candidate for water storage in the lower mantle and could have delivered water into the bottom of the mantle. To date, it still remains unclear how the presence of iron affects its elastic, rheological, vibrational, and transport properties, especially across the spin crossover. Here, we conducted high-pressure X-ray emission spectroscopy experiments on a δ-(Al$_{0.85}$Fe$_{0.15}$)OOH sample up to 53 GPa using silicone oil as the pressure transmitting medium in a diamond-anvil cell. We also carried out laser Raman measurements on δ-(Al$_{0.85}$Fe$_{0.15}$)OOH and δ-(Al$_{0.52}$Fe$_{0.48}$)OOH up to 57 and 62 GPa, respectively, using neon as the pressure-transmitting medium. Evolution of Raman spectra of δ-(Al$_{0.85}$Fe$_{0.15}$)OOH with pressure shows two new bands at 226 and 632 cm$^{-1}$ at 6.0 GPa, in agreement with the transition from an ordered (P2$_{1}$,nm) to a disordered hydrogen bonding structure (Pnnm) for δ-AlOOH. Similarly, the two new Raman bands at 155 and 15.8 GPa, indicating that the incorporation of 48 mol% FeOOH could postpone the order-disorder transition upon compression. On the other hand, the satellite peak (Kβ) intensity of δ-(Al$_{0.85}$Fe$_{0.15}$)OOH starts to decrease at ~30 GPa and it disappears completely at 42 GPa. That is, δ-(Al$_{0.85}$Fe$_{0.15}$)OOH undergoes a gradual electronic spin-pairing transition at 30–42 GPa. Furthermore, the pressure dependence of Raman shifts of δ-(Al$_{0.85}$Fe$_{0.15}$)OOH discontinuously decreases at 32–37 GPa, suggesting that the improved hydrostaticity by the use of neon pressure medium could lead to a relatively narrow spin crossover. Notably, the pressure dependence of Raman shifts and optical color of δ-(Al$_{0.52}$Fe$_{0.48}$)OOH dramatically change at 41–45 GPa, suggesting that it probably undergoes a relatively sharp spin transition in the neon pressure medium. Together with literature data on the solid solutions between δ-AlOOH and ε-FeOOH, we found that the onset pressure of the spin transition in δ-(Al,Fe)OOH increases with increasing FeOOH content. These results shed new insights into the effects of iron on the structural evolution and vibrational properties of δ-AlOOH. The presence of FeOOH in δ-AlOOH can substantially influence its high-pressure behavior and stability at the deep mantle conditions and play an important role in the deep-water cycle.

Keywords: Iron-bearing δ-AlOOH, spin transition, high pressure, X-ray emission spectroscopy, Raman spectroscopy; Volatile Elements in Differentiated Planetary Interiors

Introduction

The water cycling between the Earth’s surface and interior plays a key role in the evolution and dynamics of Earth’s interior (Mao and Mao 2020; Ohira et al. 2019; Ohtani 2005). Slab subduction and magmatism are the two key processes regulating the in-gassing and outgassing rates of water and many other volatiles. Based on geochemical and petrological evidence, the amount of water entering into the mantle through subducting slabs is in the order of (7–10)$\times$10$^{11}$ kg/year, while water returning to the surface via magmatism is (2–6.7)$\times$10$^{11}$ kg/year (Ohtani 2020). That is, (0.3–8)$\times$10$^{11}$ kg/year of water is likely transported into the Earth’s interior. Hydrous minerals are the utmost important hosts for transporting water and hydrogen into the mantle. Thus far, most hydrous minerals (e.g., serpentine, 10 Å phase, phase A, phase E) would decompose under the temperature and pressure (P-T) conditions above the topmost lower mantle. However, the pyrite-structured FeO$_2$H$_2$, the hexagonal phase [HH phase, a hexagonal ultradense hydrous phase of (Fe,Al)OOH], and δ-AlOOH phase and its solid solution with ε-FeOOH are plausibly stable under the lower-mantle P-T conditions (Ohtani 2020 and references therein). Studying the behavior of these hydrous phases at high pressure sheds light on the potential impacts of subducted hydrous materials on the structure, evolution, and geodynamics of the Earth’s deep interior (Hu et al. 2021; Liu et al. 2021; Mao and Mao 2020).

The nature of δ-AlOOH at high pressure has been extensively investigated, including crystal chemistry, phase stability, and sound velocity by both experiments and theoretical calculations (Cortona 2017; Duan et al. 2018; Li et al. 2006; Mashino et al. 2016; Ohira et al. 2019; Tsuchiya and Tsuchiya 2009; Tsuchiya...