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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 ($P2_1nm$) to a disordered hydrogen bonding structure (*Pnnm*) for δ-AlOOH. Similarly, the two new Raman bands at 155 and 539 cm^{-1} appear in δ-$(Al_{0.52}Fe_{0.48})OOH$ between 8.5 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 ($K\beta'$) 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