

SPECIAL COLLECTION: WATER IN NOMINALLY HYDROUS AND ANHYDROUS MINERALS

Raman spectroscopy of water-rich stishovite and dense high-pressure silica up to 55 GPa

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ABSTRACT

Recent studies have shown that mineral end-member phases (δ -AlOOH phase, phase H, and stishovite) with rutile-type or modified rutile-type crystal structures and solid solutions between them in the MgO-Al₂O₃-SiO₂ system can store large amounts of water and can be stable at high pressures and high temperatures relevant to the Earth's lower mantle. The Al-H charge-coupled substitution ($\text{Si}^{4+} \rightarrow \text{Al}^{3+} + \text{H}^+$) has been proposed to explain the storage capacity found in some of these phases. However, the amount of H⁺ found in some recent examples does not match the expected value if such substitution is dominant, and it is difficult to explain the larger water storage in stishovite with such a mechanism alone. An octahedral version of the hydrogarnet-like substitution ($\text{Si}^{4+} \rightarrow 4\text{H}^+$) has been proposed to explain the incorporation of protons in Al-free, water-rich stishovite. Yet, the high-pressure structural behavior of OH in this phase has not yet been measured. In this study, we report high-pressure Raman spectroscopy measurements on Al-free hydrous stishovite with 3.2 ± 0.5 wt% water up to 55 GPa. At ambient pressure, we find that the OH stretching modes in this phase have frequencies lying in between those in low-water aluminous stishovite and those in δ -AlOOH, suggesting a strength of the hydrogen bonding intermediate between these two cases. After decompression to 1 bar, we observe modes that are similar to the IR-active modes of anhydrous and hydrous stishovite, suggesting that the existence of Si defects in the crystal structure can activate the inactive modes. For both lattice and OH-stretching modes, our data show a series of changes at pressures between 24 and 28 GPa suggesting a phase transition (likely to CaCl₂-type). While some of the lattice mode behaviors are similar to what was predicted for the AlOOH polymorphs, the OH mode of our hydrous stishovite shows a positive frequency shift with pressure, which is different from δ -AlOOH. All our spectral observations suggest that water-rich pure dense silica has a distinct proton incorporation mechanism from aluminous low-water stishovite and δ -AlOOH, supporting the proposed direct substitution.

Keywords: Raman spectroscopy, free-Al hydrous stishovite, high-pressure studies, phase transition, hydrogen incorporation mechanism; Water in Nominally Hydrous and Anhydrous Minerals