

Hydride in perovskites – a possible mechanism for incorporating hydrogen in the deep earth

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The hydrogen found in the nominally anhydrous minerals (NAMs) of earth's mantle is typically conceptualized as OH⁻ groups – interstitial protons bonded to oxygen atoms. However, both experimental and theoretical work over the last two decades has demonstrated that an alternative form of hydrogen can occur in crystalline oxides: hydride. The hydride anion (H⁻) is shown to be stable in a growing list of oxide phases across a variety of chemistries and structures including: MgO, apatites, ZnO (wurtzite-type), and perovskites, among several others. Perovskite phases are of particular interest because hydride has an extremely high solubility in these phases, which are structural analogues to the most abundant phases in earth's mantle. Despite this, much about hydride in perovskites remains understudied, including its observation through common analytical techniques like infrared spectroscopy. Here, we present our experimental and theoretical work exploring hydride in perovskites, including methods of hydride incorporation and detection. We have induced hydride defect states in SrTiO₃, a cubic perovskite that is both stable at atmospheric pressure and is structurally analogous with the recently discovered davemaoite. These hydride states and their effect on SrTiO₃ were then characterized through a variety of techniques including ¹H NMR, FTIR spectroscopy and Raman spectroscopy, giving broader context to the possibility of observing hydride in geologic materials. Additionally, we explored the possibility of hydride incorporation in davemaoite via density functional theory (DFT) calculations, with theorized defect states based on the measured chemistry of natural davemaoite. Although much work remains to be done, these studies raise the possibility of mechanisms other than just the hydroxide ion for hydrogen storage and transport in the deep earth and other planetary interiors.