

# The spectroscopy of hydride in perovskites

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With only a handful of exceptions, the study of hydrogen in nominally anhydrous silicate and oxide mantle phases has focused primarily on OH<sup>-</sup> groups. This speciation of hydrogen is well established and makes intuitive sense in the context of oxide-based minerals. However, insights from materials science research have revealed that an alternate form of hydrogen is stable in crystalline oxides: the hydride ion (H<sup>-</sup>). Under highly reducing conditions, hydrogen may bond directly to cation species, taking on a negative charge and directly substituting for O<sup>2-</sup>. These substitutions are highly favorable in the (Ca,Sr,Ba)TiO<sub>3</sub> family of perovskites, where up to 20% of all O<sup>2-</sup> ions can be replaced with H<sup>-</sup>, with significant implications for material properties<sup>[1]-[4]</sup>. Given that these Ti-based materials are structural analogues to bridgemanite and davemaoite (the 1<sup>st</sup> and 3<sup>rd</sup> most abundant mantle phases, respectively), it is natural to wonder whether hydride could be a component of perovskites in the deep earth, potentially representing a large, “hidden” reservoir for hydrogen. Nonetheless, many aspects of hydride incorporation in perovskites have yet to be thoroughly investigated. This includes detection of H<sup>-</sup> via methods like infrared (IR) spectroscopy, which are suitable for *in-situ* high pressure experiments and analysis of diamond inclusion samples. Without these analytical capabilities, hydride’s importance in the mantle cannot be assessed.

In this presentation, we report our work to characterize the H<sup>-</sup> ion in titanate perovskite materials through a combination of computational and experimental techniques. We have successfully documented vibrational modes attributed to hydride incorporation in perovskites via infrared spectroscopy and find that the spectral signatures of H<sup>-</sup> can be easy to overlook and difficult to identify. This stands in direct contrast to the more widely studied and characterized OH<sup>-</sup> modes. Complimentary information provided by density functional theory (DFT) calculations and <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy is shown to be essential in interpreting and contextualizing these infrared features. Based on our findings from analogue titanate perovskites, we also propose possible mechanisms through which hydride may be incorporated into silicate perovskites and simulate their spectra via DFT. This work represents the preliminary steps toward more advanced studies of H<sup>-</sup> in silicate perovskites, which could include hydride’s solubility in the lower mantle and its effect on bulk material properties. If hydride proves to be a viable constituent of lower mantle silicates, then current models of the deep earth hydrogen budget will need to be fundamentally revised to account for this new component.

## References:

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