Phase transitions in ε-FeOOH at high pressure and ambient temperature

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ABSTRACT

Constraining the accommodation, distribution, and circulation of hydrogen in the Earth’s interior is vital to our broader understanding of the deep Earth due to the significant influence of hydrogen on the material and rheological properties of minerals. Recently, a great deal of attention has been paid to the high-pressure polymorphs of FeOOH (space groups \( P2_1nm \) and \( Pnnm \)). These structures potentially form a hydrogen-bearing solid solution with AlOOH and phase H (MgSiO\(_2\)) that may transport water (OH\(^-\)) deep into the Earth’s lower mantle. Additionally, the pyrite-type polymorph (space group \( P2\text{3} \) of FeOOH), and its potential dehydration have been linked to phenomena as diverse as the introduction of hydrogen into the inner core (Nishi et al. 2017), the formation of ultralow-velocity zones (ULVZs) (Liu et al. 2017), and the Great Oxidation Event (Hu et al. 2016). In this study, the high-pressure evolution of FeOOH was re-evaluated up to \( \approx 75 \) GPa using a combination of synchrotron-based X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and optical absorption spectroscopy. Based on these measurements, we report three principal findings: (1) pressure-induced changes in hydrogen bonding (proton disordering or hydrogen bond symmetrization) occur at substantially lower pressures in ε-FeOOH than previously reported and are unlikely to be linked to the high-spin to low-spin transition; (2) ε-FeOOH undergoes a 10\% volume collapse coincident with an isostructural \( Pnnm \rightarrow Pnnm \) transition at approximately 45 GPa; and (3) a pressure-induced band gap reduction is observed in FeOOH at pressures consistent with the previously reported spin transition (40 to 50 GPa).

Keywords: Phase transitions, infrared-spectroscopy, optical absorption spectroscopy, X-ray diffraction, spin transition; Volatile Elements in Differentiated Planetary Interiors

INTRODUCTION

The accommodation, distribution, and circulation of hydrogen in the deep Earth is key to understanding the evolution of Earth’s interior due to the significant influence of hydrogen on the material and rheological properties of high-pressure phases (e.g., Sarafian et al. 2017; Karato 2010). Geophysical observations indicate that the Earth’s upper mantle and transition zone, at least locally, host significant quantities of hydrogen (van der Meijde et al. 2003; Dixon et al. 2004; Pearson et al. 2014; Palot et al. 2016; Tschauner et al. 2018). Additionally, tomographic evidence supports the idea that subducting lithospheric plates pierce the transition zone, potentially ushering water into the Earth’s lower mantle (van der Hilst et al. 1997). Yet while hydrogen in the upper mantle and transition zone is hosted primarily in nominally anhydrous phases, these phases are not stable at the high pressure and temperature conditions of the lower mantle (Hirschmann 2006). If hydrogen introduced into the lower mantle remains in the lower mantle, it is almost certainly accommodated primarily in minor hydrous phases, because the dominant lower mantle minerals (bridgmanite, ferropericlase, and calcium silicate perovskite) do not have the same capacity for water storage (Bolfan-Casanova et al. 2002, 2003; Panero et al. 2015). A plausible lower mantle host is the isostructural FeOOH-AlOOH-MgSiO\(_2\) system.

At moderate pressures (\( \approx 6 \) GPa) goethite (ε-FeOOH, space group \( Pbnm \)), a widespread iron oxy-hydroxide, transforms into ε-FeOOH, an orthorhombic (space group \( P2_1nm, Z = 2 \)) phase composed of edge-sharing FeO\(_6\) units that are close-packed along the c-axis, with hydrogen atoms occupying the channels between these close-packed octahedra (Bendeliani et al. 1972; Pernet et al. 1975; Bolotina et al. 2008) (Fig. 1a). At increased pressure, ε-FeOOH undergoes pressure-induced hydrogen-bond symmetrization resulting in a second-order phase transition (space group \( Pnnm, Z = 2 \)) (Fig. 1c). However, the pressure at which this hydrogen bond symmetrization induced \( P2_1nm \rightarrow Pnnm \) transition occurs remains contested (Gleason et al. 2013; Xu et al. 2013; Thompson et al. 2017; Ikeda et al. 2019). At the pressures of the Earth’s lower mantle, ε-FeOOH forms a solid solution with δ-AlOOH and phase H (MgSiH\(_4\)O\(_4\)), creating a viable hydrogen reservoir with \( P-T \) stability extending from lower mantle conditions to those of the core-mantle boundary (Sano et al. 2008; Nishi et al. 2015; Xu et al. 2019).

Hydrogen bond symmetrization is the process by which the hydrogen in an asymmetrical O–H···O bonding unit becomes centered with respect to the two O atoms with increased pressure, as the longer hydrogen bridge bond (H···O) compresses more rapidly than the shorter but stiffer hydroxyl bond (O–H) (Holzapfel 1972).