High-pressure behavior of the polymorphs of FeOOH

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ABSTRACT

The high-pressure structural and electronic behavior of α-, β-, and γ-FeOOH were studied in situ using a combination of synchrotron X-ray diffraction (XRD) and X-ray emission spectroscopy (XES). We monitored α-FeOOH by XES as a function of pressure up to 85 GPa and observed an electronic spin transition that began at approximately 50 GPa, which is consistent with previous results. In the γ-FeOOH sample, we see the initiation of a spin transition at 35 GPa that remains incomplete up to 65 GPa. β-FeOOH does not show any indication of a spin transition up to 65 GPa. Analysis of the high-pressure XRD data shows that neither β-FeOOH nor γ-FeOOH transform to new crystal structures, and both amorphize above 20 GPa. Comparing our EOS results for the β and γ phases with recently published data on the α and ε phases, we found that β-FeOOH exhibits distinct behavior from the other three polymorphs, as it is significantly less compressible and does not undergo a spin transition. A systematic examination of these iron hydroxide polymorphs as a function of pressure can provide insight into the relationship between electronic spin transitions and structural transitions in these OH- and Fe3+-bearing phases that may have implications on our understanding of the water content and oxidation state of the mantle.

Keywords: Spin transitions, high-pressure studies, XES, FeOOH, XRD data

INTRODUCTION

Iron hydroxides, including FeOOH and its polymorphs, are common on the surface of the Earth, where they are abundant in soils, aquifers, and sediments. FeOOH has four polymorphs, three of which are naturally occurring: goethite (α-FeOOH), akaganeite (β-FeOOH), and lepidocrocite (γ-FeOOH). A fourth polymorph, ε-FeOOH, can be synthesized at high pressure (Bolotina et al. 2008; Gleason et al. 2008; Voigt et al. 1981). Goethite is the thermodynamically stable phase at ambient conditions, whereas akaganeite is rare and forms in Cl-rich environments like hot brines and rust in marine environments. Lepidocrocite occurs in rocks, soils, and rust and is often an oxidation product of Fe2+. Their structures consist of corner-linked double bands of FeO2(OH) octahedra (Fig. 1). α-FeOOH has double bands of edge sharing octahedra that form 2 × 1 channels. β-FeOOH also has double bands; however, they are arranged in a circular shape forming large 2 × 2 channels, which are stabilized by the presence of a variable molecule or ions such as H2O, OH−, Cl−, or NO3−. The γ-FeOOH bands are connected via hydrogen bonds (OH·O) and form corrugated 2D layers perpendicular to the b-axis. The high-pressure ε-FeOOH phase is a slightly distorted rutile structure with corner-linked single bands of edge-shared octahedra parallel to the c-axis (Otte et al. 2009). It is isostructural with δ-AlOOH, a phase that may transport hydrogen deep within the planet and potentially down to the core-mantle boundary (Sano et al. 2004; Suzuki 2010).

Based on crystal field theory, the distribution of electrons in the d orbitals in transition metal complexes depends on the ligand field geometry and the metal d-electron configurations. The spin state of iron is determined by the difference between the energy levels of Δ (the crystal field splitting parameter) and the spin pairing energy (A). Under ambient conditions, Δ is most octahedrally coordinated iron compounds is lower than A. This results in favorable energetic conditions where 3d electrons occupy both the ts orbital and the higher energy ε orbital with unpaired spins. With increasing pressure, the crystal field splitting energy increases with respect to the spin pairing energy. This can result in the spin pairing of the electrons in the lower energy ts orbital. The spin transitions of iron in lower mantle minerals may result in significant changes in their physical and chemical properties (Speziale et al. 2005)—including their density, bulk modulus, seismic velocities, electrical conductivity, radiative heat transfer, and element partitioning (Lin et al. 2013, 2008, 2007; Speziale et al. 2005; Stackhouse et al. 2007). Previous work (Gleason et al. 2013; Xu et al. 2013) showed that spin transitions take place in α-FeOOH and ε-FeOOH. Gaining insight into the high-pressure behavior and spin state of the polymorphs of FeOOH can improve our understanding of more complex hydrogen bearing compounds that may be common in the Earth’s deep interior (Williams and Hemley 2001).

EXPERIMENTAL METHODS

Sample synthesis

α-, β-, and γ-FeOOH were synthesized using the methods in Schertmann (2000). β-FeOOH was prepared following a slight modification. After dissolving