Variation of hydrogen bonded O···O distances in goethite at high pressure

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ABSTRACT

In-situ synchrotron X-ray powder diffraction experiments on goethite were performed up to 24.5 GPa using a diamond-anvil cell at BL-18C in the Photon Factory, Japan. The compression behavior of goethite is anisotropic: the a axis, which is close to the direction of the hydrogen bond, is almost twice as compressible as the b and c axes. A second-order Birch-Murnaghan fit (\(K_0 = 4\)) to the unit-cell volumes and pressures up to 24 GPa gave a bulk modulus \(K_0 = 111(2)\) GPa. The pressure medium apparently affects the compression behavior of goethite, as a sudden strain broadening occurs above 11 GPa, where solidification of the 4:1 methanol:ethanol pressure medium occurs. The crystal structure of goethite was refined by means of the Rietveld method at several pressures below 10 GPa. The main compression occurs in the “vacant channels” in the crystal structure, where the O-H···O bridges are located. The hydrogen-bonded O···O distance shortens with increasing pressure at the rate of about -0.023 Å/GPa and reaches 2.60(1) Å at 9 GPa.

INTRODUCTION

Goethite (\(\alpha\)-FeOOH) crystallizes in the orthorhombic system with space group \(Pbnm\) and is isostructural with diaspore (\(\alpha\)-AlOOH) (Sztyura et al. 1968). The structure of goethite can be described in terms of a slightly distorted hexagonally close-packed O atom arrangement with Fe atoms occupying two-thirds of the octahedral sites. There are two independent O sites, O1 and O2. The O1 atom is surrounded by three Fe atoms to form an almost planar triangle. The O2 atom is hydrogenated, and is surrounded by three Fe atoms and an H atom to form a distorted tetrahedral coordination. The hydrogen bonding connects with an O1 atom in an adjacent octahedron. The non-linear hydrogen bonding in goethite is known to be of moderate strength. As this is the most common type of hydrogen bond (Jeffrey 1997), it is important to understand their behavior as a function of pressure.

Numerous investigations of pressure-induced weak hydrogen bonding can be found in brucite-related minerals including hydrous silicates, based on spectroscopic (e.g., Kruger et al. 1989; Nguyen et al. 1994; Faust and Williams 1996), neutron diffraction (e.g., Parise et al. 1994, 1999; Kagi et al. 2000), and theoretical studies (e.g., Sherman 1991). However, a spectroscopic study of goethite by William and Guenther (1996) appears to be the only investigation that focused upon hydrogen bonding of moderate strength at high pressure. The theoretical study by Winkler et al. (2001) appears to be the only such study of diaspore, although equation-of-state studies of diaspore have been made (Ruoff and Vanderborgh 1991; Mao et al. 1994; Grevel et al. 2000). Furthermore, the bulk modulus of goethite is undetermined. In their study of goethite by Raman spectroscopy, William and Guenther (1996) observed two O-H stretching vibrations and reported that one O-H stretching frequency decreased and the other increased with increasing pressure. The positive \(\Delta v_{\text{OH}}\) was attributed to repulsive interactions between cations and H. However, the theoretical investigation by Winkler et al. (2001) predicted only increased hydrogen bonding and a concomitant weakening of the hydroxyl bond with increasing pressure, implying the more usual negative pressure dependency of \(v_{\text{OH}}\).

While good-quality X-ray diffraction data can yield approximate locations for H atoms, it is not possible to determine the details of their structural behavior because H is a very weak X-ray scatterer. However, the hydrogen-bonded O···O distances can be determined accurately by X-ray diffraction and so can provide useful information about the nature of hydrogen bonding, since the distances are often used as a criterion of hydrogen bonding. Moreover, compression of the hydrogen-bonded O···O distance may change the nature of hydrogen bonding, because it is considered that the quantum-mechanical charge-transfer contributions to the hydrogen bond energy become more important as this O···O distance shortens (e.g., Martens and Freund 1976). Nagai et al. (2000a, 2000b) reported on the pressure variation of the hydrogen bonded O···O distances in brucite and portlandite, based on the results of X-ray diffraction measurements. They suggested that a hydrogen bonded O···O distance of 2.75 Å seems to be a kind of a critical distance, since the distance in brucite is not compressed below 2.75 Å and portlandite transforms into an amorphous material when the distance becomes 2.75 Å, which, perhaps significantly, corresponds to the O\(^2\)--O\(^2\) contact distance.

Here we present the first compression data for goethite and discuss how hydrogen bonding in goethite behaves as a function of pressure, based upon pressure variation of the hydrogen bonded O···O distance derived from in-situ synchrotron X-ray diffraction experiments.

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