Single-crystal structure refinement of diaspore at 50 GPa

ALEXANDRA FRIEDRICH,†,E* EIKEN HAUSSÜHL,† REINHARD BOEHLER,‡ WOLFGANG MORGENROTH,∥ ERICK A. JUAREZ-ARELLANO,† AND BJÖRN WINKLER†

†Institut für Geowissenschaften, Abt. Kristallographie, J.W. Goethe-Universität Frankfurt, D-60438 Frankfurt am Main, Germany
‡Max-Planck-Institut für Chemie, D-55020 Mainz, Germany
∥Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

ABSTRACT

The crystal structure of diaspore, AlO(OH), has been investigated by in situ single-crystal synchrotron X-ray diffraction at ~50 GPa using the diamond-anvil cell technique. Diaspore is found to retain its structure up to 51.5 GPa at room temperature, which is more than 30 GPa above the transition pressure to δ-AlO(OH) found in quenched high-temperature experiments and derived from density functional theory calculations. The compression is anisotropic and largest for the a axis. This can be explained by the fact that the structural response to pressure is mainly due to the shortening of the hydrogen bond, which is oriented nearly parallel to the a axis. The hydrogen bond becomes significantly more symmetric with pressure up to 50 GPa.

Keywords: Diaspore, high pressure, crystal structure, synchrotron radiation, single crystal

INTRODUCTION

Diaspore, α-AlO(OH), is an interesting model system for high-pressure studies of hydrogen bonds, as it possesses a relatively high symmetry (orthorhombic), a relatively small unit cell [unit-cell volume = 117.96(8) Å³, Busing and Levy 1958], and is chemically simple. The non-linear hydrogen bond is of intermediate strength (O-H stretching frequency ν is about 3000 cm⁻¹, Ryskin 1974). The crystal structure of diaspore (space group Pbnm, Z = 4) is built from “double rutile strings” (Ewing 1935) of edge-sharing AlO(OH) octahedra (Fig. 1). These double strings are arranged parallel to the c axis and are connected via common oxygen corners. The OH groups form hydrogen bonds in the (001) plane across the channels formed by the coordination octahedra, with the O⋯O and O-H vectors tilted away from the a axis by about 31 and 20°, respectively. The oxygen atoms are arranged in a slightly distorted hexagonal close packing, with the Al atoms occupying part of the octahedral sites.

The high-pressure behavior of diaspore was studied initially by energy-dispersive powder X-ray diffraction. Experiments up to 25.5 GPa with a 4:1 methanol:ethanol mixture as the pressure medium gave a bulk modulus B₀ = 167.5 GPa (Mao et al. 1994). Experiments in a similar pressure range, but without the use of a pressure medium, gave B₀ = 230 GPa (Xu et al. 1994). No indications of a phase transition were observed in this pressure range. Another energy-dispersive X-ray diffraction study reported the (P,V,T)-equation of state of diaspore from data collected up to 7 GPa and 1073 K (Grevel et al. 2000). In that study, a significantly smaller value for B₀ = 134 GPa was found. The first theoretical study on the high-pressure behavior of diaspore predicted structural changes and elastic properties up to 50 GPa (Winkler et al. 2001). The predictions of that study were subsequently confirmed by in situ single-crystal X-ray diffraction at pressures of up to 7 GPa (Friedrich et al. 2007). In the latter study, the theoretical investigations were extended to include predictions regarding the pressure dependence of the lattice dynamics. The main findings of these papers are (1) the bulk modulus determined from experiments and theory agrees well (B₀ is around 150 GPa); (2) the compression of the crystal structure proceeds mainly by bond shortening, and particularly by compression of the hydrogen bond; (3) the hydrogen bond strength increases with pressure; (4) the hydrogen bond becomes significantly more symmetric with increasing pressure; (5) a complete symmetrization is not reached in the investigated pressure range up to 40 GPa and does not seem likely to occur in diaspore even at higher pressures; and (6) the stretching frequencies of the O-H bond decrease approximately linearly with increasing pressure, and therefore also with increasing O-H bond length and decreasing hydrogen bond length.

These findings are consistent with the results from Rietveld refinements of the structure of isostructural goethite from powder X-ray diffraction data up to 9 GPa (Nagai et al. 2003). However, the infrared spectra of goethite were interpreted in terms of a weakening of the hydrogen bond strength by bending of the O-H⋯O angle with pressure up to 10 GPa and successive strengthening at higher pressures up to 24 GPa, being mainly driven by the positions of the iron cations (Williams and Guenther 1996). The influence of the metal-hydrogen repulsion on the hydrogen-bond geometry was also derived from recent high-pressure powder neutron diffraction experiments on deuterated α-FeO(OD) up to pressures of about 7 GPa (Nagai et al. unpublished, in Parise 2006).

An extension of the experimental studies to significantly higher pressures would not only allow the further corroboration...