

Single crystal structure analysis of diaspore, $\text{AlO}(\text{OH})$, at 50 GPa

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We have performed a single-crystal structure analysis of diaspore, $\text{AlO}(\text{OH})$, at a pressure of 50 GPa. This experiment significantly extends the range of single crystal high pressure diffraction studies of phases stable at ambient conditions, i.e. not grown in situ in a DAC. We collected intensity data of $\text{AlO}(\text{OH})$ at beamline D3 at HASYLAB. A small single-crystal ($30 \times 20 \times 10 \mu\text{m}^3$, Fig. 1) was loaded together with ruby chips for pressure determination into a new type of diamond anvil cell, which was designed by R. Boehler and built at the MPI für Chemie (Mainz) [1]. As a pressure-transmitting medium compressed helium was used, which was loaded into the pressure chamber at a pressure of 2.5 kbar within a pressure vessel at the MPI Mainz.

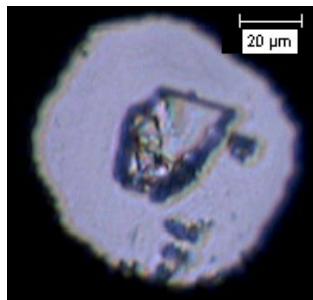


Figure 1: Single crystal of diaspore within the pressure chamber at a pressure of 50 GPa.

Data collection was performed on a HUBER four-circle diffractometer using a wavelength of 0.4 \AA . Intensity data were collected in fixed-phi mode using a point detector. The data were corrected for absorption by the crystal and the diamond-anvil cell components [2,3]. The structure refinement included the optimisation of 10 parameters with the program SHELXL97 [4] and converged to residual values of $R1 = 0.0476$ and $wR2 = 0.0862$. The hydrogen position could not be refined from these high-pressure data.

Diaspore is found to retain its structure up to 51.5 GPa at room temperature. Earlier predictions using quantum mechanics proposed a phase transition to the δ -phase at around 18 GPa [5]. Powder diffraction experiments on quenched samples, which reacted at (p, T) -conditions of $T = 1273 \text{ K}$ and $p = 19\text{-}21 \text{ GPa}$, showed the δ -phase, while at $T = 1273 \text{ K}$ and $p < 17 \text{ GPa}$ diaspore was stable [6]. This probably points to a significant influence of temperature, but it is surprising that a relatively open structure can be pressurized about 30 GPa above the transition pressure without showing peak broadening or other indications of the onset of amorphization.

We have previously investigated the structural compression of diaspore at several pressures of up to 7 GPa by in situ single-crystal X-ray diffraction at HASYLAB and of up to 50 GPa by density-functional theory [7,8]. With the experimental data at 50 GPa we can now not only confirm the strong compression of the a axis, but also the increasing anisotropy of the linear compressibilities of the b and c axes at pressures above 10 GPa, which has been predicted by density functional theory (Fig. 2). A fit of a 3rd order Birch-Murnaghan equation of state to the p, V -data results in a bulk modulus of $B_0 = 149(4) \text{ GPa}$ with its pressure derivative $B' = 4.1(2)$, which is very close to the values obtained from a fit to calculated p, V -data of $B_0 = 143.7(9) \text{ GPa}$ and $B' = 4.44(6)$ [7].

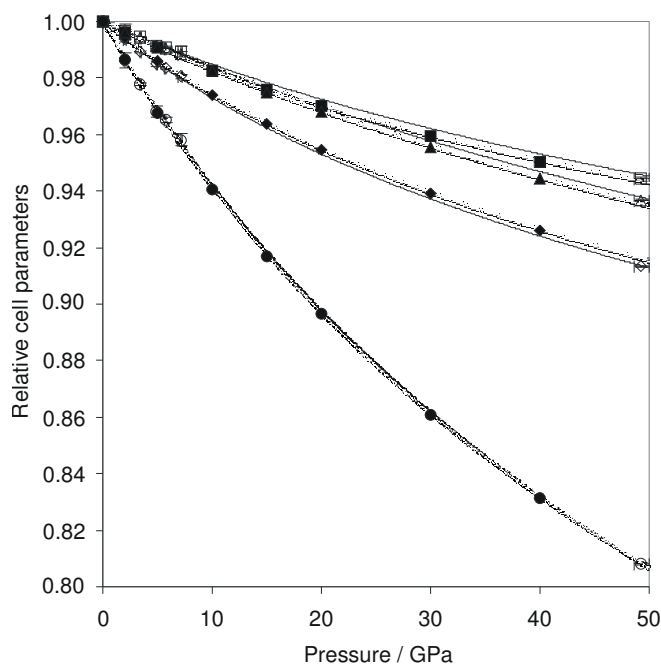


Figure 2: Pressure-dependencies of the normalized unit-cell parameters of diaspore, AlO(OH), up to 50 GPa (symbols: V/V_0 : circles, a/a_0 : diamonds, b/b_0 : squares, c/c_0 : triangles). Open symbols with error bars represent experimental data from Friedrich et al. (2006) [7] and this experiment (50 GPa), filled symbols theoretical data [7]. Fits of 3rd order Birch-Murnaghan equations of state to the experimental and theoretical data are plotted by solid and dashed lines, respectively.

The structural compression is mainly driven by the compression of the hydrogen bond, which is oriented nearly parallel to the a axis and, hence, can explain the strong compression of the a axis. In summary, this experiment confirms our earlier results obtained from density functional theory calculations [7,8].

One question addressed in this study was whether the onset of a symmetrization of the hydrogen bond, i.e. an atomic arrangement where the two O–H–O distances become similar, can be observed at high pressure. From the present results we infer that the hydrogen bond becomes significantly more symmetric with pressure up to 50 GPa. However, an extrapolation of our data implies that a complete symmetrization of the bent hydrogen bond is unlikely to occur below 100 GPa.

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References

- [1] R. Boehler, Rev. Sci. Instrum. 77, 115103 (2006).
- [2] K. Eichhorn, REDUCE, HASYLAB/DESY, Hamburg, Germany (1987)
- [3] R.J. Angel, J. Appl. Cryst. 37, 486 (2004)
- [4] G.M. Sheldrick, SHELXL97, Universität Göttingen, Germany (1997)
- [5] S. Li, R. Ahuja, and B. Johansson, Solid State Communic. 137, 101 (2006).
- [6] A. Suzuki, E. Ohtani, and T. Kamada, Phys. Chem. Minerals 27, 689 (2000)
- [7] A. Friedrich, D.J. Wilson, E. Haussühl, B. Winkler, W. Morgenroth, K. Refson, and V. Milman, Phys. Chem. Minerals, in press
- [8] B. Winkler, M. Hytha, C. Pickard, V. Milman, M. Warren, and M. Segall, Eur. J. Mineral. 13, 343 (2001)