Insight into structural changes in berlinite ($AlPO_4$) from in-situ Raman spectroscopy at high pressure and temperature

Anke Watenphul[1], Christian Schmidt[2]
[1]Deutsches Elektronen-Synchrotron, HASYLAB, Hamburg, Germany
[2]Deutsches GeoForschungsZentrum, Section 3.3, Potsdam, Germany

Berlinite ($AlPO_4$) is isomorphic to α-quartz. Their structures are related to each other by the coupled substitution 2 Si = Al + P. The SiO_4 tetrahedra along the *c*-axis in α-quartz are replaced in berlinite by alternating AlO_4 and PO_4 tetrahedra. This preferred ordering results in a doubled *c* unit-cell parameter. The positions of the vibrational modes in the Raman spectra of berlinite and α-quartz are very similar because the sum of the atomic masses of Al and P equals almost that of two Si atoms (Scott, 1971). However, detailed inspection reveals a greater complexity in the Raman spectrum of berlinite (Gregora et al., 2003).

We used in-situ Raman spectroscopy at temperatures up to 800 °C and pressures up to 10 GPa to obtain information on the structural changes in berlinite. In particular, we studied the strongest A_1-Raman lines at 462 and the 1111 cm^{-1}, which can be attributed to bending and stretching vibrations of the PO_4 tetrahedra.

The positions of both bands shift in the opposite direction with pressure and, likewise, with temperature. The 1111 cm^{-1} Raman line is accompanied by a less intense band at 1104 cm^{-1}, which likewise originates from a stretching vibration of the PO_4 tetrahedra. With increasing pressure, the 1111 cm^{-1} band shifts towards lower wavenumbers and that at 1104 cm^{-1} to higher wavenumbers. Thus, at 23 °C, both lines display the same position at about 1.4 GPa. With further increase in pressure, they become fully separated above 5 GPa. Tentatively, the opposed behavior with pressure is interpreted as being caused by the alternate succession of the AlO_4 and PO_4 tetrahedra along the *c*-axis, which permits a different compression/extension of the P-O1 and P-O2 distances.

Our results also indicate the great potential of berlinite as a secondary pressure sensor for diamond-anvil cell experiments, including studies at elevated temperatures. A relative shift, defined by the difference of the shifts in wavenumber between the 462 and the 1111 cm^{-1} lines with pressure and temperature, can be used as pressure gauge. Moreover, this sensor may be applicable at higher pressures than α-quartz (Schmidt and Ziemann, 2000) because no high-pressure polymorph isomorphic to coesite or stishovite is known so far.

References:
Gregora I. et al. (2003), Journal of Physics: Condensed Matter, 15, 4487-4501.
Schmidt C., Ziemann M.A. (2000), American Mineralogist, 85, 1725-1734.
Scott J.F. (1971), Physical Review B, 4, 1360-1366.