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Pressure-induced over-hydration and water ordering in gismondine: A synchrotron powder diffraction study

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Abstract

This paper reports the results of an in situ HP synchrotron X-ray powder diffraction investigation on the natural zeolite gismondine (ideal chemical formula $Ca_4Al_8Si_8O_{32}\cdot 16H_2O$, space group $P2_1/c$). The study was performed from P_{amb} to 7.9 GPa, and upon decompression, using methanol:ethanol:water (16:3:1) mixture (m.e.w.) as a nominally penetrating hydrostatic *P*-transmitting medium. No complete X-ray amorphization is observed up to the highest investigated pressure, and the original unit-cell parameters are almost completely recovered upon decompression. From 0.6 GPa, the water content is slightly higher than at ambient pressure, as a result of a moderate over-hydration. Moreover, at about 2 GPa, a significant water molecule system re-arrangement occurs, characterized by an ordering of part of the water molecules from four partially occupied sites to only two fully occupied ones. The over-hydration, but not the water ordering, is substantially irreversible upon pressure release. The Rietveld structural refinements of the powder patterns converged successfully up to 2.8 GPa; above this pressure, a phase transition to triclinic symmetry was observed and only the unit-cell parameters were refined. The comparison of the overall cell volume reductions and of the bulk modula of gismondine compressed between P_{amb} and 7.9 GPa in m.e.w. and in silicone oil, reveals that this is the unique zeolite with a higher compressibility in penetrating vs. non-penetrating *P*-transmitting media. This is ascribed to the re-organization of the water molecule system upon compression in m.e.w., which leaves a larger free volume inside the pores with respect to the phase compressed in silicone oil.

Keywords: Zeolite, gismondine, high pressure, compressibility, over-hydration, phase transition, crystal structure, synchrotron XRPD data