

In-situ neutron diffraction observation of hydrogen positions in portlandite under high pressure and temperature

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Ca(OH)₂, portlandite, belongs to brucite-type layered hydroxides, which is considered to be a model structure of hydrous minerals. This has hydrogen bonds within the interlayer of CaO₆ octahedral sheets. Among the other isostructural hydroxides, Ca ion in portlandite has the largest cation size, which might cause unique pressure-induced phase transitions. Previous high-pressure studies reported that portlandite undergoes a phase transition to a high-pressure (high-P) phase at 6-8 GPa and room temperature [1-3], and it transforms into another high-pressure and high-temperature (high-PT) phase at >6 GPa, >200C [4,5]. The crystal structures of these unquenchable high-P and -PT phases have been determined to be different monoclinic phases by X-ray and/or neutron diffraction measurements. According to previous neutron diffraction studies of Ca(OD)₂, repulsive D...D interaction and hydrogen bonds in portlandite becomes much stronger under high pressure up to 4.5 GPa. However, there was no in-situ neutron observation on portlandite under much higher pressure and temperature conditions, where the high-P and -PT phases are stable. Therefore, hydrogen positions in the crystal structures of portlandite under corresponding such high-PT conditions are still unknown. In the present study, in-situ neutron diffraction studies under high-PT conditions were performed in order to clarify the hydrogen positions in these portlandite polymorphs.

An initial sample of powder Ca(OD)₂ was synthesized from a mixture of CaO powder and stoichiometrically excess D₂O in an autoclave at 220C for 4 days. High-PT experiments were conducted using a 6-ram press called "Atsuhime" at a new high-PT beamline "PLANET" combined with a pulsed-neutron source at MLF, J-PARC. The neutron diffraction patterns were measured at 8.3 GPa and 400C, 200C, RT during decreasing temperature. The obtained diffraction peaks were originated from only the high-PT phase of portlandite. The crystal structure parameters and atomic positions were refined by Rietveld analytical method using GSAS software. For a model structure of the high-PT phase, the parameters, of which structure was determined by neutron diffraction data at 10 K, 0.1 MPa by Leineweber et al., 1997 [5], were used.

The structure of the high-PT phase obtained at 8.3 GPa, 400C was $a = 5.076(1)\text{Å}$, $b = 5.985(1)\text{Å}$, $c = 5.763(1)\text{Å}$, and $\beta = 100.37(7)$. Each lattice parameter of a , b , c was larger than that of [5] by 6, 2, and 4%, respectively. The β angle was smaller by 3%. In contrast, among the current results, the lattice parameters and atomic positions including hydrogen was not largely fluctuated by temperature (400C, 200C, and RT) at 8.3 GPa. The isotropic temperature factor (U_{iso}) gradually increased with increasing temperature. Based on the obtained structure of the high-P phase accompanying the displacements of CaO₆ layers and Ca atoms from the original structure of portlandite. Comparing the structure of the high-PT phase to that of the high-P phase, the phase transition mechanism can be inferred. There might be at least two positions for hydrogen in the high-P phase, one of which changed from the original position to keep stable even after the formation of new Ca-O bondings. These results agree well with those from our previous Raman and IR absorption spectroscopy measurements of OH-bonds. Therefore, it is suggested that the hydrogen bonds in portlandite are strongly affected by the phase transitions, for which the role of hydrogen bonds might be a driving force.

References

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