Synthesis and characterization of D-bearing piemontite

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Ca₀.₃₋₀.₄Al₀.₃₋₀.₄Mn⁺⁺⁺⁺₀.₃₋₀.₄Si₀.₃₋₀.₄O₁₂(OD)-piemontites were synthesized at 0.3-0.4 GPa and 500°C using hydrothermal equipment. The run products were analyzed using electron microprobe analyzer and infrared absorption spectral method, and refined using X-ray and neutron powder diffraction methods. The starting materials (s.m.s) of oxide mixture of stoichiometric compositions with p = 0.75, 1.0 and 1.1 and D₂O were used for hydrothermal synthesis experiments at 0.3-0.4 GPa and 500°C. Starging materials: Oxide mixtures heated at 850°C, and excess D₂O. Capsule systems: 1) Ag outer capsule with MnO-MnO₂ buffer + H₂O; Ag₉₀Pd₁₀ inner capsule with charge + D₂O; 2) Au outer capsule with MnO₂-MnO₂ buffer + D₂O; Ag₉₀Pd₁₀ inner capsule with charge + D₂O.

In the present synthesis experiments of deuterium-bearing piemontite using Ag-outer capsule with solid buffer + H₂O, deuterium was considerably or completely replaced by hydrogen. On the other hand, in the experiments using Au-outer capsule with solid buffer + D₂O, D-bearing piemontite was synthesized successfully. However, even in this case, seal of Au-outer capsule should be perfect, because hydrogen moves in and out inner Ag₉₀Pd₁₀ capsule.

There is no essential difference for Mn⁺⁺⁺⁺ distributions among octahedral M₁, M₂ and M₃ sites between D-bearing piemontite and H-bearing piemontite: the Mn⁺⁺⁺⁺ occupations at M₁ and M₃ in D-bearing piemontite refined using X-ray powder diffraction data are close to those of H-bearing piemontite (Nagashima and Akasaka, 2004). In this study, neutron diffraction data of a D-bearing piemontite synthesized from p = 1.0 starting material at 0.3 GPa and 500°C were measured. Although D in this piemontite was considerably replaced by H because of the use of Ag-outer capsule with solid buffer + H₂O, D-positions could be refined. Neutron diffraction study of D-bearing piemontite synthesized successfully in this study will give us useful information for the relations between cation substitutions and hydrogen bond.

Keywords: piemontite, hydrothermal synthesis, infra-red, Rietveld analysis, deuterium