American Mineralogist, Volume 95, pages 1132–1140, 2010

Uranyl phosphate sheet reconstruction during dehydration of metatorbernite [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$]

Joanne E. Stubbs,[1,*] Jeffrey E. Post,[2] David C. Elbert,[1] Peter J. Heaney,[3] and David R. Veblen[1]

[1]Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland 21218, U.S.A.
[2]Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560, U.S.A.
[3]Department of Geosciences, Pennsylvania State University, University Park, Pennsylvania 16802, U.S.A.

Abstract

The metatorbernite [$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$] structure comprises autunite-type sheets of corner-sharing uranyl square bipyramids and phosphate tetrahedra, with the interlayer region occupied by Cu^{2+} ions and molecular water. Previous studies have shown that heating induces stepwise dehydration and reduction in basal spacing. Structures of the lower hydrates have not been determined previously because suitable single crystals of these phases have yet to be prepared.

We have used synchrotron X-ray diffraction data collected during in situ, continuous heating of powdered metatorbernite to elucidate structures of its lower hydrates. Using Rietveld analysis, we have determined that autunite-type sheets remain intact through the first dehydration event above room temperature (onset 102 °C). We have discovered that the second dehydration event (onset 138 °C) triggers a major reconstruction to uranophane-type sheets, composed of chains of edge-sharing uranyl pentagonal bipyramids linked to one another by sharing edges and vertices with phosphate tetrahedra. This reconstruction enables the structure to overcome steric constraints on the minimum possible basal spacing, while maintaining Cu within the interlayer.

Four distinct phases have been identified with increasing temperature: $Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$, space group $P4/n$, a = 6.96519(23), c = 17.3102(8) Å; $Cu(UO_2)_2(PO_4)_2 \cdot 6.1H_2O$, space group $P4/n$, a = 6.95510(29), c = 16.6604(9) Å; $Cu(UO_2)_2(PO_4)_2 \cdot 3H_2O$, space group $P2_1$, a = 14.4979(23), b = 7.0159(9), c = 6.6312(10) Å, β = 107.585(14)°; and a lower hydrate with monoclinic or triclinic symmetry, $a \approx 6.7$, $b \approx 7$, $c \approx 11$ Å, β ≈ 100°. As shown here, in situ heating experiments and the Rietveld method provide fundamental insights into the crystal chemistry and structural behaviors of the important meta-autunite mineral group.

Keywords: Uranium, autunite, torbernite, metatorbernite, meta-autunite, Rietveld, synchrotron X-ray powder diffraction