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In situ dehydration of yugawaralite

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ABSTRACT

The structural response of the natural zeolite yugawaralite ($CaAl_2Si_6O_{16}\cdot 4H_2O$) upon thermally induced dehydration has been studied by Rietveld analysis of temperature-resolved powder diffraction data collected *in situ* in the temperature range 315–791 K using synchrotron radiation. The room-temperature monoclinic structure [Pc, $a = 6.73200(9)$, $b = 14.0157(2)$, $c = 10.0607(1)$ Å, $\beta = 111.189(1)$ °, $Z = 2$, at 315 K] has the Ca cations in the channels coordinated to four framework O atoms and to four water molecules, with two of the water sites (OW1 and OW4) showing positional disorder progressively disappearing as the dehydration proceeds. The yugawaralite structure reacts to the release of water molecules with small changes in the Ca-O bond distances and minor distortions of the tetrahedral framework up to about 695 K. Above this temperature the Ca coordination falls below 7 (four framework O atoms and three water molecules) and a major rearrangement in the cation coordination takes place, causing a first order phase transition involving both a large decrease in the cell volume and the change in the space group symmetry. A satisfactory structure model for the high-temperature phase stable in the range 695–791 K could not be obtained because of the complexity of the structure. A model approximately describing the average structure [Pn, $a = 12.703(1)$, $b = 13.067(1)$, $c = 9.839(1)$ Å, $\beta = 110.894(9)$, $Z = 4$, at 749 K] has been used to follow the temperature evolution of the cell parameters in the measured temperature range. This model involves a sixfold coordination of the Ca cations (five framework O atoms and one water molecule). There is no indication of significant structure changes before collapse, likely occurring when the last water molecule is expelled from the structure and the cation coordination drops below 6, as observed in other Ca-rich zeolites (i.e., laumontite, scolecite, mesolite).