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Dehydration dynamics of analcime by in situ synchrotron powder diffraction

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ABSTRACT

The continuous structural transformation of tetragonal analcime ($Na_{15.87}Al_{15.20}Si_{32.64}O_{96}\cdot 16.3H_2O$) upon dehydration was studied, using Rietveld structure analysis of temperature-resolved powder diffraction data collected using synchrotron radiation. The variation of the a-c axis length difference and normalized intensity of the (200) reflection as a function of temperature suggest that tetragonal analcime evolves toward a cubic structure at high temperature. The removal of water was accompanied by a spreading of the initial Na sites into many positions bonded to the framework O atoms. The migration of H_2O molecules through the [111] channels during dehydration caused the six-member ring apertures to open as widely as possible: this was accompanied by a twisting of the tetragonal prism, constituting the analcime framework, which led to an opposite tilting of tetrahedra connecting the prisms. These modifications induced by water diffusion are not energetically favored because they would increase the elastic energy of the system, and require a substantial thermal activation energy. The analcime framework reached a maximum distortion at about 650 K, the temperature of complete water loss, then underwent a relaxation process during which the T-O-T angles were restored to the starting value. The relative variation of cell volume associated with the opening of wide six-member ring channels during water migration, and then due to the framework relaxation process after complete dehydration, provides an explanation of the ‘‘negative thermal expansion’’ (i.e., volume contraction) effect in dehydrated analcime, which is complementary to that based on the Rigid Unit Modes theory.