Dehydration dynamics of stilbite using synchrotron X-ray powder diffraction

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ABSTRACT

The continuous structural transformation of the natural zeolite stilbite $(Na_{3.62}K_{0.44}Ba_{0.03}Ca_{6.32}Sr_{0.28}Mg_{0.04}[Fe^{3+}_{0.01}Al_{17.33}Si_{54.64}O_{144}]\cdot60H_2O)$ upon dehydration has been studied using Rietveld structure analysis of temperature-resolved powder diffraction data collected with synchrotron radiation. In the initial stage of heating, the monoclinic $F2/m$ stilbite structure (the so-called A phase) behaves as a noncollapsible framework, featuring only a slight framework distortion and a slight cell-volume contraction. At about 420 K, a first-order phase transition occurs changing the symmetry to an orthorhombic *Amma* phase, whose framework is collapsible and shows a large cell-volume contraction with temperature. The cell contraction is related to the process of T-O-T bond breaking and leads to a high-temperature stilbite phase with the same *Amma* space group and a collapsed structure similar to the previously described B phase in stellerite and barrerite. The structural refinement indicates that the dynamics of bond breaking is related to the shift of the Ca cations in the channels to achieve optimal coordination after the release of the H_2O molecules. Refined statistical occupancies of the tetrahedral atoms involved in the bond-breaking process (T1 and T1P) are consistent with a random rupture and re-formation of the T-O-T bonds. This is the first experimental study of the dynamic bond breaking of T-O-T bonds in a framework structure.