American Mineralogist, Volume 88, pages 142–150, 2003

Synchrotron X-ray diffraction study of the structure and dehydration behavior of todorokite

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ABSTRACT

Real-time, temperature-resolved synchrotron powder X-ray diffraction data and Rietveld refinements were used to investigate the behavior of the todorokite structure from 100 to 820 K. At 298 K, the lower valence cations, such as Mn^{3+}, occupy large octahedral sites at the edges of the triple chains, and four water/cation sites are in the tunnels. In our heating experiments in vacuum, todorokite began to break down at ~450 K and fully decomposed by 620 K, at which point hausmannite started to form. Our results suggest that the loss of O_2 accompanied the reduction of Mn^{4+} to Mn^{3+} and Mn^{2+}, and these reactions impelled a breakdown of the octahedral framework and the subsequent release of the tunnel water molecules. Rietveld refinements revealed a gradual thermal expansion of the todorokite structure to ~450 K. At higher temperatures, the unit-cell volume gradually decreased, primarily as a result of a decrease in *c*, and the decline in β with increasing temperature was accelerated. A mechanism for forming the inverse spinel hausmannite structure from todorokite is presented.