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Woodruffite: A new Mn oxide structure with 3 × 4 tunnels

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ABSTRACT

The mineral woodruffite, $Zn_{x/2}^{2}$ ($Mn_{i-x}^{4}Mn_{x}^{3}$)O₂·yH₂O, $x \sim 0.4$ and $y \sim 0.7$, is the first known example of a new type of Mn oxide characterized by large tunnels that measure 3 and 4 octahedra (6.9 × 9.2 Å) on a side. These tunnels are rectangular in cross-section and are the largest of any yet reported in natural or synthetic Mn oxides. The thermal stability of woodruffite is comparable to that of todorokite and other large-tunnel Mn oxide phases, breaking down at ~300 °C and eventually transforming to a spinel-type structure. The woodruffite structure may serve as a model for a new class of octahedral molecular sieves with enhanced capabilities as catalysts and selective cation-exchange agents.