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Neutron and synchrotron X-ray diffraction study of the structures and dehydration behaviors of ramsdellite and "groutellite"

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ABSTRACT

The crystal structure of ramsdellite, MnO_2, was refined using time-of-flight powder neutron diffraction data and the Rietveld method in order to assess the effects of reduction in cathodic battery materials. For the first time, we present a refined structure for "groutellite," a heretofore poorly characterized phase with ideal formula $(Mn^{4+}_{0.5}Mn^{3+}_{0.5})O_{1.5}(OH)_{0.5}$. "Groutellite" is generated synthetically as an intermediate compound during the reduction of ramsdellite to groutite (MnOOH), and it also occurs as an intergrowth in certain natural specimens of ramsdellite. The Jahn-Teller distortions in "groutellite" are confined to the **a**-**c** plane, and they result in a 6.8% unit-cell volume increase relative to ramsdellite. The Mn–O bond lengths refined for "groutellite" are consistent with the replacement of half of the Mn^{4+} and O^{2-} in ramsdellite by Mn^{3+} and $(OH)^-$, respectively. In addition, the high-temperature behaviors of ramsdellite and "groutellite" were investigated by temperature-resolved synchrotron powder X-ray diffraction from 298 to 720 K. Rietveld refinements revealed a gradual thermal expansion of the groutellite structure to ~450 K. At higher temperatures, the unit-cell volume gradually decreased, primarily as a result of a decrease in *c*.