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Neutron diffraction study of hydrogen in birnessite structures

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Abstract

The positions of hydrogen (deuterium) cations within the interlayer of synthetic Na- and K-birnessite samples have been determined for the first time using Rietveld analysis and Fourier difference syntheses, from time-of-flight powder neutron diffraction data. This study revealed that two symmetry-related D(H) positions are located ~1 Å above and below the midpoint between the split O interlayer sites in Na-birnessite. This result confirms our earlier interpretation that the split interlayer sites include O atoms from two symmetrically equivalent H_2O molecules. These molecules are oriented 180° to each other, and they are pivoted about a single set of H(D) atoms positions. The interlayer H_2O molecules in K-birnessite are oriented such that one of the H(D) atoms is pointed approximately toward the Mn octahedral layer O atoms and the other is directed approximately within the net of interlayer K/O sites. In K-birnessite, six K-O_{oct} distances are shorter than 3.35 Å, compared with only two Na-O_{oct} bond lengths in Na-birnessite, suggesting that K cations are more tightly bonded to the octahedral O atoms than are Na cations.

Keywords: Birnessite, Rietveld, neutron, hydrogen