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Water in the interlayer region of birnessite: Importance in cation exchange and structural stability

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Abstract

Birnessite is an important scavenger of trace metals in soils and aqueous environments. The basic birnessite-type structure consists of sheets of Mn octahedra separated by ~7 or ~10 Å ("buserite") interlayer regions filled with cations and water. Synthetic birnessite-like structures were produced through cation exchange reactions with synthetic Na-birnessite. The unheated, synthetic Mg^{2+}, Ca^{2+}, and Ni^{2+} layer structures have an ~10 Å interlayer spacing, whereas the other cation-exchanged synthetic birnessites and the related mineral chalcophanite have an interlayer spacing of ~7 Å. The Li^{+}, Na^{+}, K^{+}, Cs^{+}, and Pb^{2+} synthetic birnessites each contain two to three structurally different water sites, as evidenced by multiple H_2O bending and stretching modes in the infrared spectra. The complexity of the water bands in these spectra is likely related to disordering of cations on the interlayer sites. H-birnessite contains structural water and either hydroxyl, hydronium (H_3O^{+}), or both. The small difference in the width of the water stretching modes between room temperature and –180 °C indicates that the water molecules in birnessite-like structures are predominantly structurally, rather than dynamically, disordered. Most of the synthetic birnessites, including Na- and K-birnessite, undergo significant water loss at temperatures below 100 °C. There is a linear relationship between the temperature at which most of the water is lost from a given cation-exchanged birnessite and the heat of hydration of the interlayer cation. This finding implies that the interlayer water is strongly bound to the interlayer cations, and plays an important role in the thermal stability of birnessite-like structures.

Keywords: Birnessite, electron microscopy, IR spectroscopy, order-disorder, thermodynamics, XRD data