

Real-time Synchrotron X-ray Powder Diffraction Studies of the Dehydration of Synthetic Na- and K-birnessite.

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Manganese oxide minerals having the birnessite-type layer structure occur in a wide variety of geological settings, including soils, sediments, Mn crusts and nodules, and rock varnish. They readily participate in cation-exchange and oxidation-reduction reactions, and because they typically occur as coatings and fine-grained aggregates with large surface areas, they can significantly affect the chemical composition and behavior of sediments and associated aqueous systems. Also, because of their great chemical activity, synthetic birnessite-like phases are being extensively studied as possible catalysts and cation-exchange agents. Despite the importance of birnessite-like phases, many details of their atomic structures and behaviors are unknown, primarily because known natural and synthetic samples are unsuitable for single-crystal diffraction studies. In the current study, temperature-resolved, in situ powder X-ray diffraction data were collected at the National Synchrotron Light Source using imaging plates to investigate the structures and dehydration properties of synthetic Na- and K-birnessites. Samples were heated in glass capillaries in air and under vacuum, and in some cases effluents were monitored by mass spectrometry. The imaging-plate data provide nearly continuous diffraction records versus temperature, making it possible to investigate structural changes, including phase transitions, with unprecedented detail. Na-birnessite, for example, dehydrates in air via a complex process involving at least three distinct phase transformations between RT and about 125 °C. Under vacuum (about 2×10^{-6} torr) Na-birnessite dehydrates at room temperature. K-birnessite on the other hand exhibited two phase transitions below 200 °C, but was not fully dehydrated at 400 °C.

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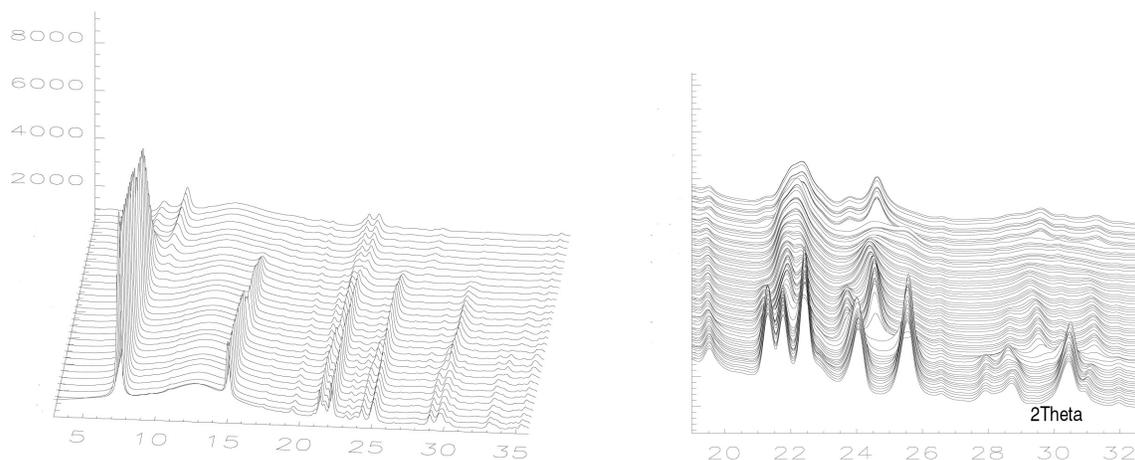


Figure 1. In situ, temperature-resolved XRD data showing dehydration and accompanying phase changes for synthetic Na-birnessite (left) and synthetic K-birnessite (right).