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# Time-resolved structural analysis of K- and Ba-exchange reactions with synthetic Na-birnessite using synchrotron X-ray diffraction

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## Abstract

Time-resolved Rietveld refinements using synchrotron X-ray diffraction (XRD) have documented real-time changes in unit-cell parameters in response to cation substitution in synthetic Na-birnessite. Potassium- and Ba-birnessite, like Na-birnessite, were found to have triclinic symmetry. Rietveld analyses of the XRD patterns for K- and Ba-exchanged birnessite revealed decreases in the *a*, *c*, and β unit-cell parameters, with a decrease of 1.7 and 0.5%, respectively, in unit-cell volume relative to Na-birnessite. Fourier electron difference syntheses revealed that the changes in the configuration of the interlayer species, and the charge, size, and hydration of the substituting cations, serve as the primary controls on changes in unit-cell parameters. Split electron density maxima with centers at (0 0 0.5) were present for Na, K, and Ba end-members; however, with increased substitution of $K^+$ for $Na^+$, the axis connecting the split-site maxima rotated from an orientation parallel to the *b*-axis to along the *a*-axis. Substitution of $Ba^{2+}$ for $Na^+$ did not result in rotation, but splitting of the interlayer site was more pronounced.

**Keywords:** Birnessite, cation exchange, synchrotron, X-ray diffraction, Mn-oxide