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Structure of synthetic Na-birnessite: Evidence for a triclinic one-layer unit cell

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ABSTRACT

The structure of a synthetic analogue of Na-birnessite (NaBi) was studied by powder X-ray diffraction (XRD). It is shown that NaBi has a one-layer triclinic structure with sub-cell parameters: a_P = 2.9513(4) Å, b_P = 2.9547(4) Å, c_P = 7.334(1) Å, α_P = 78.72(2)°, β_P = 101.79(1)°, γ_P = 122.33(1)°, and space group $P\bar{1}$. This sub-cell is equivalent to the base-centered sub-cell with parameters: a = 5.174 Å, b = 2.848 Å, c = 7.334 Å, α = 90.53°, β = 103.20°, and γ = 90.07°. A structure model has been refined using the Rietveld technique. NaBi consists of vacancy-free Mn-bearing octahedral layers whose negative charge arises mostly from the substitution of Mn^{3+} for Mn^{4+}. The departure from the hexagonal symmetry of layers results from Jahn-Teller distortion of Mn^{3+} octahedra, which are elongated along the **a** axis, segregated in Mn^{3+}-rich rows parallel to the **b** axis, and separated from each other along the **a** axis by two Mn^{4+}-rows. Structural sites of interlayer Na cations and H_2O have been determined as well as their occupancies. The sub-cells of the two NaBi modifications described by Drits et al. (1997) as types I and II likely contain four sites for interlayer species, two of which are occupied by Na and the other two by H_2O molecules. In the two NaBi varieties, these pairs of sites are split along the **c** axis and related by a center of symmetry. This splitting is consistent with the modulated structure of both NaBi types, which arises from the periodic displacement of interlayer species along the **b** axis with a periodicity $\lambda = 6b$ (Drits et al. 1997).