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Structure of synthetic monoclinic Na-rich birnessite and hexagonal birnessite: I. Results from X-ray diffraction and selected-area electron diffraction

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ABSTRACT

Synthetic Na-rich birnessite (NaBi) and its low pH form, hexagonal birnessite (HBi), were studied by X-ray and selected-area electron diffraction (XRD, SAED). SAED patterns were also obtained for synthetic Sr-exchanged birnessite (SrBi) microcrystals in which Sr was substituted for Na. XRD confirmed the one-layer monoclinic structure of NaBi and the one-layer hexagonal structure of HBi with subcell parameters a = 5.172 Å, b = 2.849 Å, c = 7.34 Å, β = 103.3° and a = 2.848 Å, c = 7.19 Å, γ = 120°, respectively. In addition to super-reflection networks, SAED patterns for NaBi and SrBi contain satellite reflections.

On the basis of these experimental obervations, structural models for NaBi and HBi are proposed. NaBi consists of almost vacancy-free Mn octahedral layers. The departure from the hexagonal symmetry of layers is caused by the Jahn-Teller distortion associated with the substitution of Mn^{3+} for Mn^{4+}. The supercell $A = 3a$ parameter arises from the ordered distribution of Mn^{3+}-rich rows parallel to [010] and separated from each other along [100] by two Mn^{4+} rows. The superstructure in the b direction of NaBi type II ($B = 3b$) comes from the ordered distribution of Na cations in the interlayer space. The maximum value of the layer negative charge is equal to 0.333 v.u. per Mn atom and is obtained when Mn^{3+}-rich rows are free of Mn^{4+}. The idealized structural formula proposed for NaBi type II is $Na_{0.333}(Mn^{4+}_{0.722}Mn^{3+}_{0.222}Mn^{2+}_{0.055})O_2$. NaBi type I has a lower amount of Mn^{3+} and its ideal composition would vary from $Na_{0.167}(Mn^{4+}_{0.833}Mn^{3+}_{0.167})O_2$ to $Na_{0.25}(Mn^{4+}_{0.75}Mn^{3+}_{0.25})O_2$. Satellites in SAED patterns of NaBi crystals result from the ordered distribution of Mn^{4+} and Mn^{2+} pairs in Mn^{3+}-rich rows with a periodicity of 6b.

The structure of HBi consists of hexagonal octahedral layers containing predominantly Mn^{4+} with variable amounts of Mn^{3+} and layer vacancies. The distribution of layer vacancies is inherited from the former Mn^{3+} distribution in NaBi. Interlayer Mn cations are located above or below vacant layer sites. The driving force of the NaBi to HBi transformation is probably the destabilization of Mn^{3+}-rich rows at low pH.