

## Structure of H-exchanged hexagonal birnessite and its mechanism of formation from Na-rich monoclinic busserite at low pH

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### ABSTRACT

The structural transformation of high pH Na-rich busserite (NaBu) to H-exchanged hexagonal birnessite (HBi) at low pH was studied by simulation of experimental X-ray diffraction patterns. Four HBi samples were prepared by equilibration of NaBu at constant pH in the range pH 5–2. The samples differ from each other by the presence of one (at pH 2 and 3) or two (at pH 4 and 5) phases, and by the structural heterogeneity of these phases which decreases with decreasing pH. The sample obtained at pH 5 is a 4:1 physical mixture of a 1H phase ( $a = 4.940 \text{ \AA}$ ,  $b = a/\sqrt{3} = 2.852 \text{ \AA}$ ,  $c = 7.235 \text{ \AA}$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ) and of a 1M phase ( $a = 4.940 \text{ \AA}$ ,  $b = a/\sqrt{3} = 2.852 \text{ \AA}$ ,  $c = 7.235 \text{ \AA}$ ,  $\beta = 119.2^\circ$ ,  $\gamma = 90^\circ$ ) in which successive layers are shifted with respect to each other by  $+a/3$  along the  $a$  axis as in chalcophanite. Both the 1H and 1M phases contain very few well-defined stacking faults at pH 5. At pH 4, the sample is a 8:5 physical mixture of a 1H phase containing 15% of monoclinic layer pairs and of a 1M phase containing 40% of orthogonal layer pairs. Any further decrease of the pH leads to the formation of a single defective 1H phase. This 1H phase contains 20% and 5% of monoclinic layer pairs at pH 3 and 2, respectively. Independent of pH, all phases contain 0.833  $\text{Mn}_{\text{layer}}$  cations, 0.167 vacant layer sites, and 0.167 interlayer Mn cations located either above or below layer vacancies per octahedron. A structural formula is established at each pH.

The origin of the observed phase and structural heterogeneities has been analyzed. 1H and 1M phases are assumed to inherit their specific structural and crystal chemical features from the two distinct NaBu modifications. NaBu type I, with a high proportion of  $\text{Mn}_{\text{layer}}^{4+}$  cations, is thought to be responsible for the monoclinic layer stacking because this configuration allows Mn cations from adjacent layers to be as far as possible from each other, thus minimizing the electrostatic repulsion between these high charge cations. In contrast, NaBu type II has a high interlayer charge induced by  $\text{Mn}_{\text{layer}}^{3+}$  for  $\text{Mn}_{\text{layer}}^{4+}$  substitutions. Consequently, the 1H phase has a high amount of interlayer protons and achieves compensation of the unfavorable overlap of layer and interlayer Mn cations, in projection on the  $ab$ -plane, by the presence of strong hydrogen bondings between layers. The higher proportion of defined stacking faults in both 1H and 1M phases at pH 4 compared to pH 5 can be attributed to the increase in reaction rate with decreasing pH. At lower pH (3 and 2) the formation of strong hydrogen bonds between adjacent layers controls the layer stacking mode and leads to the formation of a unique 1H phase. The proportion of well-defined stacking faults in this phase decreases from pH 3 to 2.