American Mineralogist, Volume 83, pages 97–118, 1998

Substructure and superstructure of four-layer Ca-exchanged birnessite

VICTOR A. DRITS,[1,2] BRUNO LANSON,[2,*] ANATOLI I. GORSHKOV,[3] AND ALAIN MANCEAU[2]

[1]Geological Institute, Russian Academy of Sciences, 7 Pyzhevsky Street, 109017 Moscow, Russia
[2]Environmental Geochemistry Group, LGIT-IRIGM, BP53, University Joseph Fourier and CNRS, 38041 Grenoble cedex 9, France
[3]Institute of Ore Mineralogy (IGEM), Russian Academy of Sciences, 35 Staromonetny Street, 109017 Moscow, Russia

ABSTRACT

Synthetic Ca-exchanged birnessite (CaBi) was studied by X-ray and selected-area electron diffraction (XRD, SAED). The substructure of CaBi may be described with a four-layer monoclinic subcell with $a = 5.150$, $b = 2.844$, $c = 4c' = 28.16$ Å, and $\beta = 90.3°$. Two different superstructures of CaBi were distinguished. CaBi type I has cell parameters $A = 3a = 15.45$, $B = 3b = 8.472$ Å. The stacking sequence in this unit cell may be described as defect-free OSOS, where successive layers are shifted relative to their predecessors by 0 (O) or $b/2$ (S) along the b axis. The complete description of stacking involves the structure of the layer itself, the structure of the interlayer, and the shift from this layer to the next one. CaBi type II can be described as a regular interstratification of $A_p = \frac{1}{2}(a - b)$, $B_p = 4b$, $\gamma = 118.9°$ and $A_p = \frac{1}{2}(a + b)$, $B_p = -4b$, $\gamma = 118.9°$ supercells that are connected by a mirror plane in projection on the a-b plane. Its stacking sequence is a random interstratification of OSOS (90%) and OOOS (10%) structural fragments. Most CaBi crystals appeared to consist of intergrown type I and type II sub-crystals.

As in Na-rich birnessite, the $A = 3a$ superstructure 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. In Mn^{3+}-rich rows heterovalent Mn cations are regularly distributed according to $Mn^{3+}Mn^{3+}Mn^{4+}$ (CaBi type I, $B = 3b$) and $Mn^{3+}Mn^{3+}Mn^{4+}Mn^{4+}$ (CaBi type II, $B = 4b$) sequences. Super-periodicities along the b axis are induced by these regular distributions of heterovalent Mn atoms in Mn^{3+}-rich rows and of associated interlayer Ca. No significant amount of layer vacancies was detected. Idealized structural formulae for CaBi type I and II are $Ca(Mn^{3+}_2Mn^{4+}_7)O_{18}$ and $Ca(Mn^{3+}_2Mn^{4+}_{10})O_{24}$, respectively.