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Structure of heavy-metal sorbed birnessite: Part 2. Results from electron diffraction

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ABSTRACT

Selected-area electron diffraction (SAED) and energy-dispersive analysis were used to study the structure of synthetic heavy-metal sorbed birnessites (MeBi). Samples were prepared by equilibrating a suspension of Na-rich buserite (NaBu) at pH 4 in the presence of various heavy metal cations (Me), including Pb, Cd, Zn, and Cu.

Five main types of SAED patterns were observed. Types I and II were observed only for ZnBi micro-crystals, and they both consist of two super-cell reflection networks related by a mirror plane parallel to the $\mathbf{a}^*$-$\mathbf{c}^*$ plane. In direct space, these twinned networks correspond to hexagonal supercells with $A_H = B_H = \sqrt{7}b/\sqrt{3}$, and $A_H = B_H = \sqrt{7}b$, for ZnBi type I and II, respectively. The supercells in the two varieties result from an ordered distribution of vacant layer octahedra capped by interlayer Zn in ZnBi layers. This distribution is described by a hexagonal cell with $A_H = \sqrt{7}b$. In ZnBi micro-crystals of type I, interstratified twinned right- and left-handed fragments are similar to chalcophanite ($ZnMn_3O_7{\cdot}3H_2O$; Wadsley 1955; Post and Appleman 1988), and distributions of vacant layer octahedra from adjacent layers are regularly shifted with respect to each other by 1/3 of the long diagonal of the hexagonal layer unit cell. In ZnBi micro-crystals of type II, distributions of vacant layer octahedra are not regularly shifted from one layer to the adjacent one.

SAED patterns of types III and IV occur for PbBi, ZnBi, and CdBi micro-crystals and contain super-cell reflections distributed parallel to $[100]^*$ with a periodicity that is not commensurate with that of the MeBi sub-structure ($a^*/2.15$ and $a^*/5.25$, respectively). The super-cell reflections result from the ordered distribution within MeBi layers of vacant layer sites capped by Me as pairs along the **a** axis. Within each pair, vacant sites are separated by $2a$ for type III, and by $5a$ for type IV. In one-layer monoclinic structures, the apparent incommensurability arises from the $+\mathbf{a}/3$ shift between adjacent layers having a similar one-dimensional periodic distribution of interlayer Me located above and below vacant octahedra sharing three corners with Mn_{layer} octahedra (TC sites). Tetrahedral coordination of these Me cations in TC sites, as in ZnBi, leads to the formation of strong H-bonds between adjacent layers. A similar incommensurate effect occurs in one-layer hexagonal MeBi if octahedrally coordinated Me cations periodically distributed along the **a** axis are located above and/or below empty tridentate cavities sharing three edges with Mn_{layer} octahedra (^{VI}TE sites, PbBi).

SAED patterns of type V contain only sub-cell reflections and were observed mostly for PbBi and CuBi micro-crystals. Three different conditions can lead to the absence of super-cell reflections: (1) a low amount of sorbed Me (PbBi); (2) the presence of Me having a scattering power similar to that of Mn on a single side of vacant layer sites (CuBi); or (3) a random distribution of interlayer species.