

MS41 O1**Crystal structure of nanocrystalline manganese oxides**

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Birnessite is a lamellar manganese oxyhydroxide (phyllosmanganate) whose layers are composed of MnO₆ octahedra. Non-stoichiometry arises from the coexistence of heterovalent Mn cations (Mn³⁺/Mn⁴⁺) and/or vacant sites, and is compensated for by the presence of interlayer cations. Despite the low natural concentration of Mn, birnessite is ubiquitous in Nature and plays a pivotal role in geochemical reactions and especially in the fate of pollutants such as organics or heavy metals. Its high reactivity arises from its high surface area, its high cationic exchange capacity, combined with adsorption and redox properties.

In addition to the presence of random stacking faults, the random interstratification of different layer types and the occurrence of well-defined stacking faults are commonly reported in layered minerals, such as phyllosmanganates. The high proportion of such defects strongly reduces the efficiency of structure refinement methods, and one effective way to determine the actual structure of defective systems is the calculation of XRD patterns using the mathematical formalism described by Drits & Tchoubar [1].

In particular, this simulation technique allowed showing that layer symmetry depends on the origin of the layer charge deficit. The symmetry of birnessite layers containing vacant octahedra is hexagonal, whereas orthogonal layer symmetry is observed for varieties containing a high proportion (~1/3) of layer Mn³⁺ cations. This distortion arises from the unique azimuthal orientation of Mn³⁺ octahedra which are distorted by the Jahn-Teller effect.

In most natural phyllosmanganates, and especially in those resulting from biological activity, the abundance of random stacking faults leads to the occurrence of nanocrystalline structures lacking three-dimensional ordering. Even for these turbostratic structures, XRD patterns exhibit noticeable modulations of the 20,11 and 31,02 bands (~2.45 and ~1.42 Å, respectively). These modulations can be used to provide relevant structural information, which includes not only unit-cell parameters but also atomic coordinates and occupancies of the different sites. This information is especially useful to improve our understanding of the interactions between natural phyllosmanganates and environmentally important heavy metals.

The usefulness of this approach will be illustrated with various synthetic and natural birnessite samples.

[1] Drits V.A. & Tchoubar C. (1990): X-ray diffraction by disordered lamellar structures. Springer Verlag, Berlin, 371 p.

MS41 O2**Te-Te interaction in minerals and inorganic compounds.** *Herta Effenberger Institut für Mineralogie und Kristallographie, Universität Wien, Vienna, Austria.*

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Compounds with tellurium atoms coordinating cations are frequently found in nature; due to the interest in their catalytical properties and semiconducting behaviour they were synthesized as well. In most of these cases the Te atoms have a formal charge of 2-. However, in some cases the Te atoms are also linked to each other and form covalently bonded pairs of chalcogen atoms. The Te—Te bond distances are similar to that of native tellurium (the infinite helices have Te—Te bond distances of 2.835(2) Å and Te—Te—Te bond angles of 96.3(2)°). Common are MTe₂ compounds crystallizing in the pyrite or marcasite type. They have dumbbells Te₂ in analogy to S₂ or Se₂. However, tellurides have a greater propensity than selenides or sulfides to exhibit interactions intermediate between a single Te—Te bond and a Te²⁺...Te²⁺ interaction. Te atoms form also Te₃ groups, which were found *e.g.*, in AgTe (empressite), Rb₄Hg₅(Te₃)₂(Te₂)₂Te₃, K₂Cu₂(Te₃)(Te₂), or K₄[Hf₃(Te₃)(Te₂)₇]. — Buckhornite, [(Pb₂Bi)S₃](AuTe₂) and nagyagite, [(Pb₃(Pb,Sb)₃S₆)(Au,Te)₃] are member of a homologue series. In buckhornite two (Pb,Bi)S sheets form one slice of the SnS archetype whereas in nagyagite four (Pb,Sb)S layers form the corresponding slice with a thickness of two SnS-archetype slabs. These layers are separated in both compounds by Au—Te *mono*-layers. In buckhornite an ordering of the Au and Te atoms on two different crystallographic sites with site symmetries *mm*2 and *m*, respectively, was observed. The symmetry elements are perpendicular to the gold-tellurium layers. The Au(III) atoms are [4] coordinated with Au—Te bond distances of 2.71 Å. The coordination figure is practically planar. The AuTe₄ configurations in buckhornite share each two *trans*-arranged Te—Te edges to form ribbons with the formula AuTe₂. The Te—Te distances are 3.52 Å and 4.11 Å for the shared and unshared edges within the AuTe₄ configuration. The Te—Te distances between the AuTe₂ ribbons are 3.34 Å and indicate weak Te—Te contacts. It is remarkable that they are shorter than the Te—Te edges within the AuTe₄ configuration. In the average nagyagite structure Te and Au paradoxically have to be assigned to one atomic position with site symmetry *m*. From this occupation results a formal square-planar (Te,Au) net. In nagyagite Au:Te varies on a wide scale (it scatters in most analyses roughly from 1:2 to 1:3), in buckhornite the ratio Au:Te is close to 1:2. In nagyagite the average (Te,Au)—(Te,Au) distance of 2.97 Å features statistically a mean value of Au—Te and Te—Te. The ratio of covalent Te—Te bonds and unbounded Te...Te contacts serve for local charge balance in accordance with the Pb,Sb ratio in the SnS archetype layer. — In this context the pseudo-binary (Au,Ag)Te₂ minerals calaverite, krennerite and sylvanite are worth to be mentioned. The average structures correspond roughly with a distorted CdI₂-structure type. Valence fluctuations are the driving force for the incommensurately modulated crystal structure of calaverite (AuTe₂). Krennerite (Au_{0.8}Ag_{0.2}Te₂) can be