

## 08-Inorganic and Mineralogical Crystallography

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ent parts of the deposit have been registered also and they correlate with geological data in a good way. Thus solution of direct problem in lab has allowed to solve a "converse" problem: "to reconstruct" a scheme of natural influence on anatase and rutile structures by analysis of "AnI". Therefore the changing of sorption properties after T-influence is one of the reasons of coexistence of gold and other noble metals with  $\text{TiO}_2$ .

PS-08.04.37

### COPPER PHOSPHATES: LIBETHENITE $\text{Cu}_2(\text{PO}_4)(\text{OH})$ AND $\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$ -SYNTHESIS AND CRYSTAL STRUCTURES.

By O. V. Yakubovich\*, Lomonosov State University and O. K. Melnikov, Inst. of Crystallography, Moscow, Russia  
Crystals of two copper phosphates have been prepared by the hydrothermal method and characterized by complete X-ray single crystal structure determination:

libethenite  $\text{Cu}_2(\text{PO}_4)(\text{OH})$ ,  $a=8.071(2)$ ,  $b=8.403(4)$ ,  $c=5.898(3)$  Å, Pnnm,  $Z=4$ ,  $\rho_{\text{calc}}=3.97\text{g/cm}^3$ ,  $R=0.0397$ ,  $R_w=0.0358$ ,  $s=1.28$ , 814 refl.

$\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$ ,  $a=8.883(3)$ ,  $b=7.556(3)$ ,  $c=5.334(1)$  Å,  $\alpha=101.33(3)$ ,  $\beta=95.80(3)$ ,  $\gamma=108.62(3)^\circ$ , P1,  $Z=2$ ,  $\rho_{\text{calc}}=4.27\text{g/cm}^3$ ,  $R=0.0310$ ,  $R_w=0.0327$ ,  $s=1.26$ , 1720 refl.

A new compound  $\text{Cu}_{2.5}\text{Mn}(\text{PO}_4)_2(\text{OH})$  with  $\text{Cu}^{2+}$ — and  $\text{Mn}^{2+}$ —cations in the same crystal were received for the first time.

The basis of both structures is formed by a framework of octahedra and five-vertex polyhedra of Cu and (Mn). All vertices of  $\text{PO}_4$ — tetrahedra are shared with the framework polyhedra. Peculiarities of  $\text{Cu}^{2+}$ — polyhedron geometry are analyzed. The positions of the hydrogen atoms are located.

A refinement of the hydrogen position in libethenite allowed to confirm a bifurcated hydrogen bond suggested earlier (Cordson A. Canad. Mineral., 1978. 16. 153-157). It is shown that libethenite is a member of structures with triangular nets in the projection along the axis of  $3n$  Å.

### PS-08.04.38 THE MODULAR INTERPRETATION OF OXYBORATE STRUCTURES.

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The structural variations of oxyborates  $\text{M}_3\text{BO}_5$  ( $\text{M} = \text{Mg}, \text{Mn}, \text{Fe}$ ) considered by Bovin et al. (Acta Cryst., 1981, A37, 28-35) according to slip and twinning mechanisms may be completely explained by the OD nature of two alternating kinds of layer building modules (BM) (Fig. 1) parallel to the slip and twinning planes and having symmetries  $\text{Pm } 2/m$  (2) and  $\text{P1 } 2/m$  (1).  $\lambda$ -operations 2 or 2m transforming a BM into itself are relating adjacent  $\text{BM}_1$  unambiguously while  $\text{BM}_2$  may be in two opposite orientations. The BMs may be denoted as H and N (11). BM-pairs  $\text{NH}=\text{b}$ ,  $\text{HN}=\text{q}$ ,  $\text{NH}=\text{d}$ ,  $\text{HN}=\text{p}$  are symmetrically and, hence, energetically equivalent (Dornberger-Schiff, Grundzüge einer OD Theorie, Berlin, 1964), and slight fluctuations in crystallization conditions and media composition may change the

BM sequence order and cause stacking faults. BM sequences may be described by sequences of BM- or BM-pair symbols. Numbers of consecutive equal letters N, H, b, d, p or q compose numerical symbols like those of Zdanov. These symbols directly correspond to the zig-zag chains of light spots imaging B-positions in HREM patterns. Symbols 2 and 2m of the  $\lambda$ -operations acting in H-BMs when used in structure notations are attributed to the intervals between equal or mirrorly equal letters (e.g. as for bb, dd or bd). Therefore they play the same role as letters h and c for close packings. According to the distribution of these operations, there are only two MDO (simple) structures satisfying the homogeneity condition: those of pinakillite (P), ... 2. 2. 2. and ludwigite (L), ... 2m. 2m. 2m. ... The other periodic structures listed by Bovin et al. (1981) are inhomogeneous (complex) as mixtures of P and L. The ratio P/L being equal to the ratio of the numbers of 2 and 2m operations is 1 : 2, 1 : 1 and 2 : 1 for the hypothetical structure (HS) in Fig. 8 of (Bovin et al., 1981), orthopinakillite (OP) and takeuchiite (T) respectively. The modular system is considered with common axes  $a_0 \sim 12.5$ ,  $b_0 \sim 3.0$ ,  $c_0 \sim 4.6$  Å ( $c_0$  being the thickness of a layer pair). For periodic structures  $\vec{a} = \vec{a}_0$ ,  $\vec{b} = \vec{b}_0$ ,  $\vec{c} = (m/5)\vec{a}_0 + n\vec{c}_0$ . In reciprocal space  $\vec{a}^* = \vec{a}_0^* - (m/5n)\vec{c}_0^*$ ,  $\vec{c}^* = \vec{c}_0^*/n$  defining the diffractive features. The m, n values are  $\pm 1, 1; 0, 2; \pm 1, 3; 0, 4; 0, 6$  for P, L, HS, OP and T respectively. A single slip corresponds to an operation sequence ... 2. 2. 2. 2m. 2m. 2. 2. 2. ..., a single twinning- to ... 2. 2m. 2. 2. 2. ... Two planes bordering a N (11) layer or an H layer may serve as slip or twin planes respectively. Their choice is thus ambiguous, the corresponding mechanisms are not convincing and may have no direct relation to reality.

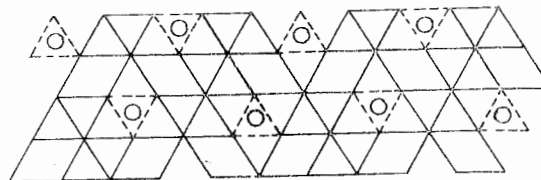


Fig. 1. Scheme of a BM quadruple NH11H. The octahedra are projecting into rhombi, circles indicate B-atoms.

### PS-08.04.39 CRYSTALLOGRAPHIC STUDY ON A SERIES OF POLYMETALLATE OXYGEN CLUSTERS.

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Polyoxoanions are important for elucidating the biological and catalytic functions of metal chalcogenide clusters; a special type of chemistry seems to be related to reduced and mixed valence clusters.

If molybdate(VI) and tungstate(VI) are reduced in acidic solution under  $\text{N}_2$  atmosphere, the resultant solution will be oxidized after exposition to air, and leads to the formation of novel and remarkable anions.

With that we call Red-Ox Reconstructing (ROR) method, we have successfully synthesized a series of different types of heteropolyanions including three new type of high-nuclearity of clusters. The types and characteristics of these structures are:

(1) Keggin-type anions: (1)  $[\text{VMo}_{12}\text{O}_{40}]^{3-}$ , space group  $\text{Fm}\bar{3}\text{m}$ ,  $a=22.334(2)$  Å,  $V=11140$  Å<sup>3</sup>,  $Z=8$ , R factor is 0.055; (2)  $[\text{VW}_{12}\text{O}_{40}]^{3-}$ , space group  $\text{P}\bar{4}3\text{m}$ ,  $a=11.027(5)$  Å,  $V=1340(11)$  Å<sup>3</sup>,  $Z=1$ , R factor is 0.054.