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 TiO_2.

PS-08.04.37 COPPER PHOSPHATES: LIBETHENITE $Cu_2(PO_4)(OH)$ AND $Cu_{2.5}Mn(PO_4)_2(OH)$ - 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 $Cu_2(PO_4)(OH)$, $a=8.071(2)$, $b=8.403(4)$, $c=5.898(3)$ Å, Pnnm, $Z=4$, $\rho_{calc}=3.97 g/cm^3$, $R=0.0397$, $R_w=0.0358$, $s=1.28$, 814 refl.

$Cu_{2.5}Mn(PO_4)_2(OH)$, $a=8.883(3)$, $b=7.556(3)$, $c=5.334(1)$ Å, $\alpha=101.33(3)$, $\beta=95.80(3)$, $\gamma=108.62(3)°$, $P\bar{1}$, $Z=2$, $\rho_{calc}=4.27 g/cm^3$, $R=0.0310$, $R_w=0.0327$, $s=1.26$, 1720 refl.

A new compound $Cu_{2.5}Mn(PO_4)_2(OH)$ with Cu^{2+}—and 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 PO_4— tetrahedra are shared with the framework polyhedra. Peculiarities of Cu^{2+}— polyhedron geometry are analized. 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 (Cordsen 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. By B. B. Zvyagin‧ and G. A. Sydorenko. Inst. of Ore Mineralogy (IGEM), Rus. Ac. Sc.‧ and Inst. of Mineral Resources, 109017 Moscow, Russia.

The structural variations of oxyborates M_3BO_5 (M = Mg, Mn, 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 twin planes and having symmetries Pm 2/m (2) and P1 2/m ($\bar{1}$). λ-operations 2 or 2m transforming a BM into itself are relating adjacent BM_1 unambiguously while BM_2 may be in two opposite orientations. The BMs may be denoted as H and N (11). BM-pairs NH = b, HN = q, NH = d, H11 = 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, 11, 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 λ-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 paly 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), orthopinakiolite (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 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 diffractional features. The m, n values are ±1, 1; 0, 2; ±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 ..2.2.2m.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.
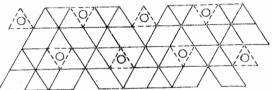

Fig. 1. Scheme of a BM quadruple NH11H. The octahedra are projecting into rhombi, circles indicate B-atoms.

PS-08.04.39 CRYSTALLOGRAPHIC STUDY ON A SERIES OF POLYMETALLATE OXYGEN CLUSTERS. By M.C.Shao,‧ G.Q. Huang, S.W. Zhang, Y.G. Wei & Y.Q. Tang, Department of Chemistry, Peking University, Beijing, 100871, P.R. China

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 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 serie of different types of heteropolyanions including three new type of high-nuclearity of clusters. The types and characteristics of these structures are:

(I) Keggin-type anions: (1) $[VMo_{12}O_{40}]^{3-}$, space group F-m$\bar{3}$m, a= 22.334(2)Å, V=11140Å³, Z=8, R factor is 0.055; (2) $[VW_{12}O_{40}]^{3-}$, space group P-$\bar{4}$3m, a=11.027(5)Å, V=1340(11)Å³, Z=1, R factor is 0.054.

(II) Keggin related anions: (1) $[AsV_{12}O_{40}(As^{III}OH)_2]^{11-}$, space group P-$\bar{4}$3m, a=10.72(2)Å, V=1231.8(9)Å^3, Z=1 R factor is 0.057; (2) $[AsV_{12}O_{40}(VO)_2]^{6-}$, space group F-ddd, a=24.707(7), b=14.983(7), c=24.455(8)Å, V=15732(7)Å^3, and Z=4, R factor is 0.059.

(III) Strandberg-type anion: $[Se_2Mo_5O_{21}]^{4-}$, space group P-2_1/n, a=9.851(2)Å, b=23.224(5)Å, c=10.456(3)Å, β=114.13(2)°, V=2183Å^3, and Z=4, R factor is 0.069.

(IV) Dawson-type anion: $[H_2V_2W_{18}O_{62}]^{4-}$, space group R-$\bar{3}$m, a=37.613(11), c=12.972(7)Å, V=15901(13)Å^3, and Z=9, R factor is 0.063.

(V)New type of high-nuclearity anions: (1)$[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ (Zhang, Huang, Shao & Tang, J. Chem. Soc., Chem. Commun., 1993, 1, 37-38); (2) $[H_6Mo_{57}Fe_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$, space group P-$6_3$/mmc, a=23.847(4), c=27.797(9)Å, V=13685(7)Å^3, and Z= 2, R factor is 0.049; (3) $[H_6Mo_{57}Fe^{II}O_{183}(NO)_6(H_2O)_{18}(MoO)_2]^{6-}$, space group P-$6_3$/mmc, a=23.868(5), c=27.512Å, V=13577Å^3, and Z=2, R factor is 0.058.

Fig. 1. Bright field micro - graph of amorphous Pb-oxides in Pb_2MoO_5 crystals.

Fig. 2. Bright field micro - graph of $PbO_{1.57}$ particle (1.5x0.4 microns). SAED from it - [315] zone axis.

Fig. 3. Bright field micro - graph of Pb_5MoO_8 particle (0.7 × 0.7 microns). SAED from it - [100] zone axis.

PS-08.04.40 **PHASE INHOMOGENEITY OF Pb₂MoO₅ SINGLE CRYSTALS.** By D. D. Nihtianova*, S. S. Angelova, L. K. Djonev, L. L. Petrov and K. P. Petrov, Institute of Applied Mineralogy, Bulgarian Academy of Sciences Rakovski str., 92, 1000 Sofia, Bulgaria.

The existence of $PbO_{1.57}$ and Pb_5MoO_8 microphases in Pb_2MoO_5 crystals was not explained earlier (Nihtianova et al, SPOC, 1989, Budapest, Booklet, p.19). Pale yellow Pb_2MoO_5 crystals, obtained by Czochralski method at different conditions, were investigated by PDA (DRON 3M), STA (STA 1500), TEM (TEM 420 Philips) and SEM (SEM 515 Philips) in order to determine the origin of the additional solid state microinclusions in them. While searching for the optimal conditions of obtaining Pb_2MoO_5 nutrient in a solid state reaction of initial oxides $2PbO + 1MoO_3$ we found out by PDA, STA and EDAX, that: 1/ the synthesis of Pb_2MoO_5 is not carried out to the end; 2/ in some experiments the system is 2-phase: predominant Pb_2MoO_5 phase and PbO (massicot) and in others 3-phase: predominant Pb_2MoO_5, PbO and Pb_2MoO_5. These data indicated unambiguously, that the appearance of amorphous Pb-oxides (Fig. 1), $PbO_{1.57}$, (Fig. 2) and Pb_2MoO_5 (Fig. 3) in Pb_2MoO_5 crystals is directly connected with the phase composition of the starting nutrient.

PS-08.04.41
THE STRUCTURAL AND PHASE TRANSFORMATIONS OF GLAUCONITES IN Na-, Ca- AND Mg-CHLORIDE MEDIA UNDER HYDROTHERMAL CONDITIONS. By E.A.Goilo, K.A.Nauruzbaev, N.V.Kotov and V.A.Frank-Kamenetskii, Department of Crystallography, State University, St. Petersburg, Russia.

X-ray diffraction studies of the products of glauconite transformations with different octahedron layer compositions have been carried out in the presence of Na, Ca and Mg under pressure of P (H2O) = 1 kbar at temperatures of 200-600°C under hydrothermal conditions in the three-days experiment. What is observed is that Fe and Fe-Mg-glauconites are very similarly formed under any experimental conditions except the appearance of Ca-trioctahedral montmorillonite at T=500°C in the presence of $CaCl_2$ and of amphibole at T= 600°C in the presence of NaCl. Therefore, it is interesting to compare the Al- and Fe-glauconite behaviour. At the minimum experimental temperature T=200° C, glauconites are not changed. However, at the temperature T=300°C and in the presence of NaCl, $CaCl_2$ and $MgCl_2$ Fe- and Fe-Mg-glauconites, unlike Al-glauconites, start to become unstable and they transform into trioctahedral montmorillonite. The following conclusions can be drawn from the crystallochemical analysis of the initial, intermediate and final phases under the experiment conditions: First of all, the composition of octahedral layer of glauconites definitely influence the transformational features under the mineralized hydrothermal condition. Fe- rich glauconites are transformed at a lower temperature, beginning from T=300°C. But at this temperature, the glauconites rich in Al are characterized by higher stability, which start to transform only at T=400°C. Secondly, the important features of structural transformation of glauconites with the increase of the experiment temperature under hydrothermal conditions is the formation of expandable trioctahedral montmorillonites. This is connected with the existence of interchangeable Na, Ca, Mg in water medium, which functions as the expandable structural stabiliser. Thirdly, with the