copper phosphates; libethinite Cu,PO₄(OH) and Cu₃(MnPO₄)₂(OH) -synthesis and crystal structures.

By O. V. Yakubovich, B. N. Belman, and O. K. Melnikov, Institute of Crystallography, Moscow, Russia

Copper phosphates have been prepared by the hydrothermal method and characterized by X-ray single crystal structure determination. Libethinite Cu₃PO₄(OH) with a = 8.07(2), b = 8.03(4), c = 5.898(3) Å, Pmmn, Z = 4, R-factor = 5.21%, R = 0.0397, Rw = 0.0358, z = 1.28, 247 refl.

Cu₃(MnPO₄)₂(OH) with a = 5.883(3), b = 7.566(3), c = 5.334 (1) Å, a = 101.33(3), b = 96.80(3), c = 108.42(3), P1, Z = 3, R-factor = 4.21%, R = 0.0390, Rw = 0.0327, z = 1.25, 1720 refl.

A new compound Cu₃MnPO₄(OH) with Cu²⁺ and Mn²⁺ 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 PO₄− tetrahedra are shared with the framework polyhedra. Peculiarities of Cu²⁺ and Mn²⁺ geometries are analyzed. The positions of the hydrogen atoms are located. A refinement of the hydrogen position in libethinite allowed to confirm a bifurcated hydrogen bond suggested earlier (Condron A. C., Canad. Mineral., 1972, 10, 153-157).

It is shown that libethinite is not a member of structures with triangular nets in the projection along the axis of 3n Å.

08-Inorganic and Mineralogical Crystallography

PS-08.04.37 THE MODULAR INTERPRETATION OF OXYBORATE STRUCTURES. By N. D. Zvyagin and G. A. Sydorenko, Institute of Ore Mineralogy (IGEM), Russian Academy of Sciences, and Institute of Mineral Resources, Moscow, Russia.

The structural variations of oxyborates M₂B₂O₆ (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 (1). In a two or three transforming a BM into itself are related adjacent BMs, unambiguously while BM may be in two opposite orientations. The BMs may be denoted as H and N (1). BMs share N ≡ H, N ≡ N, H ≡ H, H ≡ H are symmetrically and, hence, energetically equivalent (Dornberger-Schiff, Grundzüge einer OD Theorie, Berlin, 1964). Small 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-like 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 zig-zag chains of light spots imaging B positions in HREM patterns. Symbols 2 and 2m of the λ-operations arising in H-RMS when used in structure notations are attributed to the interval between equal or mirror-equal letters (e.g., as for bb, dd, or bb).

Fig. 1. Scheme of a BM quadruple NH2HH. The octahedra are projecting into rhombi, circles indicate B atoms.

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

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

If naphtholate(VI) and tamarate(VI) are reduced in acid solution under Na₂O atmosphere, the resultant solution will be esterified after exposition to air and leads to the formation of novel and remarkable anions.

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

(1) Keggin-type anion (O) [VMe₆O₆]xo, space group P-63/m, a = 22.334(2), V = 31140(2), R factor is 0.055; (2) [VMe₆O₆](H₂O)ₓ, space group P-63/m, a = 31.097(9), V = 34600(13), R factor is 0.055.
**08-Inorganic and Mineralogical Crystallography**

**Fig. 1.** Bright field micro - graph of amorphous Pb-oxides in PbMoO₄ crystals.

**Fig. 2.** Bright field micro - graph of Pb₁₉₅O₌ seventy microns. SAED from it - [20] 2000 zone axis.

**Fig. 3.** Bright field micro - graph of PbMoO₄ particle (1. 5x0. 7 microns). SAED from it - [100] zone axis.

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**PS-08.04.40**

**PHASE INHOMOGENEITY OF PbMoO₄ SINGLE CRYSTALS.**

**By D. D. Nishitianova, S. S. Angelova, L. K. Djonnev, L. L. Petrov and R. Petrov.**

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The existence of PbO₁₉₅ and PbMoO₄ microstructures in PbMoO₄ crystals was not explained earlier (Nishitianova et al., SPOC, 1989, Budapest; Booklet, p. 19). Pale yellow PbMoO₄ crystals, obtained by Czechak et al. 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 mixtures in them. While searching for the optimal conditions of obtaining PbMoO₄ nutrient in a solid state reaction of initial oxides PbO + 1 MoO₃ we found out that by a temperature of 720°C in some experiments the system is 2-phase: predominant PbMoO₄ phase and PbO (massicot) and in other 3-phase: predominant PbMoO₄, PbO and PbMoO₃. These data indicate unambiguously that the appearance of amorphous Pb-oxides (Fig. 1), PbO₁₉₅ (Fig. 2) and PbMoO₃ (Fig. 3) in PbMoO₄ crystals is directly connected with the phase composition of the starting nutrient.

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**PS-08.04.41**

**THE STRUCTURAL AND PHASE TRANSFORMATIONS OF GLAUCONITE IN Na₆-, Ca₆- AND Na₂O-CACl₂ MEDIA UNDER HYDROTHERMAL CONDITIONS.**

By E.A. Golgo, R.A. Nauruzbaev, N.V. Katkov and V.A. Frank-Kamenetski, Department of Crystallography, State University, St. Petersburg, Russia.

X-ray diffraction studies of the products of glaucleite transformations with different octahedron layer compositions have been carried out in the presence of Na₂O, CaO and NaCl by pressure of P (H₂O) - 1 kbar at temperatures of 200-600°C under hydrothermal conditions in the three-day experiment. What is observed is that Fe and Fe-Mg-glaucenites are very similarly formed under any experimental conditions except the appearance of Ca-trioctahedral montmorillonite at T=500°C in the presence of Na₂CO₃ and of amphibole at T=600°C in the presence of NaCl. Therefore, it is interesting to compare the Al- and Fe-glaucenite 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, GoCl₃ and MgCl₂ Fe- and Fe-Mg-glaucenites, unlike Al-glaucenites, start to become unstable and they transform into trioctahedral montmorillonite. The following conclusions can be drawn from the crystallographical 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 behaviour of 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 Na₂, Ca₂, Mg in water medium, which functions as the expandable structural stabilizer. Thirdly, with the