

08-Inorganic and Mineralogical Crystallography

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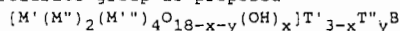
The structure is based on a framework built up by connecting [001] double chains of octahedra; wide [001] channels in the framework are occupied by a single chain of face-sharing octahedra [M(1) site] and by the Si-tetrahedra.

By putting 2.88 Si + 0.02 P in the T sites, the cell with $a = 12.02(3)$, $b = 20.22(3)$, $c = 4.732(2)$ Å (s.g. Pmcn) contains four f.u. with composition $(\text{Mg}_{0.49}\text{Ti}_{0.19}\text{Fe}_{0.01}\text{□}_{0.31})(\text{Al}_{0.71}\text{Mg}_{0.25}\text{□}_{0.04})_2$

$(\text{Al}_{0.95}\text{□}_{0.05})_4(\text{Si}_{0.94}\text{P}_{0.01}\text{□}_{0.05})_2\text{O}_{15.04}(\text{OH})_{2.96}$ B in agreement with electron- and ion-microprobe analyses. Only one hydrogen atom has been found in the difference Fourier. The further two hydrogens required by the chemical formula are disordered over more than two oxygens; their presence is confirmed by calculations of the charge distribution.

Smaller Al-free tetrahedra and lower contents of high-charge cations in the face-sharing octahedra under compression, are proposed to be the crystallochemical basis for the formation of magnesiodumortierite under the Dora-Maira metamorphic conditions.

The following general formula for the minerals of the dumortierite group is proposed



where: M' = Al, Mg, Ti, Fe, RE(?) [M(1) site]; M'' = Al, Mg [M(4) site]; M''' = Al [M(2) and M(3) sites]; T' = Si, Al, P [T(1) and T(2) sites]; T'' = Sb occurs in holtite (Hoskins, Mumme and Pryce, 1989, Min. Mag., 53, 457-463) and forms a pyramidal group with three oxygen atoms [T(1) and T(2) sites]. In all sites, particularly in M(1), vacancies can occur.

PS-08.01.31 STRUCTURAL MODEL AND POLYTYPISM IN TUNGUSITE.

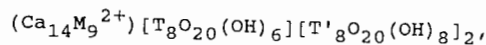
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Tungusite is a light green hydrous silicate of Ca and Fe reported from different localities of the Siberian Platform and described the first time by V.I. Kudriashova (1966, Dokl. Akad. Nauk SSSR, 171, 1167-1170).

On the basis of X-ray (powder patterns) and electron diffraction studies (selected area and oblique texture patterns) and of comparison with the crystal structures of reyerite (Merlino, 1989, Min. Mag., 52, 247-256) and gyrolite (Merlino, 1989, Min. Mag., 52, 377-387) new data on tungusite have been obtained.

No single crystals suitable for X-ray structural studies have been found and the electron diffraction shows a widespread stacking disorder along the c^* axis. The most ordered sample shows a metrically monoclinic C-centred cell, with $a = 9.66$, $b = a\sqrt{3}$, $c = 21.86$ Å, $\alpha \approx 100$, $\beta = 90$, $\gamma = 90^\circ$. By analogy with gyrolite, the structural model is based on a triclinic ($\overline{P}1$) cell with $a \approx b = 9.66$, $c = 21.86$ Å, $\alpha \approx 98.6$, $\beta = 90$, $\gamma = 120^\circ$. The proposed model maintains the $\text{S}_1\text{OS}_2\text{XS}_2\overline{\text{OS}}_1$ sequence of tetrahedral (S), octahedral (O) and complex (X) sheets reported in gyrolite by Merlino; it differs from this structure practically only for the contents of the

complex sheet X. While in gyrolite the X sheet contains only one Na and two Ca octahedra plus water molecules, in tungusite this sheet is completely filled by nine octahedra. The following ideal crystallochemical formula is derived for tungusite:



where M is mainly a bivalent with minor monovalent and trivalent cation ($\text{Fe}^{2+} \approx 6$, $\text{Na}^+ \approx 2$, $\text{Fe}^{3+} \approx 1$, in our samples); T and T' are mainly Si with, in our samples, a maximum of 2Al which should stay in T' (S_2 sheet). This type of substitutions in M requires that some OH are replaced by H_2O . Some of our samples ("white tungusite") show clearly a composition which is intermediate between tungusite and gyrolite.

With reference to the C-centred cell, possible polytypes can be derived by shifts only along the b axis ($\pm 1/9$, $\pm 2/9$, $\pm 4/9$; monoclinic cells) and along a axis as well ($\pm 1/3$, $\pm 1/2$, $\pm 1/6$; triclinic cells). The shifts are referred to the O sheets with respect to the S_1 and S_2 sheets.

PS-08.01.32

CRYSTAL STRUCTURE OF $\text{Sr}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$

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The existence of strontium perrhenate monohydrate was mentioned for the first time by Smith & Maxwell (J. Am. Chem. Soc., 1951, 73, 658-660) and proven by means of X-ray powder and TGA analysis by Wassilopoulos (Über Polinare Oxide des 4 and 7 wertigen Technetium mit Erdkalialien. Karlsruhe. Kernf. Inst. Radiochem., 1965, S. 67)

Our STA analysis of fresh $\text{Sr}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$ prepared according to Smith & Maxwell (1951) supported the existence of the monohydrate in the temperature range of 66 - 155°C. Complete powder data were evaluated (PDF 42-682; Macicek). We managed to grow single crystals of $\text{Sr}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$ from absolute CH_3OH . Crystal data: $M_r = 606.03$, orthorhombic, Pbcn (61), $a = 11.594(2)$, $b = 12.304(1)$, $c = 23.885(4)$ Å, $V = 3407$ Å³, $Z = 16$, $D_x = 4.73$ g.cm⁻³, $R = 0.042$ for 2151 reflections with $I > 2\sigma(I)$.

Coordination polyhedron of Sr(1) consists of nine oxygen atoms from eight ReO_4 tetrahedra and one water molecule at 2.548(16) - 2.686(15) Å. Sr(2) is coordinated to eight oxygen atoms from seven ReO_4 groups and the second H_2O molecule (2.507(15) - 2.814(20) Å). Sr(1) atom participates in seven double [Sr...Sr 6.175(3) - 6.530(3) Å] and one single Sr-T-Sr [Sr...Sr 6.818(3) Å] bridges, while Sr(2) forms six double [Sr...Sr 6.325(3) - 6.558(3) Å] and three single [Sr...Sr 6.632(3) - 6.818(3) Å] bridges. The ReO_4 tetrahedra have irregular geometry with Re-O distances and [O-Re-O] angles within 1.702(15) - 1.742(15) Å and [106.7(8) - 111.8(7)°]. Three of the ReO_4 groups are linked to four Sr ions, and the fourth one only to three. The non-coordinated oxygen from $\text{Re}(4)\text{O}_4$ has three closest neighbours: O(22) at 3.233(22) Å, O(23) at 3.282(23) Å and O(13) at 3.368(22) Å.

PS-08.01.33

STRUCTURES OF CALCIUM AND LEAD PERRHENATE UREA

HYDRATES. By J. Macicek*, R. Petrova, O. Angelova, Bulgarian Academy of Science, Rakovski str. 92, 1000, Sofia, (Bulgaria)

Preliminary investigation of the system $\text{M}(\text{ReO}_4)_2 \cdot \text{Urea} \cdot \text{H}_2\text{O}$, M = large divalent cations, indicate formation of 1:1:1 addition compounds. Single crystals of lead and calcium species have been studied on an Enraf-Nonius CAD4/SDP44 diffractometric system.

Ca(ReO₄)₂.Urea.H₂O: triclinic, P 1, a = 7.322(3), b = 9.088(5), c = 9.175(3)Å, α = 111.67(2), β = 91.26(2), γ = 104.89(3)°, Z = 2, D_x = 3.67 g.cm⁻³, R = 0.030 for 2104 3σ-reflections.

Pb(ReO₄)₂.Urea.H₂O: monoclinic, P 2₁/c, a = 10.283(2), b = 7.389(6), c = 14.402(8)Å, β = 99.72(1)°, Z = 4, D_x = 4.727 g.cm⁻³, R = 0.042 for 1951 3σ-reflections.

The CaO₈ environment consists of five apices of the ReO₄ tetrahedra [2.43(1)-2.52(2)Å], O atoms of two urea and one water molecules at distances 2 x 2.41(1) and 2.39(1)Å. Ca atoms are chained by alternating double Ca-O-Ca bridges of urea [Ca...Ca 3.92(1)Å] and fourfold Ca-(OReO)-Ca bridges [Ca...Ca 5.49(3)Å]. Adjacent chains are linked by pairs of Re(1)O₄ tetrahedra [Ca...Ca 6.85(2)Å] and arranged in layers parallel to the *ab*-plane. The layers are packed by H-bonds only.

The Pb atom has a nine-fold coordination of six ReO₄ apices (Pb...O 2.55(2)- 2.76(1)Å), two urea molecules [2.61(1), 2.86(1)Å], and a water molecule at 2.47(1)Å. The structure consists of layers parallel to the *bc*-plane in which the Re(1)O₄ tetrahedra form double bridges between Pb atoms (Pb...Pb 4.12(2), 6.64(2), 2 x 6.85(2)Å). The shortening of the first Pb...Pb distance is due to the complementary Pb-O-Pb urea double bridge. The layers are held together by double bridges of Re(2)O₄ tetrahedra [Pb...Pb 7.45(4)Å] and a system of H-bonds.

PS-08.01.34 NEW MEMBERS OF TRIPLE MOLYBDATE FAMILY: COMPOSITIONS, CRYSTAL STRUCTURES, THERMAL STABILITY. By R.F.Klevtsova*, L.A.Glinskaya, N.M.Kozhevnikova, Zh.G.Bazarova, P.V.Klevtsov. Institute of Inorganic Chemistry, Russian Academy of Sciences, Siberian Branch, Russia.

Triple molybdates were synthesized by solid state reactions and the complicated character of chemical interactions in the systems was established. Products of the synthesis were investigated by X-ray and DTA methods. Single crystals were obtained by spontaneous flux crystallization. The compositions are: I-Li₃Ba₂Im₃(MoO₄)₈, Im=Gd,Tm; II-NaMg₃In(MoO₄)₅, III-K₁₀MgZr₃(MoO₄)₁₂. Their crystallographic characteristics are given in the Table.

	Sp.gr.	a, Å	b, Å	c, Å	Z	N	R
I-Gd	C2/c	5.2380	12.758	19.151	2	2453	0.042
		-	91.126	-			
II	P1	7.0476	17.935	6.9849	2	4503	0.047
		87.650	100.96	92.510			
III	R3c	10.576	-	37.511	3	1166	0.026

The crystal structures were solved using single crystal data (KUMA and CAD-4, Mo K_α radiation). The characteristic features of the structures are statistically distributed atoms of bi- and trivalent metals. Structural peculiarities (size, shape, site occupancy and stacking of the coordination polyhedra) are used for interpretation of physical properties. The comparative crystal chemistry analysis of known triple molybdates has been carried out. The compounds studied melt incongruently, polymorphism was not found.

PS-08.01.35 STRUCTURAL CHEMISTRY OF BaAl₄/ThCr₂Si₂ TYPE COMPOUNDS. By G.Just and P.Paufler, Institute of Crystallography and Solid State Physics, University of Technology, Dresden, Federal Republic of Germany.

Lattice ratios *c/a* and structural parameters *x*₃ of about 180 representatives of the BaAl₄ type of structure (space group I 4/mmm) have been critically reviewed taking binary and multicomponent phases into account. Leaving out data of minor reliability a considerable scatter of experimental values in a *x*₃-*c/a* plane remains, which is classified according to the concepts of equal interatomic spacing and coordination polyhedra. Lines of equal spacings *d* were calculated for all atom positions in the unit cell up to *d* = 1.9 Å. Moreover, the coordination of all atom positions is given. Several points in the *x*₃-*c/a* plane were found to represent special structural features like coordination polyhedra with coordination numbers of 16, 18 or 20 for the barium position with characteristic packing of distorted tetrahedra. Individual space requirements of atoms are met with different spacing conditions between Al(1) and Al(2) positions. Subdivision of representatives into families behaving similarly from a point of view of crystal chemistry is discussed.

PS-08.01.36 NON-STOICHIOMETRIC V-Mo OXIDE COMPOUNDS WITH V₂O₅ STRUCTURE TYPE. By L. M. Plyasova, L. P. Solovyeva*, G. N. Kryukova, S. V. Tsybulya and T. V. Andrushkevich.

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The V-Mo oxide system was studied by X-ray analysis because such oxides serve as catalysts for oxidation of acrolein to acrylic acid. Thermal treatment of products from reaction between para-molybdate and meta-vanadate resulted in the formation of V-Mo compounds of varying composition (V₆Mo₄O₂₅, (V⁵⁺, V⁴⁺)MoO₅, VMo₃O₁₁, etc.). The structures of these compounds appear to depend on the degree of vanadium reduction and on V/Mo ratio. V_{0.85}Mo_{0.97}O₅ (V⁴⁺/V = 0.6) was selected for structural investigations. Crystal structure analysis and refinement using Rietveld method (R₁ = 0.072, R_p = 0.11) were carried out using X-ray powder diffraction data. Layers of edge-sharing octahedra of two types (Mo+V⁴⁺) and (Mo+V⁵⁺) are connected by corners. Structurally the compound is similar to the V₂O₅ type. Our results indicate that for compounds of V₂O₅ structure