**08.2—61   THE CRYSTAL STRUCTURES OF K AND Sb(III) SILICATES, $K_2Sb(OH)(Si_4O_{10})$, AND $K_2Sb_2O(Si_6O_{15})$.** By <u>V.V.Bakakin</u>, V.P.Balko, Institute of Inorganic Chemistry, Sib.Dept. of the Acad.of Sci. of the USSR, Novosibirsk, U.S.S.R.

The crystal structures of dipotassiumantimony(III)hydrotetrasilicate, $K_2Sb(OH)(Si_4O_{10})$ (I), and dipotassiumantimony(III)oxohexasilicate, $K_2Sb_2O(Si_6O_{15})$ (II), have been determined. I is monoclinic, a = 6.362, b = 10.954, c = 15.248 Å, ß = 100.63°, space group $P2_1/n$, Z = 4. II is monoclinic, a = 24.540, b = 7.760, c = 9.082 Å, ß = 102.4°, space group C2, Z = 4. Both structures were solved by the direct and Fourier methods using the diffractometer Syntex-$P2_1$ data and refined to the R-values of 0.068 and 0.078, respectively. The structures contain two-dimensional silica-oxygen motifs of topologically new type :

$(Si_4O_{10}) \rightarrow (Si_8O_{20})^{2\infty}$ and $(Si_6O_{15}) \rightarrow (Si_{12}O_{30})^{2\infty}$.
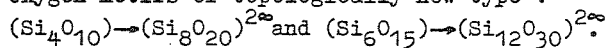
In the structure I the "vlasovite"-like chains, Si_4O_{11}, join forming a stepped corrugated net, parallel to (001). The Sb^{3+} atoms have tetragonal-pyramidal environments (Sb-OH is 1.98 and Sb-O are 2.16-2.25 Å), a lone pair E(Sb) playing a role of a sixth ligand in the trans-configuration with the OH. Both K atoms are seven-coordinated (K-O are 2.63-3.19 Å). In general features this structure is compared with that of vlasovite, $Na_2ZrSi_4O_{11}$.

The net of the structure II (with a pseudo-symmetry C2/m) can be represented as a linkage of two four-membered haradaite-like chains stretched along the b axis and one four-membered ring: $Si_{2+2}O_{12}$(the chain) + $Si_{2+2}O_{12}$ (the chain) + $Si_{2+2}O_{12}$(the ring) - O_6 = $Si_{12}O_{30}$(the net). These greatly corrugated nets, parallel to (001), are linked along the c axis by two SbO_{3+2} half-octahedra sharing the face. The Sb-O distances range from 1.97 to 2.40 Å. The channel cavities of three types contain one lone pair E(Sb), two lone pairs E(Sb) and four K atoms, respectively, with the K-K distances of 3.25-3.35 Å. The crystals were synthesized and kindly provided by M.N.Tseytlin and Kh.M.Kurbanov (Phys.-Techn.Inst., Acad. of Sci. of Tadzh. SSR, Dushanbe) along with preliminary crystallographic characteristics and an approximate chemical formula. The initial observed data have been obtained with the assistance of Yu.V.Gatilov(Inst. of Org.Chem., Sib. Dept., Acad. of Sci. of the USSR, Novosibirsk).

08.2—62   CRYSTAL STRUCTURAL STUDIES OF NEW MIXED P(Si)-Mo-V HETEROPOLYCOMPOUNDS OF THE TWELFTH ROW. R.F.Klevtsova,<u>L.P.Solovjeva</u>,L.A.Glinskaja,E.N.Yurchenko.Institute of Inorganic Chemistry,Institute of Catalysis,Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk, U.S.S.R.

The crystal structures of three heteropolycompounds with the different Mo/V ratios have been determined. The crystal data are:

(I)-tetragonal $H_5[SiMo_{11}V_1O_{40}]\cdot(30-36)H_2O$; a=12.791, c=18.131 Å, z=2, P4/m,

(II)-monoclinic $Na_3H_6[PMo_6V_6O_{40}]\cdot16H_2O$; a=13.667, b=15.260, c=11.529 Å,ß=106.98°, z=2, $P2_1/m$,

(III)-monoclinic $Na_4H_4(VO)[PMo_4V_8O_{40}]\cdot20H_2O$; a=10.870,b=21.312,c=11.654Å,ß=106.73°,z=2,$P2_1/m$.

The metal atoms (Mo and V) in the Heteropolyanions are statistically distributed according to the law of pseudo-Keggin(I) and Keggin(II and III)structures. In all these structures the anions are connected through water molecules by weak hydrogen bonds and in the structures II and III, in addition, by the Na^+cations. A characteristic feature of the structure III is the presence of the VO^{3+} group linked to four O cis-atoms of the anion. The way of the anion bonding to the outersphere cations compensating its charge is considered.

08.2—63   NEW HEXAGONAL FLUOROPEROVSKITES WITH CATION DEFICIENCY.

By E.Herdtweck, SFB 127F, Hans-Meerweinstrasse D-3500 Marburg/Lahn

Numerous hexagonal polytypes of perovskites have been found. Their structural features have been connected with the stacking periodicity of the anionic layers, leading to the 2H, 3C, 6H, 9R and 12R types.

Investigation of ternary systems $BaF_2-AF-MF_2$ (A = K,Rb,Cs; M = Ni,Fe) and $RbF-MF_2-MF_3$ ($M^{II}=M^{III}=$ Fe) reveals the existence of two new types of quaternary fluorides : $Ba_2AM_2F_9$ and $Rb_4M^{II}M^{III}_2F_{12}$.

Crystals are grown under hydrothermal high-pressure condition (3GPa, 573K, 1/2h, HF.aq, $RbF/MF_2/MF_3$) for the latter system and from molten salts. Table 1 summarizes the crystal data received from single crystal structure determinations. The crystal structures of this compounds are closly related to the $9R-CsCoF_3$-type and to the $12R-Cs_2NaCrF_6$- type respectively. All X-ray diffraction experiments performed on this phases have shown the presenceof

an ordered cation vacancy in 3b sites of the structures. Nevertheless, a remaining electron-density of about $3e^-/A^3$ and diffuse strikes observed on precession films indicate, that the assumed rhomboedric space group $R\overline{3}m$ failed.

Table 1   Hexagonal cell parameters

$Ba_2K\ Ni_2F_9$	a=b= 577.5(2)	c= 2075.6(13)pm
$Ba_2RbNi_2F_9$	a=b= 580.1(1)	c= 2099.4(2)pm
$Ba_2RbFe_2F_9$	a=b= 594.9(1)	c= 2083.7(1)pm
$Ba_2CsNi_2F_9$	a=b= 585.5(1)	c= 2120.9(9)pm
$Rb_4FeFe_2F_{12}$	a=b= 589.1(1)	c= 2903.6(2)pm

08.2—64   INVESTIGATION OF A STOICHIOMETRY OF A METASTABLE CRYSTAL PHASE OF BISMUTH CADMIUM OXIDE WITH SYLLEN'S STRUCTURE BY REITWELD'S METHOD. By S.D.Kyrik, V.A.Kutvitsky, S.V.Misjul, T.I.Karyagina; L.V.Kirensky Institute of Physics, USSR Academy of Sciences, Siberian Branch, 660036 Krasnoyarsk, USSR

The refinement of structure for bismuth cadmium oxide with composition of $5Bi_2O_3 \cdot CdO$ has been carried out by Reitweld's method. Lattice constants are a=10,220 Å, SG – I23, R_{prof}=

$$\sum |y(obs)-y(calc)| / \sum |y(obs)| = 0,082; \quad R_i =$$

$\sum |I(obs)-I(calc)| / \sum I(obs)$ (I(obs), I(calc) are the observed and calculated integral intensities of each reflection; y(obs), y(calc) are the observed and calculated profile point data). The density of charge for tetrahedral sites (2a) of 74e was obtained, that agrees with scheme of Craig and Stephenson (D.C.Craig, N.C.Stephenson, J.Solid State Chem,(1975), 15, 1). For 24f site the density of charge is 10% less than it is for Bi atom. It is explained by the substitution for the Bi part in 24f by Cd. The stoichiometry of compound corresponding by the obtained population coefficient is Bi:Cd = 19:7. Ions Cd (0,67 in the unit cell) located in (2a) lead to the shift of 2,68(0,67·4) oxide atoms being the top of octahedra. The filling of decreased octahedra is realized by Bi ions (Cd ones are too large for this purpose). The charge compensation is provided by the arrangement of 5,36 Cd ions in structure. Finally, cell contains 6Cd and 20Bi. This corresponds to the chemical analysis and to refinement of the structure.

08.3—1 $Y_{13}Pd_{40}Sn_{31}$, A NEW STRUCTURE TYPE INTERPRETED AS AN INTERGROWTH OF SIMPLE STRUCTURE BLOCKS. By K. Cenzual and E. Parthé. Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland.

$Y_{13}Pd_{40}Sn_{31}$, hexagonal, a = 19.891(7), c = 9.246(6)Å, P6/mmm, crystallizes with a new structure type containing 168 atoms in the unit cell. In a recent crystal-chemical study of the structures of rare-earth-transition metal-borides, silicides and their homologues (Parthé & Chabot (1984) in "Handbook on Physics and Chemistry of Rare Earths" Vol. 6, ch. 48) it was shown that a successful approach to the understanding and memorizing of complicated ternary alloy crystal structures is their interpretation as an intergrowth of segments of different simple, binary or ternary structures. The $Y_{13}Pd_{40}Sn_{31}$ structure can be described as an intergrowth of three kinds of segments : one is a ternary ordering variant of the $CaCu_5$-type, the second has an atom arrangement similar to that found in the neighbouring phase YPd_2Sn with $MnCu_2Al$-(Heusler) type structure (Ishikawa et al. (1982) in "Superconductivity in d- and f-Band Metals", Proc. IVth Conf., Kernforschungszentrum Karlsruhe), a derivative of the BCC W-type, and the third one consists of a column of trigonal prisms where Pd centred Sn prisms alternate with Sn centred Pd prisms.

It will further be shown that in another ternary stannide structure type, $CeNi_5Sn$ (Skolozdra et al. (1981) Sov. Phys. Crystallogr. 26, 272) binary $CaCu_5$-type slabs are intergrown with ternary Heusler type slabs.

A detailed account of the present work will be published in Acta Crystallogr. C.

08.3—2   AN ENERGETICAL INTERPRETATION OF THE αMn STRUCTURE. By K.Schubert, Max Planck Institut für Metallforschung, Inst. f. Werkstoffwiss., Stuttgart, F.R.Germany

The structure of αMn has been found for instance in the alloy system Mo-Re which may be interpreted by the two-electron-correlations model (Chem.Script.(1982)19,224). The interpretation becomes possible by the electron count Mo1,5,8-Re0,0,7 yielding for Mo3Re(Cr3Si type) cells b'b, c of the spatial correlations which obey the equations a =b'F(1)=bF(2)=cB(4) where a=crystal cell matrix, b'F=5s-electron correlation cell of the cubic face centered type, bF=4d-electron correlation cell, cB =peripheral core electron correlation cell of the cubic body centered type, (1)=unity commensurability matrix, (2)=2(1). The assumption of several spatial correlations corresponds to the existence of several energy bands in Mo-Re. At higher Re content the phase Mo2Re3(βU type) is stable. It is a contractive homotype of Mo3Re as the so called secondary layers (Frank, Kasper, Acta Cryst.(1958)11,184,12,483) go over from the Schläfli type 4↑4 to 4343↑2. The contraction is in agreement with the rule that a decrease of the b-concentration causes closer packed structures. The electron correlations satisfy a=(9.5;4.9)Å=bHT(5;3/2)=cU(√50;4.5) where HT=hexagonal isometric Bravais lattice cell in pseudo tetragonal aspect, U=tetragonal body centered isometric lattice cell. The cell bF in Mo3Re has changed to bHT in Mo2Re3 and cB to cU; for the brief notation of the commensurabilities see (Chem.Scripta (1982)19,224).The phase MoRe3(αMn type) is a stacking homeotype of βU and allows the correlations a=bC(5)=cU(√50;9) where C=cubic primitive lattice; the cell bHT in Mo2Re3 has changed to bC in MoRe3 and cU has been conserved. The correlations explain the stacking homeotypism of MoRe3 by the rule for stacking in Cu(3-N)AuZnN (Schubert,Kristallstrukturen zweikomponentiger Phasen, Berlin 1964 p.99) The electron concentration N_b^A=2.16 is compatible with the valence of Mn found by Hume-Rothery (Phil.Mag.(1948)39,89)in the mixtures Cu-Zn and Cu-Al.