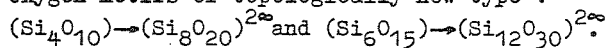


08.2-61 THE CRYSTAL STRUCTURES OF K AND Sb(III) SILICATES,  $K_2Sb(OH)(Si_4O_{10})$ , AND  $K_2Sb_2O(Si_6O_{15})$ . By V.V.Bakakin, V.P.Balko, Institute of Inorganic Chemistry, Sib.Dept. of the Acad.of Sci. of the USSR, Novosibirsk, U.S.S.R.

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,  $\beta = 100.63^\circ$ , space group  $P2_1/n$ ,  $Z = 4$ . II is monoclinic,  $a = 24.540$ ,  $b = 7.760$ ,  $c = 9.082$  Å,  $\beta = 102.4^\circ$ , 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 silic-oxygen motifs of topologically new type:



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, L.P.Solovjeva, 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  $Na_3H_6[PMo_6V_6O_{40}] \cdot 16H_2O$ ;  $a=13.667$ ,  
 $b=15.260$ ,  $c=11.529$  Å,  $\beta=106.98^\circ$ ,  $z=2$ ,  $P2_1/m$ ,

(III)-monoclinic  $Na_4H_4(VO)[PMo_4V_8O_{40}] \cdot 20H_2O$ ;  $a=$   
 $10.870$ ,  $b=21.312$ ,  $c=11.654$  Å,  $\beta=106.73^\circ$ ,  $z=2$ ,  $P2_1/m$ .

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.Herdtwack, 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<sub>2</sub> (A = K, Rb, Cs; M = Ni, Fe) and  $RbF$ -MF<sub>2</sub>-MF<sub>3</sub> ( $M^{II}=M^{III}=Fe$ ) 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 closely related to the 9R-CsCoF<sub>3</sub>-type and to the 12R-Cs<sub>2</sub>NaCrF<sub>6</sub>-type respectively. All X-ray diffraction experiments performed on this phases have shown the presence of