

$\text{Ga}_2\text{O}_6[\text{PO}_4]_3$. The dimers stringed on an two-hold axes form continuous chains along the Z axis in which the filled octahedra and the empty trigonal prisms are situated alternately. All the structure consists of a totality of indicated chains connected with each other by octahedra forming unique framework of the composition $\text{Ga}(\text{PO}_4)_2$ with large-scale spaces.

It is not difficult to notice that the obtained motive as composed from Ga-octahedra and PO_4 -tetrahedra carries a negative

charge equal to -3 for compensation of which positive cations are required. The crystal chemistry analysis of interatomic distances indicates that such positive cations can be only protons transforming free terminal oxygen atoms of phosphate groups into hydroxylic ions. Thus, by taking into account the hydrogen atoms and the water molecules the presence of which in the structure is also confirmed by DT analysis and which are statistically arranged in the above indicated vacancies, the structural formula can be expressed as $\text{GaH}_3(\text{PO}_4)_2 \cdot 2,5 \text{H}_2\text{O}$.

and Ho form zigzag chains along the axis b being connected through the general rib with the nearest symmetrically equivalent polyhedra. Such chains of Ho-polyhedra form step (zigzag) layers, parallel to planes (001), being connected by general oxygen summits between them. The layers of Ho-polyhedra being associated by general summits and ribs of Na-polyhedra, B-tetrahedra and hydrogen bonds between them, form the framework structure of sodium and holmium borates.

08.2-59 THE CRYSTAL STRUCTURE OF SODIUM AND HOLMIUM BORATE. By G.G. Jafarov, G.K. Abdullayev. The Institute of Inorganic and Physical Chemistry of the Academy of Sciences, Azerbaijan SSR, Baku, USSR.

Sodium and holmium borate $\text{NaHo}[\text{BO}_2(\text{OH})_2]\text{OH}$ was obtained under hydrothermal conditions in the system $\text{HO}_2\text{O}_3\text{-Na}_2\text{O-H}_2\text{O}$ at 400 C. The crystals are

transparent and are of lemon-yellow colour. The habitus of the crystals changes from shortly prismatic to isometric. The crystal structure was determined by single-crystal X-ray analysis (diffractometer, Mo radiation, 890 reflections, least squares refinement with anisotropic approximation, $R=0,083$). The cell dimensions are: $a=5,142(2)$, $b=6,434(4)$, $c=6,155(3)$ Å, $\beta=114,7(2)$, $Z=2$, $d_x=5,07$ g/cm³, space group $P2_1/m$. The structure has been

solved by the heavy atom method. The coordinations of Ho atoms have been determined from Patterson map. The localization of the remaining atoms (Na, O and B) was carried out from Fourier and difference electron density synthesis. The crystal structure of sodium and holmium borate consists of isolated $[\text{BO}_2(\text{OH})_2]^{3-}$

tetrahedra ($\text{B-O}, 1,480-1,524$ Å) and coordination polyhedra of metallic cations. The sodium cations are inside the distorted bicapped trigonal prisms formed by two O atoms and six OH groups ($\text{Na-O } 2,204-2,613$ Å). The holmium cations are also inside the distorted eight coordinated polyhedra formed by four oxygen atoms and four OH groups. ($\text{Ho-O } 2,322-2,686$ Å) Na

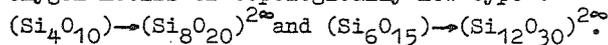
08.2-60 STRUCTURAL ANALYSIS OF SUBSTITUTED BARIUM HOLLANDITES. By R.W. Cheary, J. Kwiatkowska and J. Hodge. School of Physics & Materials, New South Wales Institute of Technology, Sydney, N.S.W. 2007, Australia.

The structures of a number of polycrystalline barium hollandites have been determined by x-ray and neutron diffraction using the Rietveld method. The purpose of this work is to establish the structural conditions required for the successful immobilisation of radioactive waste within this group of compounds. In cesium substituted hollandites

(viz $[\text{Ba}_x\text{Cs}_y][\text{Al}_{2x+y}\text{Ti}_{8-2x-y}]\text{O}_{16}$) the structural parameters for titanium, aluminium and oxygen do not change significantly with the level of cesium substitution. The only significant change occurs in the z parameter which defines the average Cs/Ba position. This increases with the level of Cs substitution indicating that these ions tend to occupy a more central location with respect to their coordinating oxygen ions. An analysis of the (Cs/Ba)-O bond length suggests a possible limit of structural stability corresponding to 0.25 cesium ions per unit cell. Electron microprobe results indicate that the level of cesium substitution is constrained by the condition that the total volume occupied per unit cell the cesium and barium remains substantially constant. Barium hollandites containing varying proportions and types of 3^+ ions on the octahedral sites have also been examined (viz $\text{Ba}_x[\text{M}_{2x}\text{Ti}_{8-2x}]\text{O}_{16}$, $\text{M} = \text{Al, Ga, Fe and Ti}$ to determine how these affect the size of the barium site.

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 silico-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.

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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-MF₂ (A = K, Rb, Cs; M = Ni, Fe) and RbF -MF₂-MF₃ ($M^{II}=M^{III}=Fe$) 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-CsCoF₃-type and to the 12R-Cs₂NaCrF₆-type respectively. All X-ray diffraction experiments performed on this phases have shown the presence of