

Oral Contributions

[MS18-04] A Polysomatic Series of Two-Dimensional Vanadates, Arsenates and Phosphates.

Olga V. Yakubovich, Ekaterina V. Yakovleva, Galina V. Kirjukhina

Department of Geology, Moscow State Lomonosov University, Russia.

E-mail: yakubol@geol.msu.ru

A family of layered vanadates, arsenates and phosphates is discussed along in terms of the modular concept. The structural characterization of two novel phases $K_2Mn_3(CO_3)[VO_4]_2$ [1] and $Na_2Ni_3(OH)_2[PO_4]_2$ allowed us concluding that these compounds can be considered as parts of one quasipolysomatic series. The $K_2Mn_3[VO_4]_2(CO_3)$ presents the first vanadate-carbonate published so far at least is as a novel crystal structure ($R = 0.022$). It is formed by two types of layers alternating along the c axis of the hexagonal unit cell. The first type parallel to the ab plane presents gibbsite-like layers of Mn octahedra sharing edges. The second type consists of Mn trigonal bipyramids linked by $[CO_3]$ triangles to form cellular layers, which are topologically identical in the ab plane to the kalsilite layers of alternating Si- and Al-tetrahedra. The $[VO_4]$ tetrahedra link the layers along the c axis by sharing all oxygen vertices with Mn polyhedra. Intercrossing channels intersect the structure in $[100]$, $[010]$, and $[110]$ directions; the K atoms are located in these channels. The monoclinic crystal structure of $Na_2Ni_3(OH)_2(PO_4)_2$ ($R = 0.026$) – the unique phosphate in this family, is formed by layers of $[NiO_4(OH)_2]$ octahedra, each sharing four edges with neighboring four Ni polyhedra. These layers are based on the hexagonal close-packing of oxygen atoms, where Ni^{2+} cations occupy 3/4 of the octahedral voids. The $[PO_4]$ tetrahedra share three oxygen vertices with Ni octahedra of one layer, while the fourth O vertex remains unshared with $[NiO_4(OH)_2]$ polyhedra. This oxygen atom plays the role of hydrogen bond acceptor, thus providing hydrogen bond linkage between

phosphate oxocomplexes and a neighboring along the c axis layer of Ni octahedra through O-H...O bonding. The $[NaO_7]$ polyhedra sharing edges also form layers parallel to the (100) plane; they alternate along the $[100]$ direction with the layers of $[NiO_4(OH)_2]$ octahedra. The group involves among two mentioned phases the minerals vésignéite, bayldonite, reppiaite, cornubite, and a series of synthetic compounds $K_2Mn_3(OH)_2[VO_4]_2$, $BaNi_2[VO_4]_2$, $BaNi_3(OH)_2[VO_4]_2$, and $Ni_5(OH)_4[AsO_4]_2$. Their crystal structures are not isotypic, but they are built of similar blocks (modules) made by a central octahedral layer filled by the atoms of d elements (e.g. Mn, Ni, or Cu) and adjacent $[VO_4]$, $[AsO_4]$, or $[PO_4]$ tetrahedra. The octahedral layers in all compounds are based on the hexagonal close-packing of oxygen atoms. They have different amount and distribution of octahedral voids within these layers of the same anionic sublattice. This kind of blocks having close dimensions are repeated in one direction in the structures of mineral reppiaite, $Mn_5[VO_4]_2(OH)_4$, isotypic synthetic arsenate, $Ni_5[AsO_4]_2(OH)_4$ and mineral cornubite $Cu_5[AsO_4]_2(OH)_4$. In the structures of $K_2Mn_3[VO_4]_2(CO_3)$, $BaNi_2[VO_4]_2$, $K_2Mn_3(OH)_2[VO_4]_2$, $BaNi_3(OH)_2[VO_4]_2$ and minerals bayldonite, $Pb(Cu, Zn)_3[AsO_4]_2(OH)_2$ and vésignéite, $BaCu_3(OH)_2[VO_4]_2$ these blocks alternate with different other structural fragments.

[1] Yakubovich O.V., Yakovleva E.V., Golovanov A.N. et al. (2013). *Inorg. Chem.* **52**. 1538-1543.

Keywords: layered crystal structure, polysomatic series, vanadate, arsenate, phosphate