MS14-O2 Synthetic phases with mineral topology: crystal chemistry and physical properties

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Novel phases prepared by hydrothermal synthesis are discussed in correlation with archetypes and derivative compounds. The $K_{2.5}Cu_5Cl(PO_4)_4(OH)_{0.5}(VO_2) \cdot H_2O$ microporous crystal structure determined at 100 K using synchrotron diffraction data, is based on a 3D anionic framework built from Cu- and V-centered five-vertex polyhedra and PO_4 tetrahedra, and includes channels with K atoms and H_2O molecules. It is a new structural representative of the topology shown by the lavendulan mineral group with structures formed by two types of alternating 2D slabs: one slab $[Cu_4X(TO_4)_4]_\infty$ (X=Cl, O; T=As, P) is common to all phases, whereas the slab content of the other set differs among the group members. This family of compounds is interpreted in terms of the modular concept as one polysomatic series.

The $Na_{2-x}Co_6(OH)_3[HPO_4][H_{x/3}PO_4]_3$ presents the first example of the ellenbergerite topology based on a 3D framework of octahedra and tetrahedra, with alkaline cations in the channels, usually occupied by transition metals. The reason for close unit-cell parameters of rather dense ellenbergerite-like and the microporous cancrinite-like Co phosphates is the nearly identical topology of their cation sublattices, where the same cations are set into diverse positions, thus providing a different distribution of the coordinating O atoms. It results in a formation of the cationic framework of Co octahedra in our case, while in the cancrinite-like phosphate Co forms a mixed anionic tetrahedral framework together with PO_4 groups. Magnetic susceptibility measurements revealed a strong antiferromagnetic interaction and magnetic transition to low temperature spin-canted phase at TN = 44 K.

The $Rb_4[Na(H_2O)_6](H_2O)_4(HV_{10}O_{28})$ crystal structure established at 100 K is formed from monoprotonated decavanadate cages of ten sharing edges V-centered octahedra, which are joint together via hydrogen bonds in one-dimensional chains. Within these chains, protons are sandwiched between neighboring polyanions. Na and Rb atoms and H_2O molecules occupy interstices flanked by the anionic chains providing additional cross-linking in the structure. Two types of interactions ensure stability of the crystal structure, which may be treated as a combination of 3D cationic framework built by Rb and Na atoms, and 1D anionic chains of decavanadate units. Structural and genetic relations among protonated and deprotonated decavanadates with inorganic cations, including minerals of the pascoite group, are discussed.

MS14-O3 Titanium and zirconium silicate ion-exchange materials for the treatment of nuclear waste

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Zeolites are commonly used as ion-exchange materials for the remediation of nuclear waste, however, they have certain drawbacks. Unlike zeolites which contain SiO_4 and AlO_4 tetrahedra, microporous titanium silicates can contain SiO_4 tetrahedra and TiO_6 octahedra and therefore structures are possible which have no traditional aluminosilicate analogues [1]. Microporous titanium silicates such as sitinakite $KNa_2Ti_4Si_2O_{13}(OH) \cdot 4H_2O$ and the synthetic niobium doped analogue are used as ion-exchange materials for the removal of Cs^+ and Sr^{2+} from nuclear waste [2,3]. To date little work in this area has been carried out using microporous zirconium silicates. The work presented here will focus on the ion-exchange properties of umbite. Umbite is a naturally occurring small pore microporous zirconium titanium silicate. The mineral is found in northern Russia and synthetic analogues, $K_2ZrSi_3O_9 \cdot H_2O$, can be prepared in the laboratory [4]. It has an orthorhombic cell with $a = 10.2977(2)$Å, $b = 13.3207(3)$Å and $c = 7.1956(1)$Å. Ion-exchange studies have been carried out and have shown that umbite has a preference for common radionuclides, such as Cs^+ and Co^{2+}, even in the presence of competing ions. Natisite is another material which has interesting ion-exchange chemistry and is a layered titanium silicate with the ideal formula Na_2TiSiO_5 [5] The structure consists of square pyramidal titanium, with the sodium cations located between the layers. This coordination environment is highly unusual for Ti. It crystallises in the tetragonal space group P4/nmm, with $a = b = 6.4967(8)$Å and $c = 5.0845(11)$Å Inclusion of zirconium in the framework has a considerable effect on ion-exchange. It was found that increasing the levels of zirconium increased the affinity towards Cs and it was also found rate of exchange of Co was increased with increasing Zr content. The Zr doped materials take up Co from an aqueous solution within minutes whereas the undoped materials needing a contact time of several hours in order to reach the same level of exchange. A combination of techniques to probe long and short range order has been used to understand this behaviour.
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