Natural and synthetic apatites recently revised as microporous materials, are characterized by flexible one-dimensional channels parallel to the c axis expanding and/or contracting to satisfy the bonding requirements of the [A]O6X polyhedrons. This flexibility is the key-property to understand why, although apatite exists generally as accessory mineral, it plays a dominant role in P-rich phase equilibria and trace element geochemistry. Because of its ability to incorporate and concentrate minor and trace elements, apatites are widely investigated for the stabilization and recycling of industrial and nuclear waste and are potentially useful in catalysis and solid oxide fuel cell electrolytes. Both natural and synthetic powdered apatites have been studied as ecomaterials to immobilize heavy metals through dissolution-precipitation or ion-exchange reaction. Approach to equilibrium is generally governed by temperature (T) and time (t) together with the reaction surface (RS). Especially sythetic hydroxyapatite has been extensively studied because of its relatively high sorption capacity, low solubility especially in basic and neutral pH, stability under reducing and oxidizing conditions; although 'ion-exchange' sensu stricto is not often demonstrated and the fixation and stabilization of many metals has been confirmed, the precise mechanisms remain poorly understood. Our results show that the ion exchange rate between a natural apatite in a Cd-rich solution is not only T-t-RS dependent, but depends drastically on the chemical gradient that sets along preferential crystallographic directions as a consequence of differential surface and near-surface absence of charge equilibrium.

Keywords: near-surface, apatite, cation-exchange

**P11.15.99**

Crystal structure of a new small — pore zirconosilicate 

Na$_2$ZrSi$_2$O$_7$·H$_2$O

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Structural and functional similarities to the framework alumosilicate-based zeolites have directed the researchers’ efforts to the less studied subclass of compounds with heterogeneous frameworks with M octahedra and T tetrahedra as basic building units (BBUs). Much attention has been paid to the investigation of zirconosilicates and their analogs. We present the synthesis and the crystal structure of the small-pore zirconosilicate Na$_2$ZrSi$_2$O$_7$·H$_2$O. The title compound is monoclinic C2/c, $a=5.476(1)$, $b=9.420(1)$, $c=13.129(1)$Å, $\beta=92.89(1)^\circ$. There is a close similarity of the cell parameters and the powder diffraction pattern to those of Na$_2$ScSi$_2$O$_7$ (Pbnm, \(a=5.35\), \(b=9.34\), \(c=13.09\)Å). Both space groups, Pbnm and C2/c are subgroups of Cmcm which allows using of suitable modified atomic coordinates of Na$_2$ScSi$_2$O$_7$ as a starting structural model for Rietveld refinement (\(Rwp=8.26\%\), \(\chi^2=3.45\)). The BBUs represented by Zr octahedra and Si tetrahedra share only vertices and build framework containing a system of channels and cavities where sodium and water lie. The stoichiometric and topological similarity of the studied phase to waterless compounds of the type A$_2$O$_7$MT$_2$O$_7$ (A=Na,K; M=Zr,Sc,Lu; T=Si,Ge) is interpreted in the light of spatial combination of BBU into larger composite building units (CBU). In turn, the three dimensional arrangement of the CBUs is presented as a condensation of \(\alpha\)-ZrP type layers. The degree of layer deformation predetermines the way of their stacking and the topologic peculiarities of the channels where the alkaline cations and/or water molecules are accommodated. The reversibility of hydration of the title compound is discussed, thus contributing to better understanding the crystal chemistry of zirconosilicates and their analogs.

Keywords: powder structure refinement, microporous material, structural similarity

**P11.15.100**

A rare-earth MOF series: Fascinating structure, efficient light emitters and promising catalysts

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The chemistry of Rare-Earth MOFs is less explored than the transition metal based MOFs, probably because Ln elements are usually regarded as unsuitable metal centres, whose coordination numbers are too high and coordination geometries are hard to control. However, the high and variable coordination numbers of Ln ions result in their important applications as catalysts for organic transformations. Besides, the interesting optical properties of some Ln cations are very well known. By using the flexible bent molecule 4,4’-(hexafluoroisopropylidene)bis(benzoic acid) as ligand, a new family of Ln-MOFs has been obtained and its structure has been solved from an intrinsically triple twinned crystal. The geometrical features of the framework explain the interesting properties shown by the obtained compounds: They have proven to be efficient light emitters, as well as promising materials as heterogeneous catalysts. The use of this flexible bent linker have given rise to the formation of three different polymorphs with molecular formula La$_2$(hfipbb) . Thus, three different networks have been found. These three nets are uninodeal pentacconnected networks, and they have unique topologies.

Keywords: metalloorganic frameworks, topology, optical properties

**P11.15.101**

Same connector, same linker, different dimensionality

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