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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 synthetic hydroxy-apatite 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

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Crystal structure of a new small – pore zirconosilicate Na₂ZrSi₂O₇·H₂O

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Structural and functional similarities to the framework aluminosilicate-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 (BBU). 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 Na₂ZrSi₂O₇·H₂O. The title compound is monoclinic *C2/c*, *a*=5.476(1), *b*=9.420(1), *c*=13.129(1)Å, β=92.89(1)°. There is a close similarity of the cell parameters and the powder diffraction pattern to those of Na₃ScSi₂O₇ (*Pbnm*, *a*=5.35, *b*=9.34, *c*=13.09Å). Both space groups, *Pbnm* and *C2/c* are subgroups of *Cmcm* which allows using of suitably modified atomic coordinates of Na₃ScSi₂O₇ as a starting structural model for Rietveld refinement (*R*_w=8.26%; χ²=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 A₂₍₃₎MT₂O₇

(A=Na,K; M=Zr,ScLu; 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 α-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

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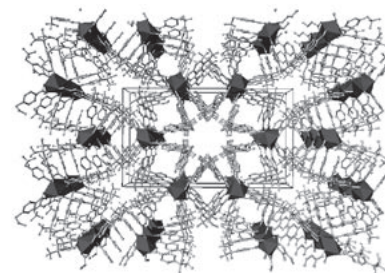
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A rare-earth MOF series: Fascinating structure, efficient light emitters and promising catalysts

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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 La₂(hfi₃pb)·3. Thus, three different networks have been found. These three nets are uninodal pentaconnected networks, and they have unique topologies.



Keywords: metallorganic frameworks, topology, optical properties

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Same connector, same linker, different dimensionality

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