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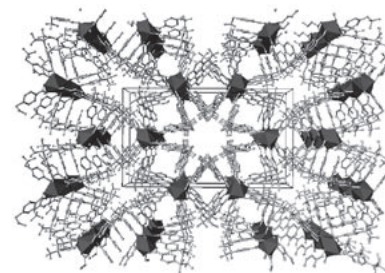
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A rare-earth MOF series: Fascinating structure, efficient light emitters and promising catalysts

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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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The disulfonate anions can be used as versatile ligands in the design of metallorganic frameworks, when they are used in combination with metals with variable coordination number. In this way, by using anthraquinone-2,6-disulfonate (AQDS) anions and rare-earth cations, ytterbium in this case, two different structural types have been obtained. The first of them, named layered rare-earth hydroxide, is a new type of crystalline material, very related to the LDH family of compounds. In the compound, cationic layers of ytterbium hydroxides are created, with molecular formula $[\text{Yb}_4(\text{OH})_{10}(\text{H}_2\text{O})_4]^{2+}$. These layers are separated by the AQDS²⁻ anions, which are not coordinated to the rare-earth cations and neutralize the charge. The SO_3^- groups of the ligand are directed towards the sheets, being connected to them by H bonds. The second type is a 3D polymeric structure. Its molecular formula is $[\text{Yb}(\text{OH})(\text{H}_2\text{O})\text{AQDS}]$, with the sulfonate groups covalently coordinated to the metallic atoms. In this structure, a completely inorganic layer is formed, with the ytterbium atoms connected between them through hydroxyl groups, or by OSO bridges, giving rise to a (6,3) honeycomb layer. The layers are joined through the whole ligand molecules, giving rise to a binodal three dimensional network, three- and penta- connected. The two types of materials have been tested as heterogeneous catalysts, showing excellent results in the reactions of oxidation of sulphides and hydrodesulphurization of thiophene.

Keywords: metalloorganic frameworks, heterogeneous catalysis, layered structures

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A new 2D germanate formed by selective coordination of the *trans* 1,2-diaminocyclohexane to Ge atoms

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ICMM9 is a new germanate, with formula $[\text{C}_6\text{H}_{10}(\text{NH}_2)_2\text{Ge}_3\text{O}_6]$. A mixture of *cis/trans* 1,2-diaminocyclohexane has been employed in the synthesis, giving rise to a layered compound in which only the *trans* molecule is present, with the nitrogen atoms covalently bonded to a germanium atom. Double layers are formed, with two different Ge atoms: one is in tetrahedral environment, and the other situated in a two-fold axis, in octahedral coordination. Tetrahedra are forming sharing vertex chains, which give rise, also by sharing vertexes with the octahedral germanium atom, to GeO_2 infinite eight-R containing layers. Every two of them are connected, in a double one, which is a new 2D binodal 4-c net, with Schläfli symbol: $(3.5^3.6^2)_2(3.5^4.8)$. Looking at the inorganic part of the structure, a correlation is established among ICMM9, pyroxene and amphibole structure types, all them having chains of sharing vertex tetrahedra and octahedral atoms. The ability of ICMM9 as heterogeneous catalyst has been examined by using it in different reactions known to be catalyzed by acid sites or basic sites. ICMM9 has proven to possess both centres and due to this bifunctional acid-base character, its activity has been examined in the synthesis of jasminaldehyde, which is usually obtained with the condensation reaction between benzaldehyde and heptanal. ICMM9 achieves 85 % conversion after 24 h of reaction time with selectivity to jasminaldehyde of > 75%.

Keywords: germanate, heterogeneous catalysis, layered compounds

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Structural characterizations of nanoporous In(III)-MOFs

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We prepared a new series of In(III)-based metal-organic frameworks and characterized them using single crystal X-ray diffraction technique. The permanent porosity of these new materials was also confirmed via N_2 and H_2 sorption analysis. Because of the unique eight coordination ability of the central In(III) ions with four polycarboxylate ligands, the new In-MOFs with various aromatic polycarboxylic acids exhibit interesting topological structures revealed by single crystal X-ray diffraction. The polycarboxylic acids such as 4,4'-biphenyldicarboxylic acid (BPDC), 2,6-naphthalenedicarboxylic acid (NDC), and 1,3,5-benzenetricarboxylic acid (BTC) could form multidimensional frameworks. For example, the In-MOF with BPDC formed a doubly-interpenetrated infinite 3D structure with 54% of solvent accessible void. The In-MOFs containing NDC and BTC exhibited catenation-free extended 3D structures having high void volumes estimated by the PLATON software, 60% and 66%, respectively. The NDC-containing In-MOF showed well-defined three independent 1D rectangular channels. The largest channel was solely occupied by water molecules which can be easily replaced by other volatile solvents. Detailed structural properties and gas storage ability of these nanoporous materials will be discussed.

Keywords: framework structures, porous materials, indium compounds

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In situ X-ray diffraction studies of host-guest properties in nanoporous spin crossover frameworks

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The targeted development of functional metal-organic frameworks, is not only a synthetic challenge, but requires parallel characterization of their often complex structure-property relationships. Among strategic efforts to introduce specific function, the incorporation of spin crossover switching centers allows for the development of new advanced functional materials for molecular-scale electronic switching and sensing devices. Recent work has shown that such spin crossover framework materials (SCOFs) can incorporate an additional level of functionality associated with their often porous natures; guest sorption/desorption in such systems, and the associated perturbation of the iron(II) coordination environment and framework structure, provide a unique avenue for investigating the spin crossover phenomenon in the solid state. To this end we have developed *in situ* synchrotron-based powder X-ray diffraction methods to simultaneously probe their guest-dependent structural and magnetic properties.

Keywords: powder and single crystal diffraction, microporous