

The magnitudes of the strains decrease outside the width of the laser beam footprint. The first laser pass induces through-thickness strains close to yield, whereafter their magnitudes decrease with increased number of laser beam passes. A comprehensive mapping of the longitudinal stresses as function of the number of laser passes is given.

Keywords: strain scanning, laser bending, residual stress

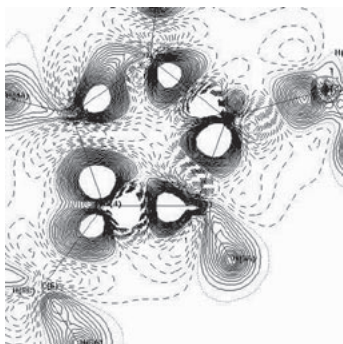
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Charge density and *in-situ* studies of ionic and ionothermally prepared materials

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X-ray diffraction is an important technique in structure determination. However zeolites and many of the porous materials we look at are notoriously difficult to grow as large single crystals. With the use of synchrotrons such as the SRS we are able to probe these fascinating structures to obtain not only initial structural models but also high resolution X-ray data sets (figure1). Our group uses stations 9.8 and 16.2 SMX to investigate these materials. We are also using the high energy dispersive beam line of 16.4 to investigate how they crystallise. We are able to produce porous materials with the use of ionic liquids which act as both a template and as a solvent reducing the number of interactions in the vessel making it easier to try and understand the mechanism.



Keywords: ionothermal prepared materials, high Resolution Charge Density, porous materials

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Hydrothermal synthesis and structural features of metal phosphates in the presence of amines

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Since the first crystalline compound, α -Zr(HPO₄)₂·H₂O, was obtained, these compounds have been extensively studied due to the possibility of relating their properties and crystalline structure, and the many potential applications. Initially, γ -Zr(H₂PO₄)(PO₄)·2H₂O, was erroneously believed to be a modification of the α -phase. Advances in the knowledge of the γ -layered structure were fundamental for the interpretation of the topotactic mechanism of formation and development of the chemistry of the γ -derivatives. Although only two crystalline forms of layered titanium phosphates are known, γ -

-Ti(HPO₄)₂·H₂O and γ -Ti(H₂PO₄)(PO₄)·2H₂O, many derivatives have been reported. Surprisingly, the γ -layered titanium phosphate is less studied than the α -phase, even though the γ -layers are more rigid, thicker, acidic and amenable to intercalation processes. More than a decade ago, we have reported the mechanism of intercalation of n-alkylamines in γ -titanium phosphate, showing that only 66% of the P-OH groups interact with the amine groups of the guest molecules. Geometrical constraints dictate that compounds with maximum intercalation usually have the empirical formula of γ -Ti(H₂PO₄)(PO₄)·1.3C_nH_{2n+1}NH₂·H₂O (with n = 1 to 6), and crystalline phases with lower amine content can also be isolated. The hydrothermal synthesis and the structural characterization of γ -titanium phosphate intercalation compounds have been only recently reported.[1,2]

[1] Mafra, L.; Almeida-Paz, F.A.; Rocha, J.; Espina, A.; Khainakov, S.A.; Garcia, J.R.; Fernandez, C., Chem. Mater. 2005, 17, 6287.

[2] Mafra, Luis; Rocha, Joao; Fernandez, Christian; Castro, German; Garcia-Granda, Santiago; Espina, Aranzazu; Khainakov, Sergei; Garcia, Jose R., Chem. Mater. 2008, 00, 0000.

Keywords: phosphates, hydrothermal synthesis, amines

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Iron incorporated in cubic mesoporous silica: Synthesis, composition and structure

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Ordered mesoporous silica (OMS) grafted with different atoms are interesting new structures with high specific surface, large pore size and uniform pore distribution for potential applications in, for example, catalysis, green chemistry and drug delivery systems. In this work, we report the direct incorporation of iron in OMS, with cubic FDU-1 structure. The structural properties of samples prepared under different conditions were investigated by Small Angle X-ray Scattering (SAXS) and large angle X-ray Diffraction (XRD). The local structure around the iron atoms was analyzed by X-ray absorption spectroscopy (XAS). The composite material is mostly formed by amorphous silica and hematite, with some amount of Fe²⁺ in the structure. The morphology, structural and textural properties were analyzed by N₂ adsorption isotherms. The variation of the synthesis pH from 1 to 3 decreased the total surface area. Rutherford Backscattering Spectrometry (RBS) was used to determine the amount of Si, O, Cl and Fe in the samples. The amount of iron inside the silica matrix depended on the preparation method, and an optimized synthesis process has been developed aiming to obtain high iron content (up to 4 wt.%) and low chlorine incorporation.

Keywords: porous materials, SAXS, EXAFS and XANES

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Cation exchange mechanism for natural apatite with a simulated Cd-polluted solution TEM-AEM and XPS

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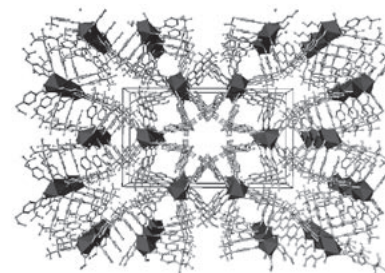
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A rare-earth MOF series: Fascinating structure, efficient light emitters and promising catalysts

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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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