

P10.06.47*Acta Cryst.* (2008). A64, C505**X-ray single-crystal study on partially guest-free melanophlogite**

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Melanophlogite (MEP), $23\text{SiO}_2 \cdot \text{M}^{12} \cdot 3\text{M}^{14}$ ($Z = 8$ for low MEP and 2 for high MEP), is a silica clathrate mineral. MEP can accommodate small gas molecules (CO_2 , CH_4 , N_2 , etc.) in the two kinds of cage-like voids, M^{12} and M^{14} . The single-crystals of guest-free MEP (GF-MEP) were obtained by heating natural guest-bearing MEP from Mt. Hamilton, California, USA at 950 or 1000°C for 6 hours. The crystal structure of GF-MEP at five different temperatures, -50, 23, 100, 200 and 400°C, was investigated with the X-ray single-crystal diffractions, which showed cubic symmetry at the five temperatures. Although Liu *et al.* (1997) suggested two phase transitions in NMR experiments, *Pm-3n* gave the most satisfactory results at all the temperatures in our study. Difference-Fourier maps, where F_c includes only framework atoms Si and O, showed that positive electron densities remained in the cages (Figure 1). It has been a common practice for the guest-molecule to substitute their form factor with those of dummy atoms having comparable numbers of electrons and sizes. The refinement using F and Mg as dummy resulted to 32.3% for M^{12} and 84.8% for M^{14} at 100°C as the occupancy factors.

Keywords: clathrate compounds, silica, single-crystal X-ray crystallography

P10.06.48*Acta Cryst.* (2008). A64, C505**Study of topotactic conversion from layered silicates to zeolites by high-temperature powder XRD**

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Recently, new synthetic route of zeolites from layered silicates as a topotactic precursor has been interested. In the topotactic conversion method, adjacent layered frameworks are bridged by dehydration-condensation, yielding one- or two-dimensional micropores in the interlayer. Several new siliceous zeolite were reported so far, i.e. CDS-1(CDO), Nu-6(2)(NSI), RUB-24(RWR) and RUB-41(RRO) from layered silicate PLS-1, Nu-6(1), RUB-18 and RUB-39, respectively. In the dehydration-condensation, basal spacings of layered silicates are shrunk dramatically and the heating conditions are important factor for obtaining highly crystalline zeolite. However, detailed structural changes from these layered silicates to zeolites have not been investigated. In this work, we investigate structural changes of various layered precursors into zeolites by a time-resolve high-temperature (TRHT) powder XRD diffraction technique. TRHT-PXRD data were collected on the Bruker D8-ADVANCE Vario-1 with MRS furnace attachment (modified Debye-Scherrer geometry using a quartz capillary tube). In case of layered silicate PLS-1, basal spacing was gradually elongated with increasing temperature up to 623 K. Then, PLS-1 was quickly changed to CDS-1 at ca. 653 K. From Rietveld refinements of intensity data at all measurement temperature, adjacent layered frameworks were

shifted parallel to layer plane and terminal silanol groups (Si-OH) were closed between adjacent layers. This finding is well agreement with the structural predictions by the molecular dynamics simulation. In case of layered silicate PREFER, structural change was gradually occurred from 543 to 843 K. Consequently, the highly crystalline FER-type zeolite was formed under sufficient airflow conditions through the capillary specimen.

Keywords: high-temperature powder diffraction, X-ray characterization of microcrystalline zeolite, layered silicates

P10.07.49*Acta Cryst.* (2008). A64, C505**New microporous and nanostructured uranium compounds**Evgeny V. Alekseev¹, Sergey V. Krivovichev², Wulf Depmeier¹¹University of Kiel, Crystallography, Ludewig-Meyn-Str. 10, Kiel, S-H, 24118, Germany, ²St. Petersburg State University, 199034 St.Petersburg, Russia, E-mail: e_v_alekseev@mail.ru

Microporous and nanostructured actinide compounds are of great interest due to their formation during alteration of spent nuclear fuel and their potential applications in nuclear industry and radiochemistry. Here we report on syntheses and structures of four new unusually highly porous uranyl compounds. Two of them is sulfate and selenate templated by the 18-crown-6-ether complexes of the H_3O^+ hydronium ions and having this chemical compositions - $(\text{H}_3\text{O})_8[(\text{H}_3\text{O})@(\text{18-crown-6})]_2[(\text{UO}_2)_{14}(\text{SO}_4)_{19}(\text{H}_2\text{O})_4](\text{H}_2\text{O})_{20.5}(1)$, $(\text{H}_2\text{O})_2\text{K}[(\text{H}_3\text{O})@(\text{18-crown-6})][(\text{UO}_2)_3(\text{SeO}_4)_5](\text{H}_2\text{O})_4$ (2). Last two compounds are first uranyl molybdates of lanthanides, they have $\text{La}_2[(\text{UO}_2)_2(\text{MoO}_4)_5(\text{H}_2\text{O})]_n\text{H}_2\text{O}$ (3), $\text{Nd}_2[(\text{UO}_2)_2(\text{MoO}_4)_5(\text{H}_2\text{O})]_n\text{H}_2\text{O}$ (4) chemical compositions. Compound 1 contains exceptionally complex $[(\text{UO}_2)_{14}(\text{SO}_4)_{19}(\text{H}_2\text{O})_4]$ microporous framework with a low framework density (FD) of 8.5 M atoms per 1000 angstrom. The largest cavity of the framework is centered approximately at (1/2; 1/2; 1/2) and has a form of a flattened disc with dimensions $\sim 20*20*8$ angstrom. Structure of 2 consists of $[(\text{UO}_2)_3(\text{SeO}_4)_5]$ uranyl selenate nanotubules extending along the a axis and forming a tetragonal rod-packing as they are separated by columns of disordered $[(\text{H}_3\text{O})@(\text{18-crown-6})]$ complexes. The external diameter of the tubule is 1.7 nm. Crown-ether complexes are templated in intertube space pseudo channels with dimension $13 * 13$ angstrom. Structures of 3 and 4 based on $[(\text{UO}_2)_2(\text{MoO}_4)_5(\text{H}_2\text{O})]$ chains these chains have width close to 2.7 nm. Maximum internal space of channels has ellipsoid form and maximum dimension $\sim 7*13$ angstrom. In to these channels are water molecules, one part of them strongly coordinated on lanthanides cations, another is disordered (zeolite-like water) in the center of these channels.

Keywords: uranium compounds, microporous solids, nanostructures

P10.07.50*Acta Cryst.* (2008). A64, C505-506**Ab initio calculation on the smallest perfect mineral: Nano-ball allophane**

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Nano-ball allophane is a naturally occurring aluminum silicate mineral with hollow spherical morphology. Diameter of the mineral is observed as 3.5 to 5.0 nm with TEM, and cation exchange experiments have proven the existence of some pores along the spherule wall. Chemical structure of the wall is similar to that of imogolite with nano-tube structure, where orthosilicates are bonded inside of gibbsite vacant site (imogolite sheet). However, whole chemical structure of the nano-ball has not been clarified. We succeeded to tentatively construct the whole chemical structure of the ball by assuming an expanded truncated octahedron composed of hexagonal imogolite sheets. By changing size of the imogolite sheets, diameters of the ball become 1.5 nm, 3.0 nm, 4.5 nm, and so on. Here we present full-structural optimization results for the nano-ball with diameter of 1.5 nm. Gaussian 03 for UNIX revision C.01 with HF/6-31G(d) method was used for calculations. The 6-coordinated Al and the 4-coordinated Si atom in the optimized structure were stable and no change in its ball shape structure. The calculated O · · · O atom distance in the vacant octahedral site that is substituted with orthosilicate has average 2.62 Å. Meanwhile, in the outer vacant octahedral sheet, the distance has average value of 4.25 Å for. It can be said that these contractions from substituted Si atom cause transformation of a planar gibbsite sheet to a material with spherical shape. Until now, there are no reports on the evidence of smallest nano-ball allophane except with diameter of 3.5 to 5.0 nm. However, our calculation result confirmed that the smallest of nano-ball allophane is stable and possible exists in the soil natural environmental.

Keywords: nano-ball allophane, *ab initio*, perfect mineral

P10.08.51

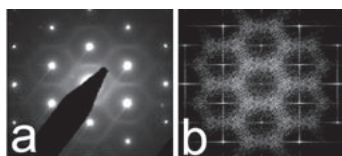
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Crystal structures and diffuse scattering of compounds with graphite-like (B,C)-nets

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The crystal structures of the new compounds $\text{Ca}(\text{B,C})_6$ (hexagonal, $a = 4.563(1)\text{\AA}$, $c = 4.396(1)\text{\AA}$) and $\text{Ca}(\text{B,C})_8$ (hexagonal, $a = 2.588(1)\text{\AA}$, $c = 4.434(1)\text{\AA}$) were determined from powder diffraction data. The compounds consist of planar graphite-like (B,C)-nets, intercalated by calcium atoms. In $\text{Ca}(\text{B,C})_6$ one third of the hexagonal prismatic voids formed by the (B,C)-layers is occupied by Ca. In $\text{Ca}(\text{B,C})_8$ the Ca-atoms are disordered, which gives rise to honeycomb-like diffuse scattering visible in the electron diffraction pattern (Fig. 1a). A model for the calcium distribution was developed and the diffuse scattering could be simulated successfully with the program DISCUS [1] (Fig. 1b).

[1] Proffen T., T., J. Appl. Cryst., 1997, 30, 171



Keywords: diffuse diffraction, powder diffraction, intercalation chemistry

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Synthesis and crystal structure of some indole derivatives complexes

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Schiff bases of hydrazone derivatives were synthesized from a condensation reaction involving hydrazones or amines and carbonyl containing compounds via reflux in ethanol for several hours. The crystal structure of the some complexes has different topology such as $\text{C}_{18}\text{H}_{20}\text{N}_8\text{S}_2\text{Ni}$ which has a layer structure.

Keywords: indole, complexes, layer structure

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Preparation of ferrites MFe_2O_4 (M=Co,Ni) nanoporous ribbons structure and their magnetic properties

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Spinel ferrites, MFe_2O_4 (M=Co, Ni), ribbons with nanoporous structure were prepared by electrospinning combined with sol-gel technology. The ribbons were formed through the agglomeration of magnetic nanoparticles with PVP as structure directing template. The length of the polycrystalline ribbons can reach several hundred micrometers and the width of the ribbons can be tuned from several micrometers to several hundred nanometers by changing the concentration of precursor. Nanoporous structure was formed during the decomposition of PVP and inorganic salts. The ribbons exhibited weak saturation magnetizations and low coercivities at room temperature, but at low temperature, saturation magnetizations and coercivities increased a lot, especially for CoFe_2O_4 ribbons, reaching to 72 emu/g and 1.45 T at 2 K respectively. These novel magnetic ribbons can potentially be used in micro/nano electronic devices, magnetic sensors and flexible magnets.

Keywords: synthesis inorganic, magnetic oxides, ferrites

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Controllable synthesis and properties of ferric oxide nanostructural materials

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The design and synthesis of nanostructural materials have been among the important research topics of nanoscience due to their