

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 $\sim 20 \times 20 \times 8$ 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 $\sim 7 \times 13$ 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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