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Open-Framework Germanate Built from the Hexagonal Packing of Rigid Cylinders

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We present a novel open-framework oxide material constructed from $Ge_{10}(O,OH)_{28}$ (Ge_{10}) oxide clusters prepared via a nonsurfactant route. The material shows two distinct pore windows of 9.43 and 4.65 Å and a low framework density structure of 12.7 Ge atoms per 1000 Å^3. The topological study leads to the recognition of a newly observed trinodal 6,7-heterocoordinated net related to the 7-coordinated **swh** net. The structure displays large rigid cylinders showing features indicating a growth mechanism by hard-sphere packing of the inorganic moiety similar to that observed in mesoporous materials.

Oxide materials with mixed coordination have attracted a strong interest because of their ability to form porous frameworks[1] and notably structures with extra large rings (≥18-rings).[2] The synthesis of crystalline materials approaching mesoporous dimensions presents fundamental questions and has significant industrial implications.[3] The discovery of SU-M,[2c] a crystalline oxide mesoporous material comparable to the MCM-48 archetype, initiated the search for its hexagonal counterpart via a nonsurfactant route. In this report, we present ASU-21, a crystalline phase displaying the sought-after hexagonal channels formed by rigid porous cylinders resulting from the cooperation between the inorganic/organic moieties and water molecules. The hard cylinders adopt a hexagonal packing, forming bimodal pores modulated by the inclusion of diprotonated 1,6-diaminohexane (DAHex) cations in the walls and suggesting the formation by a hard-sphere packing (HSP) mechanism.[3] This is in contrast with the silicogermanate SU-61,[1d] which shows monomodal hexagonally packed pores. Crystallinity is retained up to 350 °C. ASU-21 shows two distinct pore windows of 9.43 and 4.65 Å, assuming a van der Waals diameter of 2.7 Å for oxygen, and has a framework density of 12.7 Ge atoms per 1000 Å^3.

ASU-21 was prepared by hydrothermal methods from a gel of germanium dioxide, DAHex, pyridine, and water.[5] Syntheses are provided in section S1 of the Supporting Information. The structure crystallizes[6] in the orthorhombic space group *Ibam*. The chemical formula of ASU-21 is $|(C_6H_{18}N_2)_5(NH_4)_2|[Ge_{33}O_{70}(OH)_4]\cdot xH_2O$. The framework charge (12$^-$ per formula unit) is compensated for by five H_2DAHex cations and two ammonium ions. Two of the H_2DAHex cations could not be allocated by the structural refinement. The chemical formula was supported by

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(6) Single-crystal X-ray diffraction data collected on a MarCCD at 150(2) K using synchrotron radiation (λ = 1.03 Å) at the Beamline I911:2, Max Lab, Sweden. Data reduction and numerical absorption correction were applied with TwinSolve, and the structure was solved and refined by *SHELX* with nonmerohedral twins. Crystal data for ASU-21: *Ibam*, a = 49.257(10) Å, b = 28.439(6) Å, c = 14.866(3) Å, V = 20825(7) Å^3, 50 × 8 × 6 μm^3. A total of 30 028 reflections, of which 5933 are unique, were collected in the region 5.50° < θ < 30.99°. R_{int} = 0.045 for $P\bar{1}$, $R1$ = 0.0749 and $wR2$ = 0.1892 for reflections with $I > 2\sigma(I)$. Because of serious twinning, an anisotropic refinement for O atoms did not show any improvement.

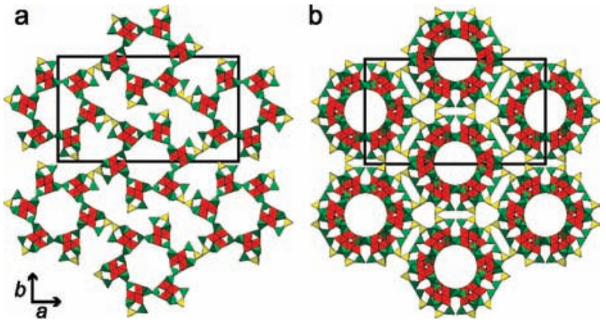

Figure 1. Polyhedral representations of ASU-21: (a) layer showing the 18- and 46-rings. (b) 3D framework showing the large cylindrical channels. GeO_6 octahedra are in red, GeO_4 tetrahedra in green, and apical additional tetrahedra in yellow.

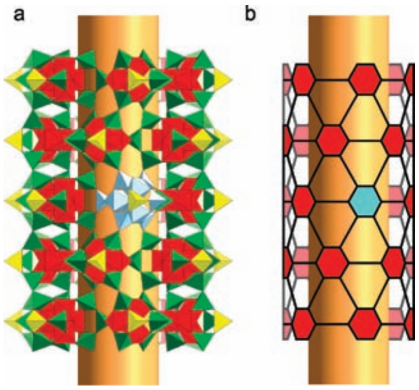

Figure 2. (a) Ge_{10} cluster arrangement forming cylindrical pores. (b) Corresponding augmented hexagonal net wrapped onto a cylinder in its highest symmetry D_{6h} ($6/mmm$). One cluster is highlighted in blue, emphasizing the 6-coordination.

Table 1. Topological Characteristics of the ASU-21 Net (V_n: Vertex Number n)

ASU-21		*Ibam*
coordination	V_1	6 16 39 74 115 160 223 300 369 446
sequence	V_2	7 21 41 74 119 167 223 292 373 461
	V_3	7 19 43 74 117 167 223 292 375 457
point symbols		V_1: $3^6.4^6.5^3$; V_2 and V_3: $3^6.4^8.5^6.6$
total point symbol		$\{3^6.4^6.5^3\}\{3^6.4^8.5^6.6\}_2$

^{13}C solid state NMR spectroscopy, elemental analysis, and the thermogravimetry (TG) trace. Na^+-exchanged samples showed a ratio Ge/Na of 4, giving indirect evidence that the pore content could be exchanged, and balanced the remaining charges (Supporting Information, sections S5 and S6).

The structure contains three crystallographic Ge_{10} clusters, capped by an extra tetrahedron in the apical position. Note that the clusters are, nevertheless, identical. A view down the *c* axis exposes a pseudolayer lying in the *ab* plane; the unit cell contains two such pseudolayers related by an inversion center. The pseudolayer consists of cycles of six Ge_{10} clusters (6-cycles) forming GeO_4/GeO_6 18-rings arranged in a hexagonal pattern with cycles of 10 Ge_{10} clusters assembled in 46-rings (Figure 1a). The pseudolayers pack along the *c* axis, constructing large cylindrical pores made from hexagonal antiprisms with a 9.43 Å opening and channels with a triangular window that can accommodate a sphere of 4.65 Å diameter, assuming a diameter of 2.7 Å for oxygen (Figure 1b). The accessible volume is about 50% and is comparable to that of SU-M.

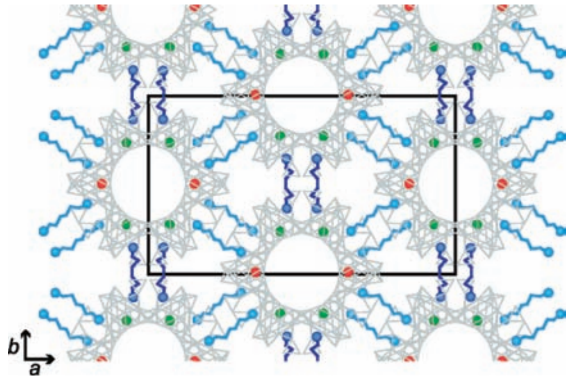

Figure 3. Location of the H_2DAHex cations (in blue) and water/ammonium ions (red/green spheres). One of the two allocated unique H_2DAHex cations is disordered (dark blue). Polyhedral gray frames represent the Ge_{10} clusters. Additional tetrahedra have been omitted for clarity.

The large pores result from the decoration of a hexagonal sheet by Ge_{10} clusters wrapped onto a cylinder. Each Ge_{10} cluster is coordinated to six others on the cylinder (Figure 2a). The highest symmetry of hexagonal net wrapped onto a cylinder is D_{6h} ($6/mmm$; Figure 2b). For the cylinders to later form 3-periodic structures while preserving this symmetry, every node must become 7-coordinated. The only default three-dimensional (3D) net in the *Reticular Chemistry Structure Resource* with 3- and 6-rings corresponding to such a structure has the **swh** topology[7] ($P6/mcc$). However, in ASU-21, the Ge_{10} geometry and orientation of the clusters are such that only two-thirds of the apical extra tetrahedra can provide bridges to the neighboring cylinders, breaking the 6-fold symmetry (Figure 1a). This leads to the recognition of a new trinodal 6,7-heterocoordinated net (Table 1 and see Supporting Information, section S8, for tiling information).

The 6-cycles in ASU-21 gyrate alternatively clockwise and anticlockwise in the *c* direction and likewise in the $a \pm b$ directions in the same pseudolayer (Figure 1a), causing a $^1/_2\, c$ shift of the adjacent cylinders. As the interactions between the cylinders responsible for the packing are relatively weak, the $^1/_2\, c$ shift of the adjacent cylinders introduces severe twinning problems (Figure S8 in the Supporting Information). Consequently, all single crystals obtained from various syntheses and examined by single-crystal X-ray diffraction lead to hexagonal prismatic crystals for which hexagonal cells were found in the first stage of the structure solution instead of the correct orthorhombic cell. In the present refinement, the three twinning domains have the proportions 39%, 41%, and 20%. Such a subtlety was recently documented for a lanthanide hybrid open framework.[8] Different height ordering may form other polymorphs. All of these features support the idea that the ASU-21 structure is formed by the assembly of rigid Ge_{10} cluster cylinders.

An intricate network of weak forces between Ge_{10} clusters, the water molecules, the ammonium ions, and the terminal amino groups of the H_2DAHex cations is at play in ASU-21. The cylinders adopt a hexagonal packing with a spacing modulated by the length of the H_2DAHex cations. Figure 3

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shows that the network involves the H_2DAHex cations and water/ammonium ions with the clusters, forming a mesh corresponding to the Archimedean tiling of a 3.4.6.4 layer (**htb**, hexagonal tungsten bronze; details are in the Supporting Information, section S7).

The selectivity of organic amines toward the formation of one structure over others remains unclear. However, the specificity of DAHex toward ASU-21 is rather striking. The 8.15 Å length of a DAHex molecule N to N relates closely to the 10.18 Å distance between four GeO_2 tetrahedra corresponding to the bridge between the cylinders. Note that the SU-M synthesis with methylpentamethylenediamine (MPDP) substituted by DAHex leads to pure ASU-21. MPDP, a positional isomer of DAHex, has a shorter N···N distance (7.47 Å). As a side note, SU-M can also be obtained as a zircogermanate using 1,4-diaminobutane (Supporting Information, section S1).

In analogy to reaction mechanisms found in mesoporous silica, while the gyroidal structure of SU-M and the hexagonal SU-61 could be the result of either a mechanism related to liquid-crystal templating or cooperative self-assembly models,[9] with the crystallization of the framework at the continuous surface, the makeup of ASU-21 shows two features that are strikingly reminiscent of the recently proposed HSP model, explaining the presence of bimodal pores in mesoporous silica. First, the cylinders result from the assembly of organic–inorganic units of Ge_{10} clusters interacting with water/ammonium ions and amino groups. Second, the twinned structure is a consequence of a mismatch in the height of the cylinders. The synthesis conditions of ASU-21, apart from a higher temperature, are relatively close to those of mesoporous materials obtained via a nonionic surfactant route using long alkylamines.

We have presented a novel Ge_{10}-based open framework with a new trinodal 6,7-heterocoordinated topology. The structure displays large rigid cylinders showing features indicating a growth mechanism by HSP of the inorganic moiety.

Acknowledgment. This phase was first prepared at Arizona State University by J. Plévert in M. O'Keeffe's group. However, they were unable to obtain a satisfactory atomic structure (private communication from M. O'Keeffe). In recognition of their work, the ASU-21 designation is retained. C.B. and J.-L.S. are funded by grants from the Wenner-Gren and Carl-Trygger Foundations, respectively. This project is supported by the Swedish Research Council (VR) and the Swedish Governmental Agency for Innovation Systems (VINNOVA) through the Berzelii Center EXSELENT. We thank the Knut and Alice Wallenberg Foundation for an equipment grant.

Supporting Information Available: Syntheses, powder X-ray diffraction patterns, TG trace, ^{13}C NMR, structure solution and refinement, a crystallographic file in CIF format, and figures of structural details and topologies. This material is available free of charge via the Internet at http://pubs.acs.org.

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