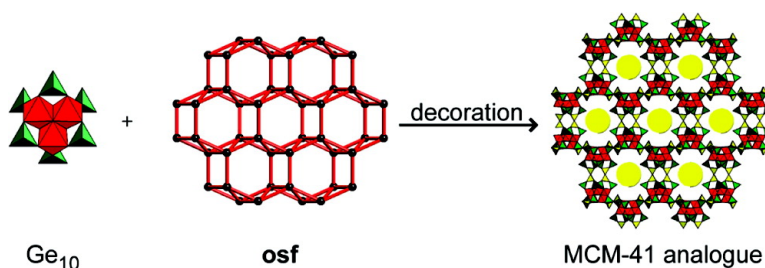Communication

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Ge10   +   osf   → decoration →   MCM-41 analogue

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An Open-Framework Silicogermanate with 26-Ring Channels Built from Seven-Coordinated (Ge,Si)$_{10}$(O,OH)$_{28}$ Clusters

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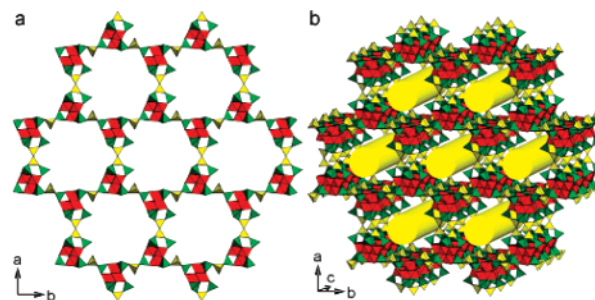
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The synthesis of open-framework oxide materials with ever-increasing pore size and decreasing framework density remains a bustling and challenging research field, as these materials are attractive for separation and catalysis applications.[1] Structures with extra-large pores are often found in phosphates,[2] phosphites,[2] and germanates.[3−4] Germanates are especially interesting because germanium can be four-, five- and six-coordinated with oxygen to form well-defined cluster building units containing a number of GeO$_n$ polyhedra. Open-framework germanates with extra-large pores are built from such clusters[3−4] and illustrate the concepts of molecular building units and scale chemistry.[5] Two germanates with 24-ring channels, ASU-16[3a] and FDU-4,[3b] are built by Ge$_7$X$_{19}$ (Ge$_7$) and Ge$_9$X$_{26−m}$ (Ge$_9$) clusters (X = O, OH, F, m = 0−1), respectively. A germanate, SU-M, with the largest pore formed by a 30-ring, is built by an even larger cluster Ge$_{10}$X$_{28}$ (Ge$_{10}$)[4] and is the first crystalline oxide with a pore opening beyond 20 Å.

In an attempt to modify the pore size and pore shape and improve the thermal stability of our germanates, the possibility of silicon substitution has been investigated. We have for the first time introduced silicon into the Ge$_7$ germanate clusters in SU-12,[6] where 14% of the tetrahedrally coordinated Ge in ASU-16[3a] was replaced by Si. The resulting framework is isostructural to ASU-16 with more circular pores and a higher thermal stability. In addition, a number of original four-coordinated silicogermanates have been synthesized[7] showing that the incorporation of silicon into the germanate cluster could lead to novel open frameworks, as the Si−O distances (1.61 Å) are shorter than the Ge−O distances (1.76 Å) and the Ge−O−Ge angles are typically smaller (130°) than Si−O−Si angles.[8]

Here we present a novel silicogermanate SU-61[9] containing 26-ring channels and built by (Ge,Si)$_{10}$ clusters. SU-61 was prepared hydrothermally from a mixture of germanium dioxide, 2-methyl-pentamethylenediamine (MPMD), tetraethylorthosilicate (TEOS), and water,[10] following a synthesis procedure similar to that of SU-M.[4] The structure was determined by single-crystal X-ray diffraction.[11] SU-61 was characterized by X-ray powder diffraction (XRPD), elemental analysis (EDS and CHN), thermogravmetric (TG) analysis, and ion exchange experiments.

SU-61 crystallizes in the orthorhombic space group *Cmcm*,[11] with pseudohexagonal unit cell dimensions. The structure is built from one unique (Ge,Si)$_{10}$ cluster and two additional unique (Ge,Si)O$_4$ tetrahedra. The (Ge,Si)$_{10}$ clusters lie on a 6^3 net corresponding to the carbon location in a graphite layer and form a layer containing 26-rings in the *ab*-plane (Figure 1a). Each 26-ring is formed by six (Ge,Si)$_{10}$ clusters connected to one another through one or two

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Figure 1. Polyhedral representation of SU-61 (a) the 26-ring layer; (b) the 3D framework showing the 26-ring channels. Octahedra and tetrahedra within the Ge$_{10}$ clusters are shown in red and green, respectively. The additional tetrahedra are in yellow.

additional (Ge,Si)O$_4$ tetrahedra and has a mirror symmetry. The layers are stacked along the *c*-axis, with adjacent layers related by a *c*-glide perpendicular to the *b*-axis and connected via the bridging oxygen to form a three-dimensional (3D) framework (Figure 1b). The framework contains two-dimensional intersecting 8- and 26-ring channels along the *b*- and *c*-axis, respectively.

The framework density (FD) of SU-61 is 10.2 (Ge,Si) atoms per 1000 Å^3. The free diameter of the 26-ring is 13.1 × 17.3 Å in SU-61, much larger than that found in the 24-ring germanate ASU-16 (8.4 × 14.5 Å) and silicogermante SU-12 (11.3 × 12.5 Å), both built from (Ge,Si)$_7$ clusters. The free diameter of the 24-ring in the germanate FDU-4, built from Ge$_9$ clusters, is even smaller (7.4 × 8.2 Å). The pore opening in SU-61 has an area comparable to that of the 30-ring in SU-M (16.7 × 22.5 Å) but is more circular. It is notable that both SU-61 and SU-M are built from the same cluster. The synthesis conditions for both compounds are also similar, the difference being the addition of TEOS to incorporate Si in SU-61. SU-61 and SU-M can be regarded as the analogues of the mesoporous hexagonal MCM-41 and cubic MCM-48, respectively.[12] While MCM-41 and MCM-48 were synthesized by using surfactant liquid crystal templating agents, SU-61 and SU-M were prepared by condensation of the (Ge,Si)$_{10}$ clusters using a small organic amine as a template. In contrast to the amorphous walls of MCM-41 and MCM-48, SU-61 and SU-M have well-defined crystalline framework walls.

We have for the first time incorporated Si into the Ge$_{10}$ clusters. The Si contents at the tetrahedral sites range from 10(1) to 30(1)% (on average 21%) and are for the two additional tetrahedra 28(1) and 78(1)%, respectively. The average T−O distance varies significantly for the tetrahedral sites, ranging from 1.607(6) to 1.742(5) Å. The large variation of the Si content in different tetrahedral sites is not yet understood. The overall Ge/Si ratio in SU-61 is 3.2 and agrees with that obtained by EDS (3.1).
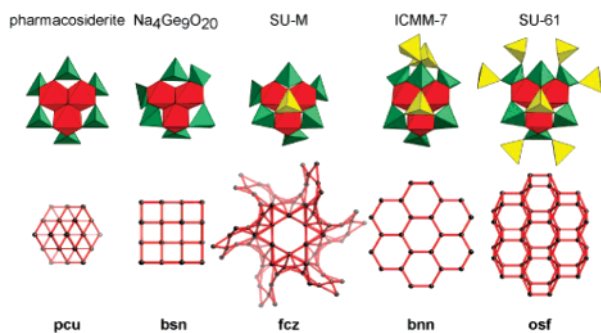
Figure 2. Above: the Ge$_{10}$ cluster and its connection to the additional tetrahedra (in yellow). Each Ge$_{10}$ cluster is built from four octahedra (in red) and six tetrahedra (in green). Below: the underlying net of different structures identified by Systre.[15]

SU-61 contains one (Ge,Si)$_{10}$O$_{27}$OH cluster, one (Ge,Si)O$_4$ tetrahedron, two (Ge,Si)O$_3$OH tetrahedra, and two protonated MPMD templates per formula unit.[9] The templates could be partially exchanged by Na$^+$, K$^+$, and Cs$^+$ ions. *In situ* X-ray powder diffraction showed that SU-61 is thermally stable up to 250 °C and has a stability similar to that of ICMM-7[3c] (250 °C) and lower than that of SU-M[4] (320 °C).

Interestingly, Ge$_{10}$ clusters can form 3D frameworks with a great structure diversity, from a dense Na$_4$Ge$_9$O$_{20}$[13](6-ring, FD = 21.6), to the relatively open Ge-pharmacosiderite[14] (8-ring, FD = 13.8) and ICMM-7[3c] (14-ring, FD = 13.0), and to the very open SU-61 (26-ring, FD = 10.2) and SU-M[4] (30-ring, FD = 7.1). All the structures contain only one unique Ge$_{10}$ cluster. The four octahedra in each Ge$_{10}$ cluster share edges and form a rather rigid unit. The six tetrahedra, on the other hand, are only two-connected to the clusters, so that they can rotate freely (Figure 2). The symmetry of the Ge$_{10}$ cluster is the highest in the Ge-pharmacosiderite ($-43m$) and lowered in other structures due to the rotation of the tetrahedra. The Ge$_{10}$ clusters in Na$_4$Ge$_9$O$_{20}$[13], SU-M,[4] and ICMM-7[3c] have lost all symmetry; in SU-61 only one mirror plane is preserved. For SU-M, ICMM-7, and SU-61, three of the tetrahedra in each Ge$_{10}$ cluster are connected by an additional tetrahedron and can no longer rotate freely. In ICMM-7 and SU-61, additional tetrahedra are connected to the clusters. In all these structures, the clusters are connected to one another in different ways: by sharing a common tetrahedron, or by sharing a bridging oxygen atom of their tetrahedra, or even via one or two additional tetrahedra.

To understand the connections of the Ge$_{10}$ clusters in the different structures, we evaluate the topology of these frameworks by studying the connectivity of the Ge$_{10}$ clusters (Figure 2). In Ge-pharmacosiderite, each Ge$_{10}$ cluster is linked to six neighboring clusters by sharing their tetrahedra. The clusters lie on a six-coordinated primitive cubic **pcu** net to form the Ge-pharmacosiderite, containing 3D intersecting 8-ring channels. In Na$_4$Ge$_9$O$_{20}$, each Ge$_{10}$ cluster is also linked to six neighboring clusters, but by sharing two common tetrahedra and linking the other four. The resulting framework is rather dense, containing only 6-rings, and corresponds to the six-coordinated β-Sn **bsn** net. The Ge$_{10}$ clusters in both SU-M[4] and ICMM-7[3c] are five-coordinated. In SU-M, they fall onto the G (gyroid) minimal surface and are located at the nodes of the **fcz** net to form a framework with two gyroidal 30-ring channels. In ICMM-7, the Ge$_{10}$ clusters lie on the boron nitride **bnn** net. On the other hand, the underlying **osf** net of SU-61 with seven-coordinated clusters had not been observed before in any crystalline structures.

We have presented a new open-framework silicogermanate SU-61 containing intersecting 8- and 26-ring channels. It has been possible to incorporate 21% Si into the tetrahedra in the Ge$_{10}$ cluster.

Numerous possible geometries arise from the observed flexibility of the tetrahedra in the Ge$_{10}$ cluster, suggesting that more exotic structures may be formed by the Ge$_{10}$ clusters.

Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, selected bond lengths and angles for SU-61. An X-ray crystallographic file (CIF). Figures of the structures and the **osf** net, XRPD patterns, and TG analysis. The material is available free of charge via the Internet at http://pubs.acs.org.

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(9) SU-61: |C$_6$H$_{16}$N$_2$H$_2$|$_2$[Ge$_{8.7}$Si$_{1.3}$O$_{16}$O$_{11/2}$OH][Ge$_{0.71}$Si$_{0.29}$O$_{4/2}$][Ge$_{0.22}$Si$_{0.78}$-O$_{3/2}$OH]$_2$.

(10) SU-61 was synthesized hydrothermally following the procedure below: 1 g of GeO$_2$ was added in 2.93 mL of water and stirred for 10 min. Then 5.43 mL of MPMD (Dytek A, Sigma-Aldrich) were slowly added, and the mixture was stirred for 10 min. Finally 0.21 g of TEOS was added. The final mixture was stirred for 30 min, transferred to a 23 mL Teflon-lined Parr autoclave, and heated at 170°C under autogenous pressure for 7 days. A typical molar ratio is GeO$_2$/H$_2$O/MPMD/TEOS = 1:17:4:0.1. The final product was colourless needle-like crystal aggregates, which were filtered, washed with deionized water and acetone, and finally dried in air at room temperature.

(11) Single crystal X-ray diffraction data were collected on an MarCCD at 297 K using a synchrotron radiation ($\lambda = 0.907$Å) at the Beamline I911: 5, Max Lab, Lund University, Sweden. Crystal data for SU-61: orthorhombic, space group *Cmcm*, $a = 34.476(3)$ Å, $b = 19.8768(17)$ Å, $c = 14.8594(8)$ Å, $V = 10183(2)$ Å^3. $2 \times 15 \times 100$ μm^3. A total of 59 924 reflections, of which 4827 are unique, were collected in the region 6.82° $< \theta < 33.12°$. Numerical absorption correction was applied. $R_{int} = 0.1543$, $R_1 = 0.0563$ for reflections with $I > 2\sigma(I)$ and 0.0701 for all reflections, $wR = 0.1590$.

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