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Design of Open-Framework Germanates by Combining Different Building Units

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Introduction

Design of open-framework oxide materials with ever-increasing pore size and decreasing framework density has been an interesting and challenging research field in chemistry, because of the important applications of these materials in separation and catalysis. Férey, O'Keeffe, and Yaghi have brought up a new concept of designing solids from molecular building units.[1] This concept is particularly useful for open-framework germanates, since germanium can be four- (tetrahedral), five- (square pyramidal or trigonal bipyramidal) and six- (octahedral) coordinated to oxygen to form well-defined cluster building units of a number of such Ge−O coordination polyhedra.[2−4] Typical cluster building units in germanates are $Ge_7O_{17}X_2$ (X = OH, F) (Ge_7)[2] and $Ge_9O_{22}X_4$ (Ge_9)[3], and they have been found in many germanate structures.[2−3] These clusters are much larger than building units found in other systems and can be used to build open-framework structures with extra-large pores and very low framework density, as predicted by Férey in terms of scale chemistry.[1] For example, different arrangements of the $Ge_7O_{17}F_2$ clusters resulted in ASU-12 with 3D interconnected 8-, 10-, and 16-ring channels[2a] and ASU-16 (also SU-12) with 24-ring channel.[2c,2e] Another example of a 24-ring germanate is FDU-4,[3g] built by pure corner-sharing $Ge_9O_{18}(OH)_4$ clusters. Recently we discovered a new cluster $Ge_{10}O_{24}X_3(Ge_{10})$ that yielded the 3D germanate structure SU-M with the lowest framework density of any inorganic material and 30-ring channels and pores extending to the mesoporous range (>20 Å).[4] If these different clusters could be combined into the same framework structure in a synthesis, we would expect much more diversity of the structures, especially those with very open frameworks and extra-large pores. However, there is only one example of open-frameworks containing more than one type of large clusters, namely SU-MB containing Ge_{10} and Ge_7 clusters,[4] where the Ge_7 clusters did not participate in building the open-framework but acted as pore-fillers to block one of the two gyroidal channels in SU-M. Here we present two germanates, denoted as SU-8 and SU-44, that are built from two different type of large clusters Ge_7 and Ge_9.

SU-8 and SU-44 were obtained hydrothermally from similar synthesis conditions as for synthesising SU-M and SU-MB, using the same structure-directing agent MPMD.[5] SU-44, but not SU-8, was synthesized in the presence of hydrofluoric acid. Both structures were determined from single-crystal X-ray diffraction.[6−7] SU-8 and SU-44 are 3D frameworks formed by GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra. With exceptions of some single GeO_2X_2 tetrahedra, the entire frameworks of both structures are built from the Ge_9 and Ge_7 clusters. These two types of clusters are structurally related, as shown in Figure 1.

The Ge_9 cluster is similar to those found in many germanate compounds.[3] One tetrahedral pair and one pair of trigonal bipyramids are connected by oxygen bridging to form a four-ring unit.

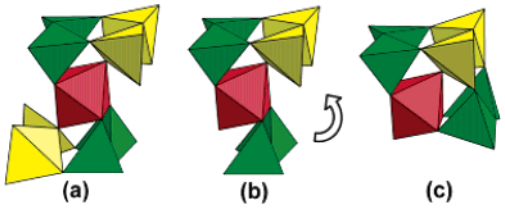

Figure 1. Schematic drawing of a Ge_9 cluster (a) transferring to a Ge_7 cluster (c) by removing one trigonal pyramidal pair in (a) and rotating the tetrahedral pair (b). GeO_6 is in red, GeO_4X in yellow, and GeO_4 in green.

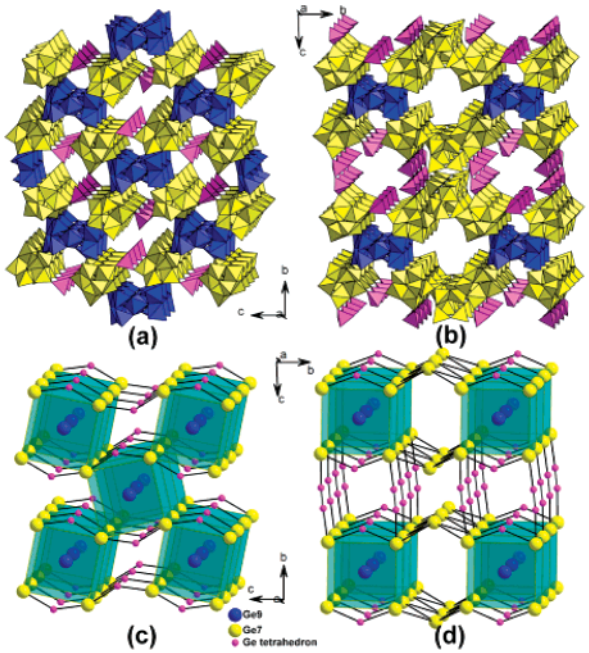

Figure 2. (a,b) Polyhedral presentation and (c,d) packing of the PBCCAs viewed along the *a*-axis for (a,c) SU-8 and (b,d) SU-44. The Ge_9 and Ge_7 clusters GeO_2X_2 tetrahedra are in blue, yellow, and purple, respectively.

Two such four-ring units are connected via an octahedron by corner-sharing to form a body-centered parallelepiped Ge_9 (Figure 1a). The two four-ring units are related by an inversion center, which is at the Ge position of the octahedron. An ideal Ge_9 cluster has the point group *2/m*. Each trigonal bipyramid has one terminal atom, and it can be either a hydroxyl group or a fluorine atom.

The Ge_7 cluster (Figure 1c) can be derived from the Ge_9 cluster by removing one of the two trigonal bipyramidal pairs in the Ge_9 cluster (Figure 1a). The tetrahedral pair connected to the removed trigonal bipyramidal pair is then rotated toward the other trigonal bipyramidal pair (Figure 1b) and linked to it by corner sharing (Figure 1c). The point group of Ge_7 cluster is *m*.

In framework structures formed by pure Ge_9 clusters, the Ge_9 clusters are often connected to form a pseudo-body-centered cluster aggregate (PBCCA).[3a,b,d,f,i,j] Each Ge_9 cluster is linked to eight other

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Ge_9 clusters through eight of its vertices (Figure 1a), one from each tetrahedron or trigonal bipyramid. The PBCCAs are arranged in a primitive manner and linked together by sharing the Ge_9 clusters to form 3D structures with only small 8- and 10-ring channels. The lack of structure diversity of these frameworks is due to the unique geometry of the Ge_9 clusters. Different framework structures may be formed if other clusters with different geometry and containing different number of vertices, for example the Ge_7 clusters can be incorporated. One such possibility could be to replace the Ge_9 clusters at the eight vertices of the PBCCA by Ge_7 clusters. This is what we discovered in the structures of SU-8 and SU-44, which are built mainly by PBCCAs with one Ge_9 cluster at the body-center and eight Ge_7 clusters at the vertices.

In SU-8, the PBCCAs are arranged in a centered manner in the *bc* plane and linked together by sharing the Ge_7 clusters to form a framework layer. The Ge_7 clusters are oriented in a *zigzag* way along the *c*-axis and further connected via additional bridging tetrahedra, $GeO_2(OH)_2$ (Figure 2a). The framework layers are stacked along the *a*-axis by sharing the Ge_7 clusters forming a 3D framework with 8- and 16-ring channels along the *a*-axis, 8-ring channels along the *b*-axis, and 8- and 10-ring channels along the *c*-axis. The free diameter of the 16-ring is 9.92 × 8.61 Å. The framework density is 11.5 Ge-atoms per 1000 Å.[3]

The PBCCA formed by one Ge_9 cluster and eight Ge_7 clusters is also present in SU-44 (Figure 2b). They are arranged in a primitive manner in the *bc* plane and linked together in the [010] direction via additional Ge_7 clusters and in the [001] direction via a pair of GeO_2X_2 tetrahedra to form a framework layer. The framework layers are stacked together along the *a*-axis by sharing the Ge_7 clusters. The final 3D framework contains 8-, 14-, 16-, and 18-rings along the *a*-axis, 8-, 10- and 18-ring channels along the *b*-axis, and 8- and 10-ring channels along the *c*-axis. The free diameters are 7.88 × 9.53 Å for the 14-ring and 10.71 × 7.94 Å for the 16-ring. The framework density is 10.2 Ge-atoms per 1000 Å.[3] The Ge_7 to Ge_9 ratios in SU-8 and SU-44 are very different, 2:1 and 6:1, respectively.

The presence of the two different clusters Ge_7 and Ge_9 in both SU-8 and SU-44 may be due to the similar synthesis conditions.[5] The common "building brick" of the two structures is the PBCCA, as illustrated in Figure 2c,d. The arrangement of the PBCCAs is pseudo-base-centered (related by a 2_1-screw axis along the *b*-axis) for SU-8 (Figure 2c) and primitive for SU-44 (Figure 2d). SU-44 can be considered as a modified SU-8, where every second PBCCA in SU-8 is replaced by two Ge_7 clusters and two pairs of GeO_2X_2 tetrahedra. The tetrahedral pair in SU-44 is disordered and occupies only 60% of the sites.

It is noted that the bridging tetrahedra that connect two Ge_7 clusters are arranged in the same way in both structures, stabilizing the PBCCAs. We also note that the bridging tetrahedra never connect directly to the tetrahedra within the Ge_7 clusters.

The concept of using scale chemistry and building units to design new open-frameworks[1b,c] can be extended from one building unit to two or more building units, as in the case of SU-8 and SU-44. If the octahedron in the Ge_9 cluster is replaced by a Ge_9 cluster and the other eight polyhedra are replaced by Ge_7 clusters, a larger building unit, namely the PBCCA unit, is formed. An A-centered arrangement of the PBCCA units results in the structure of SU-8 while a primitive arrangement results in the structure of SU-44. For SU-44, additional small "glue" units are needed to make the structure stable.

In situ X-ray powder diffraction showed that SU-8 was thermally stable up to 260 °C, while SU-44 transferred to a new phase at 200 °C and became amorphous at 250 °C.

SU-8 and SU-44 are the first examples of open-frameworks built by different large cluster building units, Ge_7 and Ge_9. We have shown that it is possible to incorporate more than one type of clusters into the same framework. A combination of different types of clusters provides new possibilities of designing more exotic frameworks with extra-large pores.

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Supporting Information Available: Structure and XRD patterns and full X-ray crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) SU-8 and SU-44 were synthesized using the same structure-directing agent as for synthesizing SU-M,[4] from a mixture of GeO_2, H_2O, and 2-methylpentamethylenediamine (MPMD) with the molar ratio of 1:40−46:10−12. In addition, hydrofluoric acid with a molar ratio of GeO_2/HF = 1:1.26 was added for the synthesis of SU-44. The final solutions were transferred to 23 ml Teflon-lined Parr autoclaves and heated under autogenous pressure at 165 °C for 21 days for SU-8 and 170 °C for 7 days for SU-44. The final products for both SU-8 and SU-44 were colorless needle-crystal aggregates. The crystals were filtered, washed first with deionized water and then with acetone, and finally dried in air at room temperature. Both samples were characterized by scanning electron microscopy (SEM), X-ray powder diffraction (XRPD), and CHN analysis. Single crystal X-ray diffraction data for SU-8 were collected at 170 K, on a STOE IPDS diffractometer equipped with an image plate system, using graphite-monochromatized Mo Kα radiation from a rotating anode. For SU-44, single crystal X-ray diffraction data were collected on a MarCCD at 297 K with a synchrotron radiation at the Beam line I911, Max Lab, Lund University, Sweden.

(6) Crystal data for SU-8: monoclinic, space group $P2_1/c$, a = 12.075(4) Å, b = 19.235(6) Å, c = 18.720(6) Å, β = 92.72(4)°, V = 4343(2) Å^3; 50 × 60 × 150 μm^3. A total of 34 095 reflections, of which 8327 are unique, were collected in the region 4.09° < θ < 25.94° (λ = 0.71073 Å). Numerical absorption correction was applied. R_{int} = 0.1356, R1 = 0.0479 for reflections with $I > 2\sigma(I)$ and 0.0951 for all reflections, wR = 0.0816.

(7) Crystal data for SU-44: triclinic, space group $P1$, a = 11.9831(7) Å, b = 20.1886(12) Å, c = 22.2361(14) Å, α = 88.240(2)°, β = 89.308(3)°, γ = 90.352(2)°, V = 5376.4(6) Å^3; 10 × 10 × 60 μm^3. A total of 34 262 reflections, of which 19131 were unique, were collected in the region 3.43° < θ < 34.53° (λ = 0.907 Å). Numerical absorption correction was applied. R_{int} = 0.0871. R_1 = 0.0788 for reflections with $I > 2\sigma(I)$ and 0.1093 for all reflections, wR = 0.2413.

(8) Anal. Calcd for $|C_6H_{16}N_2H_2]_5|[Ge_9O_{18}(OH)_4][Ge_7O_{15}(OH)]_2[GeO(OH)_2]_2$ (SU-8): C, 10.7; N, 4.1; H, 3.0%. Found: C, 11.0; N, 4.2; H 3.1%.

(9) Anal. Calcd for $|C_6H_{16}N_2H_2]_{10}|[Ge_9O_{18}X_4][Ge_7O_{15}X_2]_6[GeOX_2]_{2.85}$ (SU-44): C, 10.58; N, 4.11; H, 3.11%. Found: C, 10.7; N 4.2; H 3.1%.

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