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A Crystalline Germanate with Mesoporous 30-Ring Channels

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The design and synthesis of crystalline open-framework materials with increasing pore size is of great importance because of their wide range of applications in adsorption, separation, and catalysis.[1] Open-framework structures with extra-large pores are often found in phosphates,[2] phosphites,[3] and germanates.[4] Among all these extra-large porous compounds, open-framework germanates are of great interest, because of their unique structural features.[5] In general, germanium can be four-, five-, or six-coordinated to oxygen atoms to form well-defined cluster-building units.[6−8] Typical clusters are Ge_7X_{19} (Ge_7),[4a,b,6] Ge_9X_{26-m} (Ge_9),[4c,7] and $Ge_{10}X_{27}$ (Ge_{10})[4e,f,8] clusters (X = O, OH, F; m = 0−1). These large Ge-X cluster-building units can be linked to each other through O atoms to form various open-framework structures with large pore sizes and low framework densities as predicted by G. Férey based on "Scale Chemistry".[9] For example, ASU-16[4a] and SU-12[4b] with 24-ring channels are built from Ge_7 cluster-building units. FDU-4[4c] with 24-ring channels is built from Ge_9 clusters. SU-M[4e] with the largest pore of mesoporous 30-ring channels is built from Ge_{10} clusters. Most of the germanate structures are made of only one type of Ge−X clusters. It is believed that the combination of different types of cluster-building units in the framework can lead to an even richer structural diversity. So far, there are only three reported germanates containing different cluster-building units. SU-MB with 30-ring channels is built from Ge_{10} and Ge_7 clusters;[4e] SU-8 with 16-ring channels and SU-44 with 18-ring channels are both made of the mixture of Ge_7 and Ge_9 clusters.[10]

Herein, we present a novel germanate oxide JLG-12[11] containing 30-ring channels and built from $Ge_7O_{14}X_3$ (Ge_7) and $Ge_9O_{18}X_4$ (Ge_9) clusters. JLG-12 was prepared by the solvothermal reaction of a mixture of GeO_2, H_2O, 2-methylpentamethylenediamine (MPMD), 1,2-diaminopropane (1,2-PDA), and HF (40%).[12]

JLG-12 crystallizes in the monoclinic space group $C2/m$ with a = 46.377 (9) Å, b = 26.689 (5) Å, c = 12.107 (2) Å, β = 92.84 (3)°.[13] The framework is made of strict alternation of Ge_7 and Ge_9 clusters. Ge_7 clusters possess two sets of nonequivalent symmetry, one with Cs symmetry, and the other with $C1$ symmetry. Each Ge_7 cluster consists of one GeO_5X octahedron, two GeO_4X trigonal bipyramids, and four GeO_4 tetrahedra. The oxygen atom in the center of the Ge_7 cluster is tricoordinated to one GeO_5X and two GeO_4X polyhedra. Ge_9 clusters in JLG-12 possess two sets of nonequivalent symmetry, one with $C2h$ symmetry and the other with Ci symmetry. Each Ge_9 cluster consists of one GeO_6 octahedron, four GeO_4X trigonal bipyramids, and four GeO_4 tetrahedra. The GeO_6 octahedron is at the center of the Ge_9 cluster and connects with the other eight polyhedra through doubly and triply bridging oxygen atoms to yield a body-centered parallel-piped Ge_9 cluster. The eight polyhedra are related by an inversion center, which is at the position of the GeO_6 octahedron. The terminal group of each trigonal bipyramid or octahedron in JLG-12 can be either a hydroxy group or fluorine atom that is difficult to distinguish from X-ray diffraction alone.

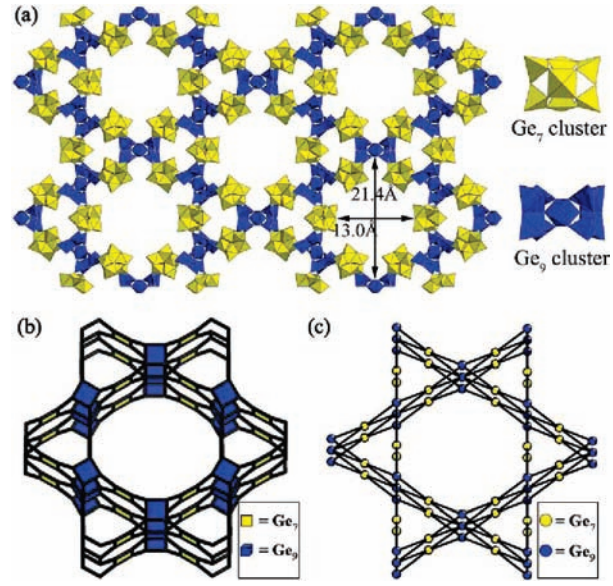

Figure 1. (a) Framework structure of JLG-12 viewed along the [001] direction. (b,c) The 3-D framework of JLG-12 interpreted as a 3-D net structure. (b) The **csq-a** net. (c) The **csq** net. The Ge_7 and Ge_9 clusters are presented in yellow and blue, respectively. The partially occupied GeX_2 moieties are not shown for clarity.

In the three-dimensional structure of JLG-12, each Ge_7 cluster connects with four neighboring Ge_9 clusters through its four GeO_4 tetrahedra, and each Ge_9 cluster connects with eight neighboring Ge_7 clusters through its four GeO_4X trigonal bipyramids and four GeO_4 tetrahedra. Such a connection gives rise to a three-dimensional open framework with parallel 30- and 12-ring channels running along the [001] direction (Figure 1a). The free diameters are 13.0 × 21.4 Å^2 for the 30-ring channel, which is comparable to those of 30-rings (10.0 × 22.4 Å^2) in SU-M. The Ge_7 to Ge_9 ratio is 2:1. The framework density (FD) of JLG-12 is 9.3 Ge atoms per 1000 Å^3, which is one of the lowest among the known open-framework materials. The accessible void volume of the 30-ring channel in JLG-12 is 8727.2 Å^3, which occupies 58% of the whole unit cell volume. According to the CHN and TG analysis, there should be 30 diprotonated MPMD molecules located in the channels of JLG-12. However, these MPMD molecules are highly disordered and could not be located unambiguously. Besides, additional partially occupied GeX_2 groups with an occupancy of 43.2% can be found inside the 30-ring channels.

The three-dimensional framework of JLG-12 can be interpreted as a 3-D net structure. If all the GeO_4 tetrahedra in the Ge_7 and Ge_9 clusters and the GeO_4X trigonal bipyramids in the Ge_9 clusters

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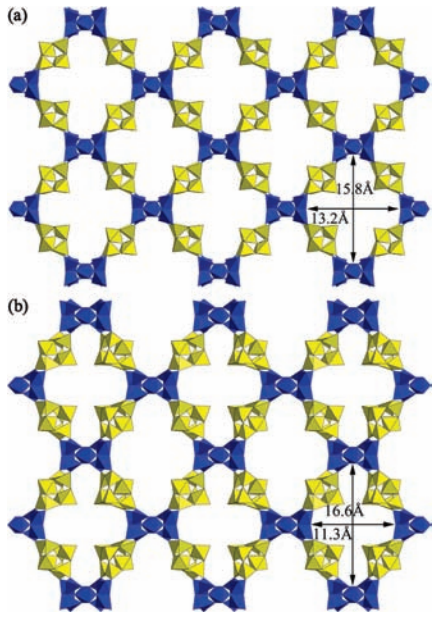

Figure 2. Hypothetical germanate frameworks. (a) The **scu-1**; (b) The **scu-2** viewed along the [001] direction.

are identified as vertices, the framework of JLG-12 will be reduced into a 3,4-heterocoordinated **csq-a** net[14] (Figure 1b). If we take the whole Ge_7 and Ge_9 clusters as vertices, the framework of JLG-12 will be further reduced into a 4,8-heterocoordinated **csq** net[14] (Figure 1c). On the other hand, the framework of JLG-12 can be considered as being constructed from introducing different cluster building units, Ge_7 and Ge_9, into a 3-D net, i.e., **csq-a** or **csq**. We, therefore, expect that, by introducing Ge_7 and Ge_9 clusters into other nets, many more open-framework germanate structures could be predicted. Figure 2 shows two hypothetical germanate frameworks generated by introducing Ge_7 and Ge_9 clusters into a 4,8-heterocoordinated **scu** net.[15] The hypothetical framework **scu-1** is in space group *Cm* with $a = 22.7443$ Å, $b = 21.0824$ Å, $c = 10.3216$ Å, $\beta = 96.828°$ and has 22-ring channels running along the [001] direction, 10-ring channels along the [010] and [110] directions, and 8-ring channels running along the [100] direction (Figure 2a). The 22-ring channel has free diameters of 13.2×15.8 Å^2, and the total accessible void volume of **scu-1** is 2943.8 Å^3, which occupies 60% of the whole unit cell. The hypothetical framework **scu-2** is found in space group *P*2/*m* with $a = 20.9012$ Å, $b = 21.9114$ Å, $c = 9.7874$ Å, $\beta = 93.2967°$. Similar to **scu-1**, the framework of **scu-2** has intersecting 22-, 10-, and 8-ring channels (Figure 2b). The 22-ring channel in **scu-2** has free diameters of 11.3×16.6 Å^2, and the total accessible void volume of **scu-2** is 2478.6 Å^3, which occupies 55% of the whole unit cell. Although these two hypothetical structures are generated using the same **scu** net, the orientations of Ge_7 clusters are different. Compared to **scu-1**, half of the Ge_7 clusters in **scu-2** are rotated by 180°, which leads to different pore geometries and symmetries.

In summary, a novel open-framework germanate JLG-12 with a mesoporous pore size has been prepared under solvothermal conditions. It consists of the largest 30-ring channels and is built from two types of cluster-building units, Ge_7 and Ge_9 clusters. The framework can be described as a 3-D net structure and viewed by introducing the Ge_7 and Ge_9 clusters into the **csq-a** or **csq** net. Many new extra-large pore open-framework germanates could be designed by using the powerful concept of "Scale Chemistry". Further development of strategies to synthesize the predicted hypothetical structures, in particular those with mesoporous channels, is of considerable interest.

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Supporting Information Available: Table of crystal data and structure refinement for JLG-12. Figures of XRD patterns, TG curve, Infrared spectrum. An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) JLG-12: $|C_6N_2H_{18}|_{30}[Ge_9O_{18}X_4]_6[Ge_7O_{14}X_3]_4[Ge_7O_{14.42}X_{2.58}]_8[GeX_2]_{1.73}$ (X = OH, F). Calcd (wt%): C, 11.27; H, 3.15; N, 4.38; TG, 24.10. Found (wt%): C, 12.17; H, 3.20; N, 4.66; TG, 23.98.

(12) JLG-12 was synthesized under solvothermal conditions. Typically, GeO_2 (0.210 g) was dispersed in a mixture of H_2O (1.0 mL) and 2-methylpentamethylenediamine (MPMD, Dytel A, Sigma-Aldrich, 5.0 mL) with constant stirring. Then, 1,2-diaminopropane (1,2-PDA, 1.0 mL) and HF (40 wt %, 0.12 mL) were added to this mixture. A homogeneous gel was formed after stirring for ~2 h. The gel was finally transferred to a 15-mL Teflon-lined stainless-steel autoclave and heated at 170°C for 12 days under static conditions. Colorless needle-shaped single crystals of JLG-12 were separated by filtration, washed with distilled water, and then dried in air. JLG-12 can also be obtained in the absence of 1,2-PDA. The addition of 1,2-PDA favored the formation of larger single crystals.

(13) Crystal data for JLG-12: monoclinic, space group *C*2/*m* (no. 12), with $a = 46.377$ (9) Å, $b = 26.689$ (5) Å, $c = 12.107$ (2) Å, $\beta = 92.84$ (3)°, $V = 14967(5)$ Å^3, $Z = 1$, $50 \times 20 \times 20$ μm^3. A total of 35 786 reflections were collected in the region $2.22° < \theta < 24.50°$, of which 12 325 were unique ($\lambda = 0.710\,73$ Å). $R_{int} = 0.1629$, $R_1 = 0.0938$ for reflections with $I > 2\sigma(I)$ and 0.1436 for all reflections.

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