DOI: 10.1002/ejic.201000363

Germanate Frameworks Constructed from Oxo Germanium Cluster Building Units

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Keywords: Microporous materials / Open frameworks / Germanium / Cluster compounds / Structure elucidation

This article describes the recent research progress in the field of crystalline germanate frameworks with oxo germanium clusters as building units. By using different amine molecules or transition-metal complexes as the structure-directing agents, new oxo germanium clusters, such as Ge_7, Ge_8, Ge_9, Ge_{10}, and $Ni@Ge_{14}$ units, have been prepared and organized into extended frameworks with chain-like, tubular, layered, slab-like, and three-dimensional structures. The combination of different types of oxo germanium clusters in the same crystalline framework provides an additional way to tune the framework structures. Besides their rich structural chemistry, the germanate frameworks exhibit interesting properties including ion-exchange, microporosity, and thermal stability, suggesting their potential application in molecular sieving and catalysis.

1. Introduction

Microporous and open-framework inorganic solids have been extensively studied because of their rich structural chemistry and potential applications in catalysis, separation, and ion-exchange.[1–3] Zeolitic aluminosilicates represent the most well-known family of such materials with pore size below 20 Å. Traditionally, zeolites are constructed from corner-sharing TO_4 tetrahedra (T = Si and Al) to form three-dimensional structures with open channels or cages.[4,5] The discovery of aluminophosphate molecular sieves by Flanigen and co-workers in 1982 opened the gates to synthesize new microporous materials with framework building elements other than Al and Si.[6] As the analogue of silicon, germanium is of particular interest in the construction of new framework structures for several reasons. First, Ge–O bond lengths in open-framework germanates are significantly larger than Si–O bond lengths in zeolite structures, which favors the presence of smaller Ge–O–Ge angles in germanate frameworks.[7] The typical value for the Ge–O–Ge angle in germanates is about 130°, which is much smaller than the typical T–O–T angle (about 145°) in zeolites. This geometrical factor is desirable for the formation

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of three-membered rings, which could lead to highly open frameworks with low framework density.[8] Second, unlike silicon that is usually tetrahedrally coordinated, germanium may be surrounded by four, five, or six oxygen atoms as a result of its larger coordination sphere. GeO_4 tetrahedra, GeO_5 square pyramids or trigonal bipyramids, and GeO_6 octahedra have been observed in germanate frameworks. By combining the different polyhedral units in the same crystalline framework, a large number of novel structures can be potentially accessed. On the other hand, the use of structure-directing agents with various charge, size, and shape is particularly effective in assisting the formation of different germanate frameworks. Furthermore, the capacity of germanium to form cluster aggregates with oxygen atoms offers great opportunities for the design and synthesis of open frameworks with large pore sizes as predicted by G. Férey on the basis of "Scale Chemistry".[9,10]

Following the pioneering work reporting the synthesis of an organically templated germanate by Xu and co-workers in 1991,[11] a large number of germanate frameworks with layered and three-dimensional structures have been synthesized and characterized.[12–17] By developing new synthetic strategies, a variety of main group and transition-metal elements have also been incorporated into germanate frameworks during the past years.[18–27] Germanate frameworks frequently consist of oxo germanium clusters as their structural building units. For simplicity, we use general terms such as Ge_7, Ge_8, Ge_9, and Ge_{10} to refer an oxo germanium cluster that contains the specified number of metal ions. These oxo germanium clusters usually occur in covalent germanate frameworks, but examples of oxo germanium clusters with isolated forms are also known.[28,29]

The synthesis of germanium frameworks is seldom carried out with isolated oxo germanium clusters as the starting materials. Instead, dense-phase GeO_2 is always used in the solution-mediated synthesis. The main solvents involved in the syntheses include water, alcohols, pyridine, DMF, amines, or their mixtures. By adding amine or other bases in the solvent, GeO_2 readily undergoes hydration to form a solution, and oxo germanium clusters of various types may exist in this solution. When the solution is heated, the oxo germanium clusters may polymerize and form framework structures under hydro/solvothermal conditions. The role of amine molecules is to direct the formation of open-framework structures. Usually, they are located in the free voids surrounded by the inorganic framework. In some instances, they have also acted as ligands to the germanium atoms in the frameworks.[30,31] To improve the crystallization of germanates, fluoride ions are often used in the syntheses. Besides their well-known mineralizing role, fluoride ions are also found in the coordination sphere of germanium. The presence of fluoride ions in germanate frameworks increases the coordination number of germanium and adds rigidity to the structure through Ge–F–Ge bonds.

This review will focus primarily on the recent advances in the synthesis of germanate frameworks based on oxo germanium clusters. Other relevant reviews are available for different types of open-framework inorganic solids.[32,33] The rich structural chemistry of germanate frameworks will be described along with their interesting properties, such as ion exchange, thermal stability, gas adsorption, and catalysis.

2. Germanate Frameworks Constructed from Ge_7 Clusters

Among various oxo germanium clusters, the Ge_7 cluster has attracted considerable attention because it has several linkage modes to produce framework structures. The oxo germanium cluster consists of seven germanium atoms with mixed coordination environments: four tetrahedral GeO_4, two trigonal bipyramidal GeO_4X (X = F, O), and one octahedral GeO_5X, as shown in Figure 1a, b. One tricoordinate oxygen atom is located at the core of the cluster and links the GeO_5X octahedron and two GeO_4X trigonal bipyramids. There are seven potential connecting sites present in such a cluster, and every polyhedral unit in this cluster can link with other clusters by sharing common oxygen atoms. So far, eight modes of linkage denoted as T^2, T^2P^2, T^4, T^4O, T^4P, T^4P^2, T^4PO, and T^4P^2O (T = tetrahedral, P = trigonal pyramidal, and O = octahedral) have been found in the known germanate frameworks, where T^2 means that a Ge_7 cluster is connected with other building units by sharing two common oxygen vertices coming from two GeO_4 tetrahedra, and other notations can be explained in the same way.

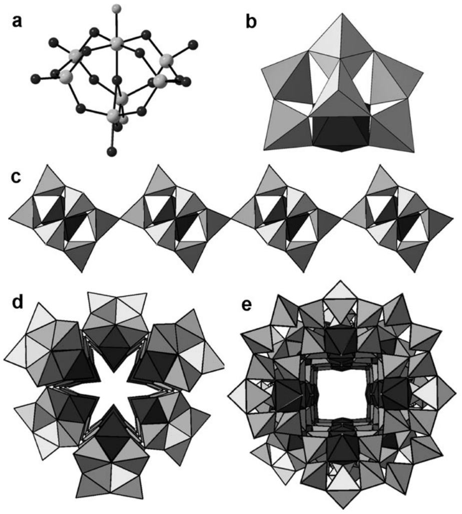

Figure 1. (a) Ball-and-stick and (b) polyhedral representation of the Ge_7 cluster that can be used as the building unit to construct chain-like structure of (c) FJ-6 and tubular structures of (d) JLG-4 and (e) JLG-5.

As shown in Figure 1c, $[Ge_7O_{13}(OH)_2F_3]\cdot Cl\cdot 2[Ni(DIEN)_2]$ (FJ-6) possesses a chain-like structure constructed from Ge_7 clusters.[34,35] Five potential connecting sites in the Ge_7 cluster are blocked by terminal F^- anions and OH^- groups, thus each Ge_7 cluster is connected with two adjacent clusters by the linkage mode T^2. An interesting aspect of FJ-6 is that the inorganic host has a molecular recognizability for the guest metal complexes, as reflected by the fact that *mer*-Ni(DIEN)$_2^{2+}$ and *s-fac*-Ni(DIEN)$_2^{2+}$ complexes are separated in an orderly fashion between the inorganic chains, and no *u-fac*-Ni(DIEN)$_2^{2+}$ complexes are found in the structure. When [Ni(1,2-PDA)$_3$]$^{2+}$ and 3-amino-1-propanol were used as the structure-directing agents, a new germanate [Ni(1,2-PDA)$_3$]$_2$(HOCH$_2$CH$_2$CH$_2$NH$_3$)$_3$(H$_3$O)$_2$[Ge$_7$O$_{14}$X$_3$]$_3$ (X = F, OH; JLG-4) with 12-membered-ring hexagonal tubular channels was synthesized under solvothermal conditions, as shown in Figure 1d.[36] The structure of JLG-4 is constructed from Ge$_7$ clusters by the linkage mode T^4. The H$_3$O$^+$ cations are encapsulated inside the 12-membered-ring tube, and the HOCH$_2$CH$_2$CH$_2$NH$_3^+$ cations are located in the ten-membered-ring windows, the –OH groups pointing into the 12-membered-ring tube. The racemic [Ni(1,2-PDA)$_3$]$^{2+}$ cations with Δ- and Λ-configurations are accommodated among individual inorganic tubes. Another tubular germanate with 12-membered-ring channels is [(C$_5$N$_2$H$_{14}$)$_4$(C$_5$N$_2$H$_{13}$)(H$_2$O)$_4$][Ge$_7$O$_{12}$O$_{4/2}$(OH)F$_2$][Ge$_7$O$_{12}$O$_{5/2}$(OH)F]$_2$[GeO$_{2/2}$(OH)$_2$] (JLG-5).[37] As shown in Figure 1e, the structure of JLG-5 is constructed from Ge$_7$ clusters by the linkage modes T^4 and T^{4}P. Remarkably, twelve Ge$_7$ clusters in the structure are linked through their common oxygen vertices to form a large 6^{8}12^6 cage with the free diameters 6.4 × 7.0 × 7.0 Å. The 6^{8}12^6 cage can be easily identified as a cuboctahedron with each of its 12 vertices decorated by a four-connected Ge$_7$ cluster. Inside the nanosized cage, there is a unique hydrogen-bonded (H$_2$O)$_{16}$ cluster, which may play an important structure-directing role in the formation of such 6^{8}12^6 cages.

The Ge$_7$ cluster is also a useful building unit to construct layered structures. Generally, every Ge$_7$ cluster is connected with four adjacent Ge$_7$ clusters by the linkage mode T^4 to form a layered structure with a 4^4 grid topology. Interestingly, the layered structure can exhibit two types of pore apertures as a result of the different arrangements of Ge$_7$ clusters in the 4^4 grid topology. The type I pore apertures have 8- and 12-membered-ring windows, as seen in Figure 2a. This kind of layered structure has been found in several germanates, including Ge$_7$O$_{14}$X$_3$·[H$_2$DACH]$_{1.5}$·2H$_2$O (ASU-20-DACH),[38] Ge$_7$O$_{14}$X$_3$·[H$_2$DAPe]$_{1.5}$·H$_2$O (ASU-20-DAPe),[38] [C$_4$N$_3$H$_{15}$]$_{1.5}$[Ge$_7$O$_{14}$X$_3$]·H$_2$O (SU-22),[39] and. Ge$_7$O$_{14}$F$_3$·0.5 [In(DIEN)$_2$]·0.5H$_3$DIEN.[40] The type II pore apertures have ten-membered-ring windows, as found in a layered germanate [C$_7$N$_2$H$_{19}$][C$_7$N$_2$H$_{20}$][Ge$_7$O$_{14}$X$_3$][GeO$_2$]$_{0.2}$·H$_2$O (SU-23, Figure 2b).[39] It should be noted that, when two type I germanate layers are connected by additional GeO$_2$X$_2$ tetrahedra, a slab-like germanate, Ge$_{14}$O$_{29}$X$_4$·[GeOX$_2$]·[H$_2$DAB]·3.8H$_2$O (ASU-19), with big cavities within its double-layered structure can be generated.[38]

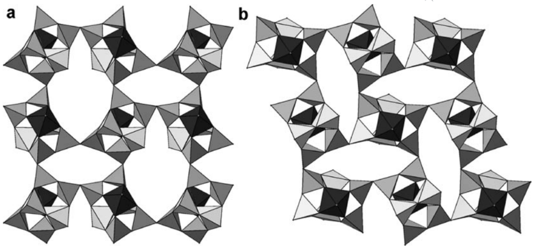

Figure 2. The Ge$_7$ cluster can be arranged in a 4^4 grid topology to form (a) a layered structure with 8-membered-ring and 12-membered-ring windows or (b) a layered structure with 10-membered-ring windows.

The most striking structural feature of germanates constructed from Ge$_7$ clusters is the presence of extra-large channels. As shown in Figure 3a, Ge$_7$O$_{14.5}$F$_2$·[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$ (ASU-12) has a three-dimensional inorganic framework with 16-membered-ring channels delimited by six Ge$_7$ clusters.[41] The protonated DMA cations in the channels can be exchanged by a wide variety of inorganic cations such as Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Ba^{2+}, Ag$^+$, Cd^{2+}, Pb^{2+}, and Tl$^+$. The Na$^+$ exchange sample exhibits microporous properties with a surface area of 250 m^2/g measured on the basis of a water sorption experiment. By using 1,4-diaminobutane as the structure-directing agent and keeping the synthesis conditions similar, a new three-dimensional germanate, Ge$_{14}$O$_{29}$F$_4$[H$_2$DAB]$_3$[DAB]$_{0.5}$·16H$_2$O (ASU-16), constructed from Ge$_7$ clusters can be prepared.[42] This compound has extra-large 24-membered-ring channels running along the [001] direction, which are delimited by eight Ge$_7$ clusters (Figure 3b). The structure of ASU-16 is quite flexible. The doping of silicon into the framework will change the pore shape from elliptical to circular.[43] The linkage mode of Ge$_7$ clusters in ASU-16 is T^{4}P, which is the same as that in ASU-12. If every Ge$_7$ cluster is described as a 5-connectd node in the network, the structure of ASU-16 is formed from a prismatic stacking of planar 4.8^2 nets along the [010] direction, and the structure of ASU-12 is formed from a prismatic stacking of 6^3 nets along the [010] direction. If Ge$_7$ clusters are connected with each other by additional GeO$_4$ tetrahedra, a new organically templated germanate, Ge$_{10}$O$_{21}$(OH)·N$_4$C$_6$H$_{21}$, with seven-membered-ring channels and pear-shape 7^{8}6^{2}5^{2}4^{4}3^2 cavities can be produced.[44] This complex cavity has internal dimensions of 10 × 8.3 Å, where the triprotonated TREN molecule is hosted.

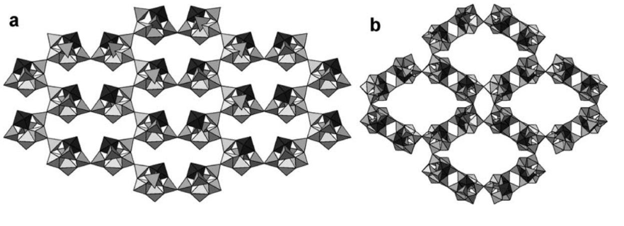

Figure 3. Polyhedral view of the three-dimensional structures of (a) ASU-12 with 16-membered-ring channels and (b) ASU-16 with 24-membered-ring channels.

3. Germanate Frameworks Constructed from Ge$_8$ Clusters

The cuboidal Ge$_8$ cluster, also known as D4R in zeolite chemistry, consists of eight GeO$_4$ tetrahedra linked through their common oxygen vertices. This oxo germanium cluster has been found in isolated form and in several covalent three-dimensional germanates with neutral frameworks (Figure 4a). In $[GeO_2]_{10}\cdot(DMA)(H_2O)$ (ASU-7), the eight corners of each Ge_8 cluster are bridged by additional GeO_2 tetrahedra to form a 4-connected net containing 12-membered-ring channels running along the [001] direction (Figure 4b).[45] ASU-7 has a previously unknown framework topology with the vertex symbols $6\cdot6\cdot6_2\cdot6_2\cdot12_8\cdot12_8$ (vertex 1) and $4\cdot6\cdot4\cdot6\cdot4\cdot6$ (vertex 2 on cube). The 12-membered-ring channel is almost circular with a diameter of 7.0 Å, calculated as the shortest oxygen-to-oxygen distance across the channel. The amine molecules with disorder reside at the center of 12-membered-ring channels and can be removed by calcination without the collapse of the structure. It is believed that the amine molecule does not play a significant role to direct the formation of the ASU-7 framework. They may act more as space-filler during the growth of the structure. Besides DMA, several linear amines, including EN, 1,3-PDA, DIEN, and APEN, can be used to synthesize germanates with ASU-7 topology.[46] By replacing DMA with DABCO in the solvothermal synthesis, other 4-connected open-framework germanates containing Ge_8 cubes, such as $[GeO_2]_{10}\cdot(DABCO)(H_2O)$ (ASU-9),[45] $[(CH_3)_3N]_6[Ge_{32}O_{64}]\cdot(H_2O)_{4.5}$ (FOS-5),[47] and $Ge_{16}O_{32}(OH)^-(C_6H_{12}N_2H)^+(C_6H_{12}N_2)\cdot1.125H_2O$ (ICMM-5),[48] could be generated as the products. The germanate net observed in ASU-9 is analogous to that found in the structure of $AlPO_4$-16. It has an open octadecasil net topology with DABCO molecules in the center of octadecahedra. Different from ASU-7 with high thermal stability, the removal of guest species in ASU-9 will make the structure collapse. The framework of FOS-5 or ICMM-5 shows tetragonal symmetry and has three-dimensional 12-membered-ring channels, which is the polymorph C of beta zeolite. The free diameters of the 12-membered-ring window are 5.8 × 6.0 Å along the [100] and [010] directions and 7.4 Å along the [001] direction. The framework density of FOS-5, defined as the number of tetrahedra per 1000 $Å^3$, is 13.9, which is one of the lowest framework densities known in 4-connected zeolitic structures. A void space analysis with the *PLATON* program indicates that the inorganic framework occupies 26% of the unit cell volume, leaving 74% as "solvent accessible" space.[49] After the removal of the guest molecules by heating to 500 °C, the structure remains stable. Moreover, ICMM-5 exhibits catalytic properties for the Michael addition reaction and the isomerization of epoxides.[48]

The Ge_8 cluster with ring aperture has been found in the open-framework structure of $(C_4N_3H_{15})[(BO_2)_2(GeO_2)_4]$ (Figure 4c).[50,51] Every Ge_8 cluster is connected with four adjacent clusters to produce a layered structure. These germanate layers are further linked by B_2O_7 dimers, forming the three-dimensional network with 8- and 12-membered-ring channels (Figure 4d). The 12-membered-ring channels, delimited by 12 GeO_4 tetrahedra, are elliptical and run along the [100] direction. There are three different 8-membered-ring channels perpendicular to the 12-membered-ring channels, which run along the [010], [01–1], and [011] directions. The shapes of these 8-membered-ring windows are the same, built by two BO_4 and six GeO_4 tetrahedra. The borogermanate has a novel zeolitic framework topology containing three-membered-ring windows. It is noteworthy that the B–O–B connection found in the structure violates Löwenstein's rule.

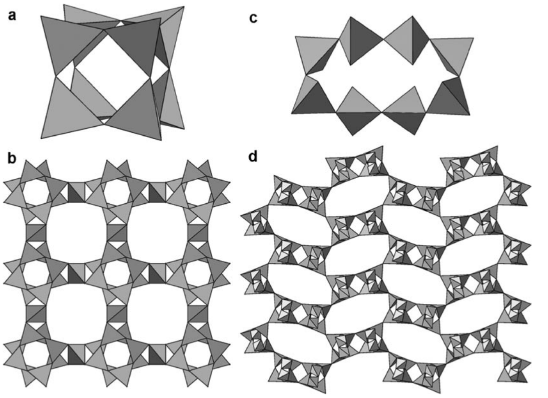

Figure 4. Polyhedral view of (a) the cuboidal Ge_8 cluster and (b) the three-dimensional structures of ASU-7 with cuboidal Ge_8 clusters linked by additional GeO_4 tetrahedra. Polyhedral view of (c) the Ge_8 cluster with ring aperture and (d) the three-dimensional structure of $(C_4N_3H_{15})[(BO_2)_2(GeO_2)_4]$ with germanate layers linked by B_2O_7 dimers.

4. Germanate Frameworks Constructed from Ge_9 Clusters

There are three types of Ge_9 clusters found in open-framework germanates. The Type I Ge_9 cluster consists of one GeO_6 octahedron, two pairs of GeO_5 trigonal bipyramids and two pairs of GeO_4 tetrahedra (Figure 5a). It has a body-centered parallelepiped configuration with the octahedrally coordinated germanium atom at the center. The tetrahedral and trigonal bipyramidal germanium atoms are connected to the centered germanium atom through bi- and tri-oordinated oxygen atoms, respectively. In the structure of $[Ge_9O_{18}(OH)_4]\cdot(H_2PIP)_2(H_2O)_{0.5}$ (ASU-14),[52] every Ge_9

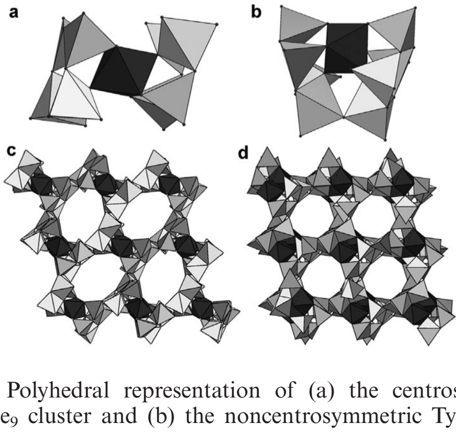

Figure 5. Polyhedral representation of (a) the centrosymmetric Type I Ge_9 cluster and (b) the noncentrosymmetric Type II Ge_9 cluster, which can be used as the building units to construct the three-dimensional structures of (c) ASU-14 and (d) ICMM-6 with eight-, ten- and ten-membered-ring channels.

cluster is connected with eight such units to form a three-dimensional structure with an open polycubane-like topology, which is reminiscent of the porous structure of aluminum cobalt phosphate (ACP-1).[53] Three intersecting channels with ten-, ten-, and eight-membered-ring apertures have been found in the germanate structure (Figure 5c). The germanate framework is flexible and can be synthesized in the presence of different structure-directing agents, such as EN, 1,3-PDA, PIP, APEN, and the $[M_2(EN)_3]^{4+}$ (M = Zn, Cd, Co) cations.[52,54–58] It is noteworthy that $[M_2(EN)_3]^{4+}$ complexes are located within the channels and attach to the inorganic wall through M–O–Ge connectivities.

Similar to the Type I Ge_9 cluster, the Type II Ge_9 cluster also contains one GeO_6 octahedron, two pairs of GeO_5 trigonal bipyramids, and two pairs of GeO_4 tetrahedra (Figure 5b). However, the geometrical arrangements of the pairs of GeO_4 tetrahedra and the pairs of GeO_5 trigonal bipyramids within the parallelepiped Ge_9 cluster are quite different. In the Type I Ge_9 cluster, the pairs are related by an inversion center and sit in a *trans* position, while in the Type II Ge_9 cluster, they sit in a *cis* position. The three-dimensional structures constructed from Type II Ge_9 clusters crystallize in chiral space groups and possess pore openings with ten-, ten-, and eight-membered rings (Figure 5d).[59,60] The chirality of the germanate frameworks may be related to their non-centrosymmetric Ge_9 building unit. In the structure of $Ge_9O_{19}(OH)_2(H_2EN)(EN)_{0.5}H_2O$ (ICMM-6),[60] the diprotonated EN cations are located in the channels and cannot be removed by heating without collapsing the structure.[60] The compound is stable in water and organic solvents and shows catalytic activity for the Michael addition reaction and acetalization of aldehydes.

The Type III Ge_9 cluster consists of one GeO_5 square bipyramid, four GeO_5 trigonal bipyramids, and four GeO_4 tetrahedra (Figure 6a, b). By using isopropylamine as the structure-directing agent, such Ge_9 clusters can be organized into a three-dimensional open-framework structure of $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$.[61] Viewed along the [001] direction, the framework has circular 16-membered-ring channels and elliptical 14-membered-ring channels (Figure 6c). The free diameter of the 16-membered-ring window is 12.6 Å and the free diameter of the 14-membered-ring window is 6.5 × 13.1 Å. The other open-framework germanate constructed from Type III Ge_9 clusters is $[Ge_9O_{17}(OH)_4][N(CH_2CH_2NH_3)_3]_{2/3}[DMF]_{1/6}(H_2O)_{11/3}$ (FDU-4).[62] The structure of this compound is templated by TREN. It has circular 12-membered-ring and 24-membered-ring channels running along the [001] direction (Figure 6d). The free diameter of the 12-membered-ring window is 9.5 Å, and the free diameter of the 24-membered-ring window is 12.7 Å. The two open-framework germanates are constructed from the same Ge_9 clusters; however, as a result of the presence of different structure-directing agents, they possess different framework topologies. If every Ge_9 cluster in the two structures is described as a 6-connected node in the network, the structure of the germanate with 14- and 16-membered-ring channels can be produced from a stacking of planar 4.8^2 nets along the [001] direction and the structure of FDU-4 is generated from a stacking of 6^3 nets along the [001] direction.

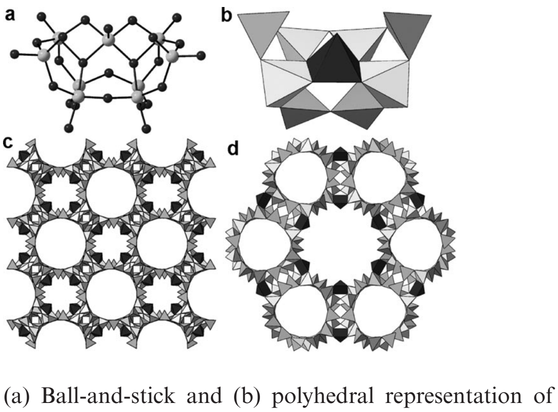

Figure 6. (a) Ball-and-stick and (b) polyhedral representation of the Type III Ge_9 cluster, which can be used as the building unit to construct the three-dimensional structures of (c) $(H_3NC_3H_7)_5(H_3O)[Ge_{18}O_{36}(OH)_6]\cdot 3H_2O$ with 14-membered-ring and 16-membered-ring channels and (d) FDU-4 with 12-membered-ring and 24-membered-ring channels.

5. Germanate Frameworks Constructed from Ge_{10} Clusters

In pure germanate frameworks, the Ge_{10} cluster is the largest structural building unit. It consists of four GeO_6 octahedra and six GeO_4 tetrahedra and has a cubane-like Ge_4O_4 unit at the core (Figure 7a, Figure 7b). When every face of the Ge_4O_4 core is covered by a GeO_4 tetrahedron, a Ge_{10} cluster is formed. Such Ge_{10} clusters have been found in the structure of dense-phase $Na_4Ge_9O_{20}$ (six-membered-ring, FD = 21.6), germanate-type pharmacosiderite (eight-membered-ring, FD = 13.8), and $|(enH_2)_2(H_2O)_{2.3}|[Ge_8O_{17}(OH)_2]$ (ten-membered-ring, FD = 13.4).[63] When additional GeO_2 tetrahedra are connected with Ge_{10} clusters, more open germanate structures can be produced. $Ge_{13}O_{26}(OH)_4[C_6N_2H_{16}](H_2O)_{1.5}$ (ICMM-7, FD = 13.0) is a three-dimensional germanate with interconnected 14-, 12-,

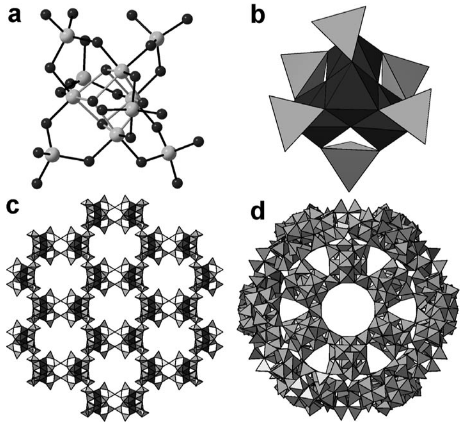

Figure 7. (a) Ball-and-stick and (b) polyhedral representation of the Ge_{10} cluster, which can be used as the building unit to construct the three-dimensional structures of (c) SU-61 with 26-membered-ring channels and (d) SU-M with mesoporous 30-membered-ring channels.

12-, and 8-membered-ring channels.[64] The 14-membered-ring channels run along the [100] direction with a pore size of 14.5 × 8.5 Å. The hydroxy groups point towards the center of the 14-membered-ring channels and line the walls of the channels, which makes the large channels more hydrophilic than other channels. The organic cations located in the 14-membered-ring channels are well ordered because of the presence of extensive host–guest H-bonding interactions. It is noteworthy that 14-membered-ring channels are rare in open-framework inorganic solids. In fact, only five zeolites (CFI, DON, OSO, SFH, and SFN) and one zirconogermanate named ASU-24 with 14-membered-ring channels have been reported.[65]

The substitution of germanium by silicon in the Ge_{10} cluster resulted in the formation of a new open-framework compound, $|C_6H_{16}N_2H_2|_2[Ge_{8.7}Si_{1.3}O_{16}O_{11/2}OH][Ge_{0.71}Si_{0.29}O_{4/2}][Ge_{0.22}Si_{0.78}O_{3/2}OH]_2$ (SU-61, FD = 10.2).[66] The structure of SU-61 contains seven-coordinate (Si, Ge)$_{10}$ clusters located on the nodes of the osf net. Six (Si, Ge)$_{10}$ clusters are linked by additional (Si, Ge)O_4 tetrahedra to form 26-membered-ring channels running along the [001] direction (Figure 7c). The pore size of the 26-membered-ring channel is 13.1 × 17.3 Å. The organic cations within the channels could be partially exchanged by Na^+, K^+, and Cs^+ cations.

So far, the most open structure constructed by Ge_{10} clusters is SU-M, $|(H_2MPMD)_2(H_2O)_x|[Ge_{10}O_{20.5}(OH)_3]$ (FD = 7.1).[67] This compound has mesoporous structure with crystalline pore walls (Figure 7d). Similar to mesoporous MCM-48, SU-M also has the symmetry of *Ia*-3*d*. It can be regarded as the crystalline analogue of MCM-48. Strikingly, SU-M is synthesized under hydrothermal conditions without using surfactants, but with an amine as the structure-direction agent. It has big cavities with inner diameters of 18.6 × 26.2 Å, which represent the largest cavities in open-framework germanates. The big cavity is connected to three other such cavities through 30-membered-ring windows to form two sets of giant gyroidal channels with opposite chirality. The 30-membered-ring window is delimited by ten Ge_{10} clusters and its free diameter is 10.0 × 22.4 Å. Despite the presence of extraframework species, SU-M exhibits permanent porosity with its BET surface area of 214 m^2g^{-1}. Ion-exchange experiments indicate that organic cations in the structure can be completely exchanged by Na^+, K^+, and Cs^+ ions.

6. Germanate Frameworks Constructed from Different Oxo Germanium Clusters

Germanate frameworks usually consist of a specified oxo germanium cluster as the structural building unit. In some instances, different oxo germanium clusters can coexist in a crystalline framework. $|(H_2MPMD)_{5.5}(H_2O)_x|\{[Ge_{10}O_{21}(OH)_2]\cdot[Ge_7O_{14}F_3]\}$ (SU-MB), for example, is a well-known open-framework germanate containing Ge_7 and Ge_{10} clusters.[67] This compound crystallizes in the chiral space group *I*4$_1$32 and can be understood as a chiral derivative of mesoporous SU-M. When one of the two gyroidal channel systems of SU-M is filled with Ge_7 clusters, the mesoporous structure of SU-MB is generated. In fact, the Ge_7 clusters in SU-M do not participate in the construction of the framework structure. They may act more as space-fillers during the growth of the open structure.

Also interesting are $|(C_6H_{16}N_2H_2)_5|[Ge_9O_{18}(OH)_4][Ge_7O_{15}(OH)]_2[GeO(OH)_2]_2$ (SU-8),[68] $|(C_6H_{16}N_2H_2)_{10}|[Ge_9O_{18}X_4][Ge_7O_{15}X_2]_6[GeOX_2]_{2.85}$ (SU-44),[68] and $|(C_6N_2H_{18})_{30}|[Ge_9O_{18}X_4][Ge_7O_{14}X_3]_4[Ge_7O_{14.42}X_{2.58}]_8[GeX_2]_{1.73}$ (JLG-12),[69] The three compounds are synthesized by using the same amine (MPMD) as the structure-directing agent. All of them have three-dimensional structures built from Ge_7 and Type I Ge_9 clusters. Each Ge_9 cluster in the three structures connects with eight neighboring Ge_7 clusters through four GeO_4X trigonal pyramids and four GeO_4 tetrahedra. Each Ge_7 cluster connects with four neighboring Ge_9 clusters in SU-8 and JLG-12, while in SU-44, each Ge_7 cluster connects with two neighboring Ge_9 clusters and two neighboring Ge_7 clusters. The Ge_7-to-Ge_9 ratios in SU-8, SU-44, and JLG-12 are 2:1, 6:1, and 2:1, respectively. The largest pore openings in SU-8, SU-44, and JLG-12 are 16-, 18-, and 30-membered rings, respectively. The pore size of the 30-membered ring in JLG-12 is 13.0 × 21.4 Å, bridging the gap between micro- and mesoporous structures. If Ge_7 and Ge_9 clusters are considered as nodes in the network, the framework of JLG-12 can be reduced into a 4,8-heterocoordinated csq net (Figure 8). By organizing the Ge_7 and Ge_9 clusters into other nets, it is expected that many more open-framework germanate structures may be produced.

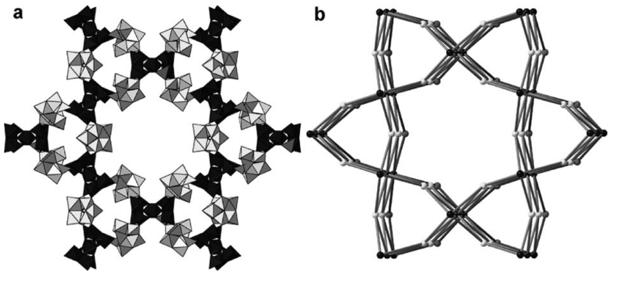

Figure 8. (a) Polyhedral representation of the three-dimensional structure of JLG-12 constructed from Ge_7 and Ge_9 clusters. (b) The structure of JLG-12 has csq topology if Ge_7 and Ge_9 clusters are considered as the nodes in the network.

7. Germanate Frameworks Constructed from M–Ge–O Clusters

To enhance the structural diversity of open-framework germanates and devise new materials with catalytic, magnetic, and photochemical properties, great efforts have been made to introduce transition metals into germanate frameworks. During the course of such investigations, some layered and three-dimensional zirconogermanates have been synthesized and characterized.[65,70–73] A notable example is $Ge_2ZrO_6F_2\cdot(H_2DAB)H_2O$ (ASU-15) with "bow tie" building units.[73] This cluster unit contains four GeO_4 tetrahedra and one ZrO_4F_2 octahedron and plays an important role in achieving two three-membered rings at each vertex of the inorganic framework. It is well known that the presence of three-membered rings in four-connected nets can lead to low framework density and large pore openings. As expected, ASU-15 has a very low framework density with an FD value of 9.1, which is comparable to the value 9.1 for ETS-10. The net of ASU-15 is closely related to that of gismondine if the zirconium atoms are removed from the centers of $ZrGe_4$ clusters and the building units are considered as Ge_4 squares. The organic species in the channels can be ion-exchanged by Na^+ cations. The exchanged solid has a Langmuir surface area of 83.9 m^2/g and can adsorb water and organic vapors such as CH_2Cl_2, CCl_4, and C_6H_{12}. An isostructural niobium germanate, $(C_6H_{18}N_2)\cdot Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$ (NGH-5), was obtained by using DACH as the structure-directing agent.[74] However, as a result of the presence of strong N–H···F hydrogen bonds, the organic cations in NGF-5 could not be ion-exchanged by Na^+, K^+, and Rb^+ ions.

In open-framework germanates, the framework cations are usually connected to each other by T–X–T linkage modes, where T is a cation and X is an anion. $Ni@Ge_{14}O_{24}(OH)_3\cdot 2Ni(L)_3$, (L = EN/1,2-PDA; denoted FJ-1a/FJ-1b) represents the first example of porous materials having T–M–T linkages (where T–M–T = Ge–Ni–Ge).[75] The inorganic framework of this compound is constructed from large $Ni@Ge_{14}$ clusters with one Ni^+ and five Ge^{2+} ions reduced from Ni^{2+} and Ge^{4+} ions by organic species under solvothermal conditions (Figure 9a, b). The Ni^+ ion is located at the core of the cluster and is bonded with five Ge^{2+} ions to yield a trigonal-bipyramidal core. Of the fourteen Ge atoms, five Ge atoms are tetrahedrally coordinated by one μ_5-Ni, and three O atoms and the remaining nine Ge atoms are bonded to four O atoms. Each $Ni@Ge_{14}$ cluster is bridged to six others by sharing common oxygen vertices to yield a three-dimensional framework with 24-membered-ring channels running along the [001] direction (Figure 9c). The 24-membered-ring channels have dimensions of about 8.3 × 13.6 Å and are intersected by two 12-membered-ring channels running along the [100] and [010] directions. Interestingly, the propellane-like shape of the 24-membered-ring channel matches the shape of the $[Ni(L)_3]^{2+}$ complex quite well. FJ-1 has the 4^96^6 framework topology if each $Ni@Ge_{14}$ cluster is considered as a node in the net (Figure 9d). The unique Ge–Ni–Ge linkages in the structure endow the compound with semiconducting properties. The optical absorption data derived from the solid-state diffuse reflectance analysis shows an optical transition with a band gap of 2.6 eV.

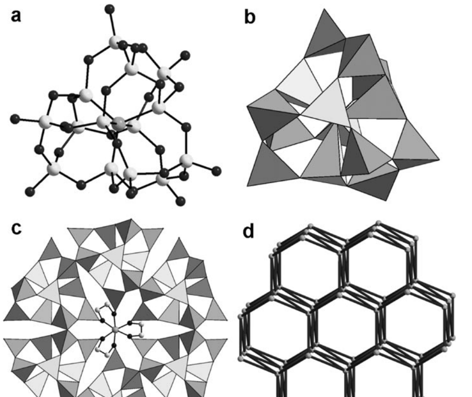

Figure 9. (a) Ball-and-stick and (b) polyhedral representation of the $Ni@Ge_{14}$ cluster, which can be used as the building unit to construct the three-dimensional structures of (c) FJ-1 with (d) 4^96^6 framework topology.

8. Conclusions

In summary, a number of germanate frameworks have been synthesized under hydro/solvothermal conditions. The inorganic frameworks of these compounds are constructed from large oxo germanium clusters and exhibit various structural dimensionalities, such as three-dimensional architectures, two-dimensional layers and slabs, and one-dimensional chains and tubes. The various oxo germanium clusters and their rich connecting modes enable researchers to design and synthesize diverse germanate frameworks by using different structure-directing agents. The pore aperture of open-framework inorganic solids containing oxo germanium clusters ranges from microporous eight-membered rings to mesoporous 30-membered rings, indicating that open-framework germanates should represent a suitable system for exploration of new crystalline porous materials with extra-large channels. With the development of new synthetic strategies and structural concepts, new oxo germanium clusters may be prepared and organized into novel extended frameworks in the near future.

Acknowledgments

We thank for the support of this work by the National Natural Science Foundation of China (Z.-E. L., Grant 20801037), National Natural Science Foundation of China (G.-Y. Y., Grant 20725101, 50872133, 20821061), and the National Program on Key Basic Research Project (973 Program, grant 2006CB932904).

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Received: April 1, 2010