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Host−Guest Symmetry and Charge Matching in Two Germanates with Intersecting Three-Dimensional Channels

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Lately there has been much research directed toward the search for microporous materials in new compositional domains.[1−7] This is, in part, because it is highly possible to obtain framework materials with novel architectures in new compositional domains and because these new materials may possess unique adsorptive and catalytic activities. The type of connectivity among framework polyhedral atoms is closely related to the local bonding geometries such as T−O−T angles (T refers to tetrahedral atoms). Different T atoms have preference for different local geometries, which in turn may lead to a novel framework geometry. For example, the Ge−O−Ge angle (usually less than 130°) is smaller than the typical Si−O−Si angle (about 140°), and some unusual topological nets have been found in germanates while the corresponding silicates have not been discovered.[8−11] By exploring different compositional domains, we will be able to discover new and potentially useful materials and further understand formation mechanism of these extended solids.

In the study of highly charged phosphate-based zeolite-type materials, we have developed synthetic strategies based on the host−guest charge-matching concept.[12−14] Such a concept was later extended to the germanate composition, resulting in the synthesis of a family of alumino- and gallo-germanate zeolite-type materials.[15−18] For tetrahedral phosphate and germanate frameworks, we have also shown that the symmetry of guest molecules can dictate the symmetry of inorganic frameworks. One of the most striking examples is the symmetry reduction of a sodalite cage from cubic all the way down to triclinic when a strong structure-directing agent, diprotonated ethylenediamine, is used.[15] Here, we examine the similar host−guest symmetry matching effect in a different class of germanate open-framework materials that are constructed on the basis of the packing of the cluster units. Two materials reported here have a bcc-packing mode of Ge_9O_{18} cluster units.

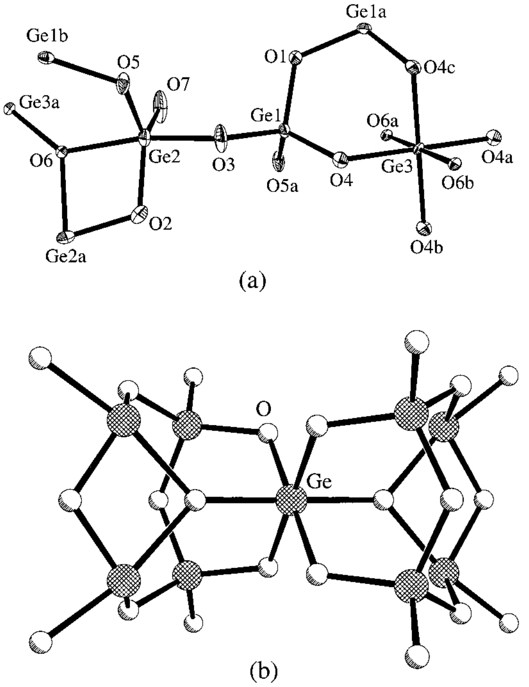

Figure 1. (a) The ORTEP view of coordination environments for Ge and O atoms in UCSB-40. Atoms having "a", "b", or "c" in their labels are symmetry-generated. Of seven unique O atoms, O1 through O5 are bridging atoms between two Ge centers and the O6 site is coordinated to three Ge atoms. The O7 site is a hydroxyl group. The Ge1 site has tetrahedral coordination and the Ge2 site is coordinated to five O atoms, one of which is a OH^-. The Ge3 site is located at the centers of the *ac* plane and the *b* axis with the 2/*m* site symmetry and is symmetry-constrained to adopt the octahedral coordination. (b) The basic building unit in UCSB-40, Ge_9O_{18}. Each oxygen atom bridging between two Ge_9O_{18} clusters is counted as half.

Clear needle-shaped crystals of UCSB-40 were synthesized by stirring a mixture of GeO_2 (1.11 g), $Zn(NO_3)_3 \cdot 6H_2O$ (0.60 g), 1,3-diaminopropane (2.82 g), distilled water (2.02 g), and ethylene glycol (11.06 g) for about 2 h. The mixture had a pH of 11.7 and was subsequently heated at 180 °C for 8 days in a Teflon-coated steel autoclave. Thick plate-shaped crystals of UCSB-41 were synthesized by stirring a mixture of GeO_2 (0.50 g), aluminum isopropoxide (0.22 g), piperazine hexahydrate (6.31 g), pyridine (8.28 g), 49 wt %

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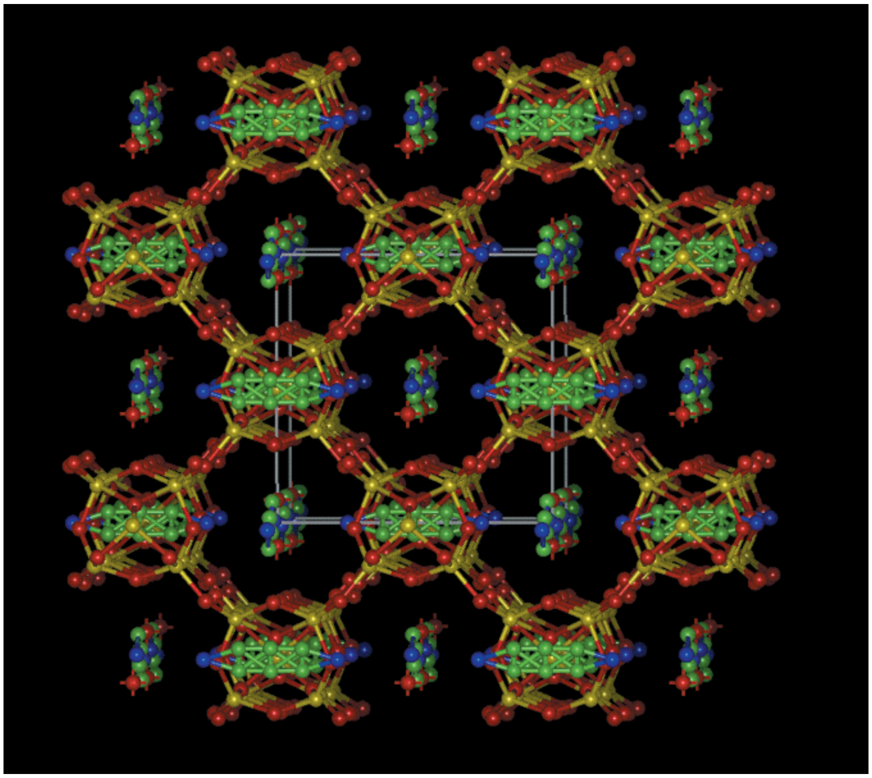

Figure 2. Projections of the three-dimensional framework down the *a* axis in UCSB-40. Colors: red, oxygen; yellow, germanium; green, carbon; blue, nitrogen.

HF (0.28 g), and ethylene glycol (2.24 g) for about 8 h. The mixture had a pH of 11.4 and was subsequently heated at 180 °C for 8 days in a Teflon-coated steel autoclave. Crystal structures of UCSB-40 and UCSB-41 were solved from room-temperature data collected on a Bruker SMART CCD diffractometer.[19]

In UCSB-40, one three-membered ring is formed between two Ge1 tetrahedra and one Ge3 octahedron (Figure 1a). Such a 3-ring is part of a larger cluster, Ge_9O_{18} (Figure 1b). These clusters are located only at the centers of the *ac* plane and the *b* axis and are therefore packed in a body-centered manner with the long axis of each Ge_9O_{18} cluster aligned along the unit cell *a* axis. Each cluster has an octahedral Ge center and at two ends of each cluster, there are eight oxygen atoms (four at each end, Figure 1b), each of which is connected to another Ge_9O_{18} cluster (Figure 2).

UCSB-40 is synthesized in fluoride-free media with 1,3-diaminopropane, whereas UCSB-41 is prepared in the HF/pyridine solution with piperazine. Despite much lower symmetry, UCSB-41 has the same framework topology as UCSB-40. In the germanate system, another example of the formation of the same framework topology from different structure-directing agents is the synthesis of ICMM-2 from $[M(NH_3)_2]^+$ (M = Cu, Ag) [9] and UCSB-46 from methylamine.[17]

UCSB-40 and -41 have the same framework topology as ASU-14.[20] We have shown here that it is possible to synthesize this framework topology in fluoride-free media and with a different structure-directing agent. Also, structure-directing agents in UCSB-41 are completely ordered, so there is no ambiguity with respect to types and locations of extraframework species. In UCSB-41, the symmetry of the inorganic framework is completely determined by ordered diprotonated piperazine molecules, all of which are located at the unit cell inversion centers. In this case, the inversion center of the lattice coincides with the molecular symmetry element (i.e., inversion center) of each individual piperazine molecule. In other words, the condensation of the inorganic framework around guest molecules is dictated by the molecular symmetry of guest molecules. Guest molecules exert their symmetry-templating effect through N—H···O type hydrogen bonding.[21,22]

In comparison, the less rigid 1,3-diaminopropane has a relatively weaker templating effect. The inorganic framework adopts the highest possible symmetry and guest molecules conform to the symmetry of the inorganic framework by adjusting their molecular conformation and adopting multiple orientations. The disorder of amine molecules in UCSB-40 can be easily understood from the symmetry consideration as shown in Figure 3.

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(19) Crystal data for UCSB-40: orthorhombic, space group *Pnnm* (no. 58), $Z = 2$, Mo Kα radiation ($\lambda = 0.71073$ Å), $2\theta_{max} = 50°$, $[Ge_9O_{18}(OH)_4]\cdot 2(NH_3CH_2CH_2CH_2NH_3)\cdot H_2O$, $a = 13.213(1)$ Å, $b = 10.056(1)$ Å, $c = 10.284(1)$ Å, $V = 1366.5(2)$ Å^3, 0.11 × 0.067 × 0.040 mm^3, refinement on F^2, $R(F) = 5.74\%$, $wR(F^2) = 12.0\%$, GOF = 1.35 for 122 parameters and 1093 unique reflections with $I > 2.0\sigma(I)$. Crystal data for UCSB-41: triclinic, space group $P\bar{1}$, $Z = 2$, $2\theta_{max} = 50°$, $[Ge_9O_{18}(OH)_4]\cdot 2R\cdot H_2O$, R = diprotonated piperazine, $a = 10.3439(4)$ Å, $b = 10.3890(4)$ Å, $c = 12.8515(1)$ Å, $\alpha = 90.761(1)°$, $\beta = 90.854(1)°$, $\gamma = 91.250(1)°$, $V = 1380.45(9)$ Å^3, 0.080 × 0.080 × 0.040 mm^3, refinement on F^2, $R(F) = 4.51\%$, $wR(F^2) = 10.4\%$, GOF = 1.31 for 414 parameters and 4274 unique reflections with $I > 2.0\sigma(I)$.

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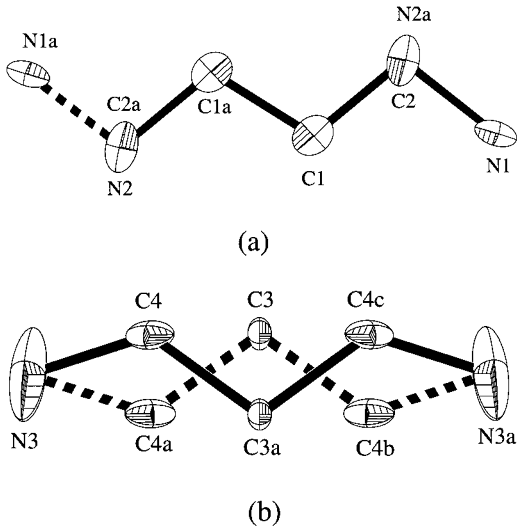

Figure 3. Two crystallographically unique amine molecules in UCSB-40: (a) the 2-fold axis is perpendicular to the molecular plane and (b) the 2-fold is within the molecular plane.

There are two types of diprotonated 1,3-diaminopropane molecules. The type I amine molecules are located at the centers of the *bc* face and the *a* axis with the *2*/*m* site symmetry. All atoms of the amine molecule are within the mirror plane. However, there are still two statistical positions, generated by the 2-fold axis perpendicular to the amine molecular plane (Figure 3). The type II amine molecules also have two different statistical positions. However, its disorder is caused by the 2-fold axis that is within the amine molecular plane (Figure 3). The type II amine molecules are located at the centers of the *ab* plane and the *c* axis. Both types of amine molecules form hydrogen bonds with framework oxygen atoms. The shortest N···O distances are 2.88 Å (type I) and 3.17 Å (type II), respectively. Type II amine molecules also form hydrogen bonds with extraframework water molecules, as discussed below.

In UCSB-40, there is one extraframework water molecule per Ge_9O_{18} cluster. This water molecule statistically occupies two positions related by an inversion center and a separation of 1.74 Å. These two positions are well-defined because water molecules are involved in relatively strong hydrogen bonds as suggested by the short O··· N contact distance of 2.78 Å. Extraframework water molecules in UCSB-41 have similar statistical disorder.

It is of interest to examine various mechanisms by which host−guest charges are matched. Because amine molecules are usually incorporated into the pores in protonated forms, it is thus necessary to examine different ways to generate negative centers surrounding framework polyhedral atom sites. The first mechanism is the incorporation of trivalent cations such as Al^{3+} and Ga^{3+} as shown in UCSB-7-type helical structures.[10] Through such a mechanism, tetrahedral coordination of all Ge sites can be maintained.[15] The second mechanism as found in UCSB-46 is to generate octahedral Ge^{4+} centers without changing the coordination type of oxygen atoms, i.e., all oxygen atoms are bicoordinated as in zeolite-type structures.[17] The third mechanism as found in UCSB-40 and UCSB-41 reported here, is the direct conversion of tetrahedral Ge^{4+} centers to higher coordination by attaching a hydroxyl group. It is noteworthy that unlike in UCSB-46, the octahedral Ge^{4+} in UCSB-40 and UCSB-41 does not serve to generate negative charges on the framework because of the tricoordination of some oxygen atoms.

In conclusion, host−guest symmetry matching is shown here to be an important synthetic parameter that can determine the characteristics of the inorganic framework or guest molecules. Three different mechanisms for host−guest charge matching in germanate-based open-framework materials is also described here. By controlling synthetic conditions that can favor one mechanism over others, it should be feasible to control the coordination of polyhedral atoms and the overall framework topology.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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