Isolation of Germanate Sheets with Three-Membered Rings: A Possible Precursor to Three-Dimensional Zeolite-Type Germanates

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Received September 13, 1999
Revised Manuscript Received October 27, 1999

The designed synthesis of self-organized inorganic and inorganic−organic composite materials is currently one of the most active research areas in solid-state chemistry.[1−5] One important aspect in the synthesis of novel materials is the development of new concepts and techniques to synthesize novel materials previously unattainable by more conventional methods. Compared to the synthesis of many molecular materials, the ability to control structural features of polymeric inorganic or inorganic−organic composite materials is still limited. However, using appropriate strategies, it is possible to design new framework materials, and in some cases, a high degree of structural control can be achieved.[6−10]

The development of new synthetic strategies depends critically on the understanding of formation mechanisms of extended inorganic solids. Unfortunately, the self-assembly process of extended inorganic frameworks is not well understood because it involves a large number of synthetic parameters such as host−guest interactions and solvent effects. Particularly intriguing is the templating effect of molecular templates (sometimes also called structure-directing agents).

Here, we report that by replacing the organic structure-directing agent, methylamine, with K^+ cations in the synthesis of germanates, we can isolate two-dimensional sheets that are building units of three zeolite-type 3D framework materials(UCSB-9, -11, and -46).[11−13] The successful synthesis of this new germanate (denoted as UCSB-9L) demonstrates that organic structure-directing agents may only exhibit their templating effects at a particular stage in the self-assembly process. During the formation of UCSB-9, -11, -46, and -9L, it appears that the condensation process that leads to the construction of two-dimensional sheets is unrelated to the presence of the organic structure-directing agent, methylamine. The templating effect of methylamine may only need to occur during the construction of the three-dimensional framework from two-dimensional sheets.

UCSB-9L was synthesized by heating a mixture of GeO_2 (0.45 g), $Ga(NO_3)_3$ (1.02 g), 8 M KOH (4.11 g), 49% HF (1.03 g), and ethylene glycol (14.76 g) at 180 °C for 8 days in a Teflon-coated steel autoclave. The product consisted of elongated transparent hexagonal plates. X-ray powder diffraction peaks between the 2θ range from 3 to 50° could be indexed using cell parameters derived from single-crystal diffraction, suggesting that no other crystalline phase was present. Qualitative elemental analyses were performed on a JEOL JSM-840A scanning electron microscope equipped with an X-ray energy dispersvie system. In addition to the dominant X-ray spectra lines from Ge and K, there were two distinct peaks. The fluorine peak height was slightly lower than that for the oxygen. The incorporation of F^- was confirmed by single-crystal structure analysis performed on a Bruker SMART CCD diffractometer.[14]

There are three unique germanium sites. Because of the three terminating F^- anions on the Ge1 site (representing 40% of all germanium sites), the Ge1 site is 3-connected to other parts of the layer even though it is octahedrally coordinated. Note that the Ge1 site is not part of the three-membered rings. The Ge2 and Ge3 sites are tetrahedrally coordinated to other parts of the sheet and they form three-membered rings as shown in Figure 1.

UCSB-9L is built from two-dimensional sheets that were previously reported to occur in structures of UCSB-9, -11, and -46. Such a sheet is constructed by linking of a secondary structural building unit denoted as 4=1, first identified in three fibrous mineral zeolites (edingtonite, natrolite, and thomsonite).[15] The 4=1 unit is a group of five tetrahedral atoms (Figure 2). Four of these atoms form a four-membered ring and the fifth one forms a bridge between two nonadjacent tetrahedral atoms of the four-membered ring. These 4=1 units can be joined into layers containing both three- and nine-membered rings (Figure 2). These sheets can then be linked through oxygen bridges to form UCSB-9 or UCSB-11. In UCSB-11, layers are stacked in the eclipsed configuration whereas in UCSB-9, layers are stacked in the staggered configuration.[12] UCSB-46 is formed by conversion of one-ninth of Ge sites from 4-connected into 6-connected polyhedral sites.[13]

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[14] Crystal data for UCSB-9L: $K_4Ge_5O_9F_6(H_2O)$, space group *Pbcn* (no. 60), $a = 6.8829(9)$ Å, $b = 11.505(3)$ Å, $c = 19.013(3)$, $V = 1505.5(5)$ Å^3, $Z = 4$, transparent plate, crystal size 0.13 × 0.053 × 0.027 mm^3, Mo Kα, $\lambda = 0.71073$ Å, $2\theta_{max} = 50°$, $R(F) = 3.44\%$, wR(F^2) = 7.01% for 119 parameters and 1017 unique reflections with $I > 2\sigma(I)$.

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10.1021/cm991143r CCC: $18.00

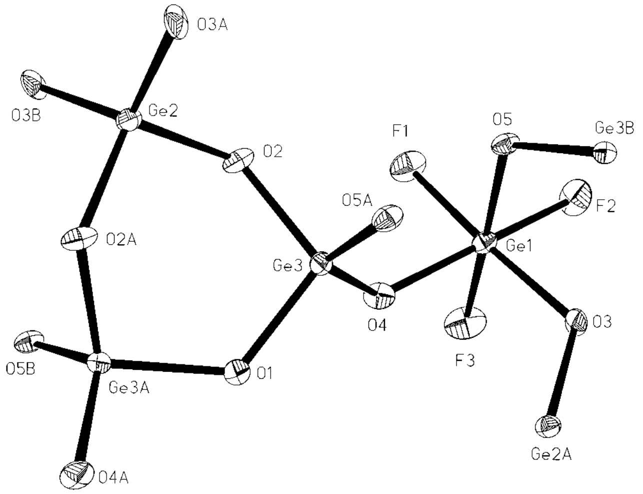

Figure 1. The ORTEP view of coordination environments for Ge cations and O anions. Atom labels having "A" or "B" refer to symmetry-generated atoms. Note that there is a 2-fold axis passing through Ge2 and O1.

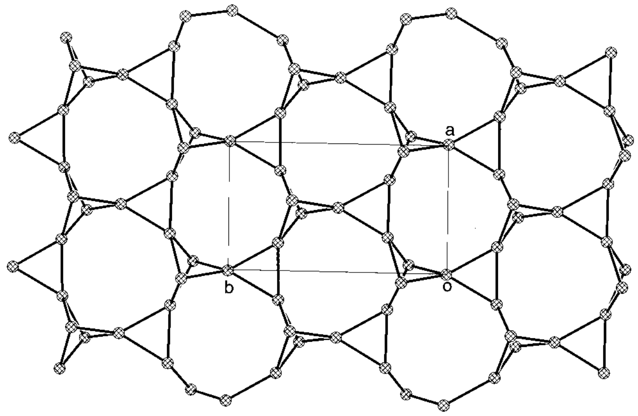

Figure 2. A nine-membered ring containing, two-dimensional sheet in UCSB-9L (also in UCSB-9, -11, and -46). Each five T-atom unit surrounded by three three-membered ring units is denoted as a 4=1 unit, first observed in natural fibrous zeolites. The bridging oxygen atoms and terminating fluorine atoms are omitted for clarity.

In UCSB-9L, these two-dimensional sheets are not linked into a 3D framework. They are stacked along the crystallographic *c* axis with alkali metal cations (K^+) and water molecules sandwiched between the sheets. The *d* spacing between two adjacent sheets is equal to half of the *c* axial length (∼9.5 Å). The stacking mode of layers in UCSB-9L is different from those found in UCSB-9, -11, and -46. The nine-membered rings of adjacent layers in UCSB-9L are still on top of each other as in UCSB-11, but each three-memberded ring in UCSB-9L is between two 4=1 units of two adjacent layers above and below (Figure 3) and vice versa. Apparently each sheet is rotated by 60° (with respect to its adjacent sheets) around an axis that passes through the center of a nine-membered ring channel.

There is an extraframework water molecule that is hydrogen-bonded to terminating F^- anions. The shortest distances from the oxygen atom of the water molecule to the three crystallographically unique fluorine anions are 2.61, 2.69, and 3.02 Å, respectively. The water molecule is statistically distributed over two crystallographic sites separated by a distance of 1.96 Å and related by an inversion center. The inclusion of extraframework water molecules is likely to serve the purpose of stabilizing both F^- anions and K^+ cations.

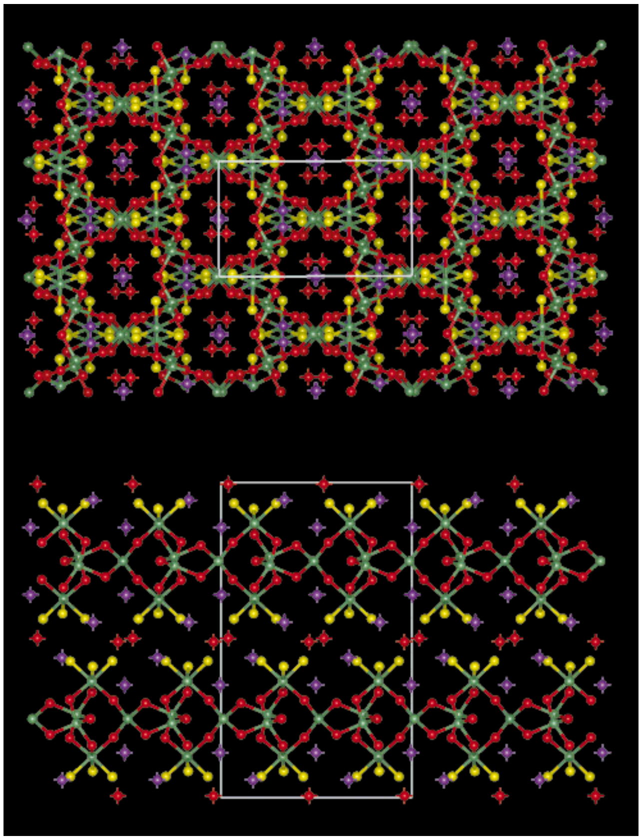

Figure 3. Unit cell packing diagrams showing the location of extraframework species and nine-membered ring channels: top, viewed down the *c* axis and perpendicular to layers; bottom, viewed down the *a* axis; red, oxygen; purple, potassium; green, germanium; yellow, fluorine.

The synthesis of UCSB-9L is a significant discovery because it leads to an isolation of two-dimensional sheets that were previously considered to be the framework building unit purely from a structural point of view. The formation of such two-dimensional sheets is apparently unrelated to organic structure-directing agents employed in the synthesis of UCSB-9, -11, and -46. It is likely that these organic molecules only template the linking of two-dimensional sheets into a 3D framework. In a more general term, the synthesis of UCSB-9, -11, -46, and -9L indicates that the templating effect may not need to be active throughout the self-assembly process, but may only need to occur in a narrow range along the reaction coordinate.

Acknowledgment. Supported in part by the National Science Foundation Grant DMR 95-20971 and a Materials Research Laboratory Corning Foundation Fellowship to P.F.

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

CM991143R