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Novel Germanate Zeolite Structures with 3-Rings

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For over half a century, zeolites have been extensively studied because of their utility in commercial processes such as catalysis and gas separation. Of fundamental importance is the synthesis of zeolitic materials with novel catalytic properties. This has led to an ever increasing interest in making zeolitic materials with new framework topologies or chemical compositions.[1]

One of the most challenging goals for synthetic chemists is the synthesis of zeolite-type structures with 3-rings (three tetrahedral atoms in a ring). It has been predicted that the 4-connected 3D nets having a maximum number of smallest possible rings may be the key to very open frameworks.[2] Unfortunately, zeolite type structures with 3-rings are relatively rare. Because lovdarite (a beryllosilicate mineral with a zeolite structure)[1] has 3-rings, an obvious synthesis strategy is to use divalent metals as framework building blocks in place of Be^{2+}, which is less desirable because of its toxicity. This has led to the synthesis of three 3-ring-containing zincosilicates in the past.[3,4]

The limited success in the synthesis of silicate-based 3-ring structures is likely due to the short Si−O bond distance and associated large T−O−T angles that do not favor the highly strained 3-ring configuration compared to rings of larger sizes (i.e., 4, 5, and 6). To make new 3-ring structures, it is necessary to consider geometrical factors that can relieve the strain inherent in a 3-ring structure.

Germanates are of particular interest because they have metal−oxygen bond distances significantly greater than those in most silicates. The large T−O distance in germanates favors smaller T−O−T angles, and we have found that these geometric factors have an important effect on both pore and cage configurations and the types of structures that are favored under particular synthesis conditions.[5] The exploration of such a compositional domain has the potential to uncover new 3-ring zeolite structures.

While most industrial applications are still based on aluminosilicate zeolites, an improved understanding of both structural and synthetic aspects of zeolites has been achieved through the studies of non-aluminosilicate-based materials. For example, the crystal structure of a substituted aluminophosphate (MAPSO-46) played a key role in the subsequent structure determination of ZSM-18, the only aluminosilicate zeolite reported to have 3-rings.[6]

Compared to silicate or phosphate zeolite-type structures, much less is known about germanate zeolite structures.[1] In gallium germanates, for example, only single-crystal structures of sodalite (the hydrated Na^+ form) and natrolite (the anhydrous Rb^+ form) analogues have been reported.[7,8,9] The natrolite analogue was made under high temperatures and high pressures, conditions obviously unsuitable for the synthesis of more open frameworks.

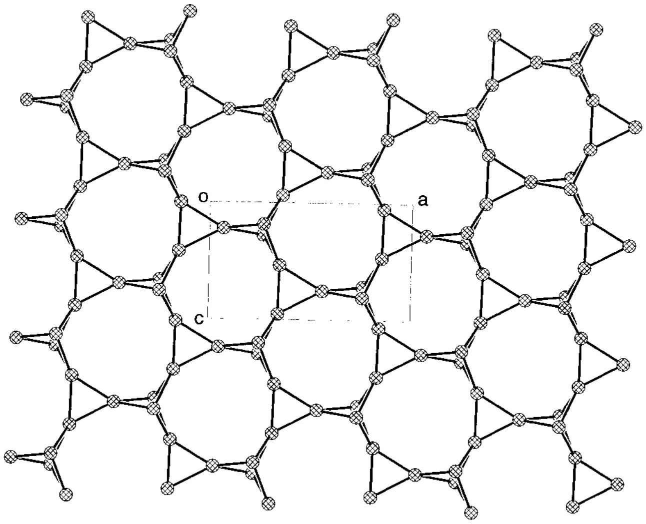

Figure 1. A unique 3-connected, 2D sheet in UCSB-9. The five T-atom unit surrounded by three 3-ring units are denoted as 4=1 units, first observed in natural fibrous zeolites. The bridging oxygen atoms are omitted for clarity.

UCSB-9 was synthesized by heating a mixture of GeO_2 (0.64 g), 40% methylamine (8.63 g), $Ga(NO_3)_3$ (1.05 g), and ethylene glycol (9.67 g) at 180 °C for eight days in a Teflon-coated steel autoclave. X-ray powder diffraction peaks can be indexed using the unit cell constants from single-crystal X-ray diffraction. Thermogravimetric and differential thermal analyses were performed in static air with a heating rate of 5 °C/min from 30 °C to 1050 °C. Between 400 °C and 600 °C, there was a one-step weight loss of 11.0% (calculated: 10.7%) accompanied by an endothermic peak. When heated at 430 °C for 3h, the sample became dark and amorphous. Quantitative elemental analysis of UCSB-9 was carried out on an electron probe microanalyzer equipped with five wavelength dispersive X-ray spectrometers. The calculated values (in mass percent based on a formula derived from the single-crystal structure analysis) and observed values in parentheses for UCSB-9 are 24.0 (21.5) Ga, 37.5 (41.5) Ge.

UCSB-9 is the first 3-ring gallogermanate zeolite-type structure and it has a previously unknown framework topology.[10] The novel tetrahedral atom configurations in UCSB-9 provide new structural subunits for the theoretical construction of new zeolite topologies. The framework structure of UCSB-9 is closely related to that of three natural zeolites (edingtonite, natrolite, and thomsonite) because they are all constructed from a secondary structural building unit denoted as 4=1 (Figure 1).[11] Such a unit has five T-atom corners (three equatorial ones and two axial ones) and is surrounded by three 3-rings in UCSB-9 (Figure 1). Each of the three equatorial ones has two free bonds and each of the two axial ones has only one free bond. In UCSB-9, by using three T-atoms at the equatorial positions, the 4=1 units are joined by 3-rings into an infinite 9-ring-containing sheet which if undistorted would have a 3-fold symmetry axis (Figure 1). Such a sheet structure correlates with the hexagonal plate-shaped crystal morphology.

The 9-ring sheets are joined through the T-atoms at the axial positions into a 3D framework structure. There are two stacking

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(1) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; Elsevier: Boston, 1996.

(2) Brunner, G. O.; Meier, W. M. *Nature* **1989**, *337*, 146−147.

(3) Annen, M. J.; Davis, M. E.; Higgins, J. B.; Schlenker, J. L. *J. Chem. Soc. Chem. Commun.* **1991**, 1175−1176.

(4) Rohrig, C.; Gies, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 63−65.

(5) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154−157.

(6) Lawton, S. L.; Rohrbaugh, W. L. *Science* **1990**, *247*, 1319−1322.

(7) Some other gallium germanate tetrahedral framework materials such as paracelsian-like strontium gallium germanate are also known, but they are not considered as open-framework structures. Calleri, M.; Gazzoni, G. *Acta Crystallgr.* **1976**, *B32*, 1196−1205.

(8) Nenoff, T. M.; Harrison, W. T. A.; Gier, T. E.; Keder, N. L.; Zaremba, C. M.; Srdanov, V. I.; Nicol, J. M.; Stucky, G. D. *Inorg. Chem.* **1994**, *33*, 2472−2480.

(9) Klaska, K. H.; Jarchow, O. *Z. Kristallogr.* **1960**, *113*, 430−444.

(10) Crystallographic data for UCSB-9: $(CH_3NH_3)_2Ga_2Ge_3O_{10}$, space group *Pnna*, $a = 12.4987(3)$ Å, $b = 14.3155(2)$ Å, $c = 7.3751(2)$ Å, $V = 1319.59(6)$ Å^3, $Z = 4$, Mo Kα, $2\theta_{max} = 56°$, $R(F) = 3.59\%$, $R_w(F^2) = 7.96\%$, GOF = 1.17 for 89 parameters and 1357 reflections with $I > 2\sigma(I)$.

(11) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*; Butterworth-Heinemann: Boston, 1992.

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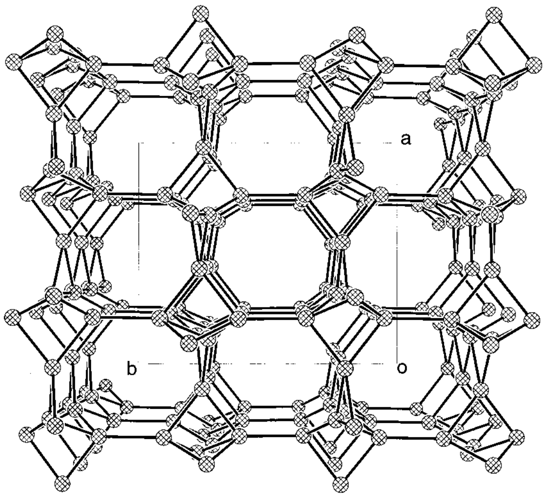

Figure 2. The projection of UCSB-9 framework down the crystallographic *c* axis showing 8-ring channels. The bridging oxygen atoms are omitted for clarity.

modes between adjacent layers and an infinite number of 3-ring structures can be generated from the combination of these two stacking modes. If all adjacent layers are stacked in the eclipsed configuration, a novel structure, UCSB-11, with a straight 9-ring channel is obtained.[12] In UCSB-9, layers are stacked in the staggered configuration with respect to 3- or 9-rings. This creates a zigzag 9-ring channel along the crystallographic *b* axis. Perpendicular to the 9-ring channel, are three intersecting 8-ring channels along the crystallographic [100], [001], and [101] directions (Figure 2).

In UCSB-9, the protonated methylamine molecule is ordered and forms hydrogen bonds with the framework oxygen atoms. The three shortest N- - -O contact distances are 2.969 Å, 2.997 Å, and 3.009 Å for N1−O3, N1−O4, and N1−O1, respectively. There are three unique T-atom sites (one is in a special position) with average T−O distances of 1.789 Å, 1.766 Å, and 1.772 Å, respectively. Because the ideal bond distances are 1.74 Å for Ge−O and 1.82 Å for Ga−O, the above average T−O distances in UCSB-9 suggest that all three sites are mixed Ge/Ga sites.[13] A similar situation exists in aluminosilicate zeolites in which it is often not possible to distinguish between Al^{3+} and Si^{4+} sites.

Previously, we reported a large number of cobalt phosphate based zeolite-type materials.[14,15] The present work extends our synthetic methodology for highly charged phosphates into a new compositional domain. In addition to UCSB-9 and UCSB-11, we have synthesized a number of other gallo- and aluminogermanate zeolite-type structures including UCSB-15AlGe and UCSB-15GaGe, the first germanates with 5-rings.[16] The fundamental synthetic parameters in the cobalt phosphate based system such as host−guest charge density matching and hydrogen-bonding-assisted self-assembly are also important factors in the synthesis of germanate-based materials. It is worth noting that large crystals (up to several millimeters) of gallo- and aluminogermanate 4-connected, 3D open-framework structures can be readily synthesized within a few days without the use of any inorganic charge-balancing cations. This is in contrast with the synthesis of aluminosilicate zeolites that almost always requires the presence of alkali metal cations.

In conclusion, we present the synthesis and structure of the first 3-ring-containing germanates and successfully extend the amine-directing synthesis methodology commonly used in phosphates and silicates into the binary germanate system. UCSB-9 and UCSB-11 are novel not only in their 3D framework topologies but also in their unusual T-atom configurations. This work opens up new synthesis areas which may lead to many new zeolite-type materials including very open 3-ring nets.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters (4 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(12) UCSB-11: $(CH_3)_4NAlGe_4O_{10}$, $a = 13.1573(2)$ Å, $c = 7.3327(2)$ Å, space group $P321$, $R(F) = 5.25\%$ for 105 parameters and 1302 reflections with $I > 2\sigma(I)$.

(13) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−767.

(14) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735−741.

(15) Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2080−2085.

(16) Bu, X.; Feng, P.; Gier, T. E.; Zhao, D.; Stucky, G. D., *J. Am. Chem. Soc.* submitted for publication, in revision.