

## Transformation of Germanium Dioxide to Microporous Germanate 4-Connected Nets

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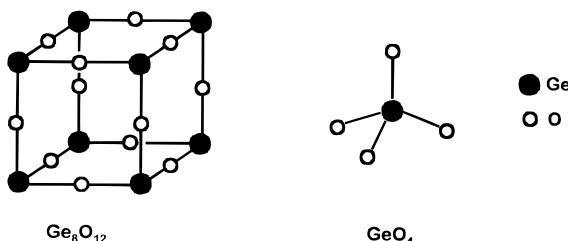
Received July 7, 1998

Extensive research efforts worldwide continue to aim for new compositions and framework topologies of zeolites and related microporous crystalline materials due to their current widespread applications in catalysis and separation technologies<sup>1–3</sup> and the advantages they present as platforms for the assembly of spatially organized molecular recognition systems.<sup>4,5</sup> Although, 4-connected nets of zeolitic silicates and aluminosilicates represent a vast, well-established, and useful class of materials,<sup>6</sup> the analogous germanates remain conspicuously absent and largely unexplored. We have employed a synthetic route similar to that employed for zeolites in the conversion of  $\text{GeO}_2$  to previously unknown, microporous germanate 4-connected nets. Here, two crystalline materials of  $\text{GeO}_2$  composition will be reported, namely,  $[\text{GeO}_2]_{10} \cdot (\text{DMA})(\text{H}_2\text{O})$ , ASU-7, (DMA = dimethylamine), and  $[\text{GeO}_2]_{10} \cdot \text{DABCO}(\text{H}_2\text{O})$ , ASU-9, (DABCO = 1,4-diazabicyclo[2.2.2]-octane), with the first possessing a remarkable new zeolite-type net containing 1-D channels and the second adopting an octadecasil net with large cages.

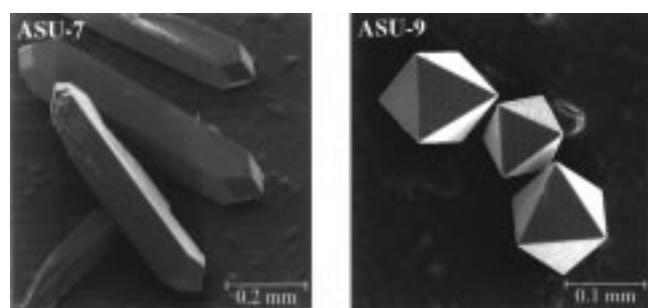
At the outset of this study, germanate framework structures have been limited to those constructed from combinations of tetrahedral  $\text{GeO}_4$ , trigonal bipyramidal  $\text{GeO}_5$ , and/or octahedral  $\text{GeO}_6$  centers<sup>7–10</sup> with no 4-connected microporous structures based solely on the  $\text{GeO}_4$  tetrahedron reported yet.

$\text{GeO}_2$  (150 mg, 1.434 mmol) was dissolved in a 40% aqueous DMA (1.26 mL, 10.04 mmol) followed by the addition of pyridine (3.20 mL, 39.78 mmol) and 48–51% aqueous HF (0.02 mL, 0.572 mmol). The solution ( $\text{pH} = 10.6$ ) was heated in a Teflon-lined vessel to 165 °C for 4 days and then cooled to room temperature to give 90 mg (56% yield based on  $\text{GeO}_2$ ) of ASU-7 as rodlike crystals (shown in Figure 1 for a selected sample). Octahedrally shaped crystals of ASU-9 (Figure 1) were obtained by a similar procedure. Here,  $\text{GeO}_2$  (50 mg, 0.478 mmol) and DABCO (250 mg, 2.232 mmol) were dissolved in water (0.45 mL) followed by the addition of pyridine (1.60 mL, 19.89 mmol) and 48–51% aqueous HF (0.02 mL, 0.572 mmol) and then the solution ( $\text{pH} = 8.8$ ) was heated to 160 °C for 2 days to give 6 mg product (10% unoptimized yield based on  $\text{GeO}_2$ ).

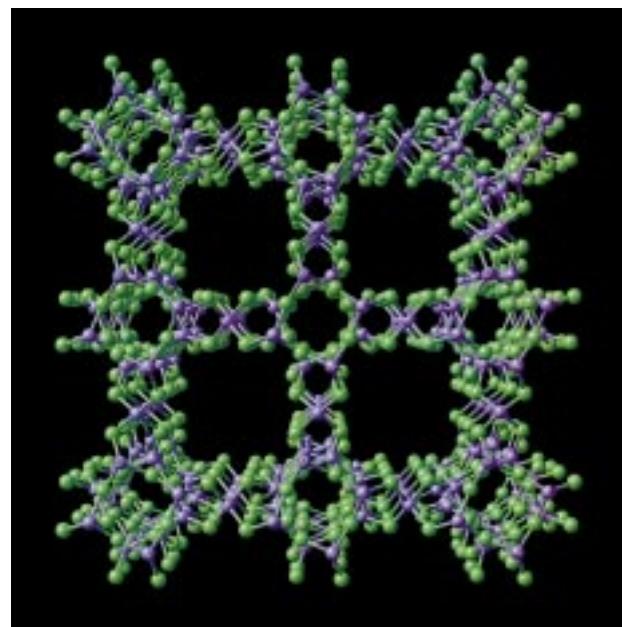
Elemental microanalysis<sup>11</sup> and single-crystal X-ray studies<sup>12</sup> on the two crystals confirmed that these conditions are ideal for transforming the original condensed structure of  $\text{GeO}_2$  into 4-connected microporous nets having cubes and tetrahedra as building blocks (shown below). In both structures, the cubes are



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**Figure 1.** SEM images showing the morphology of as-synthesized crystals of ASU-7 and ASU-9.



**Figure 2.** The crystal structure of  $[\text{GeO}_2]_{10} \cdot (\text{DMA})(\text{H}_2\text{O})$ , (ASU-7), shown along the crystallographic *c*-axis: green, O; blue, Ge. Four channels are shown with the DMA guests, and water molecules (within the germanate cubes) are omitted for clarity.

bridged by tetrahedral units that connect each of the eight corners, resulting in larger building units with distinct stereochemistry having the cubes either rotated by 45° or identically oriented with respect to other cubes along the same direction. The first arrangement belonging to ASU-7 yields a 4-connected net containing extended 1-D channels running along the crystallographic *c*-axis, where a single water molecule occupies the center of each cube and the DMA guest molecules reside in the channels (Figure 2). This is a new type of microporous net having the vertex symbols, 6·6·6<sub>2</sub>·6<sub>2</sub>·12<sub>8</sub>·12<sub>8</sub> (vertex 1) and 4·6·4·6·4·6 (vertex 2, on cube).<sup>13a</sup>

To examine the stability of this network in the absence of the DMA guests, a sample (39.9 mg) of ASU-7 was heated in a thermal gravimetric apparatus to reveal a weight loss of 5.2% at 420–540 °C corresponding to the removal of DMA and water (5.7% calculated per formula unit). Decomposition of DMA

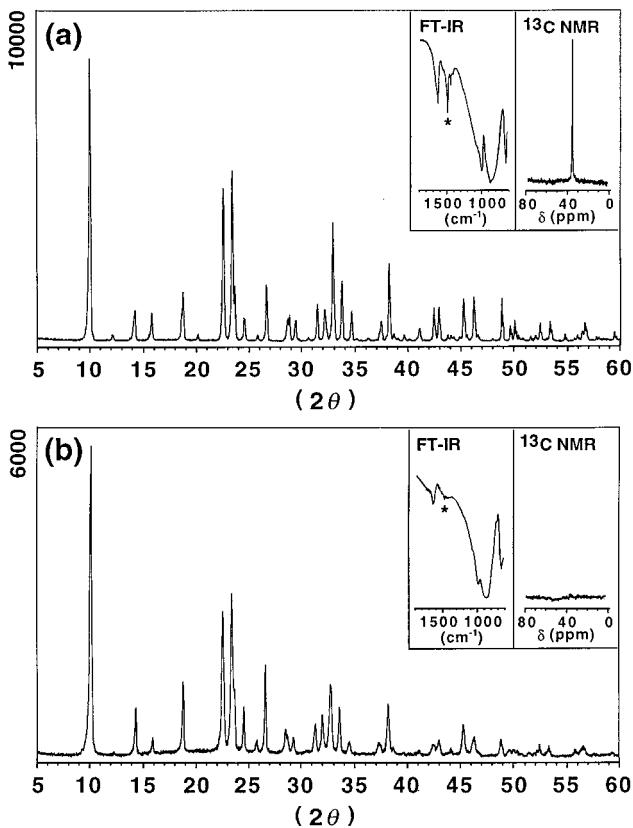
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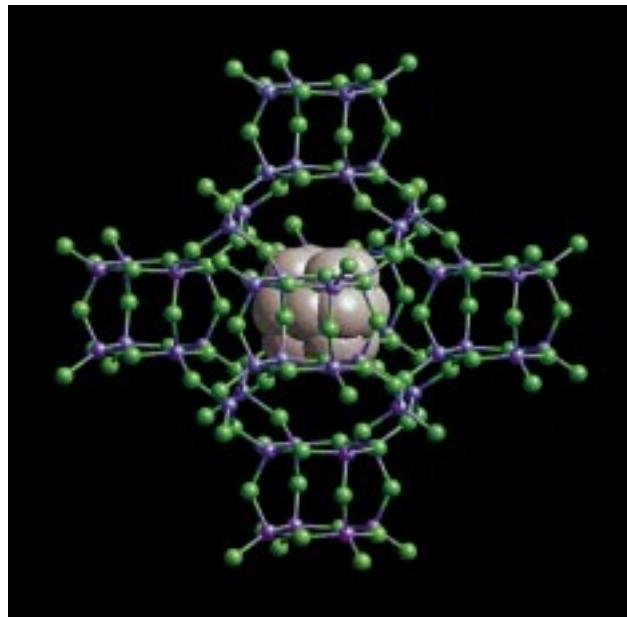
**Figure 3.** The XRPD patterns for (a) as-synthesized ASU-7 with DMA in the channels and (b) the material after calcination at 435–445 °C for 12 h. Their respective FT-IR and  $^{13}\text{C}$  CPMAS NMR spectra for the DMA region are shown in the inset.

guests from the channels was further confirmed by comparison of the FT-IR and  $^{13}\text{C}$  CPMAS spectra of the material before and after calcination (parts a and b of Figure 3), which showed a clear reduction in the  $\nu(\text{N}-\text{H})$  IR band and the absence of any NMR resonances in the expected chemical-shift range for DMA. The crystalline nature of the calcined germanate framework and its

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(11) (a) Anal. Calcd for  $\text{C}_2\text{H}_5\text{NO}_2\text{Ge}_{10}$ : C, 2.38; H, 0.89; N, 1.53; Ge, 65.60%. Found: C, 2.17; H, 0.83; N, 1.26; Ge, 65.46%. (b) Anal. Calcd for  $\text{C}_6\text{H}_{14}\text{N}_2\text{O}_2\text{Ge}_{10}$ : C, 6.31; H, 1.30; N, 2.38; Ge, 60.33%. Found: C, 6.13; H, 1.20; N, 2.38; Ge, 61.72%. A small amount of F (%) was detected: 1.12 (ASU-7) and 1.36 (ASU-9); it is believed to occupy the voids in the form of HF–guest complex.

(12) (a) Single crystals of ASU-7 are, at  $-75 \pm 2$  °C, tetragonal, space group  $P4/mcc - D_{4h}^2$  (No. 124) with  $a = 8.7795(1)$  Å,  $c = 14.4696(2)$  Å,  $V = 1115.31(2)$  Å $^3$ , and  $Z = 2$  formula units [ $d_{\text{calcd}} = 3.302$  g cm $^{-3}$ ;  $\mu_{\text{d}}(\text{Mo K}\alpha) = 13.365$  mm $^{-1}$ ]. A total of 6517 integrated reflection intensities having  $2\Theta(\text{Mo K}\alpha) < 56.60^\circ$  were produced using the Siemens/Bruker program SAINT. A total of 729 of these were independent and gave  $R_{\text{int}} = 0.046$ . All stages of weighted full-matrix least-squares refinement were conducted using  $F^2$  data with the SHELXTL-PC Version 5 software package and converged to give  $R_1$  (unweighted, based on  $F$ ) = 0.020 for 650 independent absorption-corrected reflections having  $2\Theta(\text{Mo K}\alpha) < 56.60^\circ$  and  $I > 2\sigma(I)$  and  $wR_2$  (weighted, based on  $F^2$ ) = 0.053 for 709 independent absorption-corrected reflections having  $2\Theta(\text{Mo K}\alpha) < 56.60^\circ$  and  $I > 0$ . Cube-edge oxygen atoms are both statistically disordered between two alternate sites in the lattice. {Atomic coordinates for the  $\text{GeO}_2$  framework [atom type (10 $x$ , 10 $y$ , 10 $z$ ): Ge1 (0, 5000, 2500); Ge2 (2565, 4239, 1086); O1 (1043, 3755, 1810); O2 (2010, 3595, 0); O2' (1764, 4393, 0); O3 (3257, 5936, 1557); O3' (3793, 2692, 1194)]. (b) Single crystals of ASU-9 were analyzed at  $-99 \pm 1$  °C: tetragonal, space group  $I4/m$  with  $a = 9.2314(7)$  Å,  $c = 14.096(1)$  Å,  $V = 1201.3(1)$  Å $^3$ ,  $Z = 2$ ,  $d_{\text{calcd}} = 1.593$  g cm $^{-3}$  and  $\mu_{\text{d}}(\text{Mo K}\alpha) = 0.125$  mm $^{-1}$ . Data were collected using a Siemens SMART CCD (charge coupled device) autodiffractometer using graphite-monochromated Mo K $\alpha$  radiation using 0.3°  $\omega$  scans per frame for 30 s, such that a hemisphere was collected. The structure was solved by (SHELXS-97) direct methods and the resulting structural parameters were refined by full-matrix least-squares techniques on  $F^2$  to a standard discrepancy index  $R = 0.0577$  and  $R_w = 0.1161$  with  $I > 2\sigma(I)$  and Goodness-of-fit on  $F^2 = 1.052$ . Further crystallographic details for ASU-7 and ASU-9 are provided in the deposited Supporting Information.



**Figure 4.** A fragment of crystal structure of  $[\text{GeO}_2]_{10} \cdot (\text{DABCO})(\text{H}_2\text{O})$ , ASU-9, showing how the germanate octadecahedron is filled with disordered DABCO guests (gray): green, O; blue, Ge. Water molecules within the germanate cubes are omitted for clarity.

structural stability was confirmed by the close coincidence observed between the XRPD patterns of the as-synthesized solid and that of the calcined solid.

To produce an extended cage framework, DABCO, which is a spherically shaped organic guest was used in an identical reaction mixture instead of DMA to yield ASU-9. Single-crystal X-ray analysis on this material reveals a germanate open octadecasil net topology as shown in Figure 4, where the DABCO guest molecules reside in the center of octadecahedra, and a single water molecule occupies the center of each cube. DABCO cannot be removed from the cages without the destruction of the framework; at 250 °C, this material begins to decompose. The germanate net observed for ASU-9 is analogous to that found in the structure of  $\text{AlPO}_4-16$ .<sup>13b</sup>

It is worth noting that the typical Ge–O–Ge angle (ca. 130°) observed in these compounds is lower than that found in microporous silicates for Si–O–Si (ca. 146°), which points to the possibility of yielding microporous germanates having 3-ring secondary units, a structural property predicted to impart higher stability on open frameworks and seen as essential to the achievement of very porous nets<sup>13</sup> but as yet found to be rare in zeolitic networks. Given that the synthetic strategy developed for producing ASU-7 and ASU-9 produces a germanate gel prior to applying the heating program and the facility with which the ultimate structure can be modulated by addition of the appropriate organic guest coupled to the accessibility of favorable angles for open nets, the full-development of this area is anticipated.

**Acknowledgment.** This work was supported by the National Science Foundation [CHE-9702131]. We thank Dr. Fred Hollander for the crystallography and Professor M. O’Keeffe for invaluable discussions.

**Supporting Information Available:** Crystallographic data for ASU-7 and ASU-9, including crystal structure analysis report, positional parameters, thermal parameters, and interatomic distances and angles (28 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

JA982384N

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