Chem. Mater. **1999,** *11,* 3025−3027 3025

Transformation of 4-Connected Zeolite Topologies into a Mixed 4- and 6-Connected 3-Dimensional Open Framework

Pingyun Feng, Xianhui Bu, and Galen D. Stucky*

Department of Chemistry, University of California, Santa Barbara, California 93106

Received August 9, 1999
Revised Manuscript Received September 1, 1999

Zeolites have been extensively studied due to their utility in commercial processes such as catalysis and gas separation.[1,2] Of fundamental importance is the synthesis of new zeolitic materials with novel structural properties because the utility of these crystalline materials is intimately correlated to their geometrical features.[3] The initial synthetic efforts were focused on aluminosilicates with various Si-to-Al ratios; however, the discovery of a family of aluminophosphate based microporous materials in the 1980s has spurred widespread enthusiasm in making non-aluminosilicate-type zeolitic materials.[4−8]

Compared to silicate or phosphate zeolite-type structures, much less is known about germanate zeolite structures. A few germanate zeolite analogues (e.g., sodalite and natrolite) have been known for many years;[2] however, not until recently had novel framework topologies based on tetrahedral germanium oxides been synthesized.[9−11] Germanates are of particular interest because they have metal−oxygen bond distances significantly greater than those in silicates or phosphates. Such a large T−O distance in germanates favors smaller T−O−T angles and has an important effect on framework configurations.[12] In particular, structures containing 3-rings and mixed tetrahedral−octahedral frameworks can be prepared in such a compositional domain.[9,13,14]

The framework of a zeolite structure has the general composition of AB_2, where A is a 4-connected atom (tetrahedral atoms such as Al, Si, Ge, and P) and B is any 2-connected atom (usually oxygen) which is shared between two tetrahedral atoms.[2] The topology of zeolite structures is usually viewed based on the connectivity of tetrahedral atoms. Such tetrahedral atom connectivity can be regarded mathematically as 4-connected 3-D nets, which are constructed from 3-connected 2-D sheets.[3] From a synthetic point of view, the transformation from 3-connected 2-D sheets into 4-connected 3-D nets is a condensation step involving the elimination of water molecules from hydroxyl groups and subsequent formation of T−O−T bridges (T refers to a tetrahedral atom). Here we report a different pathway from 3-connected 2-D sheets to a 3-D network. Instead of generating 4-connected 3-D nets, 3-connected 2-D sheets are joined into a mixed 4- and 6-connected 3D networks (through the elimination of both tetrahedral and oxygen atoms) in a new germanate open-framework phase denoted as UCSB-46.

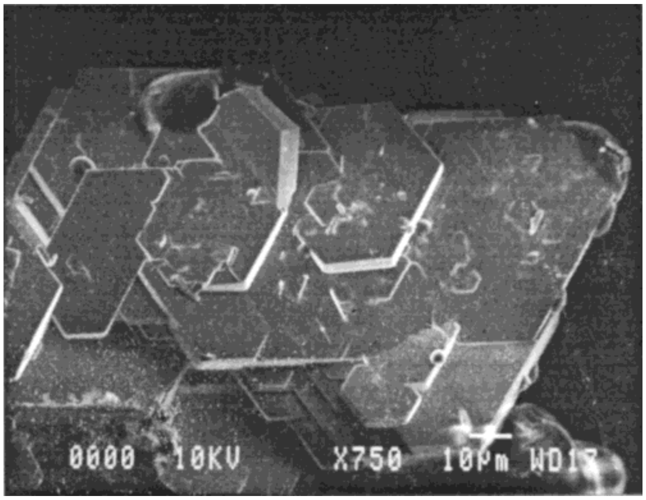

Figure 1. Scanning electron microscopy image of a cluster of crystals of UCSB-46 showing the platelike morphology.

UCSB-46 was synthesized by heating a mixture of GeO_2 (1.01 g), 40% methylamine (3.98 g), $Ga(NO_3)_3$ (0.204 g), 49% HF (0.44 g), and ethylene glycol (13.02 g) at 180 °C for 20 days in a Teflon-coated steel autoclave. The product consisted of crystals with two distinct morphologies. Most crystals were polyhedron-shaped and were identified to be UCSB-7.[10] UCSB-46 was a minor phase and was shaped like thin plates (Figure 1). A qualitative elemental analysis performed on a JEOL JSM-840A scanning electron microscope equipped with a X-ray energy dispersvie system showed that UCSB-46 did not contain gallium atoms, in agreement with results derived from the single-crystal structure analysis.[15] In the absence of HF, a related structure, UCSB-9, could be synthesized using methylamine as the structure-directing agent.[9]

The framework structure of UCSB-46 is closely related to that of UCSB-9, UCSB-11, and three natural zeolites (edingtonite, natrolite, and thomsonite) because

---

(1) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.

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

(3) Behrens, P.; Stucky, G. D. In Comprehensive Supramolecular Chemistry; Albert, G., Bein, T., Eds.; Elsevier: New York, 1996; Vol. 7, pp 721−772.

(4) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146−1147.

(5) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, A. L.; Zubieta, J.; Dye, J. L. *Chem. Mater.* **1996**, *8*, 43−53.

(6) Suib, S. T. *Curr. Opin. Solid State Sci.* **1998**, *3*, 63−70.

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

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

(9) Bu, X.; Feng, P.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 11204−11205.

(10) Bu, X.; Feng, P.; Gier, T. E.; Zhao, D.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 13389−13397.

(11) Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 10569−10570.

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

(13) Cascales, C.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruíz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2436−2439.

(14) Cascales, C.; Gutierrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 129−131.

(15) Crystal data for $(NH_4)(CH_3NH_3)(Ge_9O_{19})$, $M = 1007.4$, space group *Pnna*, $a = 12.3384(3)$ Å, $b = 23.5171(4)$ Å, $c = 7.2483(2)$ Å, $V = 2103.19(9)$ Å^3, $Z = 4$, $D_c = 3.182$ g cm^{-3}, clear thin plate, crystal size $0.093 \times 0.067 \times 0.013$ mm^3, Mo Kα, $\lambda = 0.710\,73$ Å, $\mu = 12.76$ mm^{-1}, $2\theta_{max} = 48°$, $R(F) = 6.03\%$, $wR(F^2) = 13.1\%$, GOF = 1.04 for 138 parameters and 1646 unique reflections with $I > 2.0\sigma(I)$.

10.1021/cm991118l CCC: $18.00

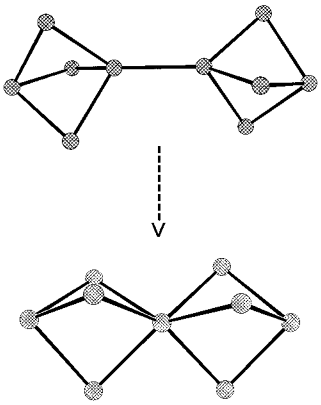

Figure 2. Consolidation of two 4=1 units into a Ge_9 cluster consisting of eight Ge tetrahedra and one Ge octahedron. Such a consolidation transforms UCSB-9, -11 type topologies into the novel 3D topology discovered in UCSB-46. The bridging oxygen atoms are omitted for clarity.

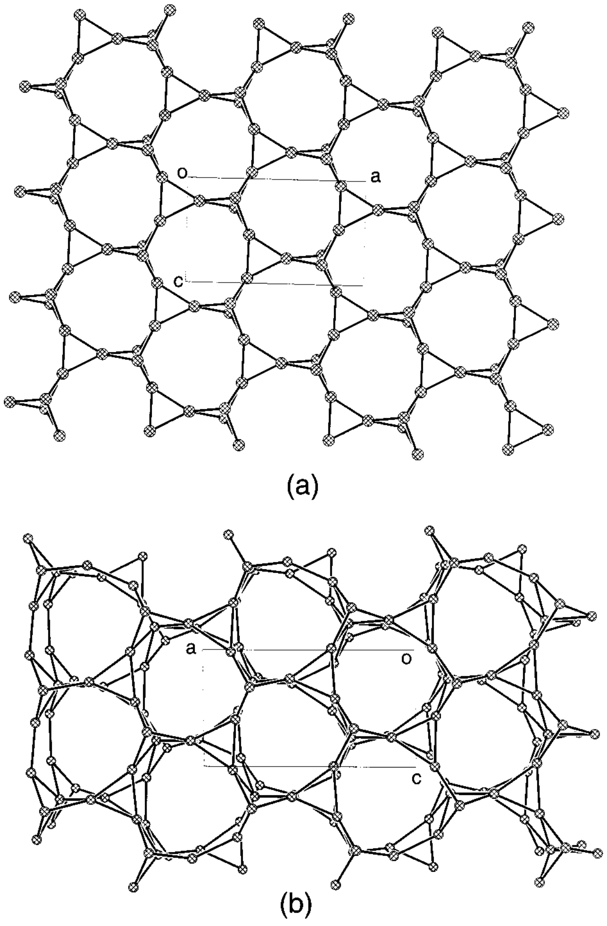

Figure 3. Transformation from 3-connected 2D sheets into a mixed 4- and 6-connected 3D framework: (a) the 3-connected 2D sheet in UCSB-9; (b) a double layer formed from two 3-cconnected 2D sheets by converting two tetrahedral Ge sites into a single octahedral site. Note that the 3-connected 2D sheet is preserved in UCSB-46. The bridging oxygen atoms are omitted for clarity.

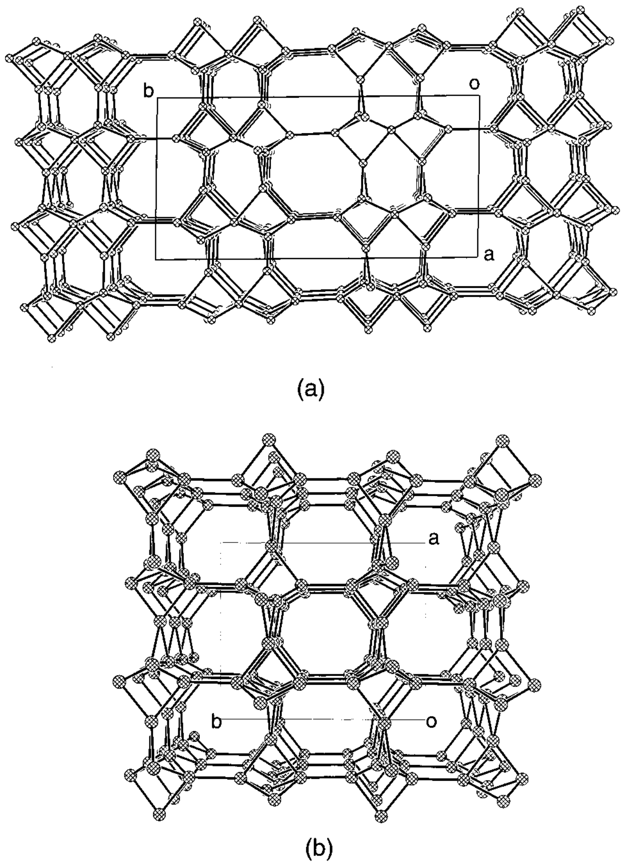

Figure 4. Comparison of the wall thickness between 8-ring channels in UCSB-9 and UCSB-46: (a) the projection of UCSB-46 framework down the crystallographic [001] direction showing 8 ring channels; (b) the similar 8-ring channels in UCSB-9. The bridging oxygen atoms are omitted for clarity.

of the presence of a secondary structural building unit denoted as 4=1.[2] 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 4-ring. These 4=1 units can be joined into layers containing 3- and 9-rings (Figure 3a). These sheets can then be linked through oxygen bridges to form UCSB-9 (Figure 4b) and UCSB-11. If all adjacent layers are stacked in the eclipsed configuration (−AAAA− sequence), UCSB-11 is obtained. In UCSB-9, layers are stacked in the staggered configuration (−ABAB− sequence).[9] An infinite number of other configurations (such as an −AABBAABB− sequence) are theoretically possible.

The framework topology of UCSB-46 is derived from the −AABBAABB− type configuration except that all T−O−T bridges between identical layers (−AA− or −BB−) are consolidated into octahedral coordinations through the following condensation (Figure 2):

$$[O_3Ge-O-GeO_3]^{-6} \rightarrow [O_3GeO_3]^{-8}$$

This leads to the formation of double layers that are perpendicular to the crystallographic *b* axis (Figure 3b). We believe that the driving force for such a consolidation is to generate negative centers on the framework in order to balance the positive species (NH_4^+ and CH_3-NH_3^+) trapped inside the channels. It should be noted that tetrahedral atoms that are part of 3-rings are not involved in the linking of layers and are therefore not affected by the tetrahedral-to-octahedral consolidation process. Also tetrahedral atoms that connect different layers (A and B) are not consolidated either and this is responsible for the generation of the intersecting 8-ring channels along [101], [10$\bar{1}$], and [001] directions in UCSB-46 (Figure 4a). In addition, UCSB-46 has zigzag

9-ring channels along the crystallographic *b* axis that coincides with the stacking direction of layers.

The consolidation process described here gives rise to a 3D framework that has eight tetrahedral Ge centers per octahedral one. This is quite uncommon even though a large number of tetrahedral–octahedral oxides are known in the literature. For one thing, oxygen atoms in many known tetrahedral–octahedral oxides are not exclusively bicoordinated between two framework polyhedral centers. One importance of such a consolidation is that it provides a mechanism for the generation of thick walls between channels (Figure 4a). This is a fundamentally important problem in the development of new zeolitic materials with large pore sizes because large pore sizes require thicker walls for sufficient thermal and hydrothermal stability.

In conclusion, using rare 3- and 9-ring containing germanates (UCSB-9, UCSB-11, and UCSB-46) as examples, we have described a novel pathway to the formation of a mixed tetrahedral-octahedral open framework. The transformation from UCSB-9, -11 type structures to UCSB-46 doubles the framework wall thickness without a sacrifice in the channel dimensionality and pore size. The host–guest charge matching (rather than the atomic size of Ge) is proposed as the driving force behind the structural transformation.

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, and anisotropic thermal parameters and a figure showing an ORTEP diagram. This material is available free of charge via the Internet at http://pubs.acs.org.

CM991118L