

A Flexible Germanate Structure Containing 24-Ring Channels and with Very Low Framework Density

Jacques Plévert,^{*,†} Travis M. Gentz,[†] Aaron Laine,[†]
Hailian Li,[†] Victor G. Young,[‡] Omar M. Yaghi,[§] and
Michael O’Keeffe[†]

Department of Chemistry and Biochemistry
Arizona State University, Tempe, Arizona 85287-1604

Department of Chemistry, University of Minnesota
Minneapolis, Minnesota 55455

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109-1055

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Oxide materials with open structures have been the subject of intense research for decades, because of their economically important applications including catalysis, separations, waste removal, and water softening. The now classical materials are the aluminosilicate zeolites whose structures are based on frameworks of corner-sharing metal–oxygen tetrahedra.¹ The pores in such materials are characterized by the size of the rings defining them, which in turn are measured by the number of metal atoms in the ring. Traditionally, rings of 8, 10, or 12 metal atoms have been denoted as small, medium, and large. The discovery² of an aluminophosphate with 18-membered rings (“extra-large”) has directed attention³ to oxide materials with even larger pores, and examples are now known of materials with 20-membered⁴ and 24-membered^{5,6} rings. Even larger rings are found *inside the cavity* of a framework with 16-membered-ring windows.⁷ All of the materials mentioned so far are phosphates,⁵ and contain a metal such as Al, V, Fe, Ni, Zn, or Ga in 5- and/or 6-coordination, with the exception of a 24-membered-ring germanate reported recently.⁶ Here we report a new germanate framework, of unusually low density, with pores based on 24-membered rings. Density in zeolite materials is often measured as *FD* (framework density) = the number of metal atoms per nm³. The lowest density zeolite is cloverite^{4a} with *FD* = 11.1 nm⁻³.

Germanate analogues of zeolites with all tetrahedral frameworks are rare,^{8a,d} but there are also a number of materials with mixed 4-, 5-, and/or 6-coordination.⁸ In the compound formulated as Ge₁₄O₂₉F₄[(CH₃)₂NH₂]₆·xH₂O (ASU-12),⁹ a novel cluster formed by condensation of four GeX₄ tetrahedra, two GeX₅ trigonal

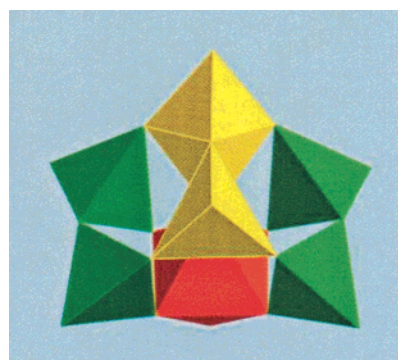


Figure 1. The building units of ASU-16 composed of seven germanate groups with coordination varying from four to six: tetrahedra green, trigonal bipyramids yellow, and octahedra red.

bipyramids, and one GeX₆ octahedron (X = O or F) was found. This material, which contains pores outlined by 16-membered rings, is one of the least dense germanates prepared to date with 12.0 Ge atoms nm⁻³ (comparable to the least dense aluminosilicate zeolites). ASU-12 was genuinely porous as shown by exchange studies.

We have now found that by using a different base, diaminobutane (DAB), but otherwise similar synthesis conditions, that a material (ASU-16) with the same building units, but with a different topology and very much lower framework density (8.6 Ge atoms nm⁻³), can be prepared. In fact, it has a lower *FD* than any of the other materials referred to in this paper, or indeed of any that we are aware of, although a few others come close.¹⁰

ASU-16 was synthesized as a pure germanate under hydrothermal conditions for 4 days at 160 °C from a mixture of germanium dioxide, water, 1,4-diaminobutane (99%, Aldrich), pyridine, and hydrofluoric acid (48 wt %) with a typical molar ratio of GeO₂:70 H₂O:12 DAB:40 pyridine:2 HF. The resulting product was washed and filtered before drying at room temperature. ASU-16 crystallizes as spherical bundles of tightly packed needles. The length of the needles rarely exceeds 100 μm. No other phases can be detected in the X-ray powder diffraction patterns.

The structure of ASU-16 was solved by single-crystal X-ray microdiffraction at the APS synchrotron source (Argonne, IL).¹¹ It is made up of two crystallographically independent clusters, identical in composition. The clusters are composed of seven germanium atoms with mixed coordination: four tetrahedral GeO₄, two trigonal bipyramidal GeO₄F, and one octahedral GeO₅F (Figure 1). One oxygen at the core of the cluster is tricoordinated

(8) For a review of germanates and comparison with silicates see: (a) O’Keeffe, M.; Yaghi, O. M. *Chem. Eur. J.* **1999**, *5*, 2796–2801. Recent papers include: (b) Cascales, C.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2436–2439. (c) Cascales, C.; Gutiérrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C.; Snejko, N. *Chem. Commun.* **2000**, 2145–2146. (d) Conradsson, T.; Dadachov, M. S.; Zou, X. D. *Microporous Mesoporous Mater.* **2000**, *41*, 183–191. (e) Dadachov, M. S.; Sun, K.; Conradsson, T.; Zou, X. *Angew. Chem., Int. Ed.* **2000**, *39*, 3674–3676. (f) Li, H.; Eddaoudi, M.; Plévert, J.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 12409–12410.

(9) Li, H.; Eddaoudi, M.; Richardson, D. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8567–8568.

(10) The previous record low was claimed to be *FD* = 9.10 nm⁻³ in a guanidinium zinc phosphate: Harrison, W. T. A.; Phillips, M. L. F. *Chem. Mater.* **1997**, *9*, 1837–1846. Other low *FD* are 9.13 nm⁻³ for Ge₂ZrO₆F₂(H₂DAB)·H₂O (ASU-15),^{8f} 9.16 nm⁻³ for another zinc phosphate,^{5c} and 9.29 nm⁻³ for “vanadium phosphate I”.⁷ For ASU-16 we use the volume as prepared, rather than the slightly smaller volume of the material used for crystal structure determination.

(11) Crystal data for ASU-16: space group *I*222, *a* = 16.9109(8) Å, *b* = 24.267(2) Å, *c* = 30.210(3) Å, *Z* = 8, *λ* = 0.5594 Å, 0.10 × 0.01 × 0.01 mm³. A total of 50669 reflections (10948 independent) were measured at 120 K. Final agreement indices are *R*₁ = 3.85%, *wR*₂ = 9.24%, *GoF* = 0.967.

[†] Arizona State University.

[‡] University of Minnesota.

[§] University of Michigan.

(1) Thomas, J. M. *Angew. Chem.* **1999**, *38*, 3588–3628.

(2) Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J. M.; Crowder, C. *Nature* **1988**, *331*, 698–699.

(3) (a) Davis, M. E. *Chem. Eur. J.* **1997**, *3*, 1745–1750. (b) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3269–3292.

(4) (a) Estermann, M.; McCusker, L. B.; Baerlocher, Ch.; Merrerouche, A.; Kessler, H. *Nature* **1991**, *352*, 320–323. (b) Jones, R. H.; Thomas, J. M.; Chen, J. S.; Xu, R. R.; Huo, Q. S.; Li, S. G.; Ma, Z. G.; Chippindale, A. M. *J. Solid State Chem.* **1993**, *102*, 204–208. (c) Lii, K. H.; Huang, Y. F. *Chem. Commun.* **1997**, 839–840. (d) Chippindale, A. M.; Peacock, K. J.; Cowley, A. R. *J. Solid State Chem.* **1999**, *145*, 379–386. (e) Walton, R. I.; Millange, F.; Loiseau, T.; O’Hare, D.; Férey, G. *Angew. Chem., Int. Ed.* **2000**, *39*, 4552–4555.

(5) (a) Yang, G.-Y.; Sevov, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 8389–8390. (b) Guillou, N.; Gao, Q.; Noguès, M.; Morris, R. E.; Hervieu, M.; Férey, G.; Cheetham, A. K. *C. R. Acad. Sci. Paris, Ser. II* **1999**, *2*, 387–392. (c) Zhu, J.; Bu, X.; Feng, P.; Stucky, G. D. *J. Am. Chem. Soc.* **2000**, *122*, 11563–11564. (d) Lin, C.-H.; Wang, S.-L.; Lii, K.-H. *J. Am. Chem. Soc.* **2001**, *123*, 4649–4650. (e) Guillou, N.; Gao, Q.; Forster, P. M.; Chang, J.-S.; Noguès, M.; Park S.-E.; Férey, G.; Cheetham, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2831–2834.

(6) Zhou, Y.; Zhu, H.; Chen, Z.; Chen, M.; Xu, Y.; Zhang, H.; Zhao, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 2166–2168.

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

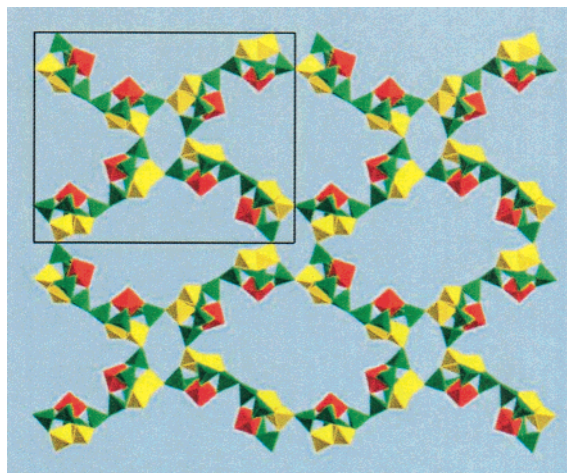


Figure 2. View of the ASU-16 framework along the 24-membered ring pore direction (view down a -axis with c -axis horizontal): tetrahedra green, trigonal bipyramids yellow, and octahedra red.

and links the octahedron to the two GeO_4F polyhedra. The heptamer shows C_{2v} symmetry and is similar to the building unit of ASU-12.⁹ In both phases, the clusters are linked to each other through five bonds by sharing the corner oxygen of the four tetrahedra and one GeO_4F unit. The new structure generated is a 3-D framework characterized by 1-D 24-membered-ring channels. The structure can be described as the stacking of sheets along the a -axis where a layer in the bc plane is formed from the assembly of units made of four clusters (Figure 2). Each cluster has one link up and one link down allowing the connection of the sheets along the a -axis, which generates new windows of 8-, 10-, and 12-membered rings perpendicular to the channel direction. The resulting 5-connected net of clusters is formed from a prismatic stacking of planar 4.8^2 nets. In contrast in ASU-12, the corresponding 5-connected net is formed from a prismatic stacking of 6^3 nets.

The channels are elliptical in shape; the smallest and the largest free diameters of the pore aperture are approximately 8.5 and 15 Å, respectively.

We assume that the singly coordinated anions in the cluster are F atoms (although they may be partly OH). This gives a charge of -6 per two-cluster unit with composition $\text{Ge}_{14}\text{O}_{29}\text{F}_4$. Elemental analysis is consistent with the negative charge of the framework being fully compensated by the presence in the structure of three molecules of the organic base DAB.¹² However, only two molecules were clearly located by X-ray analysis, which were found in the 10- and 12-membered-ring windows. Remaining species are disordered in the channels; however, thermogravimetry measurements revealed water departure at a temperature as low as 40 °C, suggesting that desorption occurs before the synchrotron

(12) Anal. Calcd for $\text{Ge}_{14}\text{O}_{29}\text{F}_4[\text{H}_3\text{DAB}]_3[\text{DAB}]_{0.5}\cdot 16\text{H}_2\text{O}$: C 7.80, H 3.75, N 4.55, Ge 47.14. Found: C 7.79, H 3.23, N 4.37, Ge 47.25. Quantitative F analysis is difficult in oxyfluorides of this type; the reported analysis of 1.3 wt % represents a lower limit, and corresponds to 1.5 F atoms per formula unit. Only at the end of this study did we appreciate fully that the material loses solvent, and possibly neutral base, slowly to the surrounding atmosphere and that this affects the elemental analysis. As discussed later in the text, this loss is manifest in a change of unit cell volume with time.

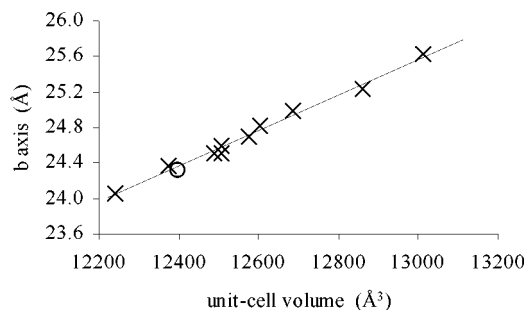


Figure 3. Correlation between the unit-cell volume and the unit-cell parameter b for a series of ASU-16 samples presenting different degrees of weight loss; the circle corresponds to single-crystal data.

data acquisition. Despite solvent loss, X-ray powder diffraction shows that the framework is stable to at least 150 °C.

The bond distances Ge–O of tetrahedral germanium vary from 1.706 to 1.784 Å, with an average value $\langle \text{Ge–O} \rangle = 1.740$ Å typical of germanium oxides. The distances Ge–O of the five-coordinated germanium bonded to bicoordinated framework oxygen are in the range 1.756–1.865 Å, the distances Ge–O to the tricoordinated oxygen located in the core of the clusters being in a different range 1.980–2.182 Å.

The bond angles Ge–O–Ge show two separated distributions. The angles Ge–O–Ge between germanium atoms within the same cluster are distributed in a narrow range around 119.2° with a standard deviation of 3.5°. On the opposite side, the five angles Ge–O–Ge connecting the clusters are in the range 133.5–146.5°. This distinction suggests that the structure can be described as an assembly of rigid clusters connected by flexible Ge–O–Ge bonds.

The structure is characterized by a truly remarkable flexibility. The volume of the unit-cell determined from full-profile fitting refinement of X-ray powder diffraction patterns shows a dramatic variation as a function of the weight loss of the samples at room temperature. For our set of samples, the volume decreases from 13010 to 12240 Å³, which corresponds to a variation of ca. 6%, without jeopardizing the integrity of the framework. The volume change of the unit-cell originates from the contraction of the b -axis, the product ac remaining constant, $ac = 509$ Å² (Figure 3). This variation is remarkable and reveals the flexibility of the Ge–O–Ge bridging bonds between the clusters and explains why the connection between the building units is not limited to form only one topology. Indeed a framework of even lower density and with larger rings can be envisaged that is based on prismatic stacking of 4.6.12 layers. This is a target of future synthesis.

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Supporting Information Available: Crystallographic data for ASU-16 (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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