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Ge$_2$ZrO$_6$F$_2$·(H$_2$DAB)H$_2$O:[1] A 4-Connected Microporous Material with "Bow Tie" Building Units and an Exceptional Proportion of 3-Rings

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Considerable effort has been, and is still being, applied to the discovery of new zeolitic oxide materials for their importance as sorbents, ion-exchangers, and catalysts.[2] An important goal is the preparation of materials with extra-large pores, which are usually defined as having rings of 12 or more T atoms (T are the metal atoms of the framework, usually in tetrahedral coordination).[3,4] One suggested way of achieving this goal, based essentially on the observation that *average* ring sizes in 4-connected nets do not vary over a very wide range,[4,5] is to design materials with a high proportion of small rings (3- or 4-rings). A small number of materials containing 3-rings have been made with frameworks containing one of Li, Zn, Be or Al, and Si; Be and P; and Ga and Ge.[6] Except for the lithosilicate RUB-23, which contains on average *one* 3-ring at each vertex, the number of 3-rings per vertex is significantly less than one.[6a]

We and others have recently pursued the preparation of germanate zeolites,[7] since they represent particularly favorable candidates for formation of frameworks with three-membered rings as the Ge−O−Ge angle (typically about 130°; contrast about 145° for Si−O−Si) allows such rings to be formed in a strain-free manner.[7a] Here we report the synthesis, structure, and porosity of the Ge$_2$ZrO$_6$F$_2$ (ASU-15) framework constructed exclusively of "bow tie" building units (SBUs) that play an important role in achieving *two* 3-rings at each vertex.

Germanium dioxide (60 mg, 0.575 mmol) and Zr(OC$_2$H$_5$)$_4$ (70 mg, 0.259 mmol) were dissolved in a mixture of water (0.4 mL) and 1,4-diaminobutane (DAB) (0.4 mL), to which pyridine (1.5 mL) and aqueous HF (1.14 mmol) were added. The solution was heated at 165 °C for 3 days in a Teflon-lined vessel. After the mixture was cooled to room-temperature, colorless rodlike crystals were recovered.

Elemental analysis and single-crystal X-ray analysis showed that the material was based on a body-centered tetragonal ($I4_1/a$) framework of composition ZrGe$_2$O$_6$ in which Ge is tetrahedrally coordinated by 4 oxygen atoms and Zr has four oxygen atoms in approximately square-planar coordination.[8] The zirconium coordination sphere is completed by two F atoms forming a *trans*-ZrO$_4$F$_2$ octahedron. The framework encloses (per unit ZrGe$_2$) one DAB molecule and one water molecule which are disordered.

The Ge−O bond lengths [1.715(5), 1.708(5), 1.756(3) 2×, average 1.734 Å] are close to the value expected (1.748 Å) for a Ge−O single bond.[9] The bond valence sums at Zr and Ge are both 4.2, close to the expected value (4.0).[9] The bond angles at O are Ge−O−Ge = 127.1(2)° and Ge−O−Zr = 137.0(2)° and 137.1(2)°. The F atoms are split between two positions close to each other. The metal−oxygen bond valence sums at O and F are approximately 1.9 and 0.6, indicating that most of the bonding to protonated DAB (H$_2$DAB) is from fluorine and that the ZrGe$_2$O$_6$ framework is essentially neutral.

The overall topology of the net can be described in terms of rods of corner-sharing GeO$_4$ tetrahedra running parallel to the *c* axis and linked into a three-dimensional network by Zr atoms forming ZrO$_4$ squares as shown in Figure 1a−c. This arrangement results in open channels running parallel to the crystallographic *a*- and *b*-axis. The metal atoms (T atoms) form a novel 4-connected net with ideal symmetry $I4_1/amd$ as illustrated in Figure 1d,e. Two corner sharing ZrGe$_2$ triangles are joined at the Zr vertex to form a planar ZrGe$_4$ "bow tie". These bow ties are further linked by sharing the Ge vertexes to make a 4-connected net in which two 3-rings meet in a *spiro* configuration at each Ge vertex. Thus two 3-rings meet at *every* vertex; the vertex symbols are $3\cdot3\cdot8\cdot10_2\cdot10\cdot10$ for Ge and $3\cdot3\cdot8\cdot8\cdot{*}\cdot{*}$ for Zr.[10] In the vertex symbol for the Zr vertex, the asterisks indicate that at two of the angles there are no rings at all, and thus this vertex is characteristic of a two-dimensional (rather than 3-dimensional) 4-connected net. Note the high density of 8- and 10-membered rings, but the absence of extra-large rings underscoring the fact that a high density of small rings, although probably necessary, is not a sufficient condition for the production of extra-large pores. However, the bow tie motif represents a new secondary building unit (SBU) that will be useful toward the assembly of new zeolite structures: if the Zr atoms are removed from the center of the bow ties they are converted into Ge$_4$ squares, and the whole net is converted into that of gismondine (zeolite code GIS)[11a] which has the same symmetry, as shown in Figure 2. This correspondence suggests other possible structures for Zr−Ge (or Zr−Si, etc.) porous frameworks.[11b]

It is worth noting that the introduction of Zr into the germanate framework by using Zr(OC$_2$H$_5$)$_4$ in the reaction mixture holds a

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(1) DAB = 1,4-diaminobutane.

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(7) (a) For a review of germanate zeolites and a comparison with silicates see: O'Keeffe, M.; Yaghi, O. M. *Chem. Eur. J.* **1999**, *5*, 2796−2801. The only new framework of zeolite-like materials in which all T atoms are Ge occurs in ASU-7 (zeolite code ASV): Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 10569−10570. (b) Gier, T. E.; Bu, X.; Feng, P.; Stucky, G. D. *Nature* **1998**, *395*, 154−157. (c) Cascales, C.; Guiterrez-Puebla, E.; Iglesias, M.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2436−2439.

(8) (a) Anal. Calcd for ZrGe$_2$O$_6$F$_2$·(C$_4$H$_{14}$N$_2$)H$_2$O: C 10.04; H 3.37; N 5.85. Found: C 9.81, H 3.18, N 5.60. (b) Single crystals of ASU-15 are tetragonal, space group $I4_1/a$, with $a = 15.323(1)$ Å, $c = 11.191(1)$ Å, $V = 2627.7(2)$ Å^3, and $Z = 4$ formula units $\{d_{calcd} = 2.581$ g cm^{-3}; μ_a(Mo Kα) = 5.38 cm$^{-1}\}$. A total of 5870 integrated reflection intensities having 2Θ(Mo Kα) < 56.60° were produced using the Siemens/Bruker program SAINT. A total of 1102 of these were independent and gave $R_{int} = 0.0365$. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL-PC Version 5 software package and converged to give $R = 0.0225$ for 912 independent absorption-corrected reflections having $I > 2\sigma(I)$.

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(12) Calcd for Na$_2$ZrGe$_2$O$_6$F$_2$·5.5H$_2$O: C, 0.0; H, 2.15; N, 0.0. Found: C, 0.31; H, 2.10; N, 0.05.

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10.1021/ja003228v CCC: $19.00

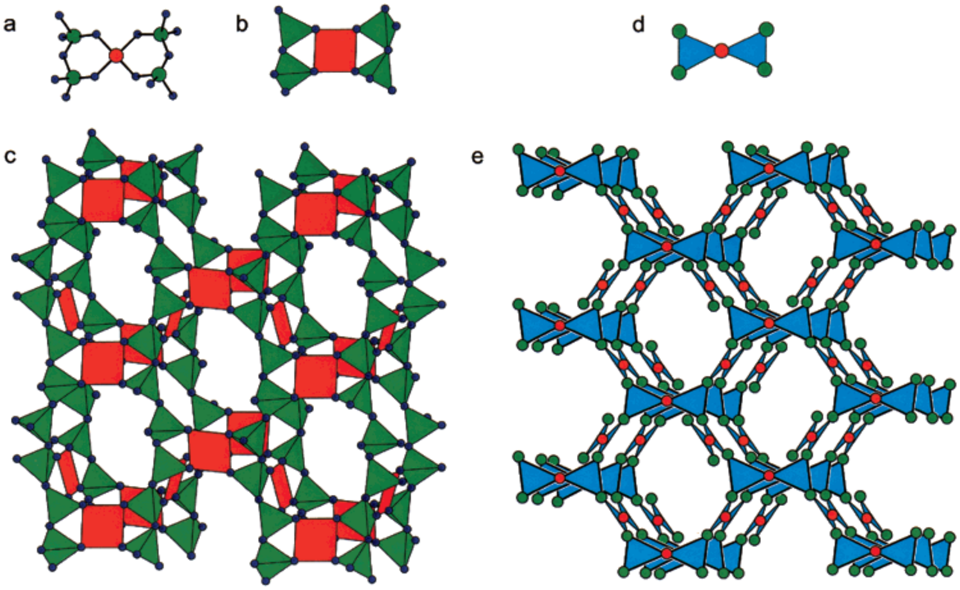

Figure 1. The $ZrGe_2O_6$ framework of ASU-15, $ZrGe_2O_6F_2\cdot(H_2DAB)H_2O$, is constructed from 3-rings shown as (a) stick-and-ball and (b) polyhedral representation. These units form a (c) 3-D network with a 2-D channel system. The *c* axis of the body-centered tetragonal ($I4_1/a$) structure is vertical on the page. It is instructive to view parts a and b as (d) "bow tie" secondary building units, which are *spiro*-connected to form (e) an ASU-15 network (Zr, red; Ge, green; O, blue).

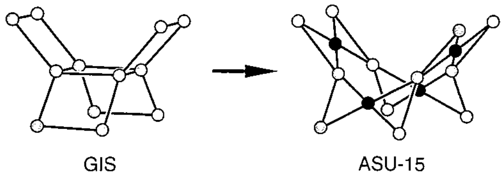

Figure 2. The relationship between the gismondine (GIS) framework and that of ASU-15.

great promise toward the preparation of other Zr containing zeolites, especially since the incorporation of such metal ions into zeolitic frameworks has been a formidable challenge thus far. Preliminary experiments aimed at investigating the likelihood of eliminating the F ions from ASU-15 to yield open zirconium sites point to a possible loss of HF at 500 °C; however, at present, it is difficult to make useful conclusions since the process appears to be complicated by side reactions of the amine guests and more significantly a concomitant loss of crystallinity of the sample.

Nevertheless, ASU-15 can be dehydrated by heating to 225 °C without loss of F ions to produce a crystalline solid with remarkable porosity. In cation exchange experiments in which crystals were immersed in 1 M $NaNO_3$(aq) solution virtually all the organic base is exchanged after 16 h at room temperature. We formulate the exchanged material as $Na_2ZrGe_2O_6F_2\cdot xH_2O$ ($x \approx 6$) on the basis of elemental analysis.[12] Its X-ray powder diffraction pattern showed sharp diffraction lines, with many found to be coincident to those observed for the as-synthesized material. On the other hand, no exchange was observed under similar conditions in $Mg(NO_3)_2$ or $Ca(NO_3)_2$.

To further confirm and evaluate the porosity of this framework, gas and vapor sorption isotherms for the exchanged sample were measured using an electromicro-gravimetric balance (CAHN 1000) setup and an already published procedure.[13] Evacuation of the sample (73.80 g) at room temperature and 5×10^{-5} Torr showed a weight loss of 15.26% corresponding to the loss of 4.4 water molecules per formula unit. N_2(g) sorption performed on the evacuated material revealed a reversible type I isotherm. The same sorption behavior was observed for water and organic vapors such as CH_2Cl_2, CCl_4, and C_6H_{12}. Similar to those of porous zeolites, the isotherms are reversible and show no hysteresis upon desorption of gases from the pores. Using the Dubinin–Raduskhvich equation, pore volumes of 0.03 cm^3/g were calculated. Assuming a monolayer coverage of N_2 the apparent Langmuir surface area was estimated at 83.9 m^2/g. These findings clearly indicate that the exchanged framework has structural stability to support permanent porosity and ion-exchange.

This study illustrates the use of bow tie units in the construction of new zeolite structures, in which it is possible to produce 3-ring units and successfully incorporate covalently linked metal ions—two important aspects to advancing zeolite chemistry and providing numerous opportunities for design of extra-large pore germanate and silicate structures.

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Supporting Information Available: Crystallographic data and N_2 sorption isotherm for ASU-15 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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