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Porous Germanates: Synthesis, Structure, and Inclusion Properties of $Ge_7O_{14.5}F_2\cdot[(CH_3)_2NH_2]_3(H_2O)_{0.86}$

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Despite the extensive growth in the syntheses and applications of new crystalline silicate-based porous materials and related molecular sieves,[1] the analogous germanate chemistry remains virtually undeveloped with only few open-frameworks reported.[2] Given that the minimum M-O-M angles in germanates are typically smaller (120−135°) than in porous silicates (140−145°), the former offers greater opportunities for the formation of three-membered rings and cluster aggregates, which are essential to achieving far more open frameworks having a structural diversity yet unobserved in silicates and their substituted derivatives.[3] Anticipating the rich chemistry promised by germanates, we have embarked on a program designed to further this area. We report here on the transformation of germanium dioxide into $Ge_7O_{14.5}F_2\cdot[(CH_3)_2NH_2]_3(H_2O)_{0.86}$ (ASU-12) using largely *nonaqueous* soft chemical means.[4] Its structure is constructed from Ge_7 cluster units linked into a 3D porous net having intersecting channels where $(CH_3)_2NH_2^+$ (DMA^+) and H_2O guests reside. We have demonstrated that DMA^+ can be reversibly exchanged for Na^+ with full retention of the integrity and periodicity of the germanate open framework structure.

Germanium dioxide (0.120 g, 1.15 mmol) was suspended in a pyridine solution (3.20 mL) containing dimethylamine (DMA) (1.40 mL of a 40% aqueous stock solution, 11.16 mmol) and hydroflouric acid (0.06 mL of an aqueous stock solution of 48.0 wt %, 1.715 mmol) to form a thick liquid/gel. This was heated to 165 °C for 4 days then cooled to room temperature to give colorless crystals of ASU-12 in 65% yield (based on GeO_2).[5] Single-crystal X-ray diffraction analysis[6] revealed a 3D network constructed from the building blocks shown in Figure 1. The core of the cluster is composed of seven germanium oxide centers arranged in C_{2v} noncrystallographic symmetry. An oxide ion (O1) occupies the center of the cluster, which is bonded to three germanium centers to give one octahedral (Ge1) and two trigonal-bipyramidal (Ge2 and Ge3) germanium centers. The remaining germanium centers are tetrahedral and do not form any close interactions to O1. Unlike Ge1 and Ge3, which have a terminal fluoride ligand, the other germanium centers (Ge2 and Ge4−Ge7) are connected to adjacent Ge_7 clusters by doubly bridging oxides (O13, O13A, O14, O15, and O15A) to yield a 3D open framework having nearly square pore apertures that range in free diameter between 4.5 and 5.0 Å (1.40 Å was used as the van der Waals radius of oxygen) as shown in Figure 2. The pores extend along the crystallographic *a* and *c* axes, and at 45° to the *a* and *b* axes resulting in a 3D intersecting channel system that is occupied by three DMA^+ guests and a partial water molecule per formula unit, the latter having an occupancy of 0.86.

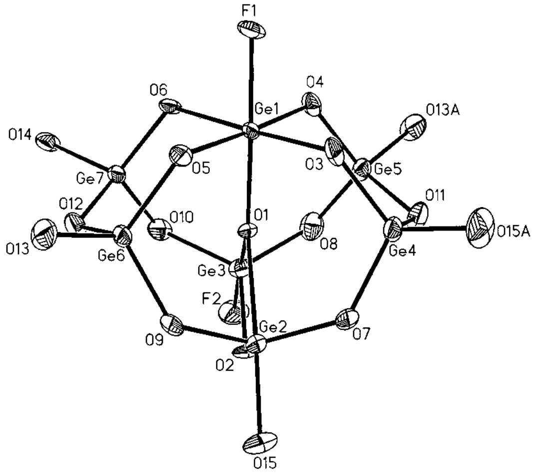

Figure 1. (a) The building block unit including the asymmetric unit present in crystalline $Ge_7O_{14.5}F_2\cdot[(CH_3)_2NH_2]_3(H_2O)_{0.86}$ with atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with an additional letter "A" are symmetry equivalent to those atoms without such designation.

Bond distances and angles within the germanate framework are unexceptional with Ge−O−Ge = 119.0(3)−133.0(4)°, Ge−O (tetrahedral Ge) = 1.717(6)−1.771(6) Å, and Ge−O (octahedral and trigonal bipyramidal) = 1.776(6)−2.187(5) Å, which are in agreement with those observed for other germanates.[2] Close examination of the guests reveal that the cations (N1−N4) and water guests (O16) are weakly hydrogen-bonded to oxygen and fluorine in the framework (N1−O6 = 2.833(10) Å, N2−F1 = 2.766(8) Å, N4−F2 = 2.756(13) Å, O16−O5 = 2.956(15) Å).

A thermal gravimetric study performed on a sample of this material showed an onset of weight loss starting at 165 °C and continuing slowly until 590 °C with a major loss of 6.5% recorded at 320 °C, which we believe is due to the partial decomposition of DMA^+ and the evolution of water from the channels. It was not possible to affect the full thermal decomposition of the DMA^+;

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(1) For example, see: (a) Breck, D. W. *Zeolite Molecular Sieves*, Wiley: New York, 1974. (b) Meier, W. M.; Olson, D. H.; Baerlocher, Ch. *Atlas of Zeolite Structure Types*; Elsevier: Boston, MA, 1996. (c) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756−768. (d) van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds. *Introduction to Zeolite Science and Practice*; Elsevier: Amsterdam, 1991. (e) Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2080−2085. (f) Pinnavaia, T. J.; Thorpe, M. F. *Access in Nanoporous Materials*; Plenum: New York, 1995. (g) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710−712.

(2) (a) Roberts, M. A.; Fitch, A. N. *Z. Kristallogr.* **1996**, *211*, 378−387. (b) Jones, R. H.; Chen, J.; Thomas, J. M.; George, A.; Hursthouse, M. B.; Xu, R.; Li, S.; Lu, Y.; Yang, G. *Chem. Mater.* **1992**, *4*, 808−812. (c) Cheng, J. C.; Xu, R.; Yang, G. *J. Chem. Soc., Dalton Trans.* **1991**, 1537−1540. (d) Cascales, C.; Gutierrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 129−131. (e) Wilson, A. J. C., Eds. *Structure Reports*; Oosthoek-Utrecht: The Netherlands, 1947−1948; Vol. 11, p 405. (h) Feng, S.; Tsai, M.; Greenblatt, M. *Chem. Mater.* **1992**, *4*, 388−393. (i) Behrens, E. A.; Sylvester, P.; Clearfield, A. *Acc. Chem. Res.* **1998**, *32*, 101−107.

(3) O'Keeffe, M.; Hyde, B. G. *Crystal Structures: I. Patterns and Symmetry*; Mineralogical Society of America: Washington, DC, 1996.

(4) The role of nonaqueous solvents in the synthesis of zeolites has been recognized: Nadimi, S.; Oliver, S.; Kuperman, A.; Lough, A.; Ozin, G.; Garces, J.; Olken, M.; Rudolf, P. In *Zeolites and Related Microporous Materials*; Weitkamp, J., Karge, H. G., Pfeifer, H., Holderich, W., Eds.; Elsevier: Amsterdam, 1994; Vol. 84, pp 93−100.

(5) Anal. Calcd for $Ge_7O_{14.5}F_2\cdot[(CH_3)_2NH_2]_3(H_2O)_{0.86}$: C, 7.73; H, 2.78; N, 4.51; Ge, 54.51; F, 4.08. Found: C, 7.62; H, 2.77; N, 4.64; Ge, 53.11; F, 3.68.

(6) Colorless prismatic single crystals of $Ge_7O_{14.5}F_2\cdot[(CH_3)_2NH_2]_3(H_2O)_{0.86}$ were analyzed at −113 ± 1 °C, monoclinic, space group *Im* (no. 8) with a = 9.3693(2) Å, b = 29.6646(6) Å, c = 8.8507(1) Å, β = 108.3400(10)°, V = 2334.98(7) Å^3, and Z = 4 formula units {d_{calcd} = 2.392 g cm^{-3}; μ(Mo Kα) = 77.04 cm^{-1}}. A full hemisphere of diffracted intensities was measured using graphite-monochromated Mo Kα radiation on a Siemens/Bruker SMART CCD System. Cell constants and an orientation matrix, obtained from least-squares refinement using the measured positions of 4450 reflections with $I > 10\sigma$ in the range $3.00 < 2\theta < 50.00°$. The Siemens/Bruker program SHELXTL-PC software package was utilized to solve the structure using "Direct Methods" techniques. 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_1 (unweighted, based on F) = 0.024 for 2447 independent absorption-corrected reflections having 2θ(Mo Kα) < 52.1° and $I > 3.00\sigma(I)$ and wR_2 (weighted, based on F^2) = 0.029 with a "goodness of fit indicator" value of 1.09.

S0002-7863(98)01391-2 CCC: $15.00

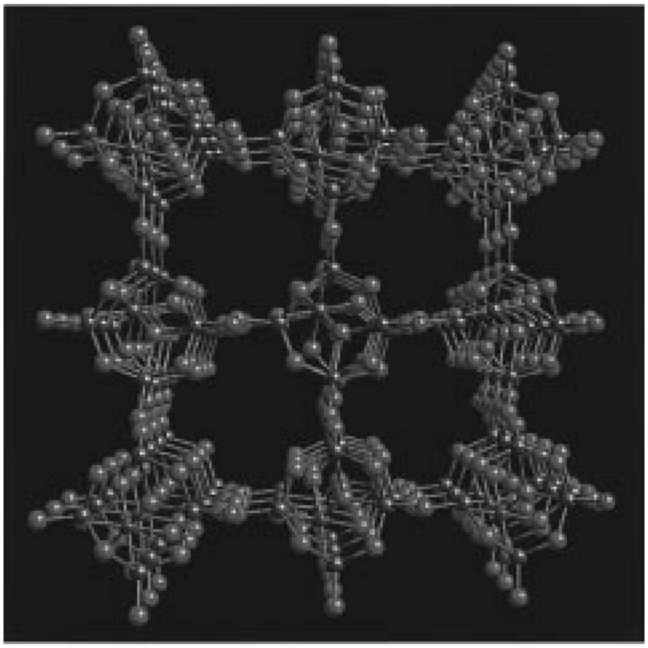

Figure 2. The crystal structure of the 3D porous framework of ASU-12 shown along 45° to the crystallographic *a* axis with Ge (blue), O (green), and F (red). The DMA^+ and water guests are omitted for clarity.

however, we found that the DMA^+ guests can be exchanged in solution. Specifically, the solution ion-exchange behavior of this material was examined by immersing a sample (200 mg) of single crystals (ca. 0.1 × 0.1 mm) in 20 mL of 5.0 M $NaNO_3$ aqueous solution for 45 min; the sample then filtered out and washed thoroughly with water, ethanol, and acetone followed by air-drying. The X-ray powder diffraction (XRPD) patterns of the original starting material (Figure 3a), having DMA^+ in the channels, and the recovered Na^+ exchanged product (Figure 3b), show similar peak intensity and relative position—indicating clearly the retention of the germanate host framework structure and its periodicity. The absence of DMA^+ in the exchanged product was confirmed by the disappearance of the strong absorption peak associated with DMA^+ at 1473 cm^{-1} in the FTIR spectra (compare insets of Figure 3a,b). The identity of the exchanged product was formulated as $Ge_7O_{14.5}F_2 \cdot Na_3(H_2O)_5$ by elemental microanalysis.[7] This confirms the absence of C and N in the sample and thus the complete exchange of Na^+ for DMA^+. The presence of hydration water molecules was established by a thermal gravimetric study on a 38.08-mg crystalline sample of this solid, which showed a weight loss of 9.8% over the temperature range 20−180 °C corresponding to the loss of five water molecules per formula unit (calculated: 9.6%).

Evidence supporting the porosity of this material was obtained by examining the water sorption isotherm of $Ge_7O_{14.5}F_2 \cdot Na_3(H_2O)_5$ using an electromicrogravimetric balance (CAHN 1000). Here, this solid was dehydrated at 96 °C for 16 h under a vacuum of 1×10^{-7} atm until no weight change was observed. Water was then introduced at room temperature in the P/P_0 range of 0.0−0.6 (P_0 = saturation pressure of 0.027 atm) to show a type I isotherm, which is typical of a microporous material. Using these data, the apparent surface area was estimated at 250 m^2/g. The plateau region of the isotherm corresponds to 10% weight gain of water or the sorption of five water molecules per formula unit, which confirms the proposed hydrated composition of the Na^+ exchanged phase.

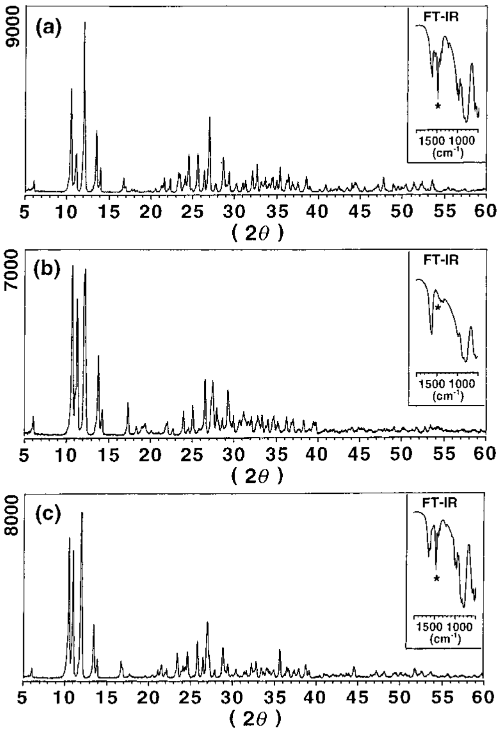

Figure 3. The XRPD patterns and FTIR spectra (insets) of the (a) as-synthesized material, $Ge_7O_{14.5}F_2 \cdot [(CH_3)_2NH_2]_3(H_2O)_{0.86}$ (ASU-12), (b) exchanged solid, $Ge_7O_{14.5}F_2 \cdot Na_3(H_2O)_5$, and (c) reexchanged solid, $Ge_7O_{14.5}F_2 \cdot [(CH_3)_2NH_2]_2Na(H_2O)_2$, resulting from the reintroduction of DMA^+ into the channels.

Upon immersing the Na^+ containing product (100 mg) in an aqueous solution of 5 M DMACl (10 mL) for 45 min, the DMA^+ peak in the FTIR reappears (inset of Figure 3c), while the XRPD pattern of this reexchanged solid (Figure 3c) appears identical to that of the original as-synthesized material (Figure 3a). Elemental microanalysis[8] showed 67% of the Na^+ can be exchanged after 45 min at room temperature; thereafter, the process is significantly slower. Nonetheless, this demonstrates the reversibility of ion exchange within the pores. It is worth noting that the shape and transparency of the crystals are largely retained throughout the ion-exchange process as revealed by optical microscopy.

Preliminary studies in this direction show that ASU-12 readily undergoes ion exchange with a wide variety of mono- and dications such as K^+, Rb^+, Cs^+, Ca^{2+}, Ba^{2+}, Ag^+, Cd^{2+}, Pb^{2+}, and Tl^+. Further studies on the ion-conduction behavior of this material are in progress.

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Supporting Information Available: Crystallographic data for $Ge_7O_{14.5}F_2 \cdot [(CH_3)_2NH_2]_3 (H_2O)_{0.86}$ (ASU-12), 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.

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[7] Anal. Calcd for $Ge_7O_{14.5}F_2 \cdot Na_3(H_2O)_5$: C, 0.00; H, 1.08; N, 0.00; Na, 7.36. Found: C, 0.21; H, 1.07; N, 0.22; Na, 6.90.

[8] Anal. Calcd for $Ge_7O_{14.5}F_2 \cdot [(CH_3)_2NH_2]_2Na(H_2O)_2$: C, 5.17; H, 2.17; N, 3.01; Na, 2.47. Found: C, 5.17; H, 2.10; N, 2.99; Na, 2.37.