Porous Germanates: Synthesis, Structure, and Inclusion Properties of GeO$_{14.4}$F$_2$[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$

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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 GeO$_{14.4}$F$_2$[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$ (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$_3$)$_2$NH$_2^+$ (DMA$^+$) and H$_2$O 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 hydrofluoric 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$_2$). Single-crystal X-ray diffraction analysis5 revealed a 3D network with full retention of the integrity and periodicity of the germanate 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.

Bond distances and angles within the germanate framework are unexceptional with Ge–O–Ge = 119.0(3)–133.0(4) Å, 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 fluorne 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$^+$.


(5) Anal. Calcd for GeO$_{14.4}$F$_2$[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$; 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.

Figure 1. (a) The building block unit including the asymmetric unit present in crystalline GeO$_{14.4}$F$_2$[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$ 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.

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(6) Colorless prismatic single crystals of GeO$_{14.4}$F$_2$[(CH$_3$)$_2$NH$_2$]$_3$(H$_2$O)$_{0.86}$ were analyzed at $-113 \pm 1^\circ C$, monoclinic, space group $\text{Pn}$ (no. 8) with $a = 3.9639(2)$ Å, $b = 29.6646(6)$ Å, $c = 8.8507(1)$ Å, $\beta = 108.3400(10)^\circ$, $V = 2334.987(7)$ Å$^3$, and $Z = 4$ formula units ($\text{d}_{\text{calc}} = 2.392$ g cm$^{-3}$; $\mu$(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 $I > 10\sigma(I)$ in the range $3.00 > 2\theta > 50.00^\circ$. The Siemens/Bruker program SHELXLT-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 $F^2$ data with the SHELXLT-PC Version 5 software package and converged to give $R_1$ (unweighted, based on $F^2$) = 0.024 for 2447 independent absorption-corrected reflections having $2(\text{Mo Kα}) < 52.1^\circ$ and $I > 3\sigma(I)$ and $wR_2$ (weighted, based on $F^2$) = 0.029 with a “goodness of fit indicator” value of 1.09.
DMA

original starting material (Figure 3a), having DMA

throughout with water, ethanol, and acetone followed by air-
solution for 45 min; the sample then filtered out and washed
+channels, and the recovered Na

elemental microanalysis. This confirms the absence of C and

of water or the sorption of five water molecules per formula unit,
plateau region of the isotherm corresponds to 10% weight gain

exchanged product was formulated as Ge7 O 14.5 F 2

spectra (compare insets of Figure 3a,b). The identity of the

P

absorption peak associated with DMA

product was confirmed by the disappearance of the strong

in the exchanged

which confirms the proposed hydrated composition of the Na+

exchanged phase.

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 showed 67% of the Na+

+Na 3 (H 2 O) 5 by
dications such as K+, Rb+, Cs+, Ba2+, Ag+, Cd2+, Pb2+, 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 GeO 14.5 F 2[(CH 3 ) 2 NH] 2 (H 2 O) 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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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.

Figure 3. The XRPD patterns and FTIR spectra (insets) of the (a) as-synthesized material, Ge 4O 1.5 F 2[(CH 3 ) 2 NH] 2 (H 2 O) 0.86 (ASU-12), (b) exchanged solid, Ge 4O 1.5 F 2Na 3 (H 2 O) 5, and (c) reexchanged solid, Ge 4O 1.5 F 2[(CH 3 ) 2 NH] 2 Na 3 (H 2 O) 5, resulting from the reintroduction of DMA+ into the channels.

Evidence supporting the porosity of this material was obtained by examining the water sorption isotherm of GeO 14.5 F 2Na 3 (H 2 O) 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/ P0 range of 0.0−0.6 ( P0 = 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 m2/g. The plateau region of the isotherm corresponds to 10% weight gain of water or the sorption of five water molecules per formula unit,

(7) Anal. Calcd for Ge 4O 14.5 F 2Na 3 (H 2 O) 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 4O 14.5 F 2[(CH 3 ) 2 NH] 2 Na 3 (H 2 O) 5: 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.