Synthesis, Structure, and Properties of a Three-Dimensional Open-Framework Niobium Fluorogermanate (NGH-5)

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The low-temperature hydrothermal synthesis and crystal structure of a new open-framework niobium germanate phase is reported. $(C_6H_{18}N_2)\cdot Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$ (NGH-5) was synthesized from GeO_2, Nb_2O_5, and HF (aq) by using 1,4-*trans*-diaminocyclohexane (1,4-DACH) as an organic structure directing agent. The structure of NGH-5 was determined ab initio by using powder X-ray diffraction techniques and consists of a negatively charged three-dimensional Nb/Ge/O/F framework containing three orthogonal channel systems. Two of the channels are delimited by 10-membered rings of NbO_5F octahedra and GeO_4 tetrahedra; the third is delimited by an 8-membered ring. Charge-balancing $(C_6H_{18}N_2)^{2+}$ cations are encapsulated within the framework and are located at the center of the 10-membered ring channels. The NGH-5 framework is characterized by a low framework density and is closely related to the recently reported zirconium germanate ASU-15.

Introduction

The synthesis of new crystalline zeolitic compositions remains a highly active field due to their widespread application in catalysis, separation, ion-exchange, and radioactive waste remediation.[1−5] Recent efforts have focused on two related goals: new compositions and the formation of large pore materials displaying large internal pore volumes. By controlling the local geometry of the framework species, one can influence the overall framework architecture. For example, the smaller Ge−O−Ge angle found in germanates relative to the Si−O−Si angle found in silicates has important structural consequences, and some unusual topological nets have been observed in germanates that have not been seen in silicates.[6−8] In particular, germanates show a markedly greater propensity for forming three-rings (i.e., three tetrahedral atoms and three oxygen atoms in a ring) which are postulated to be important for the formation of very open-framework architectures.[9] Replacement of a tetrahedral species with a species displaying higher coordination (e.g., octahedral) can also influence the framework architecture. Though relatively few have been reported (with the exception of phosphate-based materials), such mixed octahedral−tetrahedral systems display framework topologies and absorption properties that are markedly different from purely tetrahedral materials.[10]

Our own recent work has focused on open-framework niobium silicate and germanate compositions, of which a very limited number have been reported to date. The limited number of compounds is, in part, due to synthetic difficulties associated with the very low solubility of common sources of niobium in water and the consequent problem of preparing homogeneous starting mixtures. Crystallization from nonhomogeneous mixtures frequently results in the formation of amorphous or semicrystalline materials. Our approach has been to employ a two-stage process in which Nb_2O_5 is first dissolved in aqueous HF, followed by reaction with a germanium or silicon source, an organic template, water, and/or ethylene glycol. The addition of fluoride ions has been shown to be a particularly effective means of synthesizing novel structure types.[11,12] A further important synthetic principle is to make use of the well-known ability of organic species to influence the topology of the framework produced.[6,16,17] We have been exploring the hydrothermal synthesis of new open-framework niobium silicate and germanate compositions in the

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(1) Venuto, P. B. *Microporous Mater.* **1994**, *2*, 297−411.

(2) Thomas, J. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3588−3628.

(3) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633−2656.

(4) O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3−20.

(5) Férey, G. *J. Solid State Chem.* **2000**, *152*, 37−48.

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

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

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

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

(10) Rocha, J.; Anderson, M. W. *Eur. J. Inorg. Chem.* **2000**, 801−818.

(11) Guth, J. L.; Kessler, H.; Higel, J. M.; Lamblin, J. M.; Patarin, J.; Sieve, A.; Chezcau, J. M.; Wey, R. *ACS Symp. Ser.* **1989**, *398*, 176.

(12) Kessler, H. *Mater. Res. Soc. Symp. Ser.* **1991**, *233*, 47.

(13) Francis, R. J.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, in press.

(14) Altomare, A.; Burla, M. C.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Giuseppina-Moliterni, A. G.; Polidori, G.; Rizzi, R. *J. Appl. Crystallogr.* **1999**, *32*, 339−340.

(15) Larson, A. C.; Dreele, R. B. V. Los Alamos Laboratory Rep. No. La-UR-86-748; Los Alamos, NM, 1987.

(16) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751−760.

(17) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr.* **1991**, *B47*, 192−197.

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presence of both organic templates and fluoride ions, and we recently reported the first examples of organically templated open-framework niobium silicate and germanate materials.[13] We report here the synthesis, structure, and properties of $(C_6H_{18}N_2){\cdot}Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$ (designated as NGH-5; Niobium Germanate Houston-5): a new open-framework niobium germanate which has large 10-ring pores and a very low framework density. The structure is closely related to the recently reported zirconium germanate ASU-15.[19]

Experimental Section

Synthesis and Ion-Exchange. NGH-5 was synthesized by first dissolving 0.177 g of Nb_2O_5 (99.5%, Aldrich) in 0.334 g of HF solution (48 wt % in H_2O, Aldrich) at 110 °C for 4 h in a sealed polypropylene bottle. After being cooled to room temperature, this solution was combined with 0.418 g of GeO_2 (99.8%, Aldrich), 1.824 g of *trans*-1,4-diaminocyclohexane (98%, Aldrich), and 2.88 g of H_2O. This mixture was placed in a closed 23 mL Teflon-lined stainless steel autoclave and heated under autogenous hydrothermal conditions at 160°C for 5 days. After the mixture was cooled to room temperature, colorless crystals (crystal size ca. 50−100 μm) of NGH-5 were recovered as the only product of the reaction by filtration; they were washed with water and allowed to dry in air. The yield (based on Nb) was greater than 90%. Ion-exchange reactions were performed on NGH-5 by stirring 250 mg samples of the as-synthesized materials in 15 mL of 1M aqueous solutions of either sodium or potassium chloride at 60 °C for 12 h. Following this treatment, the exchanged materials were washed with water and dried in air.

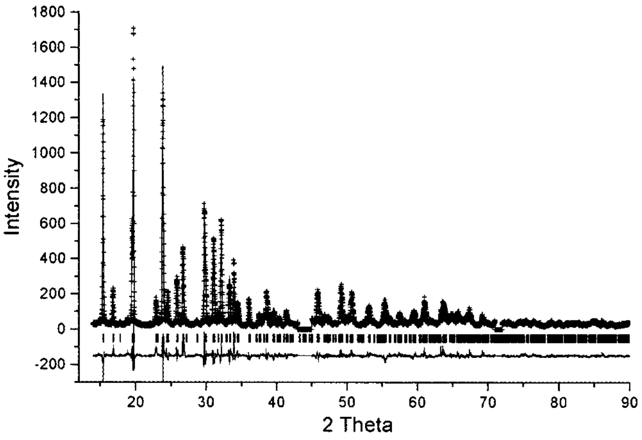

Figure 1. Observed (markers), calculated (line), and difference profiles for the Rietveld refinement of $(C_6H_{18}N_2){\cdot}Ge_2NbO_7F$ (NGH-5).

Table 1. Crystallographic Data for the Organically Templated Open-Framework Niobium Germanate $(C_6H_{18}N_2)Ge_2NbO_7F$ (NGH-5)

	NGH-5
empirical formula	$(C_6H_{18}N_2)Ge_2NbO_7F$
formula weight	484.2
crystal system	tetragonal
space group	$I4_1/a$
a (Å)	14.9152(4)
c (Å)	11.2975(3)
V (Å^3)	2513.3
Z	8
ρ_{calcd} (g cm^{-3})	2.465
geometry	Bragg−Brentano
wavelength (Å)	1.540 56
scan range (deg)	14−90
step size (deg)	0.01
R_p	12.94
R_{wp}	16.41
R_F	7.34
R_{F^2}	12.53
χ^2	1.773

Table 2. Fractional Atomic Coordinates and Thermal Factors for $(C_6H_{18}N_2)Ge_2NbO_7F$ (NGH-5)

atom	W[a]	x	y	z	U_{iso} (Å^2)
Nb(1)	8c	0	0	0	0.0314
Ge(1)	16f	0.2037(4)	0.4533(4)	0.1169(6)	0.0015
O(1)	16f	0.2606(8)	0.4919(21)	−0.0163(2)	0.015[b]
O(2)	16f	0.1915(12)	0.3291(12)	0.1319(18)	0.015[b]
O(3)	16f	0.0987(13)	0.4963(12)	0.1212(18)	0.015[b]
O(4)[c]	16f	0.0289(12)	0.8711(9)	0.0322(2)	0.015[b]
F(1)[c]	16f	0.0289(12)	0.8711(9)	0.0322(2)	0.015[b]
C(1)	16f	0.5151(24)	0.5774(12)	0.0275(27)	0.025[b]
C(2)	16f	0.4750(19)	0.5293 (21)	0.1357(17)	0.025[b]
C(3)	16f	0.5294(17)	0.4486(19)	0.0905(23)	0.025[b]
N(1)	16f	0.5094(23)	0.3873(11)	0.1901(18)	0.025[b]

[a] Wyckoff letter from International Tables. [b] Not refined. [c] From chemical analysis, the occupancies of O(4) and F(1) are 0.4 and 0.6, respectively.

Structure Determination. Powder diffraction data on NGH-5 were collected on a Scintag 2000 diffractometer using Cu Kα radiation over the range 8−100° 2θ. The pattern was indexed by using TREOR90 which gave the refined tetragonal cell $a = b = 14.9152(8)$ and $c = 11.2975(6)$ Å. Evaluation of the systematic absences allowed the space group to be determined unambiguously as $I4_1/a$ (No. 88). The structure was solved ab initio by using the direct methods package EXPO[14] from which the locations of the framework niobium, germanium, and oxygen atoms were determined. This solution was then used as the starting model in the Rietveld analysis of the structure by using the software package GSAS.[15] After initial refinement of this structural model, successive cycles of refinement and difference Fourier syntheses enabled the positions of the template atoms to be determined. For the following cycles of refinement, soft constraints were applied to the relevant carbon−carbon and carbon−nitrogen bond lengths to prevent the atoms from moving to chemically unreasonable positions. Since bulk chemical analysis (Galbraith) indicated that the germanium/niobium ratio was greater than 2, the possibility of germanium substitution at the niobium site was investigated. Addition of a germanium atom at the niobium atom position (initially with an occupancy of zero) followed by refinement of the fractional occupancies of the niobium and added germanium atoms (under the constraint that the total occupancy was always equal to one) led to a small improvement of the fit and a refined Nb/Ge ratio of 0.8:2.2, which is in excellent agreement with the analysis data. Assuming that the template molecules are doubly protonated, this implies that there must be 1.2 fluorine atoms per formula unit to maintain charge balance, giving an overall stoichiometry of $(C_6N_2H_{16}){\cdot}Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$. Bulk chemical analysis was consistent with this formulation (see below). Due to the small difference in the form factors of O and F, the location of the fluorine atom could not be determined from the X-ray data. However, by comparison with the large number of known metal oxyfluorides, it is highly likely that the fluorine atom is located at one of the two terminal positions on the niobium atom. Since both terminal atoms are located on the same crystallographic site, this site was split with a 40% O occupancy and 60% F occupancy. The final refinement consisted of 57 structural and profile parameters and proceeded smoothly to convergence, with $R_p = 12.78$, $R_{wp} = 16.23$, $R_F = 7.12$, $R_{F^2} = 12.09$ and, $\chi^2 = 1.726$. Figure 1 shows the final Rietveld fit to the data. Crystallographic data, fractional atomic coordinates and thermal parameters, and a list of selected bond lengths for NGH-5 are given in Tables 1, 2, and 3, respectively. Analysis data: found (calcd for $(C_6N_2H_{16})Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$):

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(18) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(19) Li, H.; Eddaoudi, M.; Plevert, J.; O'Keefe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 12409−12410.

Table 3. Selected Bond Distances for $(C_6H_{18}N_2)Ge_2NbO_7F$ (NGH-5)

bond	distance (Å)	bond	distance (Å)
Nb(1)−O(2) ×2	1.983(18)	C(1)−C(2)	1.538(2)
Nb(1)−O(3) ×2	2.012(19)	C(1)−C(3)	1.539(2)
Nb(1)−O(4)/F(1)[a] ×2	2.003(15)	C(2)−C(3)	1.538(20
Ge(1)−O(1)	1.819(26)	C(3)−N(1)	1.480(2)
Ge(1)−O(1)	1.771(25)		
Ge(1)−O(2)	1.869(17)		
Ge(1)−O(3)	1.693(19)		

[a] O(4) and F(1) occupy the same crystallographic position each with 40:60% occupancy.

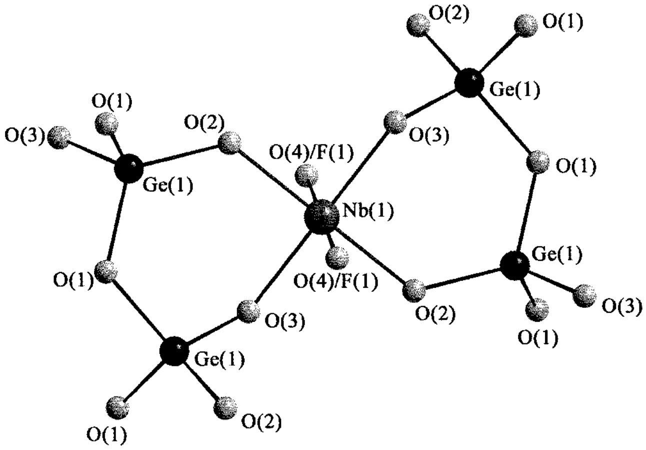

Figure 2. Framework-building unit of $(C_6H_{18}N_2)\cdot Ge_2NbO_7F$ (NGH-5), showing the local coordination around each cation, and the atomic labeling scheme.

C% 14.98 (14.95), H% 3.56 (3.33), N% 5.51 (5.81), F% 5.06 (4.73), Ge% 34.37 (33.20), Nb% 16.04 (15.43).

Thermogravimetry and IR. Thermogravimetric analyses were performed in flowing dry air on a Thermal Analysis Instruments TGA 2950 thermogravimetric analyzer. A ramp rate of 5°C min^{-1} was used in all experiments. IR spectra were collected on a Mattson FTIR 5000 spectrometer by using pressed KBr pellets of the samples.

Results and Discussion

Structure Description. The NGH-5 structure consists of a negatively charged Nb/Ge/O/F framework of ideal composition $Ge_2NbO_7F^{2-}$ encompassing diprotonated 1,4-*trans*-diaminocyclohexane (1,4-DACH) molecules. The framework-building unit along with the atomic labeling scheme is shown in Figure 2 and contains one unique Nb site, one unique Ge site, three unique O sites, and one mixed O/F site. Five O atoms and one F atom coordinate the Nb atoms in slightly distorted octahedral coordination with an average Nb−O/F bond length of 1.999(17) Å. Four of the O atoms share corners with adjacent GeO_4 tetrahedra, while the remaining O atom and F atom are terminal and statistically disordered over two positions related by a center of symmetry. The Ge atoms are tetrahedrally coordinated with an average Ge−O bond length of 1.788 Å. Each GeO_4 tetrahedron shares corners with 2 NbO_5F octahedra and two GeO_4 tetrahedra to form the three-dimensional framework structure.

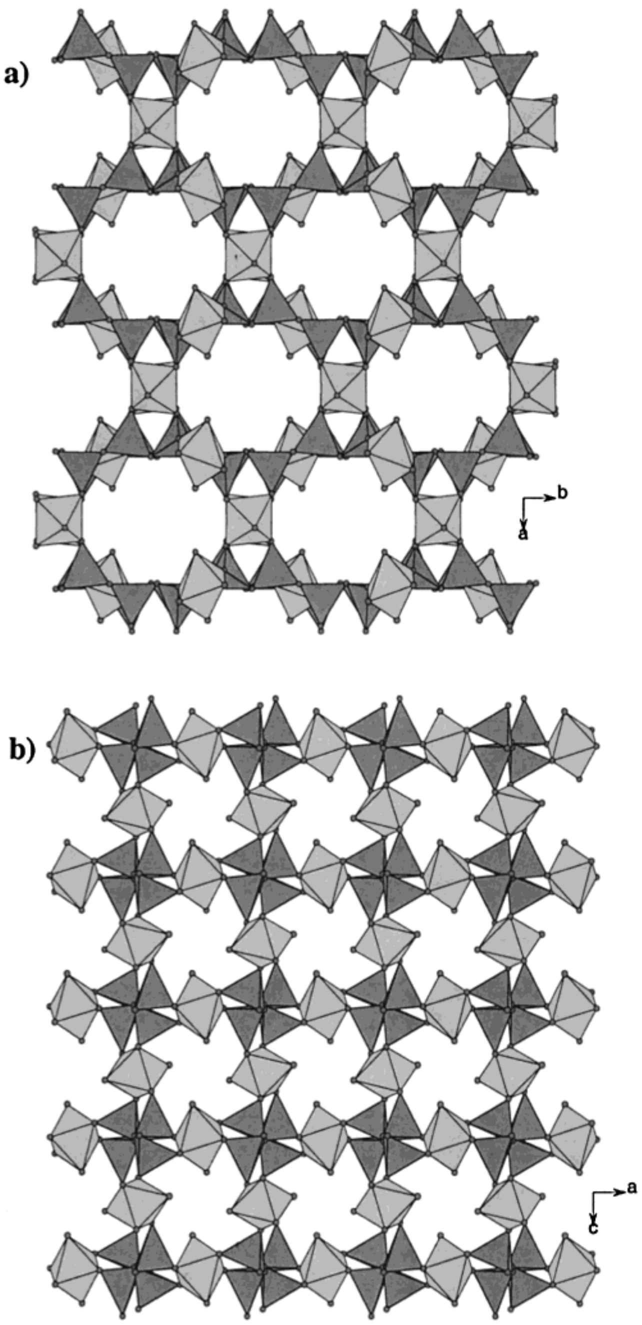

Figure 3. Polyhedral representations of the framework structure of $(C_6H_{18}N_2)\cdot Ge_2NbO_7F$ (NGH-5): (a) viewed along the crystallographic *a*-axis, showing the 10-MR channels and (b) viewed along the crystallographic *c*-axis, showing the 8-MR channels. The template molecules are omitted for clarity. In (a) the NbO_5F octahedra are shown in gray and the GeO_4 tetrahedra are shown in dark gray.

The overall framework topology of NGH-5 is shown in Figure 3. Chains of corner-shared GeO_4 tetrahedra run parallel to the crystallographic *c*-axis, which are then cross-linked in the *a* and *b* directions by NbO_5F octahedra. This connectivity results in large one-dimensional 10-ring (10-MR) channels which are constructed from two NbO_5F and eight GeO_4 units which run along the equivalent *a* and *b* crystallographic axes (Figure 3a). One-dimensional 8-ring (8-MR) channels constructed from four NbO_5F and four GeO_4 units are also formed along the crystallographic *c*-axis (Figure 3b). The 8-MR channels are almost circular in cross-section with a shortest oxygen−oxygen distance across the channel of 3.71 Å. The large 10-MR channels are elliptical in shape with dimensions of 7.2 × 9.1 Å, giving a "free-pore diameter" (using the atomic radii of Shannon[16]) of ca. 4.4 × 6.3 Å. The three channels intersect

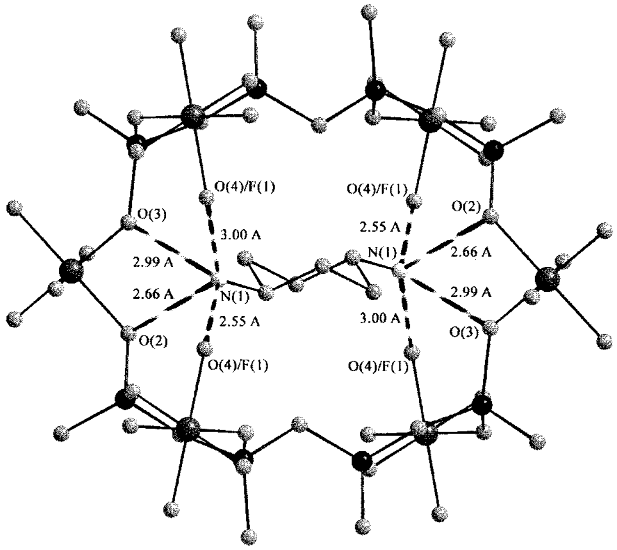

Figure 4. Detail of the location of the template cations within the 10-MR ring windows showing the hydrogen-bonding interactions (shown as dashed lines) between the template nitrogen atoms and the framework. The niobium atoms are represented as dark gray spheres, germanium atoms as black spheres, oxygen, fluorine, and carbon atoms as medium gray spheres, and nitrogen atoms as lighter gray spheres.

at roughly (0.5, 0.25, 0.875) forming a long oval-shaped cavity centered at that position. The maximum free diameter across the cavity is approximately 9.4 Å. The protonated 1,4-DACH cations are not centered within the cavity but are rather located at the centers of the 10-ring windows. Very strong hydrogen bonds are formed between the template cation, the terminal O/F atoms (N−O/F distance = 2.55 Å), and the framework O(2) atoms (N−O distance = 2.66 Å). Somewhat weaker hydrogen bonds are formed between the framework O(3) atoms and a second terminal O/F atom (N−O distances of 2.99 and 3.00 Å, respectively). The 1,4-DACH molecules are located at crystallographic inversion centers. This points to a very strong templating effect through the strong N−F and N−O hydrogen bonds, with the symmetry of the template molecule dictating the symmetry of the inorganic framework. The hydrogen-bonding pattern in NGH-5 is shown in Figure 4.

Chemical analysis gave ratios Ge/Nb = 2.2 and F/Nb = 1.2 indicating the possibility of some substitution of Ge on the Nb sites to give a composition of $Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}{}^{2-}$. Refinement of the X-ray data with this model gave a slightly improved fit and a composition close to that determined by chemical analysis. The lower than expected bond valence sums[17] for the Nb and Ge atoms of 4.73 and 3.64, respectively, are consistent with a disordered model that includes both Nb_{Nb}−O−Ge and Ge_{Nb}−O−Ge bonds.

The NGH-5 framework is an extremely open structure, with a very low framework atom density. The “openness” of microporous frameworks is often parametrized by calculating the framework density (FD = number of framework metal atoms per 1000 Å^3). NGH-5 has a FD value of 9.5 that can be compared with values of 9.1 for ETS-10 and 9.1 for ASU-15 (see below) and indicates an extremely open structure. Another way to quantify the degree of openness of a structure is to calculate the volume percentage not occupied by the framework atoms (here, Nb, Ge, O, and F) assuming typical values for the van der Waals radii of the atoms. With the use of the CALC SOLV function of the PLATON program,[18] 49% of the volume of the NGH-5 structure was found to be unoccupied by framework atoms, which again is a very high number. When the 1,4-DACH molecules were included in the calculation, essentially all the volume was occupied.

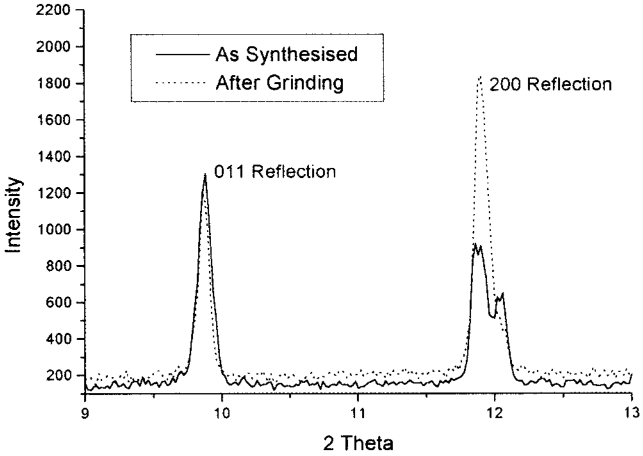

Figure 5. Detail of the low-angle regions of powder X-ray diffraction patterns of a sample of as-synthesised NGH-5 and the same sample after extensive grinding, showing the pronounced change in the 200 reflection following this treatment.

One interesting aspect of NGH-5 is the presence of numerous structural variants characterized by different values of the *a* parameter. Different batches prepared under either the same or slightly different conditions are found to display a range of *a* parameter values, and often the *h*00 reflections are either split or highly broadened. It is also found that grinding the sample leads to changes in the position and intensity of the *h*00 reflections, with the split or broadened *h*00 reflections being seen to coalesce to one peak after extensive grinding, as shown in Figure 5. The origin of this effect is not completely clear. The value of the *a* parameter can be related to the degree of twisting of the (Nb,Ge)-O_5F octahedra linking the GeO_4 chains, with a greater degree of twisting leading to a smaller value of *a*. Since these octahedra are also involved in the strong hydrogen bonding to the 1,4-DACH template, it is possible that the different structural variants may be caused by distributions of the terminal O and F atoms involved in hydrogen bonding in different domains of the same crystallite. Mechanical pressure may then cause the domains to revert to the minimum energy state. Remnants of this effect can be seen in the Rietveld plot shown in Figure 1. Close inspection of the observed and calculated diffraction patterns reveals that most of the discrepancies are caused by the variable profile shape of the diffraction lines. This is the origin of the somewhat large residuals in the Rietveld analysis and esd's of the framework oxygen atom positions.

NGH-5 is closely related to the recently reported zirconium germanate open-framework material ASU-15 reported by Li et al.[19] If the ZrF_2 unit in the ASU-15 framework is replaced by an NbOF unit, the NGH-5 framework is formed. Interestingly, ASU-15 was synthesized using 1,4-diaminobutane (1,4-DAB) as the organic template. Although this is clearly related to 1,4-

DACH, use of 1,4-DAB in the niobium germanate system results in the formation of the layered material NGH-4. This may be due to the relatively weak templating effect of the flexible 1,4-DAB molecule as opposed to the strong templating effect of the more rigid 1,4-DACH molecule. As was pointed out by Li et al., the ASU-15/NGH-5 framework can be related to the structure of gismondine. Removal of the ZrF_2 or NbOF units in ASU-15 and NGH-5, respectively, followed by condensation of the germanate groups results in the formation of the gismondine framework. A large number of three-ring units (two per vertex) are present in ASU-15/NGH-5. In structures based exclusively on tetrahedral atoms, theoretical studies[9] suggest a link between the number of three-rings and very open frameworks. The mixed octahedral−tetrahedral three-rings in ASU-15 and NGH-5 are not strictly comparable, and a large number of the previously reported octahedral−tetrahedral frameworks (e.g., ETS-4, ETS-10, VSH-1, 2, and NSH-1)[10,20,13] have very high numbers of three-rings. Nevertheless, the insertion of octahedral metal linking groups into a purely tetrahedral zeolitic framework does point to a vast potential for the formation of other very open-framework structures.

Thermal Analysis. Thermal analysis of NGH-5 in flowing dry air revealed no significant weight loss until a temperature of ca. 370 °C. Between 370 and 440 °C, a sharp weight loss of 23% occurs, followed by a further weight loss of 5% between 400 and 650°C. Calculated weight losses for combustion of the template (23.9%) and combustion of the template plus loss of HF (28.0%) are in excellent agreement with these numbers. To test the stability of the framework toward loss of the template, a sample of NGH-5 was heated in air at 420 °C for 2 h. Powder X-ray diffraction of this sample revealed an amorphous material indicating that the framework of NGH-5 is not stable toward thermal removal of the template.

Ion-Exchange Experiments. Ion-exchange experiments on NGH-5 were not successful. No significant changes in the powder X-ray diffraction patterns or IR spectra were seen after mixtures of NGH-5 were stirred in 1M solutions of $NaNO_3$, KNO_3, and $RbNO_3$ at 80 °C for 1 day. When the mixtures were heated under hydrothermal conditions at 120°C, amorphous materials were produced. This is surprising given the ease with which the 1,4-DAB cations could be exchanged from ASU-15, as reported by Li et al.[19] The difference may be related to the greater steric bulk and rigidity of 1,4-DACH relative to 1,4-DAB or, more likely, to the presence of stronger N−H···F hydrogen bonds in NGH-5.

Summary and Conclusions

In summary, we have described the simple, high yield, phase pure synthesis of a new open-framework niobium germanate phase, 1,4-DACH$Ge_{2.2}Nb_{0.8}O_{6.8}F_{1.2}$: NGH-5. The NGH-5 framework is characterized by an extremely low framework density and contains a network of two large intersecting 10-MR channels and a third smaller intersecting 8-MR channel. Although attempts to remove the organic template while keeping the framework intact have proved unsuccessful to date, given the huge variety of organic templates that could be used in these syntheses, the scope for the synthesis of further novel niobium germanate and silicate phases appears to be very large. Indeed, by the use of similar synthetic techniques, we have recently isolated further novel organically templated niobium germanate and silicate phases, including three-dimensional phases,[13] layered phases, and cluster compounds.

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(20) Wang, X.; Liu, L.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2879−2881.