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$NH_4[BGe_3O_8]$: A New Borogermanate Framework Made of Infinite-Chain Building Blocks

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A new microporous borogermanate $NH_4[BGe_3O_8]$ has been synthesized by a molten boric acid flux method with "reagent" quantities of water in which GeO_2, ethylenediamine, H_2O, and H_3BO_3 (5:8:14:25) were heated together at 513 K for 4 days. The structure consists of $\{Ge_6O_{18}\}_n$ chains, further linked together via BO_4 tetrahedra, forming a three-dimensional open framework with intersecting channel systems including one-dimensional 10-membered-ring (MR) channels. Interestingly, the infinite chains $\{Ge_6O_{18}\}_n$ as building blocks, built of alternating 4- and 6-MRs made of vertex-sharing GeO_4 tetrahedra, construct the borogermanate framework. It is noteworthy that the high viscosity of the reactive medium and the quantity of water play important roles in the formation of the compound.

Introduction

Because of their current widespread applications in catalysis, separation, ion exchange, and molecular recognition, new compositions and framework topologies of zeolites and related microporous crystalline materials have attracted extensive research efforts worldwide.[1] In zeolite science, the meaning of the term *isomorphous* substitution is the partial or total replacement of Al or Si with other tri- or tetravalent metal ions.[2] The first example of isomorphous substitution was reported by Goldsmith in 1952, concerning Ge for Si in thomsonite.[3] A major difference between tetrahedral silicate and germanate frameworks is that the Si−O−Si and Al−O−Si angles (in the absence of constraints) are in a narrow range close to 145°, whereas the Ge−O−Ge angles are close to 130°.[4] On the other hand, in contrast to Si surrounded by a tetrahedron of O atoms, in Ge zeotypes the structure of the framework can be formed by GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra. Therefore, in past decades, the research efforts have been continued with the synthesis and characterization of some new types of germanate frameworks.[5]

More recently, "attempts have also been made to incorporate elements from the third main group (B, Al, Ga) into the silicate zeolite frameworks to adjust the acid strength of zeolite-based catalysts."[6a] Boron is commonly found in trigonal or tetrahedral surroundings, and it should be a good candidate for the preparation of solids with networks similar

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to in zeolites.[7] Because of the flexible coordination geometries for both Ge and B atoms, the B−Ge−O system is likely to provide greater opportunities for the formation of new open frameworks. Although very little research has been carried out on borogermanates, some interesting structural features were already observed, such as three- and seven-rings, helical channel, and cluster.[6] Especially, the B−O−Ge angle is so small that it is even close to 114.98°.[6c]

The structure of the final product depends critically on the choice of synthetic strategies. The boric acid flux method, in which excessive melt boric acid acts as both a reaction medium and a reactant, was introduced by Williams and co-workers for the synthesis of a polyborate polymer.[8] Recently, Lin and co-workers elaborated the method and prepared a series of aluminoborates and rare-earth polyborates.[9] In our group, we successfully synthesized an ammonium fluorinated borophosphate $NH_4[BPO_4F]$ with GIS topology and other sodium borophosphates by applying this method.[10a,c] Furthermore, we extend the flux to phosphate and prepared a chlorophosphate $Na_3[CuO(HPO_4)Cl]$.[10b] More recently, Lightfoot explored a “dry” hydrothermal method using “reagent” quantities of water, which led to the isolation of a new mixed-anion framework material $Mn_2(H_2PO_4)_2(C_2O_4)$.[11]

In this paper, we applied the boric acid flux method with “reagent” quantities of water to the B−Ge−O system and prepared a new borogermanate, $NH_4[BGe_3O_8]$. X-ray analysis revealed that the crystal structure could be described as a three-dimensional (3-D) open framework built of $\{Ge_6O_{18}\}_n$ chains connected by BO_4 tetrahedra, and NH_4^+ resides in channels.

Experimental Section

Synthesis and Characterization. Crystals of $NH_4[BGe_3O_8]$ was prepared via the boric acid flux method with “reagent” quantities of water in a Teflon-lined stainless steel autoclave ($V = 40$ mL). The mixture of 3.14 g (50 mmol) of H_3BO_3 and 1.05 g (10 mmol) of GeO_2 (hexagonal phase) was homogenized by grinding and then was placed into an autoclave with a filling degree of about 20% by the initial powder reactants. After that, 1.00 mL (16 mmol) of ethylenediamine (en) and 0.50 g of H_2O (28 mmol) were added into the autoclave and stirred until the mixture became homogeneous. After a reaction time of typically 4 days at 513 K, the autoclave was removed from the furnace and allowed to cool to room temperature. The colorless crystals from the reaction were recovered by vacuum filtration, washed thoroughly with deionized water and ethanol repeatedly until the residual boric acid was completely removed, and finally dried at 333 K in air (>98% yield based on GeO_2) for further characterizations. A hot-extraction method was applied for the analysis of C, N, and H (Leco CHNS-932). Anal. Found: C, 0.09; N, 3.59; H, 0.63. Calcd for $NH_4[BGe_3O_8]$: N, 3.74; H, 1.07. This showed that en was decomposed during the reaction.

Table 1. Crystallographic Data and Refinement Parameters for $NH_4[BGe_3O_8]$

empirical formula	$NH_4[BGe_3O_8]$
fw	374.62
wavelength	Mo Kα (0.710 73 Å)
cryst syst, space group	triclinic, $P\bar{1}$ (No. 2)
unit cell dimens	$a = 7.043(4)$ Å, $\alpha = 101.98(1)°$
	$b = 7.379(4)$ Å, $\beta = 103.66(1)°$
	$c = 7.590(5)$ Å, $\gamma = 105.13(1)°$
V	354.5(4) Å^3
Z, calcd density	2, 3.510 g/cm^3
abs coeff, μ(Mo Kα), mm^{-1}	12.655
θ range for data collection	2.88−27.12°
reflns collcd/unique	1792/1513 [$R_{int} = 0.0174$]
GOF on F^2	1.011
final R indices [$I > 2\sigma(I)$]	R1^a = 0.0329, wR2^b = 0.0793
R indices (all data)	R1 = 0.0383, wR2 = 0.0810
largest diff peak and hole	−0.959 and +1.072

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

The reaction products were examined also by powder X-ray diffraction (a Rigaku D/max 2550V diffractometer, Cu Kα) to confirm their phase identity and purity. The diffraction patterns were consistent with those calculated from the structures determined by single-crystal X-ray diffraction except for a trace quantity of $(NH_4)_3HGe_7O_{16}\cdot nH_2O$. Thermogravimetric analyses and differential scanning calorimetry (TGA and DSC) were performed using STA-409PC/4/H LUXX DSC−TGA at a heating rate of 10 K min^{-1} in a flow of N_2 over the temperature range from 293 to 1123 K. IR spectra were collected on a Digilab-FTS-80 spectrophotometer using pressed KBr pellets of the sample.

Structure Determination. A colorless single crystal (0.16 × 0.16 × 0.38 mm) of $NH_4[BGe_3O_8]$ was selected under a polarizing microscope, glued to a thin glass fiber with cyanoacrylate (superglue) adhesive, and inspected for singularity. A data set was collected on a Nonius Kappa CCD diffractometer (Mo Kα radiation, $\lambda = 0.710$ 73 Å) at room temperature. The data were corrected for absorption using the *SADABS* program.[12] The structure was solved in the space group $P\bar{1}$ (No. 2) by direct methods and refined against $|F^2|$ with the aid of the *SHELXTL-97* software package.[13] All H positions were located from the difference map but were refined with fixed displacement parameters in the final refinement. Pertinent experimental details for the structure determination are presented in Table 1. Selected bond distances and angles are given in Table 2.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for $NH_4[BGe_3O_8]$[a]

Ge1−O5#1	1.750(5)	Ge3−O7#2	1.728(6)
Ge1−O2	1.711(8)	Ge3−O1	1.711(7)
Ge1−O4	1.735(11)	Ge3−O4	1.736(7)
Ge1−O8	1.720(7)	Ge3−O5	1.729(12)
Ge2−O3	1.714(9)	B1−O1	1.444(9)
Ge2−O6	1.723(6)	B1−O2#3	1.491(8)
Ge2−O7	1.754(10)	B1−O3#4	1.460(8)
Ge2−O8	1.752(7)	B1−O6#7	1.490(11)
B1−O1−Ge3	123.61(31)	B1#3−O2−Ge1	122.91(32)
B1#5−O6−Ge2	118.37(29)	B1#4−O3−Ge2	127.82(35)
Ge1−O4−Ge3	129.79(24)	Ge1#1−O5−Ge3	124.30(22)
Ge2−O7−Ge3#6	127.39(22)	Ge2−O8−Ge1	129.86(28)

Bond Valence Sums ($\sum s$)

$[BO_4]$ tetrahedron	$\sum s[B-O] = 3.05$
$[Ge(1)O_4]$ tetrahedron	$\sum s[Ge(1)-O] = 4.21$
$[Ge(2)O_3]$ tetrahedron	$\sum s[Ge(2)-O] = 4.14$
$[Ge(3)O_3]$ tetrahedron	$\sum s[Ge(3)-O] = 4.25$

[a] Symmetry transformations used to generate equivalent atoms: (#1) $1 - x, 1 - y, 1 - z$; (#2) $-1 + x, y, z$; (#3) $1 - x, 2 - y, 1 - z$; (#4) $2 - x, 2 - y, 1 - z$; (#5) $1 + x, y, 1 + z$; (#6) $1 + x, y, z$; (#7) $-1 + x, y, -1 + z$.

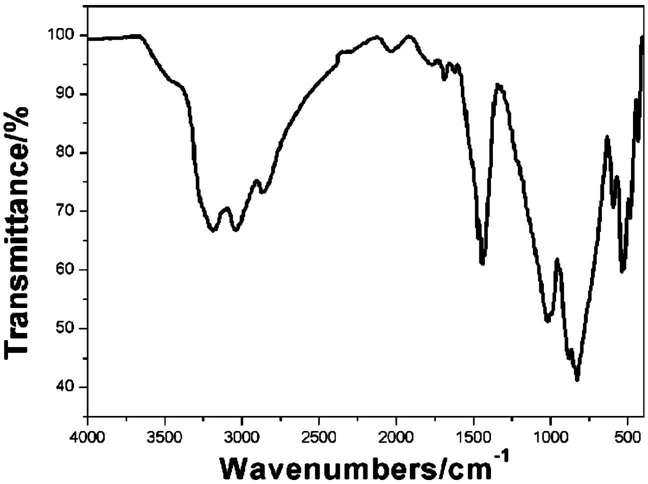

Figure 1. Fourier transform IR spectrum of $NH_4[BGe_3O_8]$.

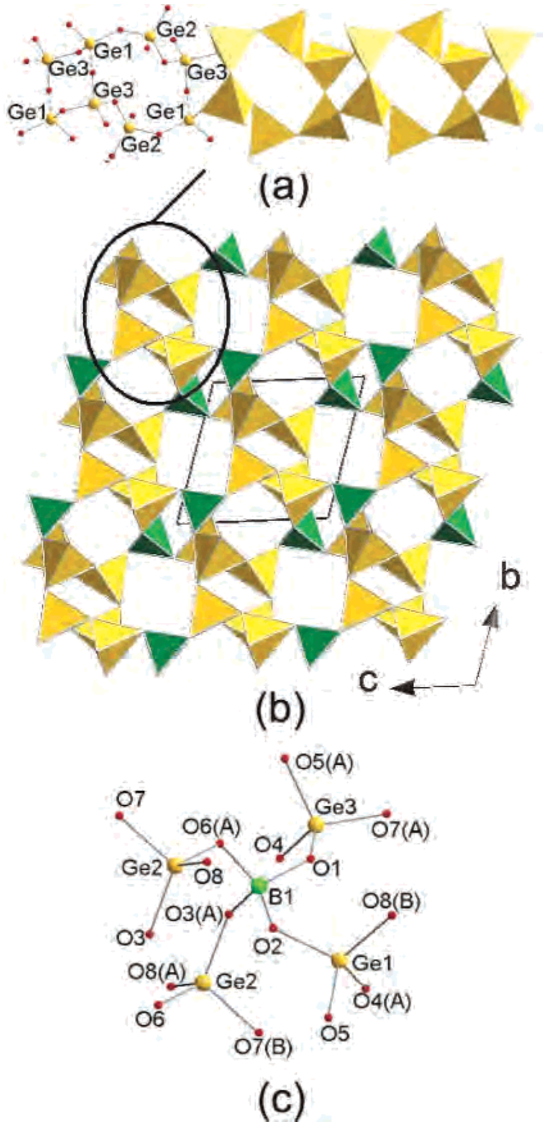

Figure 2. (a) $\{Ge_6O_{18}\}_n$ chain in $NH_4[BGe_3O_8]$. (b) Polyhedral view of $NH_4[BGe_3O_8]$ along the [100] direction, showing the connectivity of the $\{Ge_6O_{18}\}_n$ chain and BO_4 tetrahedra. (c) Connectivity of the GeO_4 and BO_4 tetrahedra.

Results and Discussions

TGA and the IR Spectrum. The IR spectrum (Digilab FTS-80) of the title compound in a KBr pellet showed bands at different positions (Figure 1). The bands at 3189−2873 and 1443 cm^{-1} can be attributed to the stretching and bending vibrations of the N−H groups, respectively. A strong band at about 1018 cm^{-1} agrees with the existence of tetrahedral BO_4 in the crystal structure.[6b,e] The peaks at 879 and 829 cm^{-1} can be assigned to an asymmetrical stretch of Ge−O of the tetrahedral Ge. The absorption bands at 598 and 540 cm^{-1} are caused by a symmetrical stretch of Ge−O. The peaks at 486 and 436 cm^{-1} are due to bending vibrations of Ge−O.[6b,e]

The TGA of the title compound (in N_2) shows a weight loss of about 7.94% from 650 to 970 K in one step. One part of the weight loss (about 4.90%) corresponds to the removal of the NH_4^+ cations (calcd 4.81%) and residue C (from the decomposition of the en molecule). The reason for the other part of the weight loss (about 3.04%) could be explained by the elimination of B (calcd 2.94%). An endothermic peak was detected at 775 K. After heating at 923 K for $^1/_2$ h, the residue is hexagonal GeO_2 from the X-ray powder diffraction result.

Crystal Structure Description. The title compound crystallizes in the triclinic space group $P\bar{1}$ and consists of $\{Ge_6O_{18}\}_n$ chains connected by BO_4 tetrahedra to form a 3-D open framework. Figure 2 illustrates the coordination environments of the central B and Ge atoms and the connectivity of the $\{Ge_6O_{18}\}_n$ chains and BO_4 tetrahedra. In the structure, all of the Ge and B centers are tetrahedrally bound to four O atoms, and all of the O atoms are μ_2-bridging. There is one crystallographically distinct B atom, and the BO_4 tetrahedra share all coordination O atoms with four GeO_4 tetrahedra by μ_2-O. $Ge(1)O_4$ and $Ge(3)O_4$ tetrahedra share one vertex with BO_4 tetrahedra, and the remaining three coordination O atoms are further connected to three GeO_4 tetrahedra by μ_2-O. $Ge(2)O_4$ tetrahedra were connected by two BO_4 tetrahedra and two GeO_4 tetrahedra via common vertexes. A 6-MR built exclusively of vertex-sharing GeO_4

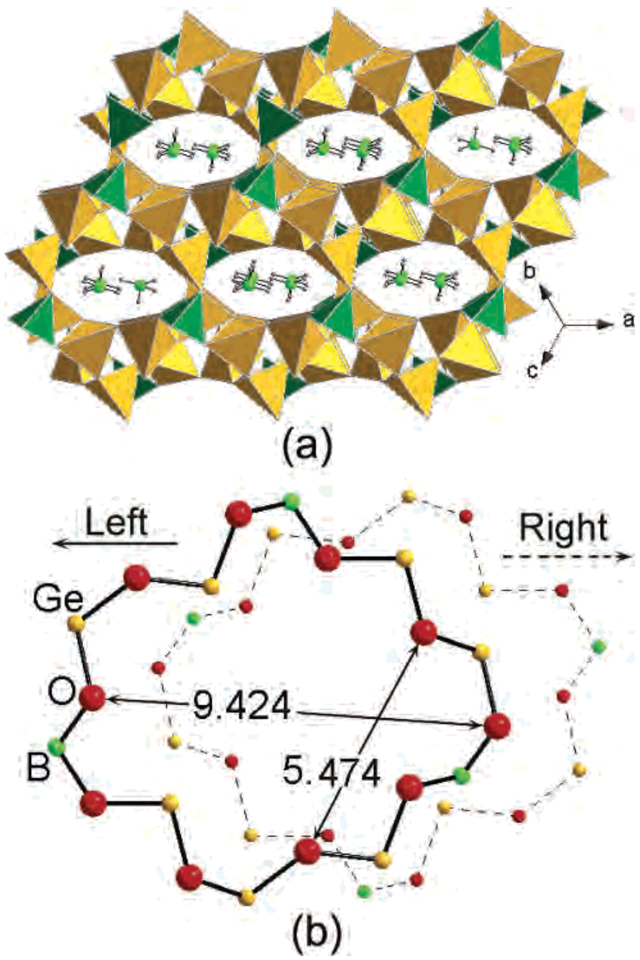

Figure 3. (a) Polyhedral view of $NH_4[BGe_3O_8]$ along the [111] direction. NH_4^+ resides in the elliptical channel: yellow tetrahedra, GeO_4; green tetrahedra, BO_4. (b) Butterfly-like 10-MR in different directions (left and right). The pore size is shown angstroms.

tetrahedra can be considered as the secondary building block (SBU) of the $\{Ge_6O_{18}\}_n$ chain. An infinite connectivity of these SBUs via vertexes forms the backbone of the chain, in which 6- and 4-MRs are arranged in an alternating fashion along the chain (Figure 2a). Along the [111] direction, there are infinite butterfly-like 10-MRs with a $(BO_4)-2(GeO_4)-(BO_4)-2(GeO_4)-(BO_4)-3(GeO_4)$ sequence arranged in an alternating direction (left and right), resulting in an elliptical channel along the [111] direction (Figure 3a). The pore aperture and ring size are shown in Figure 3b. There are also smaller 6- or 8-MR channels along the *a*, *b*, or *c* axes, resulting in 3-D intersecting channel systems.

The Ge−O distances range from 1.711 to 1.754 Å and the B−O distances from 1.444 to 1.491 Å, similar to those reported earlier.[6] The Ge−O−Ge bond angles are 124.30−129.86° and close to those reported.[6b] Interestingly, compared with Ge−O−B angles in other borogermanates with tetrahedral coordination, the smallest is 115.0°[6c] and the biggest is 131.9°;[6e] the Ge−O−B angles in $NH_4[BGe_3O_8]$ are in a wide range from 118.37° to 127.82°. In particular, no B−O−B connection is observed. The calculated bond valence sum of 3.05 for B and average 4.20 for Ge are in good agreement with the expected values of 3.0 and 4.0, respectively.[16,17] The en molecule was decomposed during the reaction in terms of element analysis. The residual NH_4^+ cations are located in the 10-MR channels, balancing the charges of the framework (Figure 3a). Furthermore, they are H-bonded to the framework; each NH_4^+ cation is H-bonded to five μ_2-O atoms. The N−H···O distances are between 2.92 and 3.33 Å.

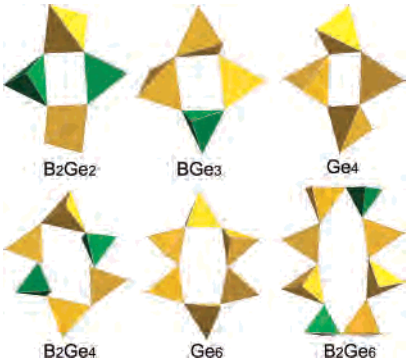

Figure 4. All types of ring fragments extracted from $NH_4[BGe_3O_8]$ (the 10-MR is shown in Figure 3) showing the structural diversity of the borogermanate system: yellow tetrahedra, GeO_4; green tetrahedra, BO_4.

Because of the wide range of bond lengths and angles, the connectivity of BO_4 and GeO_4 tetrahedra shows a great structural diversity. Such a diversity is illustrated for selected B_mGe_n ring fragments extracted from $NH_4[BGe_3O_8]$ in Figure 4. There are three types of 4-MRs with sequences of $(BO_4)-(GeO_4)-(BO_4)-(GeO_4)$, $(BO_4)-3(GeO_4)$, and $4(GeO_4)$, two types of 6-MRs with sequences of $(BO_4)-2(GeO_4)-(BO_4)-2(GeO_4)$ and $6(GeO_4)$, one type of 8-MR with a sequence of $(BO_4)-3(GeO_4)-(BO_4)-3(GeO_4)$, and the 10-MR mentioned above, which further proved that the borogermanate system should be a good candidate for the preparation of zeotype structures.

Attempts to exchange NH_4^+ with an inorganic Li^+ cation [in a LiCl(aq) solution] at room and higher temperature (333 K) failed, and the $NH_4[BGe_3O_8]$ phase transformed into $(NH_4)_3HGe_7O_{16}\cdot nH_2O$,[14] maybe due to the synthesis condition of $NH_4[BGe_3O_8]$ obtained in a trace water environment and interaction resulting from H bonding between the framework and the NH_4^+ cations.

Synthesis. The title compound was prepared by the boric acid flux method with "reagent" quantities of water. To investigate the influence of the quantities of water on products, three control experiments in the $H_3BO_3-GeO_2-en-H_2O$ system were carried out. We only changed the quantities of water and kept those of other reagents constant. All reactions were carried out in 40-mL Teflon-lined stainless steel autoclaves at 513 K for 4 days. According to the molar ratio *n* of $H_2O-H_3BO_3$, three different results were obtained. No reaction was took place when no water was added ($n = 0$). In the case of $n = 0.5$, the new phase borogermanate $NH_4[BGe_3O_8]$ was formed. With an increase of the quantity of water ($n = 2$), the $[Ge_7O_{16}]^{4-}$ cluster was formed in

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Table 3. Typical Compositions and Crystallization Products[a]

composition in a molar ratio	product
5:8:0:25 G−en−W−B	no reaction
5:8:14:25 G−en−W−B	$NH_4[BGe_3O_8]$
5:10:14:25 G−N−W−B	no reaction
5:8:56:25 G−en−W−B	$(NH_4)_3HGe_7O_{16}\cdot nH_2O$
stirring GeO_2 in concentrated aqueous ammonia[b]	$(NH_4)_3HGe_7O_{16}\cdot nH_2O$

[a] G = GeO_2, en = ethylenediamine, W = H_2O, B = H_3BO_3, N = NH_4Cl, crystallization temperature = 513 K; and crystallization time = 4 days. [b] See ref 14.

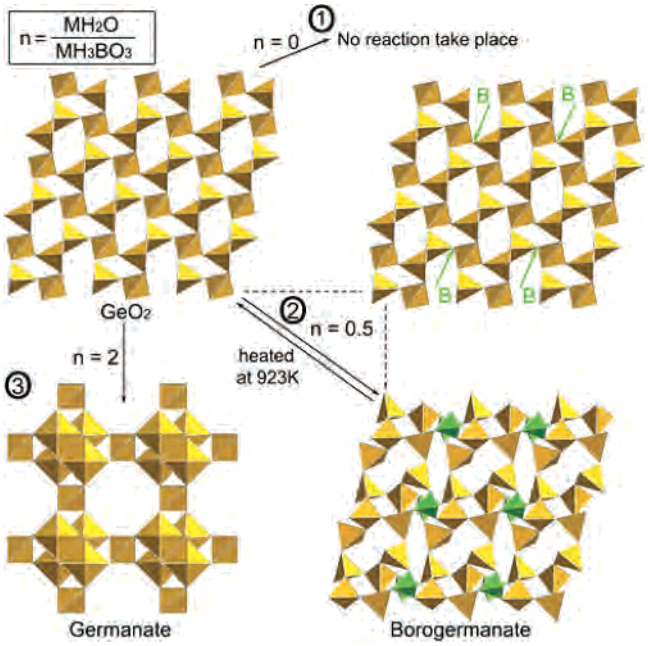

Figure 5. Schematic of the formation mechanism of $NH_4[BGe_3O_8]$ and the influence of the quantity of water on the products.

$(NH_4)_3HGe_7O_{16}\cdot nH_2O$[14] and boric acid only acts as a reaction medium. Because of the decomposition of en during synthesis, we replace en with NH_4Cl in the preparation of $NH_4[BGe_3O_8]$, but no reaction took place, which indicates that en also acts as a solvent. Compositions in molar ratios and the corresponding products in all reactions are listed in Table 3 and shown in Figure 5.

It is very interesting to compare the structures of the starting materials GeO_2 (hexagonal phase) and borogermanate $NH_4[BGe_3O_8]$ reported here. In the structure of GeO_2, we can consider that it was built of parallel $\{Ge_6O_{18}\}_n$ chains connected to each other via the Ge−O−Ge bond in *the a* plane (Figure 5). The same $\{Ge_6O_{18}\}_n$ chain is also found in the structure of $NH_4[BGe_3O_8]$, but the Ge−O−B−O−Ge bonds replaced the Ge−O−Ge bonds. The analogical structural features, the $\{Ge_6O_{18}\}_n$ chain, might be ascribed to the high viscosity of the reactive medium, in which the starting reagent cannot dissolve in molten boric acid completely. The hypothetical formation mechanism of $NH_4[BGe_3O_8]$ is shown in Figure 5. This example provides evidence that some species in molten flux can be incorporated into the ultimately isolated solid.[15] Furthermore, the successful synthesis of $NH_4[BGe_3O_8]$ shows that, in the syntheses of zeolites, we can design new structures using not only 0-D fundamental building blocks, such as rings and supertetrahedra, but also 1-D chains. Constructing new borogermanates with open frameworks using chains (as shown in $NH_4[BGe_3O_8]$) or clusters [as shown in $(NH_4)_3HGe_7O_{16}\cdot nH_2O$] is also expected.

Conclusion

A new microporous borogermanate $NH_4[BGe_3O_8]$ has been synthesized by a molten boric acid flux method with “reagent” quantities only of water. With the change of quantity of water, different open frameworks were obtained. $NH_4[BGe_3O_8]$ consists of $\{Ge_6O_{18}\}_n$ chains along the *a* axis linked together through tetrahedral borate bridges and contains 1-D channels defined by 10-MRs along the [111] direction. The infinite chains, built of vertex-sharing 6-MR $[Ge_6O_{18}]$, come from hexagonal GeO_2 as the building block to construct $NH_4[BGe_3O_8]$. This work sheds some light on the fact that it is possible to design new a borogermanate or germanate using a chain or cluster derived from a starting material as a building block in the molten flux environment, and related researches are ongoing.

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Supporting Information Available: Crystallographic data in CIF format, observed and calculated XRD patterns, and the TGA−DSC curve for $NH_4BGe_3O_8$. This material is available free of charge via the Internet at http://pubs.acs.org.

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