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Hydrothermal Synthesis and Structural Characterization of Zeolite-like Structures Based on Gallium and Aluminum Germanates

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Abstract: While extensive commercial success has been achieved through the use of organic molecules in the synthesis of aluminosilicate zeolites, the synthesis of the germanium-based zeolite structures using organic structure-directing agents is a largely unexplored area. Here we report a novel class of germanate zeolite structures prepared with inorganic cations or organic amines as structure-directing agents. These new materials possess five 4-connected 3-dimensional topologies with large (12-ring), medium (10-ring), small (8-ring), or ultrasmall (6-ring) pores. They have a variety of chemical compositions such as various Ge to Ga (or Al) ratios and exhibit interesting structural features such as helical chains and odd-membered rings. UCSB-15GaGe and UCSB-15AlGe are the first germanate-based structures with 5-rings. UCSB-7 refers to a collection of isostructural, large-pore zeolite-like structures constructed by the cross-linking of helical ribbons. UCSB-3GaGe is the only known T^{3+}/T^{4+} (T refers to tetrahedral atoms) based zeolite structure with the net 38 topology. This structure is unusual because of its very high framework charge density unsurpassed by other amine-directed zeolite structures. GaGe-SOD2 and AlGe-SOD2 (sodalite analogues) have an unusually low framework symmetry for a sodalite structure. The cubic GaGe-SOD1 (or AlGe-SOD1) and the triclinic GaGe-SOD2 (or AlGe-SOD2) are ideal examples of the compositional and structural control of the inorganic framework by structure-directing amines. GaGe-ANA1 and GaGe-ANA2, two gallogermanate analcime analogues, are noncentrosymmetric, unlike many other analcime structures.

Introduction

Zeolites are open-framework aluminosilicates constructed from corner-sharing Al and Si oxygen tetrahedra.[1] Over the past several decades, zeolites have been extensively studied because of their utility in commercial processes such as gas separation and petrochemical-based catalysis.[2] Of fundamental importance is the synthesis of zeolitic materials with novel catalytic properties. This has led to an everincreasing interest in preparing zeolitic materials with new framework topologies or chemical compositions.[3]

The discovery of a large family of aluminophosphate-based zeolite-type materials in the early 1980s has generated a widespread interest in non-aluminosilicate-based microporous materials.[4−7] Recently, a large number of phosphate-based zeolite-type structures with high framework charge densities were reported.[8,9] Here, we seek to expand the methodology developed in the synthesis of the highly charged phosphates to the germanium system. Our interest in developing germanium-based zeolite-like structures is not limited to the expansion of known zeolite structures into a new compositional domain. It is also important to understand the essential factors in the zeolite synthesis and to develop a synthesis strategy to prepare zeolite structures with previously unknown framework topologies. While a large number of zeolite structures are possible on the basis of topological considerations, only a small fraction of these have been synthesized.[10] This is in part due to the restrictive chemical factors, which favor some particular framework topologies for given chemical compositions.[11] Thus changing chemical factors by working in novel compositional domains should provide a more feasible route to new framework structures.

Germanates are of particular interest because they have metal−oxygen bond distances significantly greater than those in silicate-based materials. The large T−O distances in germanates lead to smaller T−O−T angles. We have found that these geometric factors have an important effect on the types of structures that are favored under particular synthesis conditions.[12] Another advantage of the germanate system over other non-silicate compositions is that the germanate-based materials are capable of forming both even- and odd-membered rings; thus many more framework topologies are accessible. The exploration of such a compositional domain has the potential to uncover new zeolite-like structures including 3-ring structures with low framework densities.[13]

Even in the early days of the zeolite synthesis, there were some efforts aimed at substituting Al and/or Si with other

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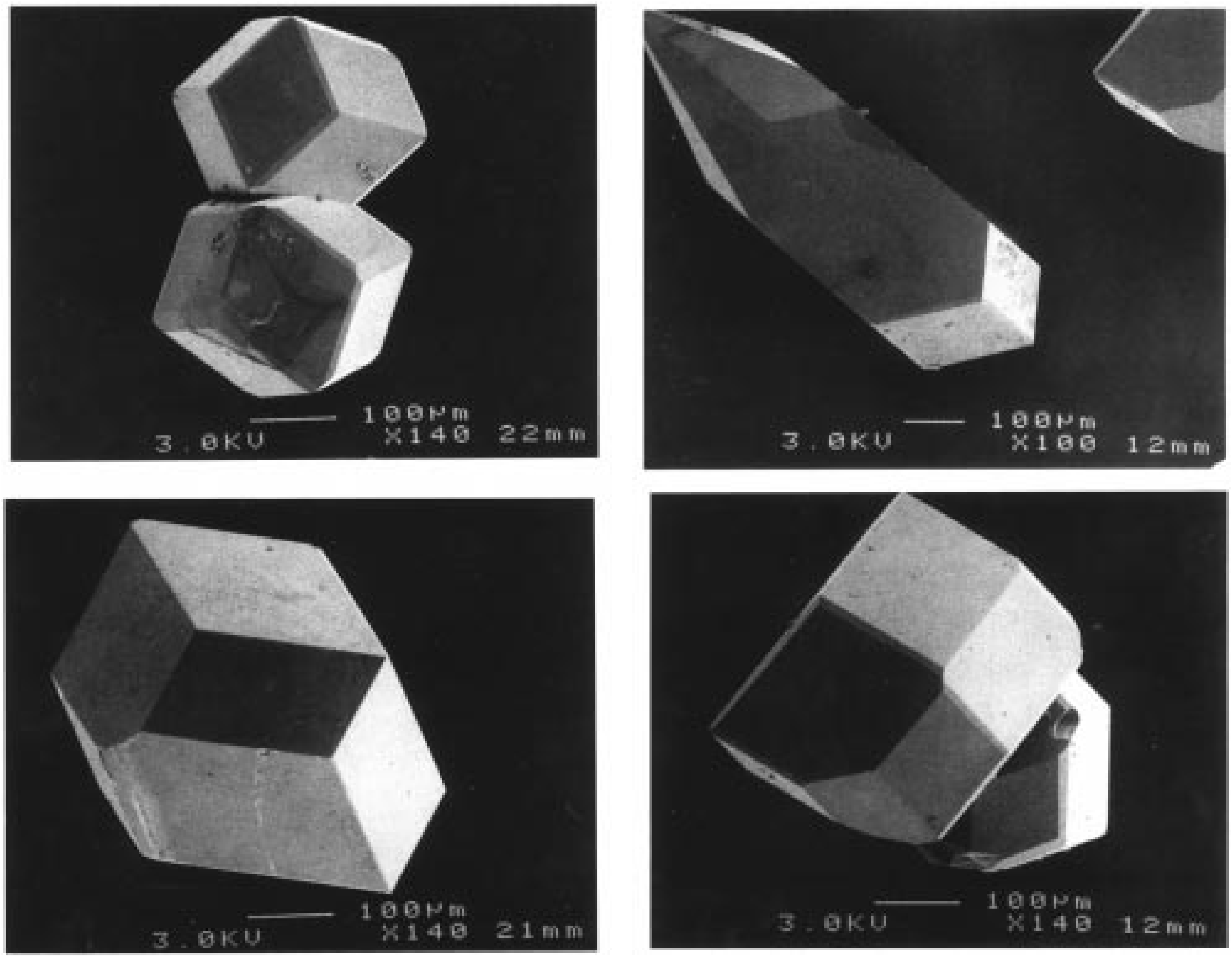

Figure 1. SEM pictures of gallogermanate UCSB-7 synthesized with *N*-(2-aminoethyl)-1,3-propanediamine showing various crystal morphologies.

tetrahedral elements such as Ga and Ge. The early synthesis of Ge^{4+}-based phases was performed in a purely inorganic system similar to that used for the synthesis of aluminosilicate zeolites, and a few phases were claimed.[14] In fact, compared to the case of silicate or phosphate structures, much less is known about germanium-based zeolite structures. In gallogermanates, only single-crystal structures of hydrated sodalite and anhydrous natrolite analogues ($Na_3[GaGeO_4]_3 \cdot 4H_2O$ and $RbGa_2Ge_3O_{10}$) have been reported.[15,16] The high pressure and high-temperature (800 bar, 750 °C) synthesis conditions for the natrolite analogue are, however, unsuitable for the synthesis of more open zeolite-like structures.

Here we report a large family of germanate zeolite structures denoted as UCSB-15GaGe, UCSB-15AlGe, UCSB-7GaGe, UCSB-7AlGe, UCSB-3GaGe, GaGe-SOD1, AlGe-SOD1, GaGe-SOD2, AlGe-SOD2, GaGe-ANA1, and GaGe-ANA2. These materials possess various Ge to Ga (or Al) ratios (1, 1.5, 2, 3, 5, etc.), demonstrating the diversity of chemical compositions that can be achieved in such a system. With the exception of the analcime analogues, these new structures were synthesized with organic molecules as structure-directing agents. A variety of amines (primary, secondary, tertiary, or quarternary; linear, branched, or cyclic) have been successfully used in the crystal growth of germanate 4-connected, 3D structures. It is noteworthy that the Ga^{3+} cations in structures reported here are strictly tetrahedrally coordinated, in contrast with many gallophosphates in which Ga^{3+} usually has a higher coordination number,[17] a configuration that in general is less desirable in the synthesis of open-framework structures.

Prior to this work, every zeolite-type structure could be prepared as either a silicate or a phosphate, or both. On such a basis, zeolite-type structures have been classified into three groups by the International Zeolite Association.[1] The work reported here creates a new group of zeolite-type structures because neither UCSB-7 nor UCSB-15 has been prepared as a silicate or phosphate.

Experimental Section

Hydrothermal Synthesis. (a) UCSB-7. UCSB-7 can have several distinct crystal morphologies even from a single synthesis batch (Figure 1). Crystals of different shapes have been studied by single-crystal X-ray diffraction and are confirmed to have identical structures. A typical procedure for the synthesis of gallogermanate UCSB-7 is given below. To a polypropylene bottle were added 0.730 g of GeO_2, 6.462 g of H_2O, 7.32 g of tris(2-aminoethyl)amine, 0.551 g of $Ga(NO_3)_3 \cdot xH_2O$, and 7.079 g of ethylene glycol. The mixture was then heated at 180

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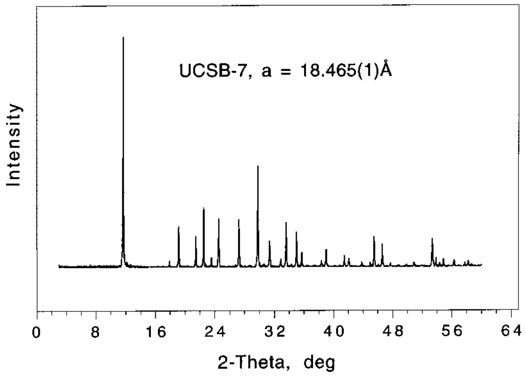

Figure 2. X-ray powder diffraction pattern of gallogermanate UCSB-7 prepared in the presence of tris(2-aminoethylamine).

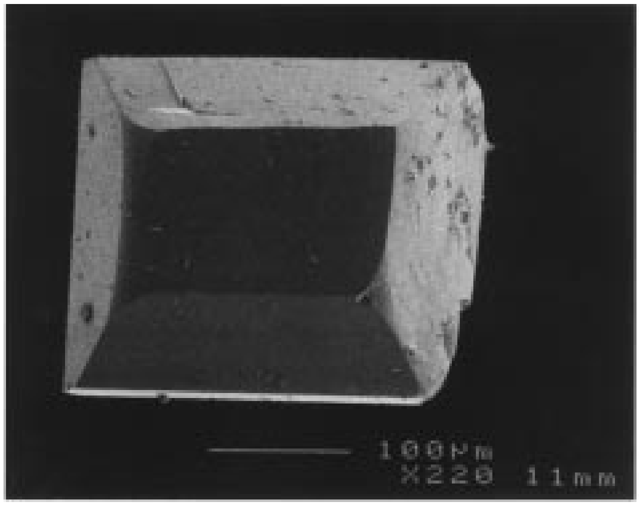

Figure 3. SEM picture of a crystal of the gallogermanate UCSB-15.

°C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. The X-ray powder pattern (Figure 2) could be indexed using a body-centered cubic cell, and no impurity lines were detected.

(b) UCSB-15GaGe. To a polypropylene bottle were added 0.454 g of GeO_2, 8.389 g of hexamethyleneimine, 1.531 g of piperazine hexahydrate, 0.244 g of $Ga(NO_3)_3{\cdot}xH_2O$, and 2.258 g of ethylene glycol. The mixture was then heated at 180 °C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Crystals of UCSB-15GaGe had a distinct crystal morphology showing the orthorhombic symmetry (Figure 3). Two other phases were UCSB-7GaGe and a piperazine-templated germanate with some Ge^{4+} sites in nontetrahedral coordinations.[18]

(c) UCSB-3GaGe and GaGe-SOD2. To a polypropylene bottle were added 0.497 g of GeO_2, 5.813 g of H_2O, 6.58 g of ethylenediamine, 0.748 g of $Ga(NO_3)_3{\cdot}xH_2O$, and 6.912 g of ethylene glycol. The mixture was then heated at 180 °C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Three different phases could be identified on the basis of the crystal morphology and single-crystal X-ray diffraction. Crystals of UCSB-3GaGe were thin-needle-shaped whereas crystals of GaGe-SOD2 were thick-plate-shaped. Crystals of UCSB-7GaGe did not have a well-defined shape and were a minor phase.

(d) GaGe-SOD1. GaGe-SOD1 was prepared by mixing GeO_2 (1.051 g), 25% aqueous tetramethylammonium hydroxide (2.840 g), $Ga(NO_3)_3{\cdot}xH_2O$ (0.472 g), and ethylene glycol (4.258 g). The mixture was then heated at 180 °C for 16 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. All crystals had a cubic morphology.

(e) GaGe-ANA1. GaGe-ANA1 was prepared by mixing GeO_2 (0.824 g), 1,4-diaminobutane (3.07 g), $Ga(NO_3)_3{\cdot}xH_2O$ (0.439 g), and ethylene glycol (0.405 g). The mixture was then heated at 180 °C for 8 days in a Teflon-coated steel autoclave. The product was recovered by filtration and washed with deionized water. Two distinct phases could be recognized on the basis of the crystal morphology and single-crystal X-ray diffraction. UCSB-7GaGe was the major phase, and crystals were in the form of thick needles (Figure 1). Crystals of GaGe-ANA1 were bowl-shaped.

(f) GaGe-ANA2. To a polypropylene bottle were added 50% aqueous CsOH (15.64 g) and a mixture of Ga_2O_3 (0.375 g) and GeO_2-(0.858 g). After an overnight soak at 100 °C, all solids were in solution. Sequential additions of concentrated HNO_3 (up to 3.737 g) were then made with overnight soaks at 100 °C. Recoveries of varying quantities of polycrystalline products (identified using X-ray powder diffraction as an analcime analogue) were made after each soak. Filtrates were saved for subsequent acidification. Finally, 0.109 g of concentrated HNO_3 was added to the last filtrate, and the mixture was sealed in a Teflon pouch and heated to 170 °C for 4 days in an autoclave. The cooled recovered product consisted of cubic crystals of GaGe-ANA2 with a typical dimension of 120 μm.

Elemental Analysis. Quantitative elemental analyses for selected materials were carried out on a Cameca SX-50 electron probe microanalyzer equipped with five wavelength-dispersive (WD) X-ray spectrometers and one energy-dispersive (ED) X-ray spectrometer. The analyses for different elements were simultaneously performed on different WD spectrometers. Calculated values (in mass percent based on the formula derived from the single-crystal structure analysis) and observed values in parentheses are as follows. UCSB-3GaGe: Ga, 29.4 (27.4); Ge, 30.6 (33.9). UCSB-7GaGe(methylamine): Ga, 15.6 (15.6); Ge, 48.7 (47.2).

Single-Crystal X-ray Crystallography. A crystal of each sample was glued to a thin glass fiber with epoxy resin and mounted on a SMART CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (Mo Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. About 1.3 hemispheres of intensity data were collected in 1321 frames with ω scans (width of 0.30° and exposure time of 30 s per frame). The empirical absorption corrections were based on the equivalent reflections, and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structures were solved by direct methods followed by successive difference Fourier methods. All calculations were performed using SHELXTL, and final full-matrix refinements were against F^2. The crystallographic results are summarized in Tables 1 and 2, and some important bond distances and angles are given in Table 3.

Results and Discussion

We will first discuss the use of the geometrical data in the evaluation of the Ge/Ga ratio and the Ge and Ga site distribution in this new family of gallogermanates. The structural correspondence between two classes of body-centered cubic zeolite-type structures (the $Im\bar{3}m$ group and the $Ia\bar{3}d$ group) will then be discussed. Finally, new gallogermanate materials will be grouped and discussed together on the basis of their framework topological types. A summary of new aluminogermanate materials isostructural with gallogermanate structures is provided in Table 4.

Ge/Ga and Al/Ge Ratios. Determining the Ge/Ga ratio is one of the most important aspects in the structural analysis of gallium germanates. The similarity in X-ray atomic scattering factor between Ge^{4+} and Ga^{3+} makes it difficult to distinguish Ge^{4+} and Ga^{3+} atomic sites in the crystal structure refinement. However, in some cases, it is possible to determine the distribution of Ga and Ge atoms by analyzing metal−oxygen (M−O) bond distances.

The ideal bond distances for Ge−O and Ga−O are 1.74 and 1.82 Å, respectively.[19] Thus, a comparison between refined M−O bond distances with these two ideal values can sometimes allow an unambiguous assignment of T-atom types to different

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Table 1. Summary of Crystal Data and Refinement Results for UCSB-3GaGe (Refined in Both Super- and Subcells), UCSB-7GaGe-dma, and UCSB-15GaGe[a−c]

	UCSB-3GaGe	UCSB-3GaGe	UCSB-7GaGe-dma	UCSB-15GaGe
formula	$(R2)Ga_2Ge_2O_8$	$(R2)Ga_2Ge_2O_8$	$(R12)GaGe_3O_8$	$(R3)GaGe_5O_{12}$
habit	thin needle	thin needle	dodecahedron	plate
color	clear translucent	clear translucent	clear translucent	clear translucent
size (μm^3)	266 × 40 × 40	266 × 40 × 40	67 × 67 × 67	226 × 106 × 13
a (Å)	10.6245(1)	15.0254(2)	18.5356(2)	7.7308(3)
b (Å)	10.6245(1)	15.0254(2)	18.5356(2)	13.3750(4)
c (Å)	8.9822(2)	8.9822(2)	18.5356(2)	14.6126(5)
V (Å^3)	1013.91(3)	2027.85(6)	6368.3(1)	1510.93(9)
Z, $2\theta_{max}$ (deg)	4, 50	8, 56	24, 56.32	4, 56.56
space group	$P4_2/n$	$P4_2/n$	$Ia\bar{3}d$	$Pnma$
no. of tot./unique data	5178/898	12 459/2430	17 425/660	8927/1914
data with $I > 2\sigma(I)$	786	1633	647	1586
no. of parameters	83	122	38	129
$R(F)$ (%)	4.27	7.37	3.79	3.27
$R_w(F^2)$ (%)	11.4	14.1	6.80	7.09
GOF	1.27	1.31	1.37	1.05

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\sigma(F)$. [b] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$. [c] R2 = $[NH_3CH_2CH_2NH_3]^{2+}$; R12 = $(CH_3)_2NH$; R3 = monoprotonated piperazine.

Table 2. Summary of Crystal Data and Refinement Results for Sodalite and Analcime Analogues[a−d]

	GaGe-SOD1	GaGe-SOD2	GaGe-ANA1	GaGe-ANA2
formula	$(R1)GaGe_5O_{12}$	$(R2)Ga_2Ge_4O_{12}$	$NH_4GaGe_2O_6$	$CsGaGe_2O_6$
habit	cube	thick plate	irregular	cube
color	clear translucent	clear translucent	clear translucent	clear translucent
size (μm^3)	133 × 133 × 133	173 × 93 × 26	186 × 133 × 93	93 × 93 × 93
a (Å)	9.0976(1)	7.1958(2)	13.6958(1)	13.9827(1)
b (Å)	9.0976(1)	7.6157(2)	13.6958(1)	13.9827(1)
c (Å)	9.0976(1)	7.6368(2)	13.6958(1)	13.9827(1)
V (Å^3)	752.98(1)	337.56(2)	2568.99(3)	2733.84(3)
Z, $2\theta_{max}$ (deg)	2, 56	1, 56.48	16, 56.62	16, 56.42
space group	$I\bar{4}3m$	$P\bar{1}$	$I\bar{4}3d$	$I\bar{4}3d$
no. of tot./unique data	2382/193	3699/1610	7549/538	7983/567
no. of data with $I > 2\sigma(I)$	193	1373	535	549
no. of parameters	15	102	32	32
$R(F)$ (%)	1.05	3.20	1.89	2.23
$R_w(F^2)$ (%)	2.51	7.03	3.92	3.94
GOF	1.28	1.05	1.23	1.13

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\sigma(F)$. [b] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$. [c] R1 = $N(CH_3)_4^+$; R2 = $[NH_3CH_2CH_2NH_3]^{2+}$. [d] Unit cell angles for GaGe-SOD2: $\alpha = 113.587(1)°$, $\beta = 109.109(1)°$, $\gamma = 100.608(1)°$.

T-atom sites. For example, in GaGe-SOD2 described below, the distribution of Ga and Ge cations among three unique tetrahedral atom sites can be determined on the basis of the average bond distances which are 1.754 Å (the Ge site), 1.752 Å (the Ge site), and 1.820 Å (the Ga site), respectively.

In some cases, the structural refinement gives a M−O distance that is between the ideal Ga−O and Ge−O distances so that it is not possible to unambiguously distinguish Ga and Ge sites. A similar problem exists in aluminosilicate zeolites, in which it is often not possible to distinguish between Al^{3+} and Si^{4+} sites. However, the M−O distances in these gallogermanates can still be quite useful in evaluating the overall Ge/Ga ratio in the structure. For example, the difference in the Ge/Ga ratios between two sodalite analogues (GaGe-SOD1 and GaGe-SOD2) is clearly reflected in the average M−O bond distances. GaGe-SOD2 has a longer average M−O distance (1.775 Å) because of its lower Ge/Ga ratio (Ge/Ga = 2). The higher Ge/Ga ratio (Ge/Ga = 5) in GaGe-SOD1 leads to a significantly shorter M−O distance (1.755 Å).

It is worth mentioning that the average M−O bond distance in aluminogermanates reported here is independent of Al/Ge ratios (Table 4) because the ideal bond distances for Ge−O and Al−O are both 1.74 Å.[19] On the other hand, the X-ray atomic scattering factors of Ge^{4+} and Al^{3+} are significantly different to allow a fairly accurate estimate of Al/Ge ratios through occupancy refinement. For example, in AlGe-SOD1, the refined occupancy factors for Ge and Al are 0.2083 and 0.0417, respectively. This gives a Ge/Al ratio of 5.00, in perfect agreement with the Ge/Al ratio derived from the charge neutrality.

T-Atom Site Selectivity. In gallogermanates, the distribution of Ge and Ga among unique tetrahedral atom sites can be highly selective. In addition to Loewenstein's aluminum avoidance rule,[20] which may be applicable to gallogermanates and thus disfavor Ga−O−Ga linkages, there are other chemical factors that could lead to a specific site selectivity. Such a site selectivity is a phenomenon occurring at the nucleation and crystallization stages and is related to the difference in local charge density of the inorganic framework. Specifically, the tetrahedral atom site selectivity is correlated with the orientation of organic molecules and the more negative region (i.e. Ga sites) should be close to the positively charged head groups of amine molecules ($R-NH_3^+$). Such an effect is illustrated by the orientation of organic molecules in the ethylenediamine sodalite analogue (GaGe-SOD2, Ge/Ga = 2). The three shortest N···O distances in GaGe-SOD2 are 2.858, 2.732, and 2.899 Å for N1−O1, N1−O3, and N1−O4, respectively. All three oxygen atoms are coordinated to the Ga site whereas only one of these O atoms is coordinated to the Ge1 site and two of these O atoms are connected to the

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Table 3. Selected Bond Distances (Å) and Angles (deg)

UCSB-15GaGe			
Ge1−O4	1.732(3)	Ge1−O3	1.736(3)
Ge1−O2	1.750(3)	Ge1−O6	1.747(2)
Ge2−O3	1.743(3)	Ge2−O2	1.744(3)
Ge2−O5	1.754(3)	Ge2−O1	1.755(3)
Ge3−O1	1.763(3)	Ge3−O5	1.766(3)
Ge3−O7	1.773(2)	Ge3−O4	1.763(3)
Ge2−O1−Ge3	131.9(2)	Ge1−O2−Ge2	132.0(2)
Ge2−O3−Ge1	139.7(2)	Ge1−O4−Ge3	130.8(2)
Ge2−O5−Ge3	129.2(2)	Ge1−O6−Ge1	134.5(2)
Ga1−O7−Ga1	137.7(2)		
UCSB-7GaGe-dma			
Ge1−O2	1.770(3)	Ge1−O2	1.773(3)
Ge1−O1	1.776(3)	Ge1−O1	1.780(3)
Ge1−O1−Ge1	123.9(2)	Ge1−O2−Ge1	127.3(2)
UCSB-3GaGesubcell			
Ge1−O3	1.736(6)	Ge1−O1	1.739(5)
Ge1−O4	1.742(4)	Ge1−O2	1.744(4)
Ga2−O1	1.797(6)	Ga2−O3	1.805(6)
Ga2−O4	1.812(5)	Ga2−O2	1.816(4)
Ge1−O1−Ga2	132.3(4)	Ge1−O2−Ga2	136.5(3)
Ge1−O3−Ga2	131.5(4)	Ge1−O4−Ga2	134.2(4)
GaGe-ANA1			
Ge1−O1	1.756(2)	Ge1−O1	1.761(2)
Ge1−O2	1.779(2)	Ge1−O2	1.786(2)
Ge1−O1−Ge1	133.3(2)	Ge1−O2−Ge1	118.23(12)
GaGe-ANA2			
Ge1−O1	1.755(3)	Ge1−O1	1.761(3)
Ge1−O2	1.774(3)	Ge1−O2	1.782(3)
Ge1−O1−Ge1	138.8(2)	Ge1−O2−Ge1	122.4(2)
GaGe-SOD1			
Ge1−O1	1.7549(8)	Ge1−O1−Ge1	132.82(11)
GaGe-SOD2			
Ge1−O6	1.738(3)	Ge1−O1	1.743(3)
Ge1−O2	1.764(3)	Ge1−O5	1.770(3)
Ge2−O3	1.739(3)	Ge2−O4	1.752(3)
Ge2−O2	1.755(3)	Ge2−O5	1.763(3)
Ga1−O6	1.806(3)	Ga1−O1	1.820(3)
Ga1−O3	1.820(3)	Ga1−O4	1.833(3)
Ge1−O1−Ga1	134.7(2)	Ge2−O2−Ge1	134.1(2)
Ge2−O3−Ga1	136.7(2)	Ge2−O4−Ga1	125.9(2)
Ge2−O5−Ge1	124.6(2)	Ge1−O6−Ga1	125.7(2)

Ge2 site. Additional evidence for the preferential orientation of amine molecules is the distance between tetrahedral atom sites and the charged amine head groups. The two shortest distances between the N site and the Ga site are 3.507 and 3.659 Å whereas the two shortest distances between the N site and the Ge site are 3.940 and 3.946 Å, demonstrating that the Ga sites (the more negative regions) are closer to the positively charged group ($R-NH_3^+$) than the Ge sites.

Cubic *I*-Centered Zeolite Structures. The ability to predict new zeolite topologies is always of great importance. Such an ability can be expanded every time a novel zeolite topology is discovered. The discovery of the UCSB-7 topology prompted us to examine zeolite-type structures with cubic body-centered symmetry. So far, seven zeolite structure types (SOD, ACO, ANA, RHO, KFI, PAU, UCSB-7) are *I*-centered cubic.[1] These materials have characteristic cell parameters (≈9 Å for SOD and ACO, ≈14 Å for ANA, ≈15 Å for RHO, ≈18 Å for KFI and UCSB-7, and ≈35 Å for PAU) and can be divided into two groups on the basis of the lattice symmetry: the $Im\bar{3}m$ group (including ACO, SOD, RHO, KFI, and PAU), and the $Ia\bar{3}d$ group (including ANA and UCSB-7). The structures in the $Im\bar{3}m$ group are cage structures and are in general more open than the channel structures in the $Ia\bar{3}d$ group.[1] The $Im\bar{3}m$ structures can be easily described on the basis of the packing of polyhedral units. On the other hand, the structures in the $Ia\bar{3}d$ group are more difficult to visualize and can be described as two independent channel systems separated by a continuous minimal surface (the gyroid surface).[21] It is tempting to suggest that, for each structure in the $Im\bar{3}m$ group, there may be a corresponding structure in the $Ia\bar{3}d$ group. Thus, on the basis of the unit cell dimension, it is suggested that ANA and RHO types form a pair and UCSB-7 (≈18 Å, $Ia\bar{3}d$) structures reported here are apparently the counterpart of the KFI type. There might be two minimal surface structures with the $Ia\bar{3}d$ symmetry (not yet found) with unit cell dimensions that match those of the SOD (or ACO) and PAU type structures. The close correspondence between materials with the $Ia\bar{3}d$ and $Im\bar{3}m$ symmetries has also been established in silica mesoporous phases with the recent discovery of the cage-structured SBA-16 ($Im\bar{3}m$) 6 years after the first report of MCM-48 ($Ia\bar{3}d$).[22,23]

UCSB-15. UCSB-15 refers to UCSB-15AlGe and UCSB-15GaGe. These two materials are the first germanium-based zeolite-type structures with 5-rings, and their framework topology has not been found previously in either natural or synthetic materials. With the synthesis of the 3-ring-containing germanates UCSB-9 and UCSB-11[13] and the 5-ring-containing UCSB-15, the structural diversity of the germanate-based system becomes evident.

The framework topology of UCSB-15 can be derived easily from a secondary building unit (SBU) denoted as 5−1 (Figure 4a).[2] In UCSB-15, two 5−1 units are stacked in an eclipsed configuration and give what we call a double 5−1 unit (Figure 4b). The double 5−1 units are joined together into a chain in which all double 5−1 units have the same orientation along the chain direction (Figure 4c). These chains are then cross-linked into a 3-dimensional framework with 1-dimensional 10-ring channels along the shortest crystallographic *a* axis (Figure 5).

The edge-sharing 4- and 6-ring chains shown in Figure 4d are generated when the double 5−1 units are joined together. The edge-sharing 4- and 6-ring chains (Figure 4d) are also present in other zeolite-type structures such as UCSB-7 and analcime analogues described below. In fact, UCSB-15 can be considered as built from the cross-linking of edge-sharing 4- and 6-ring chains with single 6-rings as the secondary building unit. Another zeolite structure with either 5−1 or single 6-rings as SBU and with 1D 10-ring channels is theta-1 (TON), but theta-1 does not contain any 4-rings and is thus a fairly dense framework with a framework density of 19.7.[24]

There are three crystallographically unique T-atom sites, and they have two different T-atom loop configurations (the AFI type and the SOD type; here we use well-known zeolite structure type codes to represent T-atom configuration types).[1] The loop configuration is a simple graph showing how many three-, or four-membered rings are associated with a given T-atom.[1] Previously, only two zeolite structure types (APD and YUG) have only these two T-atom loop configurations (the AFI type and the SOD type), but APD and YUG are small-pore

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Table 4. Summary of Crystallographic Data for Selected New Aluminogermanates[a]

	formula	space group	*a* (Å)	*b* (Å)	*c* (Å)	*R*(*F*)	M−O (Å)
AlGe-SOD1	(R1)$AlGe_5O_{12}$	$I\bar{4}3m$	9.095	9.095	9.095	2.33	1.741(1)
AlGe-SOD2	(R2)$Al_{1.62}Ge_{4.38}O_{12}$	$P\bar{1}$	7.152	7.624	7.676	4.91	1.743(5)
UCSB-7AlGe	(R3)$Al_2Ge_4O_{12}$	$Ia\bar{3}d$	18.324	18.324	18.324	5.93	1.746(5)
UCSB-15AlGe	(R4)$Al_{0.42}Ge_{5.58}O_{12}$	*Pnma*	7.781	13.382	14.620	3.42	1.745(3)

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ with $F_o > 4.0\sigma(F)$. The maximum 2θ values (Mo Kα radiation) for reflections used in the structure refinement are 50° for UCSB-7AlGe and 56° for others. Unit cell angles for AlGe-SOD2: $\alpha = 113.08°$, $\beta = 109.86°$, $\gamma = 101.24°$. M−O is the average bond distance for all unique metal atom sites in each structure. R1 = tetramethylammonium; R2 = ethylenediamine; R3 = diaminopropane; R4 = piperazine.

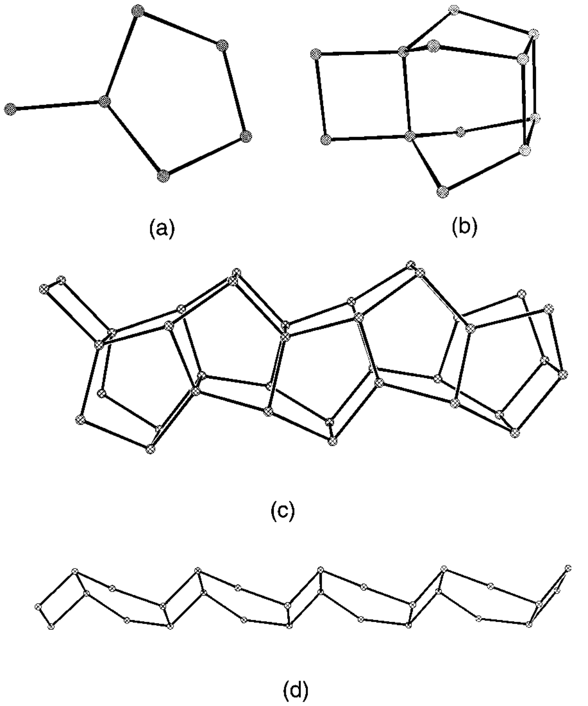

Figure 4. (a) Secondary building unit denoted as 5−1 in UCSB-15GaGe. (b) Double 5−1 units. (c) Three double 5−1 units joined into a chain. (d) Edge-sharing 4- and 6-ring chain created during the linking of the double 5−1 units. Note that the chain shown in (c) can also be considered as resulting from the coupling of two edge-sharing 4- and 6-ring chains.

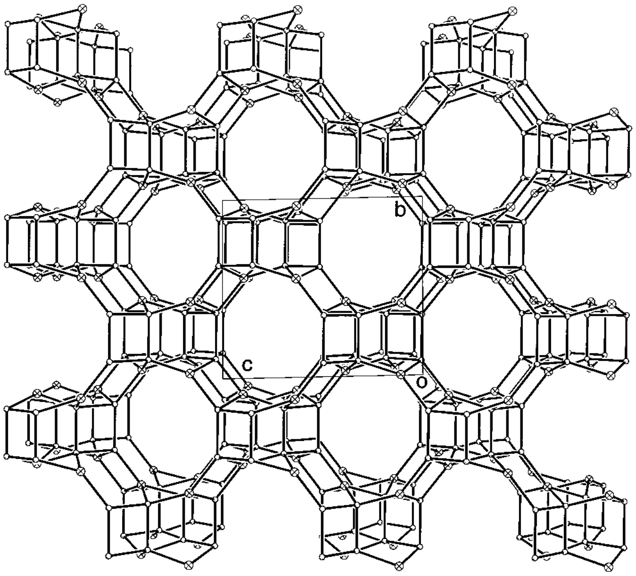

Figure 5. Projection of the framework down the crystallographic *a* axis showing the 10-ring channels in UCSB-15GaGe.

structures.[1] UCSB-15 is a medium-pore structure consisting of 4-, 5-, 6-, and 10-rings.

The framework density of UCSB-15GaGe defined as the number of T-atoms/1000 Å^3 is 15.9. Even taking into account the large ionic radii of Ga and Ge, such a framework density is fairly low considering that UCSB-15 has only 1-dimensional 10-ring channels. In comparison, ZSM-5 and ZSM-11, which are constructed from the same 5−1 units but have 3D 10-ring channels, have framework densities of 17.9 and 17.7, respectively.[1] The relatively low framework density of UCSB-15 may be due to the fact that every T-atom is involved in at least one 4-ring unit, and this is an unusual feature among 5-ring-containing zeolite structures. The large-pore zeolite mazzite is another example.

On the basis of the average M−O distances, two unique T-atom sites (labeled as Ge1 and Ge2, Table 3) are likely pure Ge sites whereas the third site (labeled as Ge3, Table 3) is a mixed Ge/Ga site with the Ge/Ga ratio unlikely to be less than 1. The presence of Ga was confirmed by the energy-dispersive X-ray spectrum performed on a JEOL scanning electron microscope. The ideal composition can be derived by assuming that piperazine molecules are monoprotonated. This gives a Ge/Ga ratio of 5, which is the same as that for GaGe-SOD1 described below. Such a composition is supported by the average M−O bond distance (1.752 Å), which is very close to that found in GaGe-SOD1 (1.755 Å, Ge/Ga = 5). Both monoprotonated and diprotonated piperazine molecules have been previously reported to structure-direct the formation of zeolite-type structures.[25,26]

Piperazine molecules have two possible orientations shown in Figure 6a, one defined by N11 and N12 and the other defined by N21 and N22. On the basis of the refined occupancy factors, the N11/N12 orientation has a much higher probability than the N21/N22 orientation (69% vs 31%). This may be because the N11/N12 orientation can form stronger hydrogen bonding with the framework oxygen atoms, as demonstrated by the shortest N- - -O distance (2.797 Å between N11 and O7 vs 3.043 Å between N21 and O3).

The monoprotonation of the piperazine molecule is correlated with the formation of hydrogen bonds. On the basis of the N- - -O contact distances, it can be concluded that, in each orientation, only one N site can form effective hydrogen bonding with framework oxygen atoms. The N- - -O distances from each nitrogen atom to the two nearest framework oxygen atoms are 2.797 and 3.500 Å for N11−O7 and N11−O5 (hydrogen bonding for N11), 3.564 and 3.642 Å for N12−O1 and N12−O7 (no or much weaker hydrogen bonding for N12), 3.043 and 3.112 Å for N21−O3 and N21−O1 (hydrogen bonding for N21), and 3.476 and 3.529 Å for N22−O5 and N22−O7 (no or much weaker hydrogen bonding for N22).

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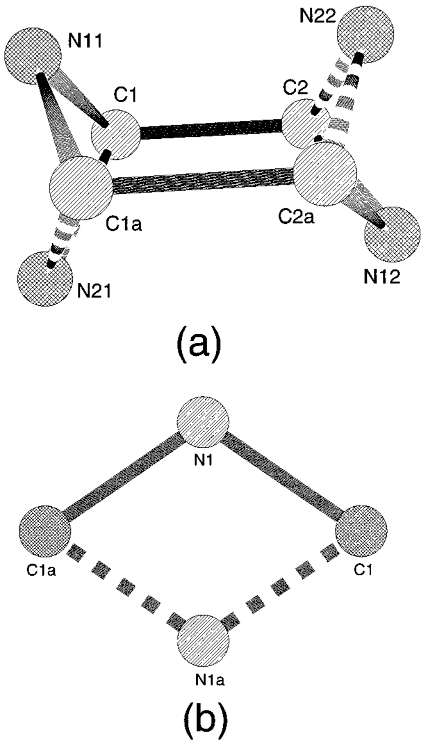

Figure 6. (a) Two possible orientations of piperazine molecules in UCSB-15GaGe. (b) Dimethylamine molecules having two statistical orientations in UCSB-7GaGe-dma.

UCSB-7. UCSB-7 refers to a large family of structures with the same framework topology but different chemical compositions. UCSB-7 structures synthesized with inorganic cations (Na^+ and K^+) have been previously reported in detail.[12] It is usually difficult to grow large crystals in the purely inorganic medium. However, when amine molecules are used as structure-directing agents in a partially nonaqueous environment, large crystals of gallo- (or alumino-) germanate UCSB-7 phases can be grown in a few days.

The framework of UCSB-7 is constructed from cross-linking of helical ribbons, and the wall structure of UCSB-7 can be described as a crystalline gyroid minimal surface similar to the disordered inorganic wall structure of mesoporous MCM-48.[27,28] The gyroid surface separates two sets of 3-dimensional, intersecting 12-ring channel systems resulting from right-handed helices and left-handed helices, forming two equal but disconnected volumes.

The helical ribbons propagate in the three cubic axial directions. Along each helical ribbon, every other 4-ring is a link between this ribbon (e.g. along the *a* axis) and the one that is perpendicular to it (e.g. along *b* or *c* axes). Therefore, for a particular ribbon, there exist two different alternating links. While mutually perpendicular helical ribbons have common links, the cylindrical voids they encompass do not intersect. From this viewpoint, the framework can be described as 3-dimensional stacking of spiral rods.

The framework density defined as the number of T-atoms/1000 Å^3 for gallogermanate UCSB-7 is approximately 14.7 depending on chemical compositions. This is comparable to that of the large cage structure ZK-5, with a framework density of 14.7.[1] There is only one type of T-atom loop configuration, which is also found exclusively in a number of important zeolite structures such as ZK-5, faujasite, and its hexagonal polymorph (EMC-2).[1] UCSB-7 and ZK-5 have nearly the same unit cell parameters and both are body-centered, but they have different space group symmetries ($Ia\bar{3}d$ for amine-directed UCSB-7 gallo- and aluminogermanate phases, $Im\bar{3}m$ for ZK-5) and completely different framework topologies.

Table 5. Organic Amines Used in the Crystal Growth of Gallo- (or alumino-) Germanate UCSB-7

methylamine
dimethylamine
diethylamine
$NH_2(CH_2)_nNH_2$, $n = 2-5$
N-methylethylenediamine
poly(ethyleneimine), $(-NHCH_2CH_2-)_x[-N(CH_2CH_2)CH_2CH_2-]_y$
tris(2-aminoethyl)amine, $(H_2NCH_2CH_2)_3N$
N-(2-aminoethyl)-1,3-propanediamine, $NH_2(CH_2)_3NH(CH_2)NH_2$
3,3′-diamino-*N*-methyldipropylamine, $CH_3N(CH_2CH_2CH_2NH_2)_2$
ethylene glycol bis(3-aminopropyl) ether, $NH_2(CH_2)_3O(CH_2)_2O(CH_2)_3NH_2$
piperazine

A large number of organic amines have been found to direct the crystallization of the UCSB-7 structure in the gallium (or aluminum) germanate composition (Table 5). In most cases, single-crystal structure refinements were performed to obtain information about the ordering of organic amines and the ordering of the Ge and Ga sites. The structural refinements were performed in both the low-symmetry space group ($I2_13$) and the high-symmetry space group ($Ia\bar{3}d$). The reason to refine structures in $I2_13$ is that this space group allows the ordering of Ga and Ge sites whereas in $Ia\bar{3}d$ only one unique T-atom site is available. For amine-directed UCSB-7 structures, the Ga and Ge ordering cannot be determined when they are refined in $I2_13$. This could result from the correlation of positional parameters because of pseudosymmetry. In cases where the Ge/Ga ratio is greater than 1, the Ge and Ga sites may be truly disordered. Thus final refinements for all amine-directed UCSB-7 phases were performed in $Ia\bar{3}d$.

Due to the high crystalline quality of UCSB-7 crystals, almost all single-crystal refinements give satisfactory *R* factors (usually below 5.0%). Atomic positions of methylamine and dimethylamine (Figure 6b) can be determined, both of which have two statistical orientations. The electron density peaks of larger amines show the orientational disorder because of the various possible orientations of the organic molecules. Such a distribution of amine molecules is not surprising considering the continuous, uniform, and multidimensional channels in UCSB-7.

UCSB-3GaGe. UCSB-3GaGe is an unusual structure because, among zeolite structures templated with only amines, it has the lowest T^{4+}/T^{3+} ratio and thus the highest framework charge density. The framework structure of UCSB-3GaGe can be viewed either as stacked 4.8.8 nets or as cross-linked bifurcated hexagonal-square (abbreviated as bhs) chains.[10] The bhs chain has not yet been found in natural zeolites, but it is known in some phosphates and one arsenate.[29,30] The high framework charge density is related to the presence of bhs chains, which is very dense compared to other double chains such as double-crankshaft chains. The highest topological symmetry for the framework of UCSB-3GaGe is $P4_2/mmc$ with

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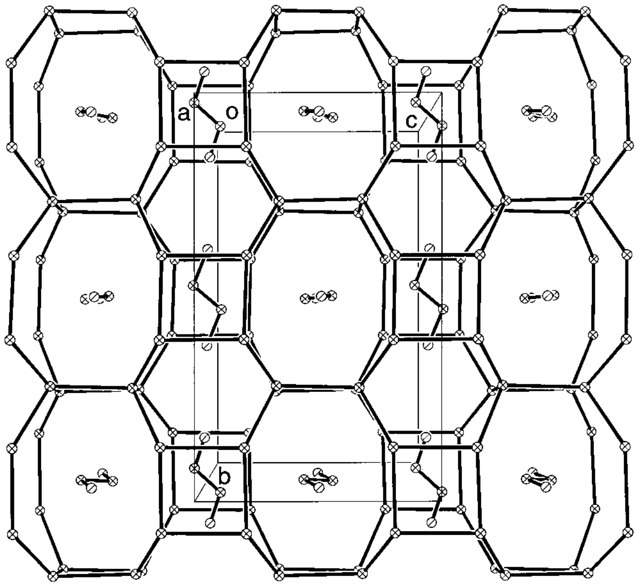

Figure 7. Eight-ring channels along the crystallographic *a* axis in UCSB-3GaGe showing ordered ethylenediamine molecules. Two different orientations of ethylenediamine molecules are shown. The bridging framework oxygen atoms are omitted for clarity.

the 4.8.8 net perpendicular to the tetragonal *c* axis and the bhs chain propagating along the *c* axis.[31] Due to the ordering of ethylenediamine molecules, the observed symmetry in actual structures is always lower (usually $P4_2/n$).[30]

The framework topology of UCSB-3GaGe (Figure 7) was proposed a long time ago as the net 38.[31] So far, such a topological type can only be constructed with protonated ethylenediamine as the structure-directing agent. This is obviously related to the fact that diprotonated ethylenediamine has a very high charge density compared to most other amines so that the host−guest charge density can be maintained. UCSB-3GaGe consists of 4-, 6-, and 8-rings and has 3-dimensional, orthogonal 8-ring channels. Its framework topology is identical to that of UCSB-3, a zincoarsenate.[30]

When refined in the subcell (a = 10.625 Å, c = 8.982 Å, space group $P4_2/n$), the average T−O distances for two unique T-atom sites are 1.740 and 1.808 Å, indicating an alternating distribution of Ga and Ge atoms. In such a subcell, the crystallographic symmetry dictates that the ethylenediamine molecule must be modeled using two statistical orientations. The subcell structure of UCSB-3GaGe is the same as that of UCSB-3 or ACP-3 (an aluminum-substituted cobalt phosphate).[30]

For UCSB-3GaGe, many supercell reflections are observed, leading to a 2-fold supercell ($a_{\text{super}} = 2^{1/2}\, a_{\text{sub}}$). The refinement in the supercell gives ordered ethylenediamine molecules, but the average T−O bond lengths for the four unique metal atom sites are not significantly different to allow the assignment of Ga and Ge atomic sites. The R factors are also significantly higher (R = 7.37%) when the refinement is performed in the supercell. This is likely due to the fact that there are not enough accurate supercell reflections to justify the refinement of the inorganic framework atoms in the supercell.

It appears that the position of amine molecules is better described in the supercell whereas the positions of framework atoms can be better modeled in the subcell. Since both of these two aspects are of interest to us, the results from both the subcell and the supercell refinements are given in Table 1.

The ordering of amines is usually a result of hydrogen bonding between framework oxygen atoms and the terminal NH_3^+ groups of the amine molecule. On the basis of the results from the supercell refinement, the three shortest distances between the N1 site and framework oxygen atoms are 2.859, 2.866, and 2.951 Å for N1−O4, N1−O8, and N1−O2, respectively, and the three shortest distances between the N2 site and framework oxygen atoms are 2.703, 2.838, and 2.906 Å for N2−O3, N2−O6, and N2−O8, respectively. Note that each ethylenediamine molecule has only one crystallographically unique N atom. These short N−O distances support the presence of N−H···O type hydrogen bonds in UCSB-3GaGe.

Analcime Analogues. The synthetic design of zeolite structures in a new compositional domain usually begins with the synthesis of a relatively dense phase such as an analcime analogue because such a phase has higher thermodynamic stability compared to more open structural types. The successful synthesis of an analcime analogue in a particular compositional domain would indicate that the framework non-oxygen atoms have a sufficiently strong tendency to adopt the tetrahedral coordination to form the more open zeolite structures. However, when anhydrous analcime analogues can only be synthesized using solid-state reactions at high temperatures or pressures, the possibility of finding other zeolite structures in the corresponding compositional domain becomes limited.

The analcime analogue has a characteristic body-centered cubic cell with a repeat length between 13 and 14 Å.[1] Such a cell is unique among 4-connected 3D nets and allows an easy identification of the analcime structural type. The most common space group for analcime analogues is $Ia\bar{3}d$, which is the space group for the mineral analcime, $Na_{16}[Al_{16}Si_{16}O_{96}]\cdot 16H_2O$.[1] However, some compositions such as $Cs_2ZnGe_5O_{12}$ are known to possess the noncentric space group $I\bar{4}3d$.[32]

In either centric or noncentric space groups, there is only one unique T-atom site, suggesting that Ga and Ge sites are not distinguishable in GaGe-ANA1 and GaGe-ANA2. However, the overall Ge/Ga ratio can be easily derived from the charge neutrality because there is no ambiguity associated with the determination of extraframework species. To our knowledge, GaGe-ANA2 is the first cesium gallium germanate known so far.

In terms of the ratio between framework T-atom sites and extraframework metal atom sites, the analcime structure type (the general formula: MT_3O_6) is between the feldspar type (MT_4O_8) and the zeolite ABW type (MT_2O_4). While feldspars with Cs^+ cations are rare, ABW and analcime structures with Cs^+ cations are very common.[33] In gallogermanate, ABW analogues have not been prepared so far. The synthetic details that lead to the preferential crystallization of either analcime or ABW phases are not yet clear. The systematic study of synthesis conditions may lead to the discovery of the germanate ABW phase and an enhanced understanding of synthetic parameters that are important in the zeolite synthesis.

Sodalite Analogues. Sodalite analogues reported here are the rare amine-directed gallo- and aluminogermanates that are analogues of an aluminosilicate, and their synthesis represents an important step in the synthesis of the germanate zeolite analogue structures. Since a variety of different amines are available, it is expected that other germanate zeolite analogues will be accessible using the synthesis approach developed here.

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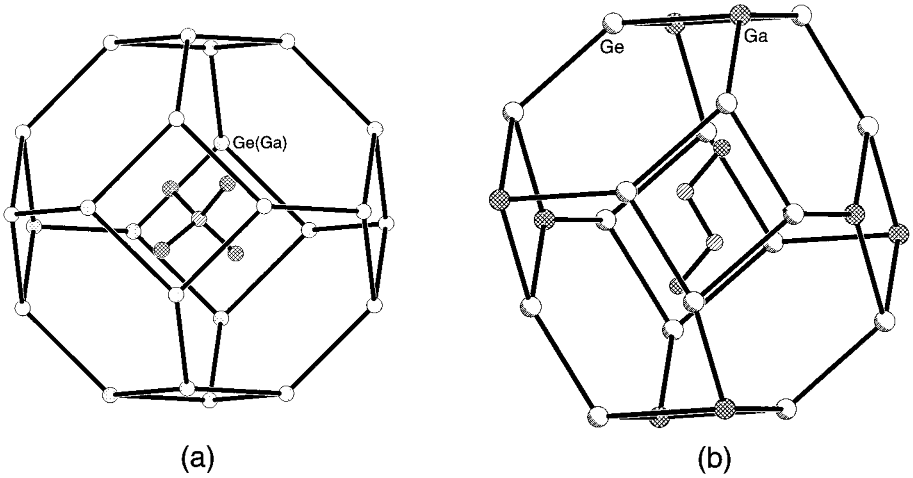

Figure 8. (a) Cubic sodalite cage in GaGe-SOD1. (b) Distorted sodalite cage in GaGe-SOD2. The bridging framework oxygen atoms are omitted for clarity.

GaGe-SOD2 is an unusual material because it embodies a number of principles in the synthesis of zeolite-type materials. These include structure-templating by host−guest charge density matching, symmetry control of the host framework by guest molecules, and T-atom site selectivity dictated by the orientation of guest molecules. Some of these principles were discussed before when several aluminum (or gallium) cobalt phosphate sodalite analogues were reported.[34] The discovery of GaGe-SOD1 and GaGe-SOD2 (Figure 8) demonstrates that these principles are generally applicable in the synthesis of zeolite-type materials and are not limited to an isolated compositional domain.

Sodalite type structures are a fascinating group of materials because the sodalite cage is the structural building block of commercially important zeolites A, X, and Y and also serves as a host for molecular clusters exhibiting various interesting properties such as photoluminescence.[35] One of the most interesting structural aspects of sodalites is the symmetry-breaking to noncubic structures because it is usually related to some fundamental structural features or synthesis mechanism.[36] While some noncubic sodalite structures are known, to our knowledge, reducing the symmetry of a sodalite structure all the way from cubic to triclinic has never been observed before.

The symmetry reduction in GaGe-SOD2 and AlGe-SOD2 is due to the ordering of ethylenediamine molecules and the strong host−guest hydrogen bonding between terminal NH_3^+ groups and framework oxygen atoms. In GaGe-SOD2, the short N- - -O distances of 2.732, 2.858, and 2.899 Å for N1−O3, N1−O1, and N1−O4 support the presence of strong N−H···O type hydrogen bonds. The protonated ethylenediamine molecules are located at the center of the sodalite cage (Figure 8). Its molecular symmetry element (inversion center) coincides with that of the sodalite cage. Thus the sodalite cage symmetry is dictated by a point group symmetry element of the amine molecule. It should be pointed out that ordered centric sodalite structures are rare. Two previous examples of ordered centric sodalite structures are the piperazine-templated sodalite analogues ACP-SOD1 and GCP-SOD1.[8]

Ethylenediamine not only dictates the symmetry of the inorganic framework but also controls the chemical composition of GaGe-SOD2. Because each diprotonated ethylenediamine molecule carries a positive charge of +2, the negative charge per sodalite cage must be −2, which can only be achieved with a Ge/Ga ratio of 2. Such a composition is very unusual for a T^{4+}/T^{3+} sodalite-type structure.

It is of interest to compare the triclinic GaGe-SOD2 and AlGe-SOD2 with the silica-sodalite containing ethylene glycol.[37] The two organic molecules are of the same shape, but they give rise to sodalite structures with very different symmetries. Because of the different basicity, ethylene glycol molecules do not form hydrogen bonds strong enough to distort the inorganic framework in the end product. Thus the inorganic framework of the silica-sodalite remains cubic and ethylene glycol molecules have to be disordered to conform to the cubic symmetry of the sodalite cage. In comparison, ethylenediamine molecules in GaGe-SOD2 and AlGe-SOD2 are completely ordered because of the strong host−guest interaction.

Conclusion. The successful synthesis of a series of gallo- and aluminogermanate zeolite-like structures with both inorganic and organic species reported here represents a significant breakthrough in the synthesis of Ge-based 4-connected 3D framework structures and opens a new synthesis area that may lead to the discovery of a large number of zeolite-type structures, some of which could have unprecedented framework topologies due to the unique geometrical factors of germanates.

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Supporting Information Available: Tables of crystal data, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic thermal parameters (26 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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