

Synthesis and Characterization of Zirconogermanates

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Received March 18, 2003

Six new zirconogermanates have been prepared under hydrothermal conditions using amines as bases. There are four new structure types (ASU-*n*) with a common motif of $ZrGe_5$. ASU-23 is a layered structure: $ZrGe_3O_8(OH)F \cdot [C_{10}H_{26}N_4] \cdot H_2O$, space group $P2_1/n$, $a = 6.7957(8)$ Å, $b = 12.700(1)$ Å, $c = 24.293(3)$ Å, $\beta = 97.936(2)^\circ$, $V = 2076.4(4)$ Å³. ASU-24 is a pillared layered structure: $Zr_3Ge_6O_{18}(OH_2)_4F_2 \cdot [C_6H_{18}N_2] \cdot [C_6H_{17}N_2]_2 \cdot 2H_2O$, space group $P2_1/n$, $a = 7.4249(3)$ Å, $b = 25.198(1)$ Å, $c = 11.3483(5)$ Å, $\beta = 90.995(1)^\circ$, $V = 2122.9(2)$ Å³. This material has the lowest framework density (FD) of any oxide material that we are aware of (FD = 8.48 metal atoms/nm³). Two other materials form three-dimensional open-frameworks, ASU-25: $ZrGe_3O_9 \cdot [C_3H_{12}N_2]$, space group $P112_1/a$, $a = 13.1994(4)$ Å, $b = 7.6828(2)$ Å, $c = 11.2373(3)$ Å, $\gamma = 91.233(3)^\circ$, $V = 1139.29(5)$ Å³. The other is ASU-26: $ZrGe_3O_9 \cdot [C_2H_{10}N_2]$, space group Pn , $a = 13.7611(3)$ Å, $b = 7.7294(2)$ Å, $c = 11.2331(3)$ Å, $\beta = 104.793(1)^\circ$, $V = 1155.21(4)$ Å³. ASU-25 is related to the mineral umbite $K_2ZrSi_3O_9 \cdot H_2O$. The germanium equivalent has been prepared through the inorganic route: $K_2ZrGe_3O_9 \cdot H_2O$, space group $P2_12_12_1$, $a = 13.6432(6)$ Å, $b = 7.4256(3)$ Å, $c = 10.3973(4)$ Å, $V = 1053.33(8)$ Å³. The structural relationships between ASU-25 and its inorganic counterpart are described. The thermal decomposition of the germanium umbite generated the cyclic trigermanate $K_2ZrGe_3O_9$, analogue of the mineral wadeite, crystallizing in the orthorhombic system, $a = 7.076$ Å, $b = 12.123$ Å, $c = 10.451$ Å, $V = 904.5$ Å³.

Introduction

Silica-based microporous solids with mixed octahedral–tetrahedral frameworks containing transition metals in octahedral coordination are well-known.¹ They form three-dimensional frameworks of interconnected octahedra and tetrahedra with large pore openings, as found in the case of the titaniumsilicate ETS-10,² where the pore rings are made of 12 metal atoms (12-membered rings, 12MRs). The zirconosilicates exist as minerals or synthetic materials and crystallize in a large variety of structures. One of the characteristics of this family of compounds is the presence in the structures of many three-membered rings (3MRs), essentially as triangles $ZrSi_2$; indeed, some frameworks are built from 3MRs only. The bridging angles Si–O–Si in these

compounds are around 130°, well below the strain-free value of 145° found in polymorphs of silica or aluminosilicates. Germanium can adopt a tetrahedral coordination in oxides in which the typical angle Ge–O–Ge is about 130°,³ making it a favorable candidate for the formation of mixed octahedral–tetrahedral frameworks. However, only a few zirconogermanates are known, generally prepared hydrothermally through the inorganic route, in the systems $M_2O-ZrO_2-GeO_2-H_2O$, where M is Na or K.^{4,5} Zirconogermanates can be prepared using organic bases, instead of alkali cations, as demonstrated in the case of ASU-15.⁶ ASU-15 is an open-framework of very low framework density (FD = 9.1), where the zirconium atom is 4-coordinated to germanate groups in a square plane with two singly coordinated fluoride ligands completing a ZrO_4F_2 octahedron.

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Here we describe the synthesis and characterization of four new zirconogermanates prepared hydrothermally using amines as bases. The four structures, which consist of one layered structure (ASU-23), one pillared layered structure (ASU-24), and two three-dimensional frameworks (ASU-25 and ASU-26), are constructed from the same motif but linked differently. ASU-25 possesses the framework topology of the mineral umbite, $K_2ZrSi_3O_9 \cdot H_2O$.⁷ We prepared the germanium equivalent $K_2ZrGe_3O_9 \cdot H_2O$. We report its structure and describe the structural relationships between the two germanate polymorphs.

Experimental Section

Synthesis. ASU-23 is obtained as a single-phase from a mixture of germanium dioxide, zirconium ethoxide, water, 1,4-bis(3-aminopropyl) piperazine (BAPP, 99%, Aldrich), pyridine, and hydrofluoric acid (48 wt %) with composition $GeO_2/0.32 ZrO_2/50 H_2O/4 BAPP/30$ pyridine/1 HF. The 3 mL solution was heated at 165 °C for 4 days in 23 mL Teflon-lined autoclaves. On the basis of crystal structure and elemental analysis, the material was formulated as $ZrGe_3O_8(OH)F \cdot H_2BAPP \cdot H_2O$. Anal. Calcd: C 17.55, H 4.12, N 8.19, F 2.78, Zr 13.33, Ge 31.82. Found: C 16.75, H 3.84, N 7.95, F 2.61, Zr 12.55, Ge 29.39.

ASU-24 is prepared using hexamethylenediamine (DAH, 98%, Aldrich) as a base. The mixture has a composition $GeO_2/ZrO_2/50 H_2O/12 DAH/40$ pyridine/1 HF and was maintained under hydrothermal conditions at 160 °C for 6 days. ASU-24 is obtained as a single phase. On the basis of the crystal structure, the solid was formulated as $Zr_3Ge_6O_{18}(OH_2)_4F_2 \cdot [H_2DAH] \cdot [HDAH]_2 \cdot 2H_2O$.

ASU-25 is prepared in a similar way using 1,3-diaminopropane (DAP, 99%, Aldrich) as a base. A typical mixture contains germanium dioxide, zirconium ethoxide, water, DAP, ethylene glycol (EG), and hydrofluoric acid (48 wt %) in molar ratio $GeO_2/0.32 ZrO_2/75 H_2O/15 DAP/50 EG/3 HF$. The solution was heated at 160 °C for 5 days in Teflon-lined autoclaves. On the basis of the crystal structure and elemental analysis, the material was formulated as $ZrGe_3O_9 \cdot H_2DAP$. Anal. Calcd: C 6.81, H 2.29, N 5.29, Zr 17.24, Ge 41.17. Found: C 7.08, H 2.33, N 5.22, Zr 18.23, Ge 41.48. A solid closely related to ASU-25 can be obtained under the same synthesis conditions using 1,2-diaminocyclohexane (DACH) as a base and substituting ethylene glycol by pyridine ($ZrGe_3O_9 \cdot H_2DACH$, space group $P112_1/a$, $a = 13.188 \text{ \AA}$, $b = 7.686 \text{ \AA}$, $c = 11.235 \text{ \AA}$, $\gamma = 91.17^\circ$).

ASU-26 is a mixture of germanium dioxide, zirconium ethoxide, water, ethylenediamine (DAE, 99% Aldrich), ethylene glycol (EG), and hydrofluoric acid (48 wt %) in molar ratio $GeO_2/0.32 ZrO_2/90 H_2O/30 DAE/50 EG/3 HF$, heated for 5 days at 180 °C. On the basis of the crystal structure, the material was formulated as $ZrGe_3O_9 \cdot H_2DAE$.

A solid $K_2ZrGe_3O_9 \cdot H_2O$ is prepared by direct dissolution of stoichiometric amounts of germanium dioxide and zirconium ethoxide in an aqueous solution of potassium hydroxide, maintained under hydrothermal treatment at 200 °C for 4 days ($GeO_2/0.32 ZrO_2/2 K_2O/300 H_2O$).

Ion exchanges were performed by treatment of the solids with an excess of 2 M NaCl aqueous solution, at room temperature for 48 h.

Structure Determination. Crystals of ASU-23 (fragment, dimensions $0.03 \times 0.12 \times 0.10 \text{ mm}^3$) and ASU-24 (needle,

dimensions $0.04 \times 0.07 \times 0.30 \text{ mm}^3$) were selected for single-crystal analysis at 159 K and room temperature, respectively. The data were collected using a SMART CCD area detector with Mo K α radiation. Absorption corrections were performed using the SADABS program.⁸ The structures were solved by direct methods using the DIRIDIF94 program⁹ (ASU-23) and the SHELLS program¹⁰ (ASU-24). The refinements were performed against all F^2 with anisotropic thermal parameters for all non-hydrogen atoms.

The structures of ASU-25 and ASU-26 were determined from X-ray powder diffraction data. Data acquisitions were performed on a Siemens D5000 diffractometer using Cu K α radiation and equipped with a graphite monochromator. ASU-25 crystallizes in the monoclinic space group $P112_1/a$: $a = 13.1994(4) \text{ \AA}$, $b = 7.6828(2) \text{ \AA}$, $c = 11.2373(3) \text{ \AA}$, $\gamma = 91.233(3)^\circ$. Its structure was determined by direct methods using the program EXPO.¹¹ Completion of the structures by Fourier difference and Rietveld refinements were performed using the GSAS software package.¹² Soft constraints were applied on distances between atoms throughout all the refinements. The powder pattern of ASU-26 can be indexed in the monoclinic crystal system with $a = 13.7611(3) \text{ \AA}$, $b = 7.7294(2) \text{ \AA}$, $c = 11.2331(3) \text{ \AA}$, and $\beta = 104.793(1)^\circ$. A structural model has been built on the basis of the similitude of cell parameters between ASU-25 and ASU-26. The structure can be described in the space groups An (standard setting, Cc) or Im (Cm), but the refinement was performed in the space group Pn (Pc) due to the presence in the powder pattern of very weak reflections with intensities I/I_{\max} about 1% or below.

Table 1 reports the crystal data for all compounds. Crystallographic details and final Rietveld refinement plots are given in the Supporting Information.

Results

In all the new structures, there is a recurrent motif $ZrGe_5$, which consists of one zirconium atom in octahedral coordination connected by corner sharing to five tetrahedral germanates forming three 3MRs (Figure 1). The octahedron is connected to four tetrahedra, roughly located within the same plane, and to a fifth tetrahedron protruding from the ensemble. The motif can form extended layered structures by sharing the four coplanar tetrahedra. Both the octahedron and the protruding tetrahedron possess dangling bonds pointing in two opposite directions, one above the layer and one below the layer.

ASU-23, $ZrGe_3O_8(OH)F \cdot H_2BAPP \cdot H_2O$, is a layered structure made of the motif $ZrGe_5$ (Figures 2 (left), and 3 (left)). The layer is formed of rows of motifs aligned in the same direction. The motifs in two contiguous rows are rotated by 60°. The protruding tetrahedron points alternatively above and below the layer plane. The layer is constructed exclu-

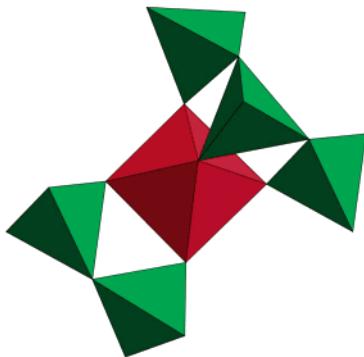
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Table 1. Crystallographic Data for ASU-*n* (*n* = 23–26) and the Germanium Equivalent of Umbite^a

compd	ASU-23	ASU-24	ASU-25	ASU-26	Ge-umbite
chemical formula	ZrGe ₃ O ₈ (OH) ₂ F·H ₂ BAPP·H ₂ O	Zr ₃ Ge ₆ O ₁₈ (OH ₂ F) ₄ F ₂ ·[H ₂ DAH]·[HDAH] ₂ ·2H ₂ O	ZrGe ₃ O ₉ ·H ₂ DAP	ZrGe ₃ O ₉ ·H ₂ DAE	K ₂ ZrGe ₃ O ₉ ·H ₂ O
cryst syst, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	monoclinic, <i>P</i> 112 ₁ / <i>a</i>	monoclinic, <i>P</i> <i>n</i>	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
cell params (Å, deg)	<i>a</i> = 6.7957(8) <i>b</i> = 12.700(1), β = 97.936(2) <i>c</i> = 24.293(3) <i>V</i> = 2076.4(4)	<i>a</i> = 7.4249(3) <i>b</i> = 25.198(1), β = 90.995(1) <i>c</i> = 11.3483(5) <i>V</i> = 2122.9(2)	<i>a</i> = 13.1994(4) <i>b</i> = 7.6828(2) <i>c</i> = 11.2373(3), γ = 91.233(3) <i>V</i> = 1139.29(5)	<i>a</i> = 13.7611(3) <i>b</i> = 7.7294(2), β = 104.793(1) <i>c</i> = 11.2331(3) <i>V</i> = 1155.21(4)	<i>a</i> = 13.6432(6) <i>b</i> = 7.4256(3) <i>c</i> = 10.3973(4) <i>V</i> = 1053.33(8)
cell volume (Å ³)					
wavelength (Å)	λ = 0.71073	λ = 0.71073	λ = 1.54059	λ = 1.54056	λ = 1.54056
indep atoms, <i>Z</i>	29, 4	31, 4	18, 4	34, 2	16, 4
final R indices ^{b,c}	R1 = 3.33%, wR2 = 2.92%	R1 = 4.54%, wR2 = 8.78%	<i>R</i> _{wp} = 9.9%, <i>R</i> _B = 3.8%	<i>R</i> _{wp} = 11.7%, <i>R</i> _B = 6.4%	<i>R</i> _{wp} = 12.6%, <i>R</i> _B = 5.5%

^a BAPP stands for 1,4-bis(3-aminopropyl) piperazine, C₁₀H₂₄N₄, DAH for hexamethylenediamine, C₆H₁₄N₂, DAP for 1,3-diaminopropane, C₃H₁₀N₂, and DAE for ethylenediamine, C₂H₈N₂. ^b R1 = $\sum |F_o| - |F_c| / \sum |F_o|$, wR2 = $[\sum w(F_o^2 - F_c^2)^2 / w(F_o)^2]^{1/2}$ for 2112 reflections satisfying $I > 2\sigma(I)$ (ASU-23) and for 3577 reflections satisfying $I > 2\sigma(I)$ (ASU-24). ^c *R*_{wp} = $[\sum w_i(y_{io} - y_{ic})^2 / \sum w_i y_{io}^2]^{1/2}$, *R*_B = $\sum |I_o - I_c| / \sum I_o$.

**Figure 1.** Structural motif ZrGes present in the four structures ASU-*n* (*n* = 23, 24, 25, 26), Ge tetrahedra green, Zr octahedron red.

sively of 3MRs, and forms 7MR openings. The angles Ge—O—Ge and Ge—O—Zr are within ranges 122.0(3)–126.3(2)°, and 126.2(2)–138.3(3)°, respectively. Bond lengths are within reasonable ranges; the average distances *d*_{Ge—O} and *d*_{Zr—O} are 1.749 and 2.070 Å, respectively. The details of the distances and angles between atoms can be found as Supporting Information. A fully ordered diprotonated BAPP molecule and one water molecule occupy the interlayer space.

The structure of ASU-24, Zr₃Ge₆O₁₈(OH₂F)₄F₂·[H₂DAH]·[HDAH]₂·2H₂O, forms a layer made of motifs of ZrGes, pillared by zirconium atoms in octahedral coordination (Figures 2 (middle) and 3 (middle)). The layer arrangement is different from the one observed in ASU-23 as all motifs are aligned in the same direction. The protruding tetrahedra point alternatively above and below the layer plane and are linked together through the intermediate of zirconium octahedra. These latter join the layers through two opposite vertices and are completed by four ligands F and H₂O, forming a square Zr(OH₂F)₄ of dangling bonds. The octahedral pillars delimit large channels with 14MR rectangular openings occupied by the amines and one water molecule. One DAH molecule is located on a center of inversion, the second is found in general position, and both are ordered. The structure shows two zirconium octahedra in two opposite environments. The first is highly coordinated, embedded in the layer and surrounded by three 3MRs. The second, in the interlayer space, shows an unusual linkage as it is connected to the remaining of the structure by only two

bonds. As a result, the structure shows a very low framework density (FD = 8.48 metal atoms per nm³), lower than the density found in ASU-15 (FD = 9.1), and even lower than any other materials we are aware of; we believe that the previous record low is held by another germanate, ASU-16 (FD = 8.6).¹³

The structure of ASU-25, ZrGe₃O₉·H₂DAP, can be described as layers of the motif ZrGe₅ directly connected, forming a three-dimensional framework ZrGe₃O₉ (Figures 2 (middle) and 3 (right-top)). The arrangement of the motifs within the layer is the same as observed in ASU-24, but the linkage of the layers is different. The octahedron is connected to the protruding tetrahedron of the next layer. The layers are staggered but straight channels with 8MR openings formed between the layers along the *b* direction. The diprotonated DAP molecules are located within the channels. ZrGe₃O₉·H₂DAP possesses the framework topology of umbite, a silicate mineral K₂ZrSi₃O₉·H₂O,⁷ but crystallizes in a different crystal system.

ASU-26, ZrGe₃O₉·H₂DAE, is a three-dimensional framework closely related to the three other structures (Figures 2 (right) and 3 (right-bottom)). The structure of ASU-26 is made of connected layers built from ZrGe₅, in which the motifs are all aligned in the layer plane and the protruding tetrahedra are all pointing in the same direction. Linking the octahedron to the protruding tetrahedron connects the layers. The rings of the layers overlap, and 7MR channels are formed along the stacking direction.

The germanium form of K-umbite has been prepared through the inorganic route and is found to be isostructural to the mineral umbite, crystallizing in the same space group *P*2₁2₁2₁. Both ZrGe₃O₉·H₂DAP and K₂ZrGe₃O₉·H₂O possess the same topology but crystallize in different space groups showing no direct group–subgroup relationships. A similar case has been observed by Clearfield and co-workers for the synthetic umbite K₂TiSi₃O₉·H₂O and its H-exchanged form K_{1.3}H_{0.7}TiSi₃O₉·H₂O,¹⁴ however, without reporting the space group relationships between the two structures. Both space

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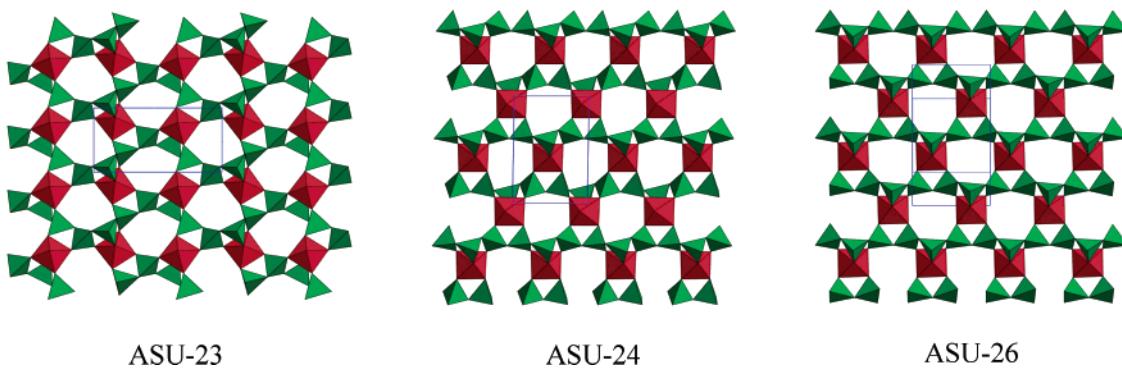


Figure 2. The oxide layer can be described as an assembly of ZrGe_5 motifs, in (left) ASU-23, (middle) ASU-24 (and ASU-25), and (right) ASU-26.

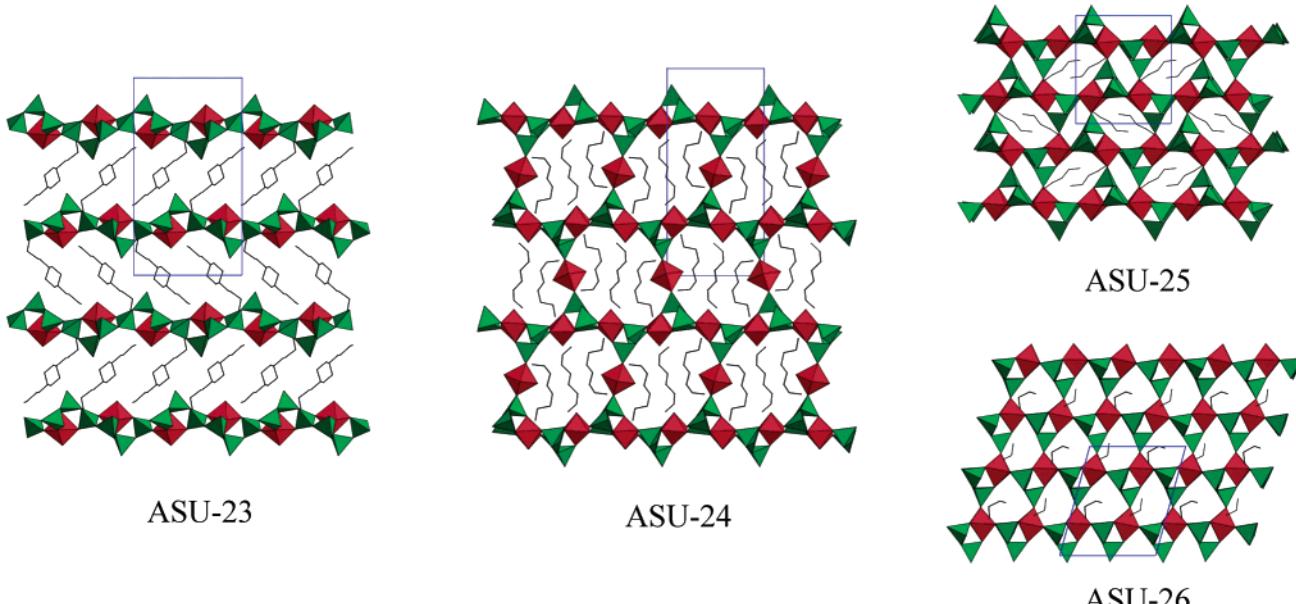


Figure 3. Stacking of layers of (left) ASU-23, (middle) ASU-24, (right-top) ASU-25, and (right-bottom) ASU-26.

groups $P2_1/a$ ($\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{DAP}$) and $P2_12_12_1$ ($\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$) are subgroups of $Pnma$. A nonconventional setting (unique) has been selected for ASU-25 to emphasize the group–subgroup relations between the two phases. The main difference observed between the two structures is the value of the interlayer Ge–O–Zr bond angles, which are about 177° and 140° for $\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{DAP}$ and $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$, respectively. The other bond angles Ge–O–Ge and Ge–O–Zr vary approximately within the same angular range for both structures, from 123° to about 140° .

The description of umbite in the space group $Pnma$ shows that the interlayer Ge–O–Zr bond is located within a mirror plane, and no constraint is imposed on the Ge–O–Zr angle. The interlayer Ge–O–Zr bond is free to bend by rotation of the motifs around the b axis. The framework experiences strong distortions as the Ge–O–Zr bond angle decreases from 180° to 140° , as evidenced by the difference of the cell parameters a and c between the two compounds (Table 1). The variation of the unit cell parameters as a function of the interlayer Ge–O–Zr angle is well described by distance least-squares (DLS) refinements of the structure.¹⁵ The origin of this effect is undoubtedly the framework adaptation to the presence of the spherical potassium cations. As a consequence, the layers of $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$ are corrugated,

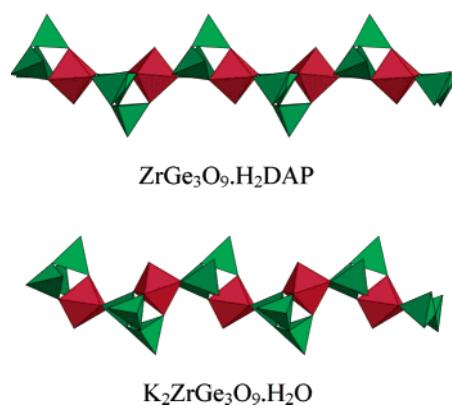


Figure 4. Comparison of the layers of umbite, projected down the b axis: (top) $\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{DAP}$ and (bottom) $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$.

while the layers of ASU-25 are relatively planar (Figure 4). The other structures prepared using organic bases show no corrugation. A second notable distortion of the umbite type

(15) The DLS refinements were performed with rigid polyhedra and a set of typical distances Ge–O and Zr–O, using the DLS-76 program¹⁶ for two Ge–O–Zr angles of 140° and 180° . The unit cells of the structures generated are the following: $a_{180} = 13.30 \text{ \AA}$, $b_{180} = 7.79 \text{ \AA}$, $c_{180} = 11.14 \text{ \AA}$, and $a_{140} = 13.75 \text{ \AA}$, $b_{140} = 7.79 \text{ \AA}$, $c_{140} = 10.46 \text{ \AA}$.

of framework is observed, accounting for the crystallization of the two phases in subgroups of *Pnma*. Both $\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$ -DAP and $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$ show a tilt of approximately 10° of the motifs around the *a* axis, perpendicular to the layers. However, in ASU-25, the tilt is alternatively clockwise and anticlockwise from one layer to the next, with respect to the presence of centers of inversion in $\text{P}2_1/a$. On the other hand, the direction of the tilt is preserved from one layer to the next in $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$, generating the acentric subgroup $\text{P}2_{12}1_2$.

Acentric structures are not uncommon in zirconosilicates. The two zirconogermanate crystals, $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$, crystallizing in crystal class 222, and ASU-26, crystallizing in class *m*, should show second-order nonlinear optical behavior, and this family of compounds may have potentially important technological properties.¹⁷

$\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$ is exchangeable by sodium cations as observed in the case of the synthetic umbite $\text{K}_2\text{ZrSi}_3\text{O}_9 \cdot \text{H}_2\text{O}$,¹⁸ but ASU-25 and ASU-26 show no exchange properties.

The frameworks of ASU-25 and ASU-26 collapse on heating before 400°C . Thermal treatment at 800°C generates the formation of quartz GeO_2 and scheelite ZrGeO_4 .^{19,20} On the other hand, thermal treatment transformed $\text{K}_2\text{ZrGe}_3\text{O}_9 \cdot \text{H}_2\text{O}$ into wadeite $\text{K}_2\text{ZrGe}_3\text{O}_9$,²¹ a structure containing cyclic trimer Ge_3O_9 , in contrast to the precursor made of chains of GeO_4 tetrahedra. The transformation occurs around 700°C , well below the temperature of transformation of the silica form, which is reported around 900°C .^{7,22} However, as the temperature increases, wadeite decomposes into scheelite.

The mineral wadeite crystallizes in the hexagonal system, but the germanate form is indexed in an orthorhombic unit cell, on the basis of the presence of additional small lines in the powder pattern: $a = 7.076\text{ \AA}$, $b = 12.123\text{ \AA}$, $c = 10.451\text{ \AA}$, $V = 904.5\text{ \AA}^3$. The orthorhombic cell is related to the hexagonal cell using the transformation $(a, a + 2b, c)$. The change of space group probably originates from small distortions in the wadeite framework. The cyclic germanates Ge_3O_9 with wadeite topology are known to crystallize in two different space groups $\text{P}6_3/m$ and $\text{P}3c1$, due to slight structural changes.²³

It is remarkable that all four ASU-*n* frameworks are formed from the same motif ZrGe_5 . Different arrangements of a central octahedron surrounded by six tetrahedra can be obtained by varying the number of 3MR ZrGe_2 units and their relative positions. All possible motifs have been generated by elementary combinatorial analysis. The motifs, where two opposite tetrahedra are part of two contiguous

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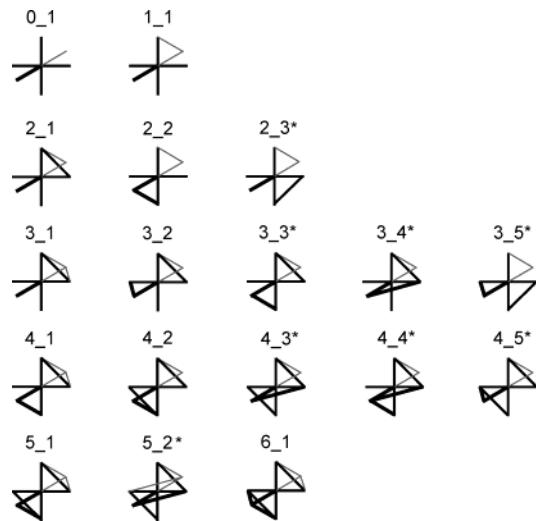


Figure 5. Combinations (18) of three-membered rings around a central octahedron have been generated; among them eight are chiral (marked with an asterisk). The most constrained arrangements have been discarded. Motif 3_2 is the motif found in the four structures ASU-*n* (*n* = 23–26).

3MRs, have been discarded because of the presence of strong geometric constraints. The 18 remaining arrangements are reported in Figure 5; the number of 3MRs varies from zero to six. As the number of contiguous 3MRs increases, the geometric constraints build up, and the motif 5_2 is the most constrained. Only a fraction of the arrangements are found in zirconosilicates, and no motifs with four 3MRs or more are known.²⁴ Eight of the motifs are chiral (marked by an asterisk in Figure 5). Among them is the well-known propeller motif (3_5) found in the zirconosilicates built on 3MRs only, such as gaidonnayite,²⁵ hilairite,²⁶ and kostylevite.²⁷ Five different motifs possess three 3MRs; the structures of ASU-*n* reported here are built from the arrangement 3_2.

The motif 3_2 can be assembled into layers, which in turn can condense into three-dimensional frameworks. The motif can adopt different arrangements within the layers, generating different possible topologies. Contiguous motifs can be aligned in the same direction or rotated by 60° , and the protruding tetrahedra can be on the same side of the layer or alternatively pointing on both sides of the layers. Four elementary combinations can be formed on the basis of those two variables. Three of them have been synthesized using amines as bases. Only the topology of ASU-25 is known as an inorganic compound, the mineral umbite.

Conclusion

Four different zirconogermanates have been prepared using amines as bases. The four structures can be described on the basis of a layer containing the recurrent motif ZrGe_5 . Different arrangements of the motif within the layer are possible. ASU-24 and ASU-25 showed the same arrangement

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as that found in the mineral umbite; ASU-23 and ASU-26 revealed two new arrangements. The layers can be isolated as observed in ASU-23, forming a two-dimensional structure, or condensed as found in ASU-25 and ASU-26, forming three-dimensional open-frameworks. ASU-24 presents an intermediate case where the layers are pillared by zirconium octahedra generating a solid with exceptionally low framework density (FD = 8.48 metal atoms per nm³).

Acknowledgment. This work was supported by National Science Foundation Grants DMR 9804817 and DMR 0103036.

Supporting Information Available: Crystallographic data for all compounds (CIF) and the Rietveld plots of three structures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC034298G