Synthesis and Characterization of Zirconogermanates

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Six new zirconogermanates have been prepared under hydrothermal conditions using amines as bases. There are four new structure types (ASU-η) with a common motif of ZrGe. ASU-23 is a layered structure: ZrGeO3(OH)F·[C10H20N2]·H2O, space group P2₁/n, a = 6.7957(8) Å, b = 12.700(1) Å, c = 24.293(3) Å, β = 97.936(2)°, V = 2076.4(4) Å³. ASU-24 is a pillared layered structure: ZrGeO3(F·[C6H18N2])·H2O·[C6H18N2]·H2O, space group P2₁/n, a = 7.4249(3) Å, b = 25.198(1) Å, c = 11.3483(5) Å, β = 90.995(1)°, 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: ZrGeO3·[C6H18N2], space group P12₁/a, a = 13.1994(4) Å, b = 7.6828(2) Å, c = 11.2373(3) Å, γ = 91.233(3)°, V = 1139.29(5) Å³. The other is ASU-26: ZrGeO3·[C6H18N2], space group Pn, a = 13.7611(3) Å, b = 7.7294(2) Å, c = 11.2331(3) Å, β = 104.793(1)°, V = 1155.21(4) Å³. ASU-25 is related to the mineral umbite K₂ZrSi₃O₉·H₂O. The germanium equivalent has been prepared through the inorganic route: K₂ZrGe₃O₉·H₂O, space group P2₁2₁2₁, a = 11.2331(3) 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 K₂ZrGe₃O₉, 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 ZrSi₂; 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 alumino-silicates. 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 M₂O₃·ZrO₂·GeO₂·H₂O, where M is Na or K.⁴ Zirconogermanates can be prepared using organic bases, instead of alkali cations, as demonstrated in the case of ASU-15.⁵ 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 ZrO₄F₂ octahedron.

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, K₂ZrSi₃O₉.⁷ We prepared the germanium equivalent K₂ZrGe₆O₁₉H₂O. 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 GeO₂/0.32 ZrO₂/50 H₂O/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 ZrGe₆O₁₈(OH₂,F)₄·F₂. Anal. Calcd: C 7.95, H 4.12, N 8.19, F 2.78, Zr 13.33, Ge 31.82. Found: C 16.75, H 0.38, N 7.68, F 2.71, Zr 13.52, Ge 31.50.

ASU-24 is prepared using hexamethylenediamine (DAH, 98%, Aldrich) as a base. The mixture has a composition GeO₂/ZrO₂/50 H₂O/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 ZrGe₆O₁₈(OH₂,F)₄·[HDAH]·[H₂DAH]·2H₂O. 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 GeO₂/0.32 ZrO₂/75 H₂O/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 ZrGe₆O₁₈H₂DAP. Anal. Calcd: C 6.81, H 2.29, N 2.29, Zr 18.23, Ge 40.17. Found: C 6.78, H 2.23, N 5.22, Zr 18.23, Ge 40.18. 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 (ZrGe₆O₁₈H₂DACH, space group P112/a, a = 13.188 Å, b = 7.686 Å, c = 11.235 Å, γ = 91.17°).

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 GeO₂/0.32 ZrO₂/90 H₂O/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 ZrGe₆O₁₈H₂DAE. A solid K₂ZrGe₆O₁₉H₂O 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 (GeO₂/0.32 ZrO₂/2 K₂O/300 H₂O).

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 × 0.12 × 0.10 mm³) and ASU-24 (needle, dimensions 0.04 × 0.07 × 0.30 mm³) 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 Kα radiation. Absorption corrections were performed using the SADABS program.⁸ The structures were solved by direct methods using the DIRDIF94 program (ASU-23) and the SHELXS program (ASU-24). The refinements were performed against all F² 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 Kα radiation and equipped with a graphite monochromator. ASU-25 crystallizes in the monoclinic space group P112/a: a = 13.1994(4) Å, b = 7.6828(2) Å, c = 11.2373(3) Å, γ = 91.233(3). Its structure was determined by direct methods using the program EXPLO.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) Å, b = 7.7294(2) Å, c = 11.2331(3) Å, and β = 104.793(1)°. A structural model has been built on the basis of the similarity 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 Iₘₙₐₓ 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 ZrGe₅, 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, ZrGe₆O₁₈(OH)₂F·H₂BAPP·H₂O, is a layered structure made of the motif ZrGe₅ (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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Within reasonable ranges; the average distances $d$ forming a square Zr(OH$_2$,F)$_4$ of dangling bonds. The second, in the interlayer space, shows an unusual linkage as it is connected to the remaining of the structure by only two molecules. 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 nm$^3$), 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, ZrGe$_3$O$_7$DAP, can be described as layers of the motif ZrGe$_3$ directly connected, forming a three-dimensional framework ZrGe$_3$O$_9$ (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. ZrGe$_3$O$_7$H$_2$DAP possesses the framework topology of umbite, a silicate mineral K$_2$ZrSi$_3$O$_9$ but crystallizes in a different crystal system.

ASU-26, ZrGe$_3$O$_7$H$_2$DAE, 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 ZrGe$_3$, 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 $P2_12_1$. Both ZrGe$_3$O$_7$H$_2$DAP and K$_2$ZrGe$_3$O$_7$H$_2$O 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 K$_2$TiSi$_3$O$_9$ and its H-exchanged form K$_2$H$_7$TiSi$_3$O$_9$H$_2$O, 14 however without reporting the space group relationships between the two structures. Both space

Figure 1. Structural motif ZrGe$_3$ present in the four structures ASU-$n$ ($n = 23, 24, 25, 26$), Ge tetrahedra green, Zr octahedron red.
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 ($c$ 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. 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, 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

Figure 2. The oxide layer can be described as an assembly of ZrGe3 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.

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) $\text{K}_2\text{ZrGe}_3\text{O}_9\cdot\text{H}_2\text{O}$.
of framework is observed, accounting for the crystallization of the two phases in subgroups of \( \text{Pnma} \). Both \( \text{ZrGe}_5\text{O}_7\text{H}_2\text{DAP} \) and \( \text{K}_2\text{ZrGe}_5\text{O}_9\text{H}_2\text{O} \) show a tilt of approximately \( 10^\circ \) 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 \( P2_1/a \). On the other hand, the direction of the tilt is preserved from one layer to the next in \( \text{K}_2\text{ZrGe}_5\text{O}_9\text{H}_2\text{O} \), generating the acenctic subgroup \( P2_12_12_1 \).

Acenctic structures are not uncommon in zirconosilicates. The two zirconogermanate crystals, \( \text{K}_2\text{ZrGe}_5\text{O}_9\text{H}_2\text{O} \), 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.\(^{17}\)

\( \text{K}_2\text{ZrGe}_5\text{O}_9\text{H}_2\text{O} \) is exchangeable by sodium cations as observed in the case of the synthetic umbite \( \text{K}_2\text{ZrSi}_3\text{O}_9\text{H}_2\text{O} \),\(^{18}\) but ASU-25 and ASU-26 show no exchange properties.

The frameworks of ASU-25 and ASU-26 collapse on heating before 400 \( ^\circ \)C. Thermal treatment at 800 \( ^\circ \)C generates the formation of quartz \( \text{GeO}_2 \) and scheelite \( \text{ZrGeO}_4 \).\(^{19,20}\) On the other hand, thermal treatment transformed \( \text{K}_2\text{ZrGe}_5\text{O}_9\text{H}_2\text{O} \) into wadeite \( \text{K}_2\text{ZrGe}_5\text{O}_9 \),\(^{21}\) a structure containing cyclic trimer \( \text{Ge}_3\text{O}_9 \), in contrast to the precursor made of chains of \( \text{GeO}_4 \) tetrahedra. The transformation occurs around 700 \( ^\circ \)C, well below the temperature of transformation of the silica form, which is reported around 900 \( ^\circ \)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: \( a = 7.076 \) Å, \( b = 12.123 \) Å, \( c = 10.451 \) Å, \( V = 904.5 \) Å\(^3\). 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 \( \text{Ge}_3\text{O}_9 \) with wadeite topology are known to crystallize in two different space groups \( P6_3/m \) and \( P3c1 \), due to slight structural changes.\(^{23}\)

It is remarkable that all four ASU-\(n \) frameworks are formed from the same motif \( \text{ZrGe}_5 \). Different arrangements of a central octahedron surrounded by six tetrahedra can be obtained by varying the number of 3MR \( \text{ZrGe}_2 \) 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...
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 nm$^3$).

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**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.

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