

First Open-Framework Zinc Germanates by a Molecular Templating Route

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Open framework microporous materials are traditionally aluminosilicates, some of which such as zeolites A, X, and Y have found widespread use in commercial applications.¹ In addition to Al³⁺ and Si⁴⁺ in aluminosilicates, other polyhedral elements can also be used to construct porous frameworks.² Among various possible compositions, metal phosphates have been shown to have a rich synthetic and structural chemistry comparable to that of aluminosilicates.^{3–11}

One compositional domain that has attracted our attention is germanium-based open-framework materials.^{12–18} One major motivation to study germanates is their ability to form 3-rings (three tetrahedral atoms and three oxygen atoms in a ring) as demonstrated recently.¹⁵ Such a structural feature has been widely believed to be the key to the synthesis of the frameworks with the lowest possible framework density.¹¹ From the earlier studies of zincosilicate tetrahedral frameworks, it has been shown that divalent zinc cations can also promote the formation of 3-ring materials.^{11,19,20} It is thus of great interest to explore zinc germanate materials to identify synthetic conditions that might lead to open framework materials with

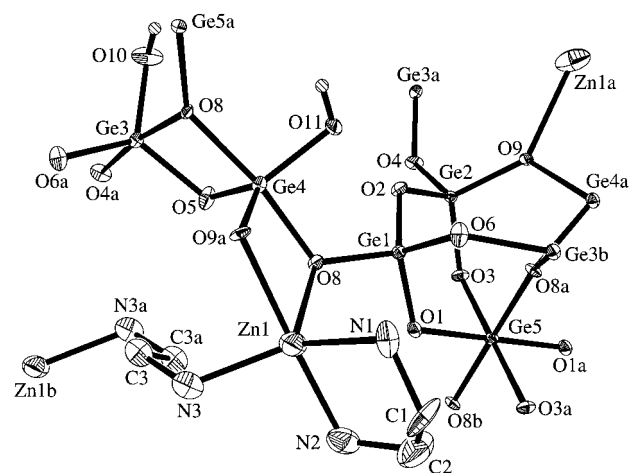


Figure 1. ORTEP view of coordination environments for Ge, Zn, and O atoms in ZnGe-1A. Atom labels having "a" or "b" refer to symmetry-generated atoms. Of 11 unique oxygen atoms, O1–O6 are bridging atoms between two germanium centers and the O7 site is coordinated to 3 Ge atoms. O8 and O9 are coordinated to 2 Ge atoms and 1 Zn atom and the remaining O10 and O11 atoms form terminal hydroxyl groups.

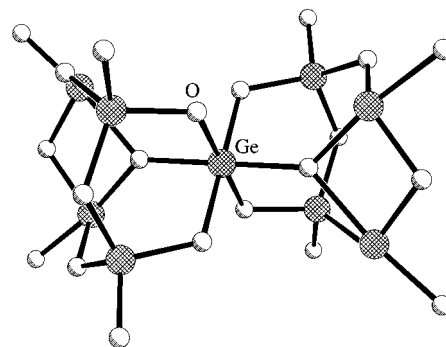


Figure 2. Basic framework building unit, Ge₉O₁₈. There are 8 oxygen atoms, 4 at each side that connect each Ge₉O₁₈ unit to other Ge₉O₁₈ clusters. Note that each oxygen atom bridging between two separate Ge₉O₁₈ clusters is counted as half.

ultralow framework density and the highest porosity. The work reported here represents one step toward such a goal.

A number of purely inorganic zinc germanates such as K₂ZnGeO₄ are known,²¹ but to our knowledge, the two zinc germanates reported here are the first amine-directed open-framework divalent metal germanates and the framework density defined as the number of polyhedral cations (Ge and Zn) in 1000 Å³ is 16.7 for both structures. Amine-directed open-framework germanates containing trivalent metals such as Ga³⁺ and Al³⁺ have already been reported.^{14,15}

Clear needle-shaped crystals of ZnGe-1A were synthesized by stirring a mixture of GeO₂ (1.19 g), Zn(NO₃)₂·6H₂O (1.15 g), ethylenediamine (5.67 g), distilled water (3.72 g), and ethylene glycol (9.38 g) for about 2.5 h. The mixture had a pH of 12.1 and was subsequently heated at 180 °C for 8 days in a Teflon-coated steel autoclave. Clear, irregularly shaped crystals of ZnGe-

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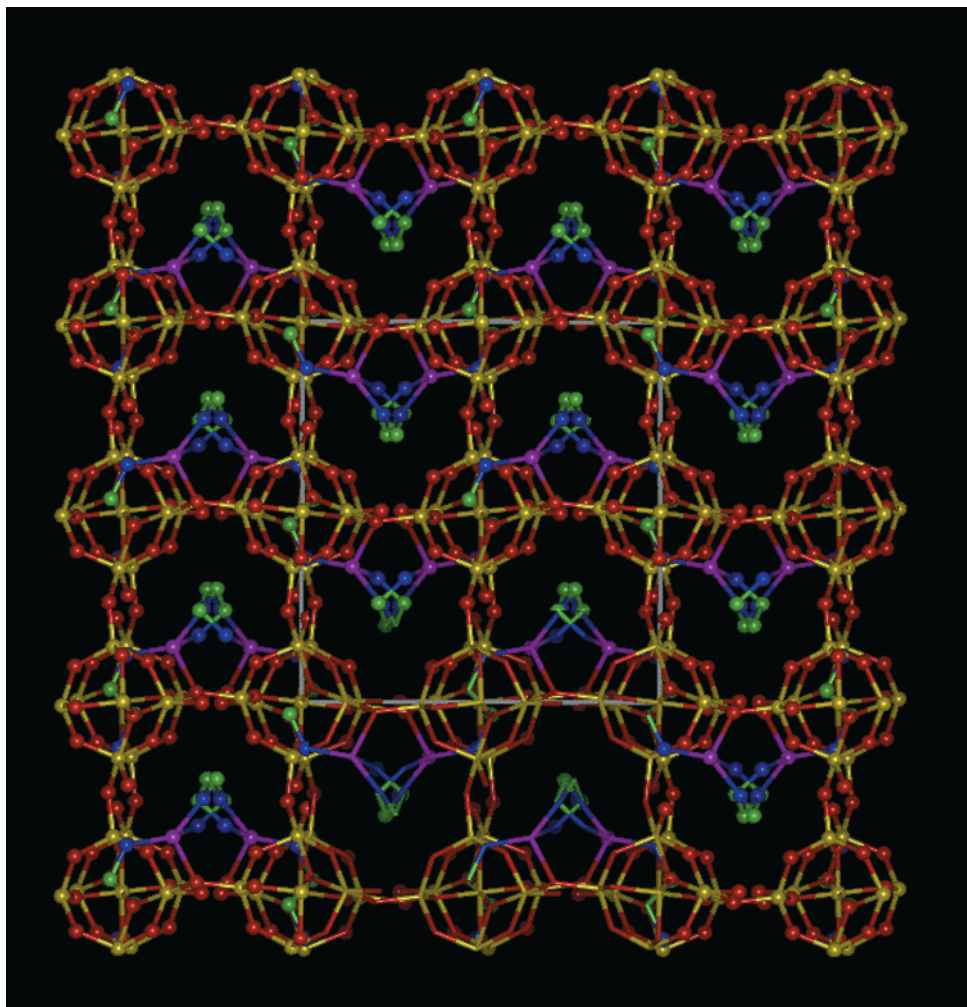


Figure 3. Unit cell packing diagram viewed down the b axis showing the location of different species and 8-ring channels in ZnGe-1A. Red, oxygen; yellow, germanium; purple, zinc; green, carbon; blue, nitrogen.

1B were synthesized by stirring a mixture of GeO_2 (1.00 g), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.92 g), ethylenediamine (4.50 g), distilled water (3.00 g), and ethylene glycol (10.29 g) for about 2.5 h. The mixture had a pH of 11.5 and was subsequently heated at 180 °C for 8 days in a Teflon-coated steel autoclave. Single-crystal structures were determined from room-temperature data collected on a Bruker SMART CCD diffractometer.²²

In ZnGe-1A, there are five unique Ge sites and only one unique Zn site (Figure 1). Ge1 and Ge2 have regular tetrahedral coordination while both Ge3 and Ge4 are coordinated to five oxygen atoms, one of which is a dangling hydroxyl group. Ge5 is located at the inversion center and is therefore constrained by symmetry to adopt the octahedral coordination. The coordination of Zn is rather unusual. Each Zn center is connected to only two framework oxygen atoms and as many as three

nitrogen atoms from two ethylenediamine molecules are coordinated to the same Zn site (Figure 1). Such a diversity of polyhedral coordinations in zinc germanates are very different from what we have observed in amine-directed trivalent metal (gallo- and alumino-) germanates.^{14,15}

In ZnGe-1A, there are several different 3-rings, including those constructed from Ge1–Ge2–Ge5, Ge1–Ge3–Ge5, and Ge2–Ge4–Ge5, respectively (Figure 1). These 3-rings are part of a larger cluster, Ge_9O_{18} (Figure 2). These clusters are located at unit cell origins and face centers (Figure 3). This is reminiscent of the distribution of Na^+ or Cl^- in the NaCl structure type. Each cluster has an octahedral Ge center, and at two ends of each cluster, there are eight oxygen atoms (four at each end, Figure 2), each of which is connected to another Ge_9O_{18} cluster. Thus, every Ge_9O_{18} cluster is connected to eight other identical clusters. Note that the long axis of each Ge_9O_{18} cluster is aligned along the crystallographic b axis.

In ZnGe-1A, there are two different types of ethylenediamine molecules. Those shown inside channels are located at general positions and two terminal NH_2 groups of each molecule are coordinated to the same Zn site (Figure 3). The other type of ethylenediamine molecules are located at unit cell edge and body centers

(22) Crystal data for ZnGe-1A: orthorhombic, space group $Pbca$ (#61), $Z = 4$, Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), $2\theta_{\text{max}} = 50^\circ$, $[\text{Ge}_9\text{O}_{18}\text{Zn}_2(\text{OH})_4] \cdot 3(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$, $a = 13.9570(1) \text{ \AA}$, $b = 12.9684(3) \text{ \AA}$, $c = 14.8453(3) \text{ \AA}$, $V = 2687.00(8) \text{ \AA}^3$, $0.19 \times 0.013 \times 0.013 \text{ mm}^3$, refinement on F^2 , $R(F) = 4.79\%$, $wR(F2) = 8.76\%$, $\text{GOF} = 1.18$ for 207 parameters and 1852 unique reflections with $I > 2.0\sigma(I)$. Crystal data for ZnGe-1B: monoclinic, space group $P2_1/c$ (#14), $Z = 4$, $2\theta_{\text{max}} = 50^\circ$, $[\text{Ge}_9\text{O}_{18}\text{Zn}_2(\text{OH})_4] \cdot 3(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$, $a = 14.9037(2) \text{ \AA}$, $b = 13.0379(1) \text{ \AA}$, $c = 14.2490(1) \text{ \AA}$, $\beta = 91.51^\circ$, $V = 2767.80(5) \text{ \AA}^3$, $0.16 \times 0.13 \times 0.11 \text{ mm}^3$, refinement on F^2 , $R(F) = 3.55\%$, $wR(F2) = 8.72\%$, $\text{GOF} = 1.10$ for 412 parameters and 3548 unique reflections with $I > 2.0\sigma(I)$.

and serve as bridges between two symmetry-related Zn sites. These bridging amine molecules do not protrude into the channels (Figure 3).

Thus, the three-dimensional framework of ZnGe-1A can be conceptually built by the following procedures. Starting with a NaCl structure with Cl^- anions at unit cell origins, the framework of ZnGe-1A can be constructed by placing Ge_9O_{18} clusters at the Cl^- sites. Through the Zn–O connection with a bond length of 2.136(5) Å, each $\text{Zn}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)$ group can then be attached to the oxygen atom that bridges two Ge_9O_{18} clusters.²³ Finally, all Na^+ sites are replaced with the second type of ethylenediamine molecules, each of which serves as a bridge between two adjacent Zn sites. A projection of the three-dimensional framework down the *b* axis is shown in Figure 3. It should be emphasized that replacing individual atoms with a cluster of atoms to obtain open-framework materials is presently both a method of the structural analysis and a synthetic strategy aimed at ultralarge cages and pores.

Thermal analysis gives a total weight loss of 16.5% up to 1000 °C, which agrees with the calculated weight loss of 16.4%. ZnGe-1A is stable up to 350 °C, but calcination at 400 °C in air for half an hour greatly broadens low-angle peaks ($\text{fwhm} > 2^\circ$) and destroys its long-range periodic ordering. Between 350 and 425 °C, there is a distinct endothermic event, accompanied by a rapid weight loss of 9.0% (calculated weight loss for two amine molecules: 9.10%). This can be best explained as the desorption of chelating ethylenediamine molecules, which are located in 8-ring channels and represent two-thirds of the total amine molecules in the structure. Between 425 and 700 °C, only 2.8% of the total weight is slowly lost. An additional 4.7% weight

(23) Another Zn–O bond with a distance of 2.268(5) Å is also formed during this process. The third closest oxygen atom to the Zn site is a hydroxyl group (O10), which is 2.70 Å away.

loss occurs within the temperature range of 700–925 °C. The last two weight losses are exothermic events, and based on the weight losses, it appears that two hydroxyl groups (calculated weight loss: 2.7%) are lost first, which is then followed by the burning of the bridging ethylenediamine molecules (calculated weight loss: 4.6%).

The framework structure of ZnGe-1B is similar to that of ZnGe-1A, but ZnGe-1B has a lower monoclinic symmetry as compared to the orthorhombic symmetry of ZnGe-1A. Like in ZnGe-1A, Ge_9O_{18} clusters and bridging ethylenediamine molecules are both located at inversion centers. On the other hand, all three unit cell axes in ZnGe-1B are longer than those in ZnGe-1A, with the largest difference being approximately 0.3 Å. Another significant change is the deviation of one of the unit cell angles from 90° by as much as 1.5° in ZnGe-1B. The structural difference between ZnGe-1A and ZnGe-1B demonstrates the flexibility of the type of the framework found in ZnGe-1A and ZnGe-1B.

In conclusion, organic molecules have been successfully used, for the first time, to synthesize open framework zinc germanates. This work is a beginning step toward incorporating divalent metals such as zinc, magnesium, and cobalt into germanium oxide frameworks in the hope to devise novel functional framework materials with low density and high porosity.

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Supporting Information Available: Tables of crystal data, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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