

**((DABCO)·ZnGe(HPO₄)₃): The First
Zinco–Germanophosphate with a Unique
Asymmetric Cage**

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Microporous materials have been extensively studied because of their applications in the fields of catalysis, ion exchange, gas separation, molecular recognition, etc. Since the first discovery of microporous aluminophosphates in 1982,¹ the elements by which microporous materials are composed have been extended to most of the transition metals and main group. A challenge for synthetic work in inorganic microporous materials is to introduce heteroatoms in one open framework, which can lead to the modification of physical and chemical properties of the parent compounds.² A series of transition elements have recently been incorporated into aluminum or gallium phosphate frameworks to give MAl(Ga)PO₄ (M = Mg, Fe, Co, Zn) with both zeolitic and new structure types.^{3–10}

Recently, interest in microporous and zeolite-analogous systems has been focused on germanate zeolite-type structures. Some germanate zeolite structures have successfully been synthesized, in which GeO₄ tetrahedral, GeO₆ octahedral, and sometimes even GeO₅ trigonal bipyramids are joined through shared corners to form frameworks.^{11–14} However, germanium phosphates are rare. Only a few M^IGe₂(PO₄)₃ (M = Ag, Cu(I), Na, Li)^{15,16} materials have been prepared by using conventional solid-state reactions, in which high temperatures over 1000 °C are needed for synthesis. Frameworks containing the zincate anion, ZnO₄⁶⁻, are also relatively uncommon, probably due to the ready hydrolysis of this species. The presence of the high charge on phosphorus helps offset the high framework charge caused by the presence of the divalent cation.¹⁷ Using organic cations as structure-directing

agents in hydrothermal ZnPO₄ synthesis has led to many novel organo–zincophosphate phases, whose crystal structures are dependent on the identity of the organic template. Actually, several zinc phosphates with interesting chiral structures have been made.^{18,19}

The aim of our work is to extend open heterometal phosphate frameworks to more transition and main group elements. Zn and Ge are chosen in the synthesis, in which the Ge⁴⁺ may help to reduce the framework charge caused by the ZnO₄⁶⁻ anion. In this paper, we report the synthesis and structure of the first zinco–germanophosphate. The unique cages in the structure are asymmetric, which will be very interesting in organic synthetic reactions and molecular recognition.

((DABCO)·ZnGe(HPO₄)₃ (USTC-1) was synthesized by heating a mixture of GeO₂ (0.5 g), ZnSO₄ (0.29 g), 70% H₃PO₄ (1.36 mL), DABCO (1,4-diazabicyclo[2,2,2] octane, 4.58 g), ethylene glycol (4 mL), and pyridine (4 mL) at 170 °C for 10 days in a Teflon-coated steel autoclave, to give colorless crystals which were insoluble in common solvents. The largest crystal size was about 2 mm long. IR spectroscopy showed that organic guests existed in the crystal. A single crystal was picked for ICP elemental analysis, which showed that the ratio of Zn:Ge is near 1:1.²⁰ The structure was revealed by single-crystal X-ray diffraction.²¹

The characteristic basic units in the crystal structure of ((DABCO)·ZnGe(HPO₄)₃ are based on 4-rings, which contain corner-sharing M(Zn or Ge) and phosphate tetrahedra. The 4-ring units link together through M(Zn or Ge)–O–P bonds to form distorted infinite 4,8-ring sheets of tetrahedra in the *ac*-crystallographic plane (Figure 1a). MO₄ and PO₄ tetrahedrons are strictly alternating in this plane. The topology of the 4,8-ring basic layer can be described as a seriously distorted 4,8² net.²² There are two different kinds of 4-membered centered-rings (4R-1 and 4R-2) and two different kinds of 8-membered centered-rings (8R-1 and 8R-2) in this sheet. The adjacent 4-ring cycles are almost perpendicular. The 4,8² net appears as a layer motif in a number of aluminosilicate structures, such as merlinoite and gismondine.²² It also can be found in some DABCO-templated phosphate structures, such as Zn₂(HPO₄)₃·H₂N₂C₆H₁₂²³ and [C₆N₂H₁₄]²⁺·2[SnPO₄]⁻·H₂O.²⁴ The layers of 4,8-ring sheets are joined through a bridging tetrahedral PO₄ group into a 3D open framework. The 4-ring units and the bridging PO₄ tetrahedra form another two infinite 8,12-ring sheets, approximately in the (1,0,-1) and (-1,1,-1)-crystallographic planes (Figure 1b and 1c), in which 8- and 12-membered rings appear alternatively. Open framework channels are constructed in three directions (Figure 2). The intersection of the channels forms a cage, in which the DABCO guest molecules are enclosed. The cage is made up of six different rings (8R1, 8R2, 8R3, 8R4, 12R1, and 12R2). Eight 4-ring units occupy the cage corners. The two 12-membered rings are adjacent. This cage is asymmetric, which is seldom seen in other zeolite type structures (Figure 3).

There are three different P atoms in this phase, all of which adopt typical tetrahedral geometry with $d_{av}[P(1)-O] = 1.544 \text{ \AA}$, $d_{av}[P(2)-O] = 1.544 \text{ \AA}$, and $d_{av}[P(3)-O] = 1.543 \text{ \AA}$. P(1) makes

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(20) Found: Zn(9.7%), Ge(11.5%). Calcd: Zn(12%), Ge(13.5%).

(21) Crystal data for USTC-1: ((DABCO)·ZnGe(HPO₄)₃), space group: triclinic, *P*-1, *a* = 9.982(6) Å, *b* = 10.000(1) Å, *c* = 9.576(4) Å, α = 97.96(3)°, β = 114.87(3)°, γ = 107.67(2)°, *V* = 768.2(7) Å³, *Z* = 2, *Mo* K α , θ_{max} = 27.49°, *R*(*F*) = 0.0690, *R*_w(*F*²) = 0.1314, GOF = 3.328.

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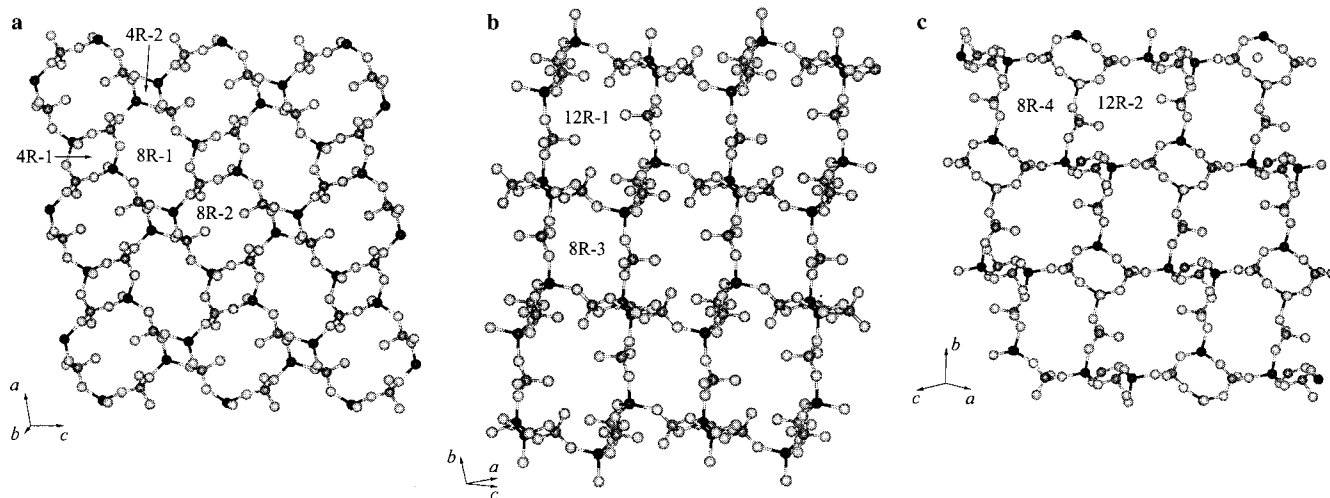


Figure 1. The figures of three sheets in the crystal structure of (DABCO)·ZnGe(HPO₄)₃ (USTC-1). (a) The figure of 4,8-ring sheet viewed down from *b* axis direction. (b, c) The figures of 8,12-ring sheets in the crystal structure. H atoms and DABCO molecules are omitted for clarity. M(Zn or Ge): black, P: dark gray, O: gray.

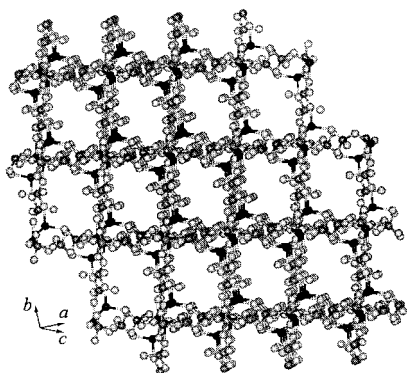


Figure 2. The view of open channels in the crystal structure. H atoms and DABCO molecules are omitted for clarity. M(Zn or Ge): black, P: dark gray, O: gray.

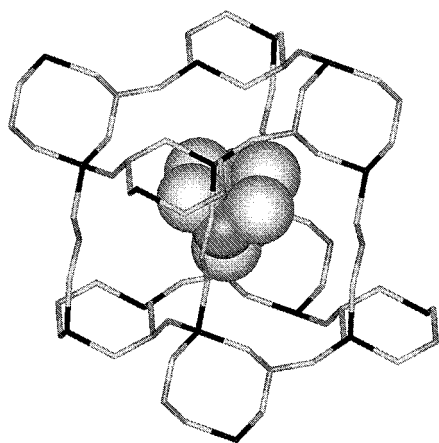


Figure 3. The figure of the asymmetric cage. H atoms and vertex oxygen atoms are omitted for clarity. M(Zn or Ge): black, P: dark gray stick, O: gray stick, C: gray ball, N: dark gray ball.

two connections via oxygen to zinc or germanium atoms and has two terminal P–O bonds. P(2) and P(3) make three P–O–M (Zn or Ge) linkages and have one terminal P–O vertex. The charge-balancing criterion requires the presence of three protons associated with the P–O bonds. P(1)–O(2) = 1.521 Å, P(2)–O(8) = 1.598 Å, and P(3)–O(10) = 1.591 Å are protonated. The framework is “interrupted”; that is, not all of the tetrahedrally coordinated atoms make four bonding connections.^{25,26} Interrupted connections have often been found with low FD values (the

number of tetrahedral atoms per 1000 Å³). In this structure, the FD value is 12.7, which is almost on the Burnner and Meier’s 4-ring boundary.²⁷ Because the X-ray scattering factors of Zn²⁺ and Ge⁴⁺ are very close, it is very difficult to distinguish the positions of these two atoms in the crystal structure. A similar situation existed in Ga³⁺/Ge⁴⁺, Zn²⁺/Ga³⁺, Co²⁺/Ga³⁺ phosphate or aluminosilicate zeolites. These sites were often considered as Ga³⁺/Ge⁴⁺, Zn²⁺/Ga³⁺, Co²⁺/Ga³⁺, or Al³⁺/Si⁴⁺ mixed sites.^{4,14,28} The ideal bond distance is 1.74 Å for Ge–O¹⁴ and 1.95 Å for Zn–O.²³ The average M–O distance (1.942 Å) in this molecule sieve is very close to the Zn–O bond length. This result may be ascribed to mixed Zn²⁺/Ge⁴⁺ sites, low symmetry, and distortion of the structure.

The DTA-TG curve of the compound showed that there were two steps of weight loss. Between 290 and 400 °C, there is about 20% weight loss, which is attributed to the DABCO (calcd 20.8%). Between 645 and 655 °C, there is another weight loss of 7.3%, which is ascribed to the dehydration of the HPO₄²⁻ anion (calcd 5.26%). Each step of the weight loss is accompanied by an endothermic peak. When heated at 400 °C for 3 h, the sample became dark. X-ray powder diffraction showed that the sample became amorphous. This means that the structure collapsed when the template molecule was removed.

In summary, we have carried out the synthesis and X-ray structure analysis of the first zinc–germanophosphate molecular sieve with a low FD value. It is worth noting that the cages in this material are asymmetric and are formed by six different tetrahedral rings. We are currently using other large guest molecular templates to synthesize new structures with larger cages. Further studies of these materials are in progress.

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Supporting Information: XRD diagram of the crystal and XRD diagram of the sample heated at 400 °C for 3 h, IR spectroscopy of the crystal, and IR spectroscopy of the sample heated at 400 °C for 3 h (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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