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PKU-9: An Aluminogermanate with a New Three-Dimensional Zeolite Framework Constructed from CGS Layers and *Spiro*-5 Units

Jie Su, Yingxia Wang,* Zheming Wang, and Jianhua Lin*

Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

Received February 20, 2009; E-mail: wangyx@pku.edu.cn; jhlin@pku.edu.cn

Zeolites have been extensively studied over many years as a result of their use in industrial applications for catalysis, ion exchange, adsorption, and separation.[1,2] The synthesis of new frameworks with large pores and low framework densities (FDs) is always a great challenge. Because of the correlation between FD and the smallest rings in tetrahedral networks,[3] it has been suggested that small rings, i.e., 3- and 4-rings, are essential for the formation of a framework with low FD.[2−4] Zeolite frameworks with 4-rings are common, but those with 3-rings are relatively rare because of the inner tension arising from this small circuit.[5] Silicon seldom forms 3-rings with oxygen atoms alone because of the short Si−O bond length (~1.61 Å) and large Si−O−Si angle (~145°); ZSM-18(**MEI**) is the only known aluminosilicate zeolite containing 3-rings.[6] On the other hand, incorporation of low-valent cations such as Be^{2+}, Zn^{2+}, and even Li^{+} in one of the tetrahedra in a 3-ring can provide the flexibility necessary to stabilize the 3-rings in the zeolite frameworks,[7−9] which indeed led to the discovery of the frameworks with very low FD, such as **OBW** (13.1 T/1000 $Å^3$) and **OSO** (13.4 T/1000 $Å^3$).[5,9] **OSO** is an extreme case in which 3-rings are the minimum rings and these 3-rings are directly corner-linked by *spiro*-5 units to form a chiral framework with large (14-ring) pores. Recently, germanates have received particular attention because the longer Ge−O bond length (~1.74 Å) and smaller Ge−O−Ge angle (~130°) may also favor the smaller rings.[10] However, 4-rings and/or double-4-rings (D4Rs) dominate in newly found germanate zeolites;[11,12] only a few germanates, such as UCSB-9(**SBN**), UCSB-11, SU-46(**SBN**), SU-16(**SOS**), FJ-17(**SOS**), and ITQ-33, contain 3-rings,[13] and none of them contains the *spiro*-5 unit, which means that no direct corner linkage of 3-rings was identified in germanate zeolites. Here we report a new aluminogermanate, $Ge_7Al_2O_{18}(C_5H_{14}N)_2$ (PKU-9). It contains a novel zeolite framework composed of **CGS** layers[14] and *spiro*-5 units and has a low framework density. To the best of our knowledge, this is the first aluminogermanate that contains *spiro*-5 units.

The reaction of a mixture of GeO_2, freshly prepared $Al(OH)_3$, trimethylethylammonium hydroxide [a structure directing agent (SDA)], and H_2O under hydrothermal conditions provided PKU-9 as colorless crystals with rhombic-like morphology. The structure of PKU-9, determined by single-crystal X-ray diffraction, is orthorhombic[15] and consists of five unique T (T = Ge, Al) positions in an asymmetric unit, all of which are tetrahedrally coordinated by oxygen. The structure refinement indicated that Al and Ge are randomly distributed in the five T sites with refined occupancies ranging from 0.22 to 0.28 for Al and 0.78 to 0.72 for Ge. According to elemental analysis [see the Supporting Information (SI)] and the requirement of charge balance, the occupancies of Al and Ge were fixed at 0.22 and 0.78 for all T positions in the final refinement, giving rise to the formula $Ge_7Al_2O_{18}(C_5H_{14}N)_2$. The ^{27}Al NMR spectrum of PKU-9 (see the SI) showed a single peak at 56.7 ppm, typical of tetrahedral aluminum.

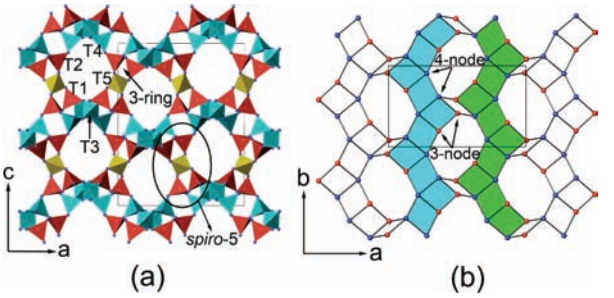

Figure 1. (a) Projection of the PKU-9 structure along the [010] direction. The T5 tetrahedra are shown in yellow, and the *spiro*-5 unit is emphasized by a circle; the tetrahedra in the **CGS** layers are shown in red and blue. (b) **CGS** layer, with the two 4-ring zigzag ladders shaded in green and cyan and the 4- and 3-noded T atoms shown in blue and red, respectively.

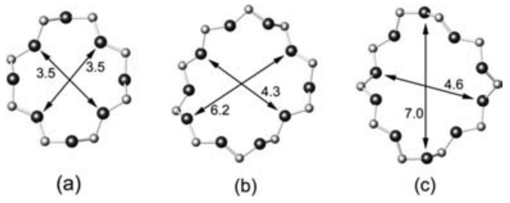

Figure 2. Views of (a) an 8-ring channel along [001], (b) a 10-ring channel along [010], and (c) a 10-ring channel along [110] or [1$\bar{1}$0]. The size of each opening (dimensions in Å) is shown.

The framework of PKU-9 can be described by wrinkled layers that are interconnected through *spiro*-5 units (Figure 1a). This wrinkled layer is in fact the fundamental layer of **CGS**, although the **CGS** framework was described in a different way in the literature.[14] Here we assign it as the **CGS** layer. The **CGS** layer is constructed by connection of 4-ring zigzag ladders (Figure 1b). These zigzag ladders, formed by the linkage of 4-rings via edge sharing in an alternating trans and cis manner, are all parallel, running along the [010] direction. Each ladder is also connected to two neighbors via 4-rings, forming the **CGS** layer with 8-ring pores in the [101] and [10$\bar{1}$] directions. The 8-rings are rather regular (Figure 2a), with an opening size of ~3.5 Å × 3.5 Å. The **CGS** layer contains two kinds of T atoms: one is 3-noded (T1 and T2, shown in red in Figure 1b) and the other 4-noded (T3 and T4, in blue). The 3-noded T atoms are in neighboring positions, so they can connect to T5 atoms to form 3-rings. Further connection of T5 atoms to another neighboring **CGS** layer results in the *spiro*-5 units and the framework of PKU-9.

The connection of the **CGS** layers by *spiro*-5 units creates three 10-ring channels perpendicular to the [001] direction. The 10-ring channels along the [010] direction, which can be clearly seen in

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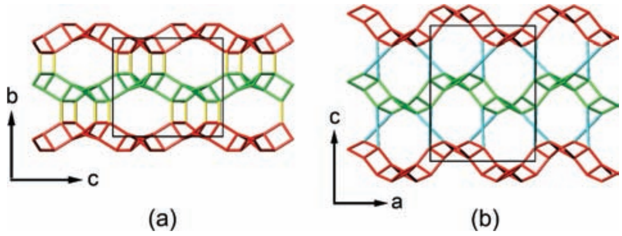

Figure 3. Comparison of the frameworks of (a) **CGS** and (b) PKU-9, in which the **CGS** layers are shown in red and green. In **CGS**, the layers are directly connected through 3-noded T atoms, while in PKU-9, they are interconnected by *spiro*-5 units.

Figure 1a, are elliptical with an effective size of ~6.2 Å × 4.3 Å (Figure 2b). The other two 10-ring channels, which run along the [110] and [1$\bar{1}$0] directions but are otherwise identical, have effective opening sizes of ~7.0 Å × 4.6 Å (Figure 2c). The three 10-ring channels intersect, and since they are all perpendicular to the 8-ring channels along [001], they also intersect with the 8-ring channels, forming a three-dimensional open framework.

It is interesting to compare the structure frameworks of PKU-9 and **CGS**. The component layers in both structures are identical, and thus, the *a* and *b* values of PKU-9 are in fact very close to *a* and *c* values of **CGS**. The only difference between the two structures is the interconnection of the layers. In the **CGS** framework, the adjacent layers are related by a mirror plane and are directly linked by the 3-noded T atoms in the **CGS** layer, as shown in Figure 3a. Such linkage creates 10-ring channels along the *a* direction in the structure. In PKU-9, the neighboring layers are related by an n-glide plane perpendicular to the *c* direction and interconnected by additional T5 atoms via *spiro*-5 units (Figure 3b). As a consequence, the distance between adjacent **CGS** layers in PKU-9 is ~3 Å larger than that in **CGS**.

In each *spiro*-5 unit, the two corner-shared 3-rings are almost perpendicularly arranged. Such a unit is not common in tetrahedral frameworks because of the inner tension. In PKU-9, the T−O distances fall into the range 1.709−1.753 Å, which is typical of Al−O or Ge−O bonds. The T−O−T angles, however, fall into two distinct groups. Within the **CGS** layer, the T−O−T angles are in the range 132.9−147.5°, whereas in the *spiro*-5 units, the T−O−T angles are significantly smaller (123.8−128.9°). It should be noted that in the other germanate zeolite frameworks containing 3-rings, the 3-rings are either not directly linked [as in UCSB-9(**SBN**)] or linked by sharing an edge [as in SU-16(**SOS**)]. PKU-9 is the first example of an aluminogermanate that contains *spiro*-5 units.

The distribution of small rings (4- and 3-rings) and their correlation with the low FD of PKU-9 is also remarkable. The 4-noded T atoms in the **CGS** layer (T3 and T4) are surrounded by three 4-rings and the 3-noded atoms (T1 and T2) by two 4-rings and one 3-ring, while T5 in the *spiro*-5 unit is surrounded only by two 3-rings. The average size of the smallest ring is 3.4, which may be responsible for the low FD of 12.6 T/1000 Å^3. In view of the compositional effect, an FD_{Si} of 13.5 T/1000 Å^3 is estimated from the ratio $d_{Ge-O}/d_{Si-O} = 1.07$.

The SDA cations are located in the 10-ring channels in the structure (see the SI), as confirmed by ^{13}C magic-angle spinning NMR, elemental analysis, and structure refinement. PKU-9 loses ~18.7% of its weight between 310 and 880 °C, consistent with the decomposition of the SDA (calcd 18.7 wt %). The framework collapses at ~400 °C, when the decomposition of the SDA occurs.

In summary, PKU-9 is a novel aluminogermanate with a remarkable new zeolite framework. The framework is constructed from **CGS** layers and *spiro*-5 units, providing an alternative view of using known zeolite layers to design and synthesize topologically new zeolites.

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Supporting Information Available: Details concerning the synthesis, chemical analysis, spectroscopy, and structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) PKU-9: orthorhombic, *Pbcn*, $a = 15.578(3)$ Å, $b = 9.1704(18)$ Å, $c = 19.993(4)$ Å, $V = 2856.1(10)$ Å^3, $Z = 4$, $R_1 = 0.0428$ for 2136 observations.

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