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A Crystalline Mesoporous Germanate with 48-Ring Channels for CO_2 Separation**

Jie Liang, Jie Su, Xiaodan Luo, Yingxia Wang, Haoquan Zheng, Hong Chen, Xiaodong Zou, Jianhua Lin,* and Junliang Sun**

Abstract: *One of the challenges in materials science has been to prepare crystalline inorganic compounds with mesopores. Although several design strategies have been developed to address the challenge, expansion of pore sizes in inorganic materials is more difficult compared to that for metal–organic frameworks. Herein, we designed a novel mesoporous germanate PKU-17 with 3D $48\times16\times16$-ring channels by introducing two large building units (Ge_{10} and Ge_7 clusters) into the same framework. The key for this design strategy is the selection of 2-propanolamine (MIPA), which serves as the terminal species to promote the crystallization of Ge_7 clusters. Moreover, it is responsible for the coexistence of Ge_{10} and Ge_7 clusters. To our knowledge, the discovery of PKU-17 sets a new record in pore sizes among germanates. It is also the first germanate that exhibits a good selectivity toward CO_2 over N_2 and CH_4.*

The design and synthesis of crystalline open-framework materials with ever-increasing pore sizes has been an interesting and challenging research field in chemistry, owing to the important applications of these materials in catalysis, gas adsorption, and separation.[1–3] Mesoporous crystalline materials with nanometer-sized pores are of particular interest as they can improve the diffusion of bulky molecules through the pores when they are used as catalysts or adsorbents. However, until now, only a few inorganic materials are reported to have mesopores in their frameworks, including SU-M,[4] JLG-12,[5] ITQ-37,[6] ITQ-43,[7] SUT-7,[8] and NTHU-13.[9] Although Wang and co-workers found that the pore size of gallium zincophosphites NTHU-13 can be expanded to 72-ring by elongating the carbon chains of templates,[9] the pore sizes of other inorganic compounds are still delimited to 30-rings.

Several design strategies were proposed to tackle this challenge.[10–14] Among them, the "scale chemistry" proposed by Férey,[10,13,14] which suggests building large-pore solids from large building units (BUs), has been perfectly implemented in germanates because germanium tends to form larger BUs than other elements. Typical germanate BUs include $Ge_7(O,OH,F)_{19}$ (Ge_7),[15] $Ge_8(O,OH)_{20}$ (Ge_8),[16] Ge_9-$(O,OH,F)_{25\text{-}26}$ (Ge_9),[17] and $Ge_{10}(O,OH)_{27}$ (Ge_{10}) clusters.[4] More than 70 germanates have been synthesized from these BUs, while only six of them contain more than one type of cluster.[4,5,16,18,19] Compared with the germanates with one specified cluster, the six "hybrid" germanates have the largest pore size of at least 16-ring and are relatively more open structures. Therefore, it is expected that the combination of different clusters into the same framework may lead to more diverse germanate structures, especially those with very open frameworks and extra-large pores.[4,5,18]

Because the Ge_7 and Ge_{10} clusters are the most frequently obtained BUs and have been found in more than 50 germanate structures, it is desirable to build new "hybrid" germanates with both Ge_7 and Ge_{10} clusters to increase the pore size. However, these two clusters seldom coexist in the same framework owing to their requirement of different synthetic conditions. The Ge_{10} cluster is always observed in structures synthesized with zero or low HF concentration, whereas the formation of Ge_7 clusters requires a high HF concentration.[19] We analyzed the connectivity of Ge_7 cluster, as proposed by Yu et al.,[38] with respect to the HF content (Supporting Information, Table S1). Our findings show that, for the germanates synthesized with HF, the Ge_7 connectivity is mostly lower than five and F^- or OH always act as terminal groups. For the five germanates synthesized without HF, the Ge_7 connectivity is equal to or higher than six, owing to the additional GeO_4 tetrahedra or ethanolamine which are connected to Ge_7 cluster as terminal species.[18,20–23] These imply that it is the replacement of OH terminals by F^-, additional GeO_4 tetrahedra, or OR groups in ethanolamine that plays a primary role in the formation of Ge_7 clusters. Thus, we propose that it might be possible to obtain 'hybrid' open frameworks built by both Ge_{10} and Ge_7 clusters by choosing other types of guest species instead of HF. Herein, we report a novel hierarchical meso- and micro-porous germanate PKU-17 containing both Ge_7 and Ge_{10} clusters in

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[*] Dr. J. Liang, X. Luo, Prof. Y. Wang, Prof. J. Lin, Prof. J. Sun
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871 (P. R. China)
E-mail: yxwang@pku.edu.cn
jhlin@pku.edu.cn
junliang.sun@pku.edu.cn

Dr. J. Liang, Dr. J. Su, Dr. H. Zheng, Dr. H. Chen, Prof. X. Zou, Prof. J. Sun
Berzelii Center EXSELENT on Porous Materials
Department of Materials and Environmental Chemistry
Stockholm University, Stockholm 10691 (Sweden)

Dr. H. Chen
Faculty of Material Science and Chemistry
China University of Geosciences, Wuhan 430074 (P.R. China)

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the framework. PKU-17 has a three-dimensional (3D) 48 × 16 × 16-ring channel system, which sets a new record of pore size of 48-ring among germanates.

PKU-17 was synthesized by using a commercially available 2-propanolamine (MIPA) as the structure-directing agent (SDA). A mixture of germanium dioxide (GeO_2), MIPA, and water with the molar ratio of 1:3.5:6 was sealed in a 23 mL Teflon-lined stainless-steel autoclave and heated at 150 °C under a static condition for 5 days. After filtration, colorless rod-like crystals with sizes about $50 \times 5 \times 5\ \mu m^3$ were obtained (Supporting Information, Figure S1c).

Synchrotron single-crystal X-ray diffraction study on PKU-17 shows that it crystallizes in the tetragonal space group $I4/m$ with $a = 48.046(3)$, $c = 18.7246(6)$ Å. The framework is constructed from two building units: Ge_7 and Ge_{10} clusters, and both are common motifs in germanates. The Ge_7 cluster consists of one GeO_6 octahedra, two GeO_5 trigonal bipyramids, and four GeO_4 tetrahedra (Figure 1 a). The Ge_{10} cluster consists of four GeO_6 octahedra and six GeO_4 tetrahedra and has a cube-like Ge_4O_4 unitat the core (Figure 1 b,c). Although the Ge_{10} and Ge_7 clusters are frequently found in germanates, their combination in the same framework is only found in SU-MB.[4] However, in SU-MB, the Ge_7 clusters do not participate in building the open-framework but act as pore-fillers to block one of the two gyroidal channels in SU-M. Thus, PKU-17 is the first germanate which contains Ge_{10} and Ge_7 clusters in its framework.

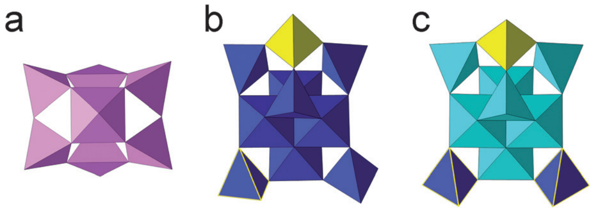

Figure 1. a) The $Ge_7O_{18}(OH)$ unit (Ge_7). b) The $Ge_{10}O_{26}(OH)_2$ cluster (Ge_{10}-I). c) The $Ge_{10}O_{25}(OH)_3$ cluster (Ge_{10}-II). See text for details. The tetrahedra highlighted with yellow edges in (b) and (c) are the tetrahedra shared by two Ge_{10} clusters. Apical additional tetrahedra are in yellow.

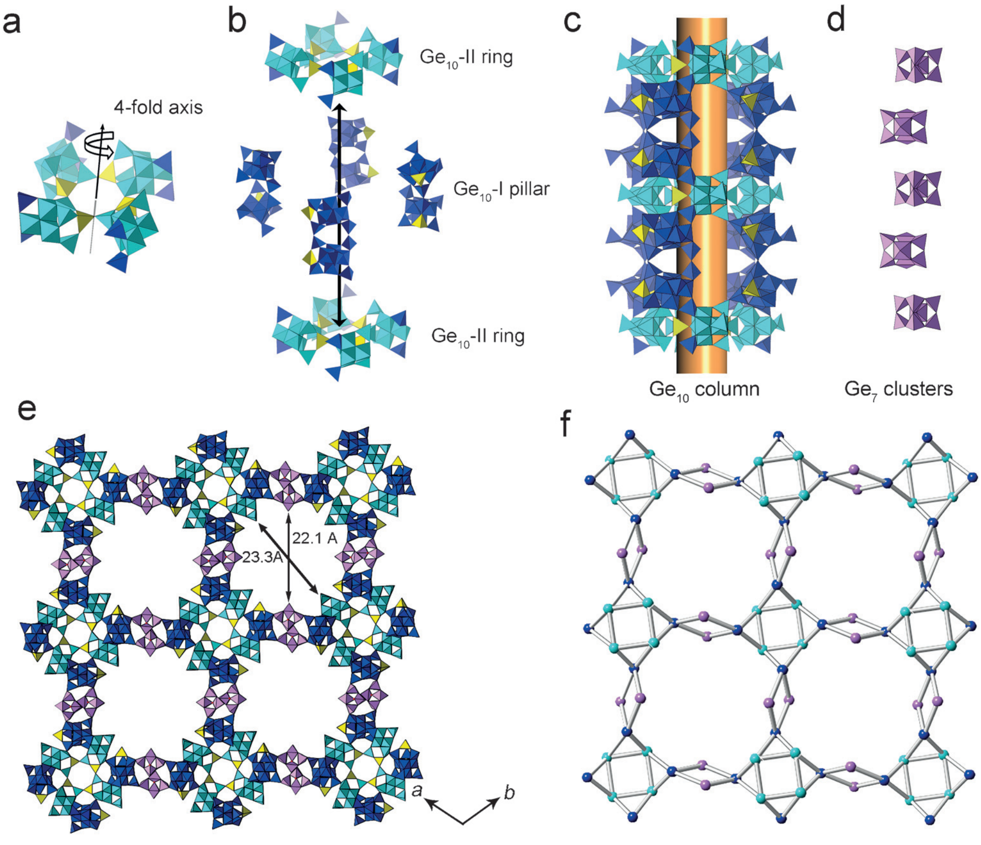

Figure 2. a) The Ge_{10}-II ring. b) Neighboring Ge_{10}-II rings are pillared by four isolated Ge_{10}-I dimers. c) A side view of the hollow Ge_{10} column. d) The staggered Ge_7 clusters with their octahedra pointing out and in. e) The projection of PKU-17 framework viewed along the [001] direction showing the 48-ring window. f) Simplified topological view of the framework. In (a–e): clusters Ge_{10}-I purple, Ge_{10}-II blue, and Ge_7 pink, apical GeO_4 tetrahedra are in yellow. In (f): cluster Ge_{10}-I blue balls, Ge_{10}-II purple balls, and Ge_7 pink balls.

The PKU-17 framework can be described by neighboring Ge_{10} columns connected by Ge_7 bridges. The rigid Ge_{10} column is aligned along the c-axis, formed by two unique Ge_{10} clusters named Ge_{10}-I and Ge_{10}-II, respectively (Figure 1 b,c). Each Ge_{10} cluster is capped with one apical GeO_4 tetrahedron. In one Ge_{10} column (Figure 2 c), four Ge_{10}-II clusters related by fourfold symmetry are connected through their apical GeO_4 tetrahedra to form a Ge_{10}-II ring (Figure 2 a), and neighboring Ge_{10}-II rings are then pillared by four isolated Ge_{10}-I dimers along the c-axis (Figure 2 b). In the ab plane, neighboring Ge_{10} columns are shifted by 1/2 c along the c-axis and connected by Ge_7 clusters, forming 48-ring channels extended along the c-axis (Figure 2 c–e). If the Ge_{10}-I, Ge_{10}-II and Ge_7 clusters are considered as three different vertices, the PKU-17 framework can be regarded as a new 4,5,6-c net (Figure 2 f). This net can be further described by a natural tiling as shown in Figure S6 in the Supporting Information.

The 48-ring channel in PKU-17 is the new record in channel sizes among germanates (Figure 3, and Supporting Information Figure S7). It is encircled by 12 Ge_{10} clusters and 4 Ge_7 clusters in the ab plane, with 12 terminal OH groups pointing towards the center. The dimension of the 48-ring is 20.6×19.4 Å^2 (assuming a van der Waals diameters of 2.7 Å

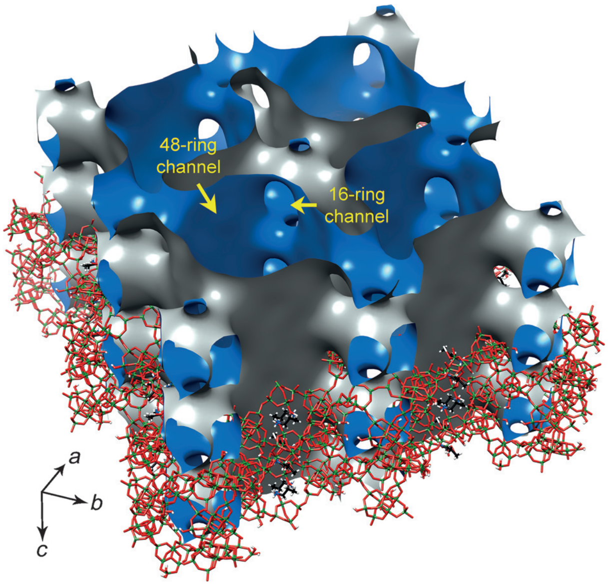

Figure 3. The channel system is partially superimposed with the structure model, showing the 48- and 16-ring channels. The blue surfaces are toward the channels while the gray surfaces are toward the framework. Ge green, O red, C black, N blue, and H white.

for oxygen) and reaches the mesopore range. Compared with the other two germanates with elliptical windows: SU-M with 30-ring (10.0×22.4 Å^2) and JLG-12 with 30-ring (13.0×21.4 Å^2),[4,5] the 48-ring window in PKU-17 is circular and has the largest pore size. Along the [100] and [010] directions, each 48-ring channel communicates with neighboring channels through 16-ring channels (8.5×5.7 Å^2), endowing PKU-17 a hierarchical meso- and micro-porous germanate structure. The framework density is 7.8 Ge atoms per 1000 Å^3, which is one of the lowest among inorganic open-framework materials. The accessible void volume of the channels in PKU-17 is 30407 Å^3, and occupies 70.3 % of the total unit cell volume.

The large channels in PKU-17 are occupied by guest molecules, which play space-filling and charge-balancing roles. According to the C,H,N elemental and thermogravimetric (TG) analyses (Supporting Information, Figure S3), 9.5 protonated MIPA and 10 water molecules are expected per formula. However, owing to the high symmetry of the framework and the disorder of guest molecules, only 2.5 protonated MIPA and 2.5 water molecules were located from the structure refinement. Interestingly, one MIPA is directly coordinated to the five-coordinate Ge atom in the Ge_7 cluster through the hydroxy group (Supporting Information, Figure S8), acting as a 'terminal' group to stabilize the Ge_7 cluster. The terminal groups play a primary role in the formation of Ge_7 cluster. They also have a great impact on the crystal growth: with the increase of the MIPA/GeO_2 ratio from 0.88 to 3.5, the morphology of PKU-17 crystal changes from nanofiber crystals to rod-like crystals with 5×5 μm^2 tetragonal sections (Supporting Information, Figure S1). This change can be explained as follows. When the MIPA content is low, the crystals grow more rapidly along the *c*-axis, corresponding to the growth of the Ge_{10} columns; with the increase of the MIPA content, faster growth is found in the *ab* plane as a result of the easier formation of Ge_7 clusters. Considering the PKU-17 framework, it is suggested that the growth of PKU-17 can be described as the assembling of Ge_{10} columns by Ge_7 clusters. A similar growth mechanism was reported in a silicogermanate zeolite ITQ-33.[24] But because of a mismatch in the height of neighboring columns, ITQ-33 has a twinned structure. We carefully checked the single-crystal X-ray diffraction data of PKU-17, and no stacking faults were found.

The N_2 adsorption isotherm was measured at 77 K to check the permanent porosity of PKU-17, and the Brunauer-Emmett-Teller (BET) surface area was determined to be 228 m^2 g^{-1}. In the N_2 adsorption isotherm (Figure 4 a), a steep N_2 uptake is observed when P/P_0 is lower than 0.01, indicating the presence of micropores; with the increase of P/P_0, the N_2 uptake increases dramatically and shows a step at $P/P_0=0.05$, indicating the presence of larger pores. The pore size distribution plot confirms that two kinds of pores are present in PKU-17: the peak located at 6.5 Å corresponding to the 16-ring micropore, and the peak at 19.8 Å corresponding to the 48-ring mesopores. Compared with other inorganic crystalline mesoporous materials with either elliptical mesoporous windows or template-occupied mesopores, PKU-17 is the

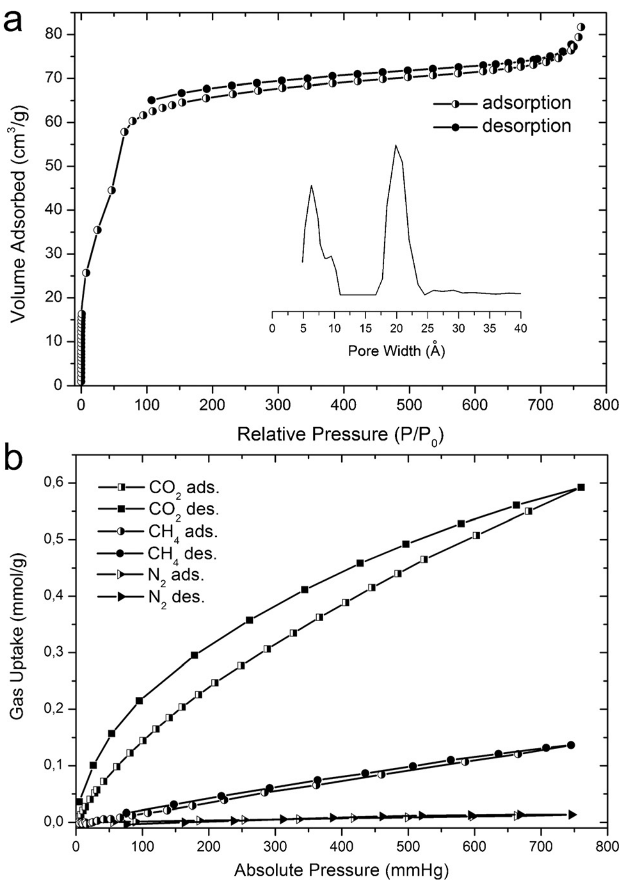

Figure 4. a) N_2 sorption isotherms at 77 K. Inset: pore-width distribution plot calculated by NLDFT using a cylinder model. b) CO_2, CH_4, and N_2 sorption isotherms at 273 K.

first inorganic framework whose mesopore was confirmed by N_2 adsorption experiments.

In light of the hierarchical channel system in PKU-17, and the existence of polar functional groups (dangling amino and hydroxy groups) which can enhance the affinity for CO_2,[25] we decided to check the selective CO_2-adsorption properties for PKU-17. As shown in Figure 4b, PKU-17 can adsorb a certain amount of CO_2, with the value of 0.6 $mmol\,g^{-1}$ at 273 K, 760 mmHg. Although the value is much lower than those of 'benchmark' microporous substrate, such as 13X zeolite (7.06 $mmol\,g^{-1}$)[26] and Cu-BTC metal–organic framework (16.5 $mmol\,g^{-1}$) at 298 K,[26] it is higher than that of mesoporous gallium zincophosphites NTHU-13 (0.32 $mmol\,g^{-1}$).[9] The lower CO_2 uptakes on PKU-17 and NTHU-13 are perhaps due to their large mesoporous channels, while CO_2 is single-layer adsorbed on the pore wall. Compared with the adsorption of CO_2, the CH_4 and N_2 adsorption isotherms (Figure 4b) show much lower uptakes of 0.14 and 0.014 $mmol\,g^{-1}$, respectively. On the basis of single-component isotherms and the Ideal Adsorbed Solution Theory,[27] the adsorption selectivity of PKU-17 for CO_2 over CH_4 is calculated to be 5.5 in a biogas stream (50% CO_2 and 50% CH_4), and 82 for CO_2 over N_2 in a flue-gas stream (15% CO_2 and 85% N_2). The CO_2/CH_4 selectivity of PKU-17 is comparable to that of Cu-BTC (ca. 4–6) at 303 K, 1 bar,[28,29] whereas the CO_2/N_2 selectivity is higher than that of Cu-BTC (21) at 298 K, 2.5 bar,[30] and lower than that of 13X zeolite (150) at 295 K, 1 bar.[31] Thus, despite the moderate CO_2 uptake, PKU-17 shows a satisfactory preference for CO_2 adsorption over CH_4 and N_2.

To better understand the CO_2 adsorption properties, the isosteric heat of adsorption was calculated from the CO_2 adsorption isotherms at two different temperatures (Supporting Information, Figure S10a). At zero-loading, the heat of adsorption of PKU-17 reaches 27 $kJ\,mol^{-1}$ (Supporting Information, Figure S10b). This value is higher than those of nonpolar or unfunctionalized analogues (lower than 20 $kJ\,mol^{-1}$),[32,33] and much lower than those amino-functionalized mesoporous silica in which the amine groups directly form bonds with CO_2 molecules (40–90 $kJ\,mol^{-1}$ for physisorption and 85–105 $kJ\,mol^{-1}$ for chemisorption).[34–37] The moderate isosteric heat of adsorption suggests that the interaction between CO_2 and PKU-17 can be attributed to the moderate/weak hydrogen bonding between CO_2 and polar functionalities, for example, NH_3^+ and OH groups. Such a weak intermolecular interaction is useful in practice: it not only effectively increases the adsorption for CO_2, but also enables the fully reversible desorption and decreases the energy cost for the absorbent regeneration (Supporting Information, Figure S11).

In summary, a novel mesoporous germanate PKU-17 with a record 48-ring pore size was synthesized by combining Ge_7 and Ge_{10} clusters in the same framework. The MIPA plays a decisive role in the synthesis as both the SDA and terminal species. N_2 adsorption confirms the permanent hierarchical porosity of PKU-17. PKU-17 exhibits a good selectivity toward CO_2 over N_2 and CH_4 at 273 K. Given the functional polar (-NH_3^+ and -OH) groups anchored on the pore wall and the accessible mesopores in the framework, PKU-17 may find application in other fields, such as immobilization of nanometer-sized molecules or biomolecules. We demonstrate herein that the use of multiple building blocks is not only an efficient strategy to build crystalline mesoporous frameworks, but also a potential route to synthesize functional porous materials with applications in catalysis, adsorption and separation, biosensors, and nanomaterials.

Keywords: cluster compounds · gas adsorption · germanates · porous materials · zeolite analogues

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