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**Zeolite Structures**

# A Germanosilicate Structure with 11 × 11 × 12-Ring Channels Solved by Electron Crystallography**

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***Abstract:*** *Zeolites have been widely used in industry owing to their ordered micropores and stable frameworks. The pore sizes and shapes are the key parameters that affect the selectivity and efficiency in their applications in catalysis, sorption, and separation. Zeolites with pores defined by 10 and 12* $TO_4$ *tetrahedra are often used for various catalytic processes. To optimize the performance of zeolites, it is extremely desirable to fine-tune the pore sizes/shapes. The first germanosilicate zeolite with a three-dimensional 11 × 11 × 12-ring channel system, PKU-16 (PKU, Peking University) is presented. Nanosized PKU-16 was structurally characterized by the new three-dimensional rotation electron diffraction (RED) technique. PKU-16 is structurally related to the zeolite β polymorph C (BEC, 12 × 12 × 12-ring channels) by rotating half of the four-rings in double mtw units.*

Zeolites are crystalline microporous materials consisting of corner-sharing $TO_4$ tetrahedra ($T = Si, Al, P, Ge, \ldots$), and they have wide industrial applications in catalysis, ion exchange, and separation.[1–7] Despite that a large number of new zeolites with three-dimensional (3D) extra-large pores have been successfully synthesized recently, such as ITQ-44 (IRR, 18 × 12 × 12-ring),[8] ITQ-43 (28 × 12 × 12-ring),[9] ITQ-37 (ITV, 30 × 30 × 30-ring)[10] and so on, stable zeolites with proper pore sizes and shapes are of great interest owing to their high selectivity. Zeolites with 8- and 10-rings are widely used in separation and ion-exchange (such as LTA, FER),[11,12] while those with 10-rings and 12-rings are efficient catalysts for the commercial applications in petrochemical industry, such as zeolite beta,[13,14] ZSM-5,[15] FAU, MOR, or FER.[16] Both zeolite beta with 12-rings and ZSM-5 with 10-rings are among the most important zeolite catalysts and used in various processes, such as hydrocarbon conversion,[17] alkylation,[18] and acylation of aromatics.[19] Owing to the medium pore size, ZSM-5 has even better shape selectivity than zeolite beta in many applications. This is also indicated by the increased academic interest in medium pore zeolites in recent years. Zeolites with mixed 10- and 12-rings also show excellent catalytic performance. For example, ITQ-39 with a 3D 12 × 10 × 10-ring channel system is an efficient catalyst for the conversion of naphtha into diesel fuel compared with zeolite beta and ZSM-5, because the 10-rings reduce the coke formation while the 12-rings facilitate the diffusion of alkylated long-chain products.[20] To further improve their catalytic performance, zeolites with finely tuned ring sizes and shapes are extremely desirable for high selectivity, especially those with large odd-numbered rings (> 10-rings), as the zeolite applications in catalysis are dominated by zeolites with even-numbered rings. Two reported zeolites with large odd-numbered rings, GaGeO-JU-64 (11 × 11 × 11-ring)[21] and ITQ-40 (16 × 16 × 15-ring),[22] are both unstable after removing guest molecules and cannot be used for catalytic applications, which could be partially due to the existence of large amounts of 3-rings. To synthesize stable zeolites with large odd-numbered rings is still challenging. PKU-16 is the first such zeolite with unique three-dimensional squashed 11-ring channels.

PKU-16 was synthesized by using a commercially available neutral amine, 4-dimethylaminopyridine (DMAP), as the organic structure-directing agent (OSDA). This OSDA has been used for the synthesis of a few zeolites.[23–25] A mixture with the batch composition of $1.0\,GeO_2{:}1.0\,TEOS{:}10.0\,H_2O{:}1.0\,DMAP{:}1.0\,HF$ was prepared and sealed in a 3 mL Teflon tube at 125 °C under static conditions for 14 days. After washing, the obtained rod-like product has crystal sizes around 40–200 nm (Supporting Information, Figure S1). Powder X-ray diffraction (PXRD) indicates that PKU-16 was stable up to 600 °C and the framework was maintained after removing OSDAs by ozone treatments in air (Supporting Information, Figures S2, S3). The chemical formula of PKU-16 was estimated as $|(C_7H_{10}N_2)_8(H_2O)_{12.2}(HF)_{5.8}|[Si_{0.59}Ge_{0.41}O_2]_{64}$ based on elemental analysis, thermogravimetric analysis, and solid-state $^{19}F$ NMR results (Experimental Section and Supporting Information, Figures S4, S5).

Owing to the peak overlapping caused by the small crystal size and being a minor phase when it was first discovered, a direct structure solution of PKU-16 from PXRD was difficult.[26] Thus, the newly developed three-dimensional

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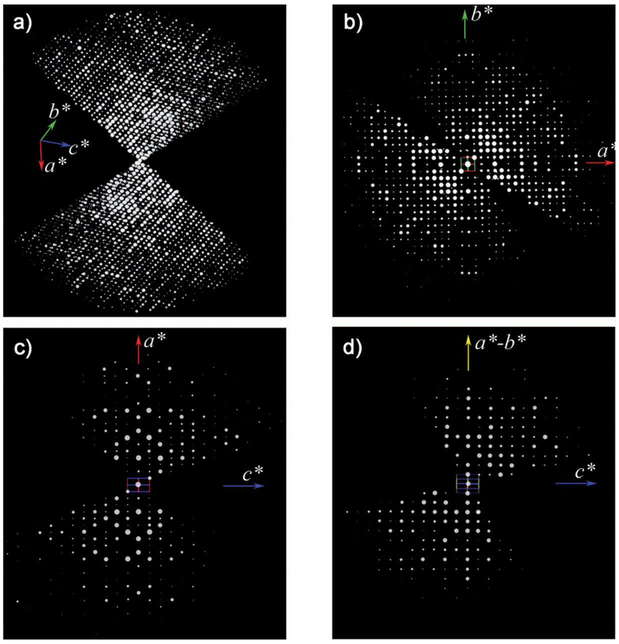

*Figure 1.* Reconstructed three-dimensional RED data. a) Overview of the data; owing to electron beam damage, the reflections at high resolution following a clockwise direction become weaker and weaker. b)–d) Selected planes in the reciprocal lattice and corresponding to *hk*0, *h*0*l*, and *hhl* planes, respectively. The reflection conditions can be obtained as: $h0l$, $h+l=2n$; $h00$, $h=2n$; $00l$, $l=2n$. Owing to dynamical effects, some reflections violate the reflection conditions.

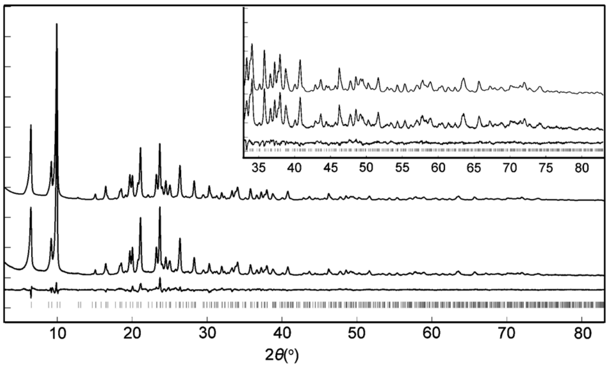

*Figure 2.* Rietveld refinement of powder X-ray diffraction for as-synthesized PKU-16. The curves from top to bottom are simulated, observed, and difference profiles respectively.

electron diffraction technique, namely rotation electron diffraction (RED)[9,27] was used to collect and process the 3D electron diffraction data for structure solution. The 3D reciprocal lattice reconstructed from the RED dataset is shown in Figure 1 a. This reciprocal lattice shows clearly a $4/mmm$ Laue symmetry with a tetragonal unit cell of $a \approx 19.04$ Å and $c \approx 11.73$ Å. The reflection conditions derived from this 3D dataset in Figure 1 indicate the possible space groups of $P4_2/mnm$, $P4nm$, and $P\bar{4}n2$. Ab initio structure solution was performed by direct methods using the program SIR2011.[28] All Si/Ge and part of oxygen atoms were located directly with the $P4_2/mnm$ symmetry, and the remaining oxygen atoms were then found from residue peaks. The framework atoms could be refined anisotropically without any restraints by SHELX97.[29] However, because of the electron beam damage during the data collection, the OSDAs in the pores could not be located from the RED data. Based on the framework structure obtained from the RED method, the synthesis condition was optimized and pure PKU-16 samples were successfully synthesized. The final Rietveld refinement was performed on the pure PKU-16 sample using the program TOPAS.[30] Similar *R*-values were obtained with different locations of OSDAs, which indicates that the OSDAs may be disordered. The force-field simulation also resulted in disordered OSDAs in the pores. Thus the OSDAs were refined as rigid bodies to compensate for the scattering power. The framework was refined with soft restraints for distances and angles. The Si/Ge ratio was fixed at 1.45 as determined by ICP-MS. The refinement converged to $R_p = 0.0575$ and $R_{wp} = 0.0738$ with $R_{exp} = 0.0479$ (Figure 2). The framework of PKU-16 can be presented by natural tiling with a transitivity of [5(13)(16)8] (Supporting Information, Figure S6 and Table S3)[31] and contains a 3D channel system.

The framework of PKU-16 is closely related to that of zeolite β polymorph C (BEC).[32–34] Both structures are constructed by the columns along the *c*-axis, which are further linked by double four rings (*d*4*r*s) to form 3D channel systems with the similar framework density about 15.1T/1000 Å$^3$. The striking difference is that the straight 3D channel system is transformed from 12 × 12 × 12 rings in BEC to 11 × 11 × 12 rings in PKU-16 (Figure 3) by a 90° rotation of single 4-rings in the center of the column. All such single 4-rings in BEC are parallel to the *c*-axis and form star-like *mor* units (Figure 4 a), while half of these 4-rings in PKU-16 (marked in black) are rotated by 90° around *a*- or *b*-axis and become perpendicular to the *c*-axis (Figure 4 b). The rotation of these single 4-rings results in a doubled unit cell in the *a*-*b* plane without altering the 12-ring channels along the *c*-axis. One important difference between the two structures is observed, as illustrated in Figure 4 c,d. BEC has round 12-ring channels, and each 4-ring contributes two T-atoms to the 12-ring (Figure 4 c). If half of the single 4-rings in BEC (marked in black) are rotated by 90° and each such 4-ring contributes only one atom to the ring, the structure of PKU-16 is formed (Figure 4 d). The 12-rings in BEC become squashed 11-rings in PKU-16, and the free diameter of the ring is changed from 6.9 × 7.0 Å for BEC to 4.6 × 6.9 Å for PKU-16, taking into account of the van der

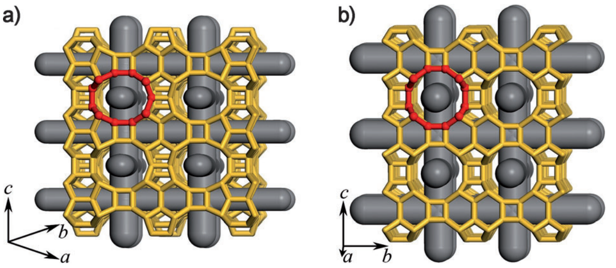

*Figure 3.* Comparison of the 3D channel systems in a) PKU-16 and b) BEC. PKU-16 has an 11 × 11 × 12 ring channel system, where the 11-ring channels are squashed with pore sizes of 4.6 × 6.9 Å, assuming the van der Waals diameter for oxygen is 2.7 Å. BEC has a 12 × 12 × 12-ring channel system. Only the T–T connections are shown for clarity.

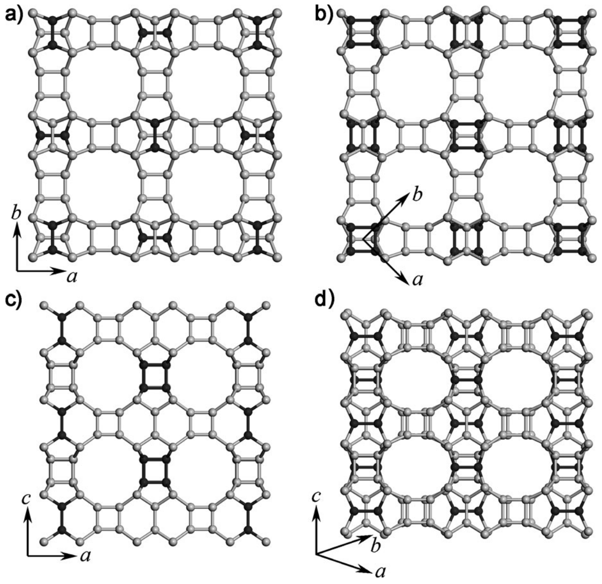

*Figure 4.* Comparison of BEC and PKU-16 frameworks. a), c) Projections of BEC; b), d) projections of PKU-16. Viewing along the *c*-axis, both structures have 12-ring channels, but part of the 4-ring in black has different orientations as shown in (a) and (b). Viewing perpendicular to the *c*-axis, BEC in (c) still has straight 12-ring channels while PKU-16 in (d) has squashed 11-ring channels. Only T–T connections are shown for clarity. The differences between the two structures are highlighted in black.

Waals radius of oxygen 1.35 Å. This agrees with the pore size obtained from $N_2$ adsorption analysis (Supporting Information, Figure S7). Note that unlike two other zeolites with large odd-numbered rings (JU-64 with 11-rings and ITQ-40 with 15-rings), where a large number of 3-rings exist in the framework, PKU-16 is formed with similar fragments as BEC with the smallest ring size of four. Thus, PKU-16 is the first stable zeolite structure with large odd-numbered rings. Owing to its special pore size and squashed shape, PKU-16 is expected to be a unique catalyst for petrochemical industry, for example the conversion of naphtha into diesel fuel, which is under investigation.

The structural relations between PKU-16 and BEC can be examined more carefully through their composite building units (CBUs). PKU-16 is constructed of three different CBUs, namely *d*4*r*, *mel*, and *stf*, while BEC is built from *d*4*r*, *mtw*, and *mor*.[35] Two mirror-symmetry related *mtw* units in BEC are shown in Figure 5 a. After rotating the blue single 4-ring in the center, it is converted into two mirror-symmetry-related *stf* units in Figure 5 b. In the meantime, the fragment shrinks along the vertical direction while expands along the horizontal directions, which resulted in a shorter *c*-axis of PKU-16 and shifted *d*4*r*s between each other in the projection shown in Figure 4 d. Force-field simulation shows that after geometry optimization, PKU-16 in a pure silica form has a reasonable framework energy (10.05 kJ mol$^{-1}$ higher than α-quartz with a formula of $SiO_2$), which is very close to that for BEC in a pure silica form (10.19 kJ mol$^{-1}$). This explains the possibility of obtaining PKU-16 with 11-rings. In fact, the flexibility of the 4-rings can be found in a number of reported zeolites, one extreme case is found in zeolites ITQ-26 (IWS)[36] and ITQ-21.[37] In ITQ-26, the 4-rings are ordered, while in ITQ-21, these 4-rings are oriented randomly in three different orientations, as shown in Figure 5 c. In ITQ-21, none of the T-atoms in these single 4-rings contributes in the formation of the channels, so the rotation of the 4-rings does not change the pore size or shape. By searching the zeolite database, more zeolites with double *mtw* CBUs could be found such as ISV,[38] MSE,[39] IWS,[36] and ITQ-39 polymorph C.[20] Based on the frameworks of ISV and MSE, three new frameworks can be built with different pore sizes and shapes, donated as ISV-i, ISV-ii and MSE-i. From the calculated framework energy (Supporting Information, Table S4), ISV-ii with 10 × 12 × 12-ring channels (Supporting Information, Figure S8a) and MSE-i with 10 × 11 × 12-ring channels (Supporting Information, Figure S8b) are energetically feasible, whereas ISV-i with an 11 × 11 × 12-ring is not. Considering that 9-rings are more frequently found in zeolites than 7-rings owing to less stress, we believe 11-rings could be as common as 9-rings by releasing the geometry stress. Note that the structure of MSE-i and MSE is hardly distinguishable by PXRD patterns owing to their similar unit-cell dimensions, and the difference in symmetry only induces changes for a few weak reflections (Supporting Information, Figure S11). For the structures of ISV and ISV-ii, they can be easily identified from PXRD owing to the large differences of the unit cell dimensions, just like BEC and PKU-16 (Supporting Information, Figures S12, S13).

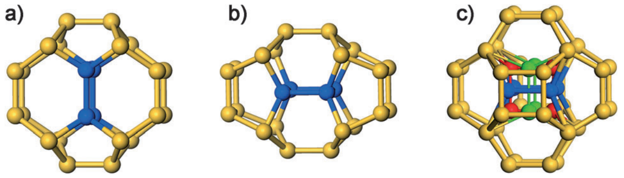

*Figure 5.* Comparison of the composite building units in three different zeolites where the 4-rings are oriented in different ways, a) double *mtw* unit in BEC; b) double *stf* unit in PKU-16; c) a composite unit in ITQ-21 with 4-rings randomly orientated in three different orientations (shown in red, green, and blue, respectively). Only T-T connections are shown for clarity.

In conclusion, we have successfully synthesized a novel zeolite containing straight 11-ring channels, PKU-16, using a simple OSDA. The newly developed RED method was used to identify this interesting phase and determine its framework structure. The structure of PKU-16 has a 3D 11 × 11 × 12-ring channel system and is closely related to zeolite β polymorph C by rotating half of single 4-rings in the double *mtw* units by 90°. PKU-16 is the first stable zeolite with large odd-numbered rings (> 10). The success of synthesizing odd-numbered rings may offer unique pore sizes and shapes for highly selective catalytic applications, which is very important to change the situation that the zeolite catalytic applications are dominated by zeolites with 10-rings and 12-rings.

## Experimental Section

4-Dimethylaminopyridine (122.0 mg, 1.0 mmol) and $GeO_2$ (104.6 mg, 1.0 mmol) were added to water (5.0 mL). The mixture was stirred using a magnetic stirrer until all germanium oxide was dissolved.

After adding TEOS (tetraethoxysilane; 208.3 mg, 1.0 mmol), the mixture was stirred for another 2 h to hydrolyze the TEOS. An aqueous HF solution (40 %, 44.0 μL, 1.0 mmol) was then added and the mixture was stirred at room temperature until the amount of water left was 180.0 mg (10.0 mmol) by weighing. The mixture was transferred into a 3 mL Teflon-lined stainless steel autoclave. The autoclave was sealed and heated to 125 °C under autogenous pressure for 14 days. The solid product was recovered by filtration and washed with distilled water.

Single-crystal rotation-electron diffraction (RED) data were collected on a JEOL JEM2100 TEM by the RED program on a $300\times250\times150$ nm crystal (goniometer tilt: $-71°$ to $+68°$; beam tilt: $-1°$ to $+1°$; exposure time: 0.5 s).[27] Totally 1264 ED frames were recorded with a step of 0.1°. The reciprocal space reconstruction and data extraction were carried out by the program RED data processing.[27] The ab initio structure solution was carried out by SIR2011,[28] and all Si and O atoms were located from the Fourier map. The structure was refined based on the RED data, which converged to an $R_1$ of 25.8 % using SHELXL97.[29] This initial model was then used for the Rietveld refinement with PXRD data by TOPAS 4.0.

Further details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-426839.

The framework energies for different framework types were calculated by the Forcite modules in Materials Studio v6.0. All frameworks were calculated in a pure silica form. The force field of COMPASS27 was used with parameters of o2z and si4z for oxygen and silicon, respectively. The Smart algorithm was used to optimize the geometry and unit cell parameters with ultrafine quality. Energies for different frameworks were compared with α-quartz in a formula of $SiO_2$ to give a relative energy as shown in the Supporting Information, Table S4. The energy of PKU-16 was also calculated with OSDAs and $F^-$ ions, and multiple minima with similar energies were found. This indicates possible disorder for the OSDAs, in consistent with the result from the Rietveld refinement.

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