

A silicogermanate with 20-ring channels directed by a simple quaternary ammonium cation†

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A silicogermanate, PKU-12, with the –CLO type of zeolite framework was hydrothermally synthesized under fluoride media using diisopropylethylmethylammonium as a structure directing agent. The formation of the silicogermanate zeolite with 20-ring channels has not only extended the –CLO family from phosphates into silicogermanates, but also demonstrated its structural diversity.

Zeolites have been extensively studied over many years due to their wide applications in catalysis, ion exchange, adsorption, and separation.¹ The synthesis of zeolites with extra-large pores has been of increasing interest to both academia and industry.² The discovery of metal phosphates from the 1980s has widely extended zeolite framework topologies and promoted the formation of zeolites with extra-large pores.³ Cloverite, a gallium phosphate, with 3D 20-ring extra-large pore systems, and coded as –CLO, has attracted considerable attention.⁴ Some transition metal ions, such as Ti⁴⁺, Mn²⁺, Co²⁺, Zn²⁺,⁵ have been doped into the cloverite framework to improve its catalytic properties, while DNL-1,⁶ an aluminophosphate with a –CLO type framework, was recently realized by applying an ionothermal synthetic route. However, up to now, its silicon or germanium analogues have not been reported. It is well known that the introduction of germanium to zeolites has led to considerable structural diversity.⁷ Since germanates often show longer Ge–O bond lengths (~1.74 Å) and smaller

Ge–O–Ge angles (~130°) in a tetrahedral framework compared with Si–O bond lengths and Si–O–Si angles in silicates, the introduction of germanium into the zeolite framework favours the formation of small rings, especially D4R (double 4-ring).⁸ A number of new zeolite framework types have emerged as silicogermanates or germanates, such as ITQ-*n*,⁹ IM-*n*,¹⁰ SU-*n*,¹¹ among which most of the silicogermanates or germanates contain D4R units. Since the –CLO framework contains extensively D4Rs, the realization of its type material as a germanate or silicogermanate is highly expected.¹²

The organocationic structure directing agent (SDA) is another important factor affecting the formation of zeolites. The size and shape of the SDA often correlate with the dimensions of the zeolite micropores or cages.¹³ The use of large, increasingly elaborate quaternary ammonium cations has been an effective strategy for the synthesis of zeolites with novel framework types. For example, IM-20,^{10c} a zeolite with 3D 12- and 10-ring channels, was obtained by a complex branched SDA 3-butyl-1-methyl-3*H*-imidazol-1-ium; ITQ-37,^{9g} an interrupted zeolite with a 3D mesoporous channel system, was templated by large dicationic organic structure directing agents. However, the syntheses of increased branching rigid SDA molecules are complex and expensive, which are not suitable for industrial application.

Here, we report the synthesis and structure of a silicogermanate with the –CLO type of framework, which is designated as PKU-12. PKU-12 was hydrothermally synthesized under fluoride media using diisopropylethylmethylammonium, a simple quaternary ammonium cation synthesized by a concise route in our lab (see ESI and Fig. S1†), as the structure directing agent.

PKU-12, crystallized in cubic morphology (Fig. S2, ESI†), was obtained from a mixture of GeO₂, fumed silica, SDA and HF at 110 °C for 15–30 days. The most suitable composition of the gel was 0.35 SiO₂: 0.65 GeO₂: 0.5 SDA: 0.5 HF: 4.5–6.0 H₂O. The conditions for the formation of pure PKU-12 are critical. Only when the ratio of Ge/Si was 0.65/0.35 and the water content in the range of 4.5–6.0 (H₂O/TO₂), pure PKU-12 could be obtained at 110 °C. A decrease of the Ge/Si ratio and an

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†Electronic supplementary information (ESI) available: The synthesis and characterization of the SDA, the composition of the initial gels and the reaction conditions, SEM image, IR spectrum, TG curve, thermal stability, tables of crystallographic information, ¹³C NMR spectrum, N₂ adsorption isotherm, EDS analysis, and crystallographic information file in CIF format. CCDC 903298. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt32231e

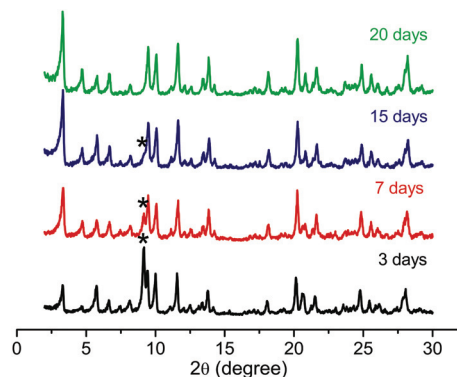


Fig. 1 XRD profiles of the products with reaction time. The peak marked with an asterisk (*) is the main peak of the D4R-C phase.

increase of the water content resulted in the appearance of ITQ-21, while a higher Ge/Si ratio and a shorter reaction time produced D4R-C,¹⁴ a compound that can be considered as a super-molecular assembly of double D4R clusters. The presence of D4R-C in the early reaction stage and its disappearance with the increasing reaction time (Fig. 1) imply that the D4R clusters act as pre-nucleation building units¹⁵ in the reaction system, which can re-organize themselves to form PKU-12.

In the spectrum of ¹³C NMR in PKU-12 (Fig. S3, ESI†), the five signals with the chemical shifts at 63.89, 53.47, 45.04, 18.39, and 10.57 ppm correspond to the responses of carbon in the groups of –NCH, –NCH₂, –NCH₃, and methyl groups in the isopropyl and ethyl groups, which are similar to those of diisopropylethylmethylammonium iodide, and indicate that the SDA cations are kept intact in PKU-12. The elemental analysis of the sample after being heated at 200 °C for 3 hours reveals the content (wt%) of 11.96, 3.44 and 1.51 for C, H and N respectively, while the ICP result provides a ratio of Si/Ge ≈ 0.45/0.55, which is also proved by EDS results (Table S2 in ESI†). Based on the results, the chemical formula for PKU-12, (Si_{0.45}Ge_{0.55})₁₉₂O₃₇₂(OH)₂₄F₂₄(C₉H₂₂N)₂₄(H₂O)₉₆, could be deduced.

The XRD pattern of PKU-12 can be indexed by a primary cubic lattice with the cell parameter $a = 26.23$ Å, which is consistent with the parameter for an ideal –CLO framework. For the gallo- or alumino-phosphate –CLO systems, a large face-centered cell with a doubled cell parameter was applied for the location of M³⁺ (M = Ga/Al) and P⁵⁺ cations in an ordered manner. However, the large cell seems not necessary for the silicogermanate since silicon and germanium ions are both +4 and can occupy the same position randomly. A tentative refinement with the super-lattice did not yield any apparent indication for the ordered distribution of Si⁴⁺ and Ge⁴⁺ in PKU-12. Then the primary cubic cell with the space group $Pm\bar{3}m$ was applied in the Rietveld analysis and the refinement converged to $R_p = 0.0467$ and $R_{wp} = 0.0619$ by the program TOPAS 3.0.^{†16} The Rietveld plots are shown in Fig. 2 and the details for the structure refinement, including the data collection conditions and the results of Rietveld analysis, are listed in Table S3.† The structure parameters and the selected bond lengths and angles are listed in Tables S4 and S5.†

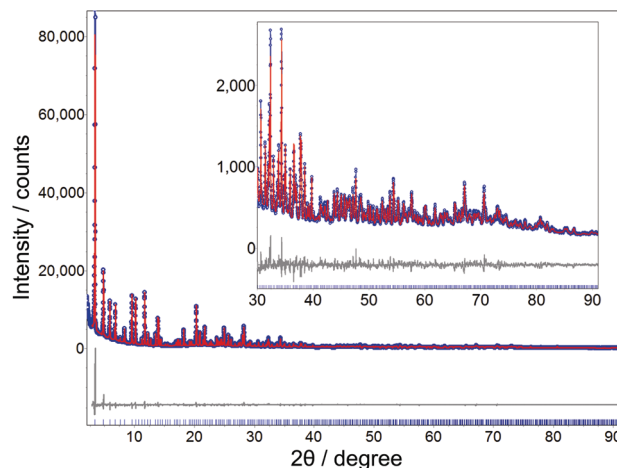


Fig. 2 X-ray Rietveld refinement plot of PKU-12. The blue circles are for the observed data. The red solid line is for the calculated data. The grey solid curve is for the difference. The vertical bars are for the positions of Bragg peaks.

An asymmetric unit of PKU-12 contains 5 crystallographically independent T atoms (T = Si or Ge) and 14 oxygen atoms in the framework. All T atoms are tetrahedrally coordinated by oxygen, while 13 oxygen atoms are shared by two T atoms and the O14 only links to T5 presenting as a hydroxyl group. Si and Ge are distributed in the five T sites with the ratios of 0.62(T1), 0.88(T2), 1.12(T3), 0.75(T4) and 0.64(T5) based on the refined occupancy results (Table S3†). The higher content of Ge in the T5 site may be due to the TOH terminal group, but it is difficult to tell the reason why Ge favors the T1 site, since the –CLO framework can be viewed as an architecture built by D4Rs, and all the five T atoms join the construction of D4R units. The T–O bond distances and T–O–T angles are reasonable in the structure. The large cavities of PKU-12 can accommodate a large amount of SDA and water molecules, but they are not orderedly distributed, then several statistic atoms are put into the cavities to compensate the electron densities due to the guest molecules in channels.

The –CLO framework consists of two types of D4Rs as the basic structural units: one is the normal D4R with eight Q4 T atoms, and the other has two terminal groups. The D4Rs connect each other, forming *lta* cages, *clo* cages, creating two sets of three-dimensional channel systems, as shown in Fig. 3. One is the eight-ring channel running through the *lta* and *clo* cages, and the other is a 20-ring channel with 30 Å supercavities at the intersections. The supercavity has an unusual clover-shaped window due to the presence of terminal hydroxyl groups.

It is believed that fluoride can induce the formation of the D4R unit and its role in the synthesis of silicates or germanates has been extensively discussed.^{17,18} The location of the fluoride ions in the structure of PKU-12 can be characterized by ¹⁹F NMR. As shown in Fig. 4(a), the strong ¹⁹F resonance at –4.3 ppm originates from the fluoride ions in D4R units formed by both Si and Ge tetrahedra, and the signals at –114 to –124 ppm may be assigned to the fluoride ions in channels for charge balance.

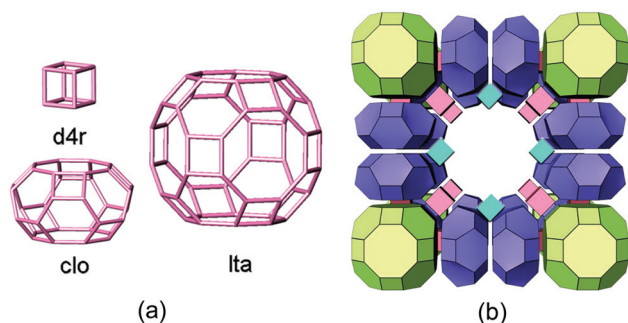


Fig. 3 Structure of PKU-12. (a) Composite building units and (b) polyhedral projection along the [100] direction. The different colours represent different composite building units.

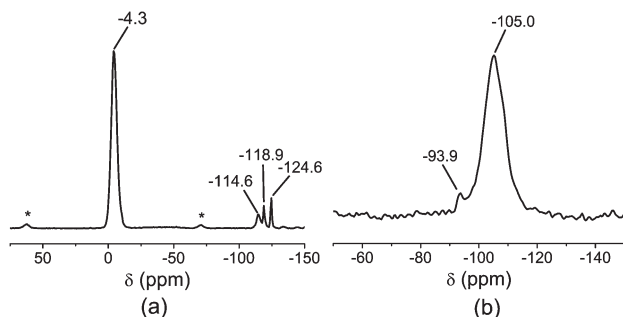


Fig. 4 Solid state NMR spectra of PKU-12. (a) ^{19}F and (b) ^{29}Si .

The ^{29}Si MASNMR spectrum of PKU-12, shown in Fig. 4(b), consists of a weak peak at -93.9 ppm and a broad band with a maximum at *ca.* -105.0 ppm, which are characteristic of $\text{HOSi}(\text{OSi})_3$ (Q^3) and $\text{Si}(\text{OSi})_4$ (Q^4) silicon sites, respectively. It confirms the presence of terminal hydroxyl groups in the PKU-12 structure.

The thermogravimetric analysis curve of PKU-12 under an air atmosphere is shown in Fig. S4.† It decomposes in three steps with a total weight loss of 24.6% between 30 and 800 °C. The XRD profiles of the calcined samples under different temperatures are shown in Fig. S5.† The framework of PKU-12 can retain to 550 °C. The powder X-ray Rietveld analysis of the calcined sample was performed and the results confirm that PKU-12 keeps the CLO-type of framework (for details, see Tables S6 and S7, Fig. S7†). The removal of the SDA molecules resulted in a shrinkage of the cell parameter to 26.18 Å. The de-template product was stable under water-free conditions, but collapsed in hours when exposed to air. It may be due to the attack of water molecules on the tetrahedral germanium; similar phenomena of framework collapse were observed in gallo- and aluminophosphate cloverite.^{4d,6}

PKU-12 has a micropore volume of $0.23 \text{ cm}^3 \text{ g}^{-1}$ and a large BET surface area of $623 \text{ m}^2 \text{ g}^{-1}$, as determined from nitrogen adsorption (Fig. S6†) and by the conventional t-plot method. We also analyzed the adsorption data using the Horvath-Kawazoe method to deduce the pore size of PKU-12. The average pore diameter for the PKU-12 sample was 13.2 Å,

which is coincident with the structural analysis result of 13.6 Å.

In summary, we have successfully synthesized the first non-phosphate analog of the $-\text{CLO}$ zeolite framework, the silicogermanate PKU-12, by using a simple SDA diisopropylethylmethylammonium hydroxide. The framework structure of PKU-12 was refined by Rietveld structure analysis using powder XRD. PKU-12 has a large pore size and a high BET surface area and shows reasonable stability under anhydrous conditions, making it a potential catalyst for the reaction of larger organic molecules.

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Notes and references

† Crystal data for PKU-12: $\text{Si}_{3.61}\text{Ge}_{4.39}\text{O}_{19.60}\text{C}_{10}\text{F}$, $M_r = 872.78$, cubic, space group $\text{Pm}\bar{3}m$, $a = 26.2373(2) \text{ Å}$, $V = 18\,061.7(4) \text{ Å}^3$, $Z = 24$, $T = 298(2) \text{ K}$, $\lambda = 1.5406 \text{ Å}$, $R_p = 0.0467$, $R_{wp} = 0.0619$, $\text{GOF} = 1.925$. CSD-423401.

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