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Zeolite Analogues

A Gallogermanate Zeolite with Eleven-Membered-Ring Channels**

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Zeolites are crystalline microporous materials composed of corner-sharing TO_4 (T = Si, Al, P, etc.) tetrahedra, and widely applied in the fields of catalysis, ion-exchange, adsorption, and separation.[1] So far, 206 types of zeolite frameworks have been identified by the Structure Commission of the International Zeolite Association (IZA-SC).[2] The importance and increasing number of applications for zeolites drives the development of new zeolite materials.[3] Germanate-based zeolites are of particular interest because of their rich structural diversity favored by the larger T–O distances and the smaller T-O-T angles of Ge atoms compared with those of Si atoms in silicate zeolites. Such geometric factors have an important effect on the formation of small rings, such as double four-membered rings (D4Rs), which are believed to be beneficial for the formation of structures with very low framework density (FD), proposed by Brunner and Meier.[4] Notably, a series of D4R-containing germanosilicate zeolites with extra-large pores has been successfully synthesized,[5] such as ITQ-33 (18 × 10 × 10 ring),[6] ITQ-43 (28 × 12 × 12 ring),[7] ITQ-44 (IRR, 18 × 12 × 12 ring),[8] and ITQ-37 (-ITV) with 30-membered-ring windows.[9] In addition, several novel germanate-based zeolites built of small rings that incorporate trivalent elements, such as B, Al, and Ga, have been discovered.[10–12] Notably, the gallogermanate zeolite GeGaO-CJ63 (JST) is constructed exclusively from 3-membered-ring units,[12] and has a structure that features a pair of chiral cages induced by chiral metal-complex templates.

The pore characteristics of zeolites such as pore dimension and pore size may fundamentally affect the shape-selective property with regards to molecular sieving and hydrocarbon transformations, which can lead to new or improved separation and catalytic processes.[3b,13] Compared with even-numbered pore openings, odd-numbered pore openings are much less frequently observed in existing zeolites. Until now, the largest odd-numbered channel openings are 15-membered-ring openings, which are found in germanosilicate ITQ-40.[14] To the best of our knowledge, there is no zeolite that possesses pore openings bordered by eleven tetrahedrally coordinated atoms. Herein, we present the synthesis and characterization of a gallogermanate zeolite $|(Ni(C_3H_{10}N_2)_3)_{36}Ni_{4.7}|[Ga_{81.4}Ge_{206.6}O_{576}]$ (denoted GaGeO-JU64, $C_3H_{10}N_2$ = 1,2-PDA = 1,2-diaminopropane). It exhibits a novel four-connected zeolite structure that possesses a three-dimensional intersecting 11-membered-ring channel system. The structure features novel $[3^{12}.4^3.6^2.11^6]$ cavities that exist as pairs of enantiomers either containing or being surrounded by chiral metal complexes used as the templates. GaGeO-JU64 has the lowest framework density (FD = 9.9 T/1000 Å^3) ever achieved in oxide zeolites.

GaGeO-JU64 was prepared by the hydrothermal reaction of a mixture of GeO_2, $Ga(NO_3)_3$, $Ni(CH_3COO)_2\cdot 4H_2O$, 1,2-PDA, and H_2O in a molar ratio of 1.00:0.39:0.24:19.17:36.76 at 180 °C for 8 days in a Teflon-lined stainless steel autoclave. The metal complex cation $[Ni(1,2\text{-PDA})_3]^{2+}$ was formed in the above reaction. The obtained pink cubic crystals were washed by deionized water and dried in air. The phase purity was confirmed by the agreement between the experimental powder X-ray diffraction (XRD) pattern and the simulated one based on structure analysis (see the Supporting Information, Figure S1). The XRD patterns of the GaGeO-JU64 sample recorded at different temperatures are shown in Figure S2 in the Supporting Information.

GaGeO-JU64 crystallizes in the $R\bar{3}$ space group (No. 148) with a = 30.0117(12) Å, and c = 37.301(3) Å. Its framework is built from TO_4 (T = Ge, Ga) tetrahedra, forming the anionic $[T_{288}O_{576}]_n^{81.4n-}$ open framework, in which 288 × T sites are occupied by both 206.6 × Ge and 81.4 × Ga atoms. Ga and Ge atoms are difficult to distinguish from each other by X-ray diffraction (See the Experimental Section). The negative charges of the framework of GaGeO-JU64 are compensated by $36\times[Ni(1,2\text{-PDA})_3]^{2+}$ cations in the void and $4.7\times Ni^{2+}$ cations trapped in the double six-membered rings (D6Rs). The ratio of Ge/Ga/Ni is about 5:2:1, which is in agreement with energy-dispersive X-ray (EDX) analysis results. The asymmetric unit contains 16 unique T atom positions and 4 unique Ni positions. The T–O distances are in the range of 1.724(8)–1.799(7) Å, and the average T–O bond length of 1.76 Å lies between the ideal Ge–O bond length (1.74 Å) and Ga–O bond length (1.82 Å). All T-O-T angles are in the range of 119.3(5)–131.8(5)°, which is reasonable for both Ge-O-Ga and Ge-O-Ge angles.

The framework of GaGeO-JU64 can be described as the combination of different characteristic building units including single six-membered rings, double six-membered rings (D6Rs), and spiro-5 units. The six-membered rings and D6Rs are connected to each other alternately by spiro-5 units to form a layer containing 11-membered-ring windows (Figure 1a). Further connection of these layers by spiro-5 units results in the three-dimensional structure with intersecting 11-membered-ring channels along three directions (Figure 1b). The 11-membered-ring channels have free diameters of 5.1 × 7.0 Å^2, 5.2 × 7.0 Å^2, 5.2 × 7.2 Å^2, and 5.3 × 6.8 Å^2 (calculated from the atomic coordinates and van der Waals diameters of

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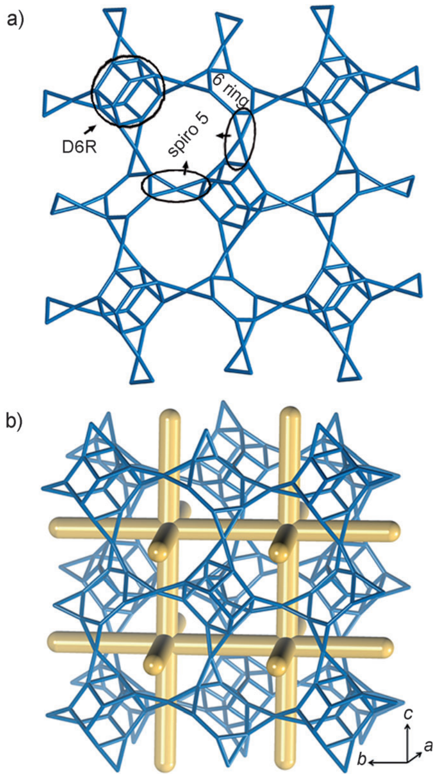

Figure 1. a) The single layer of six-membered rings (6 ring) and D6Rs connected by spiro-5 units. b) The framework of GaGeO-JU64 under the highest topological symmetry of $Pa\bar{3}$, and yellow sticks showing the three dimensional intersecting eleven-membered-ring channels.

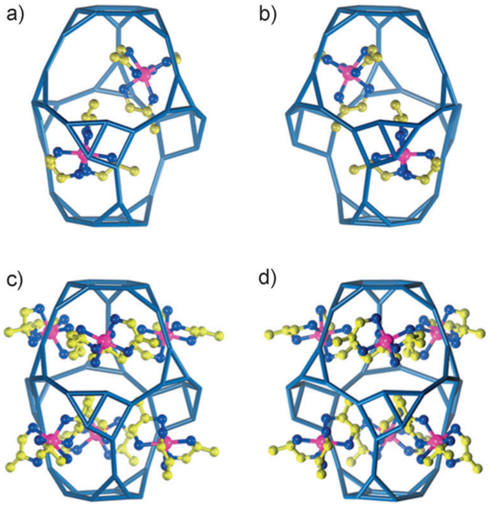

Figure 2. A pair of enantiomers of $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities of $C1$ symmetry, each of which contains a) two $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations of Δ and b) Λ configuration. Another pair of $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities of $C3$ symmetry, each of which is surrounded by c) six $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations of Λ and d) Δ configuration. All of the $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations possess $C1$ symmetry.

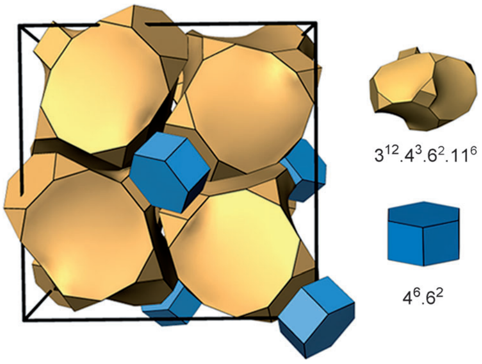

Figure 3. The tiling forming the framework net of GaGeO-JU64. The two different tiles are shown in different colors.

oxygen atoms; see the Supporting Information, Figure S3). Such 11-membered-ring channels in 4-connected zeolites are unprecedented.

Notably, the structure features two pairs of chiral $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities in $C1$ and $C3$ symmetry. Figure 2 a and b show a pair of $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities in $C1$ symmetry. Each of the $C1$ cavities contains two $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations of the same handedness. Figure 2 c and d show the other pair of $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities in $C3$ symmetry. Each $C3$ cavity is surrounded by six $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations of the same handedness. Parts of the $[Ni(1,2\text{-}PDA)_3]^{2+}$ cations protrude into the $C3$ cavities. Each $[Ni(1,2\text{-}PDA)_3]^{2+}$ cation interacts with the $[3^{12}.4^{3}.6^{2}.11^{6}]$ cavities through hydrogen bonds with N•••O distances between 2.911 and 3.341 Å.

Notice that all the Ni^{2+} cations are accommodated in the centers of the D6Rs and coordinated to six inner framework oxygen atoms from the D6Rs. The Ni–O distances vary in the range of 2.295(7)–2.363(7) Å, which are similar to the Ni–O bond distances (1.92–2.37 Å) in nickel(II) bisacetylacetone complexes.[15] Such interesting structural features have been reported in some structures, such as zeolites FAU and CHA.[16]

The framework of GaGeO-JU64 can also be envisaged in terms of natural tiling[17] (shown in Figure 3). The intrinsic symmetry of the underlying net of GaGeO-JU64, as determined by using the software Systre,[18] is $Pa\bar{3}$ (No. 205). This three-periodic net is formed by a unique natural tiling with transitivity of [4862]. The signature of this tiling is $[4^{6}.6^{2}] + 2[3^{12}.4^{3}.6^{2}.11^{6}]$, and the two types of natural tiles are connected with each other through shared faces of the four-membered and six-membered rings. In the framework of GaGeO-JU64, each $[3^{12}.4^{3}.6^{2}.11^{6}]$ tile is surrounded by four $[4^{6}.6^{2}]$ tiles, and each $[4^{6}.6^{2}]$ tile is surrounded by eight $[3^{12}.4^{3}.6^{2}.11^{6}]$ tiles.

It is worth noting that the framework energy of GaGeO-JU64 relative to quartz is 49.6 $kJ\,mol^{-1}$ calculated as a silica polymorph.[19] Therefore, GaGeO-JU64 appears not to be an energetically feasible zeolite,[20] which contradicts to our experimental discovery. Recently, our group proposed a set of universal structural criteria,[19] the use of which is more reliable for the evaluation of the chemical feasibility of a zeolite framework. According to this discovery, the local interatomic distances (LIDs), including the T–O, O–T–O, and T–O–T distances in the optimized framework of every existing zeolite should satisfy a set of rules. Similar to those of all the existing zeolites, the optimized framework of GaGeO-

JU64 obeys the new universal LID rules, thus indicating that the framework of GaGeO-JU64 should be chemically realizable. Furthermore, the LID criteria also indicate that the framework of GaGeO-JU64 can only be realized by unconventional elements, such as Ga and Ge. All these predictions agree well with our experimental work, which proves again the reliability of the new LID criteria, as well as the chemical feasibility of GaGeO-JU64.

In summary, GaGeO-JU64 represents a novel gallogermanate zeolite with an unprecedented three-dimensional intersecting 11-membered-ring channel system. The framework features chiral $[3^{12}\cdot 4^{3}\cdot 6^{2}\cdot 11^{6}]$ cavities. Hydrogen bonds exist between the chiral cavities and the chiral metal complexes. The framework of GaGeO-JU64 possesses the lowest framework density among the known oxide zeolites, and may result from the presence of spiro-5 units composed of three-membered rings according to the Brunner–Meier principle. In addition, the synthesis of GaGeO-JU64 proves again the reliability of the new LID criteria. This work opens the possibility of synthesizing zeolites with 11-ring channels, which may hold promise for improving catalytic and molecular sieving properties.

Experimental Section

Synthesis: GaGeO-JU64 was prepared under hydrothermal conditions. GeO_2 (0.158 g) was dispersed in a mixture of H_2O (1 mL) and 1,2-PDA (2.5 mL), and then $Ga(NO_3)_3$ (0.149 g) and $Ni(CH_3COO)_2\cdot 4H_2O$ (0.09 g) were added with stirring. A homogeneous gel was formed after stirring for 0.5 h. The gel was sealed in a 15 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 days without stirring. Large pink cubic single crystals were separated by filtration, washed with distilled water, and then dried in air. EDX analysis, carried out on a JSM-6700F field emission scanning electron microscope, gave an average molar ratio of Ge/Ga/Ni of 5.08:2.14:1. XRD analysis revealed that GaGeO-JU64 collapsed upon calcination at approximately 300 °C with the decomposition of occluded metal complexes.

Structure determination: A suitable single crystal of GaGeO-JU64 with dimensions of $0.4\times0.4\times0.4\ \mathrm{mm}^3$ was selected for single-crystal X-ray diffraction analysis. The data were collected on a Bruker AXS SMART APEX II diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 62011 reflections, of which 13220 were unique ($R_{\mathrm{int}} = 0.1149$), were collected in the region $1.91° < \theta < 26.37°$. The structure was solved in space group $R\bar{3}$ (No. 148). Unit-cell dimensions: $a = 30.0117(12)$, $c = 37.301(3)$ Å, $V = 29096(3)$ Å^3, and $\rho_{\mathrm{calcd}} = 2.299\ \mathrm{g\,cm^{-3}}$. The structure of GaGeO-JU64 was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL.[21] All Ge, Ga, Ni, O, C, and N positions were easily located. According to compositional analysis and the requirement of charge balance, the occupancies of Ge, Ga at each T position and Ni in D6Rs were refined and shown in the CIF files. Experimental details for the structure determination are presented in the Supporting Information, Table S1. The atomic coordinates are presented in the Supporting Information, Table S2. CCDC 915902 (GaGeO-JU64) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Topological analysis: The natural tiling was calculated by using the free software TOPOS.[17] The coordination sequences were calculated by using the software Systre[18] (see the Supporting Information, Table S3), and the program 3dt[22] was used for visualization of all the tiles.

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