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Microporous Materials

$In_2Ge_6O_{15}(OH)_2(H_2dien)$: An Open-Framework Indate Germanate with One-Dimensional 12-Ring Channels**

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The continuing demand for crystalline, microporous materials in the areas of catalysis, absorption, and ion exchange[1] has spurred increasing interest in extending the range of framework topologies and chemical compositions,[2] because the utility of these crystalline materials is intimately correlated to their geometrical features. Group 13 and 14 elements are promising candidates for framework builders of solid materials such as zeolites and aluminophosphates, as well as their isomorphically substituted forms, which are known for their high thermal stability and good optical transparency.[3] Recently, great progress has been made in the synthesis of microporous germanates.[4] Chemically, germanium is the element closest to silicon but, in contrast to silicon, which is usually tetrahedrally coordinated, it has flexible coordination behavior (GeO_4: tetrahedral, GeO_5: square-pyramidal or trigonal-bipyramidal, and GeO_6: octahedral). Importantly, its larger atomic radius results in significantly longer M−O bonds and smaller M-O-M angles than in most silicates or phosphates. These geometric factors offer greater opportunities for the formation of 3-rings and cluster aggregates which are predicted to impart higher stability on open frameworks and regarded as important factors for obtaining more open frameworks with a structural diversity not yet observed in silicates and phosphates.[5] 3-Rings are very common in germanate systems,[4d,j] and a number of compounds with large pores, and thus very low framework densities, such as ASU-12[4k] (16-ring), SU-8[4p] (16-ring), SU-44[4p] (18-ring), FDU-4[4l] (24-ring), and ASU-16[4f] (24-ring), have been made. Zou et al.[6] recently reported a crystalline mesoporous germanate (SU-M) with extra-large 30-ring channels (> 20 Å) and the lowest framework density of any inorganic material. Hence, the exploration of such a compositional domain has implications for the generation of porous solids with previously unseen framework topologies, low framework densities, and unexpected properties.

We focus on the investigation of germanates[7] and are interested in introducing the group 13 element B into this system to obtain a new class of materials, borogermanates,[8] with new framework topologies and distinct nonlinear optical properties. Compared to the lighter group 13 elements B and Al[9] and Ga,[4b–d] which have been extensively incorporated into the frameworks of germanates, indium exhibits more flexible coordination geometries (InO_4: tetrahedral, InO_6: octahedral, and InO_5: trigonal-bipyramidal),[10] similar to germanium. However, only one example of a microporous indate germanate, namely, $In_2Ge_6O_{15}(en)_2$ (en = ethylenediamine)[11] is known. As part of our ongoing study on germanates containing a group 13 element, herein we report the novel indate germanate $In_2Ge_6O_{15}(OH)_2(H_2dien)$ (**FJ-3**, dien = diethylenetriamine), in which Ge–O layers are cross-linked by In–O chains to form a three-dimensional (3D) framework with 12-ring large channels (Figure 1). It is the second example of a microporous open-framework indate germanate.

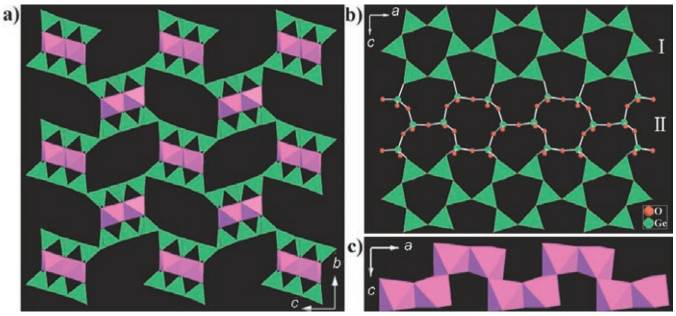

Figure 1. a) The framework structure of **FJ-3** viewed along the [100] direction, showing the 12-ring channels; the H_2dien cations are omitted for clarity. b) A Ge–O layer in **FJ-3** comprising two representations of rows of corner-sharing 6-rings in the (010) plane: row I (polyhedra) and row II (ball-and-stick). c) A zigzag In–O chain in **FJ-3** running along the [100] direction, formed by *cis*-side-sharing InO_6 octahedra. Color code: InO_6 octahedra purple, GeO_4 tetrahedra green.

Colorless rod-shaped crystals of **FJ-3** were synthesized by the solvothermal reaction of GeO_2, In_2O_3, and dien in the presence of HF as mineralizer and H_2O/pyridine as medium. Single-crystal X-ray diffraction analysis showed six unique Ge and two unique In atoms in the asymmetric unit. The Ge atoms are all tetrahedrally coordinated and the In atoms are octahedrally coordinated. The 3D framework structure of **FJ-3** is constructed from Ge–O layers linked by In–O chains (Figure 1a). The puckered germanate layer perpendicular to the [010] direction consists of corner-sharing GeO_4 tetrahedra that form a 6^3 net (Figure 1b) that has been observed in zeolitic silicates (AET, AFI, and VFI).[12] However, **FJ-3** is, to the best of our knowledge, the first germanate with such a feature. An instructive way to further understand the

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structure of such a material is to recognize that the layer net is comprised of rows of corner-sharing 6-rings running along the [100] direction, with the free bridging oxygen atom of each GeO$_4$ tetrahedron in adjacent rows pointing alternately in opposite directions of the layer plane. The adjacent rows of 6-rings are related by a translation of $1/2a$ and joined to form additional 6-rings. The In–O chains consist pairs of *cis*-edge-sharing InO$_6$ octahedra that propagate in a zigzag fashion along the [100] direction (Figure 1c). These chains establish the cohesion between neighboring germanate sheets through O6, O7, O8, O9, O13, and O16 (Figure 2a) to produce the entire 3D framework. This mode of connection gives rise to several 3- and 4-rings formed by the GeO$_4$ tetrahedra and InO$_6$ octahedra. Of the bridging anions, O7 and O9 are three-coordinate oxygen centers connected to one tetrahedrally coordinated germanium atom and two octahedrally coordinated indium atoms, respectively; the remainder are two-coordinate oxygen centers. Three-coordinate oxygen centers favor not only trigonal-bipyramidal or octahedral geometry but also 3-ring units.[4d]

The inorganic framework has 1D linear 12-ring channels running along the [100] direction, parallel to the Ge–O layers and In–O chains. The openings of the 12-ring channel are elliptical in shape and delimited by ten GeO$_4$ tetrahedra and two InO$_6$ octahedra with an approximate free-pore diameter of 3.7×8.2 Å^2 (Figure 2b), and the pore walls are built from 3-, 4-, 6-, and 8-ring windows (Figure 2c, d). Each 12-ring channel communicates with four neighboring 12-ring channels through 6-ring windows perpendicular to the main channel direction (Figure 2e). The free diameter of the 6-ring channel is approximately 2.5×3.0 Å^2 (Figure 2f).

Interestingly, each 12-ring channel in **FJ-3** is enclosed by four columnlike structural motifs running parallel along the [100] direction (Figure 1a, Figure 2e, g, h). In the complex structural motif, two rows of 6-rings from two neighboring Ge–O layers sandwich one zigzag In–O chain (Figure 2g) and are further connected by corner-sharing GeO$_4$ tetrahedra to form the 3D framework. Significantly, such a connection provides the possibility for the generation of thick walls between channels, which is of fundamental importance in the development of new zeotype materials with large pores, which require thicker walls for sufficient thermal stability. Thus, the framework structure of **FJ-3** is comparable to that of FJ-17/SU-16,[8d,g] a borogermanate likewise with H$_2$dien cations as structure-directing agents, in that both contain similar (shape and size) 1D linear 12-ring channels enclosed by four columnlike structural motifs, except that the motifs in FJ-17/SU-16 are built by alternate linking of two B$_2$O$_7$ dimers and 8-rings delimited by GeO$_4$ tetrahedra, which produces three 8-ring channels perpendicular to each 12-ring main channel. However, the framework density of **FJ-3**, defined as the number of polyhedra per 1000 Å^3, is 15.4, which is comparable to that of FJ-17/SU-16 (16.1). A PLATON[13] analysis, performed only on the framework structure, suggested a solvent-accessible volume of approximately 30.3%. The relatively low framework density of **FJ-3** may be due to the fact that each polyhedral center is involved in at least two 3- or 4-rings, the presence of which is thought to be the key to very open frameworks.[5c,12]

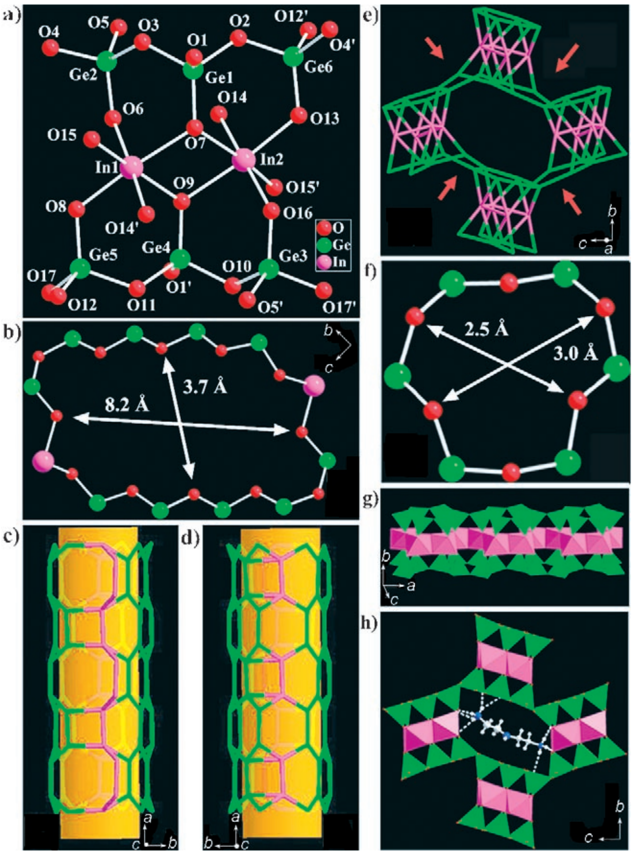

Figure 2. a) Representation of the connection between the Ge–O layers and In–O chains in **FJ-3**. b) The elliptical 12-ring opening (O···O distance not including the van der Waals radii; similarly hereinafter). c,d) The pore walls of the 12-ring channel showing 3-, 4-, 6-, and 8-ring side pockets, viewed along [00$\bar{1}$] and [001] directions, respectively; O atoms are omitted for clarity. e) The 12-ring channel interconnected by 6-ring windows to four adjacent channels; O atoms are omitted for clarity. f) The 6-ring opening. g) Polyhedral representation of the columnlike structural motif. h) Detail of the location of the H$_2$dien cation within the 12-ring channels showing the H-bonding interactions between the H$_2$dien nitrogen atoms and the framework oxygen atoms. Color code: InO$_6$ octahedra purple, GeO$_4$ tetrahedra green.

Assuming the usual valences of Ge, In, and O to be $+4$, $+3$, and -2, respectively, the framework stoichiometry of In$_2$Ge$_6$O$_{17}$ creates a net framework charge of -4, which cannot be balanced by protonated dien cations, even if dien is triply protonated. This implies that some bridging hydroxide ligands (M-O(H)-M) exist in the framework, similar to those in the FDU-4 framework.[4l] We note that O14 and O15 bridge two In atoms with In–O distances of 2.135(5)–2.168(5) Å. Such In–O distances (av 2.157(5) Å) are longer than those of the other two-coordinate O atoms (2.070(5)–2.118(5) Å), but similar to those of the three-coordinate O atoms (2.171(4)–2.211(5) Å); the bond valence sums[14] for O14 and O15, which have similar coordination environments, are 1.03 and 0.98 valence units, respectively, while those for the other O atoms are in accordance with their formal oxidation state of -2, that is, O14 and O15 belong to OH groups. This assignment is also in agreement with the proton positions observed near the oxygen atoms in the difference Fourier map. In addition, the existence of the OH groups is further evidenced by the IR spectrum showing a sharp band at 3612 cm^{-1} in the expected range for O–H stretching frequencies,[15] while the N–H and C–H stretching vibrations are observed at 3257–3451 and 2850–2923 cm^{-1}, respectively. The assignment of these peaks is usual for amine-containing germanates.[4h,l,m,7b] Thus, on the basis of charge-balance considerations, the dien molecules are assumed to be diprotonated, as is also observed in FJ-17/SU-16.[8d,g] The Ge–O distances are in the range of 1.704(5)–1.776(6) Å (av. 1.741 Å), and the O-Ge-O bond angles between 102.5 and 116.8° (av. 109.4°), which are within the range typical for germanium oxides.[16] The Ge-O-Ge angles vary between 124.0(3) and 136.2(3) and are in the expected range.

The H_2dien cations are located within the 12-ring channels of **FJ-3** and interact with the framework oxygen atoms through hydrogen bonding (Figure 2 h); each H_2dien cation is hydrogen-bonded to four columnlike structural motifs via terminal N atoms with N···O distances in the range of 2.802(8)–3.209(8) Å, and the ordered H_2dien cation is a very good "fit" for the 12-ring channel. In addition, it is noteworthy that thick walls between channels usually lead to the accumulation of framework negative charges in the process of self-assembly of microporous solids, because charge-balancing template cations are usually located in the channels. However, in **FJ-3**, the presence of three-coordinate oxygen atoms and bridging hydroxy groups serves to relieve such accumulation of negative charge on the framework. Thus, the N–H···O hydrogen-bonding interactions and host–guest shape and charge-density matching may play an important role in framework formation of **FJ-3**.[4c,d,17]

The thermogravimetric curve revealed a weight loss of 9.8 % between 275 and 410 °C, followed by a further weight loss of 3.9 % between 410 and 570 °C, which correspond to the loss of organic amine from the channels (calcd 10.1 %) and dehydration of the inorganic framework (calcd 3.3 %), respectively. The powder X-ray diffraction pattern of a sample heated for 4 h in air at 350 °C indicated collapse of the framework. Attempts to exchange H_2dien^{2+} with inorganic cations such as Na^+, K^+, and Ba^{2+} were not successful, perhaps due to the strong hydrogen-bonding interaction between the host framework and guest molecules.[8g]

To date, the vast majority of microporous materials have been constructed from tetrahedral geometries.[12,18] One important structural feature of **FJ-3** is that its inorganic network is constructed by a combination of tetrahedral and octahedral geometries, which is a promising strategy for the design of structures with novel topologies and properties.[19] For the earlier group 13 elements Al and Ga, octahedral coordination is not uncommon in microporous phosphates, but they usually exhibit tetrahedral coordination in germanates. In contrast to the Al and Ga atoms, the In atom, with its larger radius, exhibits octahedral coordination geometry in germanates $In_2Ge_6O_{15}(en)_2$[11] and **FJ-3**. The former is the only reported indate germanate with a neutral framework formed by Ge–O layers with 4-, 6-, and 8-rings pillared by $In_2O_6(en)_2$ dimers. Furthermore, germanate layers linked by chains of edge-sharing octahedra are absent from the literature on metal germanates, while layers pillared by isolated[20] and dimeric polyhedra[8g,11] have been observed.

In summary, a novel microporous indate germanate directed by an organic amine was synthesized under solvothermal conditions. The structure is characterized by germanate layers with 6^3 nets linked by chains of *cis*-edge-sharing In–O octahedra into a 3D framework that has 1D linear 12-ring channels with thick pore walls. Indate germanate **FJ-3** is novel not only in its 3D framework topology but also in its unusually high ratio of small 3- and 4-rings in each polyhedral center, which is responsible for its very open framework structure. This result expands the scope of rational design for zeotype materials by using group 13 and 14 elements as framework builders. Given the flexible coordination behaviors of germanium and indium as well as the large variety of organic molecules that could be used in this method, further investigations on the systematic synthesis of microporous indate germanates are underway.

Experimental Section

FJ-3 was synthesized under solvothermal conditions with pyridine as solvent in the presence of the structure-directing agent diethylenetriamine (dien). Typically, GeO_2 (0.15 g) was dispersed in a mixture of H_2O (1.0 mL), pyridine(5.0 mL), and dien (1.5 mL) with constant stirring. Then, In_2O_3 (0.14 g) and HF solution (40 wt %, 0.04 mL) were added to this solution. The homogeneous gel with the composition GeO_2/In_2O_3/dien/pyridine/HF/H_2O in a molar ratio of 3:1:30:124:2:110 that was formed after stirring for about 2 h was transferred to a 23-mL teflon-lined stainless steel autoclave and heated at 180 °C for 8 d under static conditions. Colorless rod-shaped crystals (13 % yield based on GeO_2) were separated from the remainder of the product by sonication, washed with distilled water, and then dried in air. The synthesis conditions for **FJ-3** are very critical: In particular, the HF not only adjusts the pH value of the reaction mixture but also act as the mineralizer that is usually necessary for the synthesis of germanates. Attempts to synthesize **FJ-3** by addition of other acids instead of HF were unsuccessful, and a higher HF content always led to a new layered germanate[21] with the same framework structure as ASU-20.[4n] In addition, only a dense GeO_2 phase was isolated when H_2O was used as solvent instead of a mixture of H_2O and pyridine. C,H,N analysis (%) calcd for $C_4H_{17}N_3In_2Ge_6O_{17}$: C 4.60, H 1.64, N 4.02; found: 4.67, H 1.71, N 4.05.

C,H,N analysis was performed on an Elemental Vario EL III analyzer. IR spectra were obtained from a powdered sample pelletized with KBr on an ABB Bomen MB 102 series IR spectrophotometer in the range 400–4000 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of 10 K min^{-1}. Powder X-ray diffraction patterns (PXRD) were collected with a PANalytical X'Pert Pro diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å).

Crystal data for **FJ-3**: $C_4H_{17}N_3In_2Ge_6O_{17}$, $M_r = 1044.37$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 9.3552(5)$, $b = 14.4053(7)$, $c = 15.3923(7)$ Å, $V = 2074.34(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 3.344$ g cm^{-1}, $\mu = 10.839$ mm^{-1}, $F(000) = 1952$, GOF = 1.068. A total of 16204 reflections (4728 independent, $R_{int} = 0.0414$) were measured at 293 K. Final agreement indices were $R1$ ($wR2$) = 0.0329 (0.0620) for 290 parameters and 4369 reflections [$I > 2\sigma(I)$]. Residual electron density: 0.815/−0.830 e Å^{-3}.

A suitable single-crystal with dimensions $0.22 \times 0.08 \times 0.07$ mm^3 was mounted on a Siemens SMART CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL97.[22] All the hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms. All non-hydrogen atoms were refined anisotropically. As a final check on the crystal symmetry, the refined atomic coordinates of **FJ-3** were processed by the program PLATON/CHACK, which checks a crystal model for (pseudo)center of symmetry. However, solution of the structure in a higher space group always resulted in a disordered structure flawed by poor geometry, thermal parameters, and high residual electron density. An ordered structure could be satisfactorily solved in the space group $P2_12_12_1$, though the determination of the absolute structure yielded a value for the Flack parameter of 0.47(1), which indicates a twinned racemate crystal.[23] The same problem was observed for a data set measured on a second crystal. Therefore, the problems in determining the absolute structure may originate from the pseudocentrosymmetry of the crystal. CCDC-629006 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.

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