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A New 2D Hybrid Indate-Germanate Based on the Linkages of $Ge_4O_{10}F_2$ Clusters and $\{In_2O_6\}$ Dimers

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A novel layered indate-germanate $InGe_2O_5F(dap)\cdot 2H_2O$ (**1**, dap = 1,2-diaminopropane) has been hydrothermally synthesized and structurally characterized. Its structure consists of $Ge_4O_{10}F_2$ clusters and In_2O_6 dimers, which are interconnected to form 4- and 6-ring layers. **1** displays luminescent emission at 422 nm.

Microporous materials with open frameworks have been intensively investigated because of their widespread applications in catalysis, ion exchange, and gas separation.[1] Since the discovery of the first germanates with open framework in the early 1990s,[2] great efforts have been devoted to the pursuit of germanate-based microporous materials with new framework topologies, low framework densities, and unexpected properties.[3] Interest in using Ge as a framework-forming element is not only because it exhibits flexible coordination behavior (tetrahedron, square-pyramid or trigonal-bipyramid, and octahedron), but also because its larger atomic radius results in the significantly longer Ge−O distances and smaller Ge−O−Ge angles than those in most silicates. These geometric factors offer greater opportunities for the formation of three rings and Ge−O 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.[4] So far, a number of the pure germanates with large pores and very low framework density have been made.[3,5] However, the germanates containing heteroatoms in their frameworks are less explored under mild solvo(hydro)thermal conditions, and only a few examples have been reported.[6]

Our recent research interest has been focused on the synthesis of microporous germanates[7] and investigating the effect of introducing heteroatoms on their framework structures.[8] Notably, the incorporation of boron into germanate leads to a new class of porous borogermanates with new architectural features and distinct nonlinear optical

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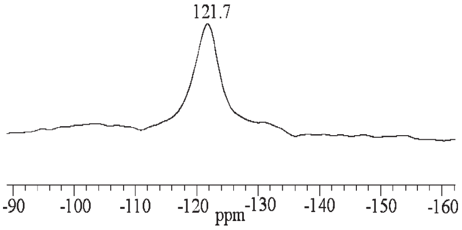

Figure 1. ^{19}F NMR of **1**.

properties.[8b,c] Being in the same group as B, In exhibits more flexible coordination geometries (tetrahedral, trigonal-bipyramidal, and octahedral).[9] However, there is little research carried out on indate-germanates under mild solvo(hydro)-thermal conditions. The limited examples include $In_2Ge_6O_{15}(en)_2$ (en = ethylenediamine) with 3D neutral In−Ge−O framework[6h] and $In_2Ge_6O_{15}(OH)_2(H_2dien)$ (dien = diethylenetriamine) with 3-D anionic In−Ge−O framework.[8a] But 2D layered indate-germanates under mild solvo(hydro)-thermal conditions have not been observed until now, to the best of our knowledge. As a continuation of this work, herein we report the synthesis and structure of the first 2D hybrid indate-germanate, $InGe_2O_5F(dap)\cdot 2H_2O$ (**1**), built by $Ge_4O_{10}F_2$ clusters and $In_2O_6(dap)_2$ dimers.

Colorless crystals of **1** were obtained by the hydrothermal reaction of In_2O_3, GeO_2, 1,2-diaminopropane (dap), and H_2O in the presence of HF at 180 °C.[10] Here, the HF used in the synthetic process not only adjusts the pH of reaction system but also apparently plays a key role in the formation of **1**, as attempts to make **1** without HF were unsuccessful. The experimental and simulated powder X-ray diffraction patterns are in good accordance with each other, indicating the phase purity of the sample (Figure S1).The ^{19}F NMR of **1** shows a single response peak at 121.7 ppm (Figure 1), which is very close to that of the reported germanium(IV) fluorides[11] and confirms the presence of the F ions in **1**.

According to the crystal structure determination,[12] the composition of **1** is $InGe_2O_5F(dap)\cdot 2H_2O$. Its asymmetric unit comprises two unique Ge, one In, one F, and five O atoms, one dap acting as bidentate ligand and two free water molecules (Figure 2a). To two Ge atoms, Ge1 is tetrahedrally coordinated GeO_3F, bonded to one F and three μ-O atoms, whereas Ge2 is coordinated by four μ-O atoms to form moderately distorted tetrahedron (GeO_4). Two GeO_3F and two GeO_4 tetrahedra are joined alternately via sharing corner to form a $Ge_4O_{10}F_2$ ring-shape cluster (Figure 2b). The In1 atom is coordinated by four O and two N atoms to form a strongly distorted octahedron; two symmetry-related octahedra share a common edge to form a dimer of $In_2O_6N_4$ with the In···In distance of 3.354(1) Å (Figure 2c), consistent with that of these known indates.[6h,8a]

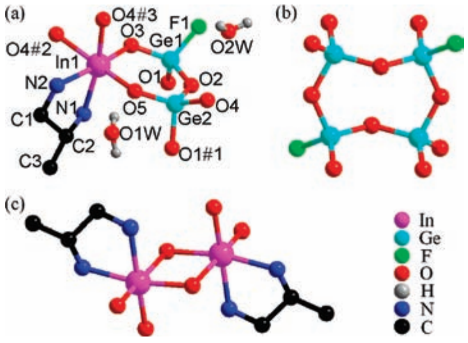

Figure 2. (a) Asymmetric unit of **1** (symmetry code: #1 $1-x, -y, 1-z$; #2 $-1+x, y, z$; #3 $1-x, 1-y, 1-z$. H atoms bonded to C and N atoms have been omitted for clarity). Ball-and-stick representations of structures of (b) $Ge_4O_{10}F_2$ cluster and (c) In_2O_6(dap) dimer, respectively.

In **1**, each $Ge_4O_{10}F_2$ cluster connects four $In_2O_6N_2$ dimers by six shared μ-O atoms, and then further connects eight such Ge-based clusters via four bridging $In_2O_6N_4$ dimers. Like the $Ge_4O_{10}F_2$ cluster, each $In_2O_6N_4$ unit also joins eight such dimers via four bridging $Ge_4O_{10}F_2$ clusters. The alternate connectivity between the $Ge_4O_{10}F_2$ clusters and the $In_2O_6N_4$ dimers by their vertex O atoms gives rise to a novel 2-D neutral $[InGe_2O_5F(dap)]_n$ layer with 4- and 6-rings (Figure 3a, S2). The interlayer has a thickness of 8.8 Å, calculated as the shortest F1 to F1 distance between the layers. This kind of the layer arrangement with 4- and 6- ring, has not been observed in the 2D germanates. The three-nine ring association seems to be more frequent.[3b,5a,13] Only a four-eight ring layer[14] and four-ten ring sheet[5b] have been reported. If the $Ge_4O_{10}F_2$ clusters and $In_2O_6N_4$ dimers can be considered as 4-connected nodes, respectively, the 2D layer can be classified as sql topological net with the total Schläfli symbol of $(4^4\cdot 6^2)(4^4\cdot 6^2)$ (Figure 3b). Although the sql topological net based on simple transition metal ion as 4-connected node is common in coordinated polymers,[15] the $Ge_4O_{10}F_2$ cluster as 4-connected node is relatively rare in the germanate system. In **1**, the H-bonding association (see Table S1 in the Supporting Information) of water molecules leads to the formation of a cyclic tetrameric water cluster $(H_2O)_4$ containing two symmetry-related O1W and O2W, whose conformation is similar to parallelogram (Figure 3c, S3). The average O···O distance within the $(H_2O)_4$ cluster is 2.87 Å, which is very close to the corresponding value of 2.85 Å found in liquid water.[16] These water

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(10) In a typical synthesis of **1**, a mixture of In_2O_3 (0.103 g) and GeO_2 (0.093 g) was dispersed to a stirring solution of H_2O (2.0 mL) and dap (2.0 mL). Then HF (0.1 mL) was added, and the stirring was continued for 11 h at room temperature. The final mixture (pH 12.5) was heated in a Teflon-lined stainless steel autoclave at 180 °C for 15 days under autogenous pressure, and was then cooled to room temperature. The crystals were washed with distilled water and then dried in air. The yield was about 52% (based on GeO_2). Anal. Calcd for **1**: C, 7.63; H, 2.99; N, 5.94. Found: C, 7.84; H, 3.06; N, 5.97. IR (KBr pellet, cm^{-1}): 3534 (m), 3436 (m), 3345 (m), 3268 (m), 2963 (w), 2873 (w), 1629 (s), 1584 (s), 1532 (s), 1468 (m), 1403 (w), 1273 (w), 1202 (w), 1150 (w), 1066 (m), 1014 (m), 878 (s), 826 (s), 781 (s), 742 (s), 587 (m), 522 (m), 419 (m).

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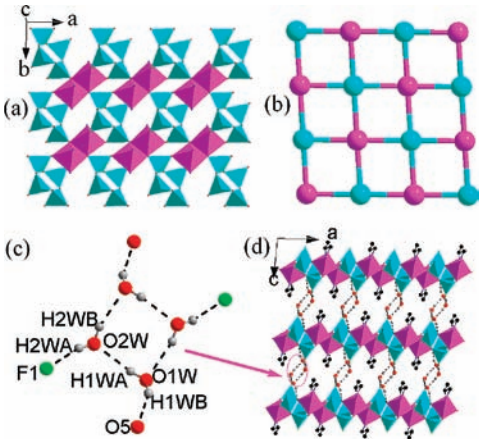

Figure 3. (a) 2D layer built by [$Ge_4O_{10}F_2$] clusters and {In_2O_6} dimers in **1** (blue, GeO_4 tetrahedron; purple, InO_4N_2 octahedron. All C and H atoms were omitted for clarity). (b) Framework topology of 1 (cyan, $Ge_4O_{10}F_2$ nodes; pink, [$In_2O_6(dap)_2$] nodes). (c) Tetrameric water cluster $(H_2O)_4$. (d) 3D supramolecular net linked by O−H···O and O−H···F H-bonds.

clusters are further linked with adjacent layers via O1W−H···O5 and O2W−H···F1 H-bonds, forming a 3D supramolecular framework (Figure 3d).

In previous literatures, organic amines are usually used as structure-directing agents to direct the formation of inorganic frameworks. Organic amines are accommodated in the free voids of the structures and are often interacted to the inorganic framework by H-bonds,[5] while the In−N distances (2.253(5)−2.268(5) Å) in **1** show that the In−N bonding has a strong covalent nature. In **1**, dap amines decorate both sides of the Ge−In−O layers (see Figure S2 in the Supporting Information).

The $Ge_4O_{12-n}X_n$ (X = OH/F; n = 0, 2, 4) unit exhibits the different linkage mode because of the presence of the terminating X group. The $Ge_4O_8(OH)_4$ cluster (n = 4) in [$Ge_8O_{12}(OH)_8F$]($C_{11}NH_{24}$)[17] containing four OH groups is linked with another $Ge_4O_8(OH)_4$ cluster via corner-sharing, forming discrete double four-ring $Ge_8O_{12}(OH)_8$ cluster. This cluster can be converted into the {Ge_8O_{20}} cluster via deprotonation of OH groups, resulting in the 3D zeolite framework.[13b] The tetrameric {Ge_4O_{12}} clusters (n = 0) in $Ge_3O_5(OH)_4$ [enH_2] are interconnected by sharing vertexes, generating the natrolite-type layer.[14] The similar heteroatom $Si_2Ge_2O_{12}$ cluster in SU-21,[18] is connected by the fifth tetrahedron GeO_4 via vertex-sharing to form a chain, which is further connected by pairs of GeO_3FN_2 octahedra, forming a layer. The linkage modes of $Ge_4O_{10}F_2$ (n = 2) in **1** is significantly different from that of the reported $Ge_4O_{12-n}X_n$ (n = 0, 4) clusters.

It is noteworthy that both the F^- ions and the organic amine molecules play an important role in the formation of the structures of **1** and $In_2Ge_6O_{15}(en)_2$ (**2**).[6h] In **2**, the Ge_4O_{12} clusters and dimeric Ge_2O_7 units are interconnected by corners to build a Ge−O layer. These layers are further pillared by $In_2O_6(en)_2$ dimers, yielding the 3D framework. But such connectivity is impossible in **1** because the Ge_2O_7 bridging units in **2** are replaced by terminal F^- ions. As a result, the 3D framework of **2** is broken down to 2-D layers. In **2**, the organic amine molecules stabilize the $In_2O_6(en)_2$ dimers and whole structure. To make the analogue of **1**, we replaced dap by en under the same synthetic conditions, but the attempts failed; colorless crystals of **2** were always isolated in high yield. In previous work,[6h] **2** has been made with different starting reactants and reaction conditions, which indicates that the organic amine plays a very important role in directing the structure formation. In general, larger organic molecules might be apt to break off some linkages and create larger spaces for themselves, such as the space between layers. Hence, **1** might be regarded as a derivative of **2** that has been "tailored" by the F^- ions and broken to layers by the space-creating dap.

The luminescent spectrum for **1** excited at 247 nm shows an emission band at 422 nm (see Figure S4 in the Supporting Information). This emission could be related to structural defect of the indate-germanate framework and the presence of organic amine molecules.[19] The similar luminescence has been observed in amine-templated gallo-/alumino-germanates, such as UCSB-7AlGe (emission band at 421 nm) and UCSB-7GaGe (emission band at 396 nm).[19] Thermogravimetric analysis of **1** was carried out in flowing air from 30 to 1000 °C with a heating rate of 10 °C/min (see Figure S5 in the Supporting Information). A three-step weight loss occurs in the range of 60−860 °C, which is related to the release of two free water molecules and the decomposition of organic amine (found, 24.2%; calcd, 23.5%).

In summary, a novel indate-germanate $InGe_2O_5F(dap)\cdot 2H_2O$ has been synthesized under mild hydrothermal conditions. **1** represents the first example of the layered indate-germanate built up from rare $Ge_4O_{10}F_2$ clusters and In_2O_6 dimers, which exhibits the unusual sql topological network in germanate chemistry. **1** can emit fluorescence at 422 nm, making **1** a good candidate for potential bluish materials. The successful synthesis of **1** opens possibilities for making other novel indate-germanates using different templates under desirable conditions. Further research on this work is in progress.

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Supporting Information Available: X-ray crystallographic file in CIF format; XRD patterns, a TGA plot, and the solid-state emission spectrum (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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