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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · MARCH 2011

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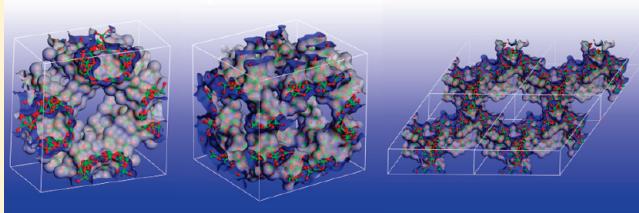
Germanates Built from $\text{Ge}_{10}(\text{O}, \text{OH})_{27-28}$ and $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ Secondary Building Units: From Systematic Study of Reported Compounds to Rational Design of Novel Structures

Maxim V. Peskov* and Xiaodong Zou*

Inorganic and Structural Chemistry and Berzelii Center EXSELENT on Porous Materials, Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden

 Supporting Information

ABSTRACT: Design of novel porous compounds is one of the fastest-growing fields of materials chemistry due to the broad range of applications including catalysis, adsorption, and separation. Open-framework germanates have shown large structure diversity and can form structures with extra-large pores. A systematic study of the structural features of the reported germanates is a key for the design of novel porous germanates. In this work, the topological study and classification of all known germanates that are built from $\text{Ge}_{10}(\text{O}, \text{OH})_{27-28}$ (Ge_{10}) or $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ (Ge_7) secondary building units, has been undertaken. We have demonstrated that the combination of topological technique and data mining provides new insights into structural chemistry of a group of compounds. We proposed an efficient and general strategy for prediction of novel structures in germanates and other chemical systems.



INTRODUCTION

Design of new porous compounds nowadays is a direction of materials chemistry attracting intensive attention of both fundamental and applied sciences. Open-framework germanates (in particular, Ge-containing zeolites) are recognized as important materials for a broad range of applications including catalysis, adsorption, and separation.^{1–4} Although certain progress in producing novel open-framework germanates has been made for the past decade,^{5,6} rational design of new structures is still a big challenge for materials chemists.⁷ One of the reasons is that there is no clear comprehension of the processes leading to the formation of porous architectures.^{8–10}

Many open-framework germanates are built from some common cluster building units.^{6,11} The cluster building unit is defined as a secondary building unit (SBU) if it occurs in diverse germanate structures and provides the basis for description and comparison of different germanate compounds.¹² Although it remains uncertain if these clusters are related to the species in solution during the crystallization of a porous germanate, the analysis of the arrangement and connectivity of the clusters in reported solids is of particular interest for the design of novel porous compounds.¹³

Examination of the topological properties and the connectivity of the building units has been conducted for a number of novel germanate compounds published for the past few years.^{11,14–16} However, there is a lack of detailed and systematic topological study of porous germanates owing to the complexity of such an analysis and perhaps some ambiguities in choice and accounting of building units. To address this

issue, we performed the analysis of known germanates with respect to the SBUs, and study of the topology and connectivity between the SBUs.

Although a number of cluster building units, for example $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ (Ge_7), $\text{Ge}_8(\text{O}, \text{OH}, \text{F})_{20}$ (Ge_8), $\text{Ge}_9(\text{O}, \text{OH}, \text{F})_{25-26}$ (Ge_9), and $\text{Ge}_{10}(\text{O}, \text{OH})_{27-28}$ (Ge_{10}), are found in open-framework germanates,^{6,7} we have chosen to concentrate our study only on those germanates that are constructed from the Ge_{10} or Ge_7 clusters.⁶ These are of particular interest due to their ability to form architectures of different dimensionality and complexity, which vary from rather simple structures (Ge-pharmacosiderite analogues,^{17,18} FJ-6¹⁹ and ICMM-7²⁰) to intricate frameworks with large unit cells (SU-M and SU-MB¹⁴). Furthermore, the Ge_{10} and Ge_7 clusters are considered as promising building units for novel germanate compounds.^{7,11}

Along with the understanding of architectures of synthetically feasible germanates, enumeration of hypothetical porous compounds is an important method of theoretical chemistry.²¹ Theoretical design of novel germanates may be applied to the exploration of novel materials with desired properties or used in the identification of potential synthetic targets. Here, we use the knowledge from the systematic study of known open-framework germanates built from the Ge_{10} and Ge_7 SBUs to the design of hypothetical open-framework germanates built from these SBUs.

Received: December 25, 2010

Revised: March 2, 2011

Published: March 29, 2011

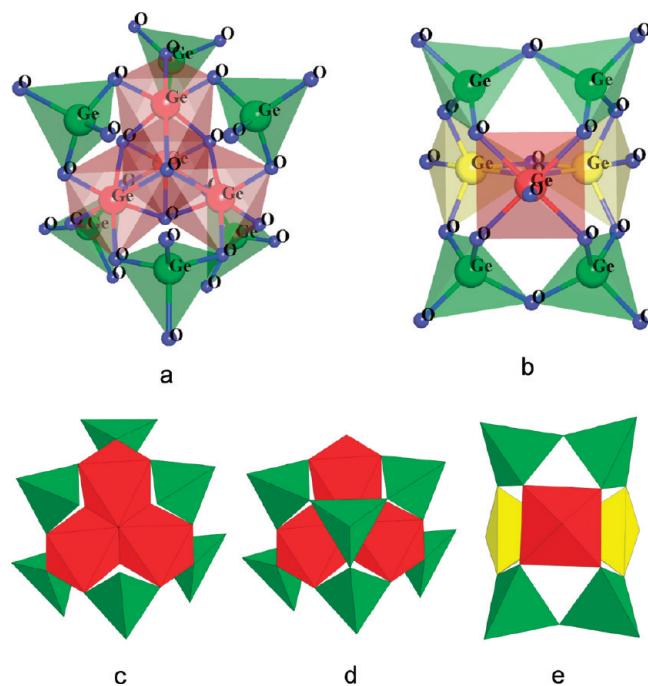


Figure 1. Shell graphs describing (a) $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ and (b) $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ clusters. Polyhedral presentation of (c) $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$, (d) $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$, and (e) $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ SBUs. The GeO_4 tetrahedra are shown in green, GeO_5 trigonal bipyramids are in yellow, and GeO_6 octahedra are in red.

■ PROGRAMS AND COMPUTATIONAL METHODS

Inorganic Crystal Structure Database (ICSD version 2010/1²²) and Cambridge Structural Database (CSD System, 2009 release²³) were used as the source of structural information on known germanates. The simplification and topological analysis of germanate structures were performed by the program package *TOPOS*.²⁴

The method of fragment matching²⁵ was used to identify the compounds containing Ge_{10} and Ge_7 clusters. The analysis of germanate structures consists of the following steps:

- 1 Chemical bonds in germanates were determined fully automatically by the program AutoCN of the package *TOPOS*,²⁴ which uses the method of intersecting spheres.²⁶ All strong interatomic interactions with the corresponding solid angles Ω_0 of more than 0.06π (1.5% of the full solid angle 4π) are included except for those between atoms with the same type of positive or negative charges.
- 2 To find the compounds containing the clusters Ge_{10} and/or Ge_7 in a database, the clusters were described by shell graphs²⁵ (parts a and b of Figure 1). The nodes of the shell graphs correspond to the atoms Ge, O, or F, and the edges indicate the strong chemical bonds between the atoms. Hence, the shell graphs describe the clusters in terms of topology, and therefore the method allows searching for compounds with given clusters regardless of their geometrical distortions. The shell graphs were prepared using the *TOPOS* package.
- 3 To study the geometrical properties of germanate frameworks, the frameworks are first decomposed into a sets of clusters, and then the coordination of the clusters are examined. This was performed using the program *IsoCryst* of the *TOPOS* package.²⁴

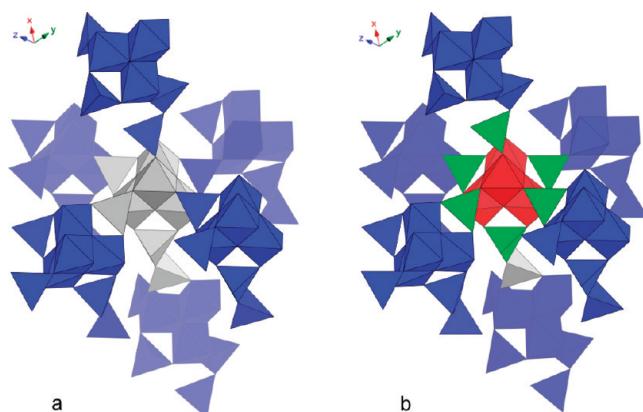


Figure 2. Different choices of the cluster building unit for describing the structure of IM-14. (a) The SBU $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ as shown in gray. (b) The $\text{Ge}_7(\text{O}, \text{OH})_{19}$ cluster as shown in red (GeO_6) and green (GeO_4).

4 Consecutive simplification of the germanate structures, analysis of their topology and identification of the corresponding nets were carried out using *TOPOS/ADS* program²⁴ supplied with the TOPOS Topological Data-bases (TTDs).²⁵ TTDs contain topological indices on the nets of several databases including Atlas of Zeolite Structure Types,¹² Reticular Chemistry Structure Resource (RCSR)²⁷ and Euclidean Patterns in Non-Euclidean Tilings (EPINET) database.²⁸

To estimate the nets features, the information about their natural tilings provided by the RCSR database²⁷ was used. In particular, tiling transitivity,²⁹ which describes how many independent vertices, edges, faces, and tiles are required to build a tiling, can serve as one of the criteria to describe the combinatorial complexity of a net.

The models of hypothetical germanates were built using Materials Studio Visualizer³⁰ and were then further optimized with the General Utility Lattice Program (GULP).³¹

■ OCCURRENCES OF GE_{10} AND GE_7 CLUSTERS IN GERMANATES

It was of interest to distinguish the compounds, where Ge_{10} or Ge_7 cluster is identified as a fragment of the structure. Generally speaking, a fragment of the structure is an atomic cluster to be considered as an SBU only if the entire structure is made up from this cluster without sharing polyhedra.¹² Allowing polyhedra to be shared between two clusters may lead to ambiguities in the description of compounds. For example, a well-known framework type in germanates, pharmacosiderite, was described as a set of $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ building units,¹¹ in spite of sharing all the GeO_4 tetrahedra. In this regard, an alternative description of the pharmacosiderite analogue, germanate LMN-1, as a set of cubane $\text{Ge}_4(\text{OH})_4$ and tetrahedral building units¹⁸ is preferable. Another example of germanates, where Ge_{10} fragments are revealed, but unlikely to be used in the description of its structure as an SBU, is IM-14³² (parts a and b of Figure 2).

To find the occurrences of Ge_{10} and Ge_7 clusters in germanate structures, we have performed systematical screening of the databases ICSD²² and CSD.²³ The procedure of searching for finite subgraphs in nets²⁵ implemented in *TOPOS*²⁴ was employed. Twenty-two germanates containing Ge_{10} clusters and 17 germanates containing Ge_7 clusters have been identified and collected. Furthermore, structures of the recently published

Table 1. Occurrences of the $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ Clusters in Germanate Structures

topological type germanate frameworks	chemical formula ^a
pharmacosiderite	$\text{Cs}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{0.7}$ (CC = 83337)
$A_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_x$ (A = Li, NH ₄ , H, Na, K, $\text{Cs}, \text{Rb } x = 0.69 - 6.00$)	$\text{Cs}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{2.262}$ (CC = 83340) $\text{Cs}_{1.77}\text{K}_{1.23}\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_4$ (CC = 99632) $\text{Ge}_7\text{O}_{12}(\text{OH})_4(\text{C}_4\text{N}_3\text{H}_{13})_{0.5}(\text{H}_2\text{O})_5$ (LMN-1a ¹⁸) $\text{Ge}_7\text{O}_{12}(\text{OH})_4(\text{H}_2\text{O})_6$ (LMN-1b ¹⁸) $(\text{H}_3\text{O})_4(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_3$ (CC = 98214) $\text{Li}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_4$ (CC = 33591) $\text{Li}_4(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{5.71}$ (CC = 80064) $\text{K}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{3.137}$ (CC = 83338) $\text{K}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_4$ (CC = 36523) $\text{KH}_3(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_3$ (CC = 34094) $(\text{NH}_4)_2\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{2.72}$ (CC = 80063) $\text{Na}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_4$ (CC = 33592) $\text{Rb}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{3.087}$ (CC = 83339) $\text{Rb}_3\text{H}(\text{Ge}_7\text{O}_{16})(\text{H}_2\text{O})_{0.69}$ (CC = 83336)
ASU-21 ⁵	$[\text{C}_6\text{H}_{16}\text{N}_2\text{H}_2]_3[\text{Ge}_{33}\text{O}_{70}(\text{OH})_4] \cdot 3\text{H}_2\text{O}$
ICMM-7 ²⁰	$[\text{C}_6\text{H}_{16}\text{N}_2\text{H}_2]_2[\text{Ge}_{13}\text{O}_{26}(\text{OH})_4](\text{H}_2\text{O})_{1.5}$
IM-14 ³²	$[\text{enH}_2]_2(\text{H}_2\text{O})_{2.3}[\text{Ge}_8\text{O}_{17}(\text{OH})_2]$
$M_4\text{Ge}_9\text{O}_{20}$ (M = Na, K)	$\text{K}_4\text{Ge}_9\text{O}_{20}$ (CC = 98215) $\text{Na}_4\text{Ge}_9\text{O}_{20}$ (CC = 68507)
SU-M ¹⁴	$[\text{C}_6\text{H}_{16}\text{N}_2\text{H}_2]_2[\text{Ge}_{10}\text{O}_{20.5}(\text{OH})_3](\text{H}_2\text{O})_x$
SU-MB ¹⁴	$[\text{C}_6\text{H}_{16}\text{N}_2\text{H}_2]_{5.5}[\text{Ge}_{10}\text{O}_{21}(\text{OH})_2] \cdot [\text{Ge}_7\text{O}_{14}\text{F}_3](\text{H}_2\text{O})_x$
SU-61 ¹¹	$[\text{C}_6\text{H}_{16}\text{N}_2\text{H}_2]_5[\text{Ge}_{8.5}\text{Si}_{1.3}\text{O}_{16}\text{O}_{5.5}(\text{OH})][\text{Ge}_{0.71}\text{Si}_{0.29}\text{O}_2]$ $[\text{Ge}_{0.22}\text{Si}_{0.78}\text{O}_{15}(\text{OH})]_2$
SU-62	
SU-67	

^a Collection codes (CC) in the ICSD are given in parentheses.

germanates ASU-21⁵ (Ge_{10}) and JLG-12³³ (Ge_7), SU-63³⁴ (Ge_7) and SU-64³⁴ (Ge_7), as well as two newly discovered Ge_{10} containing germanates (SU-62 and SU-67) have not yet been included in the databases and they are also used for our study here. Totally there are 25 germanates with GeO_4 tetrahedral and GeO_6 octahedral coordinations, and 20 germanates with GeO_4 tetrahedral, GeO_5 trigonal bipyramidal and GeO_6 octahedral coordinations.

Twenty-five germanates were found to contain Ge_{10} clusters in the structures. Topological study of their frameworks showed that they all have three-dimensional structures, which fall into only 10 different framework types (Table 1). Fifteen of the 25 germanates have the same framework type and belong to the family of Ge-pharmacosiderite analogues with the formula $A_3\text{H}[\text{Ge}_7\text{O}_{16}](\text{H}_2\text{O})_x$ (A = Li, NH₄, H, Na, K, Cs, Rb; $x = 0.69 - 6.00$). The second group is comprised of two germanates of the general formula $M_4\text{Ge}_9\text{O}_{20}$ (M = Na, K). Among the eight remaining germanates, each has its own unique framework type, including the first crystalline mesoporous germanate SU-M with gyroidal channels and its modification SU-MB.¹⁴

■ $\text{GE}_{10}(\text{O}, \text{OH})_{27}$ AND $\text{GE}_{10}(\text{O}, \text{OH})_{28}$ AS SECONDARY BUILDING UNITS

Two different Ge_{10} clusters, $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ ¹⁴ and $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ ^{11,14} have been used in discussions in reported germanates. Both Ge_{10} clusters consist of four edge-sharing octahedra surrounded

by six tetrahedra (parts c and d of Figure 1). The main difference of the two clusters is the connectivity of the tetrahedra. In $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$, all six tetrahedra are directly connected to the octahedra in the same way by sharing two of their vertices (part c of Figure 1). In $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$, only five of the six tetrahedra are directly connected to the octahedra, whereas the sixth tetrahedron connects to three of the tetrahedra, capping one side of the cluster (part d of Figure 1). The clusters are connected through the tetrahedra. Such a structural feature is responsible for distinction of geometrical and topological properties of the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ building unit. In the $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ cluster only two vertices of each of the six tetrahedra are bound (part c of Figure 1). All of these six tetrahedra can tilt themselves within a limited angle range around one of the tetrahedral edges. In the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBU, three tetrahedra are capped by a fourth tetrahedron making a robust set of 4 rings together with the octahedra in the SBU. Only two of the six tetrahedra can tilt more freely. Thus, $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ is more flexible than $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$. It is worth noting that other building units, for example the Ge_4O_{18} unit and GeO_4 tetrahedron, were also used as building units to describe the germanate LMN-1,¹⁸ a pharmacosiderite analogue.

For some germanate structures, both $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ and $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBUs can be used, whereas for other germanates only one of them may be chosen. The examples are SU-M, SU-MB, SU-62 and SU-67, where the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ cluster is an SBU. Using $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ as an SBU to describe these compounds will require sharing of some GeO_4 tetrahedra between the clusters. The $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ SBU has been previously identified in the structures of ICMM-7,²⁰ SU-61,¹¹ and ASU-21⁵ compounds.

Because of the fact that the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBU can describe a larger number of structures compared to the $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ SBU, we selected the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ for further topological analysis in this article, to achieve the consistency in the study of germanates. From now on, we use Ge_{10} exclusively for $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$. Therefore, we consider also ICMM-7, SU-61, and ASU-21, which was described previously using the $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ clusters, to be constructed from the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBUs. It is worth noting that the topologies of ICMM-7 and ASU-21 do not depend on the choices of the Ge_{10} clusters.

■ GERMANATES BUILT FROM $\text{GE}_{10}(\text{O}, \text{OH})_{27}$ SECONDARY BUILDING UNITS

Identification of structures composed of the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBU was based on the set of earlier collected occurrences of germanates containing $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ clusters. Overall, seven open-framework germanates built from $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ clusters were found: SU-M¹⁴ and SU-MB,¹⁴ SU-62, ICMM-7,²⁰ SU-61,¹¹ ASU-21,⁵ and SU-67 (Table 2).

Among the seven open-framework germanates, SU-M and SU-62 are entirely built up by direct connection of the Ge_{10} SBUs (Figure 3). No other building units are involved in the structures. The underlying nets in SU-M and SU-62 are *fcz*⁴⁸ and *svh-5-I4₁/amd*⁴⁹ respectively, both are uninodal and have three unique edges (Table 2). Each Ge_{10} is connected to five other Ge_{10} SBUs. The natural tiling for *fcz* net is built by two types of tiles,¹⁴ while that for *svh-5-I4₁/amd* net is built by only one type of tiles.

Another germanate that has a uninodal net is ICMM-7, where the Ge_{10} SBUs are connected either directly or via extra tetrahedral building units Ge_2O_7 and GeO_4 (Figure 3, Table 2). The underlying topology in ICMM-7 is *bnn*, with the transitivity

Table 2. Germanates Built from the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBU and Topological Descriptors of Their Underlying Nets

germanate	building units	coordination environment	topological features of the SBU net		
			topology	transitivity ^a	CN
SU-M	Ge_{10}	5 Ge_{10}	uninodal nets f_cz	[1342]	5
SU-62	Ge_{10}	5 Ge_{10}	svh-5-I4₁/amd	[1321]	5
ICMM-7	Ge_{10}	2 GeO_4 , 2 Ge_2O_7 , 3 Ge_{10}	bnn	[1221]	5
	Ge_2O_7	2 Ge_{10}			
	GeO_4	2 Ge_{10}			
SU-61	$(\text{Si}, \text{Ge})_3\text{O}_{10}$	4 $(\text{Ge}, \text{Si})_{10}$	binodal and 3-nodal nets novel	[2563]	4
	$(\text{Ge}, \text{Si})_{10}$	4 $(\text{Si}, \text{Ge})_3\text{O}_{10}$, 3 $(\text{Ge}, \text{Si})_{10}$			7
SU-MB	Ge_{10}	5 Ge_{10} , Ge_7	novel	[39]	6
	Ge_7	2 Ge_{10} , 2 Ge_7			4
ASU-21	Ge_{10}	5 Ge_{10} , 2 GeO_4	novel	[3873]	7
	Ge_{10}	4 Ge_{10} , 2 GeO_4			6
	GeO_4	2 Ge_{10}			
SU-67	Ge_{10}	4 Ge_{10} , 3 Ge_2O_7 , GeO_4	novel	[2763]	8
	Ge_2O_7	3 Ge_{10}			3
	GeO_4	2 Ge_{10}			

^a Hereafter, transitivity of the natural tiling [pqrs] of a net is specified as number of unique vertices (p), edges (q), faces (r), and tiles (s). If the natural tiling for a net is unknown, transitivity of the net [pq] is given instead.

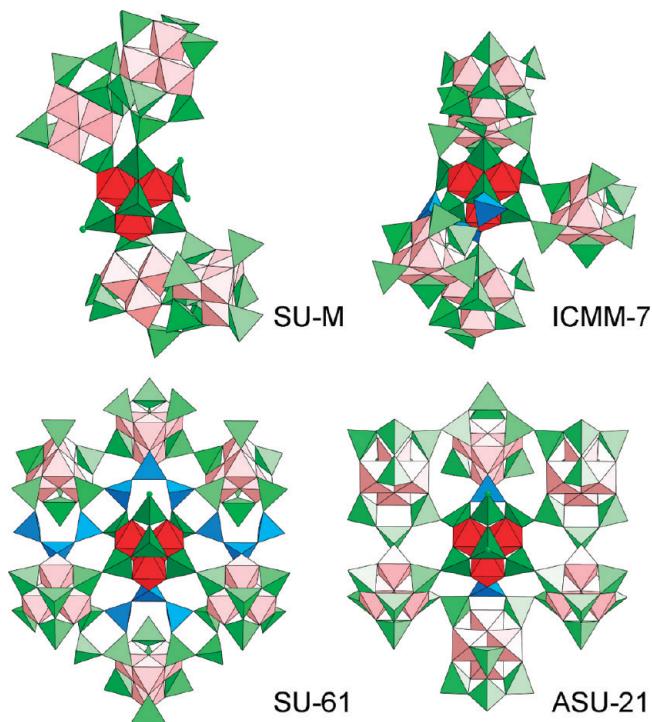


Figure 3. Coordination environment of the $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ SBU in germanates SU-M, ICMM-7, SU-61, and ASU-21. Auxiliary tetrahedra gluing $\text{Ge}_{10}\text{O}_{27}$ units are in blue. Terminal atoms O and F are depicted explicitly as solid spheres.

[1221]. An alternative building unit in ICMM-7 is a combination of a Ge_{10} unit, double tetrahedra Ge_2O_7 and a tetrahedron GeO_4 into a larger SBU $\text{Ge}_{13}(\text{O}, \text{OH})_{34}$.²⁰ However, the different choices of the SBUs did not alter the topology of the SBU net,

because the extra tetrahedral building units only provide subsidiary linkages between the Ge_{10} clusters, and the linkages between the Ge_{10} or the $\text{Ge}_{13}(\text{O}, \text{OH})_{34}$ SBUs are the same. Thus, the framework topology based on the $\text{Ge}_{13}(\text{O}, \text{OH})_{34}$ SBU is also **bnn** (Table 2).

The structures of two germanates SU-61 and SU-MB are composed of two kinds of SBUs, one is Ge_{10} and another is $(\text{Ge}, \text{Si})_3\text{O}_{10}$ in SU-61 and Ge_7 in SU-MB. As a result, SBU nets in SU-61 and SU-MB are topologically more complex: they have two and three topologically independent vertices, respectively (Table 2). Whereas the Ge_7 clusters in SU-MB only decorate the framework of SU-M by filling up a half of the big channels,¹⁴ the $(\text{Ge}, \text{Si})_3\text{O}_{10}$ units in SU-61 take part in connecting the rows of Ge_{10} clusters¹¹ (Figure 3), that is $(\text{Ge}, \text{Si})_3\text{O}_{10}$ plays a framework-forming role. The binodal SBU net in SU-61 demonstrates an example of a net following a novel topological motif (Table 2). In our previous publication, we used $\text{Ge}_{10}(\text{O}, \text{OH})_{28}$ instead of $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ here as the building unit, allowed sharing of tetrahedra between the clusters, and considered additional tetrahedra merely as spacers. The resulting underlying topology was then a simpler osf net.¹¹ Here, we will pay attention to the full representation of SBU nets where all the building units are accounted, because this is crucial for evaluation of the topology of nets.

Likewise SU-61, ASU-21⁵ (Figure 3), and SU-67 are also built from the Ge_{10} SBUs connected both directly to other Ge_{10} SBUs and via extra tetrahedral building units (Table 2).

■ OCCURRENCE AND STRUCTURAL ANALYSIS OF GERMANATES BUILT FROM $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ CLUSTERS

The Ge_7 cluster consists of one GeO_6 octahedron, two GeO_5 trigonal bipyramids and four GeO_4 tetrahedra (part e of Figure 1). It is more rigid compared to the Ge_{10} clusters because all the polyhedra are connected to at least three other polyhedra

Table 3. Germanates Built from the Ge₇(O, OH, F)₁₉ SBU and Topological Descriptors of Their Underlying Nets

germanate	building units	coordination environment	topological features of the SBU net			
			topology	dimension	transitivity	CN
uninodal nets						
FJ-6 ¹⁹	Ge ₇	2 Ge ₇		chain	[11]	2
SINMUY ³⁶	Ge ₇	4 Ge ₇	sql	layer	[11]	4
ASU-20-DACH ³⁷	Ge ₇	4 Ge ₇	sql	layer	[11]	4
ASU-20-DAPe ³⁷	Ge ₇	4 Ge ₇	sql	layer	[11]	4
SU-22 ¹⁶	Ge ₇	4 Ge ₇	sql	layer	[11]	4
SU-23 ¹⁶	Ge ₇	4 Ge ₇ , GeO ₄	sql	layer	[11]	4
	GeO ₄	Ge ₇				
SU-63 ³⁴	Ge ₇	4 Ge ₇	kgm	layer	[11]	4
JLG-4 ¹⁵	Ge ₇	4 Ge ₇		chain	[11]	4
ASU-19 ³⁷	Ge ₇	4 Ge ₇ , GeO ₄	SnS	double layer	[12]	5
	GeO ₄	2 Ge ₇				
ASU-12 ³⁸	Ge ₇	5 Ge ₇	bnn	framework	[1221]	5
ASU-16 ³⁹	Ge ₇	5 Ge ₇	fee	framework	[1342]	5
SU-12 ⁴⁰	(Ge,Si) ₇	5 (Ge,Si) ₇	fee	framework	[1342]	5
MOPBEY ⁴¹	Ge ₇	6 Ge ₃ O ₁₀	pcu	framework	[1111]	6
	Ge ₃ O ₁₀	6 Ge ₇				6
binodal and 3-nodal nets						
JLG-5 ⁴²	Ge ₇	4 Ge ₇	novel	chain	[23]	4
	Ge ₇	4 Ge ₇ , GeO ₄				5
	GeO ₄	2 Ge ₇				
SU-64 ³⁴	Ge ₇	2 Ge ₇ , 2 Ge ₉	novel	double layer	[32]	4
	Ge ₇	4 Ge ₇				4
	Ge ₉ O ₂₆	8 Ge ₇				8
STAG-1 ⁴³	Ge ₇ /Ge ₈ O ₂₀	2 Ge ₈ O ₂₁	sqc703	framework	[2341]	
	Ge ₈ O ₂₁	2 Ge ₈ O ₂₁ , 4 GeO ₄ , Ge ₇ /Ge ₈ O ₂₀				7
	GeO ₄	4 Ge ₈ O ₂₁				4
SU-8 ⁴⁴	Ge ₇	4 Ge ₉ O ₂₆ , 2 GeO ₄	sea	framework	[2243]	6
	Ge ₉ O ₂₆	8 Ge ₇				8
	GeO ₄	2 Ge ₇				
SU-44 ⁴⁴	Ge ₇	2 Ge ₇ , 2 Ge ₉ O ₂₆	novel	framework	[3497]	6
		GeO ₄ , Ge ₂ O ₇				
	Ge ₇	4 Ge ₇				4
	Ge ₉ O ₂₆	8 Ge ₇				8
	GeO ₄	2 Ge ₇				
	Ge ₂ O ₇	2 Ge ₇				
JLG-12 ³³	Ge ₇	4 Ge ₉ O ₂₆ , GeO ₄	novel	framework	[4486]	5
	Ge ₇	4 Ge ₉ O ₂₆				4
	Ge ₉ O ₂₆	8 Ge ₇				8
	GeO ₄	2 Ge ₇				
SU-MB ¹⁴	Ge ₁₀	5 Ge ₁₀ , Ge ₇	novel	framework	[39]	6
	Ge ₇	2 Ge ₁₀ , 2 Ge ₇				4

within the Ge₇ cluster and cannot rotate freely. A similar procedure as that for the Ge₁₀ clusters was applied also for the identification of germanates built from the Ge₇ clusters. The Ge₇ clusters were found in 20 open-framework germanates, including 1D, 2D, and 3D structures (Table 3). The 20 germanate compounds form 15 totally unique topologies. Among those that have the same topologies are the 3D germanate ASU-16³⁹ and its silicon-substituted analogue SU-12,⁴⁰ and the layered germanates SU-22,¹⁶ SU-23,¹⁶ SINMUY,³⁶ and ASU-20.³⁷

First, we will shortly describe germanates with simpler underlying topologies producing chainlike and layered structures.

FJ-6 is the only example of 1D germanate built from one unique Ge₇ SBU. The Ge₇ SBUs are two-connected by corner-sharing of the tetrahedra, which generates isolated rows along the *a*-axis.¹⁹

The most common coordination of the Ge₇ SBU is four, through its four GeO₄ tetrahedra (part e of Figure 1). The Ge₇ SBU with this connectivity can be abstracted as a rectangle, with a long (L) and a short (S) sides.¹⁶ One possible way of

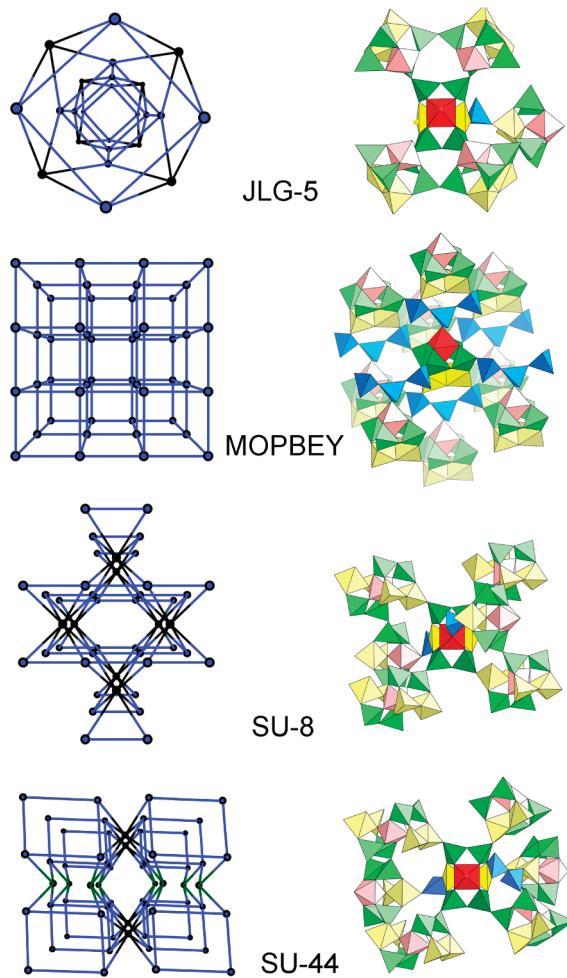


Figure 4. Coordination environment of the Ge₇ SBU in germanates JLG-5, MOPBEY, SU-8, and SU-44. (Left) The underlying nets describe the bonding between the building units in the structures and corresponding transitivities are from the top: JLG-5 chain [23], MOPBEY pcu [1111], SU-8 sea [2243], and SU-44 new 3-periodic [3497]. Topologically unique nodes are distinguished by different colors. (Right) Connection of the building units. Auxiliary tetrahedra gluing the Ge₇ SBUs are shown in blue. Terminal O and F atoms are drawn explicitly as solid spheres.

connecting the Ge₇ rectangles by vertex-sharing leads to layered structures with the 4⁴ sql topology,³⁶ as found in Ge₇O₁₄F₃·0.5 [In-(dien)₂]·0.5H₃dien·2H₂O (CCDC-628446, refcode SINMUY⁵⁰), ASU-20-DACH,³⁷ ASU-20-DAPE,³⁷ SU-22,¹⁶ and SU-23¹⁶ (Table 3). The orientation of the Ge₇ clusters and connecting sequence can be different. The different combinations can result in different compounds, as described by Bonneau et al.¹⁶ Another way to connect the Ge₇ rectangles by vertex-sharing is to follow the kagome (kgm) pattern that is observed recently in SU-63³⁴ (Table 3).

JLG-4¹⁵ has a 1D tubular structure (Table 3) with a novel uninodal topology. The SBU net of JLG-4 can be considered as 4⁴ (sql) net wrapped to a cylinder.

The structure of JLG-5 contains large 6⁸12⁶ cavities built by twelve Ge₇ clusters.⁴² Similar to the above-mentioned structures, the Ge₇ cluster in JLG-5 is connected to the neighboring Ge₇ clusters through its four GeO₄ tetrahedra. The 6⁸12⁶ cavities are further connected by additional GeO₄ to form 1D chains in

JLG-5 (Figure 4), with a novel binodal topology (Table 3). There are both four- and five-coordinated Ge₇ clusters in JLG-5.

ASU-19 and SU-64 consist of double layers of the Ge₇ SBUs, connected by extra GeO₄ tetrahedra in ASU-19 to form a herzenbergite-like structure or by the Ge₉ clusters in SU-64 forming a layered structure with an unprecedented 3-nodal topology. There are two kinds of Ge₇ clusters, both are 4-coordinated. The Ge₉ clusters are 8-coordinated.

ASU-12 has a framework built solely from Ge₇ SBUs that are linked following a rather distorted uninodal bnn net (Table 3). The Ge₇ clusters are 5-coordinated. Remarkably, bnn net, which is one of the most topologically simplest ones, has been found in the germanates built from both Ge₁₀ and Ge₇ SBUs.

ASU-16 and its silicon-substituted analogue SU-12 have a framework built from Ge₇ and (Ge,Si)₇ SBUs, respectively. The underlying topology is described by a uninodal fee net (Table 3), with three different kind of edges. The Ge₇ clusters are also 5-coordinated.

Another interesting germanate is Ge₁₀O₂₁(OH)·N₄C₆H₂₁ (MOPBEY),⁴¹ where the Ge₇ SBUs are connected into a framework via tritetrahedra Ge₃O₁₀ units (Figure 4). Although there are two kinds of SBUs in the structure, the underlying net is pcu with only one unique vertex (Table 3). Different from other uninodal 3D germanates such as ASU-12 and ASU-16 where the Ge₇ SBUs are 5-coordinated, the Ge₇ SBU in Ge₁₀O₂₁(OH)·N₄C₆H₂₁ is 6-coordinated. Thus, we can describe it as cubic close packing of the big Ge₇ clusters, while the small Ge₃O₁₀ units occupy the octahedral holes of the close packing. The relatively high framework density (15.3 Ge-atom/1000 Å³) of the germanate Ge₁₀O₂₁(OH)·N₄C₆H₂₁ is the result of the close packing.

The structure of STAG-1 is rather complex, built of four types of building units Ge₇, Ge₈O₂₀, Ge₈O₂₁ and GeO₄ (Table 3). This example shows that the plane-square coordinated Ge₇ SBUs may form frameworks only being combined with other building units. The underlying topology is described by a binodal net sqc703,²⁸ where the Ge₇ and Ge₈O₂₀ share the same positions and both are 4-coordinated.⁴³

A common feature of the 3D germanates SU-8, SU-44, SU-64 and JLG-12 is that the structures are constructed primarily from the assembly of a Ge₉ cluster connected to eight Ge₇ units.^{33,44} The results of the analysis of their underlying nets are presented in Table 3 and illustrated in Figure 4.

■ ANALYSIS OF STRUCTURAL PECULIARITIES OF GERMANATES BUILT FROM GE₁₀(O, OH)₂₇ AND GE₇(O, OH, F)₁₉ SECONDARY BUILDING UNITS

Table 3 shows how the coordination numbers (CN) of the Ge₇ SBU increase with the dimensionality of the underlying nets. For example, 4-coordinated Ge₇ SBUs prefer to form layered structures except for that of JLG-4, which is one-dimensional (Table 3). It is remarkable that the quite different building units Ge₁₀ and Ge₇ nevertheless can construct frameworks that have the common features. For example, 5-coordinated Ge₁₀ and Ge₇ SBUs often form frameworks with uninodal three-periodic underlying nets: SU-M, SU-62 and ICMM-7 are assembled from Ge₁₀ SBUs, and ASU-12, ASU-16, and SU-12 are built from Ge₇ SBUs (Tables 2 and 3). The only exception is ASU-19 with double layered structure, where the terminal atoms of the Ge₇ clusters in the double layers are fluorine instead of oxygen,³⁷ and

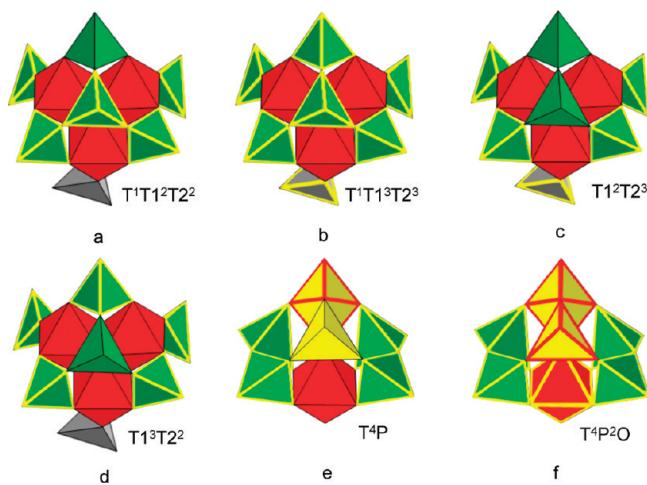


Figure 5. Coordination modes of the Ge_{10} and Ge_7 SBUs in germanates. Polyhedra that are coordinated to other SBUs are shown with enhanced edges. (a) SU-M, (b) ICMM-7, (c) SU-62, (d) the hypothetical germanates $\text{Ge}_{10}(\text{pee})$ and $\text{Ge}_{10}(\text{pcu-i})$, (e) ASU-12, SU-12, ASU-16, ASU-19, a hypothetical compound $\text{Ge}_7(\text{ttw})$ and (f) MOPBEY. Polyhedra that constitute the SBU are denoted as T (tetrahedron, green), P (trigonal bipyramidal, yellow), and O (octahedron, red). The different types of GeO_4 tetrahedra in Ge_{10} are denoted as T (the capping tetrahedron), T1 (tetrahedra linking T and the core of the Ge_{10} SBU), T2 (tetrahedra only connected to the core of the SBU). Extra GeO_4 tetrahedra are in gray.

that prevents adjacent layers from being connected into a framework (Table 3).

The above observation is only valid for those germanates with uninodal net topologies. Germanates with binodal and trinodal net topologies are built from several types of building units. The coordination number depends on the size of the building unit: lower coordination numbers are found for smaller building units (Tables 2 and 3). For the sake of simplicity, we concentrate our further study on germanates that are built on uninodal SBU nets only and leave the topologically more complex compounds for further studies.

When studying the coordination modes of the SBUs in germanates, it is important to know which SBUs are chemically bonded one to another and how the bonding is established. To address this issue, we studied the local topologies of Ge_{10} and Ge_7 SBUs in all investigated germanates with uninodal nets (parts a–f of Figure 5).

The analysis of the coordination modes of the Ge_{10} and Ge_7 SBUs shows that Ge_{10} has much more freedom in adopting new coordination modes compared to Ge_7 : all Ge_7 SBUs in the known germanate frameworks with uninodal 3-periodic nets are 5-coordinated with the same coordination mode (part e of Figure 5) except for those in MOPBEY, where they are 6-coordinated (Figure 4, and part f of Figure 5). On the contrary, among Ge_{10} -germanates with uninodal net topologies none of them have the same coordination mode of Ge_{10} (parts a–c of Figure 5).

Summarizing the topological analysis of the SBU nets of open-framework germanates built from Ge_{10} and Ge_7 clusters, the following conclusions may be drawn:

- Almost all germanates built from one kind of SBUs are based on uninodal nets (Tables 2 and 3). Although extra GeO_4 tetrahedra are present in many germanate

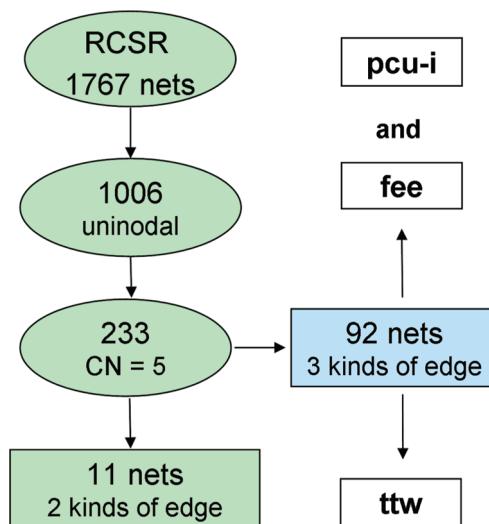


Figure 6. Scheme for screening the RCSR database against the defined criteria. As the result, nets as prototypes for hypothetical germanates built from the SBU Ge_{10} or Ge_7 are identified.

structures, for example ICMM-7 and ASU-19, they can be readily replaced by a single edge if they correspond to two-connected vertices in the underlying nets. Thus, both ICMM-7 and ASU-19 also obey this rule.

- 3D germanates built from the Ge_{10} or Ge_7 SBUs, where the SBUs are connected directly or by bridging extra tetrahedra, tend to form 5-connected SBU nets. The only exception is the germanate MOPBEY that is built of two kinds of building units (Table 3).
- The family of 5-connected uninodal nets does not have edge-transitive ones,⁴⁵ that is the number of unique edges is more than one (2 or 3, Tables 2 and 3). The only example of a 3D germanate based on an edge-transitive net is MOPBEY with the 6-connected vertex (**pcu** topology).
- The coordination mode of the Ge_7 SBU tends to be the same in all germanates, while the Ge_{10} SBU readily adapts various coordination modes.

■ DESIGN OF NOVEL OPEN-FRAMEWORK GERMANATE STRUCTURES

Analysis of underlying connectivity (topology) of the extended germanate structures provides important information on how porous architectures are constructed from certain SBUs.⁴⁶ Let us consider the combination of the above-mentioned conclusions as a set of criteria imposed on the underlying nets of a given group of compounds. Then, we search for a list of topologies that meet all these criteria and thus will more likely be adopted as underlying nets in novel structures built from the SBUs.

The last idea is important for the design of new materials since it allows to significantly reduce the number of possible alternatives of connecting building units into a framework. For example, the well-known source of nets for materials designers, RCSR database²⁷ contains totally 1767 nets. There are 1006 uninodal topologies (56.9%) and only 233 of these are 5-coordinated nets (Figure 6). If we sort those 233 nets out by the number of unique edges, it appears that only 11 nets have two

Table 4. Models of Hypothetical Open-Framework Germanates Built from $\text{Ge}_{10}(\text{O}, \text{OH})_{27}$ or $\text{Ge}_7(\text{O}, \text{OH}, \text{F})_{19}$ SBUs

germanate	unit cell	space group	wyckoff	SBU centroid	topology	SBU net
$\text{Ge}_{10}(\text{fee})$	$a = 35.0 \text{ \AA}$ $c = 22.2 \text{ \AA}$	$P4/mmm$	$16u$	(0.1639, 0.3560, 0.7391)	fee	[1342]
$\text{Ge}_{10}(\text{pcu-i})$	$a = 37.0 \text{ \AA}$ $c = 37.0 \text{ \AA}$	$P4/m$	$8l$	(0.1417, 0.1607, 0.3574) (0.1578, 0.3599, 0.1479) (0.3591, 0.1681, 0.1472)	pcu-i	[1354]
$\text{Ge}_7(\text{ttw})$	$a = 36.5 \text{ \AA}$ $c = 19.5 \text{ \AA}$ $\gamma = 120^\circ$	$P6/m$	$12l$	(0.4366, 0.6085, 0.7885)	ttw	[1342]

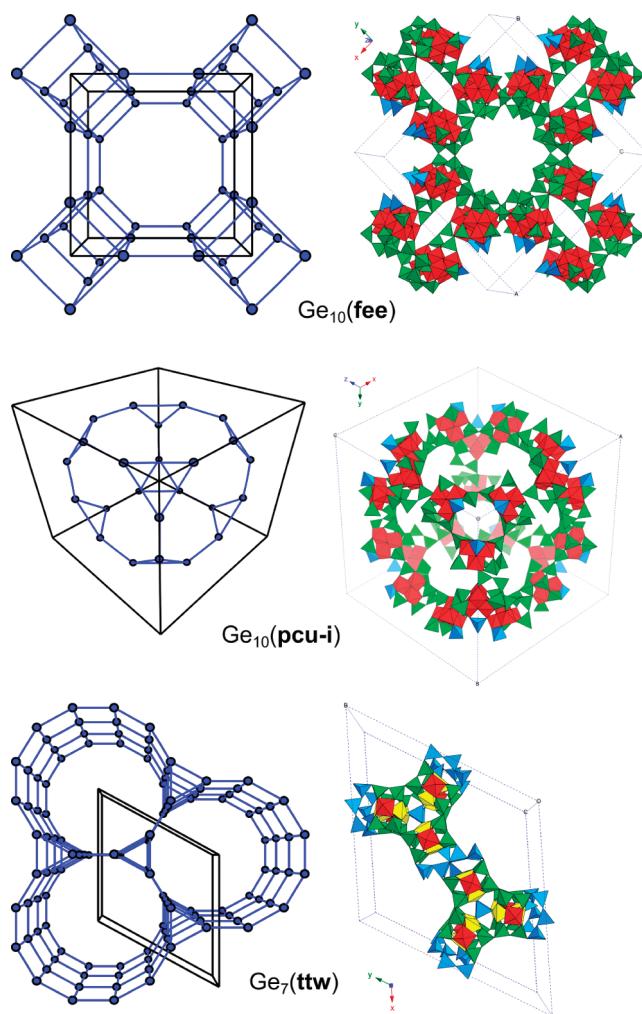


Figure 7. Models of hypothetical germanate structures built from the Ge_{10} or Ge_7 SBUs, based on the topology of **fee**, **pcu-i**, and **ttw** nets. Within the SBUs, GeO_4 tetrahedra are shown in green, GeO_5 trigonal bipyramids in yellow, and GeO_6 octahedra in red. Auxiliary tetrahedra are in blue.

unique edges and 92 are built by three kinds of edges. Out of these 11 nets only **bnn** net was adopted as the topological pattern for two germanates ICMM-7 and ASU-12 built from Ge_{10} and Ge_7 building units, respectively. The list contains a few interesting nets, for instance, the **sqp** topology recently found to be a frequently occurring net in metal–organic frameworks.²⁷

However, we have not succeeded in modeling new germanate structures based on them due to the short interatomic distances arising between the SBUs. Thus, we paid attention to the nets with three unique edges and have chosen among several candidates, **fee**, **pcu-i**, and **ttw** net, which embeddings seem to be capable to properly connect the Ge_{10} or Ge_7 clusters into 3D structures. To illustrate the concept of design new open-framework germanates, we used these nets as topological patterns to build new germanate models.

Here, we describe briefly a possible scheme that one may follow to perform the topology-based modeling of new open-framework germanate structures built from one kind of SBUs.

- The modeling starts with identifying nets from a database of topological types with a set of features meeting the criteria that were drawn up from the analysis of reported compounds built from a certain SBU. The nets should be assessed with regard to their suitability to maintain proper $\text{Ge}–\text{O}–\text{Ge}$ bond angles between the SBUs in a hypothetical germanate structure.
- The most symmetrical embedding of a net may be used as an initial model for a novel compound with further geometrical optimization of the resulting framework. The unit cell of the embedding appears to be a good starting point for determination of the asymmetric unit of the hypothetical structure.
- The SBUs should be positioned so that their centers are aligned with the vertices of the net embedding and the unit cell of the hypothetical structure is adjusted until the $\text{Ge}–\text{O}$ bond lengths are reasonable (1.7–2.0 Å).
- In addition, the SBUs need be oriented properly in order to provide the linkage with adjacent SBUs. This should be made with respect to the target coordination mode of the SBUs.

The considerable number of occurrences of the Ge_{10} and Ge_7 clusters found in germanate structures of various complexity is an evidence of their structural adjustability and capability to form diverse structures.

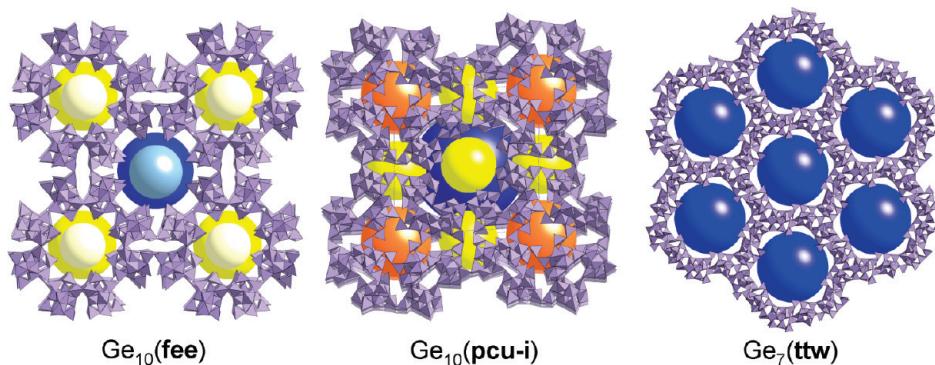
■ MODELING OF NOVEL GERMANATES BUILT FROM $\text{GE}_{10}(\text{O}, \text{OH})_{27}$ OR $\text{GE}_7(\text{O}, \text{OH}, \text{F})_{19}$ SECONDARY BUILDING UNITS

Following the above-mentioned scheme, we have modeled three hypothetical germanate structures based on the RCSR nets **fee**, **pcu-i**, and **ttw**.

The modeling of the frameworks was performed in two steps. The first step is to determine the unit cell and align the SBUs

Table 5. Structures of Energy-Minimized Hypothetical Open-Framework Germanates

germanate	unit cell		volume, Å ³	spherical pores	
				center	diameter, Å
Ge ₁₀ (fee)	<i>a</i> = 30.55 Å	α = 91.44°	16684.61	(0.9877, 0.0010, 0.9645)	16.37
	<i>b</i> = 31.09 Å	β = 90.74°		(0.4883, 0.4991, 0.9657)	14.35
	<i>c</i> = 17.57 Å	γ = 90.47°		(0.9877, 0.0010, 0.4645)	14.31
				(0.4883, 0.4991, 0.4657)	13.44
Ge ₁₀ (pcu-i)	<i>a</i> = 31.47 Å	α = 88.58°	30194.03	(0.5160, 0.5555, 0.4729)	23.77
	<i>b</i> = 31.52 Å	β = 89.80°		(0.0156, 0.0560, 0.9721)	15.47
	<i>c</i> = 30.47 Å	γ = 92.45°		(0.5148, 0.0553, 0.4716)	12.70
				(0.0179, 0.5571, 0.4711)	13.01
Ge ₇ (ttw)	<i>a</i> = 32.39 Å	α = 92.26°	13222.63	(0.5152, 0.5517, 0.9722)	12.00
	<i>b</i> = 32.60 Å	β = 90.52°		(0.9950, 0, 0.4721)	22.88
	<i>c</i> = 14.49 Å	γ = 120.02°			

**Figure 8.** Energy-minimized hypothetical germanates built from the Ge₁₀ or Ge₇ SBU, based on the topology of fee, pcu-i, and ttw nets. The spherical voids fitted into frameworks are shown: Ge₁₀(fee) *d* = 16.37 Å, blue; *d* = 14.31 Å, light blue; *d* = 14.35 Å, yellow; *d* = 13.44 Å, light yellow. Ge₁₀(pcu-i) *d* = 23.77 Å, blue; *d* = 12.70 Å, 13.01 Å, 12.00 Å, yellow; *d* = 15.47 Å, orange. Ge₇(ttw) *d* = 22.88 Å, blue.

within the unit cell. As the site symmetry of the vertex position ($4l$, C_{2v}) of the fee net embedding is higher than the intrinsic symmetry (C_1) of the Ge₁₀ SBU, the unit cell of the embedding has been expanded to place the clusters onto the general positions $16u$ of $P4/mmm$ space group. To fit the Ge₁₀ and the Ge₇ SBUs into the unit cells of pcu-i and ttw embeddings respectively, the symmetries of the embeddings have to be lowered, which was achieved by using the subgroups $P4/m$ and $P6/m$ of the space groups $Pm\bar{3}m$ and $P6/mmm$, respectively (Table 4).

The second step is to set up the mutual orientations of the SBUs by means of the Materials Studio package. As there is not any evidence that Ge₁₀ SBUs tend to be in some certain coordination mode compared to the Ge₇ SBUs, they were just oriented to get a target topology. The customary coordination mode of the Ge₇ SBUs was repeated in the hypothetical model of germanate based on the ttw net.

Eventually, the asymmetrical units of the germanate structures, which admit those topologies and take into account the symmetry of the SBUs, were built. Models of three hypothetical germanate structures were constructed in space groups $P4/mmm$, $P4/m$, and $P6/m$ using the SBUs Ge₁₀, Ge₁₀, and Ge₇, respectively (Table 4, Figure 7), which are further referred to as Ge₁₀(fee), Ge₁₀(pcu-i), and Ge₇(ttw). Extra double tetrahedra were introduced as additional linkers between the Ge₇ SBUs in

the Ge₇(ttw) model. Only extra terminal tetrahedra needed to be introduced in Ge₁₀(fee) and Ge₁₀(pcu-i), so the underlying topologies were not affected.

To optimize the initial models, we performed the energy minimization with the GULP code.³¹ The simulations were carried out under zero pressure with relaxation of atomic positions and unit cell parameters. To avoid geometrical constraints imposed by the space groups, the symmetry was lowered to $P1$. The interatomic interactions were described by the generic force field DREIDING⁴⁷ with general force constants and geometry parameters from Materials Studio DREIDING force field library. The Newton–Raphson optimization procedure was employed for system energy minimization with a gradient change tolerance of 10^{-3} and a minimal energy variation of 10^{-5} eV.

We used strong interatomic interactions both within and between the SBUs to explicitly set up the bonding within the simulated structures.

Energy minimization of the frameworks resulted in decreases of the unit cell volumes (Table 5) and led to some distortions of the SBUs, which are most probably due to the poor force-field that does not represent the open-framework germanates with mixed coordinations of GeO₄ tetrahedra, GeO₅ trigonal bipyramidal and GeO₆ octahedra. To confirm this, we performed the same energy minimization procedure for the hypothetical germanates described above to a known open-framework

germanate, ASU-12³⁸ built from the Ge₇ SBUs. Similar distortions of the polyhedra and SBUs were observed, and the *a* parameter decreased by 12.5% (Table S1 and Figure S1 of the Supporting Information). To obtain more accurate models of the hypothetical open-framework germanates with mixed Ge—O coordinations, more accurate force-field needs to be developed.

Table 5 shows the unit cell parameters as well as the pore sizes and distributions within the hypothetical germanate frameworks. The channels in the structures can be approximately described by spheres fitted within the empty spaces of the frameworks, with the diameter proportional to the channel sizes (Table 5, Figure 8). For instance, Ge₁₀(fee) consists of a series of straight 24- and 32-ring channels along the *c* axis, and their sizes are estimated by the largest spherical cavities fitted into the channels of 14.31 Å and 16.37 Å in diameter, respectively (the distances are calculated between O atoms, Table 5). The structure of Ge₁₀(pcu-i) contains intersecting 24-ring channels in three directions, built by two kinds of cages and described by the spheres of a different size (Table 5). The cages are connected via 24-ring windows (the distance between the centers of the cages is 15.21 Å). Another midsized cage described by the spherical cavity of 15.47 Å, is separated from the channel system by the relatively narrow 12-ring windows (Figure 8). Large 30-ring channels are found in the germanate structure of Ge₇(ttw) (Figure 8).

It should be noted that the enumeration of all theoretically possible frameworks alone does not give the necessary synthetic routes that may lead to the desired new structures. To address this problem, new development of rational strategies for identifying structure-directing agents and establishing synthesis routes is needed. We hope that our work will promote the development in this field.

CONCLUSIONS

The topological study of all known germanates has revealed the occurrences of the Ge₁₀ and Ge₇ clusters in 25 and 20 germanate structures, respectively. Those germanates were divided into different types in accordance with the underlying topologies. It is found that the pharmacosiderite analogue of germanates is predominate.

We have shown that Ge₇(O, OH, F)₁₉ cluster can always be considered as an SBU in all Ge₇ containing structures, whereas two alternative clusters Ge₁₀(O, OH)₂₇ and Ge₁₀(O, OH)₂₈ could be used to describe the structures containing the Ge₁₀ clusters. We chose to use the more rigid Ge₁₀(O, OH)₂₇ cluster as the SBU for the topology analysis because many germanates can be described using this SBU without the need of sharing tetrahedra between the SBUs. This will simplify the final design of novel open-framework germanates.

The connectivity of Ge₁₀(O, OH)₂₇ and Ge₇(O, OH, F)₁₉ clusters in the germanates is analyzed. Some common features were found for germanate frameworks with uninodal topologies. This formation allows to limit the number of possible topologies to be used for combinatorial enumeration of novel open-framework germanates and eventually leads to low-energy structure candidates. On the basis of this, models of three hypothetical open-framework germanates with 24 to 32 rings are proposed. We have shown that the combination of topological analysis and data mining is a powerful tool to provide insights into structural chemistry of novel porous compounds.

ASSOCIATED CONTENT

S Supporting Information. Crystallographic files (CIF) of the energy minimized hypothetical germanates structures, structural properties of the simulated ASU-12 germanate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: maxim.peskov@gmail.com (M.V.P.), xzou@mmk.su.se (X.Z.).

ACKNOWLEDGMENT

This project is supported by the Swedish Research Council (VR), the Swedish Governmental Agency for Innovation Systems (VINNOVA) and the Göran Gustafsson Foundation. M.V. P. thanks the Wenner-Gren Foundations for a postdoctoral fellowship and housing supports. We are grateful to Prof. V. A. Blatov for useful comments concerning the manuscript, and A. K. Inge and H. J. Yue for the structure information of SU-62 and SU-67, respectively.

REFERENCES

- (1) Breck, D. W. *Zeolite Molecular Sieves*; Wiley: New York, 1974.
- (2) Chen, N. Y.; Garfield, W. E.; Dwyer, F. G. *Shape Selective Catalysis in Industrial Applications*; Marcel Dekker: New York, 1989.
- (3) *Advanced Zeolite Science and Applications*; Jansen, J. C., Stöcker, M., Karge, H. G., Weitcamp, J., Eds.; Elsevier: Amsterdam, 1994.
- (4) Gandara, F.; Medina, M. E.; Snejko, N.; Gomez-Lor, B.; Iglesias, M.; Gutierrez-Puebla, E.; Monge, M. A. *Inorg. Chem.* **2008**, *47*, 6791–6795.
- (5) Bonneau, C.; Sun, J.; Sanchez-Smith, R.; Guo, B.; Zhang, D.; Inge, A. K.; Eden, M.; Zou, X. *Inorg. Chem.* **2009**, *48*, 9962–9964.
- (6) Lin, Z.-E.; Yang, G.-Y. *Eur. J. Inorg. Chem.* **2010**, *2895–2902*.
- (7) Christensen, K. E. *Cryst. Rev.* **2010**, *16*, 91–104.
- (8) Itani, L.; Liu, Y.; Zhang, W.; Bozhilov, K. N.; Delmotte, L.; Valtchev, V. *J. Am. Chem. Soc.* **2009**, *131*, 10127–10139.
- (9) Rimer, J. D.; Roth, D. D.; Vlachos, D. G.; Lobo, R. F. *Langmuir* **2007**, *23*, 2784–2791.
- (10) Wakihara, T.; Kohara, S.; Sankar, G.; Saito, S.; Sanchez-Sanchez, M.; Overweg, A. R.; Fan, W.; Ogura, M.; Okubo, T. *Phys. Chem. Chem. Phys.* **2006**, *8*, 224–227.
- (11) Christensen, K. E.; Bonneau, C.; Gustafsson, M.; Shi, L.; Sun, J.; Grins, J.; Jansson, K.; Sbille, I.; Su, B.-L.; Zou, X. *J. Am. Chem. Soc.* **2008**, *130*, 3758–3759.
- (12) Baerlocher, C.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*, 6th revised ed.; Elsevier: London, 2007.
- (13) Ferey, G. *J. Solid State Chem.* **2000**, *152*, 37–48.
- (14) Zou, X.; Conradsson, T.; Klingstedt, M.; Dadachov, M. S.; O'Keeffe, M. *Nature* **2005**, *437*, 716–719.
- (15) Pan, Q.; Li, J.; Ren, X.; Wang, Z.; Li, G.; Yu, J.; Xu, R. R. *Chem. Mater.* **2008**, *20*, 370–372.
- (16) Lei, S.; Bonneau, C.; Li, Y.; Sun, J.; Yue, H.; Zou, X. *Cryst. Growth Des.* **2008**, *8*, 3695–3699.
- (17) Roberts, M. A.; Fitch, A. N. Z. *Kristallogr.* **1996**, *211*, 378–387.
- (18) Xu, Y.; Cheng, L.; You, W. *Inorg. Chem.* **2006**, *45*, 7705–7708.
- (19) Zhang, H.-X.; Zhang, J.; Zheng, S.-T.; Yang, G.-Y. *Inorg. Chem.* **2003**, *42*, 6595–6597.
- (20) Medina, M. E.; Gutierrez-Puebla, E.; Monge, M. A.; Snejko, N. *Chem. Commun.* **2004**, 2868–2869.
- (21) Treacy, M. M. J.; Rivin, I.; Balkovsky, E.; Randall, K. H.; Foster, M. D. *Microporous Mesoporous Mater.* **2004**, *74*, 121–132.

- (22) Inorganic Crystal Structure Database (<http://www.fiz-karlsruhe.de/icsd.html>).
- (23) The Cambridge Structural Database (<http://www.ccdc.cam.ac.uk/products/csd/>).
- (24) Blatov, V. A. *IUCr Comput. Commun. Newslett.* **2006**, 4–38.
- (25) Blatov, V. A.; Proserpio, D. M. *Acta Crystallogr.* **2009**, A65, 202–212.
- (26) Blatov, V. A. *Cryst. Rev.* **2004**, 10, 249–318.
- (27) O'Keeffe, M.; Peskov, M.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, 41, 1782–1789.
- (28) Hyde, S. T.; Delgado-Friedrichs, O.; Ramsden, S. J.; Robins, V. *Solid State Sci.* **2006**, 8, 740–752.
- (29) Blatov, V. A.; Delgado-Friedrichs, O.; O'Keeffe, M.; Proserpio, D. M. *Acta Crystallogr.* **2007**, A63, 418–425.
- (30) Materials Studio (<http://accelrys.com/products/materials-studio/>).
- (31) Gale, J. D.; Rohl, A. L. *Mol. Simul.* **2003**, 29, 291–341.
- (32) Lorgouilloux, Y.; Paillaud, J.-L.; Caullet, P.; Bats, N. *Solid State Sci.* **2008**, 10, 12–19.
- (33) Ren, X.; Li, Y.; Pan, Q.; Yu, J.; Xu, R.; Xu, Y. *A. J. Am. Chem. Soc.* **2009**, 131, 14128–14129.
- (34) Guo, B.; Inge, A. K.; Bonneau, C.; Sun, J.; Christensen, K.; Yuan, Z.; Zou, X. *Inorg. Chem.* **2011**, 50, 201–207.
- (35) Blatov, V. A. *Acta Crystallogr.* **2007**, A63, 329–343.
- (36) Liu, G.-Z.; Zhang, H.-X.; Lin, Z.-E.; Zheng, S.-T.; Zhang, J.; Zhao, J.-T.; Wang, G.-M.; Yang, G.-Y. *Chem. Asian J.* **2007**, 2, 1230–1239.
- (37) Plevert, J.; Gentz, T. M.; Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Mater.* **2003**, 15, 714–718.
- (38) Li, H.; Eddaaoudi, M.; Richardson, D. A.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, 120, 8567–8568.
- (39) Plevert, J.; Gentz, T. M.; Laine, A.; Li, H.; Young, V. G.; Yaghi, O. M.; O'Keeffe, M. *J. Am. Chem. Soc.* **2001**, 123, 12706–12707.
- (40) Tang, L.; Dadachov, M. S.; Zou, X. *Chem. Mater.* **2005**, 17, 2530–2536.
- (41) Beitone, L.; Loiseau, T.; Ferey, G. *Inorg. Chem.* **2002**, 41, 3962–3966.
- (42) Pan, Q.; Li, J.; Christensen, K. E.; Bonneau, C.; Ren, X.; Shi, L.; Sun, J.; Zou, X.; Li, G.; Yu, J.; Xu, R. *Angew. Chem., Int. Ed.* **2008**, 120, 7986–7989.
- (43) Villaescusa, L. A.; Wheatley, P. S.; Morris, R. E.; Lightfoot, P. *Dalton Trans.* **2004**, 820–824.
- (44) Christensen, K. E.; Shi, L.; Conradsson, T.; Ren, T.-Z.; Dadachov, M. S.; Zou, X. *J. Am. Chem. Soc.* **2006**, 128, 14238–14239.
- (45) Delgado-Friedrichs, O.; Foster, M. D.; O'Keeffe, M.; Proserpio, D. M.; Treacy, M. M. J.; Yaghi, O. M. *J. Solid State Chem.* **2005**, 178, 2533–2554.
- (46) *Modern Methods of Crystal Structure Prediction*; Oganov, A. R., Ed.; Wiley-VCH: Weinheim, 2011.
- (47) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. *J. Phys. Chem.* **1990**, 94, 8897–8909.
- (48) Hereafter, the RCSR names are used for nets.²⁷
- (49) The net was derived from the RCSR svh net in ref 35 using net–subnet relations.
- (50) Hereafter, refcodes of compounds in CSD database are given.