Coassembly between the Largest and Smallest Metal Chalcogenide Supertetrahedral Clusters

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S *Supporting Information*

ABSTRACT: Reported here is the first crystalline inorganic−organic hybrid material combining In, Ge, and Cu. The trimetallic system undergoes a nanoscale separation into small In−Ge−S supertetrahedral T2 clusters and large In−Cu−S T5 clusters, which are further assembled into a T2−T5 mixed layer. This material reveals the long-range crystallographically ordered assembly from supertetrahedral clusters with 3 orders of difference, the largest size mismatch known so far for mixed-supertetrahedral-cluster materials. Theoretical simulations were performed to probe the contribution to the band structure by the different-sized semiconducting clusters.
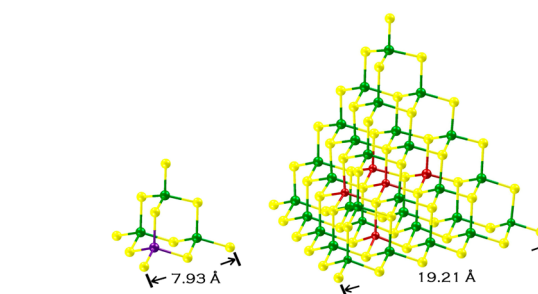
Figure 1. Size difference between the T2 and T5 supertetrahedral clusters. Color code: yellow, S; green, In; purple, In/Ge mixed sites; red, In/Cu mixed sites.

Metal chalcogenides are an important family of materials that have been widely studied for many applications such as catalysis, semiconductivity, photoluminescence, photocatalytic activity, thermoelectric property, and capture of toxic metals.[1−3] Open frameworks built from tetrahedral chalcogenide clusters beautifully represent the bottom-up self-assembly of supramolecular building blocks with precisely defined size and composition[4−11] and are distinctly different from other types of materials such as zeolites and metal−organic frameworks.[12,13] Such metal chalcogenide open frameworks preserve the structural feature of dense-phase semiconductors within a framework of 3D open architectures. As such, they are capable of integrating uniform porosity with various properties.

While different types of chalcogenide clusters are known, the supertetrahedral Tn series of clusters (n is the order of the supertetrahedral clusters and is equal to the number of MX$_4$ tetrahedra along each tetrahedral edge) represent a unique family of tetrahedral clusters whose structures can be described as the exact fragment of a well-known cubic ZnS-type lattice (Figure 1). During the past decade, researchers have synthesized supertetrahedral clusters of various sizes from T2 (e.g., Ge$_4$S$_{10}$$^{4-}$),[6a,b] T3 (e.g., In$_{10}S_{20}$$^{10-}$), T4 (e.g., Cd$_4In_{16}S_{35}$$^{14-}$), to T5 (e.g., Mn$_{13}In_{22}S_{56}$$^{20-}$) with different compositions[3,5] and demonstrated a close correlation between the properties and size/composition of the clusters.

Most framework structures are built from clusters of the same order. For example, supertetrahedral Cd$_4$In$_{16}$S$_{35}$$^{14-}$ T4 clusters are known to cross-link through corner S^{2-} sites to form 2-fold-interpenetrating diamond-type structures,[5] as well as novel structure types such as UCR-1 and UCR-8.[14] In comparison, the structures built from different-sized supertetrahedral clusters are much less known, and the structural

contribution from the nonuniform building blocks to the band structure has rarely been discussed. One interesting example of mixed-Tn-cluster frameworks is a 3D diamond-type framework formed from Ga−S T3 and Zn−Ga−S T4 clusters (the difference in the order of clusters $\Delta n = 1$).[15] The synthesis of framework structures simultaneously possessing different-sized supertetrahedral clusters is highly desirable because it creates additional compositional and structural possibilities that can be utilized to achieve a new level of property engineering.

One of the greatest challenges in the development of structures with multibuilding blocks is the potential phase separation into structures containing only each separate component. It is conceivable that structures with two or more different building blocks would likely aggregate into complicated repeating units that are generally more difficult for molecular recognition and self-repairing processes during crystallization. The growth of herocluster frameworks further faces competition from the formation of many synthetic "default" structures with single-sized clusters, which are well-known as exemplified by the T2-cluster-based structure (e.g., UCR-20),[16a] the T4-cluster-based structure (e.g., CdInS-44),[5] and T5-cluster-based structure (e.g., UCR-16).[16b] Thus, the synthesis of a material with nonuniformly sized building units, instead of macroscopic phase separation into simpler phases, is intellectually fascinating and experimentally challenging.

We recently reported one structure built from T2−T4 clusters (the difference in the order of clusters $\Delta n = 2$).[17] It has a new zeolite-type topology and demonstrates a new possibility for the coexistence of different building blocks in a structure

with topology other than the diamond type by introducing size mismatch in the tetrahedral vertex. In this work, we report the most extreme case known to date in which a two-dimensional (2D) extended framework is constructed from the largest known supertetrahedral cluster (T5) and the smallest supertetrahedral building block (T2, not considering the simplest and ubiquitous T1 unit such as InS_4; the difference in the order of clusters $\Delta n = 3$).

One of the most exceptional structural features of this new material, $[(In_3GeS_7)(Cu_5In_{30}S_{56})]^{18-}[(H_2TMDP)^{2+}]_9$ (denoted as CIS-52, TMDP = 4,4′-trimethylenedipiperidine), is that the largest and smallest supertetrahedral clusters crystallize together within the same lattice. The huge gap between two clusters is as large as 77 atoms in the total number of atoms and 13.8 times the difference in terms of volume (an edge ratio of 2.42 between T5 and T2 gives a volume ratio of $2.42^3 = 13.8$). In this structure, the T2 and T5 clusters are in a 1:1 ratio and connect with each other by sharing a bicoordinated corner sulfur atom. Each T2 cluster is connected to three T5 clusters and vice versa. Three T2 and three T5 clusters are further assembled into a six-membered ring. Notably, the ratio between two cluster building units differs significantly from the previously reported OCF-42, which is composed of T2 and T4 clusters in a 4:1 ratio. Unlike the T2 tetramer aggregates in OCF-42, which could compensate for the size difference between discrete T2 and T4 clusters, the smaller isolated T2 clusters in CIS-52 are evenly dispersed between large T5 clusters, and the resulting large size mismatch leads to a huge void space near the edge and the center of the ring, which approaches 2 nm in diameter (Figure 2). Because these
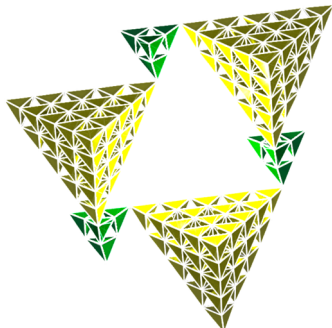

Figure 2. Three T5 and three T2 supertetrahedral clusters assembled into a six-membered ring by sharing sulfur atoms on the corner.

tetrahedral cluster nodes are only 3-connected, the fourth corner sulfur atoms all point in the axial direction to the ring, leading to a 2D honeycomb net. The adjacent layers of these hexagonal nets are further packed in a staggered fashion with dangling corners of the tetrahedron pointing toward each other. (Additional structural diagrams are given in the Supporting Information, SI.)

In the synthetic design of the covalent architecture built from supertetrahedral clusters, the local charge balance, especially surrounding the anionic species (S^{2-} in this case) plays an essential role in defining the size of the cluster. According to Pauling's electrostatic valence sum rule, to balance the local charge of the four-coordinated sulfur atom at the center of the T5 clusters, low-valent metals such as zinc or copper should be employed. In other words, the incorporation of low-valent metal ions into the synthesis promotes the formation of larger clusters. Conversely, to shrink the cluster size, higher-valent

cations such as germanium or tin would be necessary to force the sulfur into the lower coordination numbers, hence promoting the formation of T2 clusters and inhibiting the formation of the larger clusters such as T4 and T5.

In this work, we explored an unprecedented trimetallic sulfide system with three charge-complementary metal species, copper(I), indium(III), and germanium(IV). We can consider In—S as the base system. The introduced copper(I) favors the formation of T5 clusters, while the addition of germanium(IV) assists the growth of T2 clusters. The resulting trimetallic synthetic system undoubtedly possesses much more complexity and flexibility, which can lead to multiple competing crystallization processes in which other competing phases such as UCR-20 and UCR-16 may be formed as well.[16] Indeed, both T2—T2 (UCR-20) and T5—T5 (UCR-16) structures were found to crystallize, together with the targeted T2—T5 with the same amine template (Figure 2).

The synthesis of CIS-52 not only proves that two kinds of clusters with huge differences in terms of size and charge could be assembled together under the templating effect of protonated amine molecules with suitable charge density but also reveals an unusual structure with an unprecedented combination of chemical elements involving copper, indium, and germanium all in one crystal. A search of the Cambridge Structural Data shows that no phase containing copper, indium, and germanium is known. The presence of these different metal ions and their well-refined crystallographic positions is supported by single-crystal X-ray crystallography and energy-dispersive analysis of X-ray emissions (EDAX; Figure S1 in the SI). Our results also show that the different metal ions that may undergo phase separation macroscopically could be brought together first by incorporation into separate clusters and then by further assembly through sulfur bridges. Such a nanoscale separation into crystallographically ordered different-sized clusters seems to promote the coassembly of various components and lessen the chances for macroscopic phase separation.

The creation of the molecular architectures from different-sized building blocks has a general implication in property engineering based on the manipulation of artificial atoms. One interest in this system is whether the material's property is as sensitive to a change in the aggregation modes as to a change in the size of the building block. Therefore, the UV—vis spectrum of CIS-52 was measured from selected single crystals to evaluate its band gap. The measured band gap of 2.2 eV (Figure S2 in the SI) is almost the same as that of the pure T5 structures with a Cu—In—S composition. This shows that, even with the introduction of T2 clusters into the framework, the optical band still possesses T5 character. The corner sulfur atom connecting different clusters as the only channel keeps the electronic states from overlapping between adjacent clusters. Thus, the material tends to exhibit an optical gap that closely resembles that of discrete building units.

We further carried out theoretical calculation to support our findings. Because CIS-52 is the only known structure in the T2—T5 system, we had to build a hypothetical and comparable isostructure that preserves most of the local structural features of CIS-52, with the only difference being in the packing mode but with no change in connections between clusters (i.e., exactly the same components within each supertetrahedral cluster, the same dihedral angles on the bridging sulfur atom, and the same ratio between the T2 and T5 units), as shown in Figure 3. Theoretical simulations for both structures were
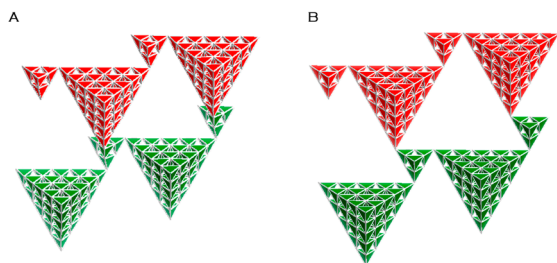
Figure 3. Difference in the stacking mode between supertetrahedral clusters in CIS-52 and its isomer: (A) stacking aggregation in CIS-52; (B) coplanar aggregation of the clusters in the hypothetical isomer.

performed on the same basis set with extended Hückel theory by using a *CAESAR* calculation package.[18,19] The calculated atom positions of the model are listed in Table S1 in the SI. The calculated density of state (DOS) plots (Figures S3 and S4 in the SI) show that, for both structures, the conduction band bottom is dominated by Cu d orbitals, while the valence band is mostly contributed from S p orbitals, which is consistent with our common understanding about semiconductors. However, there is no big difference in the total DOS between two isomers, which indicates that the electronic states in these types of materials are indeed highly localized within the clusters and the state coupling through connecting corners is quite weak. Preserving the local structural feature and yet changing the long-range order, as in this case, by shifting the stacked packing mode to the coplanar packing mode between the T2−T5 chains would not have significant effects on the band structure. This result also indicates the possibility of keeping the electronic properties undisturbed by utilizing the same ratio and size of the cluster building blocks regardless of the difference in the connection mode. In other words, the optical band of the cluster-based materials is highly dependent on its local structural feature (such as size and composition) and not strongly affected by the overall framework topology, which allows for tuning of the porosity and pore geometry while retaining similar optoelectronic properties.

In conclusion, an open-framework architecture composed of the largest and smallest supertetrahedral clusters has been synthesized. Its component complexity indicates that the mixed-building-block strategy could incorporate different metal ions (which are usually distributed in separate phases) into the same lattice by local nanoscale phase separation (instead of macroscopic phase separation into different crystalline phases). The optical gap is determined by the local structures in open-framework chalcogenides, which indicates that property engineering by cluster assembly could possibly orthogonalize the band gap from the structural features such as the coordination number, overall topology, packing density, and other long-range ordering.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, crystal data, EDAX elemental analysis, UV−vis spectrum, and atomic positions of calculated crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Yuhas, B. D.; Smeigh, A. L.; Samuel, A. P. S.; Shim, Y.; Bag, S.; Douvalis, A. P.; Wasielewski, M. R.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2011**, *133*, 7252−7255.

(2) (a) Kaib, T.; Haddadpour, S.; Kapitein, M.; Bron, P.; Schroder, C.; Eckert, H.; Roling, B.; Dehnen, S. *Chem. Mater.* **2012**, *24*, 2211−2219. (b) Lin, Y. M.; Massa, W.; Dehnen, S. *J. Am. Chem. Soc.* **2012**, *134*, 4497−4500. (c) Zhang, Z.; Zhang, J.; Wu, T.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2008**, *130*, 15238.

(3) Zheng, N. F.; Bu, X. H.; Feng, P. Y. *Nature* **2003**, *426*, 428−432.

(4) (a) Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed.* **1991**, *30*, 769−788. (b) Dance, I.; Fisher, K. *Prog. Inorg. Chem.* **1994**, *41*, 637−803.

(5) Li, H. L.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145−1147.

(6) (a) Cahill, C. L.; Parise, J. B. *Chem. Mater.* **1997**, *9*, 807−811. (b) Cahill, C. L.; Gugliotta, B.; Parise, J. B. *Chem. Commun.* **1998**, 1715−1716.

(7) (a) Soloviev, N. V.; Eichhofer, A.; Fenske, D.; Banin, U. *J. Am. Chem. Soc.* **2001**, *123*, 2354−2364. (b) Corrigan, J. F.; Fuhr, O.; Fenske, D. *Adv. Mater.* **2009**, *21*, 1867−1871.

(8) (a) Vaqueiro, P.; Romero, M. L. *J. Phys. Chem. Solids* **2007**, *68*, 1239−1243. (b) Vaqueiro, P.; Romero, M. L. *Chem. Commun.* **2007**, 3282−3284.

(9) (a) Lei, Z. X.; Zhu, Q. Y.; Zhang, X.; Luo, W.; Mu, W. Q.; Dai, J. *Inorg. Chem.* **2010**, *49*, 4385−4387. (b) Wang, Y. H.; Zhang, M. H.; Yan, Y. M.; Bian, G. Q.; Zhu, Q. Y.; Dai, J. *Inorg. Chem.* **2010**, *49*, 9731−9733.

(10) (a) Chen, Z. Y.; Luo, D. B.; Kang, M. P.; Lin, Z. *Inorg. Chem.* **2011**, *50*, 4674−4676. (b) Chen, Z. Y.; Luo, D. B.; Luo, X. C.; Kang, M. P.; Lin, Z. E. *Dalton Trans.* **2012**, *41*, 3942−3944.

(11) (a) Liu, Y.; Kanhere, P. D.; Wong, C. L.; Tian, Y. F.; Feng, Y. H.; Boey, F.; Wu, T.; Chen, H. Y.; White, T. J.; Chen, Z.; Zhang, Q. C. *J. Solid State Chem.* **2010**, *183*, 2644−2649. (b) Liu, Y.; Yu, L. M.; Loo, S. C. J.; Blair, R. G.; Zhang, Q. C. *J. Solid State Chem.* **2012**, *191*, 283−286.

(12) Luo, X. C.; Luo, D. B.; Zeng, H. M.; Gong, M. C.; Chen, Y. Q.; Lin, Z. E. *Inorg. Chem.* **2011**, *50*, 8697−8699.

(13) (a) Zhai, Q. G.; Lin, Q. P.; Wu, T.; Wang, L.; Zheng, S. T.; Bu, X. H.; Feng, P. Y. *Chem. Mater.* **2012**, *24*, 2624−2626. (b) Zhang, H. X.; Wang, F.; Yang, H.; Tan, Y. X.; Zhang, J.; Bu, X. H. *J. Am. Chem. Soc.* **2011**, *133*, 11884−11887. (c) Tan, Y. X.; Wang, F.; Kang, Y.; Zhang, J. A. *Chem. Commun.* **2011**, *47*, 770−772.

(14) (a) Wang, C.; Li, Y. Q.; Bu, X. H.; Zheng, N. F.; Zivkovic, O.; Yang, C. S.; Feng, P. Y. *J. Am. Chem. Soc.* **2001**, *123*, 11506−11507. (b) Bu, X. H.; Zheng, N. F.; Li, Y. Q.; Feng, P. Y. *J. Am. Chem. Soc.* **2003**, *125*, 6024−6025.

(15) Zheng, N.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2003**, *125*, 1138.

(16) (a) Zheng, N. F.; Bu, X. H.; Wang, B.; Feng, P. Y. *Science* **2002**, *298*, 2366−2369. (b) Bu, X. H.; Zheng, N. F.; Li, Y. Q.; Feng, P. Y. *J. Am. Chem. Soc.* **2002**, *124*, 12646−12647.

(17) Wu, T.; Wang, X. Q.; Bu, X. H.; Zhao, X.; Wang, L.; Feng, P. Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 7204−7207.

(18) Ren, J.; Liang, W.; Whangbo, M.-H. Crystal and Electronic Structure Analysis Using *CAESAR*, 1998, http://www.PrimeC.com/

(19) Crystallographic data for CIS-52: $[(In_3GeS_7)(Cu_5In_{30}S_{56})]^{18-}[(H_2TMDP)^{2+}]_9$, triclinic $P\bar{1}$, a = 21.3738(4) Å, b = 23.9400(5) Å, c = 29.1969(5) Å, α = 72.211(1)°, β = 68.980(1)°, γ = 64.472(1)°, V = 12379.8 Å³, Z = 1, T = 296 K, $2\theta_{max}$ = 45.52°, $R(F)$ = 5.71% for 1056 parameters and 9353 reflections with $I > 2\sigma(I)$.