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A crown-like heterometallic unit as the building block for a 3D In–Ge–S framework†

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Supertetrahedral clusters are the most common building blocks in constructing Group 13/14/16 microporous metal chalcogenide materials while other types of clusters are yet scarcely explored. Herein, a new crown-like building unit [In₃Ge₃S₁₆] has been obtained. The units assemble into a 3D framework [C₆H₁₄NO]₄-[In₆Ge₃S₁₇]·1.5H₂O (1) *via* a dual-connection mode and a SrSi₂ (srs)-type topology could be achieved by treating each unit as a tri-connected node.

Possessing both the semiconducting properties of metal chalcogenides and the microporous characteristics of traditional zeolites, microporous metal chalcogenide materials have extensive potential practical applications in fields such as fast-ion conductivity, ion exchange, photocatalysts, and nonlinear optical response.[1–7] Currently, the exploration of new porous structured materials coupled with practical applications remains a sustained impetus to the researchers working in this field.

The synthesis of such kinds of materials was initially achieved in Group 15 metal sulfide semiconductors, *e.g.*, the Sb–S system. Due to the presence of one lone electron pair in their orbitals, Group 15 (As, Sb) elements tend to form an anionic pyramidal MQ_3^{3-} (M = As or Sb, Q = S or Se) subunit instead of tetrahedral MQ_4^{3-} ones.[8–11] Such a tendency could be altered for Group 13 and 14 metal chalcogenides since the suitable ionic radius ratio of metal cations to chalcogen anions as well as the flexible angle of M–Q–M (M = metal cation, Q = chalcogen anion) allow the formation of a tetrahedral coordination mode surrounding each metal cation. It was due to the discovery of adamantine structures in Group 13 or 14 metal sulfides that the research boom in this sub-disciplin-

ary of microporous materials was triggered. The most distinctive feature of the structure was the formation of supertetrahedral secondary building units (SBUs) including *e.g.* Tn, Cn, Pn and Tp,q. These clusters can serve as structural building blocks to construct multidimensional inorganic or hybrid organic–inorganic frameworks through modular assembly processes.[12–23] The incorporation of lower charge metal cations (*e.g.* Cu^+, Mn^{2+}, Co^{2+}, Fe^{2+}, Zn^{2+}, Cd^{2+}) into these supertetrahedral clusters can effectively tune their size, composition and corresponding physical properties, and have been well documented in the literature.[24–26]

In this work, we report a crown-like heterometallic unit [In₃Ge₃S₁₆] which differs from the traditional supertetrahedral clusters in Group 13 and 14 metal chalcogenide systems. This uncommon unit displays a three-connected linkage mode and can assemble into a three dimensional (3D) anionic framework [In₆Ge₃S₁₇]⁴⁻ (**1a**) *via* a dually connected mode. The structural motif represented by **1** is unique among open framework chalcogenides, it also represents the first example of a three-connected metal–chalcogenide network in the $M^{3+}/M^{4+}/Q^{2-}$ system. Herein, the synthesis, crystal structure characterization, and optical property of this compound are presented.

Compound **1** was hydrothermally synthesized from the reaction of elemental In, Ge and S in the presence of *cis*-2,6-dimethylmorpholine (C₆H₁₃NO) as the template (for details, see the ESI†). Crystal structural analysis revealed that compound **1** crystallizes in the cubic space group $I2_13$. As shown in Fig. 1, there are two crystallographically distinct metal sites (In and Ge) and each of them is coordinated with four S atoms. The S atoms take either a bi- or tri-coordination mode in this compound. For the bi-coordination S atoms, S3 bridges two adjacent In atoms while S1 and S4 connect In and Ge atoms. The tri-coordination S2 atom coordinates to three In atoms. The bond lengths of In–S and Ge–S lie in the range of 2.416(2)–2.4932(8) Å and 2.192(2)–2.204(2) Å, respectively. The bond angles of S–In–S and S–Ge–S are in the range of 97.06(8)–116.30(8)° and 105.98(8)–113.22(13)°, suggesting that both InS₄ and GeS₄ tetrahedra are slightly distorted. All these values agree well with those reported previously.[27–30]

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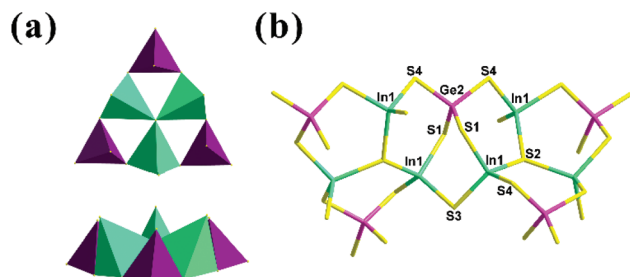
Fig. 1 (a) Different side-views of the crown-like anionic unit. Green tetrahedron stands for InS_4 and purple tetrahedron for GeS_4. (b) Dually connected fashion between two adjacent crown-like units.

When assembled into infinite structures, both InS_4 and GeS_4 tetrahedra share their neighboring tetrahedra *via* the vertex S atoms. Each GeS_4 tetrahedron is connected to four InS_4 tetrahedra while each InS_4 is connected to two GeS_4 and three other InS_4 tetrahedra (Fig. 1b). InS_4 has one more connection than GeS_4 because of the presence of the μ_3-S atom (S2), which unlikely coordinates with +4 metallic cations to avoid the violation of the traditional Pauling's rule. Such a scenario has been observed in previous supertetrahedral Tn ($n > 2$) clusters. To simplify, a crown-like repeating unit of $[In_3Ge_3S_{16}]$ in constructing the final three-dimensional framework could be extracted and each such unit is connected to its three neighboring units *via* sharing three GeS_4 tetrahedra and three bi-coordinated vertex sulfur atoms (S3).

For the repeating unit of $[In_3Ge_3S_{16}]$, all six metallic sites do not reside in the same plane due to the different distortion degrees of the two MS_4 (M = In or Ge) tetrahedra. By connecting the three corner Ge atoms and the three inner In atoms, respectively, one Ge and one In planes would be formed. The two metallic planes are parallel to each other and the distance between the two planes is about 0.6157 Å. The μ_3-S atom, as the joint of the three In atoms, resides away from the Ge plane with a distance of 1.0371 Å. The atomic arrangement of the six metal sites and this μ_3-S atom gives a crown-like unit. The repeating unit also resembles one of the four faces in the T3 cluster, but in which all six metal sites and the μ_3-chalcogen atom are almost in the same plane. Such a difference might originate from the more severe distortions of the two MS_4 tetrahedra in this crown-like unit.

The repeating unit can also be viewed as a cluster built up from one trinuclear $In_3S(S_{1/2})_9$ unit and three $Ge(S_{1/2})_4$ tetrahedra. This structural motif resembles that of $(NH_4)_4In_{12}Se_{20}$, which is a nona-nuclear cluster that is built up from the interconnections of one tri-nuclear $[In_3Se(Se_{1/2})_6(Se_{1/3})_3]$ unit and three binuclear $[In_2Se_{1/3}(Se_{1/2})_6]$ units.[31] For the two tri-nuclear units, three In atoms coordinate with 10 chalcogen atoms. However the reported structure has three more μ_3-chalcogen atoms because it is connected to binuclear units instead of simple tetrahedral units. Despite the difference in cluster composition and size, both the crown-like $[In_3Ge_3S_{16}]$ unit and the nona-nuclear unit in $(NH_4)_4In_{12}Se_{20}$ feature unusual non-Tn

clusters in hybrid group 13 and 14 metal chalcogenide microporous structures.

Each crown-like $[In_3Ge_3S_{16}]$ unit serves as a tri-coordinated block and the adjacent units are connected together *via* sharing the $Ge(2)S_4$ tetrahedron to assemble into a three dimensional framework. Besides GeS_4, one of the bi-coordination S atoms (S3) is also involved in bridging adjacent units. Prior to this, only one type of the three-connected network was achieved in the microporous metal chalcogenide system built from the asymmetric $[SbQ_3]^{3-}$ pyramid and one-apex-protonated T2 cluster $[In_4S_9SH]^{3-}$.[32] However, for Group 13 and 14 elements in the tetra-coordination mode, this trigonal-planar coordination geometry is uncommon. More impressively, omitting the Ge atoms from the crown-like unit, the tri-nuclear clusters themselves can covalently interconnect into a 3D framework *via* the bridging S3 atoms (Fig. S2 and S3, ESI†). The incorporation of Ge^{4+} can further stabilize the In–S framework and the final anionic framework $[In_6Ge_3S_{17}]^{4-}$ is yielded.

In this 3D non-Tn cluster based anionic framework, channels are identical along *a*, *b* and *c* axes and the one along *c* is illustrated in Fig. 2. Taking the van der Waals radius of atoms into account, the aperture cross section of the channels is *ca.* 13.95×8.60 Å^2. Along the [1 1 1] projection, another approximate triangular helical channel with a size of *ca.* 15.04 Å could be also observed as shown in Fig. 3. By treating each unit as a conceptually tri-connected node, a SrSi$_2$ (srs)-type topology with a point symbol of $\{10^3\}$ (Fig. 4) could be achieved. Although all framework atoms of **1** can be unambiguously determined, extra-framework guest molecules in the cavities are disordered and could not be precisely located. This is similar to those found in other open frameworks constructed from chalcogenide clusters.[23,33] The final formula is calculated from the TGA combined with elemental analysis data. Approximately 64.0% of the crystal volume is occupied by these
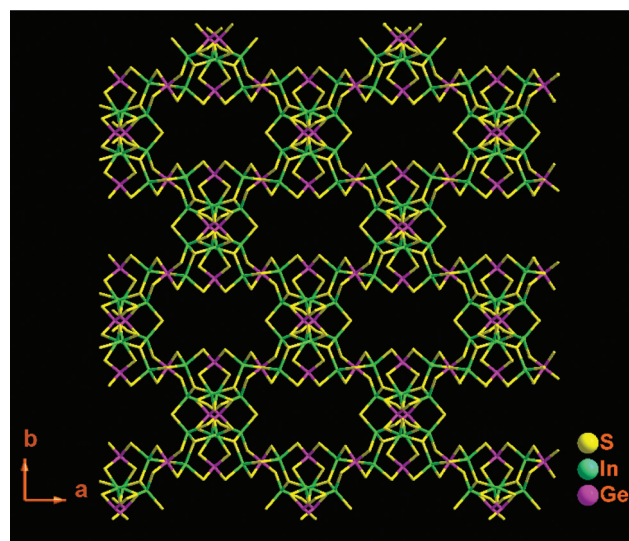

Fig. 2 View of the 3D anionic framework of compound **1** along the *c* axis.
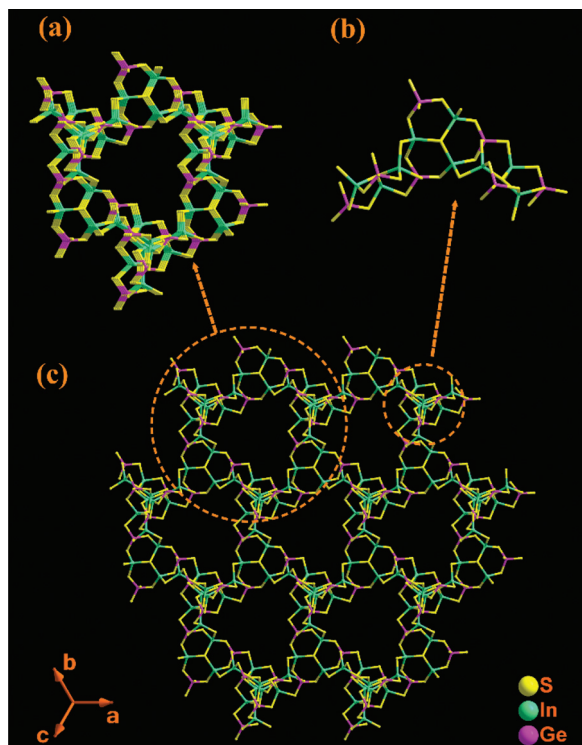
Fig. 3 (a) View of the one dimensional (1D) triangle channel of compound **1** along the [1 1 1] projection. (b) The connection mode of a trimer in a triangle pore. (c) View of the 3D anionic framework of compound **1** along the [1 1 1] projection.
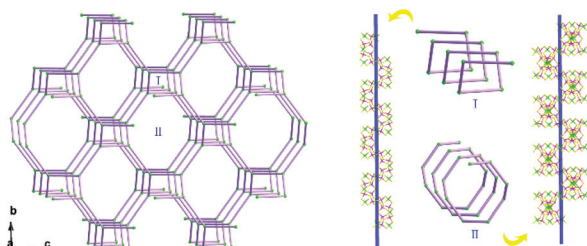

Fig. 4 View of a 3-connected topology with a srs topology for the anionic framework of compound **1**. Corner linking through sulfur atoms is shown as a straight line, green node stands for a repeating unit.

disordered extra-framework molecules as calculated by PLATON software.[34]

The optical properties of compound **1** were investigated by the solid-state diffuse-reflectance UV/Vis/NIR spectroscopy at room temperature using $BaSO_4$ powder as the 100% reflectance reference. The band gap of the compound **1** is estimated to be 2.98 eV as calculated from the reflectance data by using the Kubelka–Munk function.[35] Previous research on In/Ge/S microporous materials was mainly focused on their structural diversity and thermal stability, but not their opto-electrical properties. As a hybrid material, compared with its two binary ancestors of GeS_2 and In_2S_3, compound **1** exhibits

red and blue shifts to GeS_2 (3.2 eV)[36] and In_2S_3 (2.3 eV)[37] respectively. This value is comparable to some thiogermanates, (*e.g.*, [Mn(en)$_2$]MnGeS$_4$ (2.98 eV),[38] (CP)$_2$In$_{1.3}$Ge$_4$S$_{11}$ (2.97 eV),[39] $K_2PbGe_2S_6$ (2.85 eV)[40] and some thioindates ([In$_{40}$S$_{66}$(H$_2$O)$_8$]$^{12-}$–DBU (2.95 eV),[41] [In$_{12}$S$_{24}$H$_2$]$^{10-}$–TMDPH (3.1 eV)[42]). The variation of an absorption edge among the title compound, the bulk binaries, the thiogermanates and thioindates provides a good example of tuning their band gaps through varying their compositions and structures.

Conclusions

In summary, a new porous metal sulfide anionic open-framework with a formula of $[In_6Ge_3S_{17}]^{4-}$ is synthesized using *cis*-2,6-dimethylmorpholine as a template by a solvothermal method. Group 13 and 14 elements (Ga, In, Ge, Sn) are apt to form supertetrahedral clusters, other types of clusters are rare. To the best of our knowledge, a crown-like $[In_3Ge_3S_{16}]$ unit in **1** has never been observed before. Compound **1** is the first example of a three-connected metal–chalcogenide framework in $In^{3+}/Ge^{4+}/Q^{2-}$ (Q = S, Se and Te). This also corroborates that a heterometallic chalcogenide open-framework in this system can be formed in the absence of regular tetrahedral clusters.

Acknowledgements

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