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## COMMUNICATION

## A hybrid linkage mode between T2,2 and T3 selenide clusters

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**A multi-level 3D selenide framework in In<sup>3+</sup>/Ge<sup>4+</sup> system was synthesized. The interconnection between super-supertetrahedral T2,2 and supertetrahedral T3 clusters via their terminal Se<sup>2-</sup> leads to a previously unknown hybrid T2,2-T3 linkage mode. The synthetic realization of this material represents another new level of complexity and demonstrates the versatility in the construction and property-engineering of cluster-based semiconducting materials.**

Differing from crystalline zeolites built from inorganic oxides and lately developed coordination polymers (or metal-organic frameworks, MOFs) constructed from metallic nodes and organic spacers,<sup>1</sup> the most distinct feature of microporous metal chalcogenides is the integration of the porosity with their intrinsic semiconductivity. Such feature makes this unique family practically or potentially useful in extensive applications.<sup>2</sup> Most of their properties including electric and thermal conductivities, ion exchange capacity, photoelectrochemical and non-linear optical properties, photocatalytic activity, and so on are dependent on the constituent elements, the size of the cluster and even the organic amino or inorganic cation template. For instance, the band-gap of a specific structure can be adjusted by replacing either or both of the metallic or/and non-metallic elements in the inorganic framework. The thermal conductivity could be reduced by introducing heavier elements in the framework coupled with judicious selection of template, acting as rattling factor, in the void. To fulfil the real applications of this kind of materials, unremitting efforts should be made on their synthesis and the optimization of their properties.

Many microporous metal chalcogenides are built up from the self-assemblings of nanosized clusters that have precisely defined sizes and compositions. These nanosized clusters could be viewed as semiconducting quantum dots and serve as model systems for traditional less-well-defined colloidal nanoparticles. Therefore the properties of these non-oxide-based microporous materials can be engineered on the basis of the cluster size and composition, as well as the inter-cluster connectivity. Many known chalcogenide clusters such as Tn, Cn, Pn have been used for constructing three dimensional microporous structures,<sup>3</sup> and Tn clusters have been mostly investigated among them. For Tn clusters, they can be viewed as partial fractures of a cubic zinc blende type lattice having

four terminal chalcogen elements, typically sulfur and selenium, and are constituted of n layers of metal elements alternated by n+1 layers of chalcogen elements. So far, Tn (n = 2~5) clusters with different compositions and various sizes have been achieved<sup>3a-d</sup> and a general strategy is the combination of group 13 and 14 metallic cations such as Ga<sup>3+</sup>, In<sup>3+</sup>, Ge<sup>4+</sup> and Sn<sup>4+</sup> and low-valence transition metal cations with the presence of chalcogen elements in alkaline solutions under hydro-/solvothetical conditions.<sup>3b-d</sup>

Tn clusters can exist as isolated clusters in solutions, form neutral molecular (0D) or assemble into one-, two and three-dimensions (3D).<sup>4</sup> When assembling into high dimensional structures, both single-sized clusters and clusters with different sizes could be involved. In these cases, metal cations, organic ligands and chalcogen anions with different coordination mode (bi-, tri-, tetra-coordination chalcogen anion and even poly-sulfur chains) could serve as the linking agents between or among adjacent Tn clusters.<sup>4f,5</sup> If two or more kinds of Tn clusters were connected, hybrid supertetrahedral structures could be achieved and offer a better tuning of their properties as a result of the increases of the diversity and complexity for these materials. We recently summarized the combinations between different Tn (n=2-5) clusters and filled a T2-T3 connection mode into the six possible modes.<sup>5e,6</sup>

Besides assembling into high dimensional structures, four Tn clusters can also form super-supertetrahedral (Tp,q) clusters that can further assemble into high dimensional structures. Such open hierarchical clusters resemble traditional T2n clusters except with missing central atoms. To date, three examples have been realized in group IIIA and IVA sulfide system including T2,2, T4,2 and T5,2.<sup>5d,7</sup> The resultant pseudo T2 supertetrahedral clusters were linked via bicoordinate terminal S atom for the first two cases while, in the T5,2 cluster, unusual tetracoordinate sulfur atoms were presented in forming infinite 3D framework. Recently, Feng et al. reported a three-level of structural hierarchy in super-supertetrahedral T6-like tin oxyselenide cluster, in which the SnSe<sub>4</sub> tetrahedron, T3-[Sn<sub>10</sub>O<sub>4</sub>Se<sub>20</sub>] cluster and super-supertetrahedral cluster consisted of four T3-[Sn<sub>10</sub>O<sub>4</sub>Se<sub>20</sub>] clusters are defined as primary, secondary and tertiary building units.<sup>8</sup> This discovery is by far the only selenide example in super-supertetrahedral cluster beyond sulfide system. In forming tertiary building unit from secondary T3-[Sn<sub>10</sub>O<sub>4</sub>Se<sub>20</sub>] clusters, the edge bridges are the mixture of five bicoordinate Se<sup>2-</sup> and one dimeric [Sn<sub>2</sub>Se<sub>6</sub>]<sup>4-</sup>. Each tertiary

building unit, the T6-like tin oxyselenide cluster, coordinates with its four neighbouring clusters via a corner Se atom to form a staggered 2D square lattice.

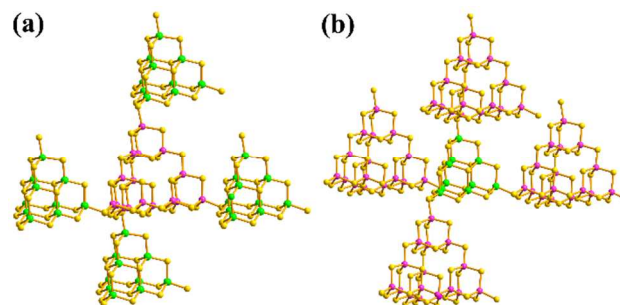
In the work reported herein, a new metal selenide multi-hierarchical microporous material constructed from hybrid clusters has been experimentally realized in a  $M^{3+}/M^{4+}/Se^{2-}$  system. Instead of forming separated phase, this compound integrates both T2 and T3 clusters in the same crystal. The inorganic anionic framework consists of a T2,2 and normal T3 clusters. This finding represents the first known super-supertetrahedral (Tp,q) cluster coexisting with other cluster in the same lattice by sharing bridge  $Se^{2-}$  and also reveals a new linkage mode denoted as T2,2–T3 in the cluster-based chalcogenides. Furthermore, compared with traditional sulfide based microporous metal chalcogenides, the development of selenide or even telluride analogues could yield semiconducting microporous materials with narrower band gap, higher electrical conductivity and lower thermal conductivity that might find applications in photocatalytic, thermoelectric and so on. However, it still remains challenging to prepare such materials due to the strong tendency for metal selenide and telluride to form non-cluster-based structures as much less supertetrahedral examples are known.<sup>3a;6b;8-9</sup>

Compound **1** was hydrothermally obtained by the reaction of elemental Ge, In and Se using piperazine (PPZ) as the traditional amine template with the presence of water at 180 °C (for details, see ESI†). An X-ray diffraction study performed on a single-crystal isolated from the reaction product reveals that compound **1** crystallizes in a tetragonal space group  $I4_1/a$ . Compound **1** features 3-D anionic framework in a new structural motif constructed from super-supertetrahedral T2,2 and supertetrahedral T3 clusters.

The T3 cluster in this structure is a regular fragment of the cubic zinc blende type lattice and comprised of ten In and twenty selenium atoms and has a formula of  $[In_{10}Se_{20}]^{6-}$ . The coordination environment for the two kinds of atoms resemble those in previous reported T3 cluster<sup>3a</sup> and follow the local charge balance theory. The ten metallic sites are four-coordinated by selenium atoms. For the twenty selenium sites, four tri-coordinated  $Se^{2-}$  atoms centre the four faces of the supertetrahedron, twelve bi-coordinated  $Se^{2-}$  atoms locate on the six edges of the supertetrahedron and the rest four occupy the terminal sites. Since each terminal  $Se^{2-}$  bridge connects adjacent T2,2 and T3 clusters, the overall T3 formula is  $[In_{10}Se_{18}]^{6-}$ . Compared with the individual T3 cluster (2.554(2) Å) obtained from the same amine template,<sup>3a</sup> the bond length of the four terminal In–Se, reported here (2.560(3) Å) is slightly longer. The corresponding bond lengths between In and  $\mu_2$ -Se or  $\mu_3$ -Se within the T3 cluster of **1** range from 2.519(3) to 2.575(3) Å and 2.611(3) to 2.622(3) Å respectively and the bond angles of Se–In–Se are between 97.02(9)–117.15(10)°, which are all comparable with reported values.

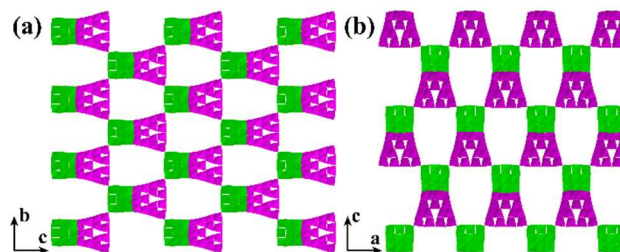
Both  $In^{3+}$  and  $Ge^{4+}$  cations are involved in forming typical T2 cluster ( $M_4Se_{10}$ ), which is condensed from four  $MSe_4$  tetrahedral (denoted as T1 cluster) primary building unit through corner-sharing selenium atoms. The metal positions are randomly occupied by Ge and In simultaneously which is similar to previous cases.<sup>7a</sup> The four T2 clusters sharing six corner selenium atoms further construct a new supertetrahedron named as T2,2 super-supertetrahedron, in which each T2 could be entirely treated as an artificial vertex atom in new supertetrahedron. In such multi-hierarchical supertetrahedron, all metal cations and chalcogen anions still have a tetrahedral coordination and a bicoordination mode, respectively. The terminal M–Se<sub>t</sub> length is 2.529(3) Å; twelve M–Se<sub>b</sub> lengths sited in a T2 cluster are in the range of 2.452(3)–2.555(3) Å; the other M–Se<sub>b</sub> lengths bridged the two neighbouring T2 clusters are between 2.466(3) to 2.501(3) Å. The bond angles of Se–M–Se are between 97.68(9)–116.35(11)°, which indicates T2 cluster is a litter distorted. The formed T2,2 super-supertetrahedron is nearly regular with the

dimensional sizes of six edges *ca.* 15.606 Å (×4) and 16.118 Å (×2) as measured between corner selenium atom sites. These values are comparable to the lateral dimensional sizes of OCF-5-ZnGaSnSe-2-MPR (15.227 Å (×4) and 15.619 Å (×2)), the largest selenide T4 cluster.<sup>3d</sup>



**Fig. 1** The connectivity of T2,2 and T3 clusters in compound **1**. Each T2,2 cluster is corner-shared to four T2-2 clusters (a) and vice versa (b). A yellow ball stands for Se, light green for In and purple for Ge–In mixed sites.

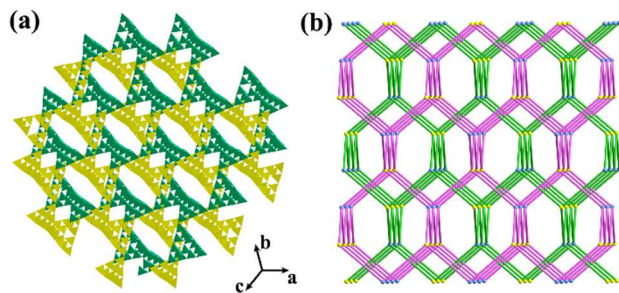
Unlink the connection mode between T2 and oxy-T3 cluster with a 1:1 ratio we reported previously,<sup>6a</sup> herein presented new linkage of T2 and regular T3 exhibits an unequal 4:1 ratio. In this structure, each T3 cluster is connected to four T2 clusters and each T2 cluster is corner-shared to three T2 and one T3 cluster (Fig. S2 in the ESI†), then four adjacent T2 clusters form a T2,2 cluster. Each T2,2 cluster is connected to four T3 clusters via terminal selenide atoms and vice versa (Fig. 1). The centre-to-centre distance between T2,2 and T3 is 14.38 Å. This alternating corner shared T2,2 and T3 clusters give rise to the formation of windows with 6-membered rings containing 21T atoms and then further generate a 3D covalent superlattice framework with an equal 1:1 ratio. The interconnection of the T2,2 and T3 units leads to two interpenetrating open frameworks with 1D triangle channels. The dimensional sizes of one edge of these triangle channel along a-axis and b-axis in the single net are both approximately 25.1 Å (Fig. 2). After interpenetrating, the dimensions of the channels changed to approximately 21.3 × 7 Å along [1 1 1] direction (Fig. 3a). By treating the supertetrahedral clusters as pseudo-tetrahedral atoms, the 3D frameworks of the chalcogenides can be simplified into very simple structure types. Hitherto, there are twelve 3D topological types realized from the assembly of this kind of clusters.<sup>2b; c; 5c; e; 6a; b; 7a; 10</sup> For compound **1**, its overall topology adopts the common double diamond lattice type in this system, similar to those of single-sized regular T3 cluster and hybrid T4-T3 cluster based structures. The observed 3D 2-fold interpenetration mode is shown in Fig 3b.



**Fig. 2** Polyhedral representation of the three-dimensional structure of the compound **1** viewed along a (a) and b-axis (b), with only one set of superlattice is shown for clarity. Green stands for T3, purple for T2,2 clusters.

Similar to other cluster-based chalcogenide structures, the extra-framework guest species (protonated amine molecules) are disordered within the large cavities and their atomic positions cannot

be determined exactly. These guest species occupy approximately 56.1% of the crystal volume as calculated by using the PLATON software<sup>11</sup> which reveals the framework is still highly open even with the formation of two interpenetrating lattices.



**Fig. 3** Two interpenetrating diamond lattices (olive and dark green) and channels (along [1 1 1] projection); (b) simplified 2-fold interpenetrating framework with dia topology (view in *ac*-plane). Corner linking through selenium atoms is shown as a straight line, bluish-violet node stands for T2,2 and yellow for T3 cluster.

The optical absorption data calculated from the reflectance data by using the Kubelka-Munk function show that compound **1** has an absorption onset at about 582 nm, corresponding to a band gap of 2.13 eV (Fig. S11, ESI†). The data further indicate that the material retains the semiconducting property of the corresponding pure inorganic dense phase.

In conclusion, a new 3D metal selenide microporous material with structural linking between semiconducting Tp,q and Tn clusters has been hydrothermally synthesized in In<sup>3+</sup>/Ge<sup>4+</sup> system. The inorganic anionic framework consists of a T2,2 and normal T3 clusters. This cluster connection through T2,2 and T3 clusters represents a new level of complexity in the supertetrahedral cluster-based system. Compared to previous reported architectures, this work shows the first case of framework containing both Tp,q and Tn clusters. This synthetic realization indicates that the “hybrid building block strategy” could fabricate new microporous semiconducting materials. It is also hypothesized that other formation of multi-sized clusters containing other Tp,q clusters such as T4,2, T3,2 may be possible in a proper synthetic condition.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Supplementary structural figures, experimental details, EDS spectra, PXRD, TGA curve and solid-state UV/Vis spectroscopy. CCDC 1033513. For ESI and crystallographic data in CIF see DOI: 10.1039/c000000x/

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