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**Solid-State Structures**

# Synthetic Control of Selenide Supertetrahedral Clusters and Three-Dimensional Co-assembly by Charge-Complementary Metal Cations**

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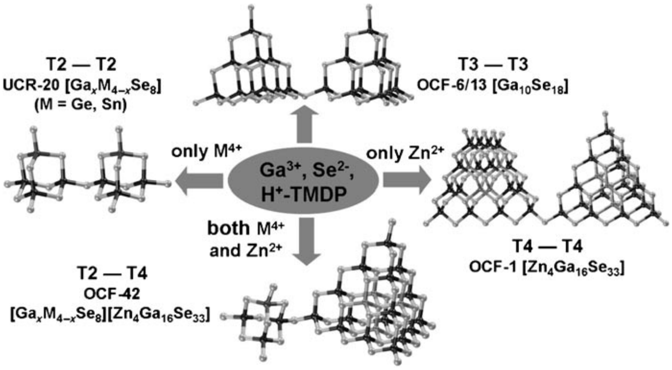
Crystalline metal chalcogenides are an important family of semiconductors that have practical or potential applications in multiple areas such as photocatalysis[1] and thermoelectrics.[2] In recent years, research on crystalline porous chalcogenides has received increasing attention because the integration of open-framework architecture and semiconducting properties could lead to multifunctional materials such as high-surface-area photocatalysts and photoelectrodes.[3,4] Furthermore, the basic structural building blocks of open-framework chalcogenides are often nanosized tetrahedral clusters that can be considered as the smallest possible semiconductor quantum dots.[5–10] Indeed quantum confinement effects have been found in such clusters.[11]

In the synthetic design of supertetrahedral clusters and their porous covalent superlattices, it has been recognized that the charge of tetrahedral metallic cations plays a key role in the determination of the cluster size.[10a,12] This is primarily because there are specific requirements for the local charge balance surrounding chalcogenide anions ($X^{2-}$, such as $S^{2-}$ or $Se^{2-}$). To form the core of large supertetrahedral clusters such as T4 and T5 clusters (e.g., T4-$[Zn_4In_{16}S_{33}]^{10-}$ and T5-$[Cu_5In_{30}S_{54}]^{13-}$), tetrahedrally coordinated $X^{2-}$ sites (in the form of $M_4X$, called anti-T1 supertetrahedral cluster) are essential. Highly charged metal cations such as $Ge^{4+}$ and $Sn^{4+}$ are known to suppress the growth of the large clusters because of their inability to form $Sn_4S^{14+}$ or $Ge_4S^{14+}$ units. In comparison, low-charged metal cations such as $Zn^{2+}$ and $Cu^+$ promote the formation of core tetrahedral $X^{2-}$ sites (e.g., $Zn_4S^{6+}$), leading to large supertetrahedral clusters (T4 or bigger).

By utilizing the above local-charge-balance principle, two distinct synthetic strategies have been developed to create open-framework chalcogenides with clusters of different sizes. The first one is based on the combination of tri- and divalent metal cations (such as $In^{3+}/Zn^{2+}$) or alternatively tri- and monovalent cations (such as $In^{3+}/Cu^+$).[8d,12] This strategy has allowed the synthesis of a series of open-framework chalcogenides containing large supertetrahedral clusters such as T4 and T5 clusters.

The second strategy is to mimic Al/Si/O zeolite compositions. By combining tetra- and trivalent cations ($M^{4+}/M^{3+}/X^{2-}$, $M^{4+} = Ge^{4+}$ or $Sn^{4+}$, $M^{3+} = Ga^{3+}$ or $In^{3+}$; $X^{2-} = S^{2-}$ or $Se^{2-}$), a family of crystalline porous semiconducting chalcogenide zeolite analogues have been made.[13] These porous chalcogenides contain only T2 clusters. The T2 cluster ($M_4X_8$) is different from larger clusters because all anionic sites in T2 are bicoordinated between two tetrahedral metal sites, an essential feature of $MX_2$ zeolite topologies. In comparison, T3 clusters contain tricoordinated $X^{2-}$ sites and T4 or larger clusters contain both tri- and tetracoordinated $X^{2-}$ sites.

The above two synthetic strategies can be unified by using trivalent chalcogenide compositions (e.g., Ga/Se, Scheme 1) as a starting point. The $M^{3+}/X^{2-}$ system normally allows the synthesis of binary T3 clusters such as $[In_{10}S_{20}]^{10-}$. The incorporation of lower-valent $M^{2+}$ or $Cu^+$ cations leads to the growth of the $M_4S$ core and larger ternary $M^{3+}/M^{2+}/X^{2-}$ (or $M^{3+}/M^+/X^{2-}$) clusters, whereas the addition of $M^{4+}$ cations suppresses the formation of both tri- and tetracoordinated $X^{2-}$ sites, leading to the formation of ternary $M^{4+}/M^{3+}/X^{2-}$ T2 clusters with bicoordinated $X^{2-}$ sites only.



**Scheme 1.** Four different strategies to create supertetrahedral clusters and their co-assemblies through charge-complementary metal cations with different oxidization states. $H^+$-TMDP is protonated 4,4′-trimethylene-dipiperidine.

In seeking to develop new synthetic strategies to create new chalcogenide open-framework materials, we hypothesized that if we combine all three charge-complementary metal cations ($M^{4+}/M^{3+}/M^{2+}$ or $M^{4+}/M^{3+}/M^+$), we might be

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able to create a new system in which both zeolite $AX_2$-type building units (e.g., T2 clusters with ternary $M^{4+}/M^{3+}/X^{2-}$ compositions) and large supertetrahedral clusters (T4, T5 or larger clusters with ternary $M^{3+}/M^{2+}/X^{2-}$ or $M^{3+}/M^{+}/X^{2-}$ compositions) can coexist. Then, by using the amine-templating strategy, these two types of clusters might be able to co-assemble into a new family of open-framework chalcogenides with unprecedented quaternary compositions and unusual topological features (Scheme 1). Such materials may lie between four-connected zeolite-type $MX_2$ frameworks and 3D superlattices of nanoclusters, which would also provide a new path towards the control of electronic, optical, and electrooptic properties of the resulting materials because of the increased diversity and complexity in chemical compositions, cluster sizes, and their patterns of organization.

Herein we report two new isostructural 3D open-framework selenides (denoted as OCF-42-ZnGaGeSe-TMDP and OCF-42-ZnGaSnSe-TMDP) that illustrate the feasibility of this synthetic strategy. It is worth noting that even though significant progress has been made in sulfides, very few 3D open-framework selenides are known.[14] To our knowledge, no 3D quaternary open-framework chalcogenides based on supertetrahedral clusters were known prior to this work, although an example of an isolated quaternary T3 cluster was reported recently.[15] Considering that chalcogenide structures built from ternary (e.g., $M^{4+}/M^{3+}/Se^{2-}$, $M^{3+}/M^{2+}/Se^{2-}$) or binary (e.g., $In^{3+}/Se^{2-}$, $Ga^{3+}/Se^{2-}$) selenide clusters are well known, it is unusual that quaternary phases are formed in our system, rather than macroscopic phase separation into compositionally simpler selenides.

Crystal structures were determined from single-crystal X-ray diffraction.[16] One of the most unusual features of the OCF-42 structures is their quaternary composition integrating three charge-complementary metal cations (Zn, Ga, Ge or Sn). The 3D open framework of the OCF-42 structures is composed of $M^{4+}/Ga^{3+}/Se^{2-}$ T2 and $Ga^{3+}/Zn^{2+}/Se^{2-}$ T4 supertetrahedral clusters. In both clusters, all metal sites are four-coordinate. For $M^{4+}/M^{3+}/Se^{2-}$ T2 clusters, all $Se^{2-}$ sites are bicoordinated, similar to $O^{2-}$ in zeolites. In comparison, in $M^{3+}/M^{2+}/Se^{2-}$ T4 clusters, in addition to 18 bicoordinated $Se^{2-}$ sites on six edges, there are also 12 tricoordinated $Se^{2-}$ ions on four faces, and one tetrahedral $Se^{2-}$ at the core of the T4 supertetrahedron. To satisfy Pauling's electrostatic valence rule, the central tetrahedral $Se^{2-}$ site is surrounded by four zinc ions to give a bond valence sum of $+2$, which is consistent with the valence of $Se^{2-}$.

The $M^{4+}/M^{3+}/Se^{2-}$ T2 clusters and $M^{3+}/M^{2+}/Se^{2-}$ T4 clusters have been reported previously; what is unprecedented in the OCF-42 compounds is their uniform and nanoscale integration. One of the greatest challenges in developing multinary compositions is the potential phase separation into simpler compositions such as ternary (e.g., $M^{3+}/M^{2+}/Se^{2-}$, $M^{4+}/M^{3+}/Se^{2-}$) and binary compositions (e.g., $Ga^{3+}/Se^{2-}$). Indeed, these simpler compositions are well known. For example, the T2 cluster is known in zeolite-type UCR-20, -21, and -22,[13] and the T4 supertetrahedral cluster ($Zn_4Ga_{16}Se_{33}$) reported herein is also found in OCF-1-ZnGaSe-TMDP.[14] In the work reported herein, instead of macroscopic phase separation into simpler ternary phases, quaternary OCF-42s are formed by integrating both T2 and T4 clusters in the same crystal.

Three-dimensional covalent open frameworks of OCF-42 compounds are formed from corner-sharing T2 and T4 clusters (Figure 1 and Figure S3 in the Supporting Information). The M-Se-M bond angles at corner sites range from 104.5 to 109.9°. Few examples of open-framework chalcogenides containing two types of supertetrahedral clusters are known.[17] Those known examples have simpler binary (e.g. In/S) or ternary compositions (e.g., Zn/In/S), which make them fundamentally different from the quaternary materials reported herein.

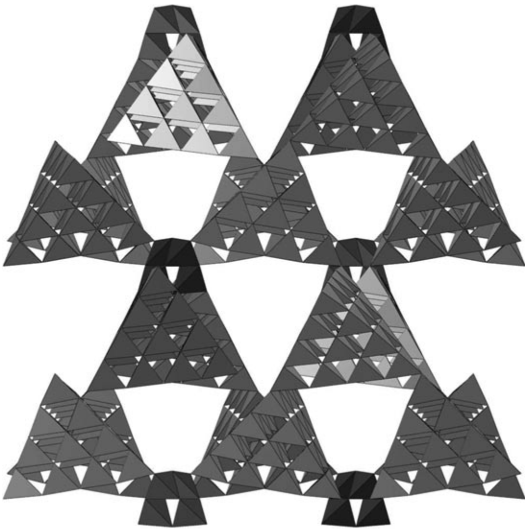

*Figure 1.* 3D open framework of OCF-42 compounds viewed along the *b* axis. Black sites represent the location of T2 clusters and gray sites represent the location of T4 clusters. The ratio between T4 and T2 clusters is 4:1.

Another uncommon feature in OCF-42 is the unequal ratio between T2 and T4 clusters. This ability to have unequal ratios represents a new way to increase the diversity of such materials. In OCF-42, instead of alternating T2 and T4 clusters, each T2 cluster is connected to four T4 clusters with a center-to-center distance of 12.03 Å, and each T4 cluster is corner-shared to one T2 and three T4 clusters (Figure S4 in the Supporting Information). Thus, the ratio between T2 and T4 clusters is 1:4.

Two distinct tetrahedral nets can be derived from OCF-42 compounds and both nets are previously unknown. For the topological analysis of the four-connected net, the T2 cluster is unique, because its four tetrahedral metal sites can be treated as four individual tetrahedral nodes, or alternatively the whole T2 cluster can be treated as a single tetrahedral node. In contrast, the T4 cluster can only be treated as a pseudotetrahedral atom, because of the presence of three- and four-coordinated $Se^{2-}$ sites. When the T2 clusters are treated as four individual nodes, the framework can be simplified into a new four-connected topology with vertex symbol of $[3.10_2.3.10_8.3.10_8][4.10_{11}.6_2.10_2.6_2.10_5]$ (Figure 2). When the T2 clusters are treated as a single tetrahedral

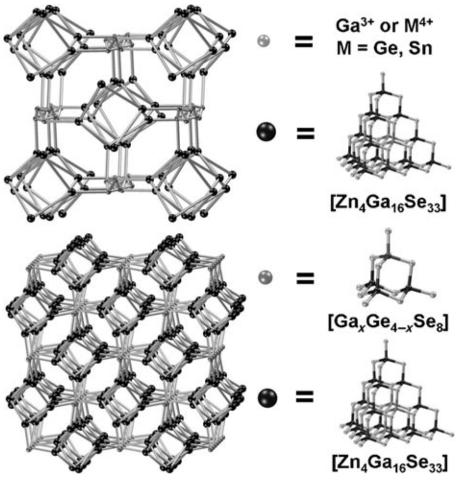

*Figure 2.* Because T2 clusters can be treated as single pseudotetrahedral sites or zeolite-type secondary building units with four tetrahedral sites, two different topological nets can be derived depending on the treatment of the T2 clusters. Top: A new non-interpenetrated zeolitic topology in OCF-42 when only the T4 clusters are considered as the artificial four-connected atoms; bottom: a new topological framework when both T2 and T4 clusters are treated as four-connected nodes.

node, the framework can also be simplified into a new four-connected topology with vertex symbol of $[8_8.8_8.8_8.8_8.8_2.8_2]$ $[4.8_{11}.6_2.8_2.6_2.8_5]$ (Figure 2 and Figure S5 in the Supporting Information).

Although all framework atoms were unambiguously determined; extra-framework species (protonated amine molecules) are disordered within the large cavities, and their atomic positions could not be determined. These disordered extra-framework species occupy approximately 64.5 % of the crystal volume as calculated using the PLATON software.[18]

Thermogravimetric analysis (Figure S6 in the Supporting Information), studied on a TA instrument SDT Q600 under a flowing $N_2$ atmosphere, followed by X-ray powder diffraction, showed that the OCF-42 compounds were stable up to 300 °C when solvent molecules trapped in the pore or adsorbed on the surface were lost (lost weight 1.6 %). An abrupt weight loss between 300 and 500 °C is attributed to the decomposition of the charge-balancing organic cations. The black residue obtained after heating the sample at 600 °C in $N_2$ shows the loss of crystallinity.

The quaternary compositions achieved add an extra freedom in the control of electronic or optical properties, such as electronic band gap. Solid-state diffuse-reflectance spectra of the OCF-42 compounds were measured on a Shimadzu UV-3101PC double-beam double monochromator spectrophotometer by using $BaSO_4$ powder as the 100 % reflectance reference. The optical absorption data calculated from reflectance data by using the Kubelka–Munk function[19] show that OCF-42-ZnGaGeSe has an absorption onset at about 855 nm, corresponding to a band gap of 1.45 eV (Figure S7 in the Supporting Information). The replacement of $Ge^{4+}$ with $Sn^{4+}$ gives a comparable band gap of 1.54 eV in OCF-42-ZnGaSnSe. The band gaps of such quaternary selenides lie between the band gaps of binary gallium selenides (OCF-6-GaSe-TMDP, 1.43 eV)[14] and some ternary selenides (such as OCF-1-ZnGaSe-TMDP, 1.76 eV;[14] $[Cd_{15}Sn_{12}Se_{46}]^{14-}$, 2.00 eV;[20] $[Cd_4Sn_3Se_{13}]^{6-}$, 2.33 eV;[20] and $[M_4(\mu_4\text{-Se})(SnSe_4)_4]^{10-}$ (M = Zn, Mn, Cd, Hg), 2.2–2.6 eV[21]), which demonstrates the possibility to tune the band gap of chalcogenides by combining different metal cations into crystals.

OCF-42 compounds are photoluminescent and can be excited with wavelength from 380 to 450 nm. When excited at 420 nm at room temperature, OCF-42-ZnGaGeSe and OCF-42-ZnGaSnSe exhibit strong photoluminescence with maximum wavelengths centered at 490 and 510 nm, respectively (Figure S8 in the Supporting Information). These transitions are attributed to the charge transfer from $Se^{2-}$-dominated valence band to $M^{4+}/Ga^{3+}/Zn^{2+}$-dominated conduction band.

In conclusion, two quaternary 3D open-framework selenides based on T2 and T4 supertetrahedral clusters have been synthesized using three types of charge-complementary (+2/+3/+4) and yet geometry-matching (all tetrahedral) metal cations such as $Zn^{2+}/Ga^{3+}/Ge^{4+}$. These charge-complementary metal cations control the cluster size and co-assembly through differing bond valence requirements of bi-, tri-, and tetracoordinated $Se^{2-}$ sites. The $M^{4+}/M^{3+}$ combination assists the formation of small T2 cluster, while the $M^{3+}/M^{2+}$ combination helps the formation of large T4 clusters. The T2 and T4 clusters are further joined into 3D covalent superlattices with an unequal 1:4 ratio, leading to a framework topology that can be simplified into two previously unknown tetrahedral nets. The formation of the quaternary $M^{4+}/M^{3+}/M^{2+}/Se^{2-}$ composition is unusual, considering that multiple competing crystallization processes for the formation of structures with simpler ternary and binary compositions are possible. The cluster-scale phase separation controlled by charge-complementary metal cations illustrates that a high degree of control is possible even in the complicated quaternary compositions.

## Experimental Section

Synthesis of OCF-42-ZnGaGeSe-TMDP: $GeO_2$ (12.1 mg, 0.116 mmol), $Ga_2O_3$ (113.2 mg, 0.604 mmol), Se (187.2 mg, 2.371 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (82.5 mg, 0.277 mmol), and TMDP (1.996 g, 9.673 mmol) were mixed with $H_2O$ (3.028 g, 168 mmol) in a 23 mL teflon-lined stainless steel autoclave and stirred for 1 h. The vessel was then sealed and heated to 200 °C for 6 days. Pale-yellow column crystals were obtained in a yield of 123.3 mg upon cooling to room temperature.

Synthesis of OCF-42-ZnGaSnSe-TMDP: $SnCl_4{\cdot}5H_2O$ (36.3 mg, 0.104 mmol), $Ga_2O_3$ (106.9 mg, 0.570 mmol)), Se (161.6 mg, 2.047 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (73.0 mg, 0.247 mmol), and TMDP (2.011 g, 9.746 mmol) were mixed with $H_2O$ (3.122 g, 173 mmol) in a 23 mL teflon-lined stainless steel autoclave and stirred for 2 h. The vessel was then sealed and heated to 200 °C for 6 days. Yellow block crystals were obtained in a yield of about 145.2 mg upon cooling to room temperature.

The phase purity was supported by PXRD (Figure S1 in the Supporting Information). The presence of di-, tri-, and tetravalent elements was confirmed by energy-dispersive X-ray (EDAX) spectroscopy performed on a scanning electron microscope (SEM) (Figure S2 in the Supporting Information). The $Sn^{4+}/Ga^{3+}$ ratios were determined by single-crystal analysis based on the large difference in the scattering power between $Sn^{4+}$ and $Ga^{3+}$ cations. The Ge/Ga ratio could not be refined reliably and the value given was estimated by comparison with OCF-42-ZnGaSnSe-TMDP.

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