

these materials could be made as aluminosilicates, the Si/Al ratio would be 3. It is worth noting that until now, no zeolites templated with organic cations only have a Si/Al ratio of 3 or lower. The synthesis of UCSB-6, UCSB-8, UCSB-10, and other highly charged phosphate-based zeolite analogs shows that it might be possible to synthesize low and intermediate silica by templating with organic cations.

While UCSB-6 and UCSB-10 have framework structures similar to EMC-2 (EMT) and faujasite (FAU), respectively, UCSB-8 has an unusual large cage consisting of 64 tetrahedral atoms. Such cage is accessible through four 12-ring windows and two 8-ring windows (Fig. 6). In comparison, the supercage in FAU-type structures is built from 48 T-atoms.

4 Microporous and Open Framework Sulfides

During the development of the above oxide-based microporous materials, two new research directions appeared in late 1980s and early 1990s. One was the synthesis of open framework sulfides initiated by Bedard, Flanigen, and coworkers [61]. Another was the development of metal-organic frameworks in which inorganic metal cations or clusters are connected with organic linkers. Metal-organic frameworks have become an important family of microporous materials and they will be discussed in the next section. Open framework chalcogenides are particularly interesting because of their potential electronic and electrooptic properties, as compared to the usual insulating properties of open framework oxides.

Like in zeolites, the tetrahedral coordination is common in metal sulfides. However, structures of open framework sulfides are substantially different from zeolites. This is mainly because of the coordination geometry of bridging sulfur anions. The typical value for the T-S-T angle in metal sulfides is between 105 and 115 degrees, much smaller than the typical T-O-T angle in zeolites that usually lies between 140 and 150 degrees. In addition, the range of the T-S-T angle is also considerably smaller than that of the T-O-T angle. While the range of the T-S-T angle is approximately between 98 and 120 degrees, the T-O-T angle can extend from about 120 to 180 degrees, depending on the type of tetrahedral atoms.

As the exploratory synthesis in zeolite and zeolite-like materials has progressed from silicates and phosphates to arsenates and germanates [62,63,64], it becomes clear that from a purely geometrical view, the research on open framework sulfides, selenides, and halides continue the trend towards large T-X distances and smaller T-X-T angles (X is an anion such as O, S, and Cl). Such trend has the potential to generate zeolite-like structures with 3-rings and exceptionally large pore sizes.

The tendency for the T-S-T angle to be close to 109 degrees has a fundamental effect on the structure of open framework sulfides. In sulfides with tetrahedral metal cations, all framework elements can adopt tetrahedral coordination. As a result, clusters with structure resembling fragments of zinc blende type lattice can be formed. These clusters are now called supertetrahedral clusters (Fig. 8).

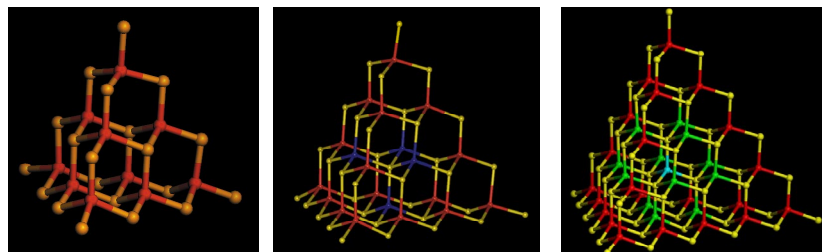


Figure 8. (left) the supertetrahedral T3 cluster, (middle) the T4 cluster. Blue sites are occupied with divalent metal cations. (right) the T5 cluster. Red: In^{3+} ; Yellow: S^{2-} ; Cyan: the core Cu^+ site. In a given cluster, only four green sites are occupied by Cu^+ ions. The occupation of green sites by Cu^+ ions is not random and follows Pauling's electrostatic valence rule.

Supertetrahedral clusters are regular tetrahedrally shaped fragments of zinc blende type lattice. They are denoted by Yaghi and O'Keeffe as T_n , where n is the number of metal layers [65,66]. One special case is T1 and it simply refers to a tetrahedral cluster such as MS_4 , where M is a metal cation. If we add an extra layer, the cluster would be shaped like an adamantane cage with the composition M_4S_{10} , called supertetrahedral T2 cluster because it consists of two metal layers. With the addition of each layer, a new supertetrahedron of a higher order will be obtained. The compositions of supertetrahedral T3, T4, and T5 clusters are $\text{M}_{10}\text{X}_{20}$ and $\text{M}_{20}\text{X}_{35}$, and $\text{M}_{35}\text{X}_{56}$ respectively. When all corners of each cluster are shared through bi-coordinated S^{2-} bridges (as in zeolites), the number of anions per cluster in the overall stoichiometry is reduced by two. While a T2 cluster consists of only bi-coordinated sulfur atoms, a T3 cluster has both bi- and tri-coordinated sulfur atoms. Starting from T4 clusters, tetrahedral coordination begins to occur for sulfur atoms inside the cluster.

At this time, the largest supertetrahedral cluster observed is the T5 cluster (Fig. 8) with the composition of $[\text{Cu}_5\text{In}_{30}\text{S}_{54}]^{13-}$ [67]. This T5 cluster occurs as part of a covalent superlattice in UCR-16 and UCR-17. So far, isolated T5 clusters have not been synthesized. The largest isolated supertetrahedral cluster known to date is T3. Some examples are $[(\text{CH}_3)_4\text{N}]_4[\text{M}_{10}\text{E}_4(\text{SPh})_{16}]$, where $M = \text{Zn}, \text{Cd}$, $E = \text{S}, \text{Se}$, and Ph is a phenyl group [68,69].

With T_n clusters as artificial tetrahedral atoms, it is possible to construct covalent superlattices with framework topologies similar to those found in zeolites. However, the ring size in terms of the number of tetrahedral atoms is increased by n times. An increase in the ring size is important because crystalline porous materials with a ring size larger than 12 are rather scarce, but highly desirable for applications involving large molecules.

4.1 Sulfides with tetravalent cations

Some zeolites such as ZSM-5 and sodalite can be made in the neutral SiO_2 form [10,56]. Neutral frameworks have also been found in microporous aluminophosphates [11] and germanates [64,70]. It is therefore reasonable to expect that microporous sulfides with a general framework composition of GeS_2 or SnS_2 may exist. The Ge-S and Sn-S systems were among the earliest compositions explored by Bedard *et al.*, when they reported their work on open framework sulfides in 1989. Thus far, a number of new compounds were found in Ge-S and Sn-S compositions, however, very few have three-dimensional framework structures. Frequently, molecular, one-dimensional, or layered structures are found in these compositions.

In the Ge-S system, the largest observed supertetrahedral cluster is T2 ($\text{Ge}_4\text{S}_{10}^{4-}$). Larger clusters such as T3 have not been found in the Ge-S system possibly because the charge on germanium is too high to satisfy the coordination environment of tri-coordinated sulfur sites that exist in clusters larger than T2. This is because of Pauling's Electrostatic Valence Rule that suggests the charge on an anion must be balanced locally by neighboring cations.

Isolated T2 clusters ($\text{Ge}_4\text{S}_{10}^{4-}$) have been found to occur [71,72,73] in the molecular compound $[(\text{CH}_3)_4\text{N}]_4\text{Ge}_4\text{S}_{10}$. One-dimensional chains of $\text{Ge}_4\text{S}_{10}^{4-}$ clusters have also been observed in a compound called DPA-GS-8 [74]. One polymorph of GeS_2 , $\delta\text{-GeS}_2$, consists of covalently linked $\text{Ge}_4\text{S}_{10}^{4-}$ clusters with a three-dimensional framework [75]. The framework topology resembles that of the diamond type lattice, however, the extra-framework space is reduced because of the presence of two interpenetrating lattices. As shown in later sections, the interpenetration can be removed by incorporating trivalent metal cations into the cluster to generate negative inorganic frameworks that can be assembled with protonated amines.

In the Sn-S system, layered structures are common [76]. Because of its large size, tin frequently forms non-tetrahedral coordination. In addition, tin may also form oxysulfides, which further complicates the synthetic design of porous tin sulfides. One rare three-dimensional framework [77] based on tin sulfide is $[\text{Sn}_5\text{S}_9\text{O}_2][\text{HN}(\text{CH}_3)_3]_2$. This material is built from T3 clusters, $[\text{Sn}_{10}\text{S}_{20}]$. Each T3 cluster has four adamantane-type cavities that can accommodate one oxygen atom per cavity to give a cluster $[\text{Sn}_{10}\text{S}_{20}\text{O}_4]^{8-}$. Because each corner sulfur atom is shared between two clusters. The overall framework formula is $[\text{Sn}_{10}\text{S}_{18}\text{O}_4]^{4-}$. The isolated form of the $[\text{Sn}_{10}\text{S}_{20}\text{O}_4]^{8-}$ cluster is also known in $\text{Cs}_8\text{Sn}_{10}\text{S}_{20}\text{O}_4 \cdot 13\text{H}_2\text{O}$ [78].

4.2 Sulfides with tetravalent and mono- or divalent cations

The early success in the preparation of open framework sulfides depended primarily on the use of mono- or divalent cations (e.g., Cu^+ , Mn^{2+}) to join together chalcogenide clusters (e.g., $\text{Ge}_4\text{S}_{10}^{4-}$). These low-charged mono- or divalent cations

help generate negative charges on the framework that are usually charge-balanced by protonated amines or quaternary ammonium cations.

One example was the synthesis of TMA-CoMnGS-2 [61]. Like many other germanium sulfides, the basic structural unit is the T2 cluster. Here, T2 clusters are joined together by three-connected $\text{Me}(\text{SH})^+$ (Me = divalent metal cations such as Co^{2+} and Mn^{2+}) units to form a framework structure. Another interesting example was the synthesis of a series of compounds with the general formula of $[(\text{CH}_3)_4\text{N}]_2\text{MGe}_4\text{S}_{10}$ (M = Mn^{2+} , Fe^{2+} , Cd^{2+}) [73,79,80]. Unlike $\delta\text{-GeS}_2$ that is an intergrowth of two diamond-type lattice (double-diamond type), $[(\text{CH}_3)_4\text{N}]_2\text{MGe}_4\text{S}_{10}$ has a non-interpenetrating diamond-type lattice (single-diamond type) in which tetrahedral carbon sites are replaced with alternating T2 and T1 clusters.

In $[(\text{CH}_3)_4\text{N}]_2\text{MGe}_4\text{S}_{10}$ and TMA-CoMnGS-2, the divalent metal cations join together four and three T2 clusters, respectively. It is also possible for a metal cation to connect to only two T2 clusters. Such is the case in $\text{CuGe}_2\text{S}_5(\text{C}_2\text{H}_5)_4\text{N}$, in which T2 clusters form the single-diamond type lattice with monovalent Cu^+ cations bridging between two T2 clusters [81].

The diamond-type lattice is very common for framework structures formed from supertetrahedral clusters. With T2 clusters, amines or ammonium cations are usually big enough to fill the framework cavity. As a result, the interpenetration of two identical lattices does not usually occur. With larger clusters, charge-balancing organic amines are often not enough to fill the extra-framework space and the double-diamond type structure becomes more common.

In addition to the single-diamond type lattice, other types of framework structures are possible. One compound, Dabco-MnGS-SB1 with a formula of $\text{MnGe}_4\text{S}_{10} \cdot \text{C}_6\text{H}_{14}\text{N}_2 \cdot 3\text{H}_2\text{O}$, has a framework structure in which T1 and T2 clusters alternate to form the zeolite ABW-type topology with a ring size of 12 tetrahedral atoms [82].

While the use of M^{2+} and M^+ cations has led to a number of open framework sulfides, it could have negative effects too. These low-charged metal sites could lower the thermal stability of the framework. The destabilizing effect of divalent cations (e.g. Co^{2+} , Mn^{2+}) in porous aluminophosphates is well known. However, unlike in phosphates, it is difficult to study the destabilizing effect of low-charged cations in open framework sulfides because the incorporation of low-charged cations in sulfides changes both chemical composition and framework type.

4.3 Sulfides with trivalent metal cations

In late 1990s, a new direction appeared when Parise, Yaghi and their coworkers reported several open framework indium sulfides [65,83]. The In-S composition is quite unique because no oxide open frameworks with similar compositions were known before. In fact, the In-O-In and Al-O-Al linkages are not expected to occur in

oxides with four-connected, three-dimensional structures. Fortunately, such a restriction does not apply to open framework sulfides.

An interesting structural feature in the In-S system is the occurrence of T3 clusters, $[\text{In}_{10}\text{S}_{18}]^{6-}$. A T3 cluster has both bi- and tri-coordinated sulfur sites. The lower charge of In^{3+} compared to Ge^{4+} and Sn^{4+} makes it possible to form tri-coordinated sulfur sites. Through the sharing of all corner sulfur atoms, open framework materials with several different framework topologies have been made. These include DMA-InS-SB1 (T3 double-diamond type) [83], ASU-31 (T3-decorated sodalite net), ASU-32 (T3-decorated CrB_4 type) [65], and ASU-34 (T3 single-diamond type) [84].

Very recently, Feng *et al.* synthesized a series of open framework materials based on T3 gallium sulfide clusters, $[\text{Ga}_{10}\text{S}_{18}]^{6-}$ [85]. Only the double-diamond type topology has been observed so far in the Ga-S system. In UCR-7GaS, T3 clusters are bridged by a sulfur atom (-S-) whereas in UCR-18GaS, one quarter of the inter-cluster linkage is through the trisulfide group (-S-S-S-).

So far, isolated T3 clusters, $[\text{In}_{10}\text{S}_{20}]^{10-}$ and $[\text{Ga}_{10}\text{S}_{20}]^{10-}$, have not been found yet even though isolated T2 clusters, $[\text{In}_4\text{S}_{10}]^{8-}$ and $[\text{Ga}_4\text{S}_{10}]^{8-}$, have been known for a while [86]. Regular supertetrahedral clusters larger than T3 have not been found in the binary In-S or Ga-S systems probably because tetrahedral sulfur atoms at the core of these clusters can not accommodate four trivalent metal cations because the positive charge surrounding the tetrahedral sulfur anion would be too high.

4.4 Sulfides with trivalent and mono- or divalent cations

To access clusters larger than T3, mono- or divalent cations need to be incorporated into the Ga-S or In-S compositions. Another motivation to incorporate mono- or divalent cations in the In-S or Ga-S synthesis conditions might be the desire to create new structures in which T3 clusters are joined together by mono- or divalent cations, in a manner similar to the assembly of $[\text{Ge}_4\text{S}_{10}]^{4-}$ clusters by mono- or divalent cations [73]. So far, mono- and divalent cations have only been observed to occur as part of a supertetrahedral cluster, not as linker units between clusters.

The first T4 cluster, $[\text{Cd}_4\text{In}_{16}\text{S}_{33}]^{10-}$, was synthesized by Yaghi, O'Keffee and coworkers in CdInS-44. In this compound, four Cd^{2+} cations are located around the core tetrahedral sulfur atom (Fig. 8). Because Cd^{2+} and In^{3+} are isoelectronic, it is difficult to distinguish Cd^{2+} and In^{3+} sites through the crystallographic refinement of X-ray diffraction data. Further evidences on the distribution of di- and trivalent cations in a T4 clusters came from UCR-1 and UCR-5 series of compounds that incorporate the first row transition metal cations such as Mn^{2+} , Fe^{2+} , Co^{2+} , and Zn^{2+} [87].

An exciting recent development is the synthesis of two superlattices (UCR-16 and UCR-17) consisting of T5 supertetrahedral clusters, $[\text{Cu}_5\text{In}_{30}\text{S}_{54}]^{13-}$ [67]. There are four tetrahedral core sulfur sites, each of which is surrounded by two In^{3+} and

two Cu^+ cations. One Cu^+ cation is located at the center of the T5 cluster and there is one Cu^+ cation on each face of the supertetrahedral cluster (Fig. 8).

Another interesting structural feature is the occurrence of hybrid superlattices. In UCR-19, T3 clusters $[\text{Ga}_{10}\text{S}_{18}]^{6-}$ and T4 clusters $[\text{Zn}_4\text{Ga}_{16}\text{S}_{33}]^{10-}$ alternate to form the double-diamond type superlattice [85]. In UCR-15, T3 clusters $[\text{Ga}_{10}\text{S}_{18}]^{6-}$ and pseudo-T5 clusters $[\text{In}_{34}\text{S}_{54}]^{6-}$ also alternate to form the double-diamond type superlattice [88]. The pseudo-T5 cluster is similar to the regular T5 cluster except that the core metal site is not occupied. The pseudo-T5 cluster has also been found with a different chemical composition in a layered superlattice with the framework composition of $[\text{Cd}_6\text{In}_{28}\text{S}_{54}]^{12-}$ [89].

4.5 Sulfides with tetravalent and trivalent cations

Open framework sulfides based on In-S and Ga-S compositions have open architectures and some have been shown to undergo ion exchange in solutions. However, to generate microporosity, it is necessary to remove a substantial amount of extra-framework species. Open framework sulfides such as indium or gallium sulfides generally do not have sufficient thermal stability to allow the removal of an adequate amount of extra-framework species to generate microporosity.

A general observation in zeolites is that the stability increases with the increasing $\text{Si}^{4+}/\text{Al}^{3+}$ ratio. It can be expected that the incorporation of tetravalent cations such as Ge^{4+} and Sn^{4+} into In-S or Ga-S compositions could lead to an increase in the thermal stability. Recently, Feng *et al.* reported a large family of chalcogenide zeolite analogs [46]. These materials were made by simultaneous triple substitutions of O^{2-} with S^{2-} or Se^{2-} , Si^{4+} with Ge^{4+} or Sn^{4+} , and Al^{3+} with Ga^{3+} or In^{3+} . All four possible $\text{M}^{4+}/\text{M}^{3+}$ combinations (Ga/Ge, Ga/Sn, In/Ge, and In/Sn) could be realized resulting in four zeolite-type topologies.

Based on the topological type, these materials are classified into four families denoted as UCR-20, UCR-21, UCR-22, and UCR-23. Each number refers to a series of materials with the same framework topology, but with different chemical compositions in either framework or extra-framework components. For example, UCR-20 can be made in all four $\text{M}^{4+}/\text{M}^{3+}$ combinations, giving rise to four sub-families denoted as UCR-20GaGeS, UCR-20GaSnS, UCR-20InGeS, and UCR-20InSnS. An individual compound is specified when both the framework composition and the type of extra-framework species are specified (e.g., UCR-20GaGeS-AEP, AEP = 1-(2-aminoethyl)piperazine).

The extra-large pore size and 3-rings are two interesting features. UCR-22 (Fig. 9) and UCR-23 have 24-ring and 16-ring windows whereas both UCR-20 (Fig. 9) and UCR-21 have 12-ring windows. These inorganic frameworks are strictly 4-connected 3-dimensional networks commonly used for the systematic description of zeolite frameworks. Unlike known zeolite structure types, a key structural feature is the presence of the adamantane-cage shaped building unit, M_4S_{10} . The M_4S_{10} unit

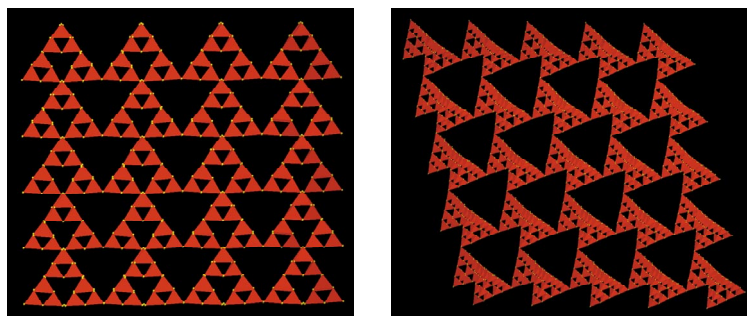


Figure 9. The three-dimensional framework of UCR-20 (left) and UCR-22 (right) families of sulfides.

consists of four 3-rings fused together. For materials reported here, the framework density defined as the number of T-atoms in 1000\AA^3 ranges from 4.4 to 6.5.

Although these chalcogenides are strictly zeolite-type tetrahedral frameworks, it is possible to view them as decoration of even simpler tetrahedral frameworks. Here, each M_4S_{10} unit can be treated as a large artificial tetrahedral atom. With this description, UCR-20 has the decorated sodalite-type structure, in which a tetrahedral site in a regular sodalite net is replaced with a M_4S_{10} unit. UCR-21 has the decorated cubic ZnS type structure. UCR-23 has the decorated CrB_4 type network in which tetrahedral boron sites are replaced with M_4S_{10} units.

Upon exchange with Cs^+ ions, the percentage of C, H, and N in UCR-20GaGeS-TAEA was dramatically reduced. The exchanged sample remained highly crystalline as the original sample. The Cs^+ exchanged UCR-20GaGeS-TAEA displayed type I isotherm characteristic of a microporous solid. This sample has a high Langmuir surface area of $807\text{m}^2/\text{g}$ and a micropore volume of $0.23\text{cm}^3/\text{g}$ despite the presence of much heavier elements (Cs, Ga, Ge, and S) compared to aluminosilicate zeolites.

5 Microporous Metal-Organic Frameworks

Currently, the synthetic design of metal-organic frameworks (also known as coordination polymers) is a very active research area [90,91]. Many new microporous materials synthesized in the past several years belong to this family. Unlike zeolites that have an inorganic host framework, in metal-organic frameworks, the three-dimensional connectivity is established by linking metal cations or clusters with bidentate or multidentate organic ligands. The resulting frameworks are hybrid frameworks between inorganic and organic building units and should be distinguished from microporous materials in which organic amines are encapsulated in the cavities of purely inorganic frameworks.