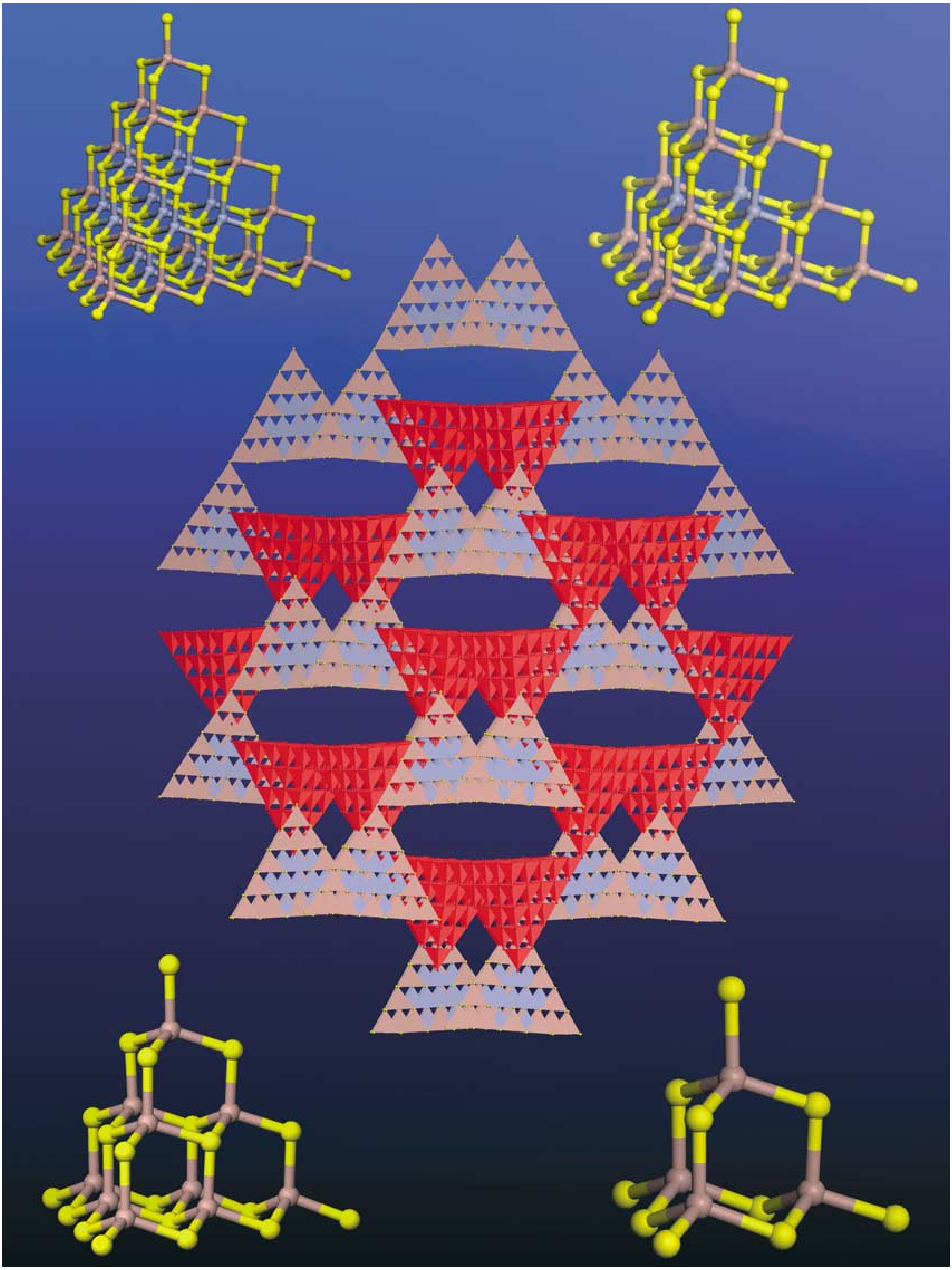

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Tetrahedral Chalcogenide Clusters and Open Frameworks

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Abstract: By integrating porosity with electrical or optical properties, microporous chalcogenides may have unique applications. Here we review recent advances and discuss concepts in the synthesis and crystal structure of tetrahedral clusters and their frameworks. These chalcogenides can be viewed as trivalent metal chalcogenides doped with tetra-, di-, or monovalent metal cations. Low-valent cations help to increase the cluster size, while high-valent cations have the opposite effect.

Keywords: chalcogens • cluster compounds • conducting materials • microporous materials • supertetrahedral clusters • transition metals • zeolites

Introduction

Because of the technological importance of porous materials, there has been a constant effort to develop new porous materials during the past several decades. The early work generally involves the substitution of framework cations (i.e., Al^{3+} or Si^{4+}) in zeolites by other cations such as Ga^{3+}, Ge^{4+}, and P^{5+}. This approach has resulted in a large number of microporous oxides, most of which are based on silicates and phosphates.[1]

The replacement of framework anions (i.e., O^{2-}) with chalcogens (e.g., S^{2-}) or organic ligands (e.g., nitriles, carboxylates, amines) represents a more recent approach for generating microporous materials. Useful concepts involving the organic ligand approach are the focus of a recent review by Yaghi et al.[2] Here, we review the recent advance related to open framework chalcogenides. Since the initial work in 1989 by Bedard, Flanigen, and their co-workers, porous chalcogenides have generated a lot of interest.[3] These chalcogenides are capable of integrating porosity with electrical or optical properties and hold promise for applications such as solid electrolytes, semiconductor electrodes, sensors, and photocatalysis.

Tetrahedral Chalcogenide Clusters

While the concept of microporous chalcogenides received wide attention after the work by Bedard et al., recent developments in porous chalcogenides also benefit from the early efforts by Krebs, Dance, and their co-workers on isolated chalcogenide clusters.[4–6] This is because many three-dimensional (3D) chalcogenides are constructed from clusters. Thus the concepts regarding the synthesis and structure of chalcogenide clusters serve as a useful guide for the development of porous chalcogenides.

A variety of chalcogenide clusters are known.[6] Here our interest is limited to tetrahedral clusters, loosely defined as those behaving like pseudo-tetrahedral atoms in an extended framework structure. Metal cations appearing in tetrahedral chalcogenide clusters are usually from Groups 12–14 (e.g., Zn, Cd, Ga, In, Ge, Sn). Other cations include Mn, Fe, Co, Cu, and Li.

The tetrahedral coordination of metal cations is common in both zeolites and chalcogenides. However, tetrahedral clusters are far more common in chalcogenides. This is related to the coordination geometry of chalcogen anions. For example, the typical value for the T–S–T angle is approximately between 105 and 115°, much smaller than the typical T–O–T angle in zeolites, which usually lies between 140 and 150°. The tendency for the T–S–T angle to be close to 109° means that in sulfides with tetrahedral cations, all framework elements can adopt tetrahedral coordination. As a result, clusters can be formed that have structures similar to the fragment of the cubic ZnS type lattice.

The most common series of tetrahedral clusters are called supertetrahedral clusters. Supertetrahedral clusters are regular, tetrahedrally shaped fragments of the cubic ZnS type

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lattice (Figure 1). They were denoted as $2^{[n]}$ by Dance et al. and recently as Tn by Yaghi et al., where n is the number of metal layers.[7,8] The compositions of T1, T2, T3, T4, and T5 clusters are MX_4, M_4X_{10}, $M_{10}X_{20}$, $M_{20}X_{35}$, and $M_{35}X_{56}$, respectively, where M is a metal cation and X is a chalcogen anion.[8]

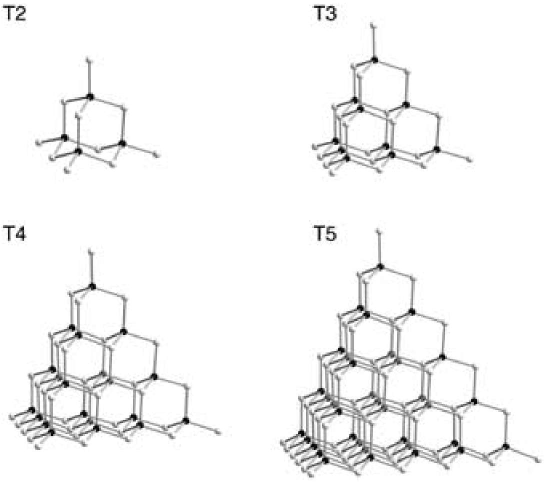

Figure 1. Ball-and-stick diagrams of T2, T3, T4, and T5 supertetrahedral clusters.

While a T2 cluster consists of only dicoordinate anions (e.g., S^{2-}), a T3 cluster has both di- and tricoordinate anions. Starting from the T4 cluster, tetrahedral coordination begins to occur for anions inside the cluster.[9,10] The coordination number of anionic sites is important, because it is related to the valence of the metal cations surrounding them. Such a relation follows Pauling's electrostatic valence rule, which states the valence of an anion is exactly or nearly equal to the sum of the electrostatic bond strengths to it from adjacent cations. Here we use the local charge-density matching concept to describe this situation, in contrast with the global charge-density matching concept that we use to describe the charge-density matching between the negative framework and the positively charged extra-framework species.

It is also helpful to distinguish between surface atoms and core atoms in a cluster. Surface atoms are those at corners, edges, and faces of the cluster, while core atoms are those inside the cluster. There are no core atoms for T1, T2, and T3 clusters. For the T4 cluster, the core atom is a single sulfur atom. For T5 or larger clusters, the core atoms constitute a T(n−4) cluster. In general, core metal cations have a valence equal to or lower than that of surface atoms.

The largest supertetrahedral cluster synthesized so far is the T5 cluster with the composition of $[M_{13}In_{22}S_{56}]^{20-}$ (M = Zn, Mn) or $[Cu_5In_{30}S_{56}]^{17-}$.[11,12] These T5 clusters occur in covalent 3D superlattices and are not known in the isolated form yet. For isolated regular supertetrahedral clusters, the largest one known so far is T3. Some examples are $[(CH_3)_4N]_4[M_{10}E_4(SPh)_{16}]$, in which M = Zn, Cd, E = S, Se, and Ph is a phenyl group.[13]

The second series of tetrahedral clusters are called penta-supertetrahedral clusters (Figure 2) denoted as $5^{[n]}$ by Dance et al. and as Pn by Feng et al.[7,14] Each Pn cluster can be conceptually constructed by coupling four Tn clusters onto each face of an anti-Tn cluster. An anti-Tn cluster is defined here as having the same geometrical feature as that of a Tn cluster; however, the positions of cations and anions are exchanged. Using this concept, a P1 cluster consists of four T1 clusters (MX_4) at corners and one anti-T1 cluster (XM_4) at the core, resulting in the composition of $(MX_4)_4(XM_4)$ (i.e., M_8X_{17}). Examples of P1 clusters include $[SCd_8(SBu)_{12}](CN)_{4/2}$ and $[K_{10}M_4Sn_4S_{17}]$ (M = Mn, Fe, Co, Zn).[7,15] A P2 cluster has the composition of $(M_4X_{10})_4(X_4M_{10})$ (i.e., $M_{26}X_{44}$). There are two examples of P2 clusters, $[Li_4In_{22}S_{44}]^{18-}$ in ICF-26 and $[Cu_{11}In_{15}Se_{16}(SePh)_{24}(PPh_3)_4]$.[14,16] Similarly, a P3 cluster has the composition of $(M_{10}X_{20})_4(X_{10}M_{20})$ (i.e., $M_{60}X_{90}$). The same procedure can be used to derive the composition of other Pn clusters. Clusters larger than P2 have not been synthesized.

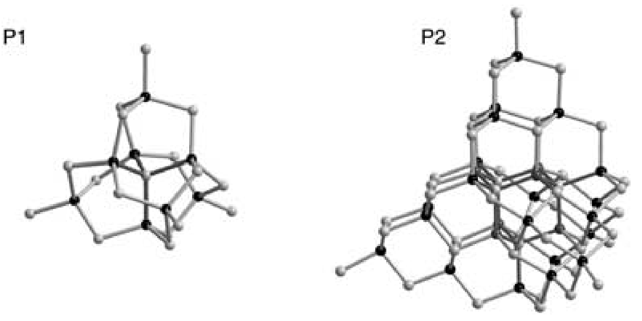

Figure 2. Ball-and-stick diagrams of P1 and P2 penta-supertetrahedral clusters.

In 1988, Dance et al. reported the first member (i.e., $[S_4Cd_{17}(SPh)_{28}]^{2-}$) of the third series of tetrahedral clusters denoted as $7^{[n]}$.[7] Recent developments in this series include the synthesis of the 3D network based on the first member with the formula of $[Cd_{17}S_4(SCH_2CH_2OH)_{26}]$ and the synthesis of an isolated cluster for the second member with the formula of $[Cd_{32}S_{14}(SC_6H_5)_{36}]\cdot 4\,DMF$.[17,18]

All above three series of clusters have no cavities inside. A series of hollow clusters can be generated if each tetrahedral site in a Tq cluster is replaced with a Tp cluster. These clusters are called super-supertetrahedral clusters and are denoted as Tp,q by Yaghi et al.[19] Two members of super-supertetrahedral clusters have been reported. One is T2,2 found in UCR-22 and ICF-22, and the other is T4,2 found in CdInS-420. The T2,2 cluster is also called the coreless T4 cluster by Feng et al., because it is similar to a regular T4 cluster without the core SM_4 anti-T1 unit (Figure 3).[20]

By adding atoms into or removing atoms from above regular tetrahedral clusters, other variations of clusters are possible. These include the coreless T5 cluster, in which the central metal site of a T5 cluster is not occupied (Figure 3) and the stuffed T2 and T3 clusters in which there is an oxygen atom in each adamantane cage.[21–24]

Chalcogenides with Tetravalent Cations

Some zeolites such as ZSM-5 and sodalite can be made in the neutral SiO_2 form. Neutral porous frameworks are also

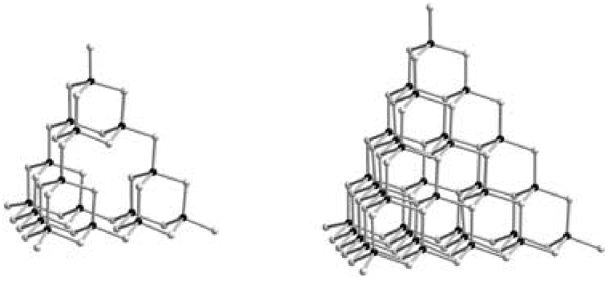

Figure 3. Ball-and-stick diagrams of coreless T4 (left) and coreless T5 (right) tetrahedral clusters.

known in $AlPO_4$ and GeO_2 forms. It is therefore reasonable to expect that open framework sulfides with the 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, Ozin, and co-workers. A number of new compounds have been made in these compositions. Frequently, molecular, one-dimensional, or layered structures are found.[24–26]

The early success in the preparation of open framework sulfides came from the use of mono- or divalent cations (e.g., Cu^+, Mn^{2+}) to join together chalcogenide clusters (e.g., $Ge_4S_{10}^{4-}$). These low-valent cations help generate negative charges on the framework that are subsequently charge-balanced by structure-directing agents. Among the most interesting examples was the synthesis of several compounds with the formula of $[(CH_3)_4N]_2[MGe_4S_{10}]$ (M = Mn^{2+}, Fe^{2+}, Cd^{2+}).[27] $[(CH_3)_4N]_2[MGe_4S_{10}]$ has a non-interpenetrating diamond type lattice (the single diamond type) with alternating T2 and T1 clusters occupying tetrahedral nodes. Another 3D solid with alternating T1 and T2 clusters is an oxyselenide, $[TMA]_2[Sn(Sn_4Se_{10}O)]$ with stuffed T2 clusters.[25]

In the Ge–S (or Ge–Se) system, the largest supertetrahedral cluster is T2. Larger clusters have not been synthesized, because the charge at cation sites is too high to satisfy the coordination environment of tricoordinate anion sites in clusters larger than T2. For the same reason, no regular T3 cluster is known in the Sn–S (or Sn–Se) system. However, there is one 3D framework with the formula $[Sn_5S_9O_2][HN(CH_3)_3]_2$.[28] This material is built from "stuffed" T3 clusters, $[Sn_{10}S_{20}O_4]^{8-}$. Each $[Sn_{10}S_{20}]$ T3 cluster has four adamantane-type cavities that can accommodate one oxygen atom per cavity to give a cluster $[Sn_{10}S_{20}O_4]^{8-}$. Because each corner sulfur atom is shared between two clusters. The overall framework formula is $[Sn_{10}S_{18}O_4]^{4-}$. The isolated form of the $[Sn_{10}S_{20}O_4]^{8-}$ cluster is also known in $[Cs_8Sn_{10}S_{20}O_4]\cdot 13H_2O$.[23]

Chalcogenides with Trivalent Cations

In late 1990s, Parise, Yaghi, and co-workers reported several open framework indium sulfides.[8,29–31] Using the In–S composition to build porous materials is quite unique, because 50% or more framework cation sites in zeolite-like oxides have a valence ≥ 4. The linkages such as In–O–In and Al–O–Al are not expected in zeolite-like oxides, because of the Loewenstein rule that states the ratio of M^{4+}/M^{3+} be larger or equal to one.

The most interesting feature in the In–S system is the occurrence of the T3 cluster, $[In_{10}S_{20}]^{10-}$. The lower charge on In^{3+} compared to Ge^{4+} and Sn^{4+} makes it possible to form tricoordinate sulfur sites needed for the formation of T3 clusters. Very recently, Feng et al. extended the In–S composition to Ga–S, Ga–Se, and In–Se compositions.[32,33] The use of the nonaqueous synthesis method is responsible for the success in the Ga–S composition.

The synthesis of the $[Cd_4In_{16}S_{35}]^{14-}$ T4 cluster by Yaghi et al.[9] shows that to access regular clusters larger than T3, divalent cations are necessary in addition to the In–S composition. Four divalent cations are needed to surround the core tetrahedral anion in T4 to achieve the local charge balance. The work by Feng et al. demonstrates that the combination of monovalent and trivalent cations could provide the required local charge matching around the tetrahedral S^{2-} site.[11]

Because Cd^{2+} and In^{3+} are isoelectronic, the unambiguous assignment of Cd^{2+} and In^{3+} sites in the $[Cd_4In_{16}S_{35}]^{14-}$ cluster is difficult through the refinement of X-ray diffraction data. Further evidence on the distribution of di- and trivalent cations in the T4 cluster comes from the UCR-1 and UCR-5 series of materials, which incorporate the first-row transition-metal cations such as Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+} in the predominantly In–S composition.[10] An exciting recent development is the synthesis of several compounds consisting of T5 clusters, $[M_{13}In_{22}S_{56}]^{20-}$ (M = Zn, Mn) and $[Cu_5In_{30}S_{54}]^{13-}$.[11,12]

Chalcogenides with Tetravalent and Trivalent Cations

In terms of chemical compositions, chalcogenides with tetravalent (M^{4+}) and trivalent (M^{3+}) metal cations bear the closest resemblance to aluminosilicate zeolites. The difficulty with the synthesis of the M^{4+}/M^{3+} chalcogenides is the phase separation, because either cation can form chalcogenides of its own. Recently, Feng and co-workers found that the use of the nonaqueous synthesis method could lead to the integration of M^{4+} and M^{3+} ions into the same framework. A series of open framework sulfides and selenides were made by combining tetravalent (i.e., Ge^{4+}, Sn^{4+}) and trivalent metal (i.e., Ga^{3+}, In^{3+}) ions.[20] The M^{4+}/M^{3+} ratio in these chalcogenides can be, however, much smaller than that in zeolites and so far falls within the range from about 1.3 to 0.21. Despite the low M^{4+}/M^{3+} ratio, some sulfides in this series possess adequate stability toward ion exchange and thermal treatment. The Cs^+ exchanged UCR-20GaGeS-TAEA (TAEA = tris(2-aminoethyl)amine) exhibits the type I isotherm typical of a microporous solid and its pore size is as large as 9.5 Å.

Assembly of Chalcogenide Clusters

As discussed above, the type of metal cations present in the solvothermal system places a limitation on the formation of individual clusters. If only the trivalent cation is present, clusters larger than T3 are unlikely to form. On the other hand, if both trivalent and divalent cations are present, the system has the flexibility to form a variety of clusters such as T3, T4, and T5.

Given the simultaneous availability of various clusters, different assemblies can be envisioned. The most common situation is for clusters of the same size to crystallize into a uniform superlattice (Figure 4). For example, in UCR-1 and UCR-8, only T4 clusters are present.[10,34] Hybrid superlattices containing clusters of the different size are also possible. For example, in UCR-19, T3 and T4 clusters alternate to form a 3D double diamond-type superlattice (Figure 4).[32] UCR-15 has an unusual structure, in which a regular T3 cluster alternates with a coreless T5 cluster to form a double diamond structure.[21]

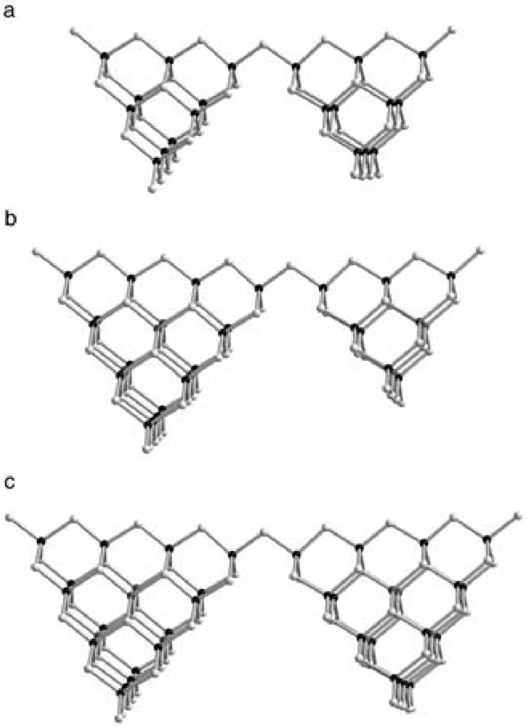

Figure 4. Three examples showing different combinations of tetrahedral clusters in 3D open framework chalcogenides: a) T3-T3, b) T3-T4, and c) T4-T4.

Tetrahedral clusters are usually joined together with a single S^{2-} (or Se^{2-}) bridge. However, in UCR-18, one fourth of the bridges are provided by polysulfur ions (S_3^{2-}) and in UCR-8, each S^{2-} bridge connects to three T4 clusters (Figure 5).[32,34]

A number of factors control the type of superlattices that can crystallize. The geometry and charge distribution of organic molecules are among the most important factors. The global charge density matching was considered to be a factor in the crystallization of UCR-15.[21] For gallium sulfides, the size of organic amines appears to correlate with the size of clusters (i.e., T3, T3-T4, or T4) in the 3D lattice.[32] Unlike in oxides, hydrogen bonding is much weaker in chalcogenides. Therefore, the host–guest electrostatic interaction, further enhanced by the highly negative framework, is expected to play a significant role in chalcogenides.

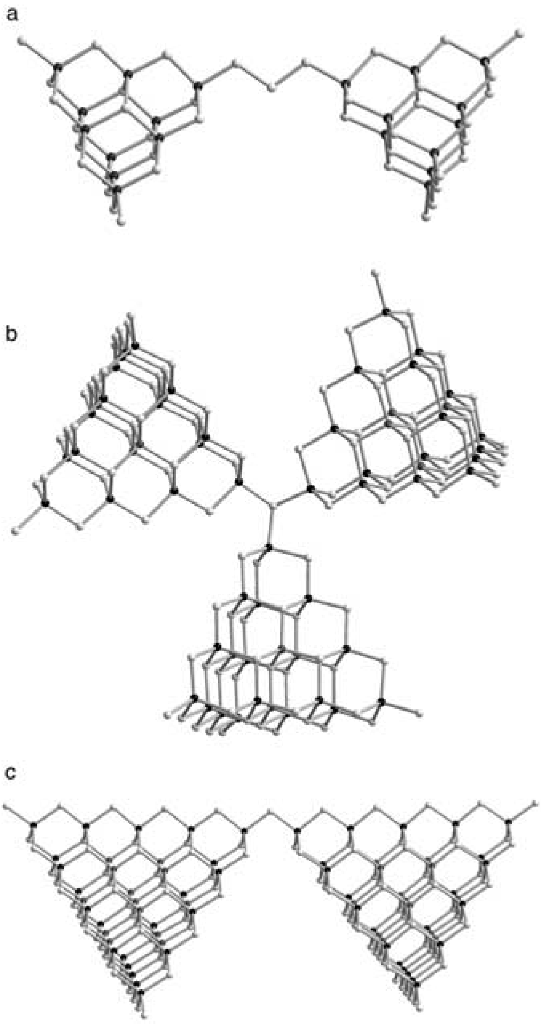

Figure 5. Examples of different bridging patterns between tetrahedral clusters: a) through the –S–S–S- bridge, b) through the tricoordinate S^{2-} bridge, and c) through the dicoordinate S^{2-} bridge.

Framework Topological Types

At least nine 3D topological types have been realized from the assembly of tetrahedral clusters (Figure 6). Among these, the single and double diamond-type lattices are by far the most common. For small T2 and T3 clusters, both single and double diamond-type structures are known.[20,29,30,35] However, for T3-T4, T4, or larger clusters such as P2 and T5, only the double diamond-type structure has been observed so far.[9,32,34]

Other structure types include ABW, CrB_4, SOD, cubic-C_3N_4, UCR-1, ICF-24, and ICF-25. The ABW type occurs

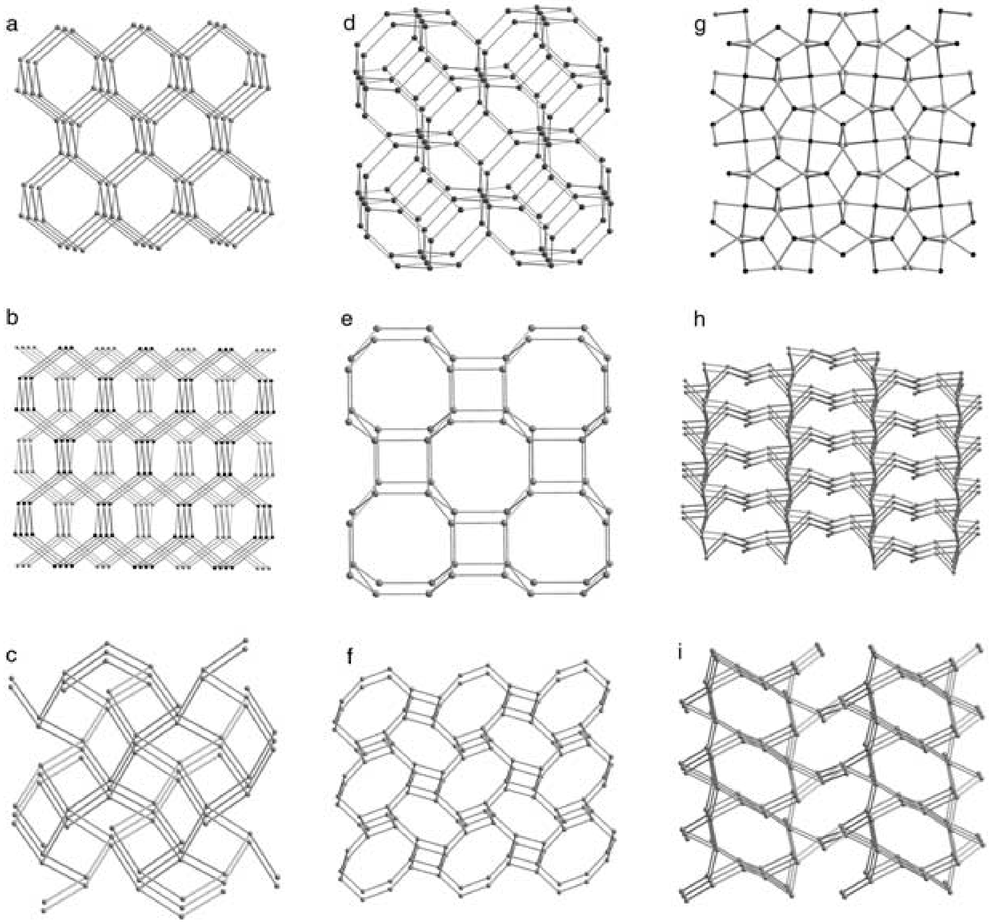

Figure 6. Examples of three-dimensional framework topologies formed from tetrahedral clusters: a) single diamond, b) double diamond, c) UCR-1, d) SOD, e) CrB_4, f) ABW, g) cubic C_3N_4, h) ICF-24, and i) ICF-25.

with T1-T2 clusters.[36] ICF-24 and ICF-25 types have only been made with T2 clusters.[12] The CrB_4 and sodalite types have been realized with either T2 or T3 clusters.[8,20] UCR-1 and cubic-C_3N_4 types only occur with the T4 cluster.[10,34]

The number of the 3D framework types remains small now. This is in part due to the inflexibility of the T–S–T angles. One new direction is to explore other linkers to bridge chalcogenide clusters. Using this strategy, Feng et al. recently prepared a 3D framework in which the cubic $[Cd_8(SPh)_{12}]^{4+}$ clusters are organized by tetradentate 1,2,4,5-tetra(4-pyridyl)benzene molecules into a three-dimensional open framework.[37]

Recent Progress

Even though zeolites were originally made from purely inorganic systems, the success of organic cations as structure-directing agents in the synthesis of high-silica zeolites and later in aluminophosphates has resulted in a nearly complete neglect of inorganic systems in the exploratory synthesis of porous materials. For over two decades, the organic approach has been chosen preferentially when a new framework composition is attempted. In the area of chalcogenides, almost all phases reported prior to the recent work by Feng et al. involve the use of organic species.[12]

Feng and co-workers took a step "backwards" and extended the traditional organic-free zeolite synthetic method to the chalcogenide system. Their work resulted in a large family of hydrated sulfides and selenides.[12] Four different tetrahedral clusters (i.e., T2, T4, T5, and coreless T4) are observed in the inorganic system. These materials, denoted as ICF-*n*, were prepared in aqueous solutions from simple inorganic salts. For example, ICF-22InS-Li can be prepared at 190 °C in 4 days by simply mixing $In(NO_3)_3 \cdot H_2O$, LiCl, and Li_2S in water.

One of the most interesting properties of these inorganic chalcogenides is fast-ion conductivity at room temperature and moderate to high humidity. In particular, lithium compounds such as ICF-22 and ICF-26 exhibit ionic conductivity significantly higher than previously known crystalline lithium compounds.[12,14]

Conclusion

Impressive synthetic successes have been achieved in the area of porous chalcogenides and related tetrahedral clusters, leading to new developments in synthetic and structural principles that will provide useful guidance for the future exploration of this intriguing and important compositional domain. Most chalcogenides described here can be viewed as trivalent metal chalcogenides doped with tetra-, di-, or monovalent cations. Incorporation of mono- or divalent cations helps to increase the size of the tetrahedral cluster (e.g., from T3 to T4 or T5), whereas the incorporation of tetravalent cations tends to lower the size of the supertetrahedral cluster from T3 to T2.

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