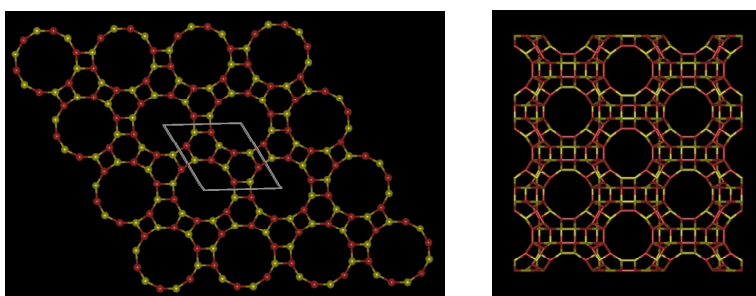


three-dimensional networks. In terms of the number of tetrahedral atoms, the tschortnerite cage is twice as large as the supercage in faujasite. However, the tschortnerite cage is accessible through 8-rings that are smaller than the 12-ring windows in faujasite.

The difficulty involving the creation of new low and intermediate silica molecular sieves is in part because of the limited choice in structure-directing agents. Traditionally, inorganic cations such as  $\text{Na}^+$  are employed and it has not been possible to synthesize zeolites with a Si/Al ratio smaller than 5 with organic cations. However, recent results demonstrate that organic cations can template the formation of  $\text{M}^{2+}$  substituted alumino- (gallo-)phosphate open frameworks in which the  $\text{M}^{2+}/\text{M}^{3+}$  molar ratio is  $\leq 1$  [49,50]. In terms of the framework charge per tetrahedral unit, this is equivalent to aluminosilicates with a Si/Al ratio  $\leq 3$ . Thus, it might be feasible to prepare low and intermediate silica zeolites using amines as structure-directing agents.

### 3 Microporous and Open Framework Phosphates

Because of the structural similarity between dense  $\text{SiO}_2$  and  $\text{AlPO}_4$  phases, the research in the 1970s on high silica or pure silica molecular sieves quickly led to the realization that it might be possible to synthesize aluminophosphate molecular sieves using the method similar to that employed for the synthesis of silicalite. In 1982, Flanigen *et al.* reported a major discovery of a new class of aluminophosphate molecular sieves ( $\text{AlPO}_4\text{-n}$ ) [11,12]. Unlike zeolites that are capable of various Si/Al ratios, the framework of these aluminophosphates consists of alternating  $\text{Al}^{3+}$  and  $\text{P}^{5+}$  sites and the overall framework is neutral with a general formula of  $\text{AlPO}_4$ .



**Figure 7.** (Left) The three-dimensional framework of  $\text{AlPO}_4\text{-5}$  consists of one-dimensional 12-ring channels. Note the alternating distribution of P and Al sites. Red: P, Yellow: Al. (right) 12-ring channels in metal (Co, Mn, Mg) substituted aluminophosphate UCSB-8.

These aluminophosphates are synthesized hydrothermally using organic amines or quaternary ammonium salts as structure-directing agents. In most cases, organic molecules are occluded into the channels or cages of  $\text{AlPO}_4$  frameworks. Because

the framework is neutral, the positive charge of organic cations is balanced by the simultaneous occlusion of OH<sup>-</sup> groups. Many of these aluminophosphates have a high thermal stability and remain crystalline after calcination at temperatures between 400-600°C. In addition to framework types already known in zeolites, new topologies have also been found in some structures including AlPO<sub>4</sub>-5 (AFI) that has a one-dimensional 12-ring channel (Fig. 7) [51].

The next family of new molecular sieves consists of a series of silicon substituted aluminophosphates [52] called silicoaluminophosphates (SAPO-n). To avoid the Si-O-P linkage, Si<sup>4+</sup> cations tend to replace P<sup>5+</sup> sites or both Al<sup>3+</sup> and P<sup>5+</sup> sites. The substitution of P<sup>5+</sup> sites by Si<sup>4+</sup> cations produces negatively charged frameworks with cation exchange properties and acidic properties. The SAPO family includes two new framework types, SAPO-40 (AFR) and SAPO-56 (AFX), not previously known in aluminosilicates, pure silica polymorphs, or aluminophosphates [30].

In addition to silicon, other elements can also be incorporated into aluminophosphates. In 1989, Wilson and Flanigen [53] reported a large family of metal aluminophosphate molecular sieves (MeAPO-n). The metal (Me) species include divalent forms of Mg, Mn, Fe, Co, and Zn (M<sup>2+</sup>). The MeAPO family represents the first demonstrated synthesis of divalent metal cations in microporous frameworks [53]. In one of these phases, CoAPO-50 (AFY) with a formula of [(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>[Co<sub>3</sub>Al<sub>5</sub>P<sub>8</sub>O<sub>32</sub>]·7H<sub>2</sub>O, approximately 37% of Al<sup>3+</sup> sites are replaced with Co<sup>2+</sup> cations [30]. For each substitution of Al<sup>3+</sup> by M<sup>2+</sup>, a negative charge develops on the framework, which is balanced by protonated amines or quaternary ammonium cations.

For a given framework topology, the framework charge is tunable in aluminosilicates by changing Si/Al ratios. However, it is fixed in binary phosphates such as aluminophosphates or cobalt phosphates [30,54]. The use of ternary compositions as in metal aluminophosphates provides the flexibility in adjusting the framework charge density. Such flexibility contributes to the development of a large variety of new framework types in metal aluminophosphates and has also led to the synthesis of a large number of phosphates with the same framework type as those in zeolites [30,50].

The MeAPSO family further extends the structural diversity and compositional variation found in the SAPO and MeAPO molecular sieves. MeAPSO can be considered as double (Si<sup>4+</sup> and M<sup>2+</sup>) substituted aluminophosphates. The MeAPSO family includes one new large pore structure MeAPSO-46 with a formula of [(C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>8</sub>[Mg<sub>6</sub>Al<sub>22</sub>P<sub>26</sub>Si<sub>2</sub>O<sub>112</sub>]·14H<sub>2</sub>O [30]. The quaternary (four different tetrahedral elements at non-trace levels) composition is rare in a microporous framework, but is obviously a promising area for future exploration.

In the two decades following Wilson and Flanigen's original discovery, there has been an explosive growth in the synthesis of open framework phosphates [13,55]. It is apparent that the MeAPO's exhibit much more structural diversity and

compositional variation than both SAPO's and MeAPSO's. However, the thermal stability of MeAPO's is generally lower than that of either  $\text{AlPO}_4$ 's or SAPO's. In general, the thermal stability of a metal aluminophosphate decreases with an increase in the concentration of divalent metal cations in the framework.

In addition to the continual exploration of  $\text{AlPO}_4$  and MeAPO compositions, many other compositions have been investigated including gallophosphates and metal gallophosphates [13]. Of particular interest is the synthesis of a family of extra-large pore phosphates with ring sizes larger than 12 tetrahedral atoms [16]. The use of the fluoride medium [34] and non-aqueous solvents [56] further enriches the structural and compositional diversity of the phosphate-based molecular sieves.

Unlike aluminophosphate molecular sieves developed by Flanigen *et al.*, new generations of phosphates such as phosphates of tin, molybdenum, vanadium [57], iron, titanium, and nickel often consist of metal cations with different coordination numbers ranging from three to six [13]. The variable coordination number helps the generation of many new metal phosphates.

In terms of the framework charge,  $\text{AlPO}_4$ 's, SAPO's, and MeAPO's closely resemble high silica and pure silica molecular sieves. This is not surprising because the synthetic breakthrough in aluminophosphate molecular sieves was based on the earlier synthetic successes in high silica and pure silica phases. However, for certain applications such as  $\text{N}_2$  selective adsorbents for air separation, it is desirable to prepare aluminophosphate-based materials that are similar to low or intermediate zeolites. Because each  $(\text{AlSi}_3\text{O}_8)^-$  unit carries the same charge as  $(\text{MAlP}_2\text{O}_8)^-$  (M is a divalent metal cation), the  $\text{M}^{2+}/\text{Al}$  ratio of 1 is equivalent to the Si/Al ratio of 3 in terms of the framework charge per tetrahedral atom. For a Si/Al ratio of 5 as in  $(\text{AlSi}_5\text{O}_{12})^-$ , the corresponding  $\text{M}^{2+}/\text{Al}$  ratio is 0.5 as in  $(\text{CoAl}_2\text{P}_3\text{O}_{12})^-$ . Therefore, to make highly charged aluminophosphates similar to low and intermediate silica, the  $\text{M}^{2+}/\text{Al}$  ratio should be higher than 0.5. Only a very small number of compounds with  $\text{M}^{2+}/\text{Al}$  ratio  $\geq 0.5$  were known prior to 1997 [30,58,59].

A significant advance occurred in 1997 when a family of highly charged metal aluminophosphates with a  $\text{M}^{2+}/\text{M}^{3+} \geq 1$  ( $\text{M}^{2+} = \text{Co}^{2+}, \text{Mn}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{M}^{3+} = \text{Al}^{3+}, \text{Ga}^{3+}$ ) were reported [49,50,60]. After over two decades of extensive research on high silica, pure silica, aluminophosphates, and other open framework materials with low-charged or neutral framework, the synthesis of these highly charged metal aluminophosphates represented a noticeable reversal towards highly charged frameworks often observed in natural zeolites. The recent work on 4-connected, three-dimensional metal sulfides and selenides further increased the framework negative charge to an unprecedented level with a  $\text{M}^{4+}/\text{M}^{3+}$  ratio as low as 0.2 [46].

Three families of open framework phosphates denoted as UCSB-6 (SBS), UCSB-8 (SBE) (Fig. 7), and UCSB-10 (SBT) demonstrate that zeolite-like structures with large pore, large cage, and multidimensional channel systems can be synthesized with a framework charge density much higher than currently known organic-templated silicates [49]. The  $\text{M}^{2+}/\text{M}^{3+}$  ratio in these phases is equal to 1. If

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).