Rich Structure Chemistry in the Aluminophosphate Family

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ABSTRACT

This Account describes a family of aluminophosphates ranging from neutral open-frameworks to anionic frameworks with fascinating structural architectures. In contrast to aluminosilicate zeolites, these aluminophosphates exhibit wealthy structural features, including extra-large micropores, mixed bonding, different structural dimensionalities, rich compositional diversities, and various stacking sequences of their 2-D sheets. The low-dimensional networks, acting as building units, can be assembled to 3-D open-frameworks via transition metal cations through a building-up process. New stoichiometries and hypothetical structural topologies can be predicted and enumerated. Computational and combinatorial approaches will greatly help to access the range of the diverse structures.

Introduction

Inorganic open-framework materials with regular pore architectures, typically known as zeolites, constitute an important area of materials science because of their widespread applications in catalysis, separation, and host–guest assemblies. Traditionally, zeolites refer to a class of crystalline aluminosilicates constructed from TO_4 tetrahedra (T = Si and Al) to form structures of composition $A_{x/n}[Si_{1-x}Al_xO_2] \cdot mH_2O$, where A is a metal cation of valence n and $0 \leq x \leq 0.5$.[1] In 1982, Wilson and co-workers developed a new class of zeolite-like molecular sieves $AlPO_4$-n (n denotes a structure type).[2] Their structures are typically built up from strict alternation of AlO_4 and PO_4 tetrahedra through corner sharing to form a neutral open-framework. Part of the Al sites can be replaced by catalytically active transition metal ions. One of the important promising areas of application shown very recently is in catalysis where aerial oxidations are possible using linear and cyclic hydrocarbons.[3] They are also available in the growing field of solvent-free industrial reactions in the important area of clean technology.[4,5]

The discovery of $AlPO_4$-n has been promoting enormous growth in the chemical diversity of open-framework metal phosphates, including aluminophosphates, gallophosphates, and zincophosphates, and transition metal phosphates,[6–8] among which aluminophosphates (hereafter denoted AlPO's) display rich variety of structures, including neutral zeolite-like open-frameworks, and a range of anionic open-frameworks with 3-dimensional (3-D) framework, 2-D layer, 1-D chain, and 0-D cluster structures. The structures of anionic AlPO's are made up of alternation of Al-centered polyhedra (AlO_4, AlO_5, AlO_6) and P-centered tetrahedra $P(O_b)_n(O_t)_{4-n}$ (b, bridging; t, terminal; n = 1, 2, 3, 4) to form diverse stoichiometries, including $AlPO_4(OH)^-$, $AlP_4O_{16}{}^{9-}$, $AlP_2O_8{}^{3-}$, $Al_2P_3O_{12}{}^{3-}$, $Al_3P_4O_{16}{}^{3-}$, $Al_3P_5O_{20}{}^{6-}$, $Al_4P_5O_{20}{}^{3-}$, $Al_5P_6O_{24}{}^{3-}$, $Al_{11}P_{12}O_{48}{}^{3-}$, $Al_{12}P_{13}O_{52}{}^{3-}$, $Al_{13}P_{18}O_{72}{}^{15-}$, and so forth (Table 1).[9–14] Their frameworks exhibit fascinating structural architectures; for example, JDF-20 has the largest channel ring size of 20 among open-framework AlPO's,[15] and AlPO-CJB1 is the first aluminophosphate molecular sieve with Brönsted acidity.[13]

The structure chemistry of open-framework AlPO's is strikingly different from that of aluminosilicate zeolites for several reasons. First, the Al atom in AlPOs can be mixed-bonded adopting four, five, and/or six coordination with oxygen,[16] in contrast to the strict occurrence of four-coordinated Al in aluminosilicate zeolites. The tetrahedral P atom can share its one, two, three, or four oxygen atoms with adjacent Al atoms. The rich stoichiometries of AlPO's are attributed to the diverse coordinations of Al and P atoms. However, in zeolites the Si/Al ratio is dependent on the states and distribution of polysilicate anions in the framework. Second, the strict alternation of Al polyhedra and P tetrahedra in AlPO's defines an even number ring of T atoms such as 8, 10, 12, 14, 18, and 20, which prevents the occurrence, for example, of five-ring units commonly encountered in aluminosilicate zeolites. Third, the diverse structures of AlPO's are greatly facilitated by utilization of various organic amine templates which interact with the host frameworks through H-bonds. As a consequence, some frameworks of AlPO's are not thermally stable compared to aluminosilicate zeolites whose structures are facilitated by some inorganic cations or quanternary ammonium cations.

In this Account, we will describe the structure chemistry of aluminophosphates with neutral open-framework, extra-large micropore, anionic 3-D, and low-dimensional framework structures. Approaches toward the design and synthesis of these materials are introduced.

Neutral Open-Framework Aluminophosphates

The initiation of aluminophosphate molecular sieves $AlPO_4$-n is based on the crystal chemistry principle that $AlPO_4$ is isoelectronic with SiO_2.[2] In $AlPO_4$-n, both Al and P atoms are tetrahedrally coordinated by oxygen atoms and alternate on the framework. There are no Al–O–Al and P–O–P connections allowed due to the Lowenstein's rule. Their Al/P ratio is exclusively of unity, and their framework is neutral in contrast to negatively charged

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Table 1. Anionic Aluminophosphates with Various Dimensionalities, Stoichiometries and Coordinations (Al/P ≤ 1)[a]

dimensionality	stoichiometry	Al and P coordinations
3-D	$Al_{12}P_{13}O_{52}^{3-}$	AlO_{4b}, AlO_{5b}, PO_{4b}
	$Al_{11}P_{12}O_{48}^{3-}$	AlO_{4b}, AlO_{6b}, PO_{4b}
	$Al_5P_6O_{24}^{3-}$	AlO_{4b}, PO_{4b}, $PO_{3b}O_t$
	$Al_4P_5O_{20}^{3-}$	AlO_{4b}, AlO_{5b}, PO_{4b}, $PO_{2b}O_{2t}$
	$Al_3P_4O_{12}^{3-}$	AlO_{4b}, $PO_{3b}O_t$
2-D	$Al_{13}P_{18}O_{72}^{15-}$	AlO_{6b}, AlO_{4b}, $PO_{3b}O_t$
	$Al_4P_5O_{20}^{3-}$	AlO_{4b}, AlO_{5b}, PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$
	$Al_3P_4O_{16}^{3-}$	AlO_{4b}, AlO_{5b}, PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$
	$Al_3P_4O_{16}^{3-}$	AlO_{4b}, $PO_{3b}O_t$
	$Al_2P_3O_{12}^{3-}$	AlO_{4b}, AlO_{5b}, PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$
	$Al_2P_3O_{12}^{3-}$	AlO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$
	$AlP_2O_8^{3-}$	$AlO_{4b}(H_2O)_2$, $PO_{2b}O_{2t}$
	$AlP_2O_8^{3-}$	AlO_{4b}, $PO_{2b}O_{2t}$
	$AlPO_4(OH)^-$	$AlO_{3b}(OH)$, $PO_{3b}Ot$
1-D	$Al_3P_5O_{20}^{6-}$	AlO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$, PO_bO_{3t}
	$AlP_2O_8^{3-}$	AlO_{4b}, $PO_{2b}O_{2t}$
	$AlP_2O_8^{3-}$	AlO_{4b}, $PO_{3b}O_t$, PO_bO_{3t}
0-D	$AlP_4O_{16}^{9-}$	AlO_{4b}, PO_bO_{3t}

[a] b, bridging oxygen; t, terminal oxygen.

aluminosilicate zeolites.[6] So far, more than 20 types of neutral open-framework aluminophosphate molecular sieves have been reported in the latest issue of the *Atlas of Zeolite Structure Types*.[17] Some aluminophosphates have structures analogous to known aluminosilicate zeolites, whereas others have not been found to have zeolite counterparts yet.

The majority of AlPO$_4$-n's possess a (4,2)-connected framework, that is, the primary building units are four-connected tetrahedral nodes (Al or P), and the bridges between those nodes are two-connected atoms (O). However, there is a number of AlPO$_4$-n that have a framework deviated from the ideal (4,2)-connection. These include the mixed-bonded framework containing five- or six-coordinated Al atoms with one or two extraframework oxygen species (OH or H$_2$O), as well as four-coordinated Al atoms.

Extra-Large Micropore Aluminophosphates

VPI-5 is the first molecular sieve that contains rings greater than 12 T-atoms.[18] It sets up the state for the development of numerous other extra-large micropore materials. Figure 1a illustrates the topology of VPI-5. It contains rings of 18 T-atoms. Its structure is made up of AlO$_4$, AlO$_4$(H$_2$O)$_2$, and PO$_4$ units. Two water molecules bond to the Al atom at the center of the fused four-rings of trans conformation.[19]

The structure of VPI-5 can transform to AlPO$_4$-8 with 14-rings of pore openings upon heating (Figure 1b).[20] During the phase transformation, the six coordination of Al is still preserved.

An interesting question is whether an aluminosilicate or a pure silica zeolite analogue of VPI-5 exists. Assuming a (4,2)-connected pure SiO$_2$ analogue of VPI-5 followed by DLS refinement,[21] energy calculation results indicate that the hypothetical analogue has an extremely high Urey−Bradley energy of 1.760 kcal/mol per SiO$_2$ unit compared to the values of 0.027, 0.120, 0.123, and 0.23 for silica zeolite CHA, LEV, ERI, and SSZ-24 analogues to AlPO$_4$-34, -35, -17, and -5, respectively. The unfavorable
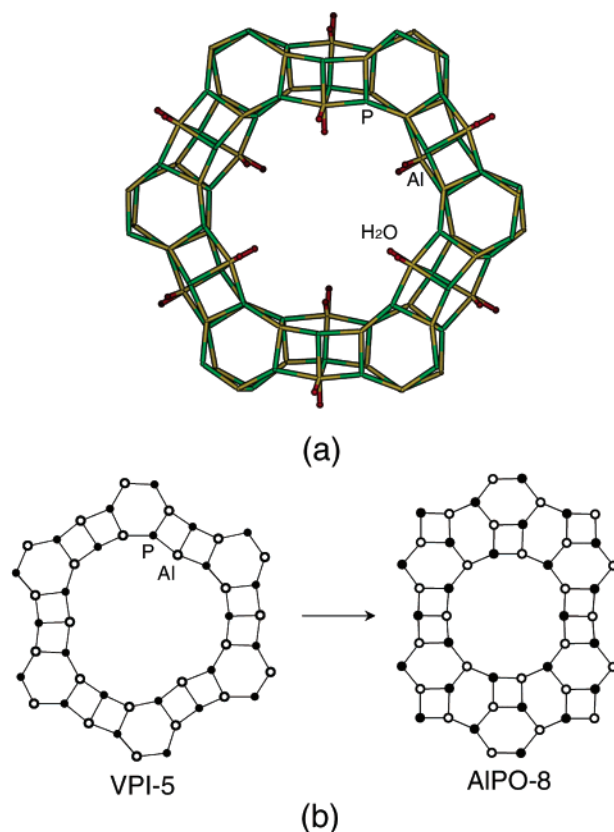

FIGURE 1. (a) Framework topology of VPI-5 (bridging oxygens are omitted). (b) Phase transformation from VPI-5 to AlPO$_4$-8 (waters are not shown).

Si(Al)−O−Si linkage in the fused edge-sharing four-rings limits the possibilities of aluminosilicate or pure silica zeolite analogue of the VPI-5 structure.

The structure of VPI-5 suggests a possible way to facilitate the formation of extra-large micropore by introducing mixed-bonded Al atoms in the framework. The alternative approach to the extra-large micropore is to make an interrupt framework. This situation is encountered in the extra-large micropore aluminophosphate JDF-20 (Jilin-Davy Farady, 20-membered ring).[15]

JDF-20, [Al$_5$P$_6$O$_{24}$H]·2Et$_3$NH·H$_2$O, contains 20-membered ring (MR) channels with elliptical apertures along *c* intersected by 10- and 8-MR rings (Figure 2). Its structure is made up of alternation of AlO$_4$ and PO$_4$ tetrahedra in which all the Al vertexes are shared, but two-thirds of the PO$_4$ tetrahedra have a terminal P−O bond. Its secondary building unit (SBU) is composed of five Al atoms and six P atoms. Its structure is featured by two types of 1-D chains along *c*, i.e., corner-sharing 4-MR chains and zigzag edge-sharing 4-MR chains. The entrance to the main channel has oxygen atoms protruding into it. Such structural feature is also found in the extra-large micropore gallophosphate cloverite.[22]

Anionic 3-D Open-Framework Aluminophosphates

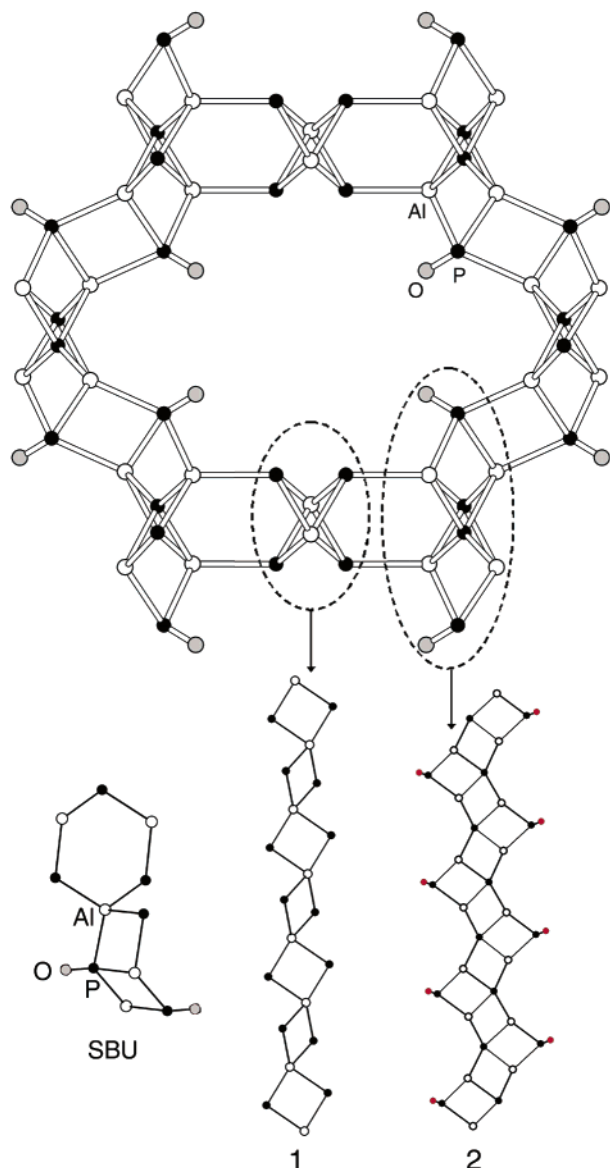It is noticed that the Al/P ratio of JDF-20 deviates from unity encountered in neutral open-framework AlPO$_4$-n.

FIGURE 2. Framework of JDF-20 (its SBU and the linear corner-sharing 4-MR chain (1) and zigzag edge-sharing 4-MR chain (2) are shown).
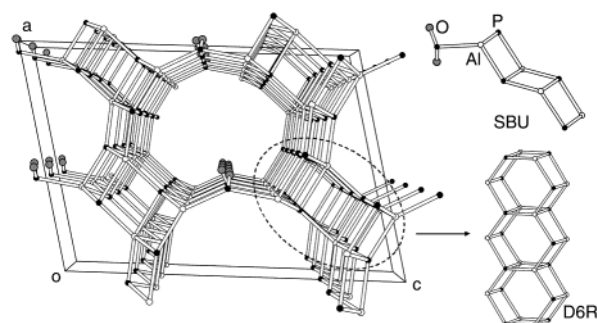

FIGURE 3. Structure of AlPO-HDA viewed along *b* (its SBU and characteristic columns of D6Rs are shown).
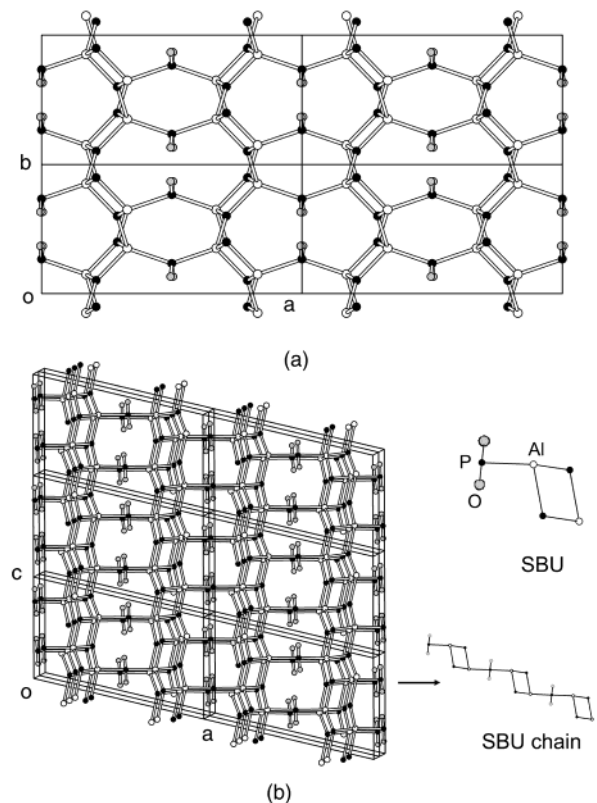
FIGURE 4. Framework of AlPO-DETA viewed along [001] (a) and [010] (b) (its SBU and SBU chain are shown).

The existence of terminal P—O bonds results in not only an interrupted structure but also an anionic framework with Al/P ratio less than 1. As with JDF-20, a number of aluminophosphates has been found to possess anionic frameworks with Al/P ratios less than unity (Table 1).

AlPO-HDA, $[Al_4P_5O_{20}H][C_6H_{18}N_2]$, has an Al/P ratio of 4/5.[23] It is made up of alternation of Al units (AlO_4 and AlO_5) and P units (PO_4, $PO_2(=O)(OH)$) to form an interrupted open-framework structure with interconnected 12- and 8-MR channels along *b* and *c*, respectively (Figure 3). Its SBU is a branched three edge-sharing 4-MRs. The framework is featured by of a series of columns of D6Rs along *b*.

$[Al_2P_3O_{12}][C_4H_{16}N_3]$ (AlPO-DETA) has an Al/P ratio of 2/3.[24] It is built up from alternation of tetrahedral AlO_4 units and PO_4 ($PO_3(=O)$ and $PO_2(=O)_2$) units via oxygens. It consists of parallel 12- and 8-MR channels along [001]

and 8-MR channels along [010] (Figure 4). Its SBU is composed of a branched 4-MR. Such SBU's are connected together to form infinite chains along *a*, which are further connected through vertex oxygens to form the 3D open-framework.

$[AlP_2O_6(OH)_2][H_3O]$ (AlPO-CJ4) has an Al/P ratio of 1/2.[25] It is constructed from alternation of AlO_6 octahedra and $PO_3(OH)$ tetrahedra via vertex oxygens to form a 3-D open framework with interconnected 8-MR channels along *a*, *b*, and *c*, respectively (Figure 5). As seen in the SBU, the Al units are solely made up of AlO_6 octahedra, with all six oxygen vertexes being shared by adjacent P atoms. The structure features a series of chiral propeller-like motifs comprised of Al-centered octahedron with three cyclic 4-MRs.

3-D anionic open-framework $[Al_9(PO_4)_{12}][C_{24}H_{91}N_{16}]\cdot 17H_2O$ with an Al/P ratio of 3/4 has also been reported.[26]
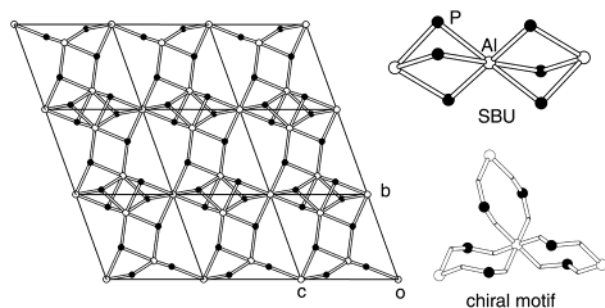
FIGURE 5. Framework of AlPO-CJ4 viewed along *c* (its SBU and chiral propeller-like motif are shown).

Its structure is made up of alternation of AlO_4 and PO_3-(=O) tetrahedra. Unlike neutral open-framework $AlPO_4$-n, the frameworks described above are all negatively charged, whose charge neutrality is achieved by protonated organic amine or water molecules occluded in the channel. These anionic AlPO's may have a potential to possess Brönsted acidity and ion-exchange capacity like aluminosilicate zeolites once the template molecules are removed to leave protons to balance the negative charges. However, for most of anionic AlPO's, the removal of the occluded templated molecules by calcination is not so successful. Efforts have been made to try to remove the templates by other ways.

$[Al_{12}P_{13}O_{52}]^{3-}$·$[(CH_2)_6N_4H_3]^{3+}$ (AlPO-CJB1) is the first aluminophosphate molecular sieve possessing Brönsted acidity upon removal of the templates by calcination.[13] Its framework is constructed by strict alternation of Al-centered polyhedra (AlO_4 and AlO_5) and P-centered PO_4 tetrahedra by sharing all oxygen atoms at vertexes to form an anionic open-framework with $Al_{12}P_{13}O_{52}^{3-}$ stoichiometry. As seen in Figure 6a, its structure is related to that of $AlPO_4$-22 (aww topology) with 8-MR pore openings along *c*.[17] In AlPO-CJB1, three kinds of cages exist, i.e., an aww cage, a P-incorporated aww cage, and an rpa cage (Figure 6b). The oxygen atoms of each PO_4 group in the P-incorporated aww cage form four normal covalent bonds with adjacent Al atoms that become five-coordinated. In contrast to neutral framework $AlPO_4$-n, the existence of AlO_5 species confers the negative charge center onto the framework of AlPO-CJB1. Since no terminal P–O groups exist, the framework of AlPO-CJB1 is stable upon removal of the occluded protonated template molecules. Protons are left to balance the negative charged framework and act as Brönsted acid centers.

Similarly, in AlPO-CJB2[12,27] the strict alternation of Al-centered polyhdra (AlO_4 and AlO_6) and PO_4 tetrahedra via all oxygen atoms forms an anionic 3-D open-framework with $[Al_{11}P_{12}O_{48}]^{3-}$ stoichiometry (Figure 7). Its framework can be viewed as to be formed by stagger stacking of a series of 4.6.12-net layers along *c*.

In summary, two situations will result in an anionic open-framework: (i) the existence of terminal P–O bonds and (ii) the occurrence of coordination numbers greater than four for Al atoms with the coordination sphere being bridging oxygens. Such situations have never been encountered in aluminosilicate zeolites. This explains why open-framework aluminophosphates show vast structural and compositional diversities compared to aluminosilicate zeolites.

Low-Dimensional Anionic Framework Aluminophosphates

Apart from a class of 3-D open-framework structures, aluminophosphates also exhibit rich diversity in a variety of low-dimensional anionic frameworks, including 2-D layers, 1-D chains, and 0-D clusters constructed from alternation of various Al and P coordinations (Table 1).

Stoichiometries of 2-D layered AlPO's are found as $AlPO_4(OH)^{-}$,[8,28] $AlP_2O_8^{3-}$,[29-31] $Al_2P_3O_{12}^{3-}$,[32,33] $Al_3P_4O_{16}^{3-}$,[29,34-48] $Al_4P_5O_{20}^{3-}$,[49] and $Al_{13}P_{18}O_{72}^{15-}$,[14] etc., among which the stoichiometry of $Al_3P_4O_{16}^{3-}$ is known in a number of 2-D layered compounds. With the exception of $[Al_3P_4O_{16}H]2-[C_3N_2H_5]$, which contains AlO_5 units,[29] the anionic sheets of $Al_3P_4O_{16}^{3-}$ are exclusively constructed from alternating AlO_4 and $PO_3(=O)$ tetrahedra. Different linkages of these tetrahedra lead to various sheet topologies. Figure 8a shows eight distinct 2-D sheet structures, including 4.6.12-,[35,39] 4.6.8(I)-,[34,38,41,47] 4.6.8(II)-,[44] 4.6(I)-,[36] 4.6(II)-,[37] 4.6(III)-,[42] 4.6(IV)-,[48] and 4.8-net.[45] Five types of SBU's for constructing the sheets are shown in the figure. Interestingly, the 2-D sheets exhibit various stacking sequences, such as AAAA,[38,41] ABAB,[34] ABCABC,[46] and ABCDEF[37] as seen in Figure 8b. The style of stacking is manipulated by the templating agent in the interlayer region which interacts with the inorganic frameworks through extensive H-bonds.[43]

A number of AlPO's also occurs as 1-D anionic chains with stoichiometry of $AlP_2O_8^{3-}$ [49-51] and $Al_3P_5O_{20}$.[6-52] The chains are made up of AlO_4 tetrahedra and $P(O-Al)_nO_{4-n}$ (n = 1, 2, 3) tetrahedra with terminal P–OH and/or P=O groups. The corner-sharing 4-MR chains (AlPO-CSC) and edge-sharing 4-MR chains (AlPO-ESC) with Al/P ratio of 1/2 have the simplest chain structures. AlPO-CSC is made up of alternation of AlO_4 and $PO_{2b}O_{2t}$ tetrahedra to form linear corner-sharing Al_2P_2 4-MRs (Figure 9a). It has been proposed that such a 1-D chain, on hydrolysis and rotation of bonds, may transform to more complex framework structures.[53] AlPO-ESC is made up of alternation of AlO_4 units and PO_4 units ($PO_{3b}O_t$ and PO_bO_{3t}) to form a zigzag ladder of fused Al_2P_2 4-MRs with pendant PO_4H side groups (Figure 9b). Our studies show that the AlPO-CSC and AlPO-ESC chains can transform to each other under suitable synthetic conditions.

Assembly of 3-D Open-Frameworks Using 1-D Chain Building Units

One important feature of low-dimensional AlPO's is the existence of terminal P–OH and/or P=O groups. This implies that they might have potential to further condense to build up 3-D framework. The intact chains or fragments of AlPO-CSC and AlPO-ESC are featured in a variety of 2-D and 3-D AlPO structures. We believe that they are fundamental building units for the formation of AlPO's. Of particular interest is the fact that these two types of
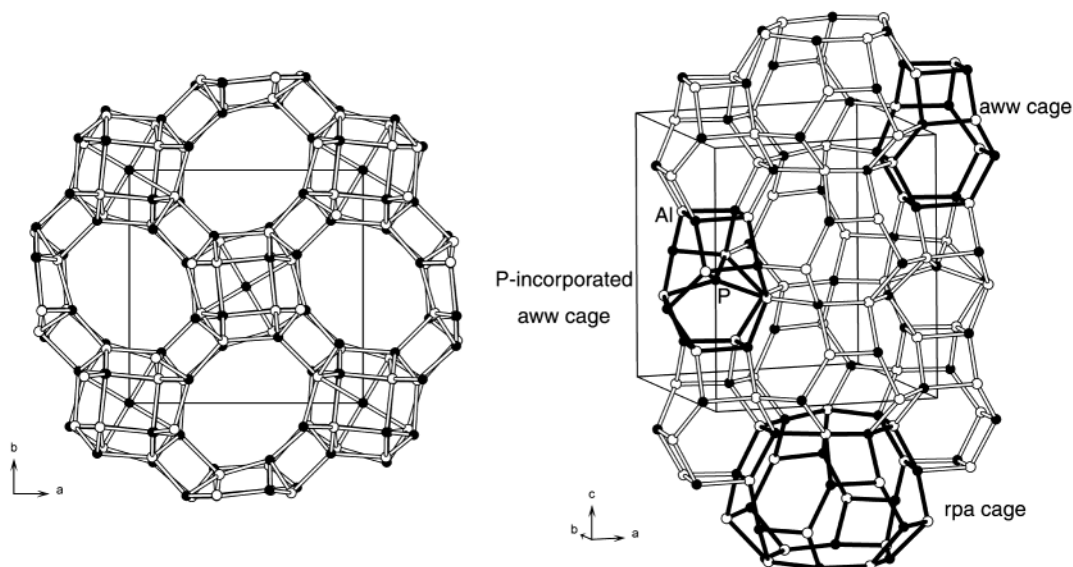
FIGURE 6. (a) Framework of AlPO-CJB1 viewed along *c*. (b) A side view showing the connection of three types of cages.
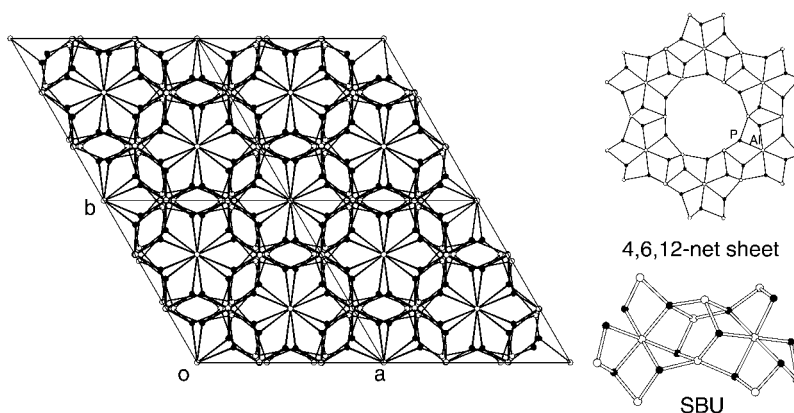

FIGURE 7. Framework of AlPO-CJB2 viewed along *c* (the 4.6.12-net sheet and SBU are shown).

chain structures have also been found in zinc phosphates and other metal phosphates. Rao et al. have made use of the Aufbau Principle to provide a wonderful demonstration how the formation of complex zinc phosphates with open architectures involves a building-up process from such simple building units.[8] Using AlPO-CSC as a building unit, 3-D open-frameworks $MAlP_2O_8 \cdot C_2N_2H_9$ have been successfully built up via transition metal cations (M = Ni^{2+}, Co^{2+}, Fe^{2+}).[54,55] Figure 10 shows the framework structure of $NiAlP_2O_8 \cdot C_2N_2H_9$. The terminal oxygen atoms attached to the 1D $AlP_2O_8^{3-}$ chains are exclusively coordinated to M^{2+}, forming O—M—O bonds. The intact AlPO-CSC chains along *a* and the $-Ni-O-Ni-$ chains along *c* are cross-linked with each other to form open-framework containing 8-MR pore openings. Our studies also show that 3-D open-framework $NiAlP_2O_8 \cdot C_2N_2H_9$ can be built up from AlPO-ESC. This indicates that AlPO-ESC might be first transformed to AlPO-CSC followed by assembly to 3-D open-framework via Ni^{2+} cations. This work provides experimental evidence that 1-D AlPO-CSC and AlPO-ESC chains are important building units for the construction of complex open-frameworks.

Stoichiometries and Coordinations of Al and P Atoms in Aluminophosphates

Aluminophosphates have been found with rich stoichiometries, which can be generally expressed as $Al_mP_nO_{4n}^{3(n-m)-}$ ($m = 1, 2, 3 ..., n = 1, 2, 3 ...$). The Al coordinations occurring in these AlPOs are four, five, and six in the form of $AlO_{3b}(OH)$, AlO_{4b}, AlO_{5b}, $AlO_{4b}(OH)$, $AlO_{4b}(OH)_2$, $AlO_{4b}(H_2O)_2$, $AlO_{4b}(OH)(H_2O)$, $AlO_{5b}(OH)$, and AlO_{6b}, while the P coordinations are solely four in the form of PO_{4b}, $PO_{3b}O_t$, $PO_{2b}O_{2t}$, and PO_bO_{3t} (b, bridging oxygens; t, terminal oxygens). Through alternation of different Al and P coordinations in the lattice, various stoichiometries can be generated. For example, the alternation of AlO_4 and $PO_{3b}O_t$ units restricts a stoichiometry of $Al_3P_4O_{16}^{3-}$. We find that the Al/P ratio and the Al and P coordinations satisfy the following equation:

$$\sum_i m_{AlO_{ib}} \times i_{AlO_{ib}} = \sum_j n_{PO_{jb}} \times j_{PO_{jb}}$$

where i (j) is the number of bridging oxygens coordinated to Al (P), m (n) is the number of AlO_{ib} (PO_{jb}) coordination, $\sum m_{AlO_{ib}} / \sum n_{PO_{jb}} = Al/P$, $i = 3, 4, 5$, and 6, corresponding to
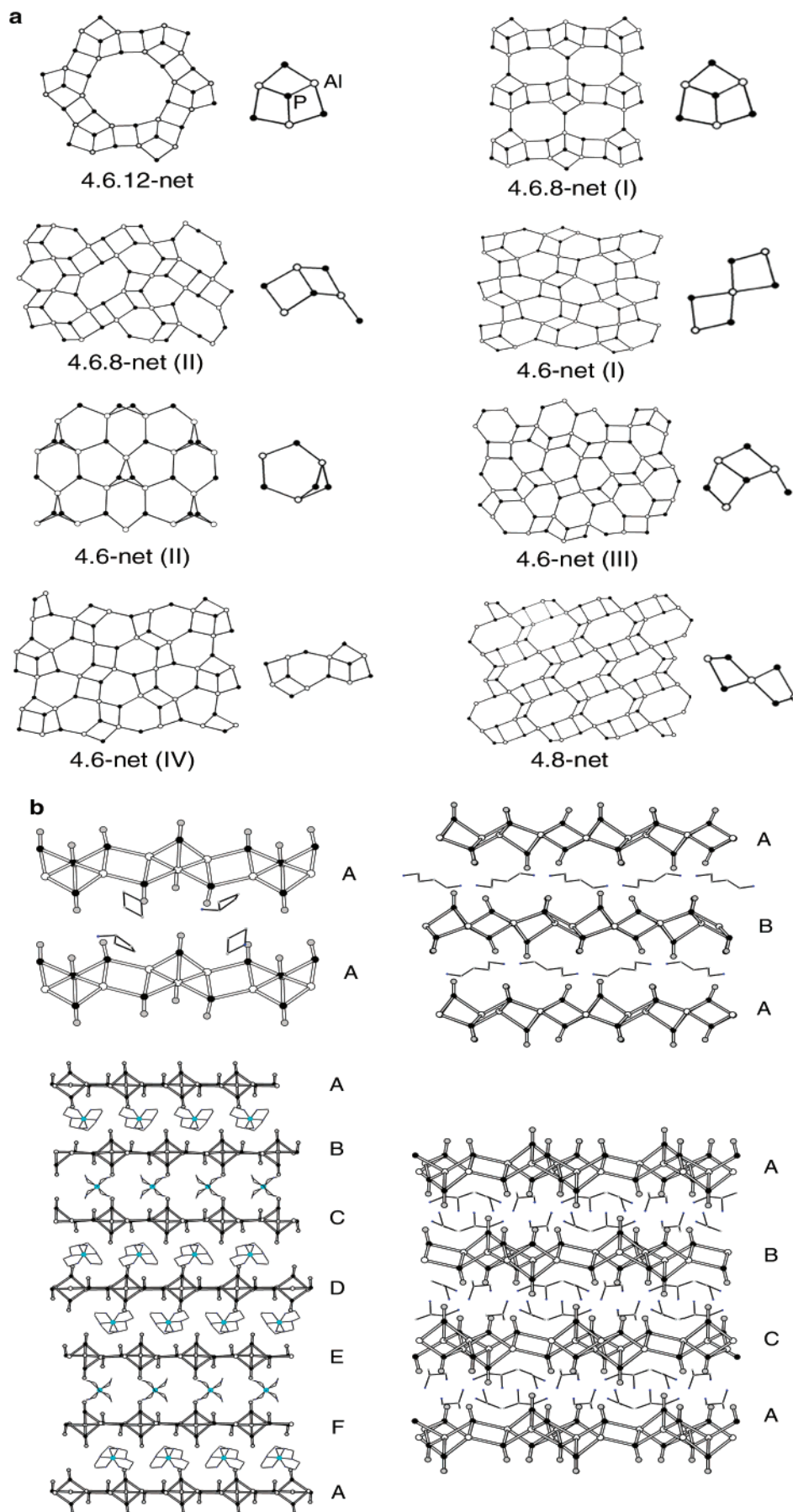
FIGURE 8. (a) Eight distinct 2-D sheet structures and their SBU's. (b) Packing of the sheets with four different stacking sequences.
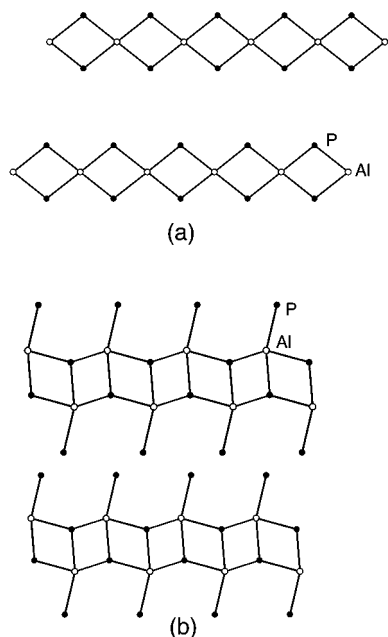
FIGURE 9. (a) Corner-sharing 4-MR chains (AlPO-CSC). (b) Edge-sharing 4-MR chains (AlPO-ESC).
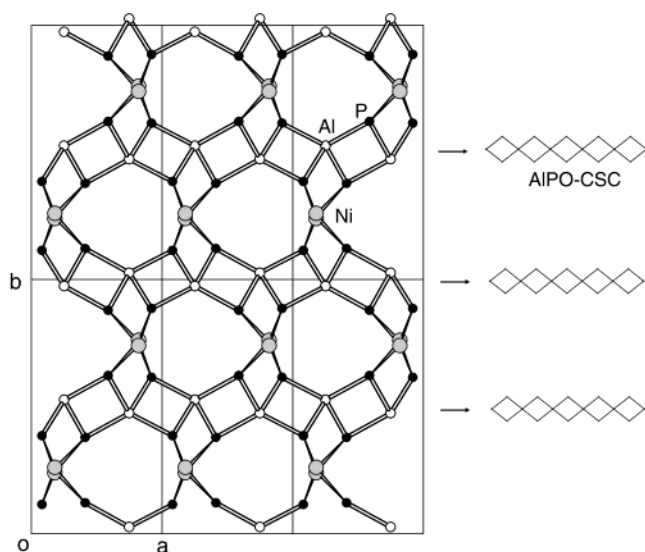

FIGURE 10. 3-D open-framework $NiAlP_2O_8 \cdot C_2N_2H_9$ (intact AlPO-CSC chains are retained in the structure).

$AlO_3(OH)$, AlO_4, AlO_5, and AlO_6 coordinations, respectively, and $j = 1, 2, 3$, and 4, corresponding to PO_4 tetrahedra with one, two, three, and four bridging oxygens, respectively. On the basis of this equation, the Al and P coordinations for a given stoichiometry can be enumerated. The importance of this equation is that coordinations for new stoichiometries, such as $Al_6P_7O_{28}^{3-}$, $Al_7O_8O_{32}^{3-}$, and so forth, could be easily enumerated. This will greatly help to design new structural topologies.

Design of Hypothetical Frameworks

Aluminophosphates exhibit rich structure chemistry because of their diverse coordinations of Al and P atoms. Understanding of their structural construction regularities allows for the search of new topologies. Using computa-

tional method, aluminophosphates with specified stoichiometry can be designed. We have developed a method to systematically enumerate the 2-D nets with $Al_3P_4O_{16}^{3-}$ stoichiometry.[56, 57]

The 2-D nets with $Al_3P_4O_{16}^{3-}$ stoichiometry are typically constructed from alternation of AlO_4 and $PO_3(=O)$ tetrahedra via vertex oxygen atoms to form a 3.4-connection. The generation of such 2-D 3.4-connected meshes must satisfies the following conditions in topology: (i) there are two types of points, a three-connected point (P atom) and a four-connected point (Al atom); (ii) the same type of points cannot be directly connected according to the Lowenstein's rule; (iii) the mesh must be expanded into a periodic 2-D net. Figure 11 shows the generation of a known 4.6.12-net starting from a hexagonal array of nodes (Figure 11a). Figure 11b illustrates the generation of a 2 × 2 mesh. By combining four child meshes (1) 3 × 2, (2) 2 × 2, (3) 3 × 2 and (4) 2 × 2 mesh, a final 5 × 4 mesh (5) is obtained (Figure 11c). This 5 × 4 mesh can be further expanded into the mesh of a 4.6.12-net in Figure 11d. Figure 11e shows the relaxed 4.6.12-net.

After a series of computer procedures are performed, over 500 distinct 3.4-connected meshes with periodic arrangements have been generated. The generated 2-D nets include all known experimental sheets, as well as a variety of hypothetical sheets. Employing such a computational methodology, new topologies for aluminophosphates with various stoichiometries can be designed on the basis of the coordinations of Al and P atoms.

Recently, Draznieks, and Férey et al. developed a method for computational design of inorganic framework by automated assembly of SBUs.[58] This will provide an excellent approach to design new open-frameworks based on various SBU's of AlPOs.

More recently, we have developed a computational methodology for the design of (4,2)-connected open-frameworks with predefined pore geometry through constrained assembly of atoms in the unit cell.[59] In this method, forbidden zones, corresponding to a porous pattern, are first defined in a unit cell, and then atoms are inserted based on specified symmetry and distance constraints (Figure 12a). For example, assuming a space group of $P6_3/mmc$, defining the pore radium of 6.0 Å and unique atoms of 2, a hypothetical open-framework consisting of extra-large micropore 18-MR channel is designed (Figure 12b). It contains columns of *gme* cages, each of which is connected through double 4-MRs. Employing this method, a number of known zeolite-like frameworks, as well as new hypothetical open-frameworks, can be generated. This method can be naturally applied to generate zeolite-like open-framework structures with extra-large micropore, crossed-linked channels, and chiral channels based on function requirements.

Computational and Combinatorial Approaches toward the Discovery of Aluminophosphates

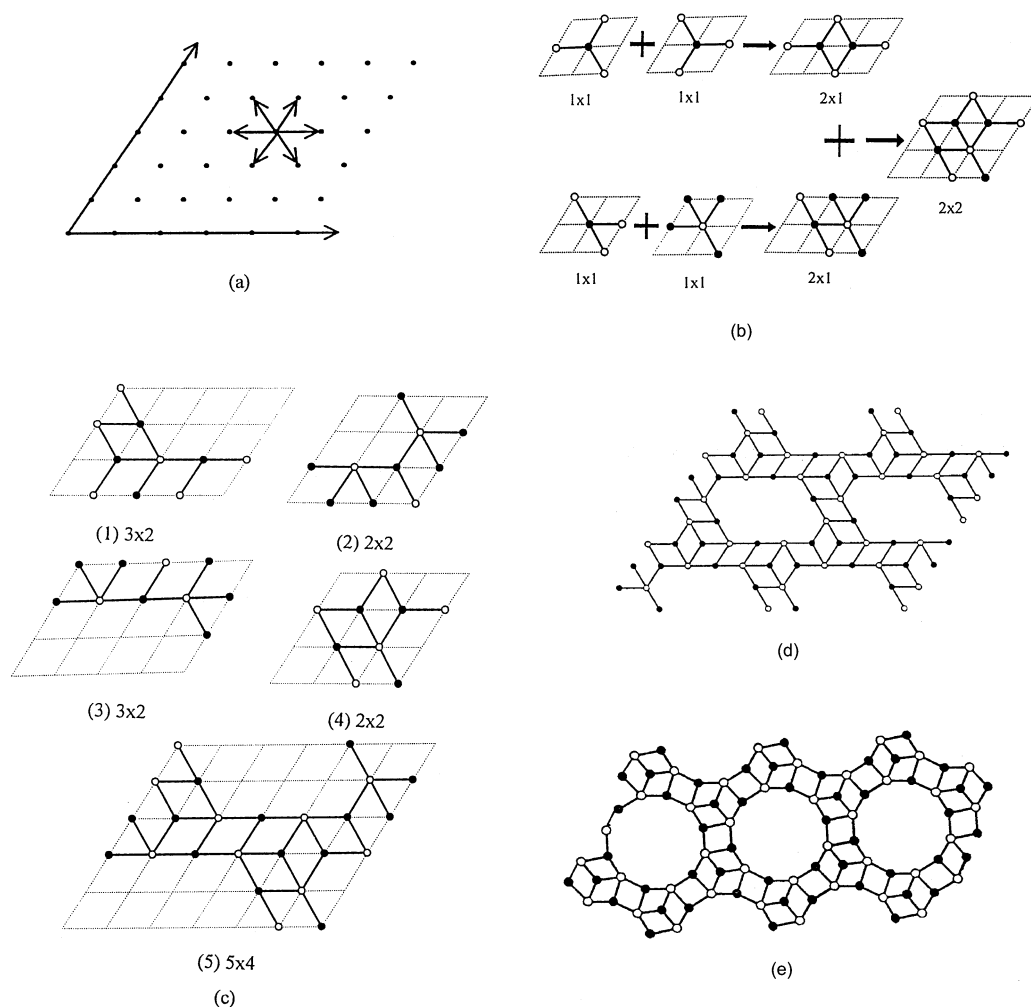Aluminophosphates show fascinating structural architectures. What is of vital importance, however, is how to

FIGURE 11. Generation procedure of a 4.6.12-net (a) axial system and unit cell of nodes in the generation of the mesh. (b) The generation of a 2 × 2 mesh. (c) The generation of a 5 × 4 mesh by combining four child meshes: (1) 3 × 2, (2) 2 × 2, (3) 3 × 2, and (4) 2 × 2. (d) The 4.6.12-net which is expanded from the 5 × 4 mesh. (e) the relaxed 4.6.12 net.

approach to such diverse structures. The open-framework structures are greatly manipulated by organic amine templating agents located in the channels, in the interlayer or interchain regions which interact with the host framework through nonbonding interactions. Toward the discovery of aluminophoshates with specified structures, the selection of suitable templates is acknowledged to be of vital importance. We have recently developed a computational methodology to examine the templating ability of organic amines in the formation of 2-D layer and 3-D open-framework AlPO's.[43,60,61] In terms of the energies of the host-template nonbonding interactions, mainly H-bonding and van der Waals interactions, the templating ability of various organic amines for the inorganic hosts can be predicted. Some suitable template candidates can be selected that have lower interaction energies with a given host. One of the successful examples is the syntheses of $Al_4P_5O_{19}(OH) \cdot C_5N_2H_{16}$ (AlPO-PDA) and $Al_4P_5O_{19}(OH) \cdot C_4N_3H_{15}$ (AlPO-DET) with structures analogous to that of AlPO-HDA by rational selection of 1,5-pentanediamine and diethylenetriamine as templates that are predicted by molecular simulations.[60]

Since 1990s, our group has built up a synthesis database for microporous materials including aluminosilicate zeolites and open-framework metal phosphates. Recently, employing KDD (knowledge discovery of Database)[62] strategy, we have successfully predicted the important synthetic factors determining the formation of aluminophosphates with 12-MR channels, with one of the successful examples being the rational synthesis of $AlPO_4$-5.[63] The KDD directed synthetic route will help to rationalize the synthesis of open-framework aluminophosphates with specified structures.

On the other hand, the methodology of combinatorial chemistry will play a significant role in the discovery of new materials. Despite a large number of aluminophosphates have been found, the space of viable structure types is infinite. Recently, combinatorial approach has been successfully applied to the hydrothermal synthesis of open-framework materials.[64] Using this approach an extensive study of complex multicomponent system is easily achieved, as shown in our recent work in the discovery of new zinc phosphates with novel framework architectures.[65] Combinatorial chemistry will demonstrate its great strength in the discovery of open-framework
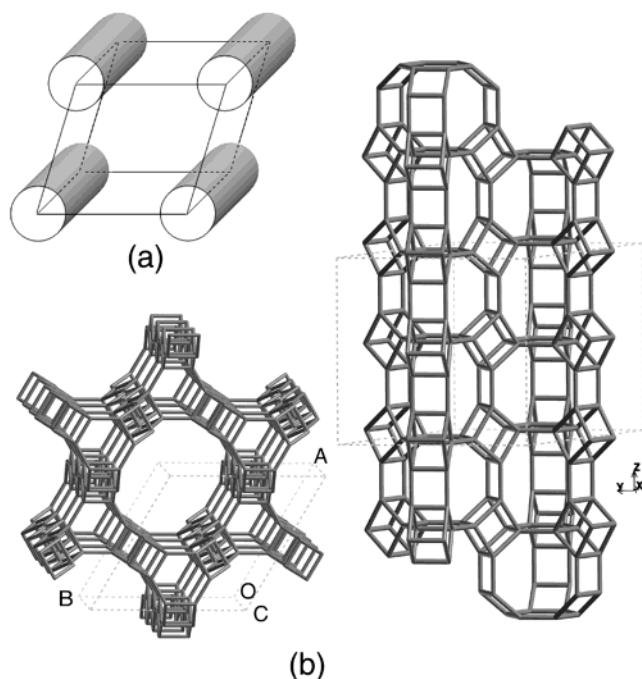
FIGURE 12. (a) The forbidden zones defined as cylinders in one unit cell. (b) The hypothetical framework containing18-MR channels with aperture dimensions of 9.4 Å x 9.4 Å (O···O distance). The refined cell parameters are $a = 16.8$ Å and $c = 14.3$ Å.

materials with new stoichiometries and interesting structural architectures and properties.

Conclusions

The fascinating structure chemistry of a variety of aluminophosphates has been elucidated in this account. Aluminophosphates have been prepared with various structural dimensionalities, such as 3-D open-frameworks, 2-D layers, and 1-D chains, and with various stoichiometries. Compared to aluminosilicate zeolites built up from TO_4 tetrahedra (T = Si, Al), aluminophosphates possess diverse structural topologies because of their rich Al and P coordinations. The increasing interest in aluminophosphates derives from not only their growing chemical and structural diversity, but also from their promising applications as catalysts. Despite the large number of aluminophosphates that have been synthesized, the number of hypothetical topologies is infinite which can be designed by computational methods. The discovery of new materials will be dependent on the new preparative strategies. The use of computational methods such as molecular simulations and KDD technique will greatly assist in the rational synthesis of aluminophosphates with specified structures. On the other hand, combinatorial approach to hydrothermal synthesis will significantly accelerate the rapid discovery of new materials.

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