

Novel Inorganic Frameworks Constructed from Double-Four-Ring (D4R) Units: Computational Design, Structures, and Lattice Energies of Silicate, Aluminophosphate, and Gallophosphate Candidates

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Abstract: The design of new and interesting inorganic frameworks is an ongoing challenge in materials sciences. New structures containing double-four-ring (D4R) units have recently received particular attention. The present work focuses on the computational design of new three-dimensional frameworks made of D4R units exclusively. In a first step, our simulations explore the possible ways to assemble predefined D4R units in 3D space using a sophisticated cascade of simulated annealing/minimizations steps (autoassembly of secondary building units method). While the existing zeotype topologies were successfully generated, new topologies were predicted including very open frameworks containing new types of cages. In a second step, lattice energy minimizations were performed to estimate the viability of these hypothetical frameworks as silicate, aluminophosphate, and gallophosphate candidates. When comparing the hypothetical structures to existing compounds, our results raise the challenging question of the appropriate chemical composition that should be aimed at for a given framework topology of interest.

Introduction

There is a growing interest in the design and representation of solids using the concept of molecular building blocks, with the aim of rationalizing the synthesis of new inorganic materials in general. In experimental chemistry, the building block concept is obviously a very useful tool to a posteriori describe and analyze existing topologies. Reversing this line of reasoning, there is a recent trend to consider the concept of building blocks as an a priori tool to reach synthetic targeted materials, that is, postulate a given local structural unit and find extended structures that either incorporate or completely consist of such “target” units. A whole series of recent articles give an excellent picture of this still emerging field in solid-state chemistry aiming at producing predicted and not-yet-synthesized structures, using intuitive and more rational a priori design approaches.¹

In such a context, the challenging task of simulating structures is of much current interest in materials sciences, chemistry, and crystallography,^{2–8} with the ultimate goal of not only simulating

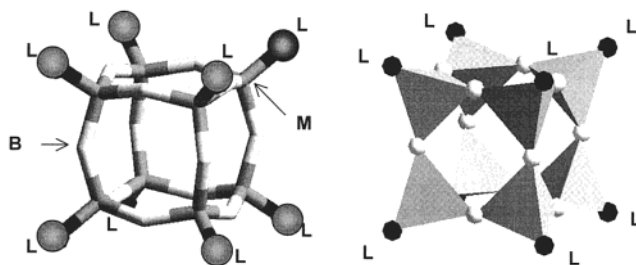


Figure 1. Cylinder (left) and polyhedral (right) representation of the D4R unit as used in the AASBU (automated assembly of secondary building units) method. L: ligand atom; B: bridging atom; M: metal atom.

existing structures but also predicting not-yet-synthesized topologies, raising the challenge to synthesis chemists to produce the simulated hypothetical structures.

In the present work, we tackle the prediction of hypothetical crystal structures constructed from double-four-ring (D4R) units using the AASBU (automated assembly of secondary building units) method.⁷ With the recent development of the AASBU method, we have integrated the concept of building block in a simulation route that generates whole libraries of known and hypothetical structures constructed from the same building block.^{7,8} The key feature of the method lies in the use of predefined topological building blocks and in the exploration of their periodical autoassembly in 3-D space through a cascade of simulated annealing/minimization steps. As a consequence, the AASBU method allows not only to rationalize the organization of the known structures but also to search for new topologies based on the same building block.

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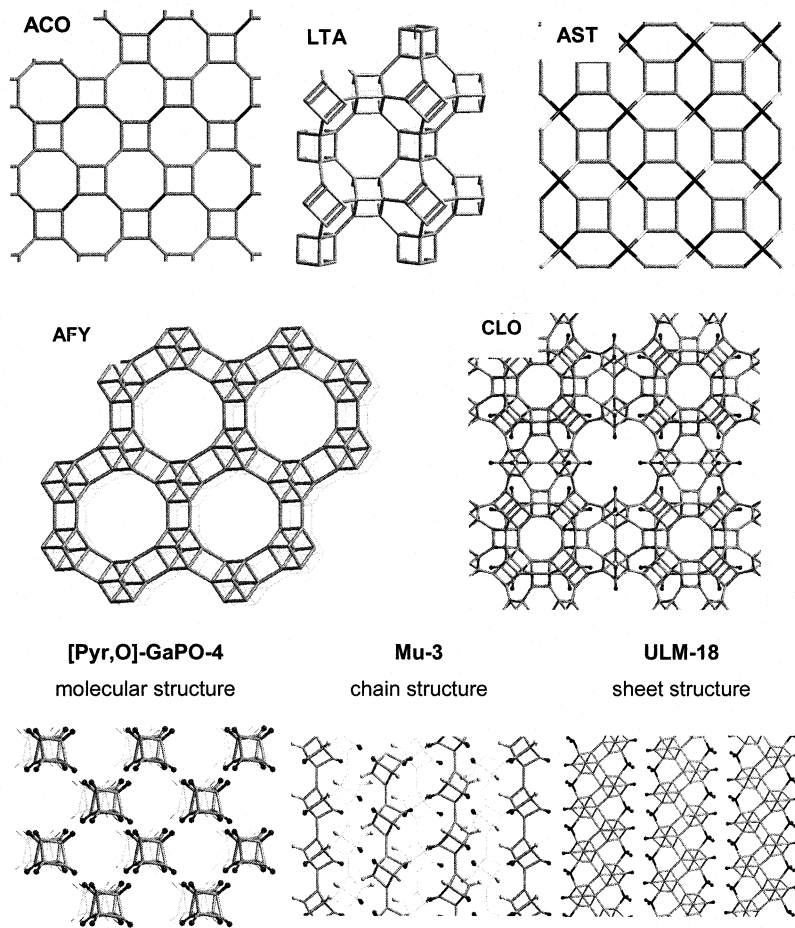


Figure 2. Selection of existing inorganic structures containing double-four-ring units, with three-dimensional structures (ACO, LTA, AST, AFY, –CLO zeotypes); sheet (ULM-18) and chain (Mu-3) structures, and molecular structure [Pyr,O]-GaPO-4. Organic molecules are omitted for clarity.

Our motivations for exploring frameworks made of D4R units directly emanate from the current interest in the study of D4R containing structures and the experimental issues related to their formation in hydrothermal synthesis. A D4R unit (see Figure 1) is made of eight corner-sharing tetrahedra MO_4 ($M = \text{metal}$). Indeed, the synthesis of new structures containing D4R units and related structural units have recently received particular attention, especially with the goal of identifying and understanding the stabilization of such units and their assembly under hydrothermal conditions.⁹ Also, there are reasons to believe that such units or related ones may be the precursors of metal phosphates which further self-assemble into one-dimensional chains, two-dimensional layered structures, or more complex three-dimensional structures.¹⁰

D4R units are commonly found in a series of existing and well-characterized inorganic structures, such as aluminophosphates or gallophosphates. Interestingly, structures made exclusively of D4R units display an important topological diversity, since they cover the whole range of possible dimensionalities (see Figure 2). Known inorganic structures containing only D4R units range from molecular arrangements of independent D4Rs, found, for example, in the recent example of [pyr,O]-GaPO-4 reported by Morris et al.⁹ or in Mu-1¹¹ and

NCUGa-1,¹² or structures made of chains (Mu-3¹³) or sheets of D4R units (ULM-18,¹⁴ to three-dimensional frameworks (Mu-2,¹⁵ ULM-5,¹⁶ Mu-15,¹⁷ Mu-5,¹⁸ cyclam-GaPO,¹⁹ C polymorph of zeolite beta²⁰). Besides Mu-5 and cyclam-GaPO where sheets of D4R are connected to one another through gallium/organic molecule complexes, most of these GaPOs contain D4R units with fluoride species occluded at their centers, suggesting at first a “templating” role of fluorinated species in the formation of D4R units during synthesis. However, recent studies on NCU-Ga-1¹² and [pyr,O]GaPO-4⁹ show they possess D4R units with occluded oxygens instead, tending to show together with a recent study²¹ that fluorine is not necessary to specifically form the DR4 unit.²² Also, there is a limited number of known existing zeotypes structures made exclusively of D4R units, that is, ACO, AFY, LTA, and –CLO.²³ Although containing D4R units, the

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AST zeotype requires the combination of D4R units with additional tetrahedral entities to generate the framework. The LTA structure exists under various chemical compositions: aluminosilicate, aluminogermanate, silico-aluminophosphate, or gallophosphate. In contrast, the ACO structure has been synthesized as a CoAlPO²⁴ only, while AFY exists as CoAlPO²⁵ and MgAlPO²⁶ compounds. Finally, the cloverite structure is well known for its very open gallophosphate framework and interesting acidic properties.²⁷ Figure 2 shows a selection of existing structures, illustrating their various dimensionalities.

Also, D4R units have been the subjects of theoretical studies. Catlow et al. have studied the role of fluorine atoms in the dodecasil structure,²⁸ while Tossell et al. have explored the distribution of Si and Al atoms in the framework of various D4R-containing structures.²⁹ The trapping of HF molecules inside D4R units of the ULM-18 structure has been studied by DFT first principle calculations.³⁰

Such a context has motivated our efforts with the aim of searching for new and open frameworks constructed from D4R units. In the first step, The AASBU method is used to generate hypothetical frameworks. In a second step, lattice energy minimizations were performed on each hypothetical framework in various candidate chemical compositions, namely, SiO₂, AlPO₄, and GaPO₄, to estimate their relative stability to existing related compounds.

Simulation methods

1. Construction of the D4R Unit. The preliminary step consisted of building the D4R unit. It was first extracted from the experimental crystal structure of cloverite. Prior to the simulations, the different atoms were labeled as follows: M, central metal atom; B, bridging atoms between M atoms; L, ligand atoms. The resulting building-unit, M₈B₁₂L₈, therefore consists of a total of 28 atoms, including 12 bridging atoms, which are not allowed to connect to other atoms during the subsequent simulation steps, and of 8 ligand atoms that are deemed to be connection points during simulations (see Figure 1).

2. Cost Function and Force Field Parameters. The rules that control the possible assembly of the D4R units are encapsulated in a cost function consisting of a Lennard-Jones-like term with a force field that essentially favors the attraction of ligand atoms to one another. In other words, this force field favors the formation of ligand••ligand “sticky-atom” pairs and allows two D4R units to assemble through L••L linkages. The interbuilding units interactions are parametrized on an atom–atom basis by a simple Lennard-Jones expression for the energy of interaction between pairs of atoms *i* and *j*, as defined in eq 1:

$$E_{ij} = \epsilon_{ij} [(r_{ij}^*/r_{ij})^{12} - 2(r_{ij}^*/r_{ij})^6] \quad (1)$$

Table 1 shows the force field parameters specifically developed to perform the assembly of D4R units. The crucial issue here is to choose force field parameters that will enforce the production of highly connected structures reproducing the type of connections known to happen in existing compounds, limiting the generation of unrealistic candidates.

Table 1. Lennard-Jones Potential Parameters Used in the Simulations for Assembling D4R Units

atom pairs	ϵ_{ij} kcal mol ⁻¹	r_{ij}^* Å
L _i ••L _j	400	0.2
M _i ••M _j	1	3.4
L _i ••M _j	50	1.8
L _i ••B _j	1	2.8

Typically, the L••L “sticky-atom” pairs are those that, when combined, form the interbuilding units linkages: these are parametrized as an attractive potential well. However, this latter term has no direct physical meaning, serving simply to “glue” together the D4R units at the linkage points during the subsequent simulation steps. To avoid unwanted configurations of D4R units, additional terms were considered. A repulsive potential between metal atoms of two different D4R units prevents two units from overlapping with each other, keeping M_i••M_j pairs distant of 3.4 Å from one another. An attractive potential between L_i••M_j pairs discourages undesirable local minima corresponding to proximate but unconnected D4R units, since it enforces a ligand atom to approach the metal atom of another D4R unit at a typical distance of 1.8 Å (chosen here so as to be close to the experimental Ga–O distances found in gallophosphates). Finally, a repulsive potential between L_i••B_j pairs was used to prevent a D4R unit from connecting to another unit through already fully connected bridging atom B.

The total cost of a given configuration of D4R units in a unit cell, E_{total} , is then computed as the sum over the set of unique building units of the Lennard-Jones terms involving dissimilar L••L, M••M, L••M, and L••B pairs, as defined in eq 2.

$$E_{\text{total}} = \sum (E_{L\cdots L} + E_{M\cdots L} + E_{M\cdots M} + E_{L\cdots B}) \quad (2)$$

The magnitude of this cost function provides an estimate of the degree of connectivity of a given arrangement of building units. In eq 2, the weight of each term is directly given by the depth of the Lennard-Jones potential well, that is, ϵ_{ij} . In the case of attracting species, the $E(L_i\cdots L_j)$ term is given a higher contribution ($\epsilon_{ij} = 400$ kcal.mol⁻¹) than the $E(L_i\cdots M_j)$ term ($\epsilon_{ij} = 50$ kcal.mol⁻¹), since L_i••L_j connections are given the stronger weight to generate connected structures. In the case of repulsive pairs, the parameters are chosen so that a penalty in the energy (positive energy) is produced when two metal atoms (M_i••M_j) or one ligand atom and a bridging atom (L_i••B_j) come too close to one another.

3. Simulation Steps for the Generation of Candidate Structures.

Once the D4R unit and assembly rules are defined, the candidate periodic structures are generated by using a cascade of simulations that entail five major steps: (i) the first step consists of a simulated annealing procedure where periodic trial arrangements of D4R units are randomly generated, within an imposed space group and an imposed number of D4R unit per asymmetric unit. In this work, it was constrained to one D4R unit per asymmetric unit to limit the computational time. The angular degrees of freedom of the D4R unit is sampled by a Metropolis Monte Carlo algorithm. At each such step, both the cell size and the distance between D4R units are adjusted to relieve close interatomic contacts, leading to successive phases of cell contractions and cell expansions. As the simulated annealing proceeds, configurations of lower cost are stored. Simulations were performed in various space groups, typically within a temperature range of 300–10⁶ K. (ii) Redundant arrangements of D4R units are removed through the comparison of radial distribution functions and simulated diffraction patterns. This way, the stored trial arrangements are reduced to a set of unique arrangements, corresponding to unique local minima. (iii) Each set of D4R unit arrangement is minimized with respect to the cost function eq 2 within the original imposed space group. This is the crucial step of the simulations where the D4R units are allowed to connect through the predefined linkage points, that is, ligand atoms, possibly leading to connected periodic arrangements of connected D4R

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units. (iv) After the minimization step, the redundant arrangements are eliminated in a similar fashion to step (ii). During all above simulation steps, the D4R units are treated as rigid bodies. (v) Finally, the pairs of sticky atoms, that is, $L\cdots L$ pairs at very short separation distances (~ 0.20 Å), are reduced to single atoms to lead to realistic crystal structures, having, for example, the ML_4 virtual composition for fully connected arrangements. The true space group symmetry of each simulated structure is then redetermined automatically by the `find_symmetry` algorithm,³¹ and is referred to as the space group of the original hypothetical framework. Additional details about the simulation steps may be found in ref 7.

The result of each simulation run is a list of candidate structures assorted with their final space group, cell parameters, and atomic positions. In this work, only three-dimensional frameworks were analyzed.

4. Lattice Energies of Candidate Structures in their SiO_2 , $AlPO_4$, and $GaPO_4$ forms.

In a last step, we have estimated the lattice energies of the above hypothetical frameworks in various candidate chemical compositions, that is, SiO_2 , $AlPO_4$, and $GaPO_4$. In contrast with the previous simulation step, such calculations allow us to estimate the chemical viability of a hypothetical structure through lattice energies calculations: in each virtual ML_4 structure, ligand atoms were substituted with oxygen atoms and metal atoms were substituted with Si to generate silicates (SiO_2), strictly alternating Al and P atoms to generate aluminophosphates with an Al/P ratio of 1 ($AlPO_4$), and strictly alternating Ga and P atoms to generate gallophosphates with a Ga/P ratio of 1 ($GaPO_4$).

To calculate lattice energies of all virtual compounds, appropriate interatomic interactions are used together with specific interatomic potentials for each chemical family as detailed below.

Here, the interatomic interactions are described by a formal charge shell model. The form of the interatomic potential chosen to describe the interaction between two ions i and j is a Buckingham potential combined with a Coulombic term to describe the electrostatic interactions:

$$E_{ij} = A_{ij} \exp(-r_{ij}/\rho_{ij}) - Cr_{ij}^{-6} + q_i q_j / r_{ij} \quad (3)$$

where q_i and q_j refer to the charges of the ions, and A_{ij} , ρ_{ij} and C_{ij} are short-range potential parameters. The electrostatic energy is calculated using an Ewald summation.³² The short-range energies are evaluated directly in real space with a cutoff of 12 Å. Ionic polarizability of the oxygen atoms is incorporated using the shell model of Dick and Overhauser³³ in which an ion is represented by a core and a shell coupled by a harmonic spring:

$$E_{\text{core-shell}} = 1/2k(r_{\text{core-shell}})^2 \quad (4)$$

where k is the core-shell spring constant.

The total energy is therefore given by the following expression:

$$E_{\text{total}} = \sum_i \sum_j A_{ij} \exp(-r_{ij}/\rho_{ij}) - Cr_{ij}^{-6} + q_i q_j / r_{ij} + \sum_{\text{Oatoms}} 1/2k(r_{\text{core-shell}})^2 \quad (5)$$

Since the chemical substitution of the hypothetical frameworks (M \rightarrow Si for silicates, M \rightarrow Al/P for AlPOs, M \rightarrow Ga/P for GaPOs) may induce changes of symmetry, the symmetry of the hypothetical crystal structure was again analyzed after energy minimizations using the

`find_symmetry` algorithm. In this work, we use force fields that have been specifically developed for studying microporous silicates,^{34,35} aluminophosphates,^{36–39} or more recently gallophosphates.^{40–42} The robustness of these force fields has been addressed through the accurate simulations of well-characterized crystal structures, yielding relative framework stabilities that are consistent with thermodynamic data when available.

Constant-pressure energy minimizations were performed using the GULP code,⁴³ that is, allowing both cell parameters and fractional coordinates to relax in the space groups of the original hypothetical frameworks.

The lattice energies yielded by minimization are dependent on the force field used, so the results given in these calculations are only meaningful when considered as relative to a reference structure. Each chemical family of compounds was compared to the quartz-type structure, its simplest and highest-density experimental isomorph, that is, α -quartz for silicates, berlinite for aluminophosphates, and $GaPO_4$ -quartz for gallophosphates. The minimized lattice energy for each structure was normalized relative to the number of metal atoms per unit cell in the structure and compared to the normalized lattice energy of their corresponding dense quartz-type polymorph. For further comparison, the lattice energies of existing zeotypes in their SiO_2 , $AlPO_4$, and $GaPO_4$ forms were also computed.

Results and Discussion

1. Simulations of Hypothetical Frameworks. Indeed, the AASBU method has the advantage that hypothetical frameworks were generated independently of the chemical nature of the D4R units. This allows us in a first step to look for new topologies: we exclusively focused on the capacity of the D4R units to connect to each other, while automatically scanning structures related to one another through topological relationships.

Rather than an exhaustive search, simulations were performed with the goal of addressing the possibility of designing new and interesting topologies using the D4R as a building unit. The simulations were performed in more than 20 space groups with an imposed number of one D4R unit per asymmetric unit. Typically, the space groups were chosen a priori mainly among low symmetry groups to reduce computational time ($P1$, $P-1$, $P2$, $P2_1$, $C2$, Pc , Cm , Cc , $P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$, $P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, $C222$, $I222$, $Pna2_1$, $P4$, $P3$, $R3$, $P23$). Each space group requires a single simulation run. For each space group, the simulations yielded the possible structures made of D4R units that are compatible with the imposed space group. Here, we want to make the distinction between the space group as imposed during the simulation itself and the space group as obtained from the final symmetry analysis of the simulated structure, referred to as the space group of the original hypothetical framework. These two may be different since arrangements of higher symmetry than that imposed may be produced.

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The final result is a list of predicted candidate structures with their final space groups, cell parameters, and atomic positions for metal and ligand atoms. A typical run required about 2 h CPU time on a Octane SGI R120000 workstation operating at 300 MHz.

As a result of each simulation run, candidate structures are ranked by decreasing degree of connectivity. Since the potential parameters were chosen to favor the connection of all ligand atoms, fully connected structures, with all eight ligand atoms of the D4R unit connected, are automatically placed on the top of the list of candidate structures with higher energies (i.e., cost function). In this study, we focus exclusively on three-dimensional frameworks, with fully or nearly fully connected D4R units, although a very large number of candidate structures with lower dimensionality were also produced during the simulations. With the exception of one candidate structure, these contain fully connected D4R units and correspond to candidate frameworks with the virtual composition ML_4 ($M = \text{metal}$, $L = \text{ligand}$).

As mentioned in the introductory section, the number of existing three-dimensional structures made exclusively of D4R units is rather limited and includes ACO, AFY, LTA, and CLO zeotypes. The known tridimensional structure types ACO, AFY, and LTA were successfully generated during the simulations. The ACO topology was obtained in various space groups: $P1$, $P-1$ (2), $C2$ (5), $C2/c$ (15), $P2_1$ (4), $P2_1/c$ (14), $C222_1$ (20), and $Pna2_1$ (34). A tilted variety was also generated in other space groups: $P2$ (3), $P2_1$ (4), $C2$ (5), Cc (9), $P2_1/c$ (14), $P222$ (16), $P2_12_12_1$ (19), and $Pna2_1$ (34). Both regular and tilted ACO-type structures are shown in Figure 3 (upper left), and the coordinates of the T atoms are given in Table 2. The symmetry of their SiO_2 energy-minimized isotypes was determined after lattice energy minimizations, which lead to $Im-3m$ for the ACO topology in agreement with the experimentally known structure²³ and to $P4/mnc$ for the tilted topology. Interestingly, lattice energies simulations reveal that the tilted form of ACO is 1.7 kJ mol^{-1} (per T site) more stable than its regular isotype in its silicate form, and 1.3 kJ mol^{-1} and 1.4 kJ mol^{-1} (per T site) more stable when considering the AlPO_4 and GaPO_4 isomorphs, respectively.

The AFY topology was generated in the $P-1$ space group exclusively, with a final symmetry of $P-31m$, while the LTA zeotype was generated in $R3$ exclusively, with a final symmetry $Pm-3m$ in its SiO_2 form. The $-CLO$ topology was not generated during our simulations. A careful analysis shows that the unit cell (volume of 125000 \AA^3) of the $-CLO$ structure contains 192 D4R units. The simulation of the $-CLO$ architecture with the AASBU method would thus require either the use of high symmetry space groups such as cubic groups or the use of lower symmetry groups with a larger number of SBUs per asymmetric unit. Both options lead to very time-consuming simulations and therefore were not considered within the scope of this study. Nevertheless, the production of the existing zeotypes may be regarded as a validation criterion of the simulation method within the family of topologies under study.

More interestingly, candidate not-yet-synthesized structures were also generated during the whole series of simulations. A handful of hypothetical three-dimensional frameworks were produced and are shown in Figure 3 (structures T1–T10). All of them possess a tridimensional structure, containing cages or

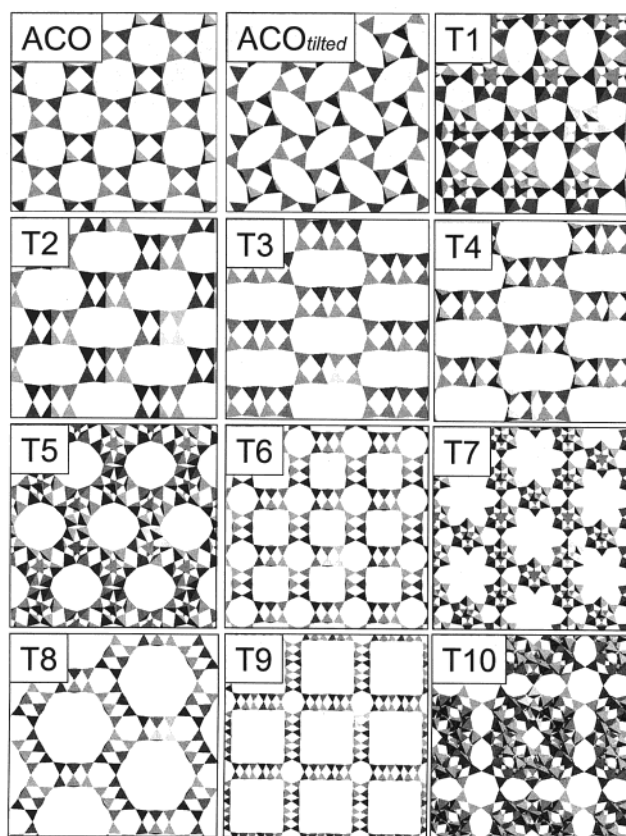


Figure 3. Hypothetical frameworks made of D4R units exclusively, as generated by the simulations. The known ACO topology was successfully predicted, together with a tilted variant, $\text{ACO}_{\text{tilted}}$.

channels. For each structure, the initial space group of the simulation run is indicated together with the final space group of the candidate structure, with the description of the tunnels in terms of direction, the number of tetrahedra that delimit the channels aperture, and their free aperture diameter. Cell parameters and coordinates of the T atoms are also given in Table 2 for each structure (coordinates of oxygen atoms are given as supplementary information). The crystal structures correspond to those obtained after lattice energy minimizations of all candidates in their SiO_2 forms, except in T7 where the interrupted framework did not allow running comparable simulations in term of composition. In this case, the structure is presented as obtained directly from the AASBU method.

Several hypothetical frameworks such as T7, T8, or T10 exhibit interesting and new open topologies, with channels above 11 \AA of free aperture (T7, T8). For example, T7 is closely related to the $-CLO$ topology. Here, the tunnels are delimited by six D4R units, instead of eight in the cloverite structure. Its “interrupted” framework similar to that of cloverite, that is, containing “pending” oxygen atoms pointing toward the channel, suggests that such a new structure could have interesting catalytic applications involving acid sites. The structure T8 reveals the three-dimensional arrangement of D4R units generating regular 18-ring channels interconnected by gmelinite cages; the channel system of this structure is closely related to that of VPI-5 (VFI type) with similar free aperture of 11.5 \AA in comparison with that of 12.7 \AA in VPI-5. Another hypothetical structure (T10) contains surprisingly large cages with a free internal diameter of 16.2 \AA ,^{424688,18} according to Smith

Table 2. Crystal Structures of Hypothetical Frameworks Constructed from D4R Units, As Obtained from the AASBU Method and after Energy Minimizations of the Silicate Forms^a

ACO $a = 9.8023 \text{ \AA}$		$Im3m$	
Si1	x/a 0.8429	y/b 0.8429	z/c 0.8429
ACO Tilted $a = 9.3036 \text{ \AA}$		$b = 9.8392 \text{ \AA}$	
Si1	x/a 0.7914	y/b 0.8946	z/c 0.3432
Structure T1 (One D4R Unit in Cm) $a = 6.689 \text{ \AA}$		$b = 13.989 \text{ \AA}$	
		$Fmmm$ $c = 28.210 \text{ \AA}$	
Si1	x/a 0.3427	y/b 1/2	z/c 0.2959
Si2	0.3392	0.3443	0.3737
Si3	0.3361	1/2	0.4470
Structure T2 (One D4R Unit in $P-1$) $a = 9.303 \text{ \AA}$		$b = 14.196 \text{ \AA}$	
		$Cmmm$ $c = 7.173 \text{ \AA}$	
Si1	x/a 0.1700	y/b 0.1520	z/c 1/2
Si2	0.1703	0	0.7928
Structure T3 (One D4R Unit in $Pna2_1$) $a = 9.472 \text{ \AA}$		$b = 20.210 \text{ \AA}$	
		$Cmcm$ $c = 10.017 \text{ \AA}$	
Si1	x/a 0.8352	y/b -0.2976	z/c 0.0957
Si2	0.1678	-0.4467	0.1024
Structure T4 (One D4R Unit in $P-1$) $a = 19.689 \text{ \AA}$		$b = 9.933 \text{ \AA}$	
		$C2/m$ $c = 11.249 \text{ \AA}$	
Si1	x/a 0.1432	y/b 0.6501	z/c 0.8955
Si2	0.0773	0.6601	0.6074
Si3	0.3031	0.6481	0.8893
Si4	0.2277	0.3419	0.5929
Structure T5 (One D4R Unit in $Pna2_1$) $a = 12.670 \text{ \AA}$		$b = 19.561 \text{ \AA}$	
		$Pna2_1$ $c = 8.153 \text{ \AA}$	
Si1	x/a 0.5895	y/b 0.5484	z/c 0.9063
Si2	0.4845	0.6654	0.6978
Si3	0.2945	0.6560	0.9208
Si4	0.5899	0.7707	0.8990
Si5	0.4011	0.7744	0.1227
Si6	0.4031	0.5536	0.1263
Si7	0.5094	0.6714	0.3245
Si8	0.6954	0.6539	0.1147
Structure T6 (One D4R Unit in $P4$) $a = 11.815 \text{ \AA}$		$c = 7.166 \text{ \AA}$	
		$P4/mmm$	
Si1	x/a 0.6334	y/b 0.1837	z/c 0
Si2	0.6340	0	0.2929
Structure T7 (One D4R Unit in $R3$) $a = 28.705 \text{ \AA}$		$c = 8.766 \text{ \AA}$	
		$R3$	
Si1	x/a 0.6107	y/b 0.7213	z/c -0.1149
Si2	0.5760	0.7851	0.0881
Si3	0.6655	0.8300	0.3288
Si4	0.6113	0.8862	-0.1063
Si5	0.7118	0.9259	0.1007
Si6	0.7101	0.7868	0.0834
Si7	0.7729	0.8882	-0.1120
Si8	0.6642	0.8314	-0.2790
Structure T8 (One D4R Unit in $P3$) $a = 16.953 \text{ \AA}$		$c = 7.176 \text{ \AA}$	
		$P6/mmm$	
Si1	x/a 0.6668	y/b 0.1470	z/c 0.0000
Si2	0.5935	0	0.7071
Structure T9 (One D4R Unit in $P4$) $a = 19.031 \text{ \AA}$		$c = 7.191 \text{ \AA}$	
		$P4/mmm$	
Si1	x/a 0.9162	y/b 0.5786	z/c 0
Si2	0.9177	0.8036	0
Si3	0.9168	0.6890	0.7066
Structure T10 (One D4R Unit in $P23$) $a = 18.870 \text{ \AA}$			
		$P-43m$	
Si1	x/a 0.9050	y/b 0.7920	z/c 0.3263
Si2	0.0013	0.6990	0.4187
Si3	0.1305	0.7603	0.3498
Si4	0.0329	0.8565	0.2541

^a For clarity, only the positions of T (Si) atoms are indicated. For comparison, the existing ACO topology and its tilted hypothetical variety are included.

notation⁴⁴ (the normal figures indicate the number of tetrahedra belonging to the ring, the exponent indicates the number of such rings in the cage). In this case, the arrangement of D4R units generates an interesting eight-ring open-framework system. The careful analysis of these new structures reveals that they contain both known and new cages (see Figure 4). Known cages include hexagonal and octagonal prisms, gmelinite and paulingite cages, and the TSC cage. The TSC cage is known from the tschermontite zeolite, which does not contain any D4R unit. The assembly of D4R units may generate a big cage (96 atoms) exclusively. Interestingly, the T10 structures contain two new cages, viz. $4^{12}8^2$ and $4^{12}6^{88}6$ according to Smith notation.⁴⁴

2. Energetics of Hypothetical Frameworks with SiO_2 , AlPO_4 , and GaPO_4 Candidate Compositions. The above generation of hypothetical frameworks immediately raises the following question: what would be a compatible chemical composition for a given topology of interest? Finding an answer is out of reach using the current computational approaches. At present, such an a posteriori choice of adequate chemical compositions requires the expertise of experimental chemists to rationalize the relationships between the corpus of already existing framework topologies and their synthesized representatives in terms of chemical compositions. The occurrence of typical topologies within given chemical composition boundaries may provide guidance for the synthesis of hypothetical frameworks. In this regard, simulations may be used to estimate the stability of hypothetical structures in various chemical compositions.

Following this line of reasoning, we have calculated the lattice energies of the above hypothetical zeotype frameworks (with exception of T7) using the GULP code⁴³ for energy minimizations, for three candidate chemical compositions, SiO_2 , AlPO_4 , and GaPO_4 , that are frequently reported for zeotype or related structures. In that purpose, the L (ligand) and M (metal) atoms of the hypothetical frameworks were assigned with the appropriate potential parameters,^{34,36,40} and the lattice energies were calculated using the potential energy function in eq 5. For generating pure silicates, metal atoms were substituted with silicon atoms and ligand atoms with oxygens. For generating structures with the AlPO_4 (GaPO_4) composition, the metal atoms of each framework were substituted according to a strict alternation of Al/P (Ga/P) atoms when possible. Lattice energy minimizations were performed in $P1$ at constant pressure, allowing cell parameters to relax, followed with a symmetry analysis of each minimized structure. The minimized lattice energy for each structure was normalized relative to the number of metal atoms in the structure (Si, Ga/P, Al/P) and compared to the normalized lattice energy of their existing dense polymorphs, α -quartz (SiO_2), α -berlinite (AlPO_4), and GaPO_4 -quartz, respectively.

For further comparison with existing structures, several frameworks were selected from the Atlas of Zeolites Framework Types:²³ ACO, AET, AFY, CFI, DON, LTA, OSO, and VFI. Their structures were energy minimized as pure silicates, as well as aluminophosphates (Al/P = 1) and gallophosphates (Ga/P = 1) when possible. Three frameworks from our selection could not be simulated as AlPO_4 and GaPO_4 (CFI, DON, OSO) since they contain rings with an odd number of tetrahedral atoms,

(44) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149.

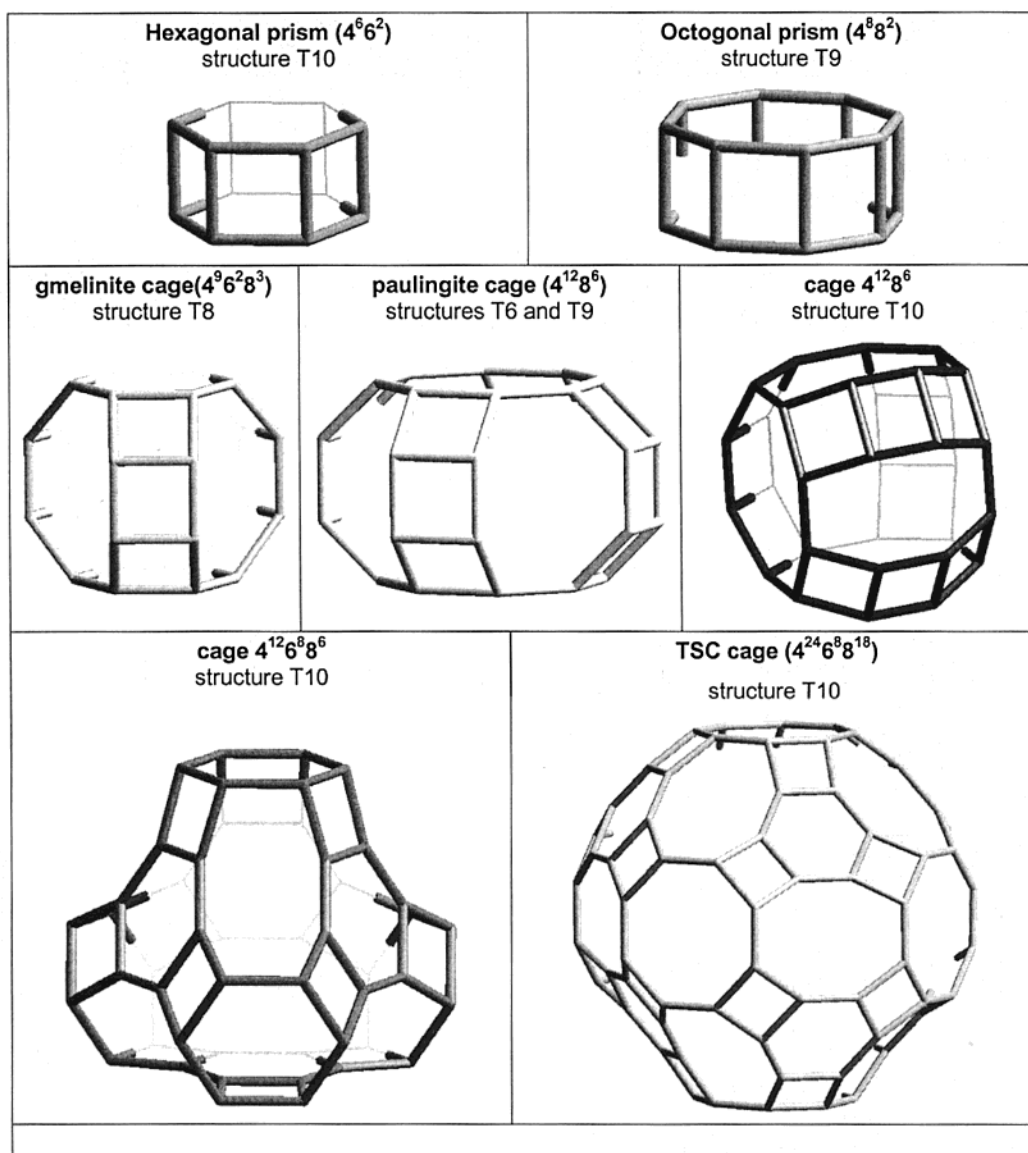


Figure 4. Both known and new cages are found in the hypothetical frameworks generated by the autoassembly of D4R units. Their names according to Smith's notation are indicated together with the frameworks where they are found.

Table 3. Selection of Known Framework Types with Their Various Existing Compositions

	silicates	aluminophosphates	gallophosphates
ACO		ACP-1 (eda)Al _{0.88} Co _{7.52} P ₈ O ₃₂	
AET		AIPO-8 Al ₃₆ P ₃₆ O ₁₄₄	
AFY		(dpa)(H ₂ O) ₇ -Co ₃ Al ₃ P ₈ O ₃₂	
CFI	CIT-5 SiO ₂		
DON	UTD-1		
	[(Cp ₂ Co) ₂ F _{1.5} (OH) _{0.5}]SiO ₂		
LTA	(H ₂ O) ₂₇ Na ₁₂ Al ₁₂ Si ₁₂ O ₄₈	AlPO ₄	[Ga ₁₂ P ₁₂ O ₄₈][(n-C ₃ H ₇) ₂ NH ₂ F] ₃
OSO	OSB-1 K ₆ (H ₂ O) ₉ (Be ₃ Si ₆ O ₁₈)		
VFI		VPI-5 (H ₂ O) ₄₂ Al ₁₈ P ₁₈ O ₇₂	

which render their structure incompatible with a strict alternation of Al/P or Ga/P atoms. Interestingly, Table 3 gives the above selected list of known zeotype frameworks with their various existing representatives in terms of chemical compositions, such as silicates, aluminosilicates, aluminophosphates, or gallophosphates. Our selection was not restricted to structures made exclusively of D4R units but rather guided by their chemical composition. Our choice was oriented toward structure types having a limited number of chemical representatives, possibly

one only among silicates, AlPOs, or GAPOs, with the exception of LTA having chemical representatives in each family.

Such a comparison between hypothetical structures and existing compounds may shed light on the chemical viability of the hypothetical frameworks simulated in this work. At this stage, we want to mention that the simulation of interrupted frameworks, that is, containing pending oxygens, such as the -CLO structure type or the hypothetical framework, T7, could not be included in this study. Indeed, the simulations of such

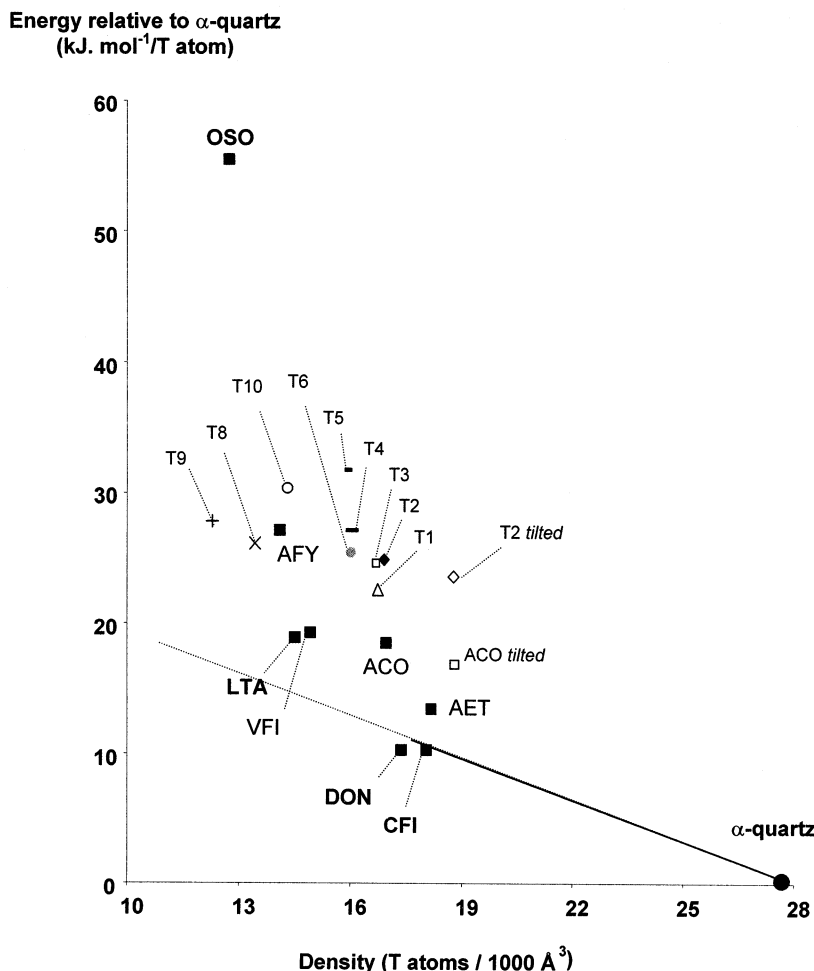


Figure 5. Plot of calculated lattice energies as a function of density for hypothetical pure silicates. Model SiO_2 structures directly built from their zeolitic analogues are also shown for comparison with their code names. The code names with bold character indicate that the structure type has experimental representatives in the chemical family of silicates or related compounds.

structures would need special treatment to restore the neutral framework required to perform energy minimizations and would prevent them from being compared to the other frameworks in this study.

Figures 5–7 plot the calculated lattice energies (normalized per T atom) of the hypothetical structures as a function of density (number of T atoms per volume units) in their SiO_2 , AlPO_4 , and GaPO_4 forms, respectively. The calculations on model silicates directly built from their zeolitic analogues are also reported in each plot with their code names.

The striking feature of the simulations is that there is an important dispersion of lattice energies of hypothetical frameworks with density in all three chemical families, SiO_2 , AlPO_4 , and GaPO_4 . All hypothetical structures appear to have relatively high lattice energies, making them particularly unstable in regard to the existing zeotype structures.

The case of pure silicate structures is particularly illustrative (Figure 5). The LTA, DON, and CFI– SiO_2 structures lie in the lower part of the energy/ density plot delimiting with the α -quartz structure the well-known linear trend of lattice energies of siliceous zeolites with density.³⁵ The line is drawn here so that it includes the existing stable pure silicate compounds, that is, quartz and CFI. This linear trend is represented as a black line in Figure 5 where the less dense structures have lower lattice energies and are to be considered as metastable phases when

Table 4. Range of T–O–T Angles (degrees) Found in the Hypothetical Frameworks Generated with D4R Units^a

T1	135.5–177.5	OSO	121.5
T2	137.8–174.2	AFY	180
T3	132.7–180	ACO	180
T4	134.5–180	ACO _{tilted}	147
T5	130.8–168.7	LTA	155.7
T6	133–173		
T8	133–175		
T9	133.5–176.9		
T10	165		

^a Angles given here correspond to those found in the pure silicate representatives after energy minimizations at constant pressure.

compared to α -quartz. Consistently, the LTA and DON structure types are known to be viable as silicates or chemically related compounds (see Table 3): the DON structure type has been synthesized in a silicate templated form, $(\text{Cp}_2\text{Co})_2\text{F}_{1.5}(\text{OH})_{0.5}\text{SiO}_2$ (Cp = cyclopentadiene), while LTA exists as a hydrated aluminosilicate, $(\text{H}_2\text{O})_{27}\text{Na}_{12}\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$.²³ Though our pure silicate models for LTA and DON are not strictly representative of the real materials, because of the presence of inframework aluminum atoms or extraframework species (template, water), their lattice energies are among the lowest ones, consistently with their experimental availability as silicates. The other structure types, ACO, VFI, AFY, and OSO are relatively unstable and possibly unviable structures as pure silicates. Since

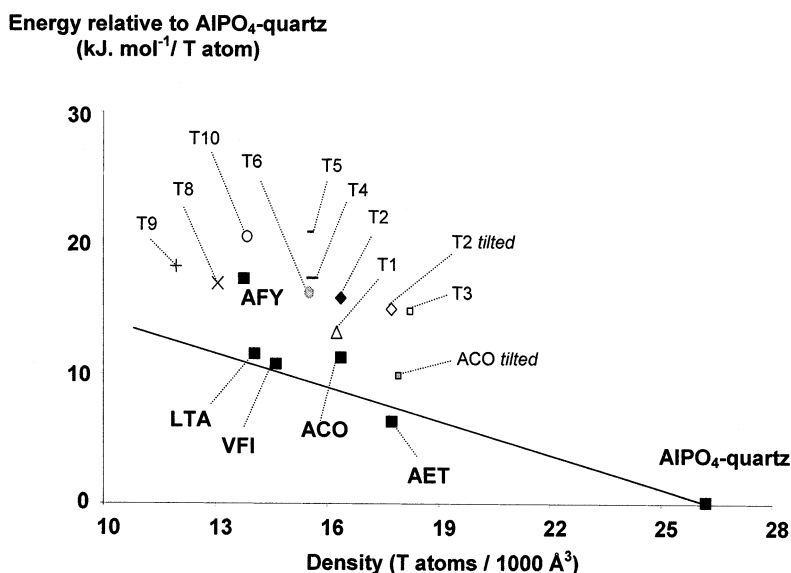


Figure 6. Plot of calculated lattice energies as a function of density for hypothetical pure aluminophosphates. Model AlPO_4 structures directly built from their zeolitic analogues are also shown for comparison on this plot with their code names. A code name with bold character indicates that the structure type has experimental representatives in the chemical family of aluminophosphates.

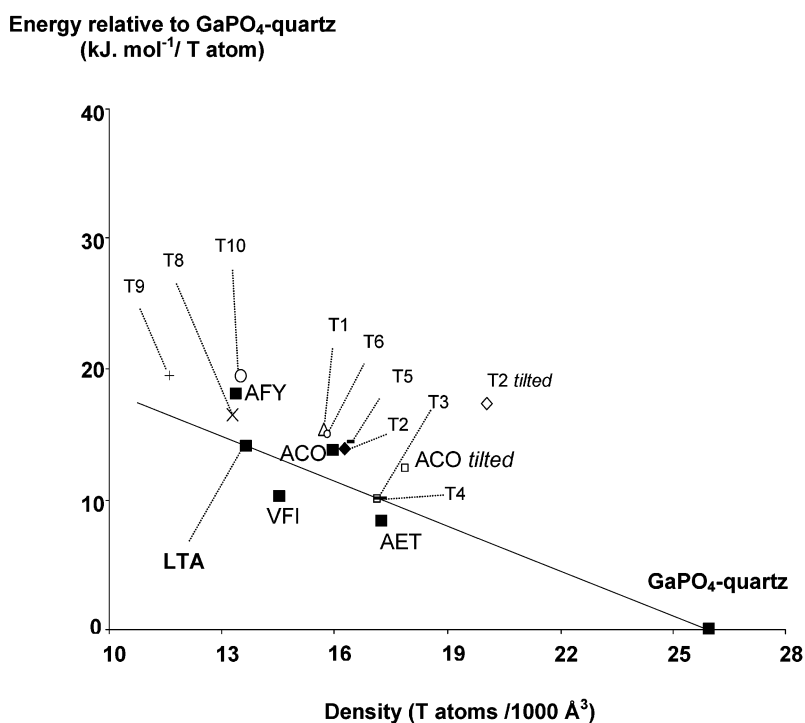


Figure 7. Plot of calculated lattice energies as a function of density for hypothetical pure gallophosphates. Model GaPO_4 structures directly built from their zeolitic analogues are also shown for comparison on this plot with their code names. A code name with bold character indicates that the structure type has experimental representatives in the chemical family of gallophosphates.

these frameworks have no pure silicate representatives, this makes our calculations consistent with their experimental unavailability so far.

While zeolite models having existing representatives in silicates belong to the (meta)stable structures, it is striking that most hypothetical SiO_2 frameworks generated in this work, T1–T10, lie in the upper part on the energy–density plot. They are systematically less stable than that expected from the monotonic energy/density relationship. A careful analysis of each structure reveals that they systematically show unrealistic structural distortions. While the Si–O–Si angles are typically found

around 147° in zeolites, they are found here to cover a wide range from 135° up to 180° in many structures. Table 4 gives a range of T–O–T angles found in the energy-minimized silicate forms of the hypothetical frameworks. In many hypothetical frameworks, the D4R units are found to be connected to one another through Si–O–Si linkages at 180° . In a similar fashion, the AFY and ACO structure types show Si–O–Si angles at 180° between all D4R units. The pure silicate form of OSO exhibits unrealistic structural features, where Si–O–Si angles are all at 127° suggesting Si–Si van der Waals contacts which are too short.⁴⁵ Such small Si–O–Si angles are known to have

large destabilizing effects in silicates.⁴⁶ Surprisingly, the tilted ACO shows all regular Si–O–Si angles around 147°, suggesting viability of the structure as a pure silicate.

However, it is striking that the OSO structure type, which is highly unstable as a pure silicate, exists as a beryllsilicate ($K_6(H_2O)Be_3Si_6O_{18}$). Such instability of the pure silicate form of OSO could emanate from repulsive interactions taking place inside the highly distorted three-membered rings. The stabilization of the framework is performed with the incorporation of inframework beryllium atoms that allows a local relaxation of the three-membered rings.⁴⁵

Indeed, the above results clearly show that the generation and the design of new open frameworks, while being now accessible with available simulation tools, raises the challenging question of their possible chemical compositions.

Our energy minimizations of the hypothetical structures (T1–T10) as aluminophosphates and gallophosphates further illustrate this issue. Figures 6 and 7 show the energy/density plots for AlPOs and GaPOs derived from both the hypothetical frameworks (T1–T10) and existing framework types. Again, the frameworks that have experimental representatives as aluminophosphates (AET, ACO, LTA, VFI, see Figure 6) and gallophosphates (LTA, see Figure 7) are among the most stable structures, delimiting a linear trend with their corresponding dense polymorphs, AlPO₄-quartz and GaPO₄-quartz, respectively. The dispersion of hypothetical AlPOs and GaPOs above

the line of existing compounds may be associated with systematic structural distortions of the frameworks. Again, the question of the appropriate chemical composition required for stabilizing such low density frameworks remains an open challenge. In that respect, the AFY structure is again illustrative: while being relatively unstable as a pure aluminophosphate, AlPO₄, it is stabilized when synthesized as a cobalt-aluminophosphate.

Conclusion

This work illustrates the computational design of new inorganic frameworks constructed from double-four-ring units. The advantage of simulation approaches such as the AASBU method is that the building unit may encapsulate a local structure of interest, such as the D4R unit, allowing us to focus on topologically related structures. The estimation of the lattice energies of about 10 new frameworks was performed in various candidate chemical compositions—SiO₂, AlPO₄, and GaPO₄—and compared to those of existing related compounds, yielding useful insight into their potential viability. The combination of the computational design of new networks together with the estimation of their potential stability in terms of chemical candidates can be a powerful strategy for the synthesis of targeted structures that possess predefined, desirable adsorption and catalytic properties.

Supporting Information Available: Tables of atomic coordinates of oxygen atoms of hypothetical frameworks (T1–T10) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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