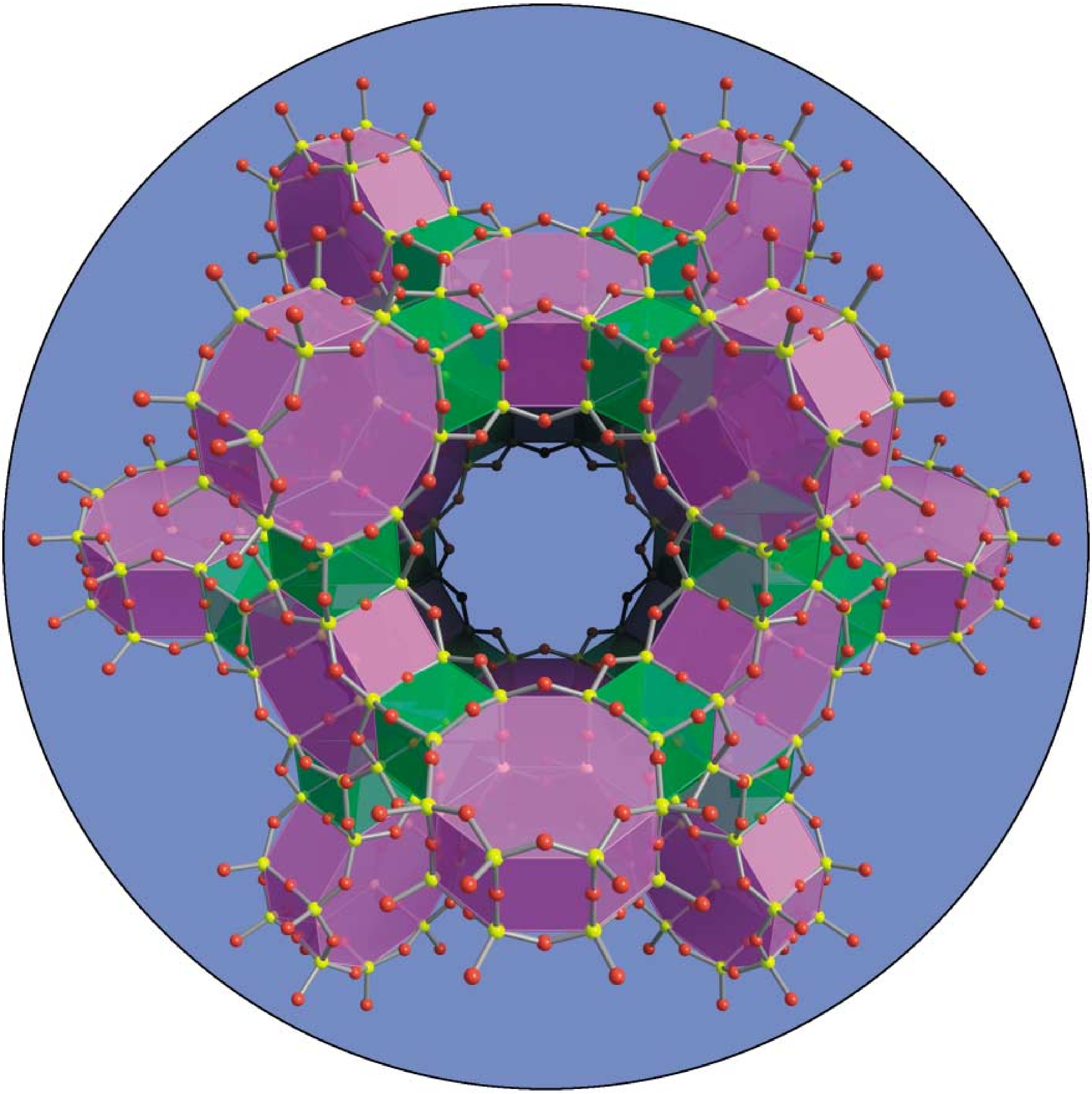
Zuschriften



Durch Einbeziehung jüngster Fortschritte in der mathematischen Pflasterungstheorie berechneten R. G. Bell und J. Klinowski et al. die hypothetischen Strukturen einer Anzahl von Zeolithgerüsten. Die Anwendung dieser Ergebnisse zum Materialdesign wird auf den folgenden Seiten diskutiert.

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Zeolite Frameworks

Structural Evaluation of Systematically Enumerated Hypothetical Uninodal Zeolites**

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The wide applications of zeolites as molecular sieves, ion exchangers, and catalysts, and their intrinsic academic interest have given rise to a large body of work on the characterization of zeolitic structures, of which 139 distinct structural types are known.[1] The design of new zeolite frameworks is a matter of considerable importance for two main reasons. Firstly, a list of chemically feasible hypothetical structures will permit the design of strategies leading to their synthesis. Secondly, X-ray diffraction patterns generated for hypothetical structures will be of considerable help in determining the structures of new materials.

The enumeration of zeolitic structures originates from the work of Wells.[2] New structures have been generated by linking together various structural subunits in new ways,[3–5] or by using computer search algorithms.[6,7] However, such methods can generate only a small fraction of possible networks, since the number of three-dimensional frameworks constructed from tetrahedral building blocks is infinite.

A completely new approach to the problem of systematic enumeration[8] is based on recent advances in mathematical tiling theory.[9] We now describe the use of simulation methods of computational chemistry to calculate the structure, lattice energy, framework density, and other structural parameters of such hypothetical frameworks. Each framework was assumed to have the empirical formula SiO_2 and optimized using a standard lattice-energy-minimization program GULP.[10] Accurate interatomic potential methods were used to calculate lattice energies of these structures relative to α-quartz. Based on relative lattice energy and on various structural features, we have devised criteria to identify frameworks that are likely to be feasible as zeolites. We describe the results for hypothetical uninodal structures (structures in which all tetrahedral sites are equivalent), which contain all 19 known uninodal zeolites, providing a control set to guide our selection of feasible structures, with the main criterion being the relative lattice energy.

A total of 294 uninodal frameworks were originally enumerated.[8] This set included nine uninodal frameworks derived from simple tilings (with tetrahedral vertex figures), and frameworks from quasi-simple tilings (with vertex figures derived from tetrahedra, but containing double edges). After removing duplicates and frameworks in which, after one initial Si–Si separation was set at 3.1 Å there remained more than three other next-neighbor Si atoms within 3.1 ± 0.2 Å, 166 uninodal structures were available for evaluation. Of these, all except two were refineable in the sense that we were able to carry out an energy-minimization calculation on their structure. Among the 164 minimized structures were 19 known zeolites, two minerals (tridymite and cristobalite) and 80 unknown zeolite topologies. The remaining structures were duplicates with the same framework topology but arising from different tilings which, in most cases, minimized to identical structures. In several cases, however, qualitatively different structures were obtained with the same topology, because different unit cell definitions can result in minimized structures with different symmetries. For example, several low- and high-symmetry forms of cristobalite and trydimite were found. While most of the structures have previously been found by model-building[4] or computer-based methods,[6] our enumeration is systematic, and ranking by relative lattice energies gives a different "order of preference" as compared to those of Boisen et al.[11] (who used a calculated force field) and Treacy et al.[6] (who relied on an empirical cost function based on the geometries of known silicate zeolites), thus giving prominence to a different subset of chemically feasible structures.

For framework-energy calculations (Figure 1), instead of considering only zeolites which exist in the purely siliceous form, we have treated all the known topologies as though they were realized as silica polymorphs. The three structures which substantially deviate from the rest are the non-silicate structure types WEI (a beryllophosphate), CZP (a zincophosphate), and OSO (a berylosilicate). OSO and WEI are frameworks containing three-membered rings, and the higher energy of these structures in the siliceous form indicates a strained framework. Figure 1 excludes structures CHI, CLO, PAR, RON, and WEN, which have interrupted frameworks. The straight line, showing the least-squares fit for all data except those for CZP, WEI and OSO, is similar to those reported by Henson et al.[12] and Aporiaye and Price,[13] and to those derived from calorimetric measurements.[14] The deviation of the relative lattice energy from the fit can be easily quantified. If the equation of the regression line is written as $y + ax + c = 0$ (where y = framework energy E_F and x = framework density D_F), then the distance of a point with coordinates (x_1, y_1) from the line is $\vartheta = |(ax_1 + y_1 + c)/a|$. Table S1 (Supporting Information) lists the values of the

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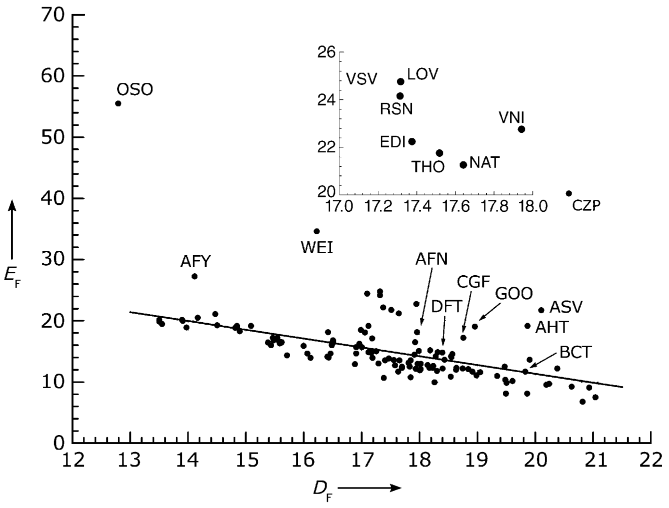

Figure 1. Framework energy (kJ mol^{-1}) with respect to α-quartz versus framework density (Si atoms per 1000 Å^3) for all known zeolitic structure types treated as silica polymorphs. The equation of the least-squares best fit line is $E_F = -1.4404 \times D_F + 40.126$ (correlation coefficient $R = -0.69$).

dimensionless deviation parameter ϑ for the structures which we consider as the most feasible.

Figure 2 gives the plot of relative framework energy versus the framework density for the known and hypothetical uninodal structures for energies below 35 kJ mol^{-1}. This identifies structures with energies falling within this range, which we consider as the most feasible. Some of these hypothetical structures have been singled out using several criteria.

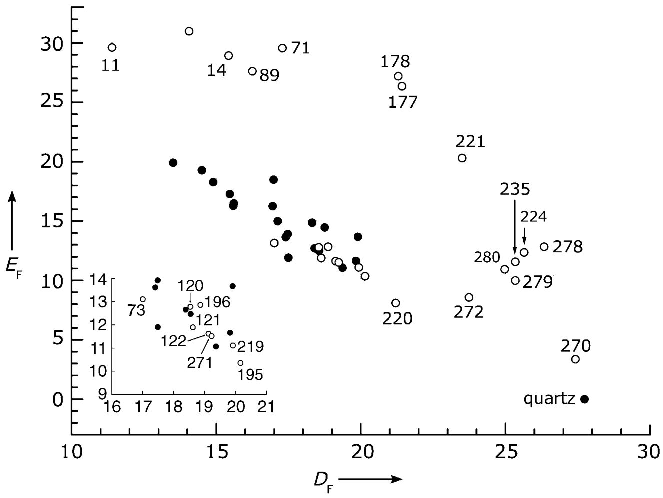

Figure 2. Framework energy with respect to α-quartz versus framework density for known (●) and hypothetical (○) uninodal zeolitic structures with framework energies below 35 kJ mol^{-1}.

Figure 3 shows the plot of relative framework density (Si atoms per 1000 Å^3) versus the number of Si atoms in the fourth coordination shell (N_4), a topological property directly related to framework density, for the known and hypothetical uninodal zeolites. For quartz, the most dense structure, $N_4 = 52$. Structures with low framework density contain large cavities and/or channels outlined by large rings. This occurs for low degrees of branching of the framework, and is reflected in the coordination sequence, which is thus a useful tool for identifying feasible zeolitic structures.[3,13]

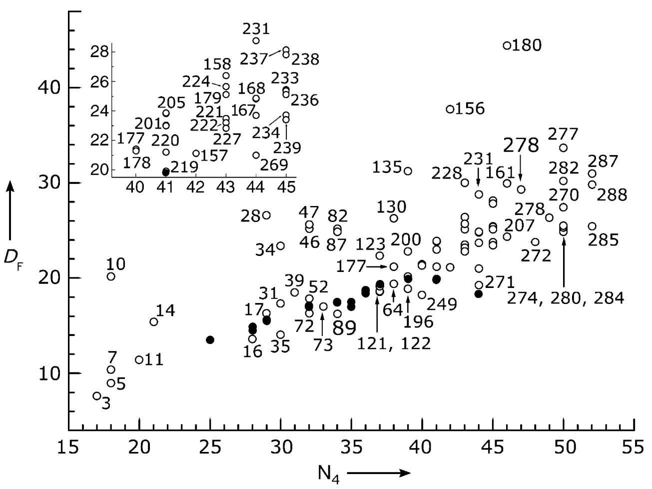

Figure 3. Framework density versus the number of Si atoms in the fourth coordination shell for known (●) and hypothetical (○) uninodal zeolitic structures.

The accessible free volume determined by a probe molecule with a radius of 1.4 Å (such as H_2O) gives an indication of the space that is available within each structure for applications in molecular sieving and catalysis. Known structures such as AST, MSO, and NON have zero accessible volume for the given size of the probe molecule. OSO has the highest accessible volume, closely followed by FAU, EMT, and SBT, all of which contain large cavities.

Low-framework-density structures are of particular interest, as they have very high accessible free volumes. Of the structures corresponding to points on the left of Figure 4, only structure 11 turns out to be energetically stable (Figure 5 a).

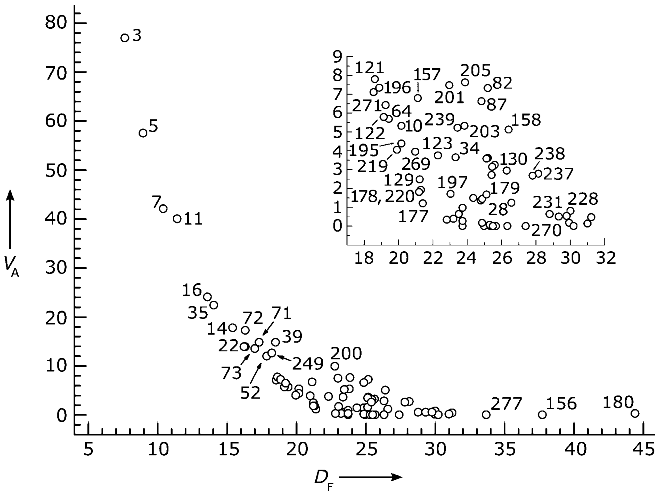

Figure 4. Accessible volume (Å^3 per Si atom) versus framework density for the hypothetical uninodal zeolites.

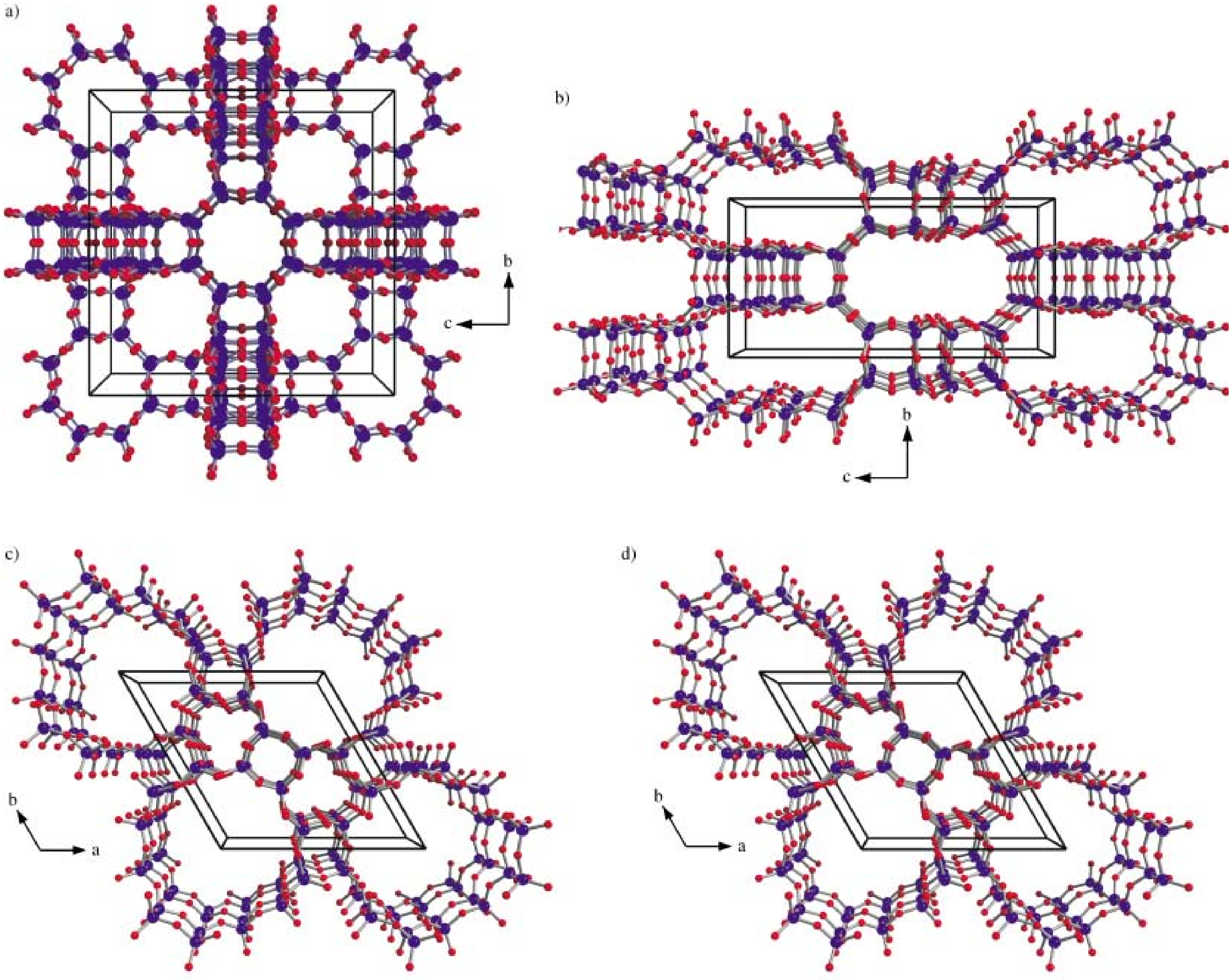

Figure 5. a) Structure 11 consists of cages connected by 4- and 8-membered rings; b) structure 14 contains two systems of elongated channels outlined by 12-membered rings (5.3×9.3 Å) running along the *a* and *b* directions of the unit cell; c) structure 71 consists of layers of 12-membered rings (7.2×7.2 Å) connected by 4- and 6-membered rings; d) structure 73 contains large channels of 12-membered rings, and narrower channels of 4- and 6-membered rings. When viewed along the *c* axis, the structure is similar to that of AFI, although the rings are connected in a different fashion along the *a* and *b* axes.

Although many of the hypothetical uninodal structures have dense frameworks, we observe a strong correlation between hypothetical structures and the known zeolite topologies. Thus one cannot rule out a structure just on the basis of the accessible free volume, even though a structure with no accessible free volume for such a small probe molecule will hardly be of interest to sorption, ion exchange, or catalysis. Figure 4 distinguishes between "favorable" hypothetical structures on the basis of their accessible free volume, but is not a suitable "filter" for feasible zeolitic topologies. Further structures of interest are: 14, 71, and 73 (Figure 5 b–d and Table S1 in Supporting Information), as well as 35, 122, 195, and 196 (not shown).

Although some of the zeolite topologies only exist as aluminum phosphates (AlPOs) or other non-silica compositions, all hypothetical structures were evaluated on the assumption that a purely siliceous composition is a good indicator of energetic stability. Evaluation of the topologies with the AlPO composition suggests that their stability is similar to that of the SiO_2 compositions,[15] and atomistic modeling of known AlPO structures shows that the correlation between energy and density for purely siliceous systems is also valid for the AlPO systems.[16]

The synthesis of microporous materials is facilitated by the use of structure-directing agents (templates), typically organic bases incorporated in the reactive mixture, which will direct the shape of the resulting framework. A given microporous structure may then be targeted by adroit choice of the template using ZEBEDDE,[17] a computational method for the de novo design of template molecules, which are "grown" within the desired inorganic framework. ZEBEDDE is already being used with a view to synthesizing the hypothetical zeolitic structures, which we have enumerated and evaluated in this work.

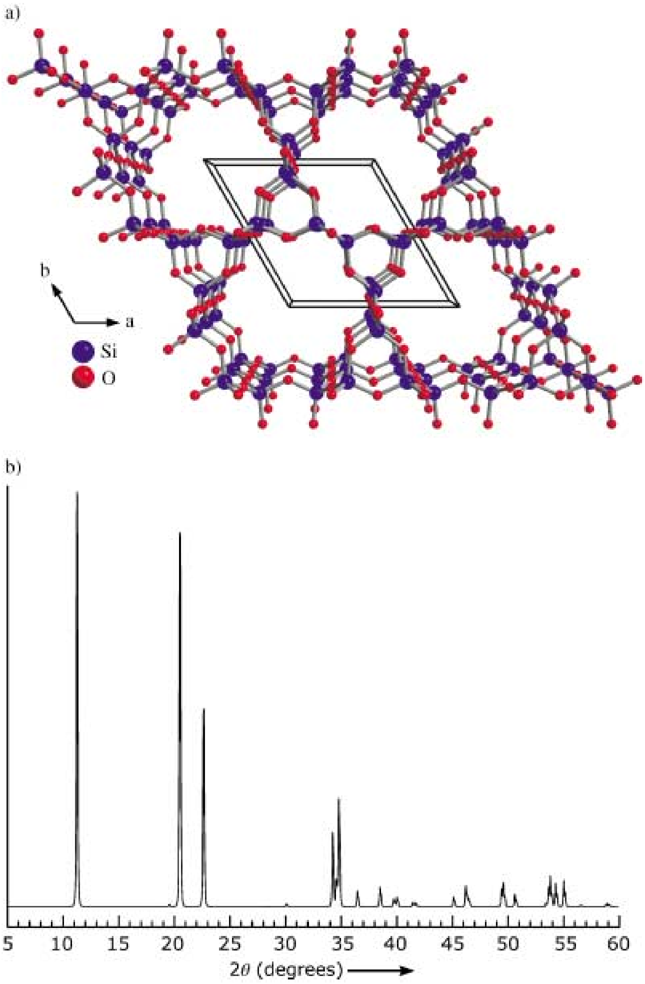

Figure 6. a) Structure 88; b) the calculated X-ray diffraction pattern for this structure.

Finally, we note that a zeolite-like material with the framework composed of phosphorus, nitrogen, and oxygen and the structure corresponding to our net 88 (Figure 6a), has recently been synthesized.[18] This was confirmed by comparing the calculated (Figure 6b) and experimental powder X-ray patterns.[18]

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