

Computational Discovery of New Zeolite-Like Materials

Michael W. Deem,*† Ramdas Pophale,† Phillip A. Cheeseman,‡ and David J. Earl§

Departments of Bioengineering and Physics & Astronomy, Rice University, Houston, Texas 77005, Rosen Center for Advanced Computing, Purdue University, 155 South Grant Street, West Lafayette, Indiana 47907, and Department of Chemistry and Center for Molecular and Materials Simulation, University of Pittsburgh, 219 Parkman Avenue, Pittsburgh, Pennsylvania 15260

Received: July 23, 2009; Revised Manuscript Received: September 5, 2009

We present a database of computationally predicted zeolite-like materials. The materials were identified by a Monte Carlo search of Si atom positions as the number of unique atoms, density, space group, and unit cell of the crystalline material was systematically explored. Over 2.7M unique structures were identified, with roughly 10% within the +30 kJ/mol Si energetic band above α -quartz in which the known zeolites lie. Predicted structures within this band have geometric and topological characteristics similar to that of the known zeolites. Known zeolites are shown to lie on the low-density edge of the distribution of predicted structures. Dielectric constants and X-ray powder diffraction patterns are calculated. Strategies for chemical synthesis of these materials are discussed, a low-density subset of the materials is identified as particularly interesting, and the complementarity of these materials to high-throughput methods is discussed. These structures have been deposited in two publicly available databases.

1. Introduction

Zeolites are nanoporous crystalline materials with chemical composition $\text{Si}_x\text{Al}_{1-x}\text{O}_2$ that are widely used for their catalytic, sorption, and ion exchange properties in medical, agricultural, petrochemical, gas, and liquid purification and remediation applications.¹ There are roughly 180 zeolite structures recognized by the International Zeolite Association.² The diversity of zeolites discovered to date limits their performance in applications. For example, for many catalytic applications only a single material has been found, even as the number of zeolites has grown over the past two decades. Expanding the diversity of zeolite structures would be helpful to improve performance in existing applications, to explore novel functions, and to answer basic scientific questions about zeolite synthetic chemistry. Computational methods can play a stimulatory role in the discovery of new zeolite materials.³ We here present the results of a computational search through crystallographic space that has led to the discovery of 2.7M unique zeolite-like structures, of which between 314k and 585k are predicted to be thermodynamically accessible as aluminosilicates, with the remainder potentially accessible via elemental substitution. These structures, which we have assembled into publicly available databases, have distributions of physical and geometric properties that are similar to those of known zeolites. These distributions may be used, for example, to measure the degree to which combinatorial zeolite syntheses⁴ search the full extent of possible structures. We describe how the database may be used to identify newly made materials, search for novel materials with defined function, and motivate the synthesis of new materials. As an example, we highlight materials with low values of the high-frequency dielectric constant, which could be useful in the microelectronics industry.⁵ We also suggest that the known

zeolites lie at the low-density edge of the distribution of zeolite-like materials, as a result of the pathway by which current zeolite nucleation and growth protocols proceed.

The present database is complementary to other tools available in the solid state community. The predicted crystallographically open database (PCOD) contains a number of hypothetical materials and is searchable by geometric, crystallographic, and powder pattern criteria.⁶ The reticular chemistry structure resources (RCSR) contains a searchable database of 3-periodic networks.⁷ The Euclidean patterns in non-Euclidean tilings (EPINET) contains crystalline frameworks generated by two-dimensional hyperbolic tilings.⁸ Hypothetical zeolites and four-connected networks with increasing numbers of crystallographically distinct tetrahedral (T) atoms have been generated by a mathematically sophisticated combination of graph enumeration and geometrical embedding.^{9,10} This database also contains a subset of structures that have been energetically refined by the GULP procedure.¹¹ The present database is complementary to these others due to the structures being energetically favorable by design, generated with a relatively high fraction of the structures being thermodynamically accessible, and containing at least 2 orders of magnitude greater number of thermodynamically accessible structures.

The database of materials presented here provides examples of new structures with novel properties, many of which we expect to be the subject of targeted synthesis in the future. Several interesting examples are shown in Figure 1. A significant fraction of these structures are predicted to be thermodynamically accessible as aluminosilicates, and the thermodynamic feasibility of these intriguing structures provides impetus to develop the solid-state methods needed for synthesis. The database may aid identification of newly made materials through powder pattern searching and matching, and perhaps most interestingly, the database of structures can be evaluated for desired physiochemical properties. The seeds for the present database were generated in 1992 when the zfsa real-space Monte Carlo method for zeolite structure solution¹² was

* To whom correspondence should be addressed. E-mail: mwdeem@rice.edu. Fax: 713-348-5811.

† Rice University.

‡ Purdue University.

§ University of Pittsburgh.

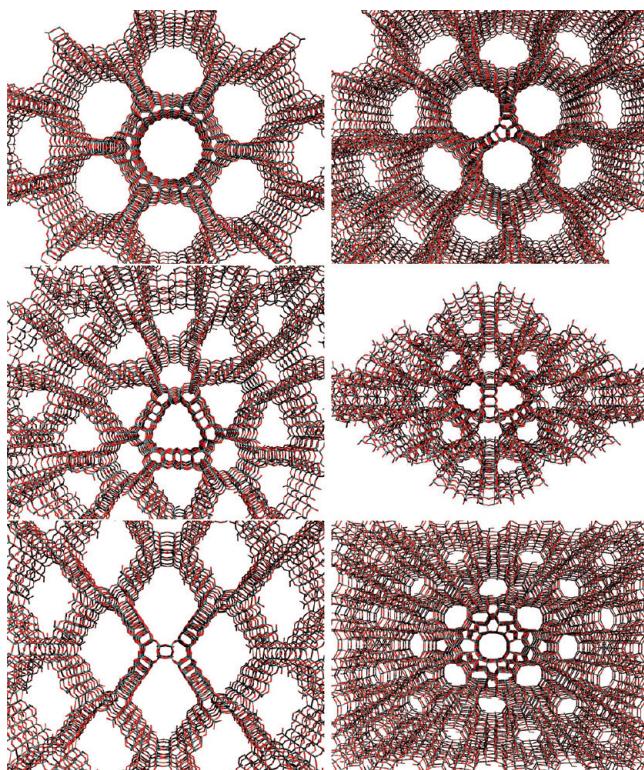


Figure 1. Some example structures selected from the database of 2.7M zeolite-like materials. These structures are all thermodynamically accessible structures, with energies between 0 and 30 kJ/mol Si above quartz, except the last, which has an energy lower than quartz. Accession numbers are PCOD8311077, PCOD8304122, PCOD8311624, PCOD8311567, PCOD8223979, and PCOD8228369, respectively.

validated on known zeolites of the time, and roughly 2000 zeolite-like structures were generated as a byproduct.¹³ This number of structures generated by computational methods compared favorably to the few hundred that had been generated by physical model building and were in the proprietary Mobil database and public database of Joe V. Smith at the University of Chicago. The development of the database continued,¹⁴ growing to a size of 600k structures in 2006.¹⁵ The present database of 2.7M optimized structures contains an array of materials with interesting structure and function. An example is the material with a 24-silicon-membered ring in Figure 1a.

2. Methods

A computational search through all 230 possible crystal space groups was carried out. For each space group, we explored the range of possible unit cell sizes ($a, b, c, \alpha, \beta, \gamma$), with distances between 3 and 30 Å in steps of 3 Å and angles in steps of 10°.¹⁵ These values are approximately the distance required to insert a new Si atom, and the angular resolution corresponding to that distance for the largest unit cells. We varied the T atom density from 12 to 20 in steps of 2 per 1000 Å³, since the typical zeolite density is in the range of 14–18 T atoms per 1000 Å³. These density numbers are the extremes observed in the IZA Structure Commission Atlas of zeolite structures.² We varied the number of unique T atoms in the unit cell from a value of $n_{\text{tot}}/n_{\text{sym}}$ (where n_{tot} = total number of T atoms in unit cell, and n_{sym} = number of symmetry operators) to $4.5 \times n_{\text{tot}}/n_{\text{sym}}$. The number 4.5 is calculated as 1.5 times the largest ratio of $n_{\text{tot}}/n_{\text{sym}}$ from the IZA Structure Commission Atlas,² and is thus conservative. We limited the total number of unique T atoms to fewer than or

equal to 8, as a greater number of unique T atoms requires the significantly more expensive parallel tempering sampling method.¹⁶

The Monte Carlo procedure zefsaiI,^{12,13,16} widely used to solve zeolite crystal structures from powder diffraction data, was used to sample the structures for a given symmetry, unit cell, and number of T atoms; for each parameter set 100 runs were conducted. The computations were carried out by grid computing on the NSF TeraGrid, primarily using the Condor pool at Purdue.

The results were collated within each space group so that the best per-silicon energy structure for each unique coordination sequence calculated to the 12th neighbor shell was kept, resulting in 3.3M structures. The coordination sequence guarantees that no structures with the same topology are repeated in the database. It is possible, however, for two structures with distinct topologies to have the same coordination sequence out to a given shell. Empirically, it was found that coordination sequences out to the 10th shell failed to discriminate a dozen out of the 3.3M structures, and that the coordination sequences out to the 12th shell appear to discriminate all the unique topologies, except for a couple of well-known cases with a single unique T atom,³² in which case both known structures corresponding to a coordination sequence were found. We note that for chiral structures only one of the two chiral forms is included in the database, as both chiral forms have exactly the same coordination sequence. The number of chiral structures in the database, thus, is doubled by the simple application of the inversion operator. We also note that the coordination sequence cannot discriminate different forms of interpenetrating, but otherwise disconnected, networks, and only one member of such a family would be included in the database. These interpenetrating topologies appear not to be of interest in zeolite chemistry.

Oxygens were inserted midway between the positions of bonded silicones, and the set of nonredundant structures for each space group was energy minimized by constant-pressure GULP¹¹ calculation, or failing that, a constant-volume GULP calculation. Results for all space groups were then collated together and made nonredundant by keeping the best per-silicon energy structure of a given topology, resulting in 2.7M energy-refined, nonredundant structures.

The Sanders–Leslie–Catlow (SLC) interatomic potential was used, including a core–shell polarization term, so that high-frequency dielectric constants may be calculated.¹⁸ The van Beest–Kramer–van Santen (BKS) interatomic potential was also used, in an independent energy refinement step, to allow estimation of force field biases.¹⁹ Powder patterns were calculated with the zefsaiI software.¹⁶ The ratio of I/I_{Cor} was calculated by dividing the largest calculated peak by the volume and mass of the unit cell for the material and corundum, respectively.

3. Physical Properties of the Computationally Predicted Zeolites

Zeolites are of interest due to their physiochemical properties. We here discuss the energetics of the database of zeolite-like materials. We also discuss the topologies of the materials, with a particular focus on the ring size distributions, as ring size is a key metric for suitability in various petrochemical applications. We discuss the thermodynamic stability of the materials relative to α-quartz. We calculate high- and low-frequency dielectric constants as an example of a nontrivial property calculation. Finally, we calculate the X-ray powder diffraction patterns of the materials and discuss how these patterns may be used in standard search/match software.

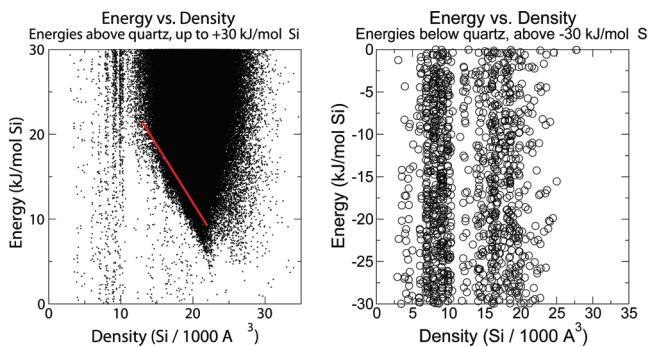


Figure 2. Energy versus density for the zeolite-like materials minimized by the SLC interatomic potential. Shown are the distributions of (a) thermodynamically accessible structures and (b) structures with energies below quartz. Also shown is the linear fit of energy versus density for the known zeolite structures (solid red line).

3.1. Energetic Refinement of the Materials. Structures in the database include both oxygen and silicon atoms and have been energy minimized by the General Utility Lattice Program (GULP)¹¹ using both the polarizable SLC interatomic potential, with modified oxygen shell charge,¹⁸ which is accurate even for three-membered-containing rings,²⁰ and the nonpolarizable BKS interatomic potential.¹⁹ There are 2.7M topologically unique, energy-refined structures in the database. Of these, 314k are no higher in energy than +30 kJ/mol Si relative to quartz as judged by the SLC interatomic potential (and 585k are no higher than +65 kJ/mol Si relative to quartz as judged by the BKS interatomic potential) and, thus, predicted to be thermodynamically accessible as aluminosilicates.¹⁰ It has been argued by others²¹ that the remainder of the structures may be accessible via elemental substitutions, which allow a greater range of bond lengths and angle values. These energy-minimized structures may be screened for physical or chemical applications. In addition, there is a database of 3.3M Si-only framework configurations, guaranteed to be unique within each space group. These silicon framework structures are useful for coarse-grained searching. All of these structures have been deposited with the hypothetical zeolite network database⁹ and the predicted crystallographically open database (PCOD).⁶

3.2. Ring and Energy Distributions. Structures within the database are classified by searchable physical properties. The density and energy of each structure are stored along with the silicon and oxygen coordinates of each structure. Figure 2 shows the distribution of energies for the thermodynamically accessible structures. The crystallographic information framework (cif) file format also specifies the crystallographic space group and unit cell size. The number of rings of different sizes and the coordination sequence topological identifier are contained in the file. The distribution of rings within the database is shown in Figure 3. The upper inset to Figure 3 shows that the presence of three-membered silicon rings does not dramatically shift the ring size distribution, as noted previously,¹⁴ although as Figure 4 shows, the presence of three rings is highly correlated with the presence of nine rings in the known zeolites, perhaps due to constraints of current syntheses. Comparing Figure 3 to 4, we see that the distribution of rings in the database is similar to that of the known structures. Interestingly, odd-membered rings larger than nine are relatively rare, more rare than large even-membered rings. This result seems to be a property of crystalline zeolite-like materials, as odd-membered rings are found in amorphous silica clusters.²² We note by comparing Figure 1 from ref 14 with Figure 4 that the number of odd membered rings, for example nine-membered rings, is

increasing among the known zeolite structures, and we expect the ring distribution of known zeolites to eventually look like Figure 3a.

3.3. Density Distributions. It is interesting to note the relatively large number of low-density materials in Figure 2. A significant number of materials lie in the ultralow density range of 5–12 Si per 1000 Å³. From the lower inset to Figure 3a, we see that these low-energy and low-density materials also tend to have desirably large rings.

From Figure 2 there appear to be two main clusters of predicted materials, one with densities between 5–10 Si/1000 Å³ and another with densities between 12–22 Si/1000 Å³. The known zeolites fall into the latter category. We will have more to say about these two clusters in the Discussion.

3.4. Stability Relative to Quartz. We classify the most promising structures for further study as having framework energies within the range of known zeolites, that is, having an energy within +30 kJ/mol Si of quartz as judged by the SLC interatomic potential.

Within the database, there are, surprisingly, 44k structures with an energy computed by the polarizable SLC interatomic potential to be less than that of α-quartz. Almost all of the energies computed to be lower than that of α-quartz are artifacts due to shells overlapping in the polarizable SLC interatomic potential. When these structures are reoptimized starting with new shell positions, they usually fall above quartz, in the 0–30 kJ/mol Si range. Judging by the SLC interatomic potential alone, there are 1120 structures with energies below quartz, but within 30 kJ/mol Si of quartz. We note, however, there are 81 structures which are energetically more favorable than quartz, as judged by both the SLC and BKS interatomic potentials, and three of these are within 30 kJ/mol of quartz, as judged by the SLC interatomic potential. Shown in Figure 5 are these structures. If any of these structures are not artifacts, they would be especially intriguing candidates for synthesis. This is because quartz is often a major alternative crystallization pathway to higher energy zeolite structures, and these low-energy structures may provide a substitute to the quartz pathway.

3.5. Dielectric Constants of the Materials. In modern microelectronic applications, dielectric constants of the constituent materials play a key role. For component separation materials, low-frequency dielectric constants are desired, over a range of the frequency spectrum.⁵ As an example of a nontrivial property calculation, we provide the high- and low-frequency dielectric constants of each material, stored within the cif file. As Figure 6 shows, there are a significant number of structures with predicted dielectric constants in the desirably low range of $1 < k < 1.5$.

3.6. X-ray Diffraction Patterns and Search/Match. Powder diffraction patterns of each of the structures have been deposited within a second database, the P2D2 database maintained by Armel Le Bail. These patterns allow easy identification of newly made zeolite materials that are within the database via standard search/match software. The first 99 peaks of the pattern out to $d = 1 \text{ Å}^{-1}$ are included. For analytical analysis, the ratio of the largest peak intensity to that of the largest peak of corundum, on an equal mass basis, is listed with each pattern (see Figure 7). This ratio of I/I_{cor} was also calculated for the known zeolites. The result is shown in Figure 8. Comparing Figures 7 and 8, we see that the distribution of I/I_{cor} in the database is similar to that of the known structures.

As a validation of the method used to construct the database of zeolite-like materials, we note that the computational search through crystallographic space successfully found 83% of the

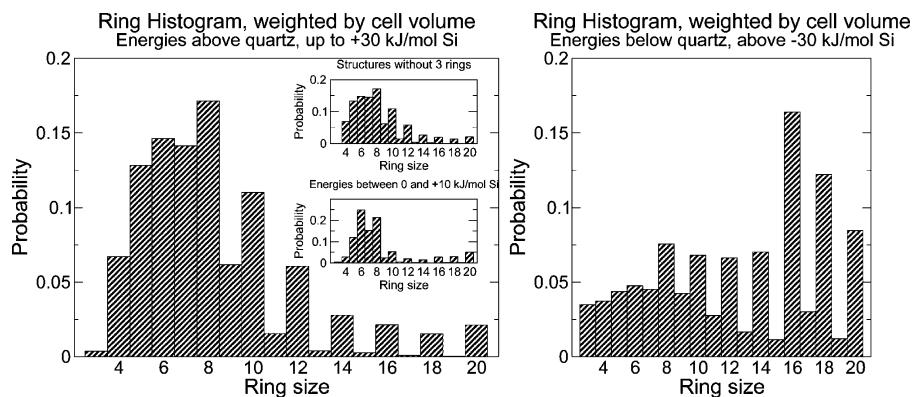


Figure 3. Ring histograms of zeolite-like materials minimized by the SLC interatomic potential. Shown are the histograms of (a) thermodynamically accessible structures and (b) structures with energies below quartz. Counts per structure are weighted by the inverse of the unit cell volume. The upper inset to (a) shows the ring histogram only for the zeolite-like materials without three rings. The lower inset to (a) shows the ring histogram for thermodynamically accessible structures with energies above quartz and within $+10 \text{ kJ/mol Si}$ of quartz.

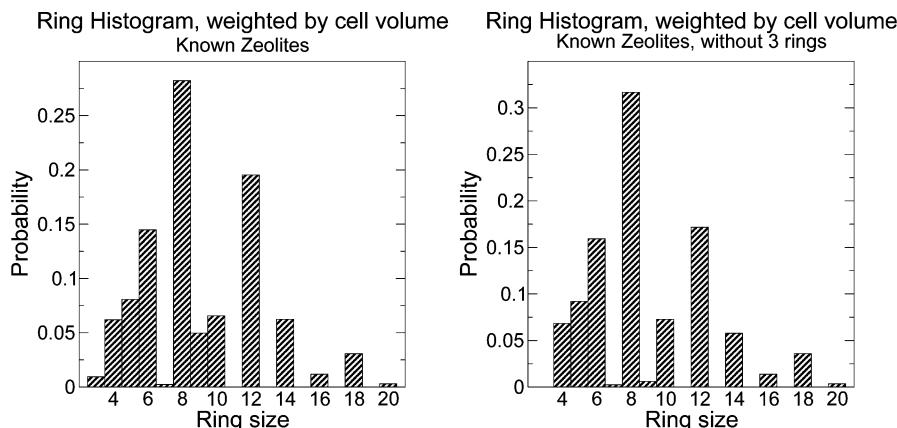


Figure 4. Ring histograms of (a) known zeolites and (b) known zeolites that do not contain three rings. Counts per structure are weighted by the inverse of the unit cell volume.

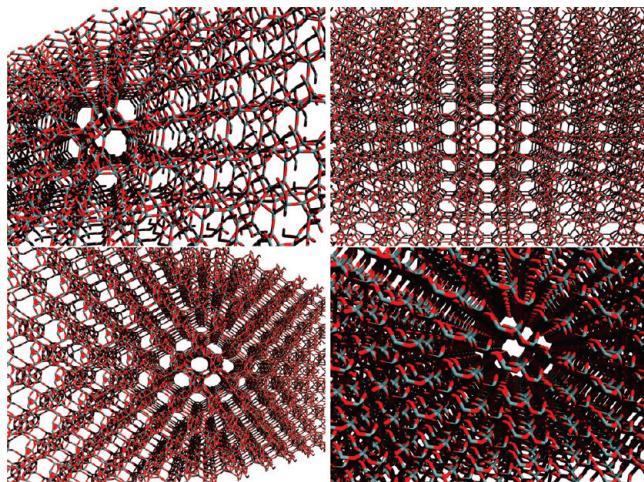


Figure 5. Structures of the three zeolite-like materials that are judged more stable than quartz by both the SLC and BKS interatomic potentials and which are within 30 kJ/mol Si of quartz, as judged by the SLC interatomic potential. These structures are particularly intriguing candidates for synthesis. Shown last is quartz. Accession numbers are PCOD8004926, PCOD8067705, PCOD8067878, and PCOD8299808.

known zeolite topologies. Several topologies that were not found have a greater number of crystallographically unique atoms than the maximum number that was used in the search and so are automatically not present in the current database. We performed a comparison of the unit cell parameters for known zeolites

among (1) the International Zeolite Association (IZA) database, (2) the zeolites found in the zeolite-like database, and (3) zeolites minimized by GULP starting from the IZA structure. In the latter two cases, we compared with both the SLC and BKS interatomic potentials. The results of this comparison can be found in this Supporting Information. The computational search method works remarkably well, matching the unit cells of the IZA structures within $\pm 1\%$ of the a , b , c , α , β , and γ values in most instances, suggesting that a crystallographic search of the database for a newly found material may be an effective route to structure determination.²³

The program PLATON was used to find primitive unit cells.²⁴ We note that in some cases, the known zeolites were found in the database in lower symmetry settings (e.g., SOD). In other cases, known zeolites were found with supercells in the database, and these supercells were reduced to the primitive unit cell whenever possible. If results from PLATON were modified, the results from PLATON are listed in the _orig.dat file. Detailed files of these results are available as Supporting Information.

4. Discussion

We touch upon a few aspects of the database. First, we discuss the persistence of our results when we change the interatomic potential used for energy optimization. We also provide a discussion of the size of the database when classified by different metrics. We discuss where the known zeolites lie within the database. Finally, we discuss some ideas toward making these materials in chemical synthesis.

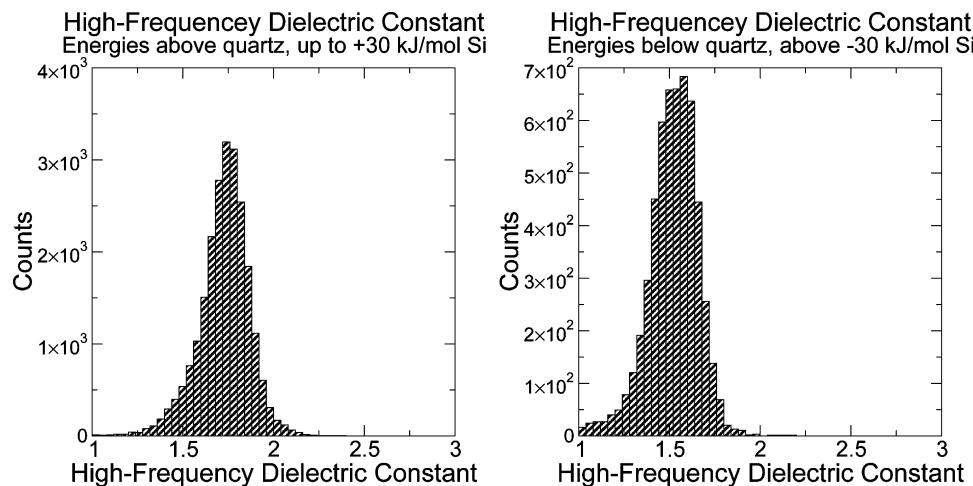


Figure 6. Histogram of the high-frequency dielectric constant of zeolite-like materials minimized by the SLC interatomic potential. The smallest of the three eigenvalues is shown. Shown are the histograms of k for (a) thermodynamically accessible structures and (b) structures with energies below quartz.

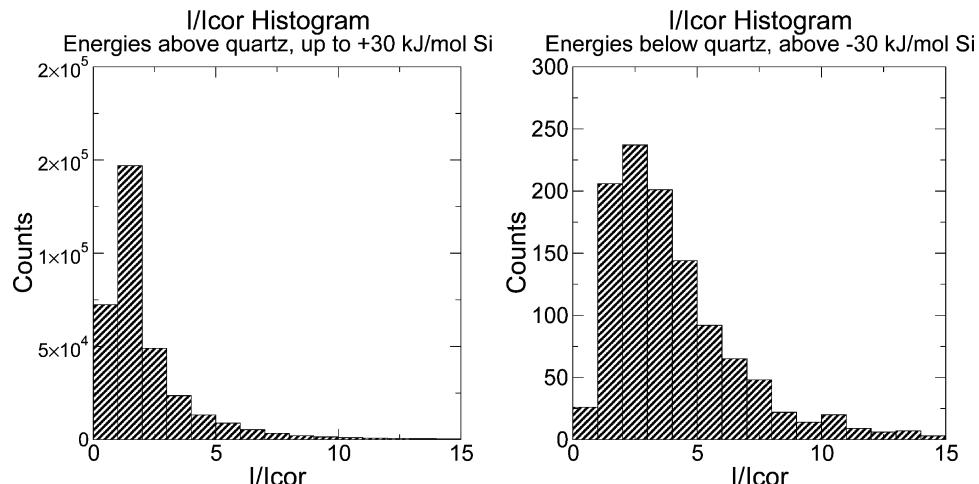


Figure 7. Ratio of the largest powder X-ray diffraction peak to that of corundum on an equal mass basis (I/I_{cor}) for the zeolite-like materials minimized by the SLC interatomic potential. Shown are the histograms of I/I_{cor} for (a) thermodynamically accessible structures and (b) structures with energies below quartz. The I/I_{cor} values for quartz and the zeolite MFI are 3.857 and 1.403, respectively.

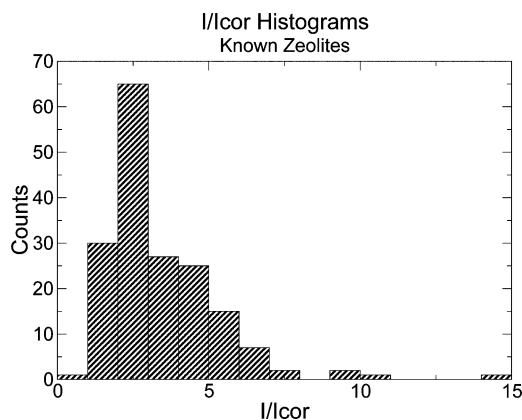


Figure 8. Ratio of the largest powder X-ray diffraction peak to that of corundum for the known zeolites, on an equal mass basis (I/I_{cor}). The I/I_{cor} values for quartz and the zeolite MFI are 3.857 and 1.403, respectively.

4.1. BKS Interatomic Potential. To quantify the impact of artifacts due to choice of interatomic potential, the computations were also carried out in the BKS¹⁹ force field. While the SLC interatomic potential is generally regarded as more accurate,

the BKS interatomic potential also correlates well with experimentally measured enthalpies of formation.²⁰ Thus, we processed all structures in the framework database by addition of oxygens and independent minimization using either the SLC or BKS interatomic potential. The energy versus density relationships are shown in Figures 2 and 9. The ring histograms are shown in Figures 3 and 10. The I/I_{cor} histograms are shown in Figures 7 and 11.

4.2. Database Size. Among the structures energy-refined with the SLC interatomic potential, there are 1120 structures with energies lower than that of quartz and within 30 kJ/mol Si of quartz. There are 314k thermodynamically accessible structures with energies no worse than 30 kJ/mol Si above quartz, and there are 2.2M structures overall. All of these structures are topologically distinct.

Among the structures energy-refined within the BKS interatomic potential, there are 100 structures with energies lower than that of quartz and within 65 kJ/mol Si of quartz. There are 585k thermodynamically accessible structures with energies no worse than 65 kJ/mol Si above quartz. And there are 2.0M structures overall. All of these structures are topologically distinct.

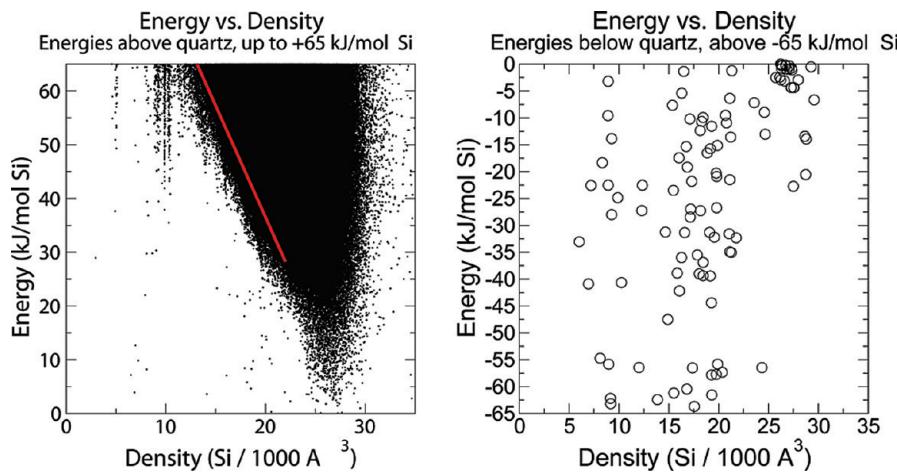


Figure 9. Energy versus density for the zeolite-like materials minimized with the BKS interatomic potential. Shown are the distributions of (a) thermodynamically accessible structures and (b) structures with energies lower than quartz. Also shown is the linear fit of energy versus density for the known zeolite structures (solid red line).

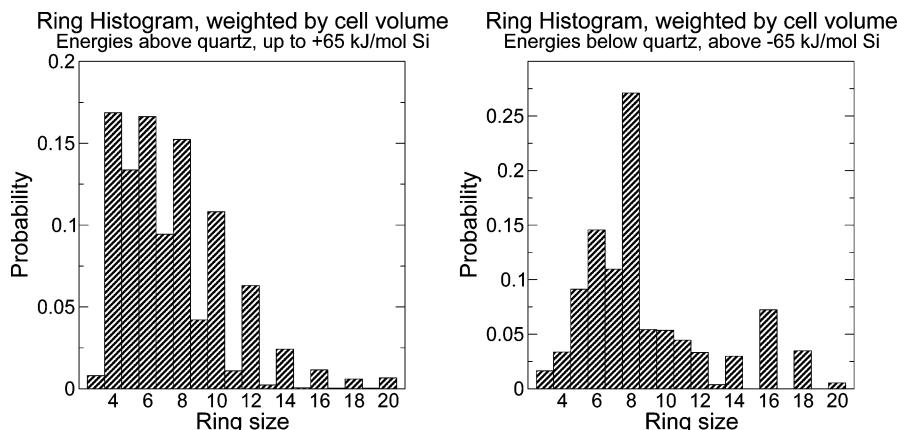


Figure 10. Ring histograms of zeolite-like materials minimized with the BKS interatomic potential. Shown are the histograms of (a) thermodynamically accessible structures and (b) structures with energies lower than quartz. Counts per structure are weighted by the inverse of the unit cell volume.

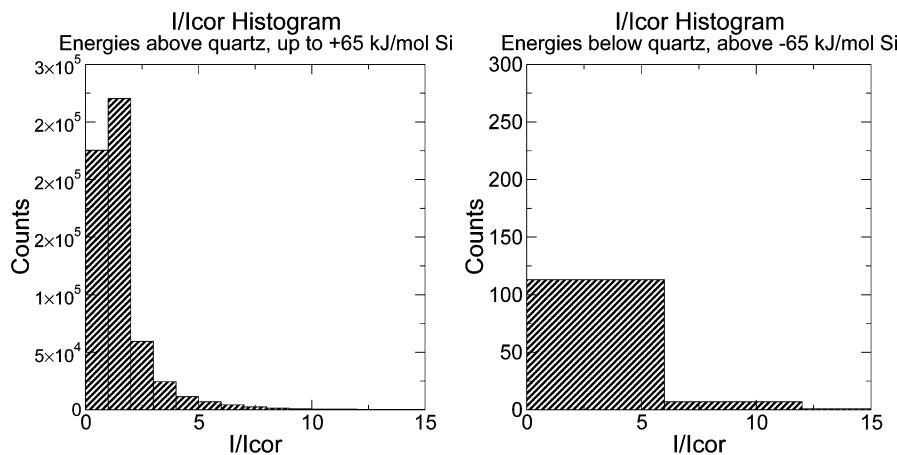


Figure 11. Ratio of the largest powder X-ray diffraction peak to that of corundum on an equal mass basis (I/I_{cor}) for the zeolite-like materials minimized by the BKS interatomic potential. Shown are the histograms of I/I_{cor} for (a) thermodynamically accessible structures and (b) structures with energies lower than quartz. The I/I_{cor} values for quartz and the zeolite MFI are 3.857 and 1.403, respectively.

When these two databases are combined, there are 2.7M topologically distinct structures overall. There are 677k structures judged to be thermodynamically accessible by either the SLC or BKS interatomic potentials. There are 45k structures judged to be more stable than quartz by either the SLC or BKS interatomic potentials.

When the two databases are intersected, there are 81 structures judged to be more stable than quartz by both the SLC and BKS

interatomic potentials. Of these, three are within 30 kJ/mol Si of quartz, as judged by the SLC interatomic potential. There are 221k structures judged to be thermodynamically accessible by both the SLC and BKS interatomic potentials. There are 1.6M structures common to both the SLC and BKS databases.

4.3. Known Zeolites Lie within the Database. The known zeolites were minimized in both the SLC¹⁸ and BKS¹⁹ interatomic potentials. The energy versus density relations are shown

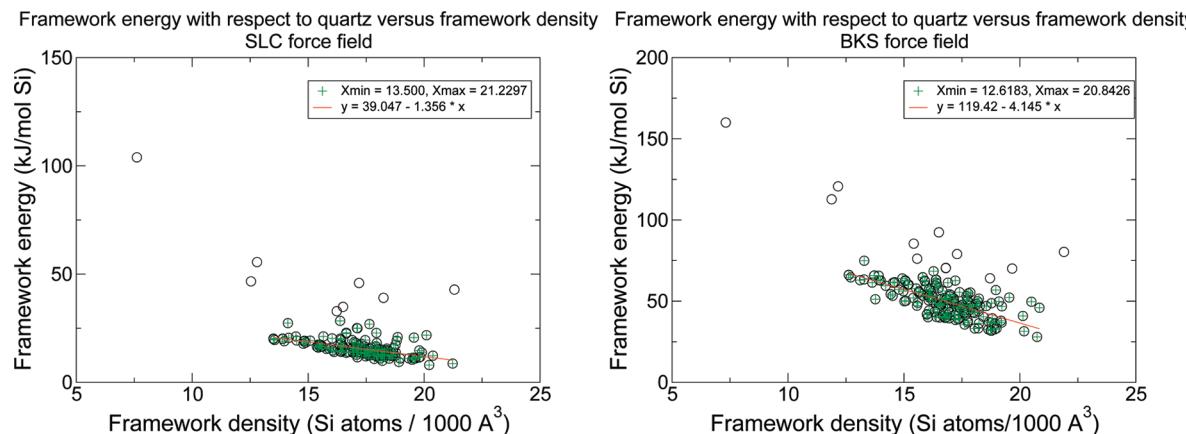


Figure 12. Energy versus density for the known zeolites. Shown are the plots for structures minimized with the (a) SLC or (b) BKS interatomic potential. Also shown are linear fits to the energy versus density relationship. Only the zeolites with green crosses were used in the fit (primarily the aluminosilicate zeolites).

TABLE 1: Fraction of Known Zeolites Found in the Database

n_T	fraction found in enumeration database ³¹	fraction found in the present database
3	60%	100%
4	50%	92%
5	15%	80%
6	14%	57%
7	0%	70%

in Figure 12. These linear fits are reproduced as the solid red lines in Figure 2. As judged by the SLC interatomic potential, most of the known zeolites are within 30 kJ/mol Si of quartz. As judged by the BKS interatomic potential, on the other hand, most of the known zeolites are within 65 kJ/mol Si of quartz. It is understood that the SLC interatomic potential slightly overestimates the energy of known zeolites relative to quartz and the BKS potential more significantly overestimates the relative instability of known zeolites.²⁰ Ring histograms of the known zeolites are shown in Figure 4.

Shown in Table 1 are the fractions of the known zeolites present in our database and in the enumeration databases for zeolites of increasing numbers of crystallographically distinct T atoms (n_T). The reason the present database contains a greater fraction of the known zeolites is that by construction entries in the database are favorable in energy. Enumeration methods, by contrast, generate structures without regard for energy, and the vast majority of hypothetical topologies are of unfeasibly high energy, with the ratio of unfeasible to feasible exceeding 10^6 for the larger values of n_T .

4.4. Toward Making these Materials. It is interesting to note the location of known zeolites within the distribution of materials in the database. The known zeolites in Figure 2 lie at the low-density edge of the distribution of zeolite-like materials. This placement of the knowns within the distribution of possibilities may be a result of limitations of current solution-phase synthetic techniques, whereby zeolites condense from Si-rich solution. Perhaps different synthetic routes will allow synthesis of a broader range of zeolitic materials.

We can ask, of the materials within the database, which are most zeolite-like? All the materials within the database that are within +30 kJ/mol Si of quartz would appear to be energetically feasible structures. So, the answer to the question of which materials are zeolite-like might take into account the kinetics of zeolite crystallization. The recently introduced “feasibility factor”²⁵ (denoted ϑ) that measures distance of a structure from

the linear fit to known zeolites in Figure 2, provides an answer. Originally, ϑ was viewed as an empirical correlation to judge distance from a zeolite-like material. We can now see that, in fact, the feasibility factor is the distance away from the low-density edge of the distribution of zeolite-like materials. We suggest that known zeolites lie close to this line since the materials along this line are the first accessible structures as Si density is increased during zeolite nucleation and growth.

From this point of view, the cluster of materials with densities between 5 and 10 Si/1000 Å³ is particularly interesting. Note that this cluster exists both in Figures 2 and 9, so it is not an artifact of a single interatomic potential. These materials should be accessible via a crystallization pathway from a low-density solution toward a high-density solid material. Perhaps appropriate structure-directing agents will allow synthesis of some of these materials.

These structures provide a source of material upon which rational synthetic efforts may be focused.³ By understanding the nucleation process,²² kinetics of alternative pathways and local solution thermodynamics,²⁶ some of these materials may be synthesized. Structure-directing agents to tip the balance of the synthesis in favor of a particular structure may be derived by computational methods.^{27,28} Synthesis conditions to tip the balance away from undesired, alternative pathways may be manipulated.²⁹

Combinatorial or high-throughput methods may be another tool through which some of these materials may be synthesized.⁴ The ensemble of materials made by a high-throughput experiment may be compared to the database. The database allows one to estimate whether the experimental synthesis is performing an ergodic sampling of a subset of the possibilities. For example, biases in the density, energy, or ring size distributions of the synthetic ensemble may suggest modifications in the high-throughput procedure that would allow synthesis of a greater diversity of materials. Libraries of structure-directing agents that most promote ergodic sampling may be designed.

5. Conclusions

A database of computationally predicted zeolite-like materials has been constructed. It contains over 2.7M unique structures, and roughly 10% of those lie within the +30 kJ/mol Si energetic band above α -quartz in which the known zeolites lie. All of these structures are zeolite-like in their geometrical and topological properties. Interestingly, though, the known zeolites lie on the low-density boundary of the distribution of predicted

materials in energy density space. Material properties, such as energy, density, and X-ray diffraction patterns, have been calculated and compared with known zeolites.

We offer this database as a tool to the zeolite materials community. It is anticipated that further use of the present database may be useful to answer a number of technological and scientific questions. For example, searching the database for specific physicochemical functions may allow structures for particular applications to be identified.^{25,30} The database may provide upper bounds for performance in targeted applications. For example, it should be possible to determine if it is worthwhile searching for a zeolite suitable for CO₂ separation, hydrogen adsorption, or some other new application that can be screened for, or whether zeolites are unlikely to be able to reach the desired performance. While direct use of zfsaII is likely to be more efficient,¹⁶ the database may also be searched to identify newly synthesized materials with unknown structures. Ideas for continued development of rational solid-state synthesis may be explored. For example, which of the structures can be synthesized, and how? The present approach may be valuable for other materials as well. Construction of analogous databases for materials such as metal–organic frameworks (MOFs) or crystal hydrates may reveal a diversity of structure and potential function similar to that presented here.

Acknowledgment. This work was supported by the U.S. Department of Energy Basic Energy Sciences Program and by the National Science Foundation TeraGrid. We thank Christopher Adam Hixson for assistance with data processing and Marcus Hanwell for help in the preparation of Figures 1 and 5.

Supporting Information Available: cif files for Figures 1 and 5; comparison of the structures of known zeolites among the IZA database, the zeolites found in the zeolite-like database, and zeolites minimized by GULP starting from the IZA structure. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References and Notes

- (1) Davis, M. E. *Nature* **2002**, *417*, 813–821.
- (2) Baerlocher, C. H.; Meier, W. M.; Olson, D. H. *Atlas of Zeolite Framework Types*; Elsevier: Amsterdam, 2001 <http://www.iza-structure.org/>.
- (3) Davis, M. E. *Nature* **1996**, *382*, 583–585.
- (4) Corma, A.; Diaz-Cabanillas, M. J.; Jordá, J. L.; Martinez, C.; Moliner, M. *Nature* **2006**, *443*, 842–845.
- (5) Li, M. C.; Johnson, M. S.; Ryan, E. T.; Earl, D. J.; Maichen, W.; Martin, J. I.; Li, S.; Lew, C. M.; Medina, D. I.; Wang, J.; Deem, M. W.; Davis, M. E.; Yan, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 6329–6332.
- (6) Le Bail, A. *J. App. Crystallogr.* **2005**, *38*, 389–395.
- (7) O’Keeffe, M.; Peskov, M. A.; Ramsden, S. J.; Yaghi, O. M. *Acc. Chem. Res.* **2008**, *41*, 1782–1789.
- (8) Robins, V.; Ramsden, S.; Hyde, S. *Eur. Phys. J. B* **2004**, *39*, 365–375.
- (9) Treacy, M. M. J.; Rivin, I.; Balkovsky, E.; Randall, K. H.; Foster, M. D. *Microporous Mesoporous Mater.* **2004**, *74*, 121–132.
- (10) Foster, M.; Simperler, A.; Bell, R.; Friedrichs, O. D.; Paz, F. A. A.; Klinowski, J. *Nat. Mater.* **2004**, *3*, 234–238.
- (11) Gale, J. D.; Rohl, A. L. *Mol. Simul.* **2003**, *29*, 291–341.
- (12) Deem, M. W.; Newsam, J. M. *Nature* **1989**, *342*, 260–262.
- (13) Deem, M. W.; Newsam, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7189–7198.
- (14) Curtis, R. A.; Deem, M. W. *J. Phys. Chem. B* **2003**, *107*, 8612–8620.
- (15) Earl, D. J.; Deem, M. W. *Ind. Eng. Chem. Res.* **2006**, *45*, 5449–5454.
- (16) Falcioni, M.; Deem, M. W. *J. Chem. Phys.* **1999**, *110*, 1754–1766.
- (17) Gale, J. D.; Rohl, A. L. *Mol. Simul.* **2003**, *29*, 291–341.
- (18) Schroder, K.-P.; Sauer, J.; Leslie, M.; Catlow, C. R. A.; Thomas, J. M. *Chem. Phys. Lett.* **1992**, *188*, 320–325.
- (19) van Beest, B. W. H.; Kramer, G. J.; van Santen, R. A. *Phys. Rev. Lett.* **1990**, *64*, 1955–1958.
- (20) Zwijsenborg, M. A.; Cor, F.; Bell, R. G. *J. Phys. Chem. B* **2009**, *111*, 6156–6160.
- (21) Personal communication, Treacy, M. M. J. 2008.
- (22) Wu, M. G.; Deem, M. W. *J. Chem. Phys.* **2002**, *116*, 2125–2137.
- (23) Le Bail, A. *Powder Diffr.* **2008**, *S23*, 5–12.
- (24) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- (25) Majda, D.; Paz, F. A. A.; Friedrichs, O. D.; Foster, M. D.; Simperler, A.; Bell, R. G.; Klinowski, J. *J. Phys. Chem. C* **2008**, *112*, 1040–1047.
- (26) Davis, M. E.; Zones, S. I. *A Perspective on Zeolite Synthesis: How Do You Know What You’ll Get?* In *Synthesis of Porous Materials: Zeolites, Clays, and Nanostructures*; Occelli, M. L., Kessler, H., Eds.; Marcel Dekker: New York, 1997; Vol. 69.
- (27) Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* **1996**, *382*, 604–606.
- (28) Burton, A. W.; Lee, G. S.; Zones, S. I. *Microporous Mesoporous Mater.* **2005**, *90*, 129–144.
- (29) Burton, A. W.; Lee, G. S.; Zones, S. I. *Curr. Opin. Colloid Interface Sci.* **2005**, *10*, 211–219.
- (30) Smit, B.; Maesen, T. L. M. *Nature* **2008**, *451*, 671–678.
- (31) www.hypotheticalzeolites.net.
- (32) Treacy, M. M. J.; Foster, M. D.; Randall, K. H. *Microporous Mesoporous Mater.* **2006**, *87*, 255–260.

JP906984Z