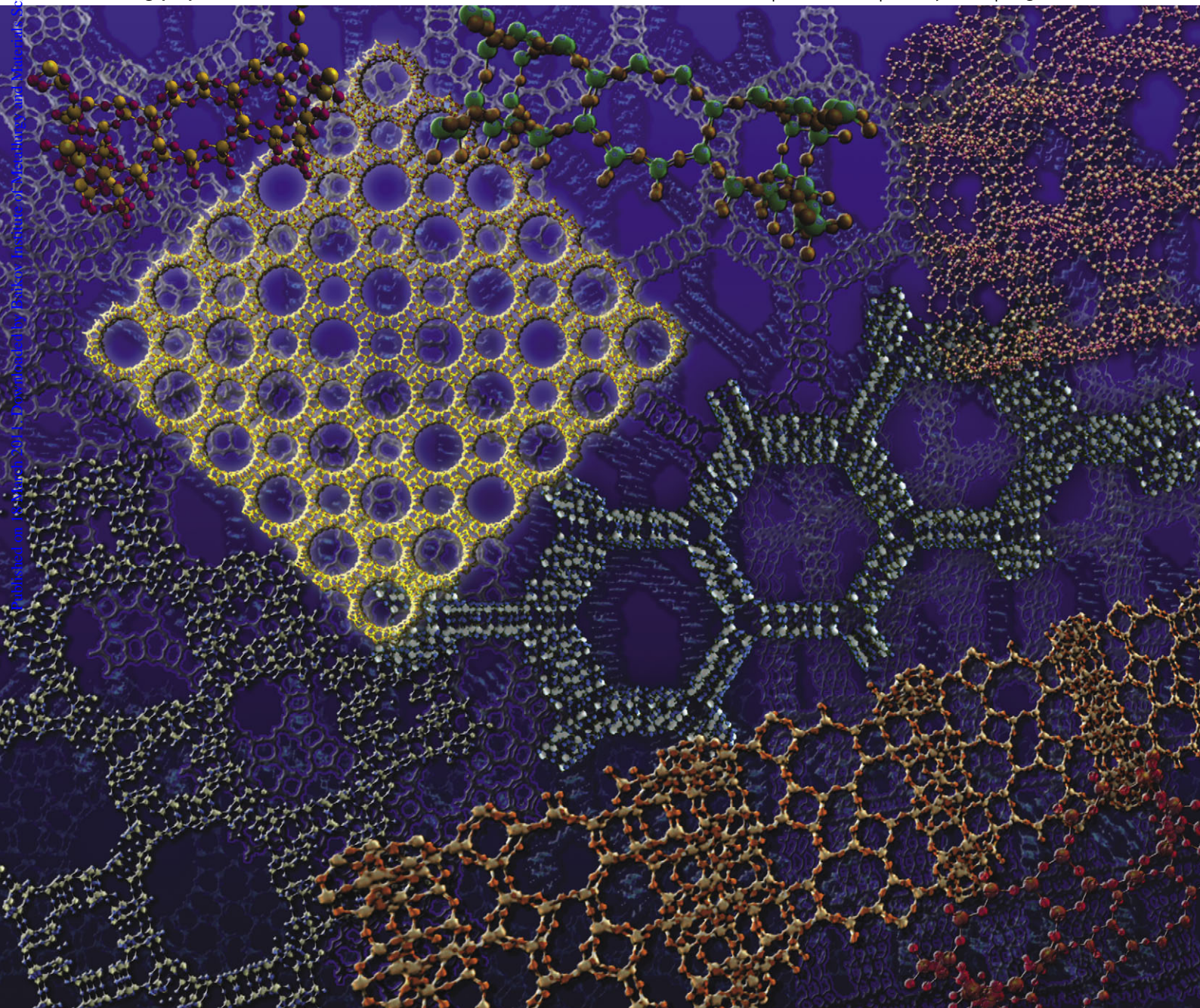


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COVER ARTICLE

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A database of new zeolite-like materials

PERSPECTIVE

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Recent advances and perspectives in four-component Dirac–Kohn–Sham calculations



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A database of new zeolite-like materials†

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We here describe a database of computationally predicted zeolite-like materials. These crystals were discovered by a Monte Carlo search for zeolite-like materials. Positions of Si atoms as well as unit cell, space group, density, and number of crystallographically unique atoms were explored in the construction of this database. The database contains over 2.6 M unique structures. Roughly 15% of these are within +30 kJ mol⁻¹ Si of α -quartz, the band in which most of the known zeolites lie. These structures have topological, geometrical, and diffraction characteristics that are similar to those of known zeolites. The database is the result of refinement by two interatomic potentials that both satisfy the Pauli exclusion principle. The database has been deposited in the publicly available PCOD database and in www.hypotheticalzeolites.net/database/deem/.

1. Introduction

Zeolites are crystalline materials widely used in industrial applications for ion exchange, catalysis, and separations.¹ Roughly 190 zeolite structures are recognized by the International Zeolite Association.² Many promising applications lack for want of a suitable zeolite material, and discovery and characterization of new zeolites is an open synthetic challenge. Expanding the library of available structures would be helpful both to provide a range of options for materials similar to those used in existing applications and to offer wholly new materials with potentially new function.

Computational methods can stimulate the search for and discovery of new zeolite materials.³ In a previous work, we reported on a first-generation database of new zeolite-like materials.⁴ We here refine the approach, with interatomic potentials that satisfy the Pauli exclusion principle. These more recent structures are what we recommend for use in screening studies.

In the solid state community discovery, rational design, and synthesis of crystalline materials is a challenging problem. Our database complements other efforts to tackle the discovery part of this problem. The reticular chemistry structure resources (RCSR) is a searchable database of 3-periodic nets representing 1600 metal-organic frameworks.⁵ The predicted crystallography open database (PCOD) is a database of enumerated inorganic compounds, and is searchable by geometric, crystallographic and powder pattern criteria.⁶ The Euclidean patterns in

non-Euclidean tilings (EPINET), searchable using geometrical and topological properties, is a database of three-dimensional periodic nets generated from 2-dimensional hyperbolic tilings.⁷ Researchers have used a combination of graph enumeration and geometrical embedding techniques to create a database of periodic 4-connected graphs and hypothetical zeolites with up to 7 distinct tetrahedral (T) atoms for several high mirror symmetry space groups.^{8,9} A subset of structures in this database have been refined energetically using the GULP suite of programs.¹⁰ In comparison to these databases, the structures described here are energetically favorable by design, and the present database contains a higher fraction of structures that are thermodynamically accessible. The number of energetically-favorable, unique structures in the present database is at least two orders of magnitude greater than in these other databases. These characteristics make our database complementary to the efforts that precede it.

This database of materials offers examples of intriguing new structures with very likely a plethora of novel properties. We expect that promising materials will be identified through screening this database, and some of these materials will be sought after targeted synthesis. A few interesting structures are shown in Fig. 1. A significant fraction of the whole database is within the energetic band in which known zeolites lie. When new materials are synthesized, they may be sought in the database by search/match procedures, and this use of the database is a novel means of structure solution. Of equal if not more interest is screening of the database for materials with desired properties. It is our hope that the presentation of the database here will stimulate these applications.

This paper is organized as follows. In the Methods section, we discuss the Monte Carlo procedure used to sample the space of zeolite-like materials. In the Results section, we provide an overview of the structures in the database. We describe the ring size, energy, and density distributions. We present diffraction patterns and dielectric constants as example property

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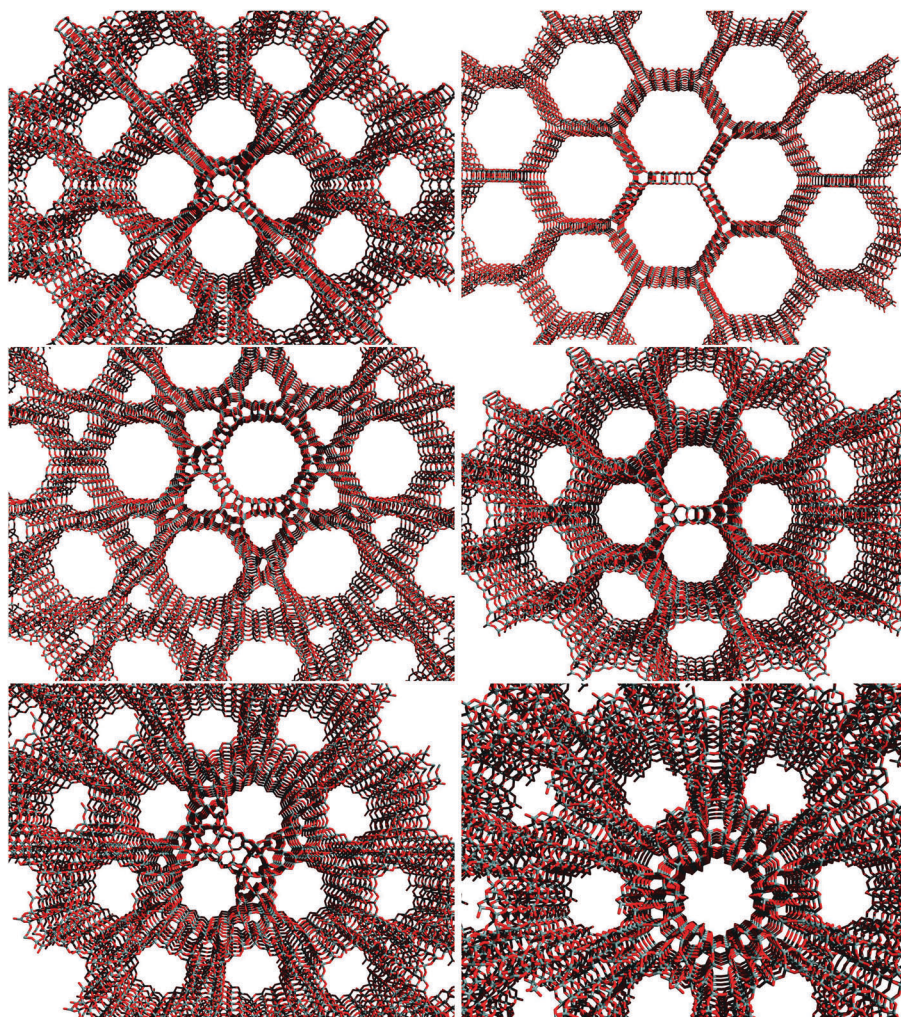


Fig. 1 Examples of some computationally predicted zeolite-like structures. Top four are structures with energies above α -quartz, within $+30 \text{ kJ mol}^{-1}$ Si. Bottom two are structures with energies below α -quartz, within -30 kJ mol^{-1} Si. The PCOD accession numbers are 8292630, 8308100, 8326129, 8325731, 8331490, and 8332116.

calculations. In the Discussion section we compare the results from the SLC and BKS interatomic potentials. We point out the intriguing band of materials with density near $9 \text{ Si}/1000 \text{ \AA}^3$. We also comment on the significance of enforcing the Pauli exclusion principle in the interatomic potentials. We explain how the database is being used as a tool by the zeolite community for a rational design of materials tailor made for specific applications. To that end we cite examples of relevant ongoing research in areas including carbon sequestration. Finally, we present our conclusions.

2. Methods

All 230 crystal space groups were examined. For each space group, unit cells with edges from 3 to 30 \AA in steps of 3 \AA were examined. Symmetry allowed angles were examined in steps of 10° . The Si atom density was varied from 10 to 20 per 1000 \AA^3 in steps of 2 per 1000 \AA^3 , covering the range of typical zeolite densities.² The number of unique T atoms in the unit cell was varied 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 limit of 4.5 was conservatively calculated as 1.5 times the largest value of $n_{\text{tot}}/n_{\text{sym}}$ in the IZA Structure Commission Atlas.² The total number of unique T atoms was limited to no greater than 8, because a greater number of unique T atoms require the parallel tempering sampling method, which is significantly more computationally expensive.¹¹

A Monte Carlo procedure termed zefsII^{11–13} was used to sample the Si atom positions with a weight given by the negative exponential of a zeolite Hamiltonian. For a given number of Si atoms, unit cell, and symmetry, 100 simulated annealing runs were carried out. Computations were performed on the Condor pool at Purdue of the NSF TeraGrid.

This procedure samples low-energy zeolite-like structures. Unique structures were identified by calculating the coordination sequence to the 12th neighbor shell. By this procedure, no structure with the same topology is repeated in the database. As a result, however, for chiral structures, only one of the two chiral forms is present in the final database. The other may be generated by inverting the chirality. In addition, a small number of distinct structures, but with the same coordination sequence, are represented by only one member of their

family; this phenomenon is rare and tends to occur only for structures with a small number of crystallographically unique Si atoms.⁴

Unique structures identified by the Monte Carlo procedure were further optimized by inserting oxygen atoms at the midpoints between silicons that share a bridging oxygen. Constant pressure energy minimization was carried out by GULP,¹⁰ and if that failed by constant volume energy minimization. Results for all space groups were combined and again made non-redundant by calculation of the coordination sequence. Only the lowest energy, in kJ mol^{-1} Si, instance of each unique structure was deposited into the final database.

Two interatomic potentials were used: the Sanders–Leslie–Catlow (SLC),¹⁴ which includes a core–shell polarization term, and the van Beest–Kramer–van Santen (BKS).¹⁵ The former includes a shell model for electronic polarization and so allows calculation of the high-frequency dielectric constant. These potentials were modified to eliminate the negative energy divergence that occurs when atoms or shells overlap. In particular, the potential between atoms or shells was linearly extrapolated with constant slope to a large, positive intercept at zero separation, starting at the small value of the separation for which the curvature of the potential changes sign. Powder patterns were calculated *via* zefsaII.¹¹ The standard analytical analysis ratio I/I_{cor} was calculated for the material and corundum, respectively, by dividing the largest calculated peak by the volume and mass of the unit cell for the material.

3. Results

3.1 Database size

Over 2.3 M unique structures exist in the SLC database, and over 2.0 M unique structures exist in the BKS database. When combined, there are over 2.6 M unique structures in total. There are over 330k structures within $+30 \text{ kJ mol}^{-1}$ Si of α -quartz in the SLC database, and over 590k within $+65 \text{ kJ mol}^{-1}$ Si of α -quartz in the BKS database. These structures are judged to be thermodynamically accessible and hence especially interesting from the point of view of synthesis of novel zeolites.

3.2 Ring size distributions

While less often calculated, details of ring geometries of zeolites are of prime interest to synthetic chemists and in applications. For many applications, desired function is thought to dictate the likely ring geometry and topology of the material. We show in Fig. 2 ring size distributions for the predicted structures. These distributions are similar to that of known zeolites for the smaller rings. The computational results predict, however, that more large-membered rings should exist.

3.3 Energy and density distributions

The known zeolites have been shown to lie along a line in energy/density space.¹⁶ In Fig. 3 we show the distribution of predicted zeolite-like structures within $+30 \text{ kJ mol}^{-1}$ Si of α -quartz. As previously observed,⁴ there is a band of structures with densities between $12\text{--}22 \text{ Si}/1000 \text{ \AA}^3$ and one with densities between $5\text{--}10 \text{ Si}/1000 \text{ \AA}^3$. The known zeolites lie along the low-density edge of the distribution of predicted structures.

With the interatomic potentials corrected to satisfy the Pauli exclusion principle, there are very few structures with energies below that of quartz. For the SLC potential, there are only two within -30 kJ mol^{-1} Si of α -quartz, and both are shown in Fig. 1. There are none for the BKS potential within -65 kJ mol^{-1} Si of α -quartz.

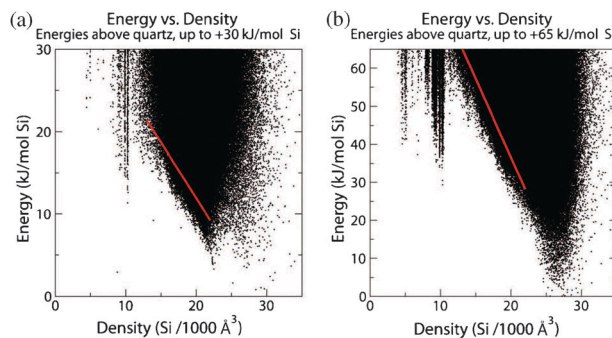


Fig. 3 Energy–density plots for the (a) SLC structures and (b) BKS structures. Also shown (red line) is the least-squares fit to the known zeolite structures.

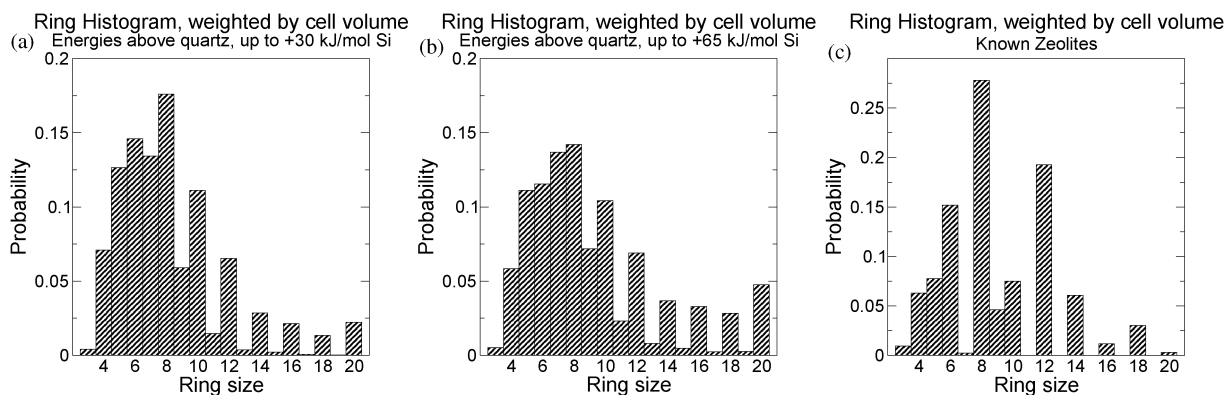


Fig. 2 Ring size distributions for the (a) SLC structures, (b) BKS structures, and (c) known zeolites. The distributions of the computationally-predicted materials (a–b) are similar to that of the known zeolites (c), except for indicating a greater presence of large rings, and 7-membered rings, in these computationally predicted materials.

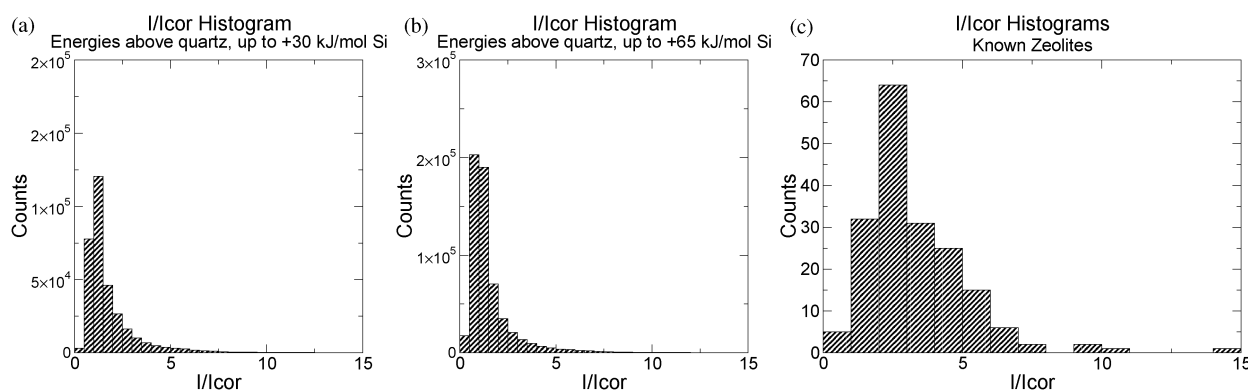


Fig. 4 The distribution of the ratio of the largest XRD peak relative to that of corundum, I/I_{cor} , a standard analytical analysis ratio. (a) SLC structures, (b) BKS structures, and (c) known zeolites. The distribution of predicted structures is similar to that of the known zeolites.

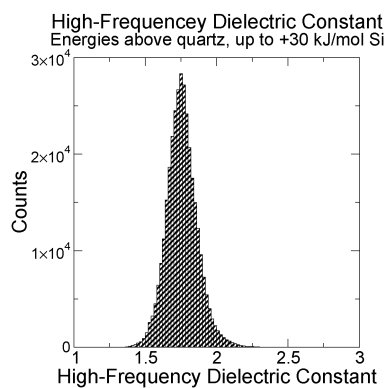


Fig. 5 Distribution of dielectric constants for the SLC structures. The distribution extends into the desirable range below $k = 1.6$.

3.4 Diffraction patterns and I/I_{cor}

Powder diffraction patterns are routinely measured to characterize zeolites. XRD patterns for all the materials were calculated and deposited in the PCOD database, according to the P2D2 format. These patterns allow possible identification of newly made materials. In Fig. 4 the analytical analysis ratio I/I_{cor} is shown. For both databases, the results are similar to that of known zeolites.⁴

3.5 Dielectric constants

Zeolites show promise as low- k insulating materials in micro-electronic applications.¹⁷ As an example, we calculated both the low- k and high- k dielectric constants. These values are stored within the cif files. Fig. 5 shows that many of the materials have dielectric constants in the desirably low range of $1 < k < 1.5$.

4. Discussion

The SLC interatomic potential is generally regarded as accurate for zeolites.¹⁸ In order to quantify the impact of artifacts introduced by choice of interatomic potential, we also carried out computations using the BKS¹⁵ interatomic potential. The BKS interatomic potential has been shown to correlate with experimentally measured enthalpies of formation.¹⁸ Thus, we added oxygen atoms to all the structures

in the framework atoms and processed them through independent energy minimization with both SLC and BKS interatomic potentials.

An implication of the present results is the importance of enforcing the Pauli exclusion principle. Both of these interatomic potentials can generate large negative energy values when atoms or shells overlap. This unphysical feature can generate unphysical structures. It is clear from the ring-size distribution in Fig. 2 that the structures from both interatomic potentials, when modified to satisfy the Pauli exclusion principle, are more similar to each other than they were for the unmodified interatomic potentials.⁴

Thus, a key feature of the present database is that structural anomalies resulting from infinite energies in the SLC or BKS interatomic potentials due to atom overlaps have been largely eliminated. The present database contains only 1343 structures that are judged to be more stable than α -quartz by either the modified SLC or BKS interatomic potential. The vast majority of these are artifacts, although the two that are within $-30 \text{ kJ mol}^{-1} \text{ Si}$ of α -quartz shown in Fig. 1 are intriguing (artifacts). This result is an improvement by orders of magnitude over the previous version of the database,⁴ which contained a greater number of these artifacts of the interatomic potential. Thus, it is clear that the modification of the interatomic potential to enforce the Pauli exclusion principle has been largely successful in curbing the negative energy divergence. As such, confidence in the validity of the structures in the present database has increased. Consequently, we are more confident in offering this version of the database as an useful tool to the zeolite material community.

The band of materials with densities between $5\text{--}10 \text{ Si}/1000 \text{ \AA}^3$, which exists in both the SLC and BKS database, is of particular interest. Since this band of materials is found with both interatomic potentials, we are reasonably confident that this is not a bias introduced by the choice of interatomic potential. This low-density band is a range of high interest, because large-pore zeolites are expected to be found here. It is expected that several materials in this band will have interesting catalytic and sorption properties. Structures with double four- and double three-ring, if obtained, are expected to fall in this band.¹⁹ In fact, zeolites with densities falling in this range have recently been synthesized.^{19,20}

Large ring and pore zeolites are of intense interest for applications and hence to the synthetic field. We see in Fig. 2 and 3 an abundance of low-energy, large-ring materials. We hope that the existence of these predicted materials, including many near the low-density edge of the distribution in Fig. 3, will spur attempts at synthesis.

We would like to note here that researchers are currently exploring the possibilities that our database provides. David Sholl's group at Georgia Tech carried out a pore analysis of a subset of structures²¹ to understand adsorption and diffusion properties for simple molecules. They calculated, among other properties, the largest cavities available for adsorption and the size of the largest molecules that can diffuse through these materials. They also calculated Henry's constant and diffusion activation energies for adsorbed CH₄ and H₂. They further compared these properties with those experimentally obtained for the 190 known zeolites. Berend Smit's group at Berkley has been looking at our database structures from the point of view of carbon sequestration.²² Using the similarity principle, with AFX, a zeolite with the highest CO₂/CH₄ selectivity, as their query structure, they screened the database for structures that exhibited similar properties. This set of structures was subjected to more detailed Grand Canonical Monte Carlo simulations to verify the properties. With this approach they were able to identify structures that exhibited adsorption selectivity for CO₂ in excess of 100, much higher than those reported in the literature.²³ The goal of these studies is to identify structures with promising properties for further modeling and possible synthesis. From that point of view it is vital to have a high quality database as a starting point. Our efforts here go a long way in ensuring quality by removing the bias introduced due to limitations in the original interatomic potentials. Thus, this manuscript plays an important role in the development of a nascent research area that holds great promise for solving some challenging scientific and engineering materials problems.

5. Conclusion

We have constructed a database of computationally predicted zeolite-like materials. It contains over 2.6 M unique structures, roughly 10% of which lie in the thermodynamically accessible region where all the known zeolites can be found. Physicochemical properties such as energy, density, X-ray diffraction patterns, ring-size distributions, and I/I_{cor} have been calculated for these structures and compared with known zeolites. This comparison has shown the structures to be zeolite-like in their geometrical and topological properties. Also, structures from both SLC and BKS interatomic potentials are more similar to each other as compared with those in the previous version⁴ of the database. In addition, the negative divergence observed in the energies has been mitigated to a great extent by modification of the SLC and BKS interatomic potentials to obey the Pauli exclusion principle. Together these points illustrate that this database is indeed a significant refinement and improvement over the previous version and that it is now suitable for applied use.

This database is offered as a tool for the zeolite material community. It could be explored further to answer several

questions. As an example, the database could be searched based on certain physicochemical criteria^{16,24} to identify structures for a particular application, say structures with low-dielectric constant and high Young's modulus that are important in the field of dielectrics for microelectronics.¹⁷ The database could answer questions related to the upper bounds for performance pertaining to some targeted applications among zeolites. For example, are any zeolites worth pursuing in industrial CO₂ separation,²⁵ H₂ adsorption, or any other new applications. Or are zeolites as a class of materials unsuitable to reach desired performance objectives in these applications. While using zefsaII directly is likely to be more efficient,¹¹ a search across the database could enable identification of newly synthesized zeolites with unknown structures. Finally, we believe this database to be an important step toward the rational synthesis of solid-state materials. The subset of thermodynamically accessible structures can be explored to decide which of these structures could be synthesized and how. Substitutions with other metals may yield structures more amenable to synthesis. The present approach may serve as a guide for construction of analogous databases for other materials such as metal-organic frameworks (MOFs) or crystal hydrates. Diversity in structures and possible functionality among these classes of materials could reveal themselves through such efforts.

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