Communication

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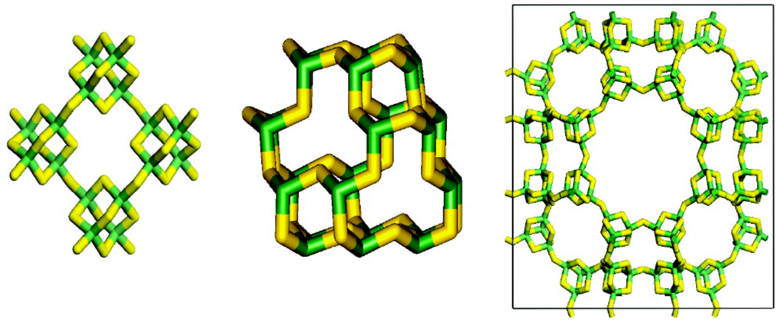

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Dramatic Differences between the Energy Landscapes of SiO_2 and SiS_2 Zeotype Materials

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Crystalline nanoporous materials known as zeotypes, including aluminosilicate zeolites, silicas, and aluminophosphates are of great industrial importance in a variety of technologies, such as catalysis, separation, and ion-exchange. The potentially enhanced range of applications for new structures with, for instance, larger pore sizes or novel electronic properties continues to drive the quest for new materials. The framework structures of zeotype materials are all based on 4-connected nets, and recent years have seen an enormous effort to enumerate, via theoretical approaches, all such nets.[1] The 10000+ hypothetical nets so far generated show that the zeotype structural landscape is much richer than expected from the 176 currently synthesized or naturally occurring frameworks. However, it is predicted that the majority of these hypothetical frameworks are thermodynamically unfeasible as siliceous materials because they can only be realized with severely distorted TX_4 tetrahedra[2] and have heats of formation tens of kJ/mol (SiO_2) higher than any currently hydrothermally synthesized material.[1d,f] Changes of the chemical composition to GeO_2 or $AlPO_4$ do not appear to alter this conclusion.[2,3] Recently, however, the previously hypothetical RWY framework (where the T-atoms of the sodalite framework are replaced with supertetrahedral T_4X_6 units, see Figure 1), which we would deem unfeasible in a siliceous form, was synthesized as the gallium germanium sulfide material UCR-20.[4] This inspired us to study in detail the energy landscape of tetrahedral sulfide (TS_4) materials and compare it with that of silica.

Here as a first step we carry out periodic density functional theory (DFT) calculations on SiS_2 materials. The polymorphs studied included two known phases: tetragonal[5] (isostructural to cristobalite, dia topology) and orthorhombic[6] (consisting of a packing of two-ring chains) and four model crystalline materials whose topologies correspond to the dense framework quartz (qtz) and the nanoporous frameworks SOD, CHA, and RWY. For comparison we also performed similar calculations on SiO_2 versions of the same crystals. The total energies and optimized geometries of the different SiO_2 and SiS_2 materials were obtained using the PBE[7] and PBE0[8] functionals and localized orbitals as implemented in the Crystal 06 code.[9] Orthorhombic SiS_2 was modeled as an isolated two-ring chain to circumvent problems with the poor description in DFT of the weak intrachain interactions. Frequencies of the γ-point phonons were calculated for each framework to verify that all optimized structures were true minima with respect to the internal coordinates. The latter is important since, with the exception of tetragonal and orthorhombic SiS_2, the starting structures for the SiS_2 materials could only be approximate and thus may optimize to n-order saddle points if left unchecked. Finally, the degree of distortion of the tetrahedra compared to an ideal tetrahedron (all X−T−X angles equal to 109.45° and all T−X bonds the same length) was assessed by the GASP code of Wells and co-workers.[10]

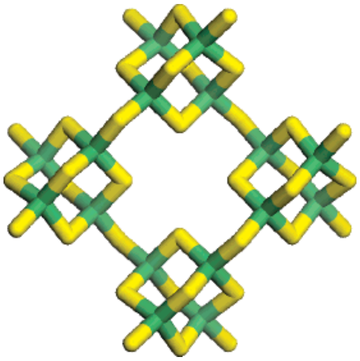

Figure 1. Fragment of RWY structure showing supertetrahedral units.

Table 1. Total Energies Relative to Quartz, Total Tetrahedral Distortion, and Average Si−X−Si Angle for the PBE0 Optimized SiO_2 and SiS_2 Materials

	E (kJ/mol SiX_2)		TTD (Å)		⟨Si–X–Si⟩ (deg)	
	SiO_2	SiS_2	SiO_2	SiS_2	SiO_2	SiS_2
qtz	0	0	2.2×10^{-2}	1.9×10^{-1}	141	119
dia	2	−33	3.4×10^{-2}	1.7×10^{-1}	141	112
SOD	7	−31	2.3×10^{-2}	1.1×10^{-1}	144	111
CHA	9	1	3.0×10^{-2}	3.1×10^{-1}	147	116
RWY	46	−37	7.1×10^{-2}	1.5×10^{-1}	123	105
two-chain		−41		2.0×10^{-1}		81

Table 1 gives the total energies (in kJ/mol relative to the respective quartz structure), total tetrahedral distortion values and average Si−X−Si angles of the different SiO_2 and SiS_2 materials, optimized using the PBE0 functional. The PBE functional gave essentially the same data, reinforcing our confidence in the results. While the silica materials show the expected energetic ordering with quartz as lowest energy structure, in line with experiment, the SiS_2 energetic landscape appears to be dramatically different. So much so that, as sulfide, supertetrahedral RWY lies between the experimentally prepared tetragonal and orthorhombic SiS_2 structures in terms of its thermodynamic stability. Furthermore, it is also much more stable than those frameworks which share the structure of low-energy silica polymorphs (e.g., quartz), strongly suggesting that sulfur holds the key to its successful synthesis. The other structure considered with small rings, the two-ring chain of orthorhombic SiS_2, is also considerably stabilized when going from SiO_2 to SiS_2. The SiS_2 two-ring chain is found to lie lowest in energy of all SiS_2 materials consistent with the fact that it can be experimentally purified through sublimation[6] and will be further stabilized by intrachain interactions not taken in account here, while its silica version (Silica-W[11]) was previously predicted to lie ∼120 kJ/mol SiO_2 above quartz.[12]

The tetrahedral distortion values are given in Table 1 in terms of the rms length of the vectors linking the X atom positions of

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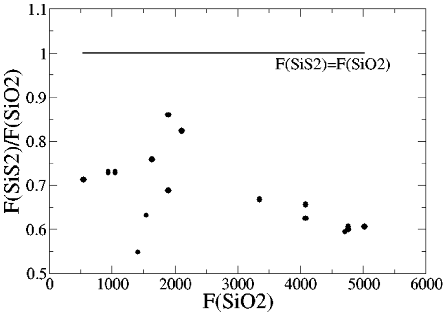

Figure 2. Ratio of SiS_2 and SiO_2 pseudofrequencies calculated for quartz, plotted against the pseudofrequencies for the SiO_2 structure.

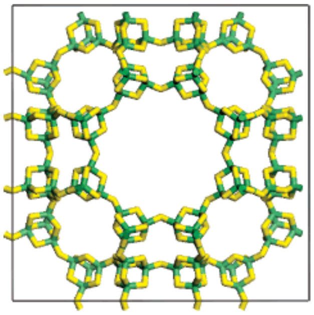

Figure 3. Unit cell of dt2_10 hypothetical zeolite structure.

the tetrahedra in the optimized structures and their idealization. These demonstrate that the sulfide materials are all considerably more distorted than their silica analogues. In SiO_2 form, values of the order of 2×10^{-2} Å are typical of experimentally known silica polymorphs such as quartz, cristobalite, or high-silica zeolites such as MFI.[2] The RWY and two-chain structures have significantly higher values, outside the range observed in real siliceous materials and consistent with their much higher energies.

Among the sulfide materials, a different picture emerges. The values of the tetrahedral distortion, including that of the experimentally known tetragonal SiS_2 material, are between 1×10^{-1} and 3.5×10^{-1} Å, one order of magnitude higher than for SiO_2. This implies that "normal" distortion in SiS_2 is greater than in SiO_2. Quartz, tetragonal SiS_2, SOD, and CHA all have similar values, comparable to that of RWY, whereas as silica their relative distortion is much lower. It is also striking that RWY is even more distorted as sulfide than in a silica form, though without an analogous energy penalty. This increase in tetrahedral distortion is accompanied by an overall decrease of the intertetrahedral Si−X−Si angles. The latter appears to reflect a preference of SiS_2 for smaller Si−X−Si angles than silica. This analysis is supported by the fact that the data in Table 1 show an approximate correlation between the average Si−S−Si angle and the relative stability: the smaller the average Si−S−Si angle is (i.e., the richer the structure is in two and three rings), the more stable a SiS_2 material is predicted to be.

The dramatic change in the energy landscape is thus most likely due to the combination of a preference of sulfides for smaller intertetrahedral Si−X−Si angles and an increased tolerance of SiS_2 for (tetrahedral) distortion compared to silica. The latter contribution is probably critical and the result of the smaller electrostatic cost due to the less ionic bonding in sulfides compared with oxides (as discussed by us in ref 13). The change in the relative ease with which the framework tetrahedra may be distorted is reflected in an increased flexibility of the material. This is seen clearly when comparing the pseudofrequencies of SiO_2 and SiS_2 quartz (i.e., the frequencies obtained with all the atomic masses set equal to one for comparison). The calculated pseudofrequencies are, depending on the particular mode in question, 10 to 50% lower for SiS_2 than for SiO_2 quartz (see Figure 2), suggesting a similar decrease in all generalized force constants.

Our calculations thus strongly suggest that SiS_2 and related sulfide compositions are ideally suited to the synthesis of frameworks whose structural units are inherently strained as SiO_2, such as supertetrahedra, two- and three-rings; an example is the hypothetical framework dt2_10[1g] (see Figure 3), which our calculations predicts to lie as sulfide at least 26 kJ/mol below quartz compared with 46 kJ/mol above quartz as silica. Targeting sulfide chemistry could therefore be highly productive in terms of synthesis of novel nanoporous structures, including the growing number of hypothetical nets generated computationally.

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Supporting Information Available: Full details of the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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