The Si-Ge substitutional series in the chiral STW
Zeolite Structure Type

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Supporting Information

Methodology

Calculation of the energy of the configurations: Effective Hamiltonian approach

The incorporation of heteroatoms in a zeolite framework might generate a large configurational space of possible atomic distribution. For simplicity, we will concern only on binary
Table S1: Details of the number of configurations used for each Ge content

| Ge/Si substitutions | Total number of configurations | Number of inequivalent configurations |
|---------------------|-------------------------------|--------------------------------------|
| 1                   | 60                            | 5                                    |
| 2                   | 1770                          | 165                                  |
| 3                   | 34220                         | 2855                                 |
| 4                   | 487635                        | 40890/1507*                          |

*a* The number of configurations considered in the calculations is shown in bold type.

Composition, for instance in the case of the present case Si-Ge distribution. Symmetry consideration, by using the SOD program, allows us to map all non-equivalent configurations up to 4 Ge atoms by unit cell. Since the cell contains 60 tetrahedral sites and the symmetry of the pure silica STW zeolite framework is relatively low (space group # 178), with 4 Ge atoms by unit cell there are already more than 40 thousand configurations. Even by using interatomic potential based calculations, this is already a heavy computational effort. For larger increase of the minority element in the binary solid solution, the number of configurations increases exponentially and therefore it is not possible to compute their energy. To deal with this, we turn to the recently developed Effective Hamiltonian (EH) approach, which parametrise the atom–atom interaction in a simple numerical function. In this way, the energy of millions of configurations can be evaluated at a small computational cost. Nevertheless, the method implies an initial high cost, since all configurations having 2 Ge (for STW a total of 165) and 3 Ge (2855 configurations) are needed first to submit to full energy relaxation, including atomic coordinates and cell parameters. Since Ge atoms confers large structural flexibility to the framework, those configurations having 4 Ge atoms, with either 4 nearest Ge neighbours or 3 Ge neighbours plus a 4th Ge atom as second next nearest neighbour, were also considered for the parameterisation of the EH. The set of zeolites considered with 4 Ge atoms has 1507 configurations.

The EH is based on consideration that the entrance of a heteroatom can be treated as a defect. First the substitution energies for isolated Ge atoms in the five distinct T sites are computed and after that, the interaction energies with the addition of new Ge atoms are
computed. We therefore parameterise the effective Hamiltonian as follows:

1. Firstly, the perturbation energy to substitute a Ge atom, $\Delta E(\vec{r}_i)$, is calculated using the Mott-Littleton methodology for each unique tetrahedral site $\vec{r}_i$.

$$\Delta E(\vec{r}_i) = E_i - E_0$$  \hspace{1cm} (S1)

where $E_0$ and $E_i$ are the lattice energies computed with GULP using the interatomic potential of pure silica structures and structures with one Ge/Si substitutions.

2. We then consider a pair interaction energy denoted as $\Delta E(\vec{r}_i, \vec{r}_j)$, where $\vec{r}_i$ and $\vec{r}_j$ are two tetrahedral sites, and is computed as the difference in energy between the individual energies for placing Ge atoms at sites $i$ and $j$ (i.e. $\Delta E(\vec{r}_i)$ and $\Delta E(\vec{r}_j)$ from above) and the energy found when both sites are occupied in a periodic calculation. The perturbation energy is given by:

$$\Delta E(\vec{r}_i, \vec{r}_j) = E_{ij} - \Delta E(\vec{r}_i) - \Delta E(\vec{r}_j) - E_0$$  \hspace{1cm} (S2)

where $E_{ij}$ is the lattice energy of structures with two Ge/Si substitutions.

3. Idem for trios and quartets of atoms.

$$\Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k) = E_{ijk} - \Delta E(\vec{r}_i, \vec{r}_j) - \Delta E(\vec{r}_i, \vec{r}_k) - \Delta E(\vec{r}_j, \vec{r}_k) - \Delta E(\vec{r}_i, \vec{r}_j) - \Delta E(\vec{r}_i, \vec{r}_k) - \Delta E(\vec{r}_j, \vec{r}_k) - E_0$$  \hspace{1cm} (S3)

$$\Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k, \vec{r}_l) = E_{ijkl} - \Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k) - \Delta E(\vec{r}_j, \vec{r}_k, \vec{r}_l) - \Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k, \vec{r}_l) - \Delta E(\vec{r}_i, \vec{r}_j) - \Delta E(\vec{r}_i, \vec{r}_k) - \Delta E(\vec{r}_j, \vec{r}_k) - \Delta E(\vec{r}_i, \vec{r}_l) - \Delta E(\vec{r}_j, \vec{r}_l) - \Delta E(\vec{r}_k, \vec{r}_l) - E_0$$  \hspace{1cm} (S4)

where $\{\ldots\}^{ijk}$ and $\{\ldots\}^{ijkl}$ represent all the summation terms, which are combinations of the $ijk$ and $ijkl$ indices, respectively.
Then, an effective approximate lattice energy of $N$ Si/Ge substitutions is being calculated as:

$$
H = E_0 + \sum_i \Delta E(\vec{r}_i) + \sum_{ij} \Delta E(\vec{r}_i, \vec{r}_j) + \sum_{ijk} \Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k) + \sum_{ijkl} \Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k, \vec{r}_l) + O(\vec{r}^N) \tag{S5}
$$

where $i, j, k, l$-indexes run on the total number of configurations. Is useful to adapt the Equation S5 with a tensor notation using the Einstein summation convention:

$$
H(N) = E_0 + \epsilon_i S^i + \rho_{ij} S^i S^j + \theta_{ijk} S^i S^j S^k + \phi_{ijkl} S^i S^j S^k S^l \tag{S6}
$$

where $S^i$ are spin-type variables which with 1 or 0 represent the presence or absence, respectively, of Ge atom in the crystallographic $i$-position, $\epsilon := \{\Delta E(\vec{r}_i)\}$, $\rho := \{\Delta E(\vec{r}_i, \vec{r}_j)\}$, $\theta := \{\Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k)\}$ and $\phi := \{\Delta E(\vec{r}_i, \vec{r}_j, \vec{r}_k, \vec{r}_l)\}$. We can readapt the Equation S6 to sum on the inequivalent configurations using a dictionary, $\delta$, which connects each configuration with the calculated equivalent configuration.

$$
H(N) = E_0 + \epsilon_i \delta^i S^i + \rho_{\alpha\beta} \delta^\alpha S^i S^j + \theta_{\alpha\beta\gamma} \delta^\alpha \delta^\beta S^i S^j S^k + \phi_{\alpha\beta\gamma\delta} \delta^\alpha \delta^\beta \delta^\gamma S^i S^j S^k S^l\tag{S7}
$$

Results
Table S2: Summary of synthesis results at 175 °C

| Geₓf  | Time (hours) | Yield (wt. %) | Phase\(^{a}\)          |
|-------|--------------|---------------|-------------------------|
| 0     | 27           | 31.1          | amorphous (+ HPM-1)     |
| 0     | 48           | 21.2          | HPM-1                   |
| 0     | 143          | 29.7          | HPM-1                   |
| 0     | 264          | 29.6          | HPM-1                   |
| 0.009 | 25           | 22.5          | HPM-1 + amorphous       |
| 0.009 | 48           | 23.7          | HPM-1                   |
| 0.009 | 144          | 23.7          | HPM-1                   |
| 0.019 | 25           | 25.1          | HPM-1                   |
| 0.019 | 48           | 24.1          | HPM-1                   |
| 0.019 | 144          | 25.4          | HPM-1                   |
| 0.019 | 240          | 25.4          | HPM-1                   |
| 0.032 | 25           | 27.1          | HPM-1                   |
| 0.032 | 48           | 27.9          | HPM-1                   |
| 0.032 | 144          | 26.16         | HPM-1                   |
| 0.032 | 240          | 26.3          | HPM-1                   |
| 0.09  | 25           | 33.1          | HPM-1                   |
| 0.09  | 48           | 31.4          | HPM-1                   |
| 0.09  | 144          | 32.2          | HPM-1                   |
| 0.09  | 240          | 34.4          | HPM-1                   |
| 0.166 | 25           | 34.4          | HPM-1                   |
| 0.166 | 48           | 34.5          | HPM-1                   |
| 0.166 | 144          | 33.3          | HPM-1                   |
| 0.166 | 237          | 36.1          | HPM-1                   |
| 0.2   | 25           | 36.4          | HPM-1                   |
| 0.2   | 48           | 35.7          | HPM-1                   |
| 0.2   | 144          | 36.1          | HPM-1                   |
| 0.2   | 240          | 35.5          | HPM-1                   |
| 0.4   | 25           | 39.3          | HPM-1                   |
| 0.4   | 48           | 39.7          | HPM-1                   |
| 0.4   | 144          | 38.0          | HPM-1                   |
| 0.4   | 240          | 37.9          | HPM-1                   |
| 0.6   | 25           | 24.9          | HPM-1                   |
| 0.6   | 48           | 26.8          | HPM-1                   |
| 0.6   | 144          | 27.6          | HPM-1                   |
| 0.6   | 240          | 32.5          | HPM-1                   |
| 0.8   | 25           | 25.4          | HPM-1                   |
| 0.8   | 48           | 23.3          | HPM-1                   |
| 0.8   | 144          | 26.6          | HPM-1                   |
| 0.9   | 25           | 5.5           | HPM-1                   |
| 0.9   | 48           | 18.1          | HPM-1                   |
| 0.9   | 144          | 21.8          | HPM-1                   |
| 1     | 27           | 0             | - \(^{b}\)              |
| 1     | 113          | 1.7           | HPM-1                   |
| 1     | 200          | 2.6           | Q+Arg (+HPM-1)\(^{c}\)  |
| 1     | 96           | 10.4          | HPM-1 (+Q)\(^{c,d}\)    |
| 1     | 102          | 9.5           | HPM-1 +Q\(^{c,d}\)      |

\(^{a}\) Major phases are listed first, very minor phases appear between parentheses. \(^{b}\) No solids could be collected. \(^{c}\) Q is the Quartz-like and Arg is the Argutite-like GeO\(_2\) phases. \(^{d}\) The last two entries correspond to a different synthesis run in the same nominal conditions as the preceeding ones.
Figure S2: Cell parameters vs Ge\textsubscript{f} computed with the EH.

Figure S3: Some of the energy-minimised D4Rs configurations. They are classified according to the resonance. Some structural distortions are distinguishable with respect to the configuration of pure silica.
Figure S4: Infrared species of STW zeolites obtained from gels with $Ge_f = 0, 0.01, 0.09, 0.17, 0.4, 0.6, 0.8, 0.9$ and 1 (from bottom to top)
Figure S5: FESEM images of HPM-1 zeolites prepared at different Ge\textsubscript{f} levels.

Figure S6: Thermograms of HPM-1 zeolites prepared at different Ge\textsubscript{f} levels.
Figure S7: Direct irradiation $^{29}\text{Si}$ MAS spectra of (Ge,Si)-STW with $\text{Ge}_f = 0.00$, 0.166, 0.20, 0.40, 0.60 and 0.80 (from bottom to top). For every spectra 2048 scans were acquired. Recycle delays are 60s for the pure silica sample and 180s for the rest.

Figure S8: Difference between calculated and experimental chemical shifts for each $^{19}\text{F}$ resonance according to our assignment (see main text).
Rietveld details

The starting model for Rietveld refinement of samples prepared with Ge\(f\)=0.4, 0.6 and 1 was the refined structure of pure silica HPM-1,\(^{2}\) in space group \(P6_122\) modified to have the unit cell dimensions determined from conventional powder XRD data and a Ge occupation of all crystallographic positions initially set at 0.4, 0.6 and 1.0, respectively (Si occupancies of 0.6, 0.4 and 0.0, respectively). Although the sample with Ge\(f\) = 1 appeared as phase-pure in the conventional XRD pattern, synchrotron radiation showed the presence of small traces of quartz-like GeO\(_2\), and the corresponding regions were excluded from the refinement. A Lobanov and Alte da Veiga absorption correction was applied.\(^{5}\) Scale factor, unit cell and profile parameters were refined, with a shifted Chebyschev function initially with 16 fixed parameters to simulate the background. Then, the Ge, Si, O and F atoms were allowed to move, initially with soft restraints on T-O and O-O distances and with Ge and Si in each crystallographic site constrained to move together. Then, the position and orientation of the organic SDA was refined as a rigid body consisting of the imidazolium ring with the three methyl substituents as a rigid unit plus the ethyl group as a satellite that could freely rotate along the C2-C9 bond. The hydrogen atoms were omitted but the fractional occupancies of the C atoms were adjusted to account for the electrons of the bonded H. The weight of the distance restraints was gradually reduced and eventually eliminated. In the final stages of the refinements, atom displacement factors (grouped by atom type), background and fractional occupancies of Ge and Si in each crystallographic site (constrained to amount to a full occupancy of each site) were included in the refinement. Final crystallographic data are summarized in Tables S3, the final Rietveld plots are given in Figures S9, S10 and S11 and the corresponding cif files are provided as supplementary material.
Figure S9: Observed (+) and calculated (solid line) powder X-ray diffractograms for as-made Ge,Si-HPM-1 with $Ge_f = 0.4$ refined in space group $P6_122$. Vertical tic marks indicate the positions of allowed reflections. The lower trace is the difference plot. $\lambda=0.56383 \text{ Å}$.

Figure S10: Observed (+) and calculated (solid line) powder X-ray diffractograms for as-made Ge,Si-HPM-1 with $Ge_f = 0.6$ refined in space group $P6_122$. Vertical tic marks indicate the positions of allowed reflections. The lower trace is the difference plot. $\lambda=0.56383 \text{ Å}$.
Table S3: Crystallographic and Experimental Parameters for the Rietveld Refinement of as-made Ge,Si-HPM-1 phases (wavelength: 0.56383 Å, Temperature 293K)

| Nominal $Ge_f$ | 0.4 | 0.6 | 1  |
|---------------|-----|-----|----|
| Refined $Ge_f$| 0.396 | 0.574 | -  |
| 2θ range      | 2.00-38.32 | 2.00-33.97 | 2.50-44.9 |
| no. of data points | 3733 | 3198 | 4241 |
| no. of reflections | 1327 | 977 | 1792 |
| Space Group   | $P6_22$ | $P6_22$ | $P6_22$ |
| unit cell parameters (Å) |      |      |      |
| $a, b$        | 12.09289(16) | 12.16714(17) | 12.42671(11) |
| $c$           | 30.0839(5) | 30.2519(6) | 30.6310(5) |
| Cell volume ($Å^3$) | 3810.01(12) | 3878.46(13) | 4096.41(8) |
| Residuals     |      |      |      |
| $R_{wp}$      | 3.06% | 2.82% | 3.66% |
| $R_p$         | 2.36% | 2.23% | 2.65% |
| $R_{F^2}$     | 7.76% | 7.53% | 10.58% |
| reduced $\chi^2$ | 2.513 | 2.527 | 3.98 |

Figure S11: Observed (+) and calculated (solid line) powder X-ray diffractograms for as-made Ge-HPM-1 ($Ge_f = 1.0$) refined in space group $P6_22$. Vertical tic marks indicate the positions of allowed reflections. The lower trace is the difference plot. $\lambda=0.56383$ Å.
Table S4: Average bond distances and angles in Ge,Si-HPM-1 phases

|                  | Average distance (Å) | \( Ge_f = 0.4 \) | \( Ge_f = 0.6 \) | \( Ge_f = 1 \) |
|------------------|----------------------|------------------|------------------|------------------|
| T1-O             | 1.654                | 1.662            | 1.668            |
| T2-O             | 1.656                | 1.670            | 1.714            |
| T3-O             | 1.637                | 1.647            | 1.706            |
| T4-O             | 1.667                | 1.689            | 1.724            |
| T5-O             | 1.635                | 1.642            | 1.724            |
| T1-F             | 2.57                 | 2.63             | 2.57             |
| T2-F             | 2.79                 | 2.76             | 2.89             |
| T3-F             | 2.70                 | 2.71             | 2.72             |
| T4-F             | 2.74                 | 2.75             | 2.75             |

|                  | Average angle (°)    |                 |                 |                 |
|------------------|----------------------|------------------|------------------|------------------|
| O-T1-O           | 109.3                | 109.2            | 109.2            |
| O-T2-O           | 109.4                | 109.4            | 109.3            |
| O-T3-O           | 109.1                | 109.0            | 109.4            |
| O-T4-O           | 109.4                | 109.4            | 109.2            |
| O-T5-O           | 109.4                | 109.4            | 109.6            |
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