Local Environment and Dynamic Behavior of Fluoride Anions in Silicogermanate Zeolites: A Computational Study of the AST Framework

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In silicogermanate zeolites containing double four-ring (d4r) building units, the germanium atoms preferentially occupy the corners of these cube-like units. While this general behaviour is well known, the absence of long-range order precludes a determination of the preferred arrangements of Si and Ge atoms at the corners of d4r cages by means of crystallographic methods. If fluoride anions are present during the synthesis, these are incorporated into the d4r cages. Due to the sensitivity of the $^{19}$F chemical shift to the local environment, NMR experiments can provide indirect insights into the predominant (Si,Ge) arrangements. However, conflicting interpretations have been reported, both with regard to the preference for, or avoidance of, Ge-O-Ge linkages, and concerning the equilibrium position of fluorine inside the cage, where fluorine might either occupy the cage centre or participate in a partly covalent Ge-F bond. In order to shed light on the energetically preferred local arrangements, periodic electronic structure calculations in the framework of dispersion-corrected density functional theory (DFT) were performed. The AST framework was used as a suitable model system, as this zeolite is synthetically accessible across the range of $(\text{Si}_{1-n}\text{Ge}_n\text{O}_2)$ compositions $(0 \leq n \leq 1)$. DFT structure optimisations for (Si,Ge)-AST systems containing fluoride anions and organic cations revealed that arrangements of Si and Ge at the cage vertices which maximise the number of Ge-O-Ge linkages are energetically preferred, and that fluorine tends to form relatively short (~2.2 to 2.4 Å) bonds to Ge atoms that are surrounded by Ge-O-Ge linkages. The preference for Ge-O-Ge linkages disappears in the absence of fluorine, pointing to a “templating” effect of the anions. In addition to the prediction of equilibrium structures, DFT-based Molecular Dynamics calculations were performed for selected AST models in order to analyse the dynamics of fluoride anions confined to d4r cages. These calculations showed that the freedom of movement of fluorine varies markedly depending on the local environment, and that it correlates with the average Ge-F distance (short Ge-F bonds = restricted motion). An analysis of the Ge-F radial distribution functions provided no evidence for a coexistence of separate local energy minima at the cage centre and in the proximity of a germanium atom for any of the systems considered. The computational approach pursued in this work provides important new insights into the local structure of silicogermanate zeolites with d4r units, enhancing the atomic-level understanding of these materials. In particular, the findings presented here constitute valuable complementary information that can aid the interpretation of experimental data.
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Local environment and dynamic behaviour of fluoride anions in silicogermanate zeolites: A computational study of the AST framework

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Abstract

In silicogermanate zeolites containing double four-ring (d4r) building units, the germanium atoms preferentially occupy the corners of these cube-like units. While this general behaviour is well known,
the absence of long-range order precludes a determination of the preferred arrangements of Si and Ge atoms at the corners of \textit{d4r} cages by means of crystallographic methods. If fluoride anions are present during the synthesis, these are incorporated into the \textit{d4r} cages. Due to the sensitivity of the $^{19}$F chemical shift to the local environment, NMR experiments can provide indirect insights into the predominant (Si,Ge) arrangements. However, conflicting interpretations have been reported, both with regard to the preference for, or avoidance of, Ge-O-Ge linkages, and concerning the equilibrium position of fluorine inside the cage, where fluorine might either occupy the cage centre or participate in a partly covalent Ge-F bond. In order to shed light on the energetically preferred local arrangements, periodic electronic structure calculations in the framework of dispersion-corrected density functional theory (DFT) were performed. The AST framework was used as a suitable model system, as this zeolite is synthetically accessible across the range of (Si$_{1-n}$/Ge$_n$)$_2$O$_2$ compositions ($0 \leq n \leq 1$). DFT structure optimisations for (Si,Ge)-AST systems containing fluoride anions and organic cations revealed that arrangements of Si and Ge at the cage vertices which maximise the number of Ge-O-Ge linkages are energetically preferred, and that fluorine tends to form relatively short (~2.2 to 2.4 Å) bonds to Ge atoms that are surrounded by Ge-O-Ge linkages. The preference for Ge-O-Ge linkages disappears in the absence of fluorine, pointing to a “templating” effect of the anions. In addition to the prediction of equilibrium structures, DFT-based Molecular Dynamics calculations were performed for selected AST models in order to analyse the dynamics of fluoride anions confined to \textit{d4r} cages. These calculations showed that the freedom of movement of fluorine varies markedly depending on the local environment, and that it correlates with the average Ge-F distance (short Ge-F bonds = restricted motion). An analysis of the Ge-F radial distribution functions provided no evidence for a coexistence of separate local energy minima at the cage centre and in the proximity of a germanium atom for any of the systems considered. The computational approach pursued in this work provides important new insights into the local structure of silicogermanate zeolites with \textit{d4r} units, enhancing the atomic-level understanding of these materials. In particular, the findings presented here constitute valuable complementary information that can aid the interpretation of experimental data.
1. Introduction

Sparked by the increased interest in novel porous materials for various applications (catalysis, separation, energy storage etc.), the last 20 years have seen major advances in the field of silicogermanate zeolites, neutral-framework zeolites in which the tetrahedral sites (T sites) are occupied by silicon and germanium. While a few zeolite frameworks, like AST, are accessible both in pure-SiO$_2$ form and as silicogermanates with various Ge contents, there are also many instances where the incorporation of Ge stabilises frameworks that are not accessible in all-silica or aluminosilicate composition.$^1$ Some of these frameworks have very large pore openings, two of the most spectacular examples being the mesoporous zeolite ITQ-37, with pore apertures surrounded by 30 T atoms,$^2$ and ITQ-44, which possesses 18-ring pore apertures and has an exceptionally low framework density.$^3$

Besides efforts in the direct synthesis, it has been shown that frameworks which are composed of Si-rich sheets connected by Ge-rich building units can be disassembled through selective Ge removal, and the layers reassembled to form new materials.$^4,5$ This ADOR (assembly-disassembly-organisation-reassembly) approach has led to the discovery of several new zeolites that are not accessible through conventional synthesis routes.$^6$

The equilibrium Ge-O-Ge angle (≈130 deg) is smaller than the corresponding Si-O-Si angle (≈145 deg).$^7$ As the formation of small (three- or four-membered) rings requires rather low T-O-T angles, the incorporation of germanium stabilises such small rings. In particular, the presence of germanium may lead to the preferred formation of double four-ring ($d_4r$) units, which are stabilised by small T-O-T angles (typically <140 degrees).$^8,9$ Different experimental methods have provided evidence that Ge preferentially occupies the vertices of the $d_4r$ cages: In favourable cases, a direct refinement of the occupancies of different T sites by Si and Ge from X-ray diffraction data is possible.$^{10-13}$ Indirect information on the Ge siting can be obtained from $^{19}$F and $^{29}$Si solid-state NMR experiments, and such studies have been performed – among other systems – for ITQ-7 (ISV framework),$^{14}$ ITQ-17 (BEC framework),$^{11}$ ITQ-13 (ITH),$^{15,16}$ and (Si,Ge) analogues of octadecasil (AST framework).$^{17}$ Besides the experimental work, a preference of Ge for the $d_4r$ unit has also been found in computational
modelling studies using a variety of techniques, comprising force field calculations,\textsuperscript{9,11,12} Hartree-Fock calculations for small cluster models,\textsuperscript{14} and periodic density functional theory (DFT) calculations.\textsuperscript{18–20} In systems with a mixed occupation of the vertices of a \textit{d4r} unit by Si and Ge, the distribution of the two elements exhibits no long-range ordering, precluding a determination of preferred arrangements by means of crystallographic methods. Some information on the local ordering can be inferred from $^{29}\text{Si}$-NMR spectroscopy. However, the influence of nearest-neighbour Ge atoms on the $^{29}\text{Si}$ chemical shift is relatively small, and contributions of several Ge atoms do not show a strictly additive behaviour.\textsuperscript{21} In zeolites synthesised via the fluoride route, fluoride anions tend to be incorporated in the smallest cage available in the structure, and they are therefore typically located in \textit{d4r} cages if such building units are present.\textsuperscript{22} Because the $^{19}\text{F}$ chemical shift depends on the composition of the \textit{d4r} cage, $^{19}\text{F}$-NMR experiments can provide insights into the local environment. It is well established that (8Si,0Ge) \textit{d4r} cages give rise to a signal at -38 ppm (relative to CFCl$_3$),\textsuperscript{17,23} whereas (0Si,8Ge) \textit{d4r} cages result in a signal at ~-15 ppm\textsuperscript{17,22} (throughout this work, we use ((8-$x$)Si, $x$Ge) as a shorthand notation to represent the occupation of the eight vertices of the \textit{d4r} unit by 8-$x$ Si and $x$ Ge atoms). Other signals appearing at -20 ppm and -8 ppm in mixed (Si,Ge) systems were mostly interpreted as being due to (7Si,1Ge)/(6Si,2Ge) and (5Si,3Ge)/(4Si,4Ge) \textit{d4r} units, respectively.\textsuperscript{11,12,14,15,17,24–26} As an interpretation on the basis of experimental data alone may lead to ambiguities, complementary computational investigations were carried out by Sastre and co-workers: Using a combination of force field based calculations (to optimise the structures) and DFT calculations (to predict NMR shifts), they found that the computed NMR shifts for mixed (Si,Ge) systems agree much better with experiment when the F atom is not located at the centre of the cage, but displaced towards a Ge atom.\textsuperscript{26,27} For several systems, the calculations delivered pentacoordinated germanium with Ge-F bond distances in the range of 1.9 to 2.0 Å. The local environment of the pentacoordinated Ge atom, specifically the number of adjacent Ge-O-Ge linkages along edges of the \textit{d4r} cage, was found to be a dominant factor in determining the chemical shift. This was corroborated in recent work on STW zeolite by Rigo et al., who found three distinguishable Ge environments on the basis of a combination of NMR experiments and DFT calculations:\textsuperscript{13} (1) “Isolated” Ge atoms surrounded only by Ge-O-Si linkages: Ge(Ge)$_0$, (2) Ge atoms surrounded by one or two Ge-O-Ge linkages along the cage edges: Ge(Ge)$_1$ and (Ge(Ge)$_2$),
(3) Ge atoms surrounded by three Ge-O-Ge linkages: Ge(Ge)$_3$ (the fourth T-O-T linkage, which has no documented impact on the NMR shift, points away from the $d4r$ cage, so three is the highest possible number of Ge-O-Ge linkages along cage edges).

The AST zeolite framework was synthesised in pure-silica form by Caullet et al., who labelled it “octadecasil” to emphasise its clathrasil nature. A pure-GeO$_2$ AST dubbed ASU-9 was later reported by Yaghi and Li, and mixed (Si,Ge)-AST frameworks were prepared by Wang et al. and by Tang. AST-type zeolites were also used as model systems in the aforementioned computational studies by Sastre and co-workers. According to a Rietveld refinement of the GeO$_2$-AST end member by Wang et al., the F atoms are located at the centre of the $d4r$ cage, however, a large isotropic displacement factor indicates rather large freedom of motion. A slight splitting of the $^{19}$F-NMR signal in this system was interpreted as being due to a displacement of fluorine from the cage centre, pointing to the possibility of coexisting off-centre local minima, as proposed earlier by Villaescusa et al. on the basis of semiempirical calculations. Si-NMR results for mixed (Si,Ge) systems led to the conclusion that there is a preference for an alternating arrangement of Si and Ge, i.e. an avoidance of Ge-O-Ge linkages.

To clarify the rationale behind the present work, it is useful to point out some conflicting observations in the existing literature:

(1) As discussed above, some NMR results have been interpreted as being indicative of an avoidance of Ge-O-Ge linkages, e.g. for (Si,Ge)-AST. Force field based simulations on ITQ-21 and AST-type frameworks provided evidence for an energetic “penalty” for the formation of Ge-O-Ge linkages, with the relative energy increasing roughly linearly with increasing number of such linkages. Conversely, a DFT study by Kamakoti and Barckholtz of the BEC framework delivered an arrangement in which two Ge atoms occupy adjacent cage vertices, i.e. in which a Ge-O-Ge link is present, to be the most favourable scenario for a (6Si,2Ge) $d4r$ cage. A configuration with two Ge-O-Ge linkages was found to be the most stable distribution for a (5Si,3Ge) $d4r$ cage. Other computational studies using electronic structure methods did not predict an energetic penalty for the formation of Ge-
O-Ge linkages.\textsuperscript{14,19} In fact, recent NMR studies on ITQ-13 and STW-type silicogermanates delivered evidence for a presence of Ge-O-Ge linkages at relatively low overall Ge contents.\textsuperscript{13,16}

(2) Crystallographic investigations on SiO\textsubscript{2} - and GeO\textsubscript{2} -zeolites and mixed (Si,Ge) systems containing \textit{d4r} units always located fluorine at the centre of the cage,\textsuperscript{12,17,23,31–33} whereas some NMR studies have pointed to an off-centre displacement in Ge-containing systems.\textsuperscript{17,30} While there is no direct experimental evidence for the presence of Ge-F bonds, the computational studies by Sastre and co-workers, which were validated against experimental NMR data, point to the existence of pentacoordinated germanium atoms in both GeO\textsubscript{2} -AST (\textit{d}(Ge-F) \approx 2.2 \text{"Å") and in mixed (Si,Ge) systems (\textit{d}(Ge-F) \approx 1.9 to 2.0 \text{"Å")}.\textsuperscript{26,27,34}

To address the first point, structure optimisations using dispersion-corrected DFT were performed for models of (Si,Ge)-AST across the full compositional range. AST was chosen as a convenient model due to its relative simplicity (two non-equivalent T sites, 20 T atoms in the conventional unit cell, Fig. 1) and due to the fact that it is synthetically accessible for essentially any Ge content. Calculations were performed for structure models including fluoride anions and tetramethylammonium cations, dubbed (TMA,F)-AST, and for models of the bare AST framework. On the basis of the calculations, the energetically preferred arrangements of Si and Ge were determined, and it was attempted to identify trends regarding the preference for, or avoidance of, certain arrangements.

With regard to the second point, the structure optimisations for (TMA,F)-AST models also deliver insights into the preferred fluorine positions and, thus, the presence or absence of pentacoordinated Ge atoms. Another interesting aspect is the dynamic behaviour of fluorine in the \textit{d4r} cage: For example, it is conceivable that several local minima exist within one cage – e.g. one at the centre and another one close to a Ge atom – and that fluorine atoms “hop” between minima over time. To elucidate the dynamic behaviour, DFT-based Molecular Dynamics (MD) calculations were performed for selected models of (TMA,F)-AST.
2. Models and methods

2.1 Models of AST structure

The AST framework is a relatively simple one, as it can be assembled from two types of natural tiles, namely cube-like $d4r$ cages (t-cub tile, face symbol $[4^6]$) and larger octadecahedral $ast$ cages (t-trd tile, face symbol $[4^6\cdot6^{12}]$).\textsuperscript{35,36} Crystallographic investigations have established that fluorine atoms occupy
the centre of the $d4r$ cages, whereas the organic structure directing agents (OSDAs), also called "templates", reside in the $ast$ cages.\textsuperscript{23,31} There are two distinct T sites in the structure: The T1 site corresponds to the vertices of the $d4r$ cage, with the three surrounding T1-O-T1 linkages forming edges of the cage. The fourth linkage from each T1 corner forms a connection to the T2 site, which is connected to T1 sites belonging to four different $d4r$ cages. In the cubic aristotype of AST, the T1-O-T2 linkage is linear. However, the actual symmetry of both as-made and calcined all-silica AST (octadecasil) is tetragonal (space group $I4/m$), thereby avoiding linear T-O-T linkages.\textsuperscript{23,31,37} Tetragonal symmetry was also found for GeO$_2$-AST and for most mixed (Si,Ge) systems.\textsuperscript{17,29}

The starting models used in the calculations for OSDA-containing AST included tetramethylammonium (TMA) molecules, as this is a fairly simple OSDA that has been successfully used to direct the synthesis of SiO$_2$-AST (octadecasil).\textsuperscript{23,31} One complication arises, as the OSDA is disordered in the experimentally determined structure, and an ordering requires a lowering of the symmetry. Different relative orientations of the OSDA molecules in adjacent cages would lead to different resulting space groups. In the present work, an orientation was chosen that retains the body-centering of the lattice, leading to a structure in space group $I4$ (Fig. 1). While (Si,Ge)-AST and GeO$_2$-AST systems have not been synthesised with TMA, the reported syntheses used other alkylammonium OSDAs.\textsuperscript{17,29} In addition to the pure-SiO$_2$ and pure-GeO$_2$ end members, models with Ge contents $n$(Ge) ranging from 0.1 to 0.9 were prepared. These models do no longer possess tetragonal symmetry (unless in very few special cases), but it was assumed that the body centering is preserved, \textit{i.e.} the $d4r$ units at the centre and at the corners of the pseudo-tetragonal unit cell have an identical arrangement of Si and Ge. The arrangements considered, which were generated for a model of a single $d4r$ cage using the Supercell code,\textsuperscript{38} are visualised in Fig. 2. The labelling scheme to designate these systems makes use of a) the number of Si and Ge atoms occupying the vertices of the cage, b) the point group symmetry of the (Si,Ge) arrangement, and c) the number of Ge-O-Ge linkages (this is dropped from the label if there is only one (Si,Ge) distribution). For example, AST_{(4Si,4Ge)}C$_{4v}$4GeGe has 4 Si and 4 Ge atoms at the vertices of the $d4r$ cages, which are arranged in a way that the point group symmetry of the (Si,Ge) distribution is $C_{4v}$ – this corresponds to an occupation of all corners of one face by Ge, and therefore 4 Ge-O-Ge linkages (the edges of that
According to Kamakoti & Barckholtz’s study of BEC, an occupation of up to 4 T sites per $d4r$ unit by Ge is energetically favourable. Beyond that, other T sites are occupied. To account for a possible occupation of the T2 site by germanium, comparisons between models in which T2 is occupied either by Si or by Ge were made for compositions ranging from $n(\text{Ge}) = 0.5$ (10 Si and 10 Ge per unit cell) to $n(\text{Ge}) = 0.8$ (4 Si and 16 Ge per unit cell). T2 = Si was assumed for $n(\text{Ge})$ up to 0.4 and T2 = Ge for $n(\text{Ge}) = 0.9$. A mixed occupancy of the T2 site by Ge and Si was not considered. If the T2 site is occupied by Si, it is omitted from the label (except in the case of $\text{AST}_{(0\text{Si,8Ge})}\_O_{h,T2Si}$), but if it is occupied by Ge, the designator “T2Ge” is appended to the label.

We have to note that the symmetry of (TMA,F)-AST, which is tetragonal, is reduced with respect to the cubic aristotype. Therefore, the $d4r$ cages possess two different types of edges (T-O-T linkages), along the tetragonal $c$-axis and perpendicular to it. If this was accounted for in the setup of the model systems, a larger number of configurations than those shown in Fig. 2 would arise. For example, two neighbouring Ge atoms in the $\text{AST}_{6\text{Si,2Ge}}\_C_{2v,1}\text{GeGe}$ model could be linked along $c$ or perpendicular to $c$. Test calculations for a few models indicated that the energy differences between such different configurations are small, and therefore only one arrangement of Si and Ge at the cage vertices was considered for each case. It has to be noted that different observations were made in a DFT study of BEC by Kamakoti and Barckholtz. However, in that system, the T-O-T angles at the edges of the $d4r$ unit vary considerably, and the occupancy of neighbouring T sites by Ge is energetically favoured when they are connected via a “deformable” T-O-T linkage, i.e. a link that allows the formation of a small T-O-T angle. Though not equivalent by symmetry, the T-O-T angles at all edges of the $d4r$ cages of SiO$_2$-AST are very similar (138 to 141 degrees).
Fig. 2 Visualisation of (Si,Ge) distributions at the vertices of a \(d_{4r}\) unit.

2.2 Computational details

DFT structure optimisations and DFT-based MD calculations were performed using the CP2K code (version 2.6.2, installed on the HLRN supercomputer “Konrad”), which uses a hybrid Gaussian and plane wave scheme.\(^{39,40}\) All calculations used the PBE exchange-correlation functional in conjunction with the “Grimme-type” D3 dispersion correction,\(^{41,42}\) a plane wave energy cutoff of 600 Ry, and Goedecker-Teter-Hutter pseudopotentials devised by Krack.\(^{43}\) Only the gamma point was used to
sample the first Brillouin zone. All calculations used Gaussian “MOLOPT” basis sets that are included in the current distribution of CP2K. The structure optimisations used triple-zeta (TZVP) basis sets, as it was found that these give a much more accurate difference in lattice energy between SiO₂-AST and quartz than double-zeta (DZVP) basis sets (TZVP: 11.6 kJ mol⁻¹; DZVP: 16.1 kJ mol⁻¹, experiment: 10.9 kJ mol⁻¹). However, both basis sets were found result in very similar equilibrium structures, justifying the use of the less demanding DZVP basis in the MD simulations.

The structure optimisations were performed for the conventional unit cell of tetragonal AST. All atomic coordinates and the lattice parameters were optimised, fixing the symmetry of the lattice to tetragonal (a = b, all angles = 90 degrees). The optimisations used the following convergence criteria: Maximal geometry change = 2⋅10⁻⁵ bohr, maximal residual force = 1⋅10⁻⁶ Ha bohr⁻¹, maximal pressure deviation = 0.01 GPa. The MD simulations took the optimised structures as starting point and used a 2×2×1 supercell. MD simulations were performed in the canonical (NVT) ensemble for a temperature of 298 K, using a Nosé-Hoover thermostat with a timestep of 0.5 ps and a time constant of 50 fs. To improve the statistics, three independent trajectories were run for each system, with each trajectory consisting of an equilibration stage of 2.5 ps (5000 steps) and a production stage of 7.5 ps (15000 steps). All results presented below correspond to averages over three trajectories. For the analysis of the production part of each MD trajectory, the root mean square displacements (RMSD) of all elements and radial distribution functions (RDF) of selected pairs of elements were computed using the VMD software, version 1.9.3.

3. Results and discussion

3.1 Equilibrium structures of the end members: SiO₂-AST and GeO₂-AST

Initial DFT structure optimisations were performed for the end members SiO₂-AST and GeO₂-AST, both with and without TMA template and F anions. The resulting lattice parameters are shown in Table 1, together with experimental data, where available. For SiO₂-AST, the computed lattice parameters agree reasonably well with experiment, although there is a systematic tendency to
overestimate the length of the $c$-axis, while underestimating $a$. Similar findings have been discussed in more detail in previous benchmarking work.\textsuperscript{46,47} For (TMA,F)-GeO$_2$-AST, the $c$-axis is overestimated even more markedly. However, it has to be considered that the experimental sample contained a different OSDA than the model used in the calculations (dimethylammonium instead of TMA), and that the dimensions of the OSDA will affect the equilibrium lattice parameters.

In addition to the lattice parameters, we also evaluated the difference in DFT energy per TO$_2$ unit between template-free SiO$_2$-AST/GeO$_2$-AST and $\alpha$-quartz/quartz-type GeO$_2$ ($\Delta E_{\text{DFT}}$). This quantity can be taken as a realistic approximation to the enthalpy of transition $\Delta H_{\text{trans}}$.\textsuperscript{46–48} The enthalpy of transition of SiO$_2$-AST has been determined as 10.9±1.2 kJ mol$^{-1}$ per formula unit using solution calorimetry experiments.\textsuperscript{49} The DFT-calculated energy difference is within the experimental error limits, amounting to 11.6 kJ mol$^{-1}$. Calculations for several other all-silica zeolites and $\alpha$-cristobalite, summarised in the electronic supplementary information (ESI), provided similarly good agreement, giving confidence in the predictions of the relative stability of AST systems, presented below. We may note that calculations using the plane-wave code CASTEP and employing similar dispersion-corrected DFT methods gave $\Delta E_{\text{DFT}}$ values in the same range: A (so far unpublished) energy difference of 10.9 kJ mol$^{-1}$ was obtained with the PBE-D2 functional,\textsuperscript{46} and the PBEsol-D2 functional delivered 11.4 kJ mol$^{-1}$.\textsuperscript{47} The calculated $\Delta E_{\text{DFT}}$ for GeO$_2$-AST with respect to quartz-type GeO$_2$ is approximately 1.5 times as large as for the silica systems, amounting to 17.7 kJ mol$^{-1}$. This is in line with experimental findings, as an increase in metastability (corresponding to larger values of $\Delta H_{\text{trans}}$) with increasing germanium content has been observed in calorimetric experiments on silicogermanate zeolites.\textsuperscript{50}

In the (TMA,F)-systems, the fluorine atoms occupy the centre of the $d4r$ cages, as shown in Fig. 3. Due to the longer bond length of Ge-O bonds in comparison to Si-O bonds, this cage has larger dimensions in (TMA,F)-GeO$_2$-AST, with an edge length of ~3.24 Å and a body diagonal of 5.62 Å, compared to (TMA,F)-SiO$_2$-AST with dimensions of ~3.05 Å and 5.30 Å, respectively. As noted above, a central position of fluorine has been observed in various crystallographic studies of as-synthesised zeolites containing $d4r$ units, and in molecular, anionic $d4r$-like [T$_8$O$_{12}$(OH)$_8$F]$^-$ units.\textsuperscript{30,51,52} High-level wave-function based calculations for these molecular systems pointed to a
moderately strong non-covalent interaction ("tetrel bonding"), but no off-centre displacement of fluorine.\textsuperscript{53} On the contrary, both force field and DFT-PBE calculations by Sastre and Gale for as-synthesised GeO\textsubscript{2}-AST predicted a displacement of F towards one Ge atom, with a Ge-F distance of \(~2.17\,\text{Å}\), indicating a significant covalent bonding component.\textsuperscript{34} These contrasting findings could indicate the presence of different local minima within one cage, a point to which we return in the context of the MD calculations.

**Table 1** Lattice parameters and unit cell volumes of pure end members, SiO\textsubscript{2}- and GeO\textsubscript{2}-AST, as obtained from DFT calculations, and comparison to experimental values (where available).

|                  | \(a / \text{Å}\) | \(c / \text{Å}\) | \(V / \text{Å}^3\) |
|------------------|------------------|------------------|-------------------|
| (TMA,F)-SiO\textsubscript{2}-AST | DFT | 8.970 | 13.605 | 1094.7 |
|                  | Exp\textsuperscript{31} | 9.068 | 13.438 | 1105.0 |
| SiO\textsubscript{2}-AST | DFT | 9.122 | 13.727 | 1142.2 |
|                  | Exp\textsuperscript{37} | 9.255 | 13.501 | 1156.4 |
| (TMA,F)-GeO\textsubscript{2}-AST | DFT | 9.151 | 14.635 | 1225.5 |
|                  | Exp\textsuperscript{37} | 9.271 | 14.349 | 1233.3 |
| GeO\textsubscript{2}-AST | DFT | 9.074 | 14.505 | 1194.3 |

**Fig. 3** Fluorine environment in (TMA,F)-AST systems: SiO\textsubscript{2}-AST, GeO\textsubscript{2}-AST, and AST\textsubscript{\(7\text{Si,1Ge}\)}\textsubscript{\(C_3\nu\)}. Selected interatomic distances are given in Å.
3.2 Equilibrium structures of (TMA,F)-AST across the compositional range

With regard to (TMA,F)-AST models across the range of compositions, we first take a brief look at
the evolution of the DFT-optimised lattice parameters $a$ and $c$ as a function of the Ge content, shown
in Fig. 4. As expected, both lattice parameters increase with $n$(Ge). In the composition range from
$n$(Ge) = 0.5 to 0.8, there is a marked dependence on the occupation of the T2 site, with models with T2
= Ge having a longer $c$-axis and shorter $a$-axis than models with T2 = Si. Experimental values are also
included in Fig. 4. The quantitative deviations between DFT and experiment can, at least in part,
be explained with the presence of a different OSDA in all experimental samples except SiO$_2$-AST. It
is, however, interesting to observe that the GeO$_2$-AST sample has a shorter $a$-axis than most (Si,Ge)
systems, whereas its $c$-axis is about 0.3 Å longer than that of the most Ge-rich (Si,Ge) sample (where
$n$(Ge) = 0.833). In the light of the relationships discussed above, this might indicate that the T2 site is
preferentially occupied by Si even in Ge-rich samples. As we will see below, the calculations predict
T2 = Si to be preferred up to $n$(Ge) = 0.7.

![Evolution of lattice parameters](image)

**Fig. 4** Evolution of lattice parameters $c$ (top panel) and $a$ (bottom panel) of (TMA,F)-AST as a
function of germanium content. Experimental values are included for comparison.
In the following, we concentrate on the relative stabilities of different (Si,Ge) distributions for a given Ge content, and on the environment of the fluorine atoms in the most stable structures. To analyse this in a systematic fashion, we present the most significant findings for each composition from \( n(\text{Ge}) = 0.1 \) to 0.9. The relative energies and shortest Ge-F distances for all models are compiled in Table 2, and fluorine environments of selected models are shown in Fig. 3, 5, and 6. In these figures, Ge-F distances of less than 2.4 Å are indicated using thick bicoulor lines, like covalent bonds, whereas distances between 2.4 and 2.7 Å are represented using thin grey lines (Ge-F distances above 2.7 Å are not shown). Of course, the choice of a distance of 2.4 Å as a threshold is entirely arbitrary. In reality, there will be a more or less smooth transition between short, partly covalent Ge-F bonds and long non-covalent Ge-F contacts.

\( n(\text{Ge}) = 0.1 \): In \( \text{AST}_{(7\text{Si},1\text{Ge})}C_{3v} \), fluorine is situated in a qualitatively different location than in the \( \text{SiO}_2 \) and GeO\(_2\) end members discussed above (Fig. 3). The fluorine atom is located much closer to the Ge atom than to all other vertices of the \( d4r \) cage, with a Ge-F distance of 2.20 Å. This pronounced displacement from the cage centre indicates a degree of covalent Ge-F bonding. Upon coordination of fluorine, the coordination environment of Ge distorts away from a tetrahedral environment without reaching the bond angles of 90 and 120 degrees of a perfect trigonal-bipyramidal arrangement. While the Ge-O bonds in the plane perpendicular to the Ge-F bond have essentially the same length as those in \( \text{GeO}_2\)-AST (1.77 Å), the apical Ge-O bond is elongated modestly to 1.79 Å. Qualitatively, the formation of pentacoordinated Ge agrees with the previous computational predictions by Sastre and co-workers.\(^{27}\) However, their calculations delivered a much shorter Ge-F distance of 1.89 Å.

\( n(\text{Ge}) = 0.2 \): The fluorine environment in the optimised (6Si,2Ge) models is shown in Fig. 5. Of the three distinct arrangements, the configuration in which two Ge atoms are located at adjacent vertices, forming a Ge-O-Ge link, is energetically most favourable. In this system, the fluorine atom has short contacts to both Ge atoms, with the Ge-F distances being slightly longer than that found above for \( \text{AST}_{(7\text{Si},1\text{Ge})}C_{3v} \). In the other two models, which are energetically less favourable by 10 and 13 kJ mol\(^{-1}\) (per \( d4r \) unit), respectively, fluorine is also located at a similar distance from both Ge atoms, but the Ge-F distances are significantly longer.
Fig. 5 Fluorine environment in three (TMA,F)-AST models having $n(\text{Ge}) = 0.2$. Selected interatomic distances are given in Å.

$n(\text{Ge}) = 0.3$: For this composition, the lowest-energy model is $\text{AST}_{(5\text{Si},3\text{Ge})}_C2v\text{-}2\text{GeGe}$, where one germanium atom participates in two Ge-O-Ge links. As is visible in Fig. 6, fluorine forms a rather short Ge-F bond to this Ge(Ge)$_2$ atom, whereas the distances to the other two Ge atoms are significantly longer. Unlike in the $n(\text{Ge}) = 0.2$ case, where the energetically preferred model is the only system having a short Ge-F bond, such a bond is also found in the second best system, $\text{AST}_{(5\text{Si},3\text{Ge})}_C3v\text{-}1\text{GeGe}$.

$n(\text{Ge}) = 0.4$: The complexity increases further for this composition, with a total of six distinct (Si,Ge) distributions. All in all, the tendency observed above is corroborated: The energetically most favourable model $\text{AST}_{(4\text{Si},4\text{Ge})}_C4v\text{-}3\text{GeGe}$ contains one Ge(Ge)$_3$ atom, and fluorine is bonded to this atom, with a short Ge-F distance of 2.25 Å (Fig. 6). There is, however, a second configuration with longer Ge-F distances that is almost identical in energy. In this $\text{AST}_{(4\text{Si},4\text{Ge})}_C4v\text{-}4\text{GeGe}$ model, also shown in Fig. 6, the four germanium atoms surround one face of the $d4r$ unit. The fluorine atom is displaced from the cage centre towards this face, with four rather similar Ge-F distances ranging from 2.42 to 2.54 Å.

$n(\text{Ge}) = 0.5$: This is the first composition for which models with T2 = Si and T2 = Ge were compared, in addition to considering different (Si,Ge) distributions within the $d4r$ unit. The most favourable model has T2 = Si and is 5 kJ mol$^{-1}$ lower in energy than the best T2 = Ge case. Again, it possesses the
largest possible number (five) of Ge-O-Ge linkages (Fig. 6). In this configuration, fluorine is displaced towards one of the Ge(Ge)$_3$ atoms, but the shortest Ge-F distance of 2.42 Å is notably longer than in the systems with lower Ge contents.

$n(\text{Ge}) = 0.6$: A total of nine different models were included for this composition. As above, the model with T2 = Si and with the largest number of Ge-O-Ge linkages constitutes the energetically preferred (Si,Ge) distribution (Fig. 6). However, two of the models with T2 = Ge are within ~1 kJ mol$^{-1}$ of this system, so the T2 site might be partially occupied by Ge in a real system. The (Si,Ge) distribution within the $d4r$ unit in these two systems corresponds to the two best models found above for the $n(\text{Ge}) = 0.4$ case, and the fluorine environments are similar to the corresponding ones for the (4Si,4Ge) models visualised in Fig. 6.

$n(\text{Ge}) = 0.7$: For this composition, only one model with T2 = Si remains, in which seven vertices of the $d4r$ unit are occupied by Ge. This distribution is 1.5 kJ mol$^{-1}$ higher in energy than a model with T2 = Ge and a distribution of Si and Ge on the vertices corresponding to that of AST$_{(3\text{Si,5Ge})_C_{2v}5\text{GeGe}}$. This trend continues for $n(\text{Ge}) = 0.8$, where the energy difference between the preferred model and the only model with T2 = Si is increased to 2.5 kJ mol$^{-1}$ (although still small in absolute terms). The fluorine environment in the preferred AST$_{(2\text{Si,6Ge})_C_{2v}7\text{GeGe}_{T2}\text{Ge}}$ system is largely similar to that shown in Fig. 6 for the analogous T2 = Si case.

$n(\text{Ge}) = 0.9$: As for $n(\text{Ge}) = 0.1$, only one distribution remains at this high Ge content, in which seven of the eight cage vertices are occupied by Ge. The fluorine atom is displaced from the cage centre towards the Ge atom that lies at the vertex opposite the only Si atom (Fig. 6), forming a Ge-F contact having an intermediate length of 2.38 Å.

Altogether, we can summarise the observations as follows: Progressive occupation of the available T1 positions by germanium is preferred over occupation of the T2 site up to fairly high Ge contents of ~0.6, indicating that each $d4r$ cage can accommodate up to six Ge atoms at its vertices without energetic “penalty”. With regard to fluorine, the formation of short Ge-F bonds (~2.2 to 2.3 Å) is
preferred at Ge contents up to $n$(Ge) = 0.4. Such bonds are preferentially formed with Ge atoms that are linked to other Ge atoms, leading to an energetic preference for models having the largest possible number of Ge-O-Ge linkages. At higher Ge contents, fluorine occupies a more central location in the cage, but it nevertheless tends to form one fairly short contact (~2.4 Å) with a Ge(Ge)$_3$ atom.

**Fig. 6** Fluorine environment in energetically preferred (TMA,F)-AST structures for $n$(Ge) = 0.3, 0.4 (where two structures are very close in energy), 0.5, 0.6, and 0.9. Selected interatomic distances are given in Å.
Table 2: Summary of results of DFT optimisations for models with different Ge contents and Ge arrangements. $\Delta E_{DFT}$ gives the energy difference with respect to the energetically most favourable model for a given composition (per d4r unit). $d$(Ge-F) corresponds to the shortest Ge-F distance. Ge(Ge)/Ge(Ge)$_2$/Ge(Ge)$_3$/Ge(Ge)$_4$ gives the number of Ge atoms that are surrounded by three/two/one/no Ge-O-Ge linkages within one d4r unit.

| SiO$_2$-AST                  | n(Ge) | T2  | Ge(Ge)$_3$/Ge(Ge)$_2$/Ge(Ge)$_1$/Ge(Ge)$_0$ | (TMA,F)-AST | $d$(Ge-F) / Å | $\Delta E_{DFT}$ / kJ mol$^{-1}$ | Template-free AST | $\Delta E_{DFT}$ / kJ mol$^{-1}$ |
|-------------------------------|-------|-----|-----------------------------------------------|-------------|----------------|------------------------------------|-------------------|-------------------------------------|
| SiO$_2$-AST                   |       |     |                                               |             |                |                                    |                   |                                     |
| AST$_{(7Si,1Ge)}_C_{n}$       |  0.1  | Si  | 0/0/0/1                                       |             | 2.20           |                                    |                   |                                     |
| AST$_{(6Si,2Ge)}_C_{2Ge}$     |  0.2  | Si  | 0/0/2/0                                       |             | 2.26           | 0.0                  | 6.0               |                                     |
| AST$_{(6Si,2Ge)}_C_{2Ge}$     |  0.2  | Si  | 0/0/0/2                                       |             | 2.45           | 9.8                  | 5.0               |                                     |
| AST$_{(6Si,2Ge)}_D_{0Ge}$     |  0.2  | Si  | 0/0/0/2                                       |             | 2.61           | 13.2                 | 0.0               |                                     |
| AST$_{(5Si,3Ge)}_C_{2Ge}$     |  0.3  | Si  | 0/2/1/0                                       |             | 2.27           | 0.0                  | 0.0               |                                     |
| AST$_{(5Si,3Ge)}_C_{2Ge}$     |  0.3  | Si  | 0/0/2/1                                       |             | 2.22           | 5.3                  | 2.6               |                                     |
| AST$_{(5Si,3Ge)}_C_{0Ge}$     |  0.3  | Si  | 0/0/0/3                                       |             | 2.53           | 13.0                 | 4.0               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.4  | Si  | 0/4/0/0                                       |             | 2.42           | 0.2                  | 6.3               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.4  | Si  | 1/0/3/0                                       |             | 2.17           | 0.0                  | 8.1               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.4  | Si  | 0/2/2/0                                       |             | 2.31           | 2.6                  | 0.0               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.4  | Si  | 0/0/0/4                                       |             | 2.64           | 14.0                 | 2.3               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.4  | Si  | 0/1/2/1                                       |             | 2.42           | 7.2                  | 4.1               |                                     |
| AST$_{(4Si,4Ge)}_T_{4Ge}$     |  0.4  | Si  | 0/0/0/4                                       |             | 2.58           | 16.8                 | 8.2               |                                     |
| AST$_{(3Si,5Ge)}_C_{5Ge}$     |  0.5  | Si  | 1/3/1/0                                       |             | 2.42           | 0.0                  | 5.5               |                                     |
| AST$_{(3Si,5Ge)}_C_{4Ge}$     |  0.5  | Si  | 0/3/2/0                                       |             | 2.50           | 6.4                  | 3.4               |                                     |
| AST$_{(3Si,5Ge)}_C_{3Ge}$     |  0.5  | Si  | 1/0/3/1                                       |             | 2.39           | 5.3                  | 8.0               |                                     |
| AST$_{(5Si,3Ge)}_C_{2Ge}$     |  0.5  | Ge  | 0/2/1/0                                       |             | 2.27           | 5.4                  | 1.5               |                                     |
| AST$_{(5Si,3Ge)}_C_{1Ge}$     |  0.5  | Ge  | 0/0/2/1                                       |             | 2.21           | 11.4                 | 0.0               |                                     |
| AST$_{(5Si,3Ge)}_C_{0Ge}$     |  0.5  | Ge  | 0/0/0/3                                       |             | 2.52           | 20.7                 | 2.8               |                                     |
| AST$_{(2Si,6Ge)}_C_{7Ge}$     |  0.6  | Si  | 2/4/0/0                                       |             | 2.40           | 0.0                  | 5.1               |                                     |
| AST$_{(2Si,6Ge)}_C_{6Ge}$     |  0.6  | Si  | 2/2/2/0                                       |             | 2.50           | 1.9                  | 6.9               |                                     |
| AST$_{(2Si,6Ge)}_D_{6Ge}$     |  0.6  | Si  | 0/6/0/0                                       |             | 2.70           | 6.6                  | 4.0               |                                     |
| AST$_{(4Si,4Ge)}_C_{8Ge}$     |  0.6  | Ge  | 0/4/0/0                                       |             | 2.37           | 1.0                  | 4.0               |                                     |
| AST$_{(4Si,4Ge)}_C_{8Ge}$     |  0.6  | Ge  | 1/0/3/0                                       |             | 2.18           | 1.2                  | 4.0               |                                     |
| AST$_{(4Si,4Ge)}_D_{8Ge}$     |  0.6  | Ge  | 0/2/2/0                                       |             | 2.32           | 3.3                  | 0.0               |                                     |
| AST$_{(4Si,4Ge)}_D_{8Ge}$     |  0.6  | Ge  | 0/0/4/0                                       |             | 2.66           | 17.1                 | 1.6               |                                     |
| AST$_{(4Si,4Ge)}_C_{2Ge}$     |  0.6  | Ge  | 0/1/2/1                                       |             | 2.47           | 9.3                  | 1.3               |                                     |
| AST$_{(4Si,4Ge)}_T_{0Ge}$     |  0.6  | Ge  | 0/0/0/4                                       |             | 2.67           | 21.2                 | 8.7               |                                     |
| AST$_{(1Si,7Ge)}_C_{2Ge}$     |  0.7  | Si  | 4/3/0/0                                       |             | 2.47           | 1.5                  | 6.4               |                                     |
| AST$_{(3Si,5Ge)}_C_{5Ge}$     |  0.7  | Ge  | 1/3/1/0                                       |             | 2.40           | 0.0                  | 3.4               |                                     |
| AST$_{(3Si,5Ge)}_C_{4Ge}$     |  0.7  | Ge  | 0/3/2/0                                       |             | 2.39           | 5.5                  | 0.0               |                                     |
| AST$_{(3Si,5Ge)}_C_{3Ge}$     |  0.7  | Ge  | 1/0/3/1                                       |             | 2.30           | 3.5                  | 5.6               |                                     |
| AST$_{(5Si,8Ge)}_O_{4Ge}$     |  0.8  | Si  | 8/0/0/0                                       |             | 2.77           | 2.7                  | 5.4               |                                     |
| AST$_{(2Si,6Ge)}_C_{7Ge}$     |  0.8  | Ge  | 2/4/0/0                                       |             | 2.33           | 0.0                  | 1.7               |                                     |
| AST$_{(2Si,6Ge)}_C_{6Ge}$     |  0.8  | Ge  | 2/2/2/0                                       |             | 2.44           | 3.8                  | 3.4               |                                     |
| AST$_{(2Si,6Ge)}_D_{6Ge}$     |  0.8  | Ge  | 0/6/0/0                                       |             | 2.69           | 8.2                  | 0.0               |                                     |
| AST$_{(1Si,7Ge)}_C_{4Ge}$     |  0.9  | Ge  | 4/3/0/0                                       |             | 2.38           |                      |                   |                                     |
| GeO$_2$-AST                   |  1.0  | Ge  | 8/0/0/0                                       |             | 2.81           |                      |                   |                                     |
As a final remark to this section, we compare the present results to the earlier force field based calculations by Sastre and co-workers.\textsuperscript{26} Their calculations for AST models containing 2, 3, and 4 Ge atoms in one \textit{d4r} unit delivered a completely different energetic ordering: For each case, systems having no Ge-O-Ge link at all were found to be the energetically favoured configurations (\textit{AST}_{(6Si,2Ge)}\textit{C}_{2v}\textit{GeGe}, \textit{AST}_{(5Si,3Ge)}\textit{C}_{3v}\textit{0GeGe}, and \textit{AST}_{(4Si,4Ge)}\textit{T}_{d}\textit{0GeGe} in the nomenclature of the present work). These models also exhibited the shortest Ge-F distances (with 1.9 to 2.0 \AA). On the other hand, DFT-based predictions of the $^{19}$F-NMR shifts agreed best with experimental observations for the \textit{AST}_{(6Si,2Ge)}\textit{C}_{2v}\textit{1GeGe}, \textit{AST}_{(5Si,3Ge)}\textit{C}_{2v}\textit{2GeGe}, and \textit{AST}_{(4Si,4Ge)}\textit{D}_{2h}\textit{2GeGe} models. Interestingly, the former two are the lowest-energy configurations for the respective compositions in the present study. Because these arrangements appeared thermodynamically unlikely on the basis of the force field calculations, Sastre and co-workers attributed the apparent preference to form \textit{d4r} cages with Ge-O-Ge linkages to kinetic effects. However, the present DFT results indicate that the energetic ordering obtained in the force field calculations may be unreliable.

3.3 Equilibrium structures of template-free AST across the compositional range

Having made detailed predictions of the energetically favoured (Si,Ge) arrangements for AST frameworks containing TMA molecules and fluoride anions, it is now interesting to assess whether the energetic ordering of the configurations changes when the non-framework species are removed from the structure. The energy differences $\Delta E_{DFT}$ obtained for models of the bare AST framework are included in Table 2. First of all, it is worth noting that the range of $\Delta E_{DFT}$ values for a given composition is considerably smaller for template-free framework models: The difference between the most and least favourable arrangements never exceeds 9 kJ mol$^{-1}$ (per \textit{d4r} unit), whereas it amounts to more than 20 kJ mol$^{-1}$ for some Ge contents in the case of (TMA,F)-AST. Secondly, the energetic ordering changes for all compositions except \textit{n}(Ge) = 0.3. In particular, models with $T2 = Ge$ are now favoured from \textit{n}(Ge) = 0.5 onwards. An inspection of the unit cell volumes (ESI, Fig. S1) shows that these models have systematically smaller volumes than those with $T2 = Si$. In contrast, the volume of
the (TMA,F)-AST systems increases with Ge content, but does not vary appreciably for a given composition. Unlike for the template-containing systems, where (Si,Ge) arrangements having a larger number of Ge-O-Ge linkages are preferred, there is no such clear trend for the template-free models. Taken together, it can be concluded that the presence of fluoride anions and organic templates has a significant impact on the relative stability of different (Si,Ge) arrangements. This should be kept in mind when comparing results from calculations for template-free zeolite models to experimental findings: Assuming that no rearrangement of the T atoms occurs upon template removal, the more likely configurations in calcined samples will correspond to those that are energetically favoured in the as-synthesised (template-containing) material, at least from a purely thermodynamic perspective (the potential influence of kinetic effects is much more challenging to address).

3.4 Dynamics of fluoride anions confined to $d4r$ cages

As shown in the previous parts, the presence of localised Ge-F bonds depends on the heterogeneity of the environment. One might now wonder whether there could be several coexisting local minima for fluorine inside the cage, e.g. one at the centre and another one in the proximity of a Ge atom, only one of which would be found in a static DFT optimisation. In order to sample a significant part of the potential energy surface, constrained optimisations were performed in which the position of fluorine was varied along the body diagonal of the $d4r$ cage. These optimisations were performed for SiO$_2$-AST, GeO$_2$-AST and AST$_{(7Si,1Ge)}$-$C_3v$, starting from the DFT-optimised structures. The coordinates of the atoms forming vertices and edges of the cage were optimised, whereas those of fluorine and of all other framework and non-framework atoms were held fixed. The resulting potential energy curves are shown in Fig. 7 a). For both SiO$_2$-AST and GeO$_2$-AST, the energy minimum is located at the centre of the cage, and the energy increases smoothly when moving towards a corner. There is a good correspondence between the potential energy curve obtained for SiO$_2$-AST and that calculated by Goesten et al. for fluorine at the centre of a silsesquioxane model of a $d4r$ unit.$^{54}$ The potential well is somewhat wider for GeO$_2$-AST than for SiO$_2$-AST due to the larger dimensions of the $d4r$ cage. For AST$_{(7Si,1Ge)}$-$C_3v$, an asymmetric potential energy curve is found, with an energy
minimum that is located at a distance of ~2.2 Å from the germanium atom, in accordance with the Ge-F distance obtained from the optimisation. If fluorine is placed at the centre of the cage, the energy is about 8 kJ mol\(^{-1}\) higher, and there are no indications for a secondary local minimum at the centre (or elsewhere along the body diagonal).

**Fig. 7** Top: Potential energy curve for a displacement of fluorine along the body diagonal of the \(d4r\) cage in \(\text{SiO}_2\)-AST, \(\text{GeO}_2\)-AST, and \(\text{AST}_{(7\text{Si},1\text{Ge})}\)_C\(_{3v}\). Bottom: T-F radial distribution functions for the same three systems. Vertical lines indicate T-F distances in the DFT-optimised structures.

In order to sample the potential energy surface more comprehensively, \textit{ab-initio} MD simulations were performed for the systems visualised in Fig. 3, 5, and 6, thus, at least one model was considered for each composition of the \(d4r\) cage from \((8\text{Si},0\text{Ge})\) to \((0\text{Si},8\text{Ge})\). To start with, the root mean square displacements were evaluated for all elements (note that the RMSDs were calculated using the average coordinates from the 7.5 ps trajectories as reference). The RMSDs obtained for \(\text{SiO}_2\)-AST, \(\text{GeO}_2\)-AST, and \(\text{AST}_{(7\text{Si},1\text{Ge})}\)_C\(_{3v}\), are compiled in Table 3. For the T atoms, a slightly larger RMSD is found for
Ge in GeO$_2$-AST (0.17 Å) compared to Si in SiO$_2$-AST (0.14 Å), despite the larger mass of germanium. This can be explained with the reduced rigidity of Ge-O bonds compared to Si-O bonds, leading to an increased freedom of motion of the atoms at the centre of the TO$_4$ tetrahedra. For oxygen, the RMSDs are essentially identical for all three models (0.22 Å), as one would expect for isostructural systems. Very pronounced differences among the three systems are found for fluorine: For SiO$_2$-AST, the RMSD of 0.28 Å reflects the larger freedom of motion of the tetrel-bonded fluorine atoms as compared to the (slightly lighter) oxygen atoms, which are held in place through directional Si-O bonds. The increased RMSD of fluorine in GeO$_2$-AST of 0.36 Å can be attributed to the larger dimensions of the d$_{4r}$ cage, permitting larger displacements from the cage centre, in line with the wider potential well found above. For AST$_{(7Si,1Ge)}_C$$_{3v}$, where fluorine participates in a Ge-F bond, the RMSD is decreased to 0.22 Å, thus being virtually the same as for the oxygen atoms. This clearly shows that the fluoride anions lose a significant portion of their freedom of motion upon formation of Ge-F bonds, corroborating the localised (partly covalent) nature of these bonds. With regard to the TMA molecules, the RMSD of the nitrogen atoms is only moderately larger than that of fluorine confined to d$_{4r}$ cages, whereas the RMSDs of C and H atoms are much larger. As the nitrogen atom constitutes the centre of mass of the TMA molecule, its small RMSD indicates that the overall displacement of the TMA molecules within the ast cages is only modest. The increased RMSDs of the atoms belonging to the methyl “arms” can be attributed to rotations of the TMA molecule about its centre of mass. The larger dimensions of the ast cage in GeO$_2$-AST as compared to SiO$_2$-AST lead to an increased motion of the TMA molecules, reflected by systematically larger RMSDs.

**Table 3** Root mean square displacements of all elements present in (TMA,F)-AST as obtained from MD calculations.

|          | SiO$_2$-AST  | GeO$_2$-AST | AST$_{(7Si,1Ge)}_C$$_{3v}$ |
|----------|--------------|--------------|-----------------------------|
| RMSD / Å | 0.14 +/- 0.02 | 0.17 +/- 0.02 | 0.14 +/- 0.02               |
| Si       | 0.22 +/- 0.02 | 0.22 +/- 0.02 | 0.23 +/- 0.02               |
| Ge       | 0.28 +/- 0.04 | 0.36 +/- 0.05 | 0.22 +/- 0.04               |
| O        | 0.96 +/- 0.12 | 1.07 +/- 0.12 | 0.91 +/- 0.15               |
| F        | 0.33 +/- 0.05 | 0.40 +/- 0.06 | 0.31 +/- 0.05               |
| C        | 1.32 +/- 0.17 | 1.46 +/- 0.17 | 1.25 +/- 0.21               |
| N        | 1.15 +/- 0.17 | 1.20 +/- 0.17 | 1.10 +/- 0.20               |
| H        | 1.05 +/- 0.17 | 1.19 +/- 0.17 | 1.04 +/- 0.20               |
The RMSDs for other mixed (Si,Ge) systems are compiled in the ESI. As the analysis of the RMSDs of the other elements reveals no trends apart from those already mentioned, the following discussion will focus on the RMSD of fluorine atoms, shown in Table 4. For the three systems with $n$(Ge) = 0.2, the RMSD varies from 0.23 Å for AST\textsubscript{6Si,2Ge}\textsubscript{C\textsubscript{2v}}GeGe, the system having a localised Ge-F bond with $d$(Ge-F) = 2.26 Å, to 0.32 Å for AST\textsubscript{6Si,2Ge}\textsubscript{D\textsubscript{3d}}GeGe, where fluorine resides almost at the cage centre (Fig. 5). This evolution agrees with the trend identified in the previous paragraph, and one might now expect that the reduction of the freedom of motion of fluorine is an entirely “local” phenomenon that depends solely on the interaction with the closest germanium atom. However, when plotting the values for all systems compiled in Table 4 against the shortest Ge-F distance (ESI – Fig. S2), it is apparent that there is no perfect correlation, as there are some systems where the RMSDs are much larger than what would be expected from the shortest Ge-F distance. In contrast, an alternative plot that uses the average Ge-F distance, calculated over all $x$ Ge-F contacts within the ((8-$x$Si,$x$Ge)$d_{4r}$ unit, shows a near-perfect correlation for all systems (Fig. S2). Thus, the freedom of motion of fluorine depends not only on the nearest neighbouring Ge atom in the equilibrium structure, but also on the presence of, and distance to, other Ge atoms in the $d_{4r}$ cage: When there is only one short Ge-F contact, or two Ge-F contacts that are similarly short, as in AST\textsubscript{6Si,2Ge}\textsubscript{C\textsubscript{2v}}GeGe, fluorine remains rather confined to its equilibrium position at the temperature considered, with an RMSD that hardly exceeds that of strongly bonded framework oxygen atoms. However, when there are additional germanium atoms that are further away, attractive secondary interactions with these atoms cause a more dynamic behaviour.
Table 4: Shortest and average Ge-F distances (obtained from static DFT optimisations), median Ge-F distances, RMSDs of fluorine atoms. The error in the MD median Ge-F distances is estimated to be +/-0.02 Å.

| n(Ge) | SiO$_2$-AST | AST$_{7Si,1Ge}$-C$_{3v}$ | AST$_{6Si,2Ge}$-C$_{2v}$ | AST$_{6Si,2Ge}$-D$_{3d}$ | AST$_{5Si,3Ge}$-C$_{s}$ | AST$_{4Si,4Ge}$-C$_{4v}$ | AST$_{4Si,4Ge}$-C$_{3v}$ | AST$_{3Si,5Ge}$-C$_{5}$ | AST$_{2Si,6Ge}$-C$_{2d}$ | AST$_{1Si,7Ge}$-C$_{3v}$-T$_2$Ge | GeO$_2$-AST |
|-------|-------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|       | n(Ge) | Shortest $d$(Ge-F) / Å | Average $d$(Ge-F) / Å | Median $d$(Ge-F) / Å | RMSD(F) / Å |
| 0.0   |       | -                | -                | -                | 0.28 +/- 0.04  |
| 0.1   |       | 2.20             | 2.20             | 2.20             | 0.22 +/- 0.04  |
| 0.2   |       | 2.26             | 2.28             | 2.30             | 0.23 +/- 0.04  |
| 0.2   |       | 2.45             | 2.50             | 2.46             | 0.27 +/- 0.04  |
| 0.2   |       | 2.61             | 2.66             | 2.64             | 0.32 +/- 0.05  |
| 0.3   |       | 2.27             | 2.40             | 2.42             | 0.25 +/- 0.04  |
| 0.4   |       | 2.42             | 2.48             | 2.50             | 0.26 +/- 0.04  |
| 0.4   |       | 2.17             | 2.50             | 2.53             | 0.26 +/- 0.04  |
| 0.5   |       | 2.42             | 2.62             | 2.59             | 0.28 +/- 0.04  |
| 0.6   |       | 2.40             | 2.69             | 2.67             | 0.29 +/- 0.04  |
| 0.9   |       | 2.38             | 2.76             | 2.74             | 0.32 +/- 0.05  |
| 1.0   |       | 2.81             | 2.81             | 2.78             | 0.36 +/- 0.05  |

The first peaks in the T-F radial distribution functions $g(r)$, which correspond to the distances between the fluorine atom in a $d4r$ cage and the T atoms at the cage vertices, are shown in Fig.s 7 b), 8, and 9 (the RDFs were always normalised in a way that the cumulative $g(r)$ for the first maximum corresponds to the number of Si or Ge atoms at the vertices of the cage). Furthermore, the median Ge-F distances, which mark the separation between lower and upper 50% of the Ge-F distances within the first peak, are included in Table 4. First of all, it is worth pointing out that the median Ge-F distances obtained from the MD calculations are always within 0.04 Å of the average $d$(Ge-F) value measured in the DFT-optimised structures. If there were some cases in which fluorine atoms moved from one local minimum to another one during the MD run, and remained confined to that minimum for a longer period of time, it could be expected that there were more pronounced deviations between the two values.

The RDFs of SiO$_2$-AST and GeO$_2$-AST, shown in Fig. 7 b), reveal an essentially symmetric distribution of the T-F distances around a maximum value that coincides with the equilibrium distance in the DFT-optimised structures. As expected from the larger cage dimensions and the wider potential well, the RDF peak for GeO$_2$-AST is broader than for SiO$_2$-AST. On the side of short T-F distances, however, both curves resemble each other, and T-F distances below 2.3 Å are essentially absent in
both of them. In agreement with the findings from the static calculations, there are no indications for short Ge-F bonds in the pure-GeO\(_2\) system. For the case of AST\(_{(7Si,1Ge)}\)_C\(_{3v}\), also shown in Fig. 7b), there are two well-separated peaks for the Ge-F and Si-F distances in the RDF, with the position of the maxima corresponding to the (average) distances in the DFT-optimised structure. The Ge-F RDF has a rather sharp maximum, as one can expect from the presence of a localised bond that limits the freedom of motion. If there was a possibility for fluorine to relocate to a secondary local minimum at or near the cage centre, one would expect a significant amount of Ge-F distances between of 2.6 to 2.7 Å, however, the value of \(g(r)\) in this distance range is close to zero. Moreover, the curve falls to zero for Ge-F distances below 2.0 Å. Thus, the MD calculations provide no evidence for the existence of very short Ge-F bonds with a length of ~1.9 Å, which have been proposed in previous computational studies.\(^{26,27}\)

Altogether, the findings for the simplest systems corroborate that there is only one local minimum for fluorine in each case, located at the cage centre for the pure end members, and at a distance of about 2.2 Å from the Ge atom for AST\(_{(7Si,1Ge)}\)_C\(_{3v}\). The situation becomes inevitably more complex – and less straightforward to analyse – when several corners of the d4r cage are occupied by germanium, where a broadening of the RDF peaks will be caused by a combination of dynamic effects and the presence of different Ge-F distances. Nevertheless, the inspection of the RDFs can deliver useful insights. Fig. 8 visualises the RDFs for all three systems having 6 Si and 2 Ge atoms at the cage vertices. For the energetically preferred AST\(_{(6Si,2Ge)}\)_C\(_{2v}\)\(_{0GeGe}\) model, the T-F RDFs show no unusual features, with smooth distributions around the equilibrium T-F distances. As there are two similarly short Ge-F bonds in this system, a motion of fluorine towards either of the two Ge atoms will cause only a minor broadening of the \(g(r)\) curve. In AST\(_{(6Si,2Ge)}\)_C\(_{2v}\)\(_{0GeGe}\), the maximum is shifted towards shorter distances when compared to the equilibrium distances in the DFT-optimised structure, both of which are close to 2.5 Å. The rather large values of \(g(r)\) between 2.1 and 2.3 Å indicate that there is a significant probability for fluorine to be displaced from its equilibrium position towards either of the two Ge atoms. The most interesting observations can be made for AST\(_{(6Si,2Ge)}\)_D\(_{3h}\)\(_{0GeGe}\), where the Ge-F RDF exhibits one very broad maximum with similar \(g(r)\) values from 2.2 to 2.9 Å. In contrast, the Si-F RDF has a narrower distribution that resembles that
of SiO$_2$-AST. Apparently, the fluorine atoms move primarily along the body diagonal connecting the two Ge atoms, while maintaining rather similar distances to the surrounding Si atoms. For this particular case, additional calculations of potential energy curves analogous to those presented in Fig. 7 were performed, considering displacements of the fluorine atom along the Ge-Ge body diagonal and along one of the Si-Si body diagonals. The resulting curves, shown in Fig. S3, show a very shallow potential well along the Ge-Ge diagonal: A displacement from the centre towards either of the Ge atoms by 0.3 Å incurs an energy increase of only ~2 kJ mol$^{-1}$, whereas a displacement of the same magnitude towards an Si atom leads to an increase of about 6 kJ mol$^{-1}$. This anisotropy of the potential energy surface explains the rather peculiar shape of the Ge-F RDF observed above. While the environment of the Ge atoms is identical to that in the system with only one Ge atom, AST$_{(7Si,1Ge)}$ $C_{3v}$, there are no local minima at Ge-F distances of ~2.2 Å. This indicates that the overall (Si,Ge) arrangement at the vertices of the $d4r$ cage, rather than the local environment of the Ge atoms, governs the relative stability of short Ge-F bonds compared to the centre-of-cage position of fluorine.

**Fig. 8** T-F RDFs for three (TMA,F)-AST models having $n$(Ge) = 0.2. Vertical lines indicate T-F distances in the DFT-optimised structures.

The radial distribution functions for systems with higher Ge contents are shown in Fig. 9. Here, symmetric maxima in the Ge-F RDF appear for those systems where the distances between fluorine and germanium in the equilibrium structure are relatively similar, whereas the maxima for models
having one or two short Ge-F contacts are asymmetric. Altogether, the radial distribution functions can be well described by assuming a statistic displacement of fluorine around its equilibrium position. Interestingly, even in the Ge-rich $d_4r$ cages, the average location of fluorine lies much closer to the Ge atoms than to the Si atoms: For example, the median Si-F distance in AST$_{(1Si,7Ge)}$C$_{3v}$T$_2$Ge amounts to 2.98 Å, and is thus almost 0.25 Å longer than the median Ge-F distance. In other words, the presence of a single Si atom at one of the vertices produces a significant anisotropy in the potential energy surface, which is pronounced enough to be clearly detectable even when the thermal motion of fluorine at 298 K is accounted for.

![Fig. 9 T-F RDFs for energetically preferred (TMA,F)-AST models having $n(\text{Ge}) = 0.3, 0.4$ (two models), 0.5, 0.6, and 0.9 (see Fig. 6). Vertical lines indicate T-F distances in the DFT-optimised structures.](image-url)
4. Concluding remarks

On the basis of the calculations presented above, the following conclusions can be drawn with regard to the preferred arrangements of Si and Ge at the \(d4r\) cages of AST frameworks, the equilibrium locations of fluorine, and its dynamic behaviour: In fluoride-containing mixed (Si,Ge) systems, arrangements that maximise the number of Ge-O-Ge linkages are energetically favoured. In the absence of fluorine, the computations predict a different energetic ordering without a clear trend. These findings strongly indicate that the presence of fluoride has a significant impact on the thermodynamically most stable (Si,Ge) arrangement, i.e. that there is a “templating effect”. This may be particularly relevant for frameworks that can be synthesised both in the presence and in the absence of fluoride anions, where the most probable local structure may differ depending on the synthesis route. As a caveat in the interpretation of the DFT results, it has to be mentioned that the energetic ordering of different distributions depends on the “deformability” of the T-O-T linkages in the structure, thus, on the framework type.\(^{18,55}\) Therefore, the trends developed above for AST are not necessarily valid for other frameworks with \(d4r\) building units. In this context, it is worth noting that EXAFS results indicated that Ge atoms preferentially locate at a single face of a (4Si,4Ge) \(d4r\) cage in IM-12 (UTL),\(^5\) whereas a detailed NMR study showed that other arrangements are predominant in ITQ-13 and ITQ-22.\(^5^5\)

With regard to the equilibrium position of fluorine, the calculations provide no evidence for the formation of pentacoordinated Ge atoms in GeO\(_2\)-AST, where fluorine resides at the centre of the cage, as in SiO\(_2\)-AST. Formation of a relatively short Ge-F bond of \(~2.2\) Å occurs in (7Si,1Ge) \(d4r\) cages. Such short bonds are also prominent in \(d4r\) cages containing 2, 3, or 4 Ge atoms if the Ge atoms are located at neighbouring vertices (many Ge-O-Ge linkages). At higher Ge contents, fluorine still tends to maintain shorter Ge-F than Si-F contacts, but there is no longer a formation of pentacoordinated germanium atoms. Neither DFT-based MD simulations nor calculations of the potential energy curve along the body diagonal of the \(d4r\) cage provide any indications for a coexistence of distinct local minima at the cage centre and in the proximity of a Ge atom. By and large, the fluorine atoms oscillate about the equilibrium positions obtained from the DFT optimisations.
at 298 K. Their freedom of motion, as measured through the RMSD, is correlated with the average Ge-F distance: If there is only a single Ge-F bond, the motion of fluorine is quite restricted, with an RMSD similar to that of the framework oxygen atoms, but if there are several Ge atoms in the vicinity, pairwise interactions with all these atoms lead to increased oscillations.

Altogether, the present study provides significant new insights into the local structure of fluoride-containing (and fluoride-free) silicogermanate $d4r$ units, insights that are not accessible through crystallographic methods, and may only be obtained indirectly via NMR spectroscopy or other spectroscopic methods. To this end, the results presented here should be of considerable value for future experimental studies of $d4r$-containing silicogermanate zeolites, e.g. in the context of an in-depth characterisation of new materials obtained via hydrothermal or ADOR-based synthesis routes.

In order to predict quantities that are directly measurable experimentally, we are currently working on a DFT-based prediction of the $^{19}$F-NMR shifts of different models (Si,Ge)-AST. Going beyond the AST framework, future computational work should consider a range of framework types in order to assess the differences and common features of various silicogermanate zeolites.

Conflicts of interest

There are no conflicts to declare.

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Local environment and dynamic behaviour of fluoride anions in silicogermanate zeolites: A computational study of the AST framework

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\textbf{SUPPORTING INFORMATION}

(1) \textbf{CP2K input files}

The ZIP archive contains two CP2K input files for a geometry optimisation (CP2K\_optimisation.inp) and for an MD calculation (CP2K\_MD.inp). Both input files read the starting structure from an example CIF file, which is also supplied (AST\_SiO2\_TMA\_I-4.cif).

The additional input files that are needed to run the calculations can be obtained from the CP2K repository at https://github.com/cp2k/cp2k/tree/master/cp2k/data:

- **BASIS\_MOLOPT**: MOLOPT basis sets, incorporating TZVP basis sets from BASIS\_MOLOPT\_UCL
- **POTENTIALS**: GTH pseudopotentials
- **dftd3.dat**: Coefficients for D3 dispersion correction
Comparison of DFT energy differences to experimental enthalpies of transition

DFT structure optimisations were performed for 16 all-silica zeolites, $\alpha$-cristobalite as well as $\alpha$-quartz (as reference). The difference in the total energy per SiO$_2$ formula unit was calculated as:

$$\Delta E_{\text{DFT}} = E_{\text{DFT}}(\text{zeolite})/N - E_{\text{DFT}}(\text{quartz})/3$$

Here, $E_{\text{DFT}}$ is the DFT total energy obtained from the CP2K calculations (PBE-D3 functional, TZVP basis set), and $N$ is the number of formula units in the zeolite unit cell.

Table S1: DFT energy differences $\Delta E_{\text{DFT}}$ and experimental enthalpies of transition $\Delta H_{\text{trans}}$. The absolute deviation between the two values is given as $\text{dev}_{\text{abs}}$. Systems for which $\text{dev}_{\text{abs}} \leq 1$ kJ mol$^{-1}$ are highlighted in green, those where $\text{dev}_{\text{abs}} \geq 2$ kJ mol$^{-1}$ are highlighted in red.

|          | $\Delta E_{\text{DFT}}$ / kJ mol$^{-1}$ | $\Delta H_{\text{trans}}$ / kJ mol$^{-1}$ | $\text{dev}_{\text{abs}}$ / kJ mol$^{-1}$ |
|----------|----------------------------------------|------------------------------------------|------------------------------------------|
| $\alpha$-cristobalite | 2.3 | 2.8 | -0.5 |
| AFI      | 8.9 | 7.2 | 1.7 |
| AST      | 11.6 | 10.9 ± 1.2 | 0.7 |
| BEA      | 12.1 | 9.3 ± 0.8 | 2.8 |
| CFI      | 8.8 | 8.8 ± 0.8 | 0.0 |
| CHA      | 13.4 | 11.4 ± 1.5 | 2.0 |
| FAU      | 13.6 | 13.6 | 0.0 |
| FER      | 9.8 | 6.6 | 3.2 |
| IFR      | 10.9 | 10 ± 1.2 | 0.9 |
| ISV      | 14.1 | 14.4 ± 1.1 | 0.3 |
| ITE      | 11.7 | 10.1 ± 1.2 | 1.6 |
| MEI      | 14.0 | 13.9 ± 0.4 | 0.1 |
| MEL      | 9.7 | 8.2 ± 1.3 | 1.5 |
| MFI      | 8.8 | 6.8 ± 0.8 | 2.0 |
| MTW      | 6.8 | 8.7 | -1.9 |
| MWW      | 12.3 | 10.4 ± 1.5 | 1.9 |
| SIT      | 12.1 | 9.2 ± 1.2 | 2.9 |

The mean of absolute errors of 1.4 kJ mol$^{-1}$ is only moderately larger than that obtained in CASTEP calculations using the PBEsol-D2 functional in previous work (1.1 kJ mol$^{-1}$) and smaller than the MAEs of the PBEsol-TS and PBE0-D2 functionals reported in the same study.$^2$
(3) Lattice parameters and unit cell volumes of template-free AST

Table S2: Lattice parameters and unit cell volumes of (TMA,F)-AST and template-free AST as obtained from DFT optimisations.

| n(Ge) | AST_(7Si,1Ge)_C_n | SiO_2-AST | (TMA,F)-AST | Template-free AST |
|-------|-------------------|-----------|-------------|-------------------|
|       |                   |           | m | a / Å | c / Å | V / Å³ | m | a / Å | c / Å | V / Å³ |
| 0     | SiO_2-AST         |           | 0 | 8.970 | 13.605 | 1094.7 | 9.122 | 13.727 | 1142.2 |
| 0.1   | AST_(7Si,1Ge)_C_n | 1        | 9.007 | 13.676 | 1109.5 | 9.160 | 13.778 | 1156.1 |
| 0.2   | AST_(6Si,2Ge)_C_n | 0.1    | 9.028 | 13.754 | 1121.0 | 9.151 | 13.855 | 1160.2 |
| 0.2   | AST_(6Si,2Ge)_C_n | 0.0   | 9.050 | 13.731 | 1124.6 | 9.16  | 13.839 | 1161.2 |
| 0.2   | AST_(6Si,2Ge)_C_n | 0.0   | 9.065 | 13.696 | 1125.5 | 9.168 | 13.854 | 1164.5 |
| 0.3   | AST_(5Si,3Ge)_C_n | 0.1    | 9.069 | 13.817 | 1136.4 | 9.152 | 13.849 | 1169.1 |
| 0.3   | AST_(5Si,3Ge)_C_n | 0.2   | 9.065 | 13.846 | 1137.8 | 9.155 | 13.949 | 1169.1 |
| 0.3   | AST_(5Si,3Ge)_C_n | 0.2   | 9.088 | 13.819 | 1141.3 | 9.168 | 13.93  | 1170.9 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.1    | 9.105 | 13.895 | 1151.9 | 9.185 | 13.897 | 1172.4 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.2   | 9.108 | 13.890 | 1152.3 | 9.173 | 13.909 | 1170.4 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.2   | 9.124 | 13.868 | 1154.5 | 9.198 | 13.876 | 1174.0 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.2    | 9.123 | 13.877 | 1155.0 | 9.145 | 13.966 | 1168.0 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.2  | 9.115 | 13.882 | 1153.4 | 9.181 | 13.988 | 1172.5 |
| 0.4   | AST_(4Si,4Ge)_C_n | 0.2  | 9.146 | 13.871 | 1155.0 | 9.175 | 13.885 | 1168.9 |
| 0.5   | AST_(3Si,5Ge)_C_n | 0.1    | 9.152 | 13.950 | 1168.4 | 9.234 | 13.948 | 1189.3 |
| 0.5   | AST_(3Si,5Ge)_C_n | 0.2   | 9.156 | 13.957 | 1170.0 | 9.191 | 13.988 | 1181.6 |
| 0.5   | AST_(3Si,5Ge)_C_n | 0.2   | 9.168 | 13.956 | 1173.0 | 9.178 | 13.988 | 1178.3 |
| 0.5   | AST_(5Si,3Ge)_C_n | 0.5    | 9.059 | 14.112 | 1158.1 | 8.985 | 14.214 | 1147.5 |
| 0.5   | AST_(5Si,3Ge)_C_n | 0.5   | 9.061 | 14.103 | 1157.9 | 9.032 | 14.211 | 1159.3 |
| 0.5   | AST_(5Si,3Ge)_C_n | 0.5   | 9.059 | 14.133 | 1159.8 | 8.933 | 14.278 | 1139.4 |
| 0.6   | AST_(2Si,6Ge)_C_n | 0.6    | 9.208 | 14.014 | 1188.2 | 9.204 | 13.997 | 1186.0 |
| 0.6   | AST_(2Si,6Ge)_C_n | 0.6    | 9.192 | 14.041 | 1186.4 | 9.179 | 14.057 | 1184.4 |
| 0.6   | AST_(2Si,6Ge)_C_n | 0.6   | 9.187 | 14.043 | 1185.2 | 9.222 | 14.033 | 1193.4 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6    | 9.107 | 14.162 | 1174.6 | 9.043 | 14.234 | 1164.0 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6   | 9.123 | 14.177 | 1179.9 | 8.99 | 14.267 | 1153.1 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6   | 9.098 | 14.200 | 1175.4 | 8.983 | 14.280 | 1152.3 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6   | 9.114 | 14.167 | 1176.8 | 9.072 | 14.198 | 1168.5 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6  | 9.101 | 14.171 | 1173.8 | 9.062 | 14.175 | 1164.1 |
| 0.6   | AST_(4Si,4Ge)_C_n | 0.6  | 9.147 | 14.165 | 1185.2 | 9.055 | 14.249 | 1168.3 |
| 0.7   | AST_(1Si,7Ge)_C_n | 0.7    | 9.214 | 14.123 | 1199.0 | 9.200 | 14.06  | 1190.0 |
| 0.7   | AST_(3Si,5Ge)_C_n | 0.7   | 9.151 | 14.255 | 1193.7 | 9.064 | 14.281 | 1173.3 |
| 0.7   | AST_(3Si,5Ge)_C_n | 0.7   | 9.124 | 14.289 | 1189.5 | 8.982 | 14.336 | 1156.6 |
| 0.7   | AST_(3Si,5Ge)_C_n | 0.7   | 9.123 | 14.305 | 1190.6 | 9.041 | 14.324 | 1170.8 |
| 0.8   | AST_(0Si,8Ge)_O_n | 0.8    | 9.218 | 14.232 | 1209.3 | 9.262 | 14.150 | 1213.9 |
| 0.8   | AST_(2Si,6Ge)_C_n | 0.8    | 9.150 | 14.360 | 1202.3 | 9.128 | 14.287 | 1190.4 |
| 0.8   | AST_(2Si,6Ge)_C_n | 0.8    | 9.159 | 14.341 | 1203.0 | 9.079 | 14.372 | 1184.7 |
| 0.9   | AST_(1Si,7Ge)_C_n | 0.9    | 9.186 | 14.451 | 1219.4 | 9.060 | 14.426 | 1184.1 |
| 1.0   | GeO_2-AST         | 1.0 | 9.151 | 14.635 | 1225.5 | 9.074 | 14.505 | 1194.3 |
Figure S1: Evolution of unit cell volumes of (TMA,F)-AST and template-free AST as a function of germanium content. For (TMA,F)-AST, experimental values are included for comparison.³⁻⁶

(4) Root mean square displacements

Table S3: Root mean square displacements (in Å) of all elements in all models of (TMA,F)-AST for which MD simulations were performed.

|                | Si  | Ge  | O   | F   | C   | N   | H   |
|----------------|-----|-----|-----|-----|-----|-----|-----|
| SiO₂-AST       | 0.14| -   | 0.22| 0.28| 0.96| 0.33| 1.32|
|                | +/- 0.02 | +/- 0.02 | +/- 0.04 | +/- 0.12 | +/- 0.05 | +/- 0.17 |
| AST_7Si_1Ge_C3v| 0.14| 0.14| 0.23| 0.22| 0.91| 0.31| 1.25|
|                | +/- 0.02 | +/- 0.02 | +/- 0.02 | +/- 0.04 | +/- 0.15 | +/- 0.05 | +/- 0.21 |
| AST_6Si_2Ge_C2v1GeGe | 0.15| 0.16| 0.24| 0.23| 0.87| 0.28| 1.20|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.16 | +/- 0.05 | +/- 0.22 |
| AST_6Si_2Ge_C2v0GeGe | 0.15| 0.16| 0.24| 0.27| 0.95| 0.33| 1.31|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.15 | +/- 0.05 | +/- 0.21 |
| AST_6Si_2Ge_D3d0GeGe | 0.15| 0.16| 0.25| 0.32| 0.92| 0.33| 1.27|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.05 | +/- 0.13 | +/- 0.05 | +/- 0.18 |
| AST_5Si_3Ge_C2v2GeGe | 0.15| 0.17| 0.25| 0.25| 1.04| 0.34| 1.44|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.18 | +/- 0.05 | +/- 0.26 |
| AST_4Si_4Ge_C4v4GeGe | 0.15| 0.18| 0.25| 0.26| 1.13| 0.35| 1.56|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.13 | +/- 0.05 | +/- 0.18 |
| AST_4Si_4Ge_C3v3GeGe | 0.16| 0.18| 0.25| 0.26| 1.00| 0.36| 1.33|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.10 | +/- 0.06 | +/- 0.15 |
| AST_3Si_5Ge_C5v5GeGe | 0.15| 0.17| 0.23| 0.28| 1.04| 0.36| 1.43|
|                | +/- 0.02 | +/- 0.02 | +/- 0.03 | +/- 0.04 | +/- 0.16 | +/- 0.05 | +/- 0.23 |
| AST_2Si_6Ge_C2v7GeGe | 0.14| 0.16| 0.20| 0.29| 1.14| 0.35| 1.56|
|                | +/- 0.02 | +/- 0.01 | +/- 0.02 | +/- 0.04 | +/- 0.12 | +/- 0.05 | +/- 0.16 |
| AST_1Si_7Ge_C7vT2Ge | 0.15| 0.16| 0.22| 0.32| 0.97| 0.36| 1.33|
|                | +/- 0.02 | +/- 0.01 | +/- 0.01 | +/- 0.05 | +/- 0.14 | +/- 0.06 | +/- 0.20 |
| GeO₂-AST       | -   | +/-.02 | +/- 0.02 | +/- 0.05 | +/- 0.12 | +/- 0.06 | +/- 0.17 |
Figure S2: Plot of the RMSD of fluorine against the shortest Ge-F distance (left) and the average Ge-F distance (right). Linear regressions delivered correlation coefficients $R^2 = 0.74$ when using the shortest Ge-F distances, and $R^2 = 0.90$ when using the average Ge-F distances.

(4) Potential energy curve for AST$_{6}$Si$_{2}$Ge$_{D_{3d}}$0GeGe

Figure S3: Left: Visualisation of fluorine displacement along the Ge-Ge and Si-Si body diagonals in the $d_{4r}$ cage of AST$_{6}$Si$_{2}$Ge$_{D_{3d}}$0GeGe. Right: Potential energy curves calculated for fluorine displacements along these diagonals (Ge-Ge = green, Si-Si = yellow).

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