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Slicing of diamond – A guide to deriving sp$^3$-Si allotropes

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Abstract

Silicon is the most important material for solar cells. However, its low conversion rate/quantum efficiency require a rather high material consumption. Thus, researchers undertake enormous experimental and theoretical efforts to find alternative Si allotropes with a better efficiency and in the ideal case a direct electronic band gap. In recent years and months many new allotropic Si structures have been reported, however often described incoherently and without context to existing structures. Our approach allows a classification of many of these allotropes and a relation of their structures to substructures of e.g. known Zintl phases. For this so-called “chemi-inspired” search for promising Si structures we present a “construction kit” as a guide to introducing a large number of tetrahedral Si allotropes, all derived by a modification of the pristine cubic diamond structure. In addition, this approach allows to realize structural (topological) relationships between experimentally accessible Zintl phases of different composition such as open tetrahedral frameworks to a yet unknown extent, including even known phase transitions of specific Zintl phases. In topological, structural and computational analyses (on a DFT-PBE0/SVP level of theory) we show the close relationship of ten low-energy Si structures derived from the cubic diamond modification; five of them are new, and some show quasi-direct band gaps. A simple deviation of this approach enables the construction of many more tetrahedral structures.

1. Silicon is seeking for another crystal structure

Silicon, the higher homologue of carbon, is one of the most consistently studied elements. It adopts the cubic diamond modification as its ground-state phase α-Si. This material is a semiconductor with a fairly small indirect band gap, but a large direct band gap that only photons in the ultraviolet light region can overcome. Due to the poor energy conversion in solar cells and the high material consumption, researchers are pushed to find other modifications –
at the best thin film devices with direct band gaps—of this environmentally and toxicologically harmless and easily accessible element just to be able to face the demand of replacing fossil fuels.\cite{1}

As the properties of a material are strongly linked to its structure, the discovery of novel Si modifications is seen as a highly important goal.\cite{2} There is a vast variety of systematic investigations towards Si allotropes, which can be classified by means of the network formation or its function. Most interesting are tetrahedral Si networks, which have been suggested (predominantly on the basis of computational results) for covalent Si allotropes, and which allow to keep the sp$^3$ hybridization of the Si atom in its ground state modification; some with promising physical properties.\cite{3} Most of them have a lower density than $\alpha$-Si and therefore can also function as possible hosts for host-guest frameworks, e.g. for the use in lithium ion batteries\cite{4} or thermoelectric applications.\cite{5}

Lately, several new Si allotropes have been reported, and the efficiency of various computational structure search methods for the discovery of structures with comparably small unit cells has been demonstrated in a series of publications.\cite{3c,6} The approaches range from random search\cite{6h} or swarm methods\cite{6b,6c}, over the use of a genetic algorithm\cite{6a}, or the intuitive modulation of known substructures\cite{7} or geometric forms\cite{6g} and the modulation of Kelvin structures\cite{6j} to the derivation of new structures from analogous carbon\cite{3b,8} or silica structures\cite{6h}, well-known framework structures as clathrates\cite{9}, or the variation of the cubic diamond structure\cite{6d,6k}.

2. **Intermetallic compounds as a source for chemi-inspired silicon allotropes**

Several of the newly discovered tetrahedral Si networks topologically correspond to known and experimentally accessible structures. The recently reported T12 structure\cite{6b} (Figure 1c) discovered by the “swarm method” adopts the topology of the known structure of CdP$_2$.\cite{10}

A topological space consisting of tetrahedrally connected nodes is quite common in multinary intermetallic compounds. For example, the recently discovered Li$_2$BSi$_2$ represents an open tetrahedral framework structure in which all B and Si atoms are four-fold covalently connected, and the Li atoms are located in channels.\cite{11} The resulting tetrahedral framework of Si and B atoms named **tum** is an interesting starting model for the computational modelling of a Si allotrope, when the positions of the B atoms are also occupied by Si atoms. Relaxation of the Si framework results in a novel Si structure (Figure 1d). We call this approach of searching for analogies to existing structures with rather different compositions a “**chemi-inspired search**”.
A similar procedure has also been applied for example for theoretical investigations on sp$^3$-carbon modifications by using zeolite-type compounds and replacing the tetrahedral SiO$_4$ building units by single C atoms.$^{[12]}$ Vice versa, predictions show that Li insertion can be achieved with appropriate B substitution within the framework in carbon clathrates.$^{[13]}$

Figure 1. “Chemi-inspired” frameworks as proposed for Si allotropes. a) and b) The networks mep and mtn correspond to the well-known clathrate I and II structures, respectively.$^{[14]}$ c) The theoretically proposed Si-network T12 with the topology of the intermetallic compounds α-CdP$_2$ and β-CdP$_2$.$^{[8b, 10, 15]}$ d) The network tum1 based on the B-Si net in LiBSi$_2$.$^{[11]}$ e) The network unj (also called ngs$^{[7a]}$) first
identified by Blasé et al. for Ga/Sn frameworks\cite{16} as a Si-structure with a reasonably small energy difference compared to \(\alpha\)-Si. f) The network unj2 has been observed for an Na-Zn-Sn phase being structurally related to unj.\cite{17}

Examples of “chemi-inspired” frameworks are shown in Figure 1. Among them there are the well-known clathrate compounds composed of polyhedral Si atom cages as building blocks. They have been described in analogy to space-filling arrangements of polyhedral cages, and many structures have a dual relationship to intermetallic Frank-Kasper phases. Clathrate I (Figure 1a) is known since the discovery of gas hydrates and is realized in many other chemical systems.\cite{18} Several clathrate frameworks are possible candidates for allotropic Si networks,\cite{9,19} and there is an emerging interest in (guest-free) clathrates of type II (Figure 1b), since they are discussed as promising and realizable candidates\cite{20} for photovoltaic applications. They show direct and, via formation of Si/Ge alloys, tunable band gaps\cite{21} and are predicted to be the most stable clathrate type for such Group 14 element modifications\cite{9,19} beside related hexagonal polytypes\cite{9,22}. For Si and Ge, the clathrate II structure has also been realized experimentally.\cite{23}

Four-connected networks with tetravalent element atoms are also found in a number of ternary silicides, germanides and stannides. Chemi-inspired networks, as they are presented in this work, have been derived from the two isotypic Na\(_5\)T\(_{2+}\)Sn\(_{10−x}\) phases (\(x \approx 0.5\); \(T = \text{Zn, Hg}\))\cite{24} showing a novel \(T\)-Sn network with realgar-like structural motifs, which is analogous to the B-Si substructure of LiBSi\(_2\) (tum).\cite{11} A substructure with helical channels in only one direction as it occurs in NaGaSn\(_5\),\cite{25} NaInSn\(_5\),\cite{16b} NaGaSn\(_5\),\cite{16a} and \(hP\)-Na\(_2\)ZnSn\(_5\)\cite{17} has already been investigated as theoretical element modification for C\cite{26}, Si\cite{6h,7a,26} Ge,\cite{6h,7a,26b} and Sn,\cite{26b} and is known as unj (Figure 1e). \(t\)-Na\(_2\)ZnSn\(_5\)\cite{17} contains even more fascinating non-intersecting helical channels in two perpendicular directions to give an open framework which is closely related to unj\cite{16a},\(^1\) and which is named here unj2 (Figure 1f) to emphasis this relationship. Within this work, we show that this new Si allotrope possesses a quasi-direct band gap. The Si and Ge frameworks of the Zintl phases NaLi\(_3\)Si\(_6\) and Na\(_7\)Ge\(_{12}\) as structure models for the so-called allo-Si or allo-Ge, respectively, give rise to another set of four-connected networks.\cite{17,27} The oxidative delithiation and formation of covalent bonds between the layers featuring four-, three- and two-connected atoms have led to new structures in the laboratory.\cite{17b,18b}

\(^1\) Notably, the computationally investigated structure was not only deduced from NaGaSn\(_5\) (done in \cite{7a}), but was also rediscovered via random search approaches for C\cite{26b} and Si\cite{6h,26b}.
but many more networks can be obtained with different stacking and interconnection patterns, which has been shown both experimentally \(^{27a, 27c}\) and computationally\(^{7a, 27b, 27c}\).

### 3. Slicing of diamond for chemi-inspired Si materials

From this overview of existing and at a first view incoherent chemi-inspired Si-networks, it is a short way to get such networks organized. The phase transition between \(hP\)-Na\(_2\)ZnSn\(_5\) and \(tI\)-Na\(_2\)ZnSn\(_5\), which was topologically explained by a small shift of atom positions and an induced bond cleavage, followed by a reorganization of the positions, also showed an interesting relationship to the cubic diamond ground state modification of Si.\(^{17}\) We now expand this approach, which results in a vast variety of allotropic structures, all bearing a tetrahedral connection. In this work, we elucidate the association between structures of known Zintl compounds as well as the possibility of the construction of new Si allotropes. We describe a group of ten covalent Si network structures, five of which are new and five are well-known as binary networks of other elements or as theoretically predicted low-energy Si phases. They cover nets such as \(\text{unj}\)\(^{16a}\), \(\text{tum}\)\(^{11}\) and \(\text{W2}\)\(^{28}\) and are constructed based on a unique scheme that is strongly linked to the description of the structural relations between various Zn/Sn networks\(^{17}\). All presented networks are based on a three-atom thick slab obtained by slicing the cubic diamond structure. The nets built of fourfold-connected sp\(^3\)-hybridized Si atoms are constructed by connecting the slices in a chemi-inspired way and are investigated by quantum chemical methods (DFT-PBE0/SVP level of theory).

As many of such networks have already been presented in the literature with very different names, we labeled these ten structures (there are more to be generated as shown in the outlook at the end of this article) according to their structural relationships and their natural tiling\(^{29}\) with the point symbol.\(^{30}\) Furthermore we include the crystallographic Pearson symbol that simplifies the chemi-inspired correlation to experimental findings, e.g. for ternary phases following the Zintl concept. The correlation between the stability of the structures and the structural parameters such as bond lengths, bond angles, ring sizes, and average number of faces per tile is investigated.

Finally, we note that recent experimental work led to the discovery of such predicted Si-networks, either via classical synthesis\(^{7b, 31}\) or by the use of ultrafast laser-induced confined microexplosion.\(^{32}\)

The basis of the networks of the proposed polytypes is constructed from a three-atom thick slab of the cubic diamond structure (\(\alpha\)-Si) oriented parallel to the (100) plane (Figure 2a and 2b). The slab contains four-bonded (\(4b\)-Si) and two-bonded Si atoms (\(2b\)-Si). The labels \(U\) (upper)
and \( L \) (lower) are used to refer to 2\( b \)-Si atoms above (\( U \)) and below (\( L \)) the plane through the 4\( b \)-Si atoms. The stacking of the slabs and the formation of both intra- and inter-layer bonds between 2\( b \)-Si atoms (Figure 2c and 2d, respectively) result in a series of four-connected networks and reveal previously unknown relationships between structures.

**Figure 2.** a) Cubic diamond structure (\( \alpha \)-Si). The bonds represented by thin lines are intersected to obtain the slabs (slicing parallel to the (100) plane). b) The resulting 2\( \times \)2 three-atom thick slab with four-
bonded (4b-Si) and two-bonded atoms (2b-Si) with filled gray and filled black (U) or white (L) spheres, respectively. The repeating unit of the eight-membered ring of the slab is highlighted in yellow. c) Intra-layer bond formation within an eight-membered ring as repeating unit of the diamond slab and the resulting structural motifs. d) The construction of two different atom layers A and B using the 2x2 superstructure shown in b) and with different connections within the eight-membered rings. Bonds within the layer are displayed as dashed lines for above (solid black) and below (open white). The resulting layers are shown as larger 4x4 units for A and B.

In an eight-membered ring unit, highlighted in yellow in Figure 2b, there are four possibilities for bond formation between 2b atoms on opposite sides (Figure 2c): the formation of two intra-layer bonds (U–U and L–L) yields a realgar-like structural unit, one U–U or one L–L bond transforms it into two edge-sharing five-membered rings. Though the two corresponding eight-atom units are equivalent, the motifs are distinguished as hump (U–U) and dell (L–L) in order to facilitate the description. Finally, a distorted eight-membered ring is generated in case all 2b-Si atoms of a ring are engaged in bonds within neighboring units. This set of four tiles – realgar, hump, dell, and ring – allows a description of all layers which can be constructed if each 2b-Si atom (U, L) of the diamond slab gets involved in one intra-layer bond. The resulting three-bonded atoms (3b-Si) allow for connecting the layers into three-dimensional networks. Based on the arrangement of the 2x2 tiles, a total of five different periodic layers can be generated, but only two of them are needed for the construction of various structures of experimentally accessible Zintl phases, and are thus discussed in this work: Layer A is built exclusively from hump and dell tiles, whereas layer B features all four different tiles (Figure 2d).

Inter-layer bonds are formed between type L and type U atoms of adjacent layers. In order to minimize the distances between the 3b atoms, the layers are shifted with respect to each other with shift vectors given as superscripts 1–6 in Table 1 and Figure 3a. Based on a primitive slab stacking the superscripts 1, 5, and 6 correspond to the shift vectors (¼, ¼), (¾, ¼), and (¼, ¾), respectively (one example is shown in Figure 3b). Alternatively, short contacts occur by a rotation of one slab by 90° (marked by an asterisk in Table 1; Figure 3b shows one example for such a stacking) and additional shift vectors (½, 0), (0, ½) and (½, ½) which are given as
superscripts 2, 3, and 4, respectively. The two presented stacking modes are referred to offset stacking and screw stacking, respectively. In Table 1, the stacking modes of all considered networks relative to the 2×2 tile-sized repeating units of layers A and B are described.

Figure 3. Layer stacking. a) A 2×2 section of the basic layer X to form layers A or B (Figure 2). Superscript numbers 1, 5, 6, 2, 3, and 4 indicate the position of the next layer by applying shift vectors along the diagonals (¼, ¼), (¾, ¼) and (¼, ¾) and along the axes (½,0), (0, ½) and (½, ½), respectively. b) Top: top view of an example of an offset shift with the upper red layer being shifted by (¼, ¼), with respect to the grey one; bottom: side view with interlayer connections. c) Top: top view of an example with the second layer X* being rotated by 90° (* denotes rotation by 90°), bottom: connections between basic layer X and X*. Top view with upper, red layer slightly inclined for clarity. Atoms of the lower and upper layer are represented as grey and red spheres, respectively. Different color shades are used to indicate the positioning of the atoms in the projection direction, black and dark red correspond to U, grey and red to 4b-Si, white and orange to L. Inter-layer bonds are represented as blue lines.

Type A layer (Figure 2d) which can be described as a puckered layer of five-membered rings, is formed by offset stacking of the networks of the known compounds NaGaSn₂[25], NaInSn₂[35], NaGaSn₅[16a], and hP-Na₂ZnSn₅ as well as the related Zn-Sn network of tI-Na₂ZnSn₅[17]. Type

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2 An arrangement as sketched in Figure 3 has been described[33] among a collection of some hypothetical structures based on the three-atom thick diamond slab known from tetragonal HP-LiGe[34]. Various stacking and interconnection patterns for the layers were considered in the work of Sherwood and Hoffmann[33], but none including a conversion of the layers themselves as it is described in the present manuscript.
A layer also occurs as part of the Sn partial structure of NaSn₅.[36] Structures including this layer have already been studied computationally.[6h, 7a, 26] The best-known network formed of this layer is **unj** or **ngs** that we will rename as **unj1** for showing further polytypic networks of the **unj** structure. Type B layers and applying a screw (or glide reflection) stacking gives the **T-Sn** networks of the isotypic Na₅T₂₊ₓSn₁₀₋ₓ phases (x ≈ 0.5; T = Zn, Hg)[24] and the B-Si network of LiBSi₂ (tum).[11]
4. **Three-dimensional silicon networks constructed by different stacking sequences of layer type A (1–6).**

The framework **unj1** (Figures 1a and 4) is the result of the simple combination of two three-atom slabs A (Figure 4a) and A\textsuperscript{1} [shift vector (1/4, 1/4)]. The network is described in space group \( P6_122 \) (no. 178) with 12 Si atoms per unit cell, all at Wyckoff position 6\( b \). This combination leads to one-dimensional helical channels with a six-membered helical winding (shown with green color in Figure 4b). The natural tiling of this structure is described with \([5^2.8^2]\) polyhedra that are staggered with a screw angle of 60° above each other (Figure 4c), resulting in an average ring size of 6.50. The point symbol for this network is \{5\textsuperscript{5}.8\}.

**Figure 4.** The network of **unj1** (1) that is identical to **unj**\textsuperscript{[16a]} or **ngs**\textsuperscript{[7a]}. a) Top view of the basic layer A. b) Side view of the combination of layers A and A\textsuperscript{1} with the resulting helix in green and the additional inter-layer bonds in blue. c) Tessellation with space filling \([5^2.8^2]\) polyhedra resulting from the natural tiling. d) The stacking sequence AA\textsuperscript{1} (compare to Figure 3) viewing along the \( c \) axis with parallel helical channels and with view perpendicular to the helical channels. The helical channels are shown in green.
Table 1. Characterization of the structures 1 – 10. Labels related to the polytypes, the stacking sequence according to the description in the text and in Figure 3, Pearson symbol, space group (no.), natural tiling and related framework topologies of intermetallic compounds as well as networks obtained from calculations (italic) are given. The formula for the natural tiling also contains the numbers of symmetry-independent tiles and not only the ratio of different tiles. Networks 1–6 are built of layer A; networks 7–10 are constructed using layer B. The stacking mode is explained in the section above.

<table>
<thead>
<tr>
<th>No.</th>
<th>label</th>
<th>stacking sequence</th>
<th>Pearson symbol 1)</th>
<th>space group (no.)</th>
<th>natural tiling</th>
<th>experimentally accessible networks/calculated networks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>unj1</td>
<td>A A² / A A²</td>
<td>hP12-Si</td>
<td>P6₁/22 (178)/P6₃22 (179) ²</td>
<td>[5²,8²]</td>
<td>unj [16a] (NaGaSn₂) [25] NaNInSn₂ [16b] NaGaSn₂ [16a] hP-Na₂ZnSn₅ [17]) C [26], Si [6h, 7a, 26] Ge [6h, 7a, 26b], Sn [26b]</td>
</tr>
<tr>
<td>2</td>
<td>unj2</td>
<td>A A² A³ A³</td>
<td>tP24-Si</td>
<td>I42d (122)</td>
<td>2[5²,8²]</td>
<td>tI-Na₂ZnSn₅ [17]</td>
</tr>
<tr>
<td>3</td>
<td>unj3</td>
<td>A A² A³ A³</td>
<td>tP24-Si</td>
<td>P4₂₁c (114)</td>
<td>3[5²,8²]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>W2</td>
<td>A A⁶</td>
<td>tP12-Si</td>
<td>P4₂/nmm (136)</td>
<td>[4²,5²,6¹]</td>
<td>W2 [28a]</td>
</tr>
<tr>
<td>5</td>
<td>T12</td>
<td>A A¹*</td>
<td>tP12-Si</td>
<td>P4₂/nmc (138)</td>
<td>[5²,7²] + [5²,6²,7²]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>unj4</td>
<td>A A¹* A⁶* A¹</td>
<td>oP24-Si</td>
<td>Pmna (52)</td>
<td>[5²,7²] + 3[5²,8²] + [5²,6²,7²]</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>tum2</td>
<td>B B¹</td>
<td>oC48-Si</td>
<td>C22₂,₁ (20)</td>
<td>2[8¹] + [5¹] + 2[5²,8²] + [8¹] + 2[5²,8²] + [5³]</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>tum1</td>
<td>B B¹*</td>
<td>tP24-Si</td>
<td>P4₂/nmc (137)</td>
<td>[5¹] + 2[5²,7²] + [7¹] + 4[5²,6²,7²]</td>
<td>Na₅T₂₋ₓSn₁₀₋ₓ phases (x ≈ 0.5; T = Zn, Hg) [24], tum (LiBSi₂) [11]</td>
</tr>
<tr>
<td>9</td>
<td>tum3</td>
<td>B B¹* B² B²*</td>
<td>tI₆-Si</td>
<td>I₄₃/amd (141)</td>
<td>[5¹] + 2[5²,7²] + 7¹ + 4[5²,6²,7²]</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>tum4</td>
<td>B B¹* B² B³*</td>
<td>oI₄-Si</td>
<td>Immm (71)</td>
<td>2[5¹] + 2[5²,7²] + 2[6²,10³] + 4[5²,6²,7²] + [5¹,10³] + 7¹,10³ + 2[4²,5²,6²]</td>
<td>Based on zeolite PCOD8292325 [37]</td>
</tr>
</tbody>
</table>

1) The symbol specifies (by two italic letters) the Bravais lattice (with the lower case letter for the crystal system and the upper case letter for the lattice type), and the number corresponds to the number of atoms in the unit cell.

2) The two enantiomorphs are described with different space groups.
The enantiomeric structure, which is described in space group \( P6_522 \) (no. 179), results from the stacking sequence \( \text{AA}^5 \) and shows right-handed helices instead of the left-handed ones in unj1 (1).

Helical channels, which do not run parallel but perpendicular to each other, are generated by the stacking sequence \( \text{AA}^1\text{A}^2\text{A}^5 \) (Figure 5a, left). The topology of the resulting network unj2 (2) is identical to the Sn/Zn partial structure observed in the ternary phase \( tI-\text{Na}_2\text{ZnSn}_5 \), which even displays the same space group \( I4 \overline{2}d \) (no. 122). The Si allotrope 2 thus is the result of the formal replacement of the Sn and Zn by Si atoms.\(^3\) The network has two symmetry-independent \([5^2.8^2]\) tiles shown in Figure 5a, right, as green and orange polyhedra. The band structure reveals a quasi-direct band gap of 2.62 eV (Figure 9). Interestingly, the ternary intermetallic compound \( \text{Na}_2\text{ZnSn}_5 \) undergoes a thermally induced phase transition from \( hP-\text{Na}_2\text{ZnSn}_5 \) to \( tI-\text{Na}_2\text{ZnSn}_5 \) with simultaneous ordering of the Zn and Sn atoms which are statistically distributed in \( hP-\text{Na}_2\text{ZnSn}_5 \), and thus a related transition from unj1 to unj2 could also occur for the Si allotrope (probably at higher temperatures due to the more stable Si-Si bonds).\(^{17}\)

Double layers of helices that alternate with respect to their orientation occur in unj3 (3) as the result of the stacking sequence \( \text{AA}^1\text{AA}^5 \). The structure can be described in space group \( P\overline{4}2_1c \) with five symmetry-independent and overall 24 Si atoms in the unit cell.\(^4\) This network contains three symmetry-independent \([5^2.8^2]\) tiles (Figure 5b).

A rotation applied in addition to the shifting of the layers leads to \( \text{A}^* \), and the most simple stacking sequence \( \text{AA}^* \) results in the known structure \( \text{W2} \) (4) the topology of which has been described before as a possible solution to the so-called Kelvin problem (Figure 5c).\(^{28}\) The

\(^3\) The \( 4b\)-Si atoms of the slab occupy two Wyckoff positions, \( 4a \) and \( 4b \), whereas the Si atoms that are part of the inter-layer bond have 16\( e \) site symmetry.

\(^4\) The initial \( 4b\)-Si atoms occupy three different Wyckoff positions, \( 2a \), \( 2b \), and \( 4d \). The Si atoms at positions \( 4d \) alternatingly contribute to the upper and the lower helix with the same handedness resulting in a parallel arrangement, whereas the Si atoms located at Wyckoff positions \( 2a \) and \( 2b \) are responsible for the perpendicular disposal of these pairs. The newly connected Si atoms occupy the two independent Wyckoff positions \( 8e \).
structure can be described in space group $P4_2/nmn$ (no. 136) with two symmetry-independent Si atoms and a small unit cell of 12 atoms.\(^5\) Instead of helices, a single convex, space filling \([^{4\mathrm{g}5\mathrm{h}}6\mathrm{i}]\) polyhedron represents the basic building unit. This polyhedron with a small average ring size of 5.14 also arises from nature tiling (Figure 5c, right). The polyhedra share their coplanar hexagonal faces, and - according to the tetragonal symmetry - they form two columns oriented perpendicular to each other (Figure 5c, left). \textbf{W2} based on layer A is a polytype of \textbf{unj1}, \textbf{unj2} and \textbf{unj3}, and the top view of this network reveals the Cairo tiling of layer A (Figure 5c, middle).

Interestingly, the known network \textbf{T12}\(^{[6b]}\) (5) also belongs to this group and is obtained by the stacking sequence AA\(^3\#\). The network contains helical chains related to those observed in \textbf{unj1}, but in 5 they adopt the form of a \textit{twin loop wire}, and they are interconnected via five- and seven-membered rings. The natural tiling is \([5^{2.7^2}\text{ and }5^{2.6^{2.7^2}}\) (pink and blue, respectively, Figure 5d, right) resulting in an average ring size of 6.0, which is identical to the average ring size of \(\alpha\)-Si. The tetragonal unit cell of 5 with space group $P4_2/nnc$ (no. 138) comprises only 12 atoms on two symmetry-independent sites. Even though \(\alpha\)-\(^{[15a,15c]}\) and \(\beta\text{-CdP}_2\)\(^{[15b]}\) crystallize in different space groups, the topologies of the nets are virtually identical. Thus 5 is a \textit{chemi-inspired} variant of the CdP\(_2\) structure type.

Finally, network \textbf{unj4} (6) is a stacking variant combining the characteristics of \textbf{unj2} (2) and \textbf{T12} (5). It is obtained from the stacking of four layers with the sequence AA\(^3\#\)A\(^6\#\)A\(^1\) (Figure 5e). Notably, the layers A\(^3\#\) and A\(^6\#\) as well as the layers A\(^1\) and A\(^6\#\) have the same relative orientation towards each other as A and A\(^1\) and A and A\(^3\#\), respectively. The symmetry of the network is described in space group $Pnna$ (no. 52) with four symmetry-independent Si atoms per unit cell.\(^6\) From Figure 5 it becomes obvious that the structural characteristics of 2 and 5 are merged to give 6. (Figure 5e, left; view along the c axis). The network is combined of one \([5^{2.7^2}\) (pink), three \([5^{2.8^2}\) (green, always connected to one left- and one right-handed helix per unit cell) and one \([5^{2.6^{2.7^2}}\) polyhedra (blue) resulting in an average ring size of 6.27 (Figure 5e, right).

\(^5\)The \textit{initial} 4b-Si is at Wyckoff position 4d, and the newly connected ones are located at position 8j.

\(^6\)The \textit{initial} 4b-Si occupy the two Wyckoff positions 4d and the newly connected ones Wyckoff positions 8e. Every second \textit{initial} 4b-Si contributes to the chains above and below linking the helix with the zigzag chain. The other one does not contribute to any chain.
Figure 5. Networks arising from various combinations of layer type A. a) **unj2** (2) with the stacking sequence $AA^1A^2A^5$ (left) and a representation of the tiling (different colors indicate the two symmetry-independent sites, right). b) **unj3** (3) related to **unj2** with the sequence $AA^1A^5$ and double layers of helical channels shown in green and orange. c) Stacking sequence $AA^*$ and view perpendicular to and along the stacking direction as well as the tiling for the resulting $W2$ structure (4). The view along the stacking direction is identical to the Cairo tiling of layer A itself (middle). Two symmetry-dependent $[4^2.5^6.6^1]$ tiles of the repeating unit in the unit cell (right). Hexagonal rings in the resulting polyhedra are shown with red and blue color (left and middle). d) **T12** (5) obtained by the stacking sequence $AA^3*$. The zigzag chains along the $b$ direction shown in blue adopt the form of a *twin loop wire*. The polyhedra (right side) from the natural tiling are $[5^2.7^2]$ (pink) and $[5^2.6^2.7^2]$ (blue). e) **unj4** (6) with the stacking sequence $AA^3*A^6*AA^1$ corresponds to a combination of **unj2** (2) and **T12** (5). The helical part of the structure is marked in green, the zigzag chains in dark and medium blue; right, a representation of the natural tiling of this structure. The right-handed helices are built from $[5^2.8^2]$ tiles (green), separated by blue $[5^2.6^2.7^2]$ and pink $[5^2.7^2]$ tiles.
5. **Three-dimensional silicon networks constructed by different stacking sequences of layer type B (7−10).**

Layer B, which contains all four possible tiles in the 2×2 unit, can also be stacked in either an offset or a screw mode (Figure 3 and 6a). The four stacking variants under consideration, one offset and three screw stackings, can be distinguished by the different relative arrangement of the realgar units with respect to each other. All structures contain linear channels, which are in principle capable of hosting small atoms such as Li and thus are interesting candidates for ion conductors.

The structure of tum2 (7) is constructed by the stacking sequence BB\(^1\), which results in a network with direct bonds between the realgar units (Figures 6b and 6c) and with channels of five- and eight-membered rings (Figures 6b, 6c, and 6d). The structure is described in space group \(\text{C222}_1\) (no. 20) with seven symmetry-independent Si positions.\(^7\) The natural tiling of this network consists of two \([8^3]\), one \([5^4]\), two \([5^2.8^2]\), two \([8^4]\), two \([5^4.8^2]\), and one \([5^8]\) polyhedra resulting in an average ring size of 6.29 (Figure 6e).

The network of tum1 (8) is constructed by the stacking sequence BB\(^*\). In contrast to tum2, there are no direct bonds between realgar units in adjacent layers, but the realgar units of one layer are placed on top of the ring units of the other. This pattern leads to additional six- and seven-membered rings beside the five-membered rings of the realgar unit (Figure 7a). Natural tiling leads to one \([5^4]\) (realgar), two \([5^2.7^2]\), one \([7^4]\) and four \([5^2.6^2.7^2]\) polyhedra (Figure 7a, middle right), with the latter four symmetry-dependent polyhedra (light blue in Figure 7a, right) enclosing the realgar unit. The average ring size of 6.0 is equivalent to the situation in \(\alpha\)-Si.

\(^7\) Two are occupied by the initial 4b-Si.
Figure 6. The network of tum2 (7) resulting from an offset stacking BB\(^1\). a) A 4×4 section of layer B used to build the structures of 7 - 10. b) Side view of the BB\(^1\) stacking sequence. Realgar units are shown in yellow, inter-layer bonds in blue. c) Directly connected realgar units of a BB\(^1\) sequence. d) Parallel projection on the BB\(^1\) sequence showing the arrangement of five- and eight-membered rings beside the realgar units. e) Natural tiling with \([8^8]\) (purple and pink), \([5^4]\) (yellow), \([5^2.8^2]\) (green), \([8^8]\) (light blue), \([5^4.8^2]\) (red; no visible in this projection), and \([5^8]\) (orange) polyhedra. For clarity, one realgar unit of the next unit cell in the stacking direction \(c\) is also shown.

Most interestingly, this novel Si structure is topologically identical to the Si-B network in the Zintl phase LiBSi\(_2\)\(^8\). In this open tetrahedral framework the Li atoms are located in channels, and the possibility of lithium ion conductivity has been discussed.\(^{[11]}\) Thus the Si structure tum1 constructed from a two-layer sequence of B is chemi-inspired by the ternary phase LiBSi\(_2\). To solid state chemists such a description is familiar from the so-called Zintl-Klemm concept. According to the salt-like description of intermetallic compounds, the Li atoms donate their valence electron to the boron atoms, which then adopt, with respect to their number of valence electrons, the bonding characteristics of a tetrel element (pseudo-element concept). Thus, a network with exclusively tetrahedrally connected atoms (despite some distortion) arises, which has been introduced as tum. However, our approach has revealed the existence of related polytypes, and thus the label tum1 is more appropriate.\(^{[11]}\) Like the ternary phase LiSiB\(_2\), the

\(^8\) And to the T-Sn networks in the Na\(_5\)T\(_{2+x}\)Sn\(_{10-x}\) phases (\(x \approx 0.5\); \(T = Zn, Hg\))\(^{[24]}\).
structure tum1 is described in space group $P4_{2}/nmc$ (no. 137); in other words tum1-Si corresponds to a defect structure of LiSiB$_2$ with all Li positions empty.

The network of tum3 (9) is constructed from four layers with the stacking sequence BB$^{3*}$B$^{4}$B$^{2*}$ and is very similar to that of tum1 (8). It can be described in space group $I4_{1}/amd$ (no. 141) with only three symmetry-independent Si positions. The average ring size is again 6.00 based on the natural tiling of one [5$^4$], two [5$^2$.7$^2$], one [7$^4$], and four [5$^2$.6$^2$.7$^2$] polyhedra and thus is identical to that in tum1 (8). The structure also contains channels of five-, six- and seven-membered rings, however, with a different arrangement than in tum1 (Figure 7b). The difference between these two structures, which is also evident from their relative energies (see Computational Analysis), becomes obvious from the larger units that are formed by the realgar unit and four surrounding [5$^2$.6$^2$.7$^2$] tiles. Although these units appear in both structures, they share one face with the neighboring unit perpendicular to the stacking in the structure of tum1 (8) (Figure 7a, right), whereas they are sharing two faces in tum3 (9) (Figure 7b, right).

A small variation of the stacking sequence to BB$^{+}$B$^2$B$^{3*}$ leads to the network of tum4 (10) with space group Immm (no. 71) and five symmetry-independent Si positions (Figure 7c). The network also shows blocks of five- and six-membered ring channels arranged in an up and down mode along the $b$ axis, which is already known from the structures tum1 and tum3. Along the $b$ axis, tum4 and tum3 are identical, but the view along the $a$ axis reveals that tum4 contains a new channel system with large channels of ten-membered rings, which are separated by blocks of two five-membered ring channels. The latter are connected by channels of the four-membered rings and separated by a row of six-membered ring channels. The realgar units are either directly connected under formation of a four-membered ring, or they are located above an eight-membered ring (Figure 7c, middle). The tiling is described by seven different polyhedra, which are represented in Figure 7c and Table 1. The unique structural features of this structure are an average ring size of 6.11 and the presence of three tiles with ten-membered rings.

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*The initial 4b-Si atoms are located at Wyckoff position 16g, the others at positions 16h.*
Figure 7. The networks 8 – 10 as polytypes of tum. a) tum1 (8) constructed by a two-layer stacking sequence as it is also observed in the Si-B network of LiBSi2. The tetragonal symmetry reveals two identical directions of the channels. Middle left: Arrangement of the realgar units. Middle right: Space filling polyhedra by natural tiling: [5^4] (red), [5^2,7^2] (green), [7^4] (purple), [5^2,6^2,7^2] (all symmetry-dependent, light blue). Right: Two realgar units, each enclosed by four [5^2,6^2,7^2] tiles (for clarity reasons shown in light and dark blue, even though they are symmetry-dependent). b) Representations of tum3 (9) as described for Figure 7a. The variation in the stacking sequence leads to a different arrangement of the channels, which - due to the tetragonal symmetry - run in two directions. c) Representations of tum4 (10) as described for Figure 7a (except for the figure to the right). Along the b axis the structural characteristics of 10 and 9 are identical, but they are less strained in 10, and parallel to the a axis, ten-membered ring channels are formed. The broken-off bonds indicate another six realgar units that are paired at the edges of the eight-membered ring. Right: polyhedral representation of the natural tiling [5^4] (yellow and pink), [5^2,7^2] (pink and green), [6^2,10^2] (orange), [5^2,6^2,7^2] (light blue), [5^4,10^2] (green), [7^4,10^2] (red), [4^2,5^4,6^2] (blue).
6. Structural and Computational analysis

All structures presented here are derived from the same two-dimensional cutouts of the well-known α-Si modification. Small distortions and stacking of the layers lead to three-dimensional networks with exclusively four bonded Si atoms, which show - in contrast to the situation in α-Si – also ring sizes other than six. The principle of “natural tiling”\cite{29} allows a systematic characterization of the various structures based on space-filling polyhedra. For the energetically most favorable structure, α-Si, the natural tiling is [6\textsuperscript{1}], and thus the average ring size is six, and the average number of faces per tile is four. The average ring sizes of the newly constructed networks are at least six, except for structure 4 (W2\textsuperscript{28}), which contains the [4\textsuperscript{2}.5\textsuperscript{8}.6\textsuperscript{4}] tile with 14 faces and is therefore the structure with the largest face to tile ratio. The four chemi-inspired structures derived on the basis of existing topologies in Zintl-phases, also have an average ring size of 6 or 6.5, and the average number of faces per tile for these structures is either 4, as seen for α-Si, or 5 (Figure 8a-b, Table 2).

All vertices in the structures are covalently four-connected atoms, and thus the minimum and maximum bond angles and bond lengths are crucial parameters for the stability of the networks. Besides the tiling, these structural parameters also have an influence on the total energy of the Si polymorphs, and their optimization on a PBE0/SVP-level of theory has been performed. The total energy of all structures is compared to that of the α-Si structure optimized at the same level of theory. For chemi-inspired networks arising from known Zintl-phases and based on layer A, we found that all angles lie between 102.8° (T12 (5)) and 130.1° (unj2 (2)). Networks based on layer B like tum1 (8) show angles in the less narrow range from 93.9° to 125.5°. Interestingly, the Si–Si distances of all networks lie between 2.28 and 2.52 Å, whereas the bond lengths in the chemi-inspired variants are within the narrower range of 2.34 - 2.45 Å, and even narrower for layer A structures (2.35 - 2.41 Å) like unj2 (2) and T12 (5). The relative atomic volumes of the discussed networks are all between 20.98 Å\textsuperscript{3} (T12 (5)) and 23.20 Å\textsuperscript{3} (W2 (4)), and thus slightly larger as in α-Si (20.29 Å\textsuperscript{3}). Thus, the procedure of slicing diamond and stacking the resulting layers differently leads to less dense networks, and the chemi-inspired structures are found again at the lower limit (tum1 (8) with 21.31 Å\textsuperscript{3} and unj2 (2) with 22.12 Å\textsuperscript{3}; Figure 8c-e).
Figure 8. Diagrams to illustrate the deviations of structural parameters of 1 – 10 as compared to α-Si. Chemi-inspired frameworks are marked with an asterisk, bold frames indicate new structures. a) The average ring sizes. The horizontal line represents the value for α-Si. Structures with smaller ring sizes do not necessarily correspond to more dense structures. b) The size of the tiles is best represented by the average number of faces per tile; the horizontal line represents the value for α-Si. c) Smallest and largest Si-Si-Si bond angle. d) The range of Si-Si bond lengths. The horizontal line represents the corresponding value of α-Si (2.36 Å) calculated on the same level of theory. e) The average atomic volume of the atoms. The horizontal line represents the corresponding value of α-Si (20.29 Å³).
The total energies $\Delta E_{\text{net}}$ per atom have been calculated and compared to the value of $\alpha$-Si which is set to 0.00 kJ mol$^{-1}$ (Equation 1).

$$\Delta E_{\text{net}} = \frac{E_{\text{total}}^\text{net}}{\text{no. atoms}} - \frac{E_{\text{total}}^{\alpha-Si}}{2}$$  \hspace{1cm} \text{(Equation 1)}

Remarkably, all chemi-inspired networks (1, 2, 5, and 8) are only slightly less stable than $\alpha$-Si with a maximum of $\Delta E_{\text{net}} = 11.1$ kJ mol$^{-1}$ for unj2 (2). The structure with the lowest relative energy is T12 (5), which has independently been found by a swarm method.$^{[6b]}$ Among the networks with relatively low energies unj3 (3) and unj4 (6) have not been described previously, neither as a possible structure for Si, nor as a topological equivalent to the covalent framework of a Zintl phase. These networks as well as T12 are vice versa promising candidates for substructure nets of Zintl-phases.

The predicted band gaps span a range from 1.79 eV for tum3 (9) to 3.01 eV for unj1 (1); chemi-inspired networks have gaps between 2.28 eV (T12 (5)) and 3.01 eV (unj1 (1)). All structures show indirect band gaps, however, the gaps of four Si-allotropes are quasi-direct: unj2 (2), tum2 (7), tum3 (9), and tum4 (10). Of these, only unj2 (2) with helical channels running perpendicular to each other without intercepting has been found in a Zintl-phase. Its predicted indirect band gap is 2.62 eV, but the same band also shows a direct gap of 2.74 eV (Figure 9, all other band structures are shown in the Supporting Information).

Notably, for all stacking variants with structural features of two structures, corresponding intermediate values are found for the relative energy and band gap, as can be seen for 3 (between 1 and 2) and 6 (between 2 and 5). Structure 4 has the lowest density with a relative atomic volume of 23.20 Å$^3$, which is the result of the large polyhedra that comprise 14 faces. Especially the flat four-membered rings cause strain in the 4b-Si network, and thus the relative energy of $\Delta E=15.2$ kJ mol$^{-1}$ is higher than for all other networks built of layer A. Consequently, network tum4 (10) built of layer B with the highest relative energy also contains flat four membered rings.
**Figure 9.** The relative energies (a) and band-gaps (b) of Si allotropes 1 - 10 compared to α-Si. Chemi-inspired frameworks are marked with an asterisk. (Bold frames indicate new networks).
**Figure 9.** Band structure of unj2 (2). a) Band structure along high symmetry points in an energy window around the Fermi level ($E_F$). The top of the valence band, which is set to zero, and the bottom of the conduction band are shown as green lines. b) Cut-out of a) showing the direct ($E_d$, blue line) and the indirect ($E_i$, orange line) band gap. These band situation is considered as “quasi-direct”.
Table 2. Parameters discussed in the text. (The corresponding values for $\alpha$-Si optimized on the same level of theory are: bond length 2.36 Å, angles 109.4°, ring size 6, atom volume 20.29 Å³, indirect band gap 1.87 eV).

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7. Computational Details

All structures were derived following the procedure described in the construction part above. The structures were first optimized with the CRYSTAL09 program package\cite{38} using Density Functional Theory with the Perdew-Burke-Ernzerhof exchange-correlation functional (DFT-PBE)\cite{39}. The Si atoms were described using a modified split-valence + polarization basis set composed of Gaussian-type functions\cite{9}. Both the lattice and atomic parameters were allowed to relax without any symmetry restrictions (feasible in space group \textit{P}1 (No. 1)). The initial cell parameters are $a = b = 7.6805$ Å and $c = 9.7758$ Å, if the structure is built stacking two layers, or $c = 19.5516$ Å, if the structure is built stacking four layers. The shrinking factor (SHRINK) to determine the $k$-mesh for the reciprocal space sampling is 4 for lattice parameters $< 15$ Å and 2 for lattice parameters $> 15$ Å, generating 16 to 20 $k$-points in the irreducible part of the Brillouin zone. Tight tolerance factors of 7, 7, 7, 7, 14 are used for the evaluation of the Coulomb and exchange integrals (TOLINTEG). Default optimization convergence thresholds and large integration grid (LGRID) for the density functional part were applied in this first optimization. The space groups of the structures were determined with FINDSYM\cite{40} at a tolerance of 0.1. In the resulting space group, the structures are re-optimized using the Perdew-Burke-Ernzerhof hybrid density functional method (DFT-PBE0)\cite{39,41}, while the structure is able to relax both, the lattice and atomic parameters within the constraints given by symmetry. The shrinking factors are 8 for lattice parameters $\leq 15$ Å and 4 for lattice parameters $> 15$ Å, generating a mesh of 75 to 300 $k$-points in the irreducible part of the Brillouin zone. For this second step, tighter tolerance factors of 8, 8, 8, 8, 16 for the Coulomb and exchange integrals were applied, as well as default optimization thresholds and extra-large integration grids (XLGRID) for the density functional parts. The local minimum character of all structures was confirmed with a harmonic frequency calculation\cite{42}. For the calculations of the band structures, the properties package of CRYSTAL09 was used. After finding the optimal path in the irreducible part of the Brillouin zone\cite{43}, the structure was investigated with 400 $k$-points along the path. The natural tiling\cite{29,30} of all networks was determined using the TOPOS4.0 program package\cite{44} to be able to compare the ring sizes and for identifying some networks\cite{45}.
8. Conclusion and Outlook

An easy to use construction kit as a guide to deriving novel silicon structures is presented. Our approach is based on a simple, three-atomic cutout of the diamond structure, and different stacking sequences with shifted or rotated layers of the same type have been used to build up a total of ten structures. The results obtained by this procedure also revealed a relationship between the new frameworks and already known ones, which, however, have not been considered as polytypes before. For instance it disclosed a so far not considered relation between the diamond structure and previously reported, possible Si structures. Furthermore, it displayed several new topologically related structures, which have not been considered yet as possible Si allotropes. The construction kit also deliveres topologies, which are also found in ternary intermetallic compounds with a substructure of exclusively four-connected atoms that follow the Zintl-Klemm concept. Vice versa, this finding may also inspire an alternative way for the search of new Si-topologies by analyzing the frameworks or substructures of intermetallic compounds, which then may be called "chemi-inspired search". As already mentioned, some of the networks obtained by the applied stacking of two layers have already been known without being considered as a polytype, but we have used this approach also to derive five as yet completely unknown network structures (one derives from a predicted zeolite framework with all Si connected via O bridges[37]). Three out of the ten derived structures have been found as polyanionic substructures in Zintl phases. The atom positions of two of those have been considered here for the first time as model for Si structures.

We presented a comprehensive topological and structural discussion of all ten networks, we calculated their band structures, and compared their energies and powder XRD patterns. The Si allotropes derived from chemi-inspired frameworks show the smallest energy difference to α-Si, and their bond lengths and bond angles lie in a narrow range, indicating a low degree of distortion from local tetrahedral symmetry. Furthermore, the two chemi-inspired structures unj1 and unj2 may show another interesting feature: for the corresponding ternary intermetallic phases hP-Na2ZnSn3 and tI-Na2ZnSn3 a temperature-induced phase transition was observed,[17] which could probably also be expected for the ‘defect variants’ hP-Si and tI-Si. Actually, multiple phase transitions can be envisioned to switch between different Si allotropes derived from the construction kit.

However, our construction kit has not been exhausted yet, and new frameworks, based on another three modifications of the three-atom thick α-Si layer as introduced in Chapter 3 and derived with the relatively small 2×2 supercell of the diamond structure, will be presented in a
forthcoming paper. The atom layers in Figure 10 (left and middle) are built of all four kinds of distortion variants shown in Figure 2c, the right one is built of only realgar-type units and eight-membered rings.

Figure 10. Three more layers that can be constructed with the herein presented set of eight-atom units. The left and middle layer are superimposable onto each other by a mirror plane, nevertheless for a description of the polytypes, it is worth to distinguish between them. The 2×2 repeating unit for each layer is highlighted.

9. Acknowledgement

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10. References


