High-pressure phases and transitions of the layered alkaline earth nitridosilicates SrSiN$_2$ and BaSiN$_2$

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Abstract
We investigate the high-pressure phase diagram of SrSiN$_2$ and BaSiN$_2$ with density-functional calculation. Searching a manifold of possible candidate structures, we propose new structural modifications of SrSiN$_2$ and BaSiN$_2$ attainable in high-pressure experiments. The monoclinic ground state of SrSiN$_2$ transforms at 3 GPa into an orthorhombic BaSiN$_2$ type. At 14 GPa a CaSiN$_2$-type structure becomes the most stable configuration of SrSiN$_2$. A hitherto unknown $Pbcm$ modification is adopted at 85 GPa and, finally, at 131 GPa a LiFeO$_2$-type structure. The higher homologue BaSiN$_2$ transforms to a CaSiN$_2$ type at 41 GPa and further to a $Pbcm$ modification at 105 GPa. Both systems follow the pressure-coordination rule: the coordination environment of Si increases from tetrahedral through trigonal bipyramidal to octahedral. Some high-pressure phases are related in structure through simple group–subgroup mechanisms, indicating displacive phase transformations with low activation barriers.

Supplementary data are available from stacks.iop.org/JPhysCM/21/275408

1. Introduction
In our continuing interest in nitridosilicates, their structural modifications and potential high-pressure phases, we investigate SrSiN$_2$ and BaSiN$_2$. Previously we reported on BeSiN$_2$, MgSiN$_2$ and CaSiN$_2$ [1]. Their ground state modifications resemble those of stuffed $\beta$-cristobalite variants. The structures with the smaller alkaline earth ions (Be, Mg) can alternatively be described as ordered wurtzite structures. High-pressure phases of BeSiN$_2$, MgSiN$_2$ and CaSiN$_2$ are proposed to adopt chalcopyrite-type structures and, finally, adopt ordered NaCl super-structures with sixfold coordination of Si.

SrSiN$_2$ and BaSiN$_2$ [2], on the contrary, differ considerably from the other three MSiN$_2$ compounds. While they comprise Si$_4$ tetrahedra as well, these tetrahedra do not form three-dimensional networks. Instead, layers are formed by connecting ‘bowtie’ units Si$_3$N$_6$ (pairs of edge-sharing tetrahedra) through common corners. BaSiN$_2$ crystallizes in the orthorhombic space group $Cmca$ (no 64), whereas SrSiN$_2$ adopts a monoclinic distorted variant ($P2_1/c$, no 14) of the same structure. The different structural behaviour at ambient pressure may be attributed to the larger size of the alkaline earth ion. An interesting question is how such structures may behave if high pressure is applied.

In this work, we report the optimized geometries of ambient pressure SrSiN$_2$ and BaSiN$_2$. We further set out to investigate candidate high-pressure phases by scanning over a manifold of ABX$_2$ structures. Anticipating our results, we will predict four high-pressure phases of SrSiN$_2$ and two for BaSiN$_2$, with SrSiN$_2$ showing the first transition as early as 3 GPa. We will also address possible mechanism of the encountered phase transformations on the basis of group–subgroup relations.

2. Methods
Structural optimizations, total energies, and properties are calculated within density-functional theory (DFT) [3], for
which we use a standard plane-wave/pseudopotential approach as implemented in the Vienna ab initio simulation package (VASP) [4]. The generalized gradient approximation (GGA) [5] together with the projector-augmented-wave (PAW) [6] method is employed to accurately compute relative enthalpies between structures with different coordination environments. For comparison, we also computed all structures using the local density approximation (LDA).

An energy cut-off of 500 eV for the expansion of the wavefunction into the plane-wave basis is chosen. Appropriate k-point grids (see table A1 in supplementary data available at stacks.iop.org/JPhysCM/21/275408) according to the Monkhorst–Pack scheme [7] facilitate Brillouin-zone integration.

Candidates for high-pressure phases of the ABX₂ type were collected from the ICSD [8]. In total, we investigated more than 15 hypothetical polymorphs of MSiN₂. All structural parameters, positions as well as cell parameters, are then optimized for the given composition. Convergence is achieved when residual forces are below 5 \( \times 10^{-3} \) eV Å\(^{-1}\). The symmetry after structure optimization is checked via the subroutine ADDSYM in the program PLATON [9]. Complete crystallographic data of the optimized positions for all presented structures are given in the supplementary data (available at stacks.iop.org/JPhysCM/21/275408).

Pressure is simulated by changing the volume of the cell and optimizing the structure again under the constraint of constant volume. The resulting energy–volume (\( E-V \)) graph is fitted with the Murnaghan equation of state (EOS) [10] to yield the bulk modulus \( B_0 \). We obtain further the pressure from the \( E-V \) graph by numerical differentiation of a Murnaghan EOS fit to the data, \( p = -\partial E / \partial V \). The enthalpy \( H \) of a structure is calculated via \( H = E + pV \). We neglect entropy contributions between solid-state structures, making the enthalpy difference \( \Delta H \) the measure to identify phase transformations. This approach is justified, because entropy differences between solid-state crystal structures are typically small in comparison to changes of \( \Delta H \) within 1 GPa of pressure change.

3. Results

3.1. SrSiN₂

\( \alpha \)-SrSiN₂ crystallizes with monoclinic space group \( P2₁/c \) (no 14) in a layered structure [2] (figure 1). The basic structural motifs are pairs of edge-sharing SiN₄ tetrahedra, which are connected further through corners to other tetrahedra pairs (figure 1). Sr\(^{2+} \) ions are located between the layers, with each Sr\(^{2+} \) ion eightfold coordinated by N. Noteworthily, the monoclinic structure of \( \alpha \)-SrSiN₂ is a distortion of the more symmetric orthorhombic structure of BaSiN₂ (space group \( Cmca \), no 64 [2], see also figure 1).

The results of our calculations—phase diagrams of SrSiN₂—are given in figure 2. Note that we present energy–volume and enthalpy–pressure data for the relevant structures only. In total we computed more than a dozen candidates. According to figure 2, the first structural transition appears as early as 3 GPa. It is a transition from the monoclinic ground state of SrSiN₂ (we assign the label \( \alpha \) to this structure) to an orthorhombic high-pressure phase (denoted \( \beta \)-SrSiN₂) with BaSiN₂-type structure. Since both structures are closely related, this transition comes as no surprise. Due to the small enthalpy differences, some caution is advised, since the estimated transition pressure may be significantly influenced by further entropy contributions as well as methodological imperfections. Nevertheless, the smallness of the transition pressure should make it possible to realize the new compound in standard high-pressure equipment, including high-volume presses.

\( \beta \)-SrSiN₂ remains the most stable polymorph up to 14 GPa, when \( \gamma \)-SrSiN₂ comes into existence. \( \gamma \)-SrSiN₂ adopts another orthorhombic structure (space group \( Pbcn \), no 61) resembling that of CaSiN₂. This structure, in which corner-sharing SiN₄ tetrahedra form a three-dimensional network, can be derived from the idealized \( \beta \)-cristobalite structure through a D₁-type distortion (figure 1) [2]. With SrSiN₂ adopting the structure of the lower homologue CaSiN₂ at high pressure, the system follows an unusual path. Typical in high-pressure science is the opposite trend, with many examples given in [11].

A third high-pressure modification, \( \delta \)-SrSiN₂, will appear at 85 GPa. It adopts a hitherto unknown orthorhombic structure (space group \( Pbcm \) (no 57)), which results from a distortion of the CaSiN₂ type (figure 1). \( \delta \)-SrSiN₂ comprises Si in

![Figure 1. Crystal structures of SrSiN₂ and BaSiN₂ polymorphs: (1) \( \alpha \)-SrSiN₂, view along [010] (SiN₄ tetrahedra drawn light grey, Sr atoms between the SiN₄ tetrahedra layers); (2) \( \alpha \)-BaSiN₂, view along [001] (SiN₄ tetrahedra drawn light grey, Ba atoms between the SiN₄ tetrahedra layers); (3) Imma structure; top, view along [001]; bottom, edge- and corner-sharing SiN₅ trigonal bipyramids (SiN₅ trigonal bipyramids light grey, metal atoms in channels); (4) \( Pbcm \) structure; left, view along [001]; right, edge- and corner-sharing SiN₅ trigonal bipyramids (SiN₅ trigonal bipyramids light grey, metal atoms in channels); (5) \( \alpha \)-CaSiN₂, view along [010] (SiN₄ tetrahedra drawn light grey); (6) m-LiFeO₂ (left, octahedral layer, view along [001]; right, stacking of octahedral layers, view along [010]).](image-url)

![Diagram showing crystal structures of SrSiN₂ and BaSiN₂ polymorphs.](image-url)
trigonal bipyramidal coordination. It thus takes some 85 GPa to increase the coordination of Si from four to five. Sr on the other hand remains octahedrally coordinated (figure 1). A summary of the sequence of structures of SrSiN₂ as pressure increases is shown in figure 3. A sweep of all polymorphs, which renders it the most compressible among the SrSiN₂ polymorphs.

Figure 3. Sequence of structures of SrSiN₂; transition pressures and density changes are indicated along the arrow.

Zero-pressure energies, volumes and densities as well as bulk moduli of the five modifications of SrSiN₂ are given in table 1. δ-SrSiN₂ has the lowest bulk modulus (33 GPa) of all polymorphs, which renders it the most compressible among the SrSiN₂ polymorphs. We attribute this finding to an exceptionally large compressibility of some Si–N bonds in this structure.

3.2. BaSiN₂

Our results of energy–volume calculations for different BaSiN₂ polymorphs are shown in figure 4, which also includes the corresponding enthalpy–pressure diagram. The layered ground state modification α-BaSiN₂ with orthorhombic space group symmetry (Cmca, no 64) [2] remains the most stable modification of BaSiN₂ up to 41 GPa. At this pressure a CaSiN₂-type modification (see figure 1, labelled β-BaSiN₂) will form. The three-dimensional network of corner-sharing Si₅N₄ tetrahedra found in β-BaSiN₂ will then gradually distort into a structure comprising edge-sharing trigonal bipyramids. We denote this structure γ-BaSiN₂, and it adopts the aforementioned Pbcm structure of δ-SrSiN₂ (figure 1). A transformation process is finished at a pressure of 105 GPa. Therefore, BaSiN₂ follows a similar structural development as SrSiN₂. However, an all-octahedral structure of BaSiN₂ will not appear for pressures up to 150 GPa.

The complete sequence of high-pressure phases of BaSiN₂ together with transition pressures and density changes is illustrated in figure 5. In table 2 we collect zero-pressure energies, volumes and densities as well as bulk moduli of the three modifications of BaSiN₂.

Table 1. E₀, V₀, B₀ and ρ₀ for α-, β-, γ-, δ- and ε-SrSiN₂.

<table>
<thead>
<tr>
<th>Modification</th>
<th>E₀/f.u. (eV)</th>
<th>V₀/f.u. (10⁶ pm³)</th>
<th>B₀ (GPa)</th>
<th>ρ₀ (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-SrSiN₂</td>
<td>-28.633</td>
<td>56.34</td>
<td>102</td>
<td>3.24</td>
</tr>
<tr>
<td>β-SrSiN₂</td>
<td>-28.623</td>
<td>56.00</td>
<td>104</td>
<td>4.26</td>
</tr>
<tr>
<td>γ-SrSiN₂</td>
<td>-28.452</td>
<td>53.41</td>
<td>125</td>
<td>4.47</td>
</tr>
<tr>
<td>δ-SrSiN₂</td>
<td>-27.110</td>
<td>53.15</td>
<td>33</td>
<td>4.49</td>
</tr>
<tr>
<td>ε-SrSiN₂</td>
<td>-25.658</td>
<td>46.28</td>
<td>163</td>
<td>5.16</td>
</tr>
</tbody>
</table>

Table 2. E₀, V₀, B₀ and ρ₀ for α-, β- and γ-BaSiN₂.

<table>
<thead>
<tr>
<th>Modification</th>
<th>E₀/f.u. (eV)</th>
<th>V₀/f.u. (10⁶ pm³)</th>
<th>B₀ (GPa)</th>
<th>ρ₀ (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-BaSiN₂</td>
<td>-28.7114</td>
<td>62.50</td>
<td>89</td>
<td>5.14</td>
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<tr>
<td>β-BaSiN₂</td>
<td>-28.2975</td>
<td>59.12</td>
<td>129</td>
<td>5.43</td>
</tr>
<tr>
<td>γ-BaSiN₂</td>
<td>-26.699</td>
<td>55.40</td>
<td>135</td>
<td>5.80</td>
</tr>
</tbody>
</table>
Figure 4. Left, energy–volume ($E-V$) phase diagram of $\alpha$, $\beta$, $\gamma$- and $\gamma'$-BaSiN$_2$, calculated within the GGA. Each symbol represents a calculation. The inset shows the $E-V$ curves of $\gamma$-BaSiN$_2$ and of $\gamma'$-BaSiN$_2$ (symmetry fixed to $Imma$). Right, enthalpy–pressure ($H-p$) diagram for the transition of $\alpha$-BaSiN$_2$ into $\beta$-BaSiN$_2$ ($p_t = 43$ GPa) and into $\gamma$-BaSiN$_2$ ($p_t = 105$ GPa) as well as of $\gamma'$-BaSiN$_2$ ($Imma$) into $\gamma$-BaSiN$_2$ ($Pbcm$) ($p_t = 32–35$ GPa).

Figure 5. Sequence of structures of BaSiN$_2$ including transition pressures and changes in density.

since $\beta$- and then at lower pressures $\alpha$-BaSiN$_2$ are even more favourable. Moreover, above 35 GPa the lower-symmetry $\gamma$-BaSiN$_2$ is favoured over $\gamma'$-BaSiN$_2$, if we constrain the symmetry of the latter. The tight structural relation between $\gamma$- and $\gamma'$-BaSiN$_2$ (a comparison of atomic positions in the $Pbcm$ and $Imma$ structures is given in supplementary data available at stacks.iop.org/JPhysCM/21/275408), however, let us hypothesize that $\gamma$-BaSiN$_2$ cannot be quenched to zero pressure. Instead, it may be that we observe a progressive distortion from the $Pbcm$ structure to an $Imma$ structure. The $Imma$ structure of $\gamma'$-BaSiN$_2$, finally, optimizes upon further pressure reduction towards a low-density, low-coordinated structure.

4. Discussion

We propose four high-pressure phases of SrSiN$_2$. The first transition occurs already as low as 3 GPa, from the monoclinic $\alpha$-SrSiN$_2$ to a higher-symmetry orthorhombic structure. This transformation follows the pressure-homologue rule [13], according to which high-pressure conditions favour the formation of phases with the structure of heavier homologues. Presumably, this displacive phase transformation will have a low activation energy barrier, because only small displacements of the atoms (compare supplementary data available at stacks.iop.org/JPhysCM/21/275408) suffice to make the transformation (figure 7). Indeed, this will make a quenching of $\beta$-SrSiN$_2$ a true challenge. Nevertheless, the orthorhombic $\beta$-phase of SrSiN$_2$ should be detectable in in situ experiments, e.g. in the DAC.

Interestingly, the proposed transformation $\beta$-SrSiN$_2$ $\rightarrow$ $\gamma$-SrSiN$_2$ (with CaSiN$_2$-type structure) then does not follow the aforementioned empirical ‘rule’. Unlike so many silicate structures [11], the nitridosilicates SrSiN$_2$ and BaSiN$_2$ adopt the structure of a smaller homologue at high pressure. The nature of this phase transformation is unambiguously reconstructive: the connection pattern of SiN$_4$ tetrahedra changes fundamentally, and a layered structure is converted into an extended, three-dimensional network.

Transforming $\gamma$- into $\delta$-SrSiN$_2$ again is a displacive process. It follows a klassengleiche ($k2$) group–subgroup relation pathway from orthorhombic $Pbca$ ($\gamma$-SrSiN$_2$) to $Pbcm$ ($\delta$-SrSiN$_2$) (cf figure 6 and supplementary data available at stacks.iop.org/JPhysCM/21/275408). Like the transformation from $\alpha$- to $\beta$-SrSiN$_2$, we can expect this

Figure 6. Illustrating the group–subgroup relation between the high-symmetry $Imma$ structure, the $Pbcm$ type, and CaSiN$_2$ ($Pbca$). These structures may appear in the phase diagram of BaSiN$_2$ as $\beta$ (right, CaSiN$_2$ type), $\gamma$ (middle, $Pbcm$ structure), and $\gamma'$-BaSiN$_2$ (left, $Imma$ structure).
the m-LiFeO2-type structure was found up to 150 GPa. As we
note, it has to be noted that upon pressure reduction the Si–
bonding of the SiN5 trigonal bipyramids in δ-SrSiN2 become too long (compare supplementary data available at
stacks.iop.org/JPhysCM/21/275408). Therefore, it is most
likely that this phase re-transforms into δ-SrSiN2 or turns
amorphous at lower pressures.

The fourth phase transition occurs at very high pressures
(131 GPa), achieving a further increase of the coordination
number of Si from five to six. By adopting the m-LiFeO2-type
structure, a superstructure of the rock-salt structure type
(12), ε-SrSiN2 finally follows the trend we have already discovered
for BeSiN2, MgSiN2 and CaSiN2 [1].

BaSiN2 adheres to the same high-pressure structure
sequence as SrSiN2. From orthorhombic \textit{Cmca} \ BaSiN2
it transforms into a \textit{Cmca} structure, followed by the displaceable phase transformation into the \textit{Pbcm}-type
structure (figure 6 and supplementary data available at
stacks.iop.org/JPhysCM/21/275408). No transformation into
the m-LiFeO2-type structure was found up to 150 GPa. As
we already noted, the \textit{Pbcm} structure of \textit{γ}-BaSiN2 may distort through a cascade of higher-symmetry structures into a very
open structure with low density and high energy. Since the nature of the \textit{β}/\textit{γ}-phase transformation is also displaceive, this
process will compete with the re-transformation into \textit{β}-BaSiN2
upon pressure release. \textit{γ}-BaSiN2 may thus be observed \textit{in situ}
only.

5. Summary

We calculated the high-pressure phase diagram of SrSiN2
and BaSiN2. Our results let us propose several new
modifications of SrSiN2 and BaSiN2 surpassing the layered
ground state modifications upon compression. Ultimately, Si
will exhibit coordination numbers higher than four in both
systems. δ-SrSiN2 and \textit{γ}-BaSiN2 both exhibit SiN4 trigonal
bipyramids, while \textit{ε}-SrSiN2 even comprises SiN6 octahedra.
Interestingly, both phase systems at one point violate the empirical pressure-homologue rule, as they both adopt a
CaSiN2-type modification at high pressure. Furthermore, we
describe an as-yet unknown \textit{Pbcm}-type high-pressure phase
for both SrSiN2 and BaSiN2 (δ-SrSiN2 and \textit{γ}-BaSiN2). As all
transition pressures are calculated to values below 150 GPa,
there are good chances to observe the new phases in \textit{in situ}
DAC experiments. Some of the new phases can hopefully be
quenched to ambient pressure.

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\begin{figure}[h]
\centering
\textbf{Figure 7.} Group–subgroup relation of the BaSiN2 and the SrSiN2
structure. Unit cell drawn: (1) solid line, \textit{Pbcm}; (2) dashed line,
\textit{Cmca}.
\end{figure}