Pathways to metastable nitride structures

Peter Kroll*

*Institut für Anorganische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen (RWTH), Professor-Pirlet-Strasse 1,
D-52056 Aachen, Germany*

Abstract

The structure types of spinel and willemite-II are related by a Bain correspondence. γ-Si$_3$N$_4$ can, therefore, transform into wII-Si$_3$N$_4$ by a diffusionless mechanism. We calculate the activation barrier for this process from the spinel into the energetically more favorable wII modification of Si$_3$N$_4$ and Ge$_3$N$_4$ to 0.92 eV and 0.56 eV/f.u., respectively. We predict that the spinel modification is a suitable precursor for the synthesis of the wII modification, which otherwise is metastable throughout the enthalpy–pressure phase diagram of Si$_3$N$_4$ and Ge$_3$N$_4$ and thus not accessible via standard pressure techniques using equilibrium thermodynamics. To allow a phase identification we provide the calculated Raman-spectra of both wII-Si$_3$N$_4$ and wII-Ge$_3$N$_4$ and compare them with those of the spinel modifications.
$\copyright$ 2003 Elsevier Inc. All rights reserved.

1. Introduction

The recent synthesis of cubic phases of Si$_3$N$_4$ [1–3] and Ge$_3$N$_4$ [4,5] provided new nitride materials based on the spinel structure. The brilliant synthetic work carried out in high-pressure laboratories was supported and complemented by detailed theoretical calculations which furthered the understanding of the new materials and their properties as well as of the corresponding phase diagrams [1,6–12]. The importance and the applicability of the new spinel nitride materials is now well established. Meanwhile, both γ-Si$_3$N$_4$ and γ-Ge$_3$N$_4$ can be produced in large amounts by shock-synthesis and start to be commercially available [13,14].

In the primary paper, the phase diagram shown for Si$_3$N$_4$, which is prototypic for both Si$_3$N$_4$ and Ge$_3$N$_4$, indicated a third phase, denoted w-Si$_3$N$_4$ [1]. w-Si$_3$N$_4$, or better wII-Si$_3$N$_4$ (we will use this notation from now on), is an intermediate between the phenacite (β-Si$_3$N$_4$) and spinel modifications (γ-Si$_3$N$_4$) of Si$_3$N$_4$ in both energy and volume. Hence, at zero pressure, while the phenacite structure constitutes the ground state, the wII structure is energetically more favorable than the spinel phase. The spinel type, however, can be synthesized at high-pressures and quenched to ambient conditions. The

wII modification, on the contrary, was never synthesized directly. Moreover, it was not even drawn into further considerations of the phase diagram, although experiments sometimes showed phase contents that could not be identified [15].

In this paper we will do some justice to this phase, which is yet another cubic polymorph of Si$_3$N$_4$. We will first explain comprehensively why it is not possible to synthesize a pure wII-Si$_3$N$_4$ under equilibrium conditions. Then we will point out strategies to synthesize a nitride compound with this structure anyway: first pursuing the standard equilibrium route, but then utilizing a genuine close relationship of the spinel and wII structure.

2. Computational method

We employed detailed first-principles calculations to access the phase diagrams presented in this paper. In particular, we used the VASP program to optimize structural parameters and total energies [16–19]. This implementation of density functional theory methods combines a plane-wave basis set with the total energy pseudopotential approach. The exchange-correlation energy of the electrons is treated within the generalized-gradient approximation (GGA) of Perdew and Wang [20]. Our particular choice of the GGA is

*Fax: +49-241-809288.
 E-mail address: peter.kroll@ac.rwth-aachen.de.

based on the fact that gradient corrections offer significant improvements when structures with different environments for the atoms are compared with each other. While the LDA fails to reproduce the experimental transition pressures and tends to favor higher coordinated structures (and transition states), the GGA performs much better on this behalf. We use the local density approximation (LDA) for the calculation of vibrational frequencies, however, as it yields a better description of elastic and vibrational properties. All results rely on well-converged structures with respect to cut-off energy (500 eV), residual forces ($<5 \times 10^{-3}$ eV/Å) and **k**-point sampling. A Monkhorst–Pack mesh of $3 \times 3 \times 4$, $3 \times 3 \times 8$, $4 \times 4 \times 4$, and $4 \times 4 \times 4$ **k**-points was used for the structures of α, β, wII, and spinel, respectively. The geometries calculated along the reaction coordinate necessitate a $4 \times 4 \times 4$-mesh for correct evaluation of the relative energies. The method overall is known for its accuracy; recent applications to related materials systems under pressure treated SiO_2 [21,22], Si_3N_4 [1,8], Si_2N_2O [23], and P_3N_5 [24].

3. Results

3.1. Crystal structures

The spinel structure of γ-Si_3N_4 adopts the space group symmetry $Fd\bar{3}m$ (227). It comprises Si in two different environments: tetrahedrally coordinated Si in $8a$ $(0,0,0)$, and octahedrally coordinated Si in $16d$ $(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$. The anions are located in position $32e$ (x,x,x), with the free positional parameter $x = \frac{3}{8} + x_{sp}$. If $x_{sp} = 0$, the anions are at the points of a face centered cubic lattice (fcc). For all spinel structures the parameter x_{sp} is very close to zero. The crystal structure of γ-Si_3N_4 can thus be completely described by two parameters: the lattice constant, a, and the positional parameter of the anions, x_{sp}.

The willemite-II type was first proposed by Teter and Hemley as a low-compressible modification of carbon nitride, C_3N_4 [25]. It is derived from a high-pressure phase of a zinc silicate, Zn_2SiO_4, denoted willemite-II,

and we will use the notation wII for this structure type. On replacing the cations (Zn and Si) by Si, or C or Ge, and the anions (O) by N, the tetragonal structure readily relaxes towards the more symmetrical cubic ground state. The structure of wII-Si_3N_4 then has the space group symmetry $I\bar{4}3d$ (220). Si atoms are in $12a$ $(\frac{7}{8}, 0, \frac{1}{4})$, and N atoms are in $16c$ (x,x,x), which has the free positional parameter $x = \frac{1}{4} + x_{wII}$. Hence, the crystallographic structure also is described by two parameters only: the lattice constant a and the positional parameter x_{wII}. Interestingly, for $x_{wII} = 0$, the anions form a body centered cubic lattice (bcc). If $x = \frac{1}{32}$, a perfect local tetrahedral coordination of the cations is achieved. For $x = \frac{1}{24}$, the local environment of the anions is perfectly trigonal planar. Similar to the lowest energy modification of β-Si_3N_4, the wII structure is an assembly of corner-connected tetrahedra, with each three tetrahedra sharing a common corner.

The results of our calculations of spinel and wII structures of C_3N_4, Si_3N_4, and Ge_3N_4 are given in Table 1. The calculations for C_3N_4 and Si_3N_4 indicate a particular balance between the two situations of a perfect tetrahedral local environment of the cations and a perfect local trigonal planar environment of the anions. It is worthy to note that for all three-phase systems, the wII structure is energetically more favorable than the spinel structure. The difference is small for Si_3N_4 and Ge_3N_4, but extremely large for C_3N_4. The latter information may bring some enlightenment on speculations of a spinel C_3N_4 [26], and will be of use for the discussion of the influence of carbon impurities on the phase diagram of Si_3N_4 or Ge_3N_4 later on.

Besides these two cubic polymorphs, we calculated the hexagonal α and β modifications. Both structures, α-Si_3N_4 and β-Si_3N_4 can be described as an assembly of corner-sharing SiN_4 tetrahedra, with each three tetrahedra sharing a common corner. β-Si_3N_4 is derived from phenacite (Be_2SiO_4), if all cations in phenacite are replaced by Si and the anions by N. α-Si_3N_4 is related to β-Si_3N_4 by a c-glide operation. Above all, there is one very important consequence of this glide operation: the stacking of trigonal N atoms along the c-axis found in the β-phase does not occur in the α-phase. While for

Table 1
Structural parameter (lattice constant, volume per formula unit, and anion positional parameter) for spinel and wII structures of C_3N_4, Si_3N_4, and Ge_3N_4

	Spinel (γ)			wII structure			ΔE(wII-γ) (eV/f.u.)
	a (Å)	V (Å³/f.u.)	x_{sp}	a (Å)	V (Å³/f.u.)	x_{wII}	
C_3N_4	6.7824	39.00	0.0058	5.4438	40.33	0.0340	−7.19
Si_3N_4	7.7729	58.70	0.0074	6.4747	67.86	0.0314	−0.39
Ge_3N_4	8.3091	71.66	0.0082	6.8652	80.89	0.0276	−0.31

ΔE is the energy difference between the two structure types; negative values indicate the preference of the wII type. All results are obtained within the GGA.

Si_3N_4 and Ge_3N_4 this difference apparently has only negligible effects for a preference of one phase over the other, the consequences are drastic for C_3N_4: the typical C–N single bond length (1.45 Å) is considerably shorter than the Si–N bond length (1.73 Å). All distances in the crystal structure, therefore, are scaled appropriately. Consequently, the c-axis in β-C_3N_4 is also shorter, causing a rather close contact of the trigonal N atoms. As a result there is repulsion between the electron lone-pairs of these trigonal N atoms and the energy of β-C_3N_4 is significantly higher than that of α-C_3N_4 [27]. We calculate an energy difference of 0.2 eV per formula unit for the zero pressure geometries. The effect is even more pronounced under pressure.

3.2. Variation of energy and enthalpy under pressure

The internal energy E as a function of the volume V of three polymorphs of Si_3N_4 is shown in Fig. 1 on the left side. The order considering both energy and volume is from β-Si_3N_4 to wII-Si_3N_4 and γ-Si_3N_4; with β-Si_3N_4 being the phase with lowest energy and highest volume. One may be tempted to interpret the graph in such ways that, on compressing β-Si_3N_4, the ensemble will always adopt the structure with the lowest internal energy: it first follows the E–V curve of β-Si_3N_4, than switches to that of wII-Si_3N_4, and finally trails on the E–V curve of γ-Si_3N_4. This point of view, however, is wrong. We know from thermodynamics that in equilibrium a system will always adopt the structure with the lowest free enthalpy, the Gibbs free energy G, instead. A transformation between two phases is then driven by the difference of free enthalpy, $\Delta G = \Delta E + p\Delta V - T\Delta S$. At high pressures, the contribution due to the entropy difference, $T\Delta S$, is typically small in comparison to the enthalpy difference $\Delta H = \Delta E + p\Delta V$. Therefore, the enthalpy difference ΔH is a good measure to compare relative stability of solid state structures under pressure and to access the phase diagram under equilibrium conditions.

The enthalpy H is calculated via $H = E + pV$; the E–V graph is used to extract the pressure $p = -\partial E/\partial V$

by numerical differentiation of a spline fit to the data. The enthalpy difference ΔH, finally, is plotted with respect to a reference phase. The results we obtain for the Si_3N_4 phases are plotted in Fig. 1 on the right side.

This graph demonstrates that β-Si_3N_4 transforms to γ-Si_3N_4, but not to wII-Si_3N_4. The transition pressure $p_t^{\beta \to \gamma}$ is calculated to 12 GPa, matching almost perfectly the experimental results [2]. wII-Si_3N_4 has no region within the enthalpy–pressure phase diagram, where it becomes the preferred modification of Si_3N_4. It is, of course, also possible to obtain $p_t^{\beta \to \gamma}$ using the common-tangent method. This method just corresponds to the localization of the point of zero enthalpy difference, $\Delta H = 0$, in the E–V graph. If a spinel modification would not exist or if, by some mechanism, the $\beta \to \gamma$ transformation could be suppressed, we would observe a transition β-Si_3N_4 to wII-Si_3N_4 at 20 GPa. Once synthesized at high pressures, γ-Si_3N_4 should transform back to β-Si_3N_4 at 12 GPa under equilibrium conditions, since with decreasing pressure β-Si_3N_4 becomes thermodynamically more stable again. Below 7 GPa even the wII-Si_3N_4 modification becomes more favorable than γ-Si_3N_4. The spinel modification of Si_3N_4, nevertheless, can be quenched without a phase transformation. Thus, it is possible to obtain a phase that is thermodynamically metastable at zero pressure. And indeed, the kinetic (thermal) stability of γ-Si_3N_4 in argon is remarkable, up to 1600 K at ambient pressure [13]. This indicates a substantial activation barrier for the transformation back into the energetically quite more favorable β-Si_3N_4.

3.3. Strategies for a synthesis of a wII structure

The arguments given above show that wII-Si_3N_4 is a thermodynamical unstable modification of Si_3N_4 throughout the phase diagram. At zero pressure, wII-Si_3N_4 would, nevertheless, be metastable in a similar way as γ-Si_3N_4 is: its decomposition would be kinetically hindered. So, is it possible to get a nitride wII phase anyway? After all, in chemistry the synthesis of metastable compounds is ubiquitous.
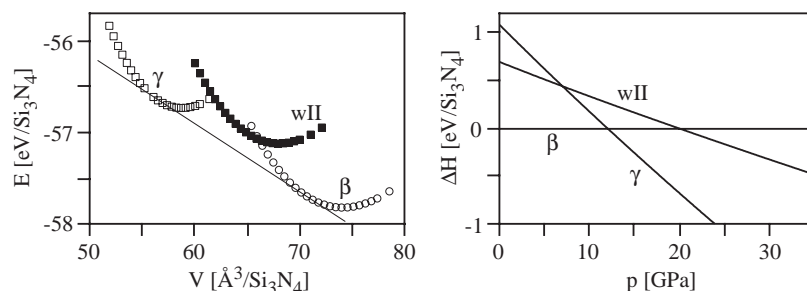

Fig. 1. Energy–volume (E–V) (left) and enthalpy–pressure (ΔH–p) diagrams (right, relative to β-Si_3N_4) of β-Si_3N_4, wII-Si_3N_4, and γ-Si_3N_4. The line in the left graph is the common tangent for β-Si_3N_4 and γ-Si_3N_4. Its slope yields the transition pressure of the $\beta \to \gamma$ transition. All results were calculated using the GGA.
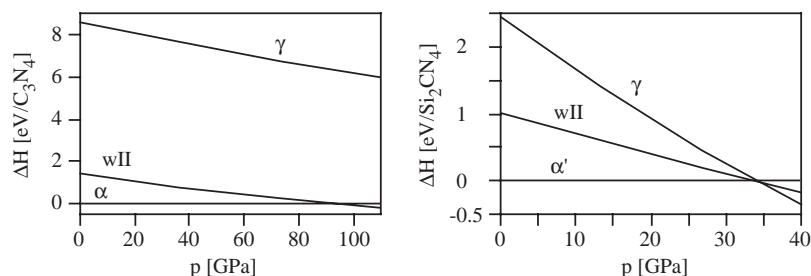
Fig. 2. Enthalpy–pressure (ΔH–p) diagrams of C_3N_4 (left) and Si_2CN_4 (right). All results were calculated using the GGA.

3.3.1. Manipulating the relative energies of spinel and wII

One approach we may pursue, still thinking in terms of equilibrium thermodynamics, is to modify the relative energies of the three phases. The goal then is to bring the energy of the wII phase below the common tangent of the $\beta \rightarrow \gamma$ transition, see the E–V in Fig. 1. Approximately 0.5 eV/f.u. (7 atoms) would be necessary to achieve this for Si_3N_4. Alternatively, one may try to push the energy of the spinel modification upwards. Within the ΔH–p diagram both approaches would then cause the corresponding curve of the wII phase to cross the reference line of the ground state structure at lower pressures in comparison to the spinel modification. This balancing of the relative energies may be induced by impurities or by rather drastic manipulations of the reaction conditions, such as a template synthesis. Considering the first approach a partial substitution of silicon by carbon might become very useful, as within the C_3N_4 phase system wII-C_3N_4 is much more favorable than γ-C_3N_4, see again the results of Table 1. With regard to the enthalpy–pressure phase diagram of C_3N_4, which is shown in Fig. 2, on the left side, we see that α-C_3N_4 is the most favorable C_3N_4 phase with tetrahedral carbon. If it can be synthesized and used as a precursor, it might transform into wII-C_3N_4 at pressures exceeding 90 GPa. A further transformation into a spinel modification will not happen for accessible pressures. If we now assume linear interpolation (Vegards's law) between C_3N_4 and Si_3N_4 to be valid (as well as the existence of an appropriate crystal modification), we can estimate that a willemite-II phase can be synthesized for the composition Si_2CN_4. The hypothesis is corroborated by our explicit calculations the enthalpy–pressure phase diagram of Si_2N_4, shown in Fig. 2, on the right side. We used an α-type modification of Si_2CN_4 as reference phase.[1]

3.3.2. Exploiting the kinetics of the transition

The second approach to synthesize wII-Si_3N_4 concentrates on the kinetics of the phase transition more than on equilibrium conditions. It utilizes the fact that below 7 GPa wII-Si_3N_4 is indeed more favorable than γ-Si_3N_4. Thus, at low pressures γ-Si_3N_4 has the option to either transform into wII-Si_3N_4 or into β-Si_3N_4. While the latter structure is more favorable in energy, the direction γ-Si_3N_4 will choose nevertheless depends on the energy necessary to activate the transformation. The transformation $\gamma \rightarrow \beta$ certainly is reconstructive and necessitates the breaking and the rearrangements of many bonds. An activation barrier, therefore, can roughly be estimated with the typical bond energy of Si_3N_4, which in turn can be extracted from Fig. 1, left side, to be approximately 4.8 eV; a typical value for the energy of a covalent bond. The activation barrier of the $\gamma \rightarrow$ wII transformation, however, will come out significantly lower than that.

3.4. Structural relation between the spinel and wII structure

As a matter of fact, the activation barrier of the $\gamma \rightarrow$ wII transition can be computed directly. To facilitate this, we first show that the spinel structure and the structure of willemite-II are related and connected by a *continuous* path. The relation follows a mechanism well known in structural transformations, namely the Bain correspondence [29], which is illustrated in Fig. 3.

The Bain correspondence then connects the anion arrangement in the spinel structure, which is approximately fcc, to the arrangements of anions in the wII structure, which is approximately bcc, as we have indicated earlier. While the Bain strain only transforms the anion sublattice (except for a marginal distortion of the ideal arrangements), the cations are related by an additional shuffle distortion. Si atoms of γ-Si_3N_4, which are octahedrally coordinated, shuffle towards an edge of the octahedron and become tetrahedrally coordinated. The effective coordination change of the cations during the transformation is shown in Fig. 4.

The structural relation is comprehended easily in more formal terms. Spinel has the space group symmetry $Fd\bar{3}m$ and the wII structure adopts $I\bar{4}3d$. A common subgroup of both structures thus is $I\bar{4}2d$ (122). The appropriate description of both wII-Si_3N_4 and

---

[1] Of more than a dozen substitution patterns, a structure related to α-Si_3N_4 (instead of one to β-Si_3N_4) came out as the energetically most favorable modification of Si_2CN_4. For yet another modification of Si_2CN_4, see [28].
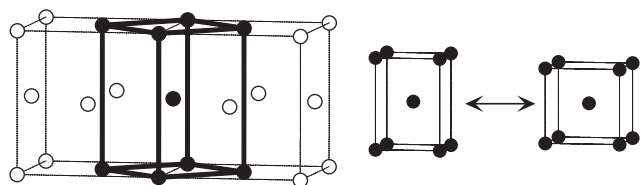
Fig. 3. The Bain correspondence connects the crystal lattice of fcc and bcc by a homogeneous strain. The left side shows two unit cells of the fcc lattice, and inscribed a body centered tetragonal (bct) cell with appropriate ratio c/a, representing the same structure. The right side illustrates the Bain strain that transforms the bct to the bcc and vice versa.
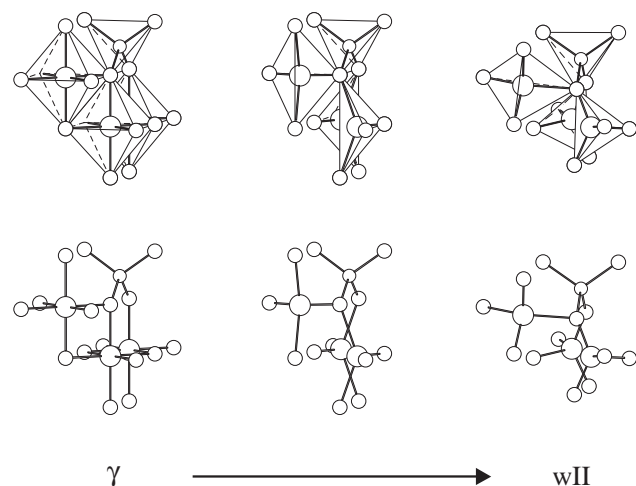

Fig. 4. Polyhedral view (upper panel) and ball-and-stick representation (lower panel) of the coordination change of the octahedral cations (large unfilled circles) in spinel during the transformation to wII. The tetrahedral cations (small unfilled circles) are unaffected. The transformation consists of a Bain strain of the anion lattice (filled circles) plus a shuffle distortion of the octahedral cations.

Table 2
Crystallographic description of the spinel and the wII structure using the common space group $I\bar{4}2d$ (122)

| Atom | Wy | γ-Si$_3$N$_4$ | | | wII-Si$_3$N$_4$ | | |
| | | $a = a_{sp},\ c/a = \sqrt{2}$ | | | $a = c = a_{wII}$ | | |
		x	y	z	x	y	z
Si1	4a	0	0	0	0	0	0
Si2	8d	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{8}$	$\frac{5}{8}$	$\frac{1}{4}$	$\frac{1}{8}$
N	16e	0	$\frac{1}{4} - 2x_{sp}$	$\frac{3}{8} + x_{sp}$	x_{wII}	$\frac{1}{4} + x_{wII}$	$\frac{3}{8} + x_{wII}$

a_{sp} and a_{wII} are lattice constants, x_{sp} and x_{wII} the anion positional parameter of conventional settings of spinel and wII structures, respectively. Wy denotes the Wyckhoff position.

γ-Si$_3$N$_4$ using this space group is given in Table 2. Apparently, the differences between the crystal coordinates are small: the Si1 position, tetrahedral in both γ-Si$_3$N$_4$ and wII-Si$_3$N$_4$, is identical, the Si2 position, octahedral Si in γ-Si$_3$N$_4$, but tetrahedral in wII-Si$_3$N$_4$, shifts by $\frac{1}{8}$ along the $\langle 100 \rangle$ direction, and the anion position shifts by a vector which is even shorter. It can thus easily be deciphered that the spinel structure can be transformed into the wII structure along a path which retains the space group symmetry $I\bar{4}2d$. The most significant differences between the two structures, however, are the lattice constants a and c, which are connected by the homogenous Bain strain.

3.5. Calculating the energy profile along the reaction coordinate

A transformation between the two structures of wII-Si$_3$N$_4$ and γ-Si$_3$N$_4$, that retains the space group symmetry $I\bar{4}2d$, can then be described as a reaction along a path within the six-dimensional configuration space, defined by the lattice constants a and c of the tetragonal cell, the x-coordinate of the Si2 position, and the three coordinates of the anion position.[2] Instead of a and c, we choose the cell volume V and the ratio of lattice constants c/a as alternative descriptors. The calculation of the complete six-dimensional potential energy surface (PES), however, would be too expensive. As a first approximation of the transformation path, we constructed a reaction coordinate by simultaneous linear interpolation of all six free structural parameter. Static calculations of these intermediate geometries yield a reliable upper boundary of the activation barrier. The approximation can be improved by some energy minimization. We allowed the anions within the structure to relax, still keeping cell parameter $(V, c/a)$ and cation position (x_{Si2}) fixed. It is worthy to note that the anions still move along a continuous path.

The results of these calculations are shown in Fig. 5. We estimate a barrier of 1.02 eV/f.u. Si$_3$N$_4$ for the $\gamma \to$ wII transformation in Si$_3$N$_4$ from the static calculations. Optimizing the energy profile by relaxing the anion position yields a value of 0.92 eV. In comparison to the typical bond energy of a Si–N bond, which is necessary to break during a reconstructive process, this is a significantly smaller barrier. The energy barrier *per atom* along the optimized path is about 0.13 eV. Translated into a kinetic energy this corresponds to a temperature of about 1500 K, which matches the experimental decomposition temperatures of γ-Si$_3$N$_4$ suspiciously close [13]. We accessed the energy profile a second time within the same approach. This time we used the cell volumes of γ-Si$_3$N$_4$ and wII-Si$_3$N$_4$ calculated at 7 GPa, which is the pressure of equal enthalpy of both structures. Only minor differences of the energy profile are found.

The same formalism was applied to the transformation between γ-Ge$_3$N$_4$ and a still hypothetical wII-Ge$_3$N$_4$.

---

[2] Although both γ-Si$_3$N$_4$ and wII-Si$_3$N$_4$ are described with one parameter for the anion position, an intermediate between these two antipodes does not follow this simple description.
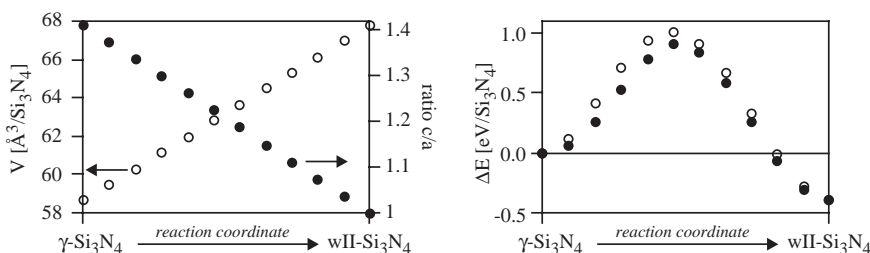
Fig. 5. Left: Volume (open circles) and ratio of lattice constants c/a (filled circles) defining the reaction coordinate of the γ-$Si_3N_4 \rightarrow$ wII-Si_3N_4 transition. Note that we used the tetragonal setting of the spinel structure. The position of the second cation (x_{Si2}) was interpolated between $\frac{1}{2}$ and $\frac{5}{8}$. Right: Energy profile along the reaction coordinate. Open circles are for static calculations (all six free parameter interpolated simultaneously), filled circles for the optimized profile (interpolating only V, ratio c/a, and x_{Si2}, while optimizing the anion positions). The interpolation was done linearly for 11 points between γ-Si_3N_4 and wII-Si_3N_4.
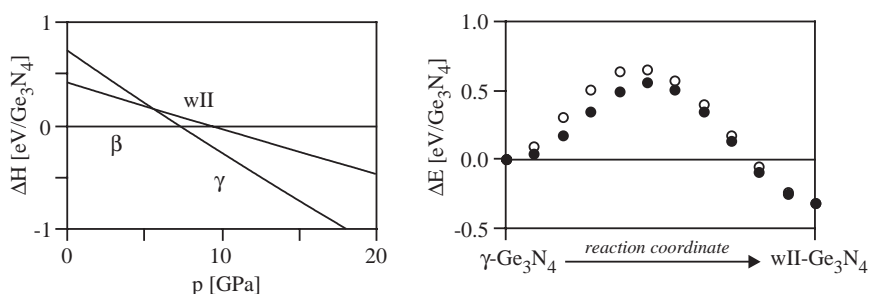

Fig. 6. Left: Enthalpy–pressure (ΔH–p) diagrams (right, relative to β-Ge_3N_4) of β-Ge_3N_4, wII-Ge_3N_4, and γ-Ge_3N_4. Right: Energy profile of the $\gamma \rightarrow$ wII transformation. Open circles are for static calculations (all six free parameter interpolated simultaneously), filled circles for the optimized profile (interpolating only V, ratio c/a, and x_{Si2}, while optimizing the anion positions). The interpolation was done linearly for 11 points between γ-Ge_3N_4 and wII-Ge_3N_4.

The enthalpy–pressure (ΔH–p) diagram of Ge_3N_4 is shown in Fig. 6, on the left. Overall, the trends are comparable to those of Si_3N_4, while the actual energy differences between the phases are slightly smaller. The transition pressure $p_t^{\beta \rightarrow \gamma}$ is calculated to 7 GPa, somewhat lower than experimental results [4,5]. Once synthesized, γ-Ge_3N_4 might transform to wII-Ge_3N_4 at pressures below 5.5 GPa. It is worth noting that the enthalpy difference to β-Ge_3N_4 at this point is significantly lower than for the Si_3N_4 counterpart. For the structures at zero pressure, we constructed a path between γ-Ge_3N_4 and wII-Ge_3N_4 in a similar way as done before for Si_3N_4. The activation barrier came out 0.66 eV from static calculations. Additional relaxations of the anions lowered this value to 0.56 eV. Taken *per atom*, this energy corresponds to merely 930 K, or 650°C.

3.6. Vibrational spectra of spinel and wII phases

The different lattice constants of spinel and wII will allow a distinction between the two phases based on diffraction methods. Another typical analytic tool for phase identification, especially in the diamond-anvil cell, is the micro-Raman technique. Consequently, we calculated the zone-center vibrational spectra of the wII and spinel polymorphs of Si_3N_4 and Ge_3N_4. The

Table 3
Calculated frequencies of Raman-active zone-center phonon modes of wII-Si_3N_4 and wII-Ge_3N_4 (in cm^{-1})

	E	T_2	E	T_2	T_2	T_2	A_1	E	T_2
wII-Si_3N_4	939	902	851	849	690	380	336	329	279
wII-Ge_3N_4	842	767	731	715	428	239	199	214	171

assessment is made within the LDA and is based on the LDA-optimized structure, because the LDA usually yields a better description of elastic and vibrational properties. The point groups of spinel and the wII structure are O_h and T_d, respectively. The group theoretical analysis yields 5 Raman-active modes for the spinel structure distributed as $A_{1g} + E_g + 3T_{2g}$ and 9 Raman-active modes for the wII structure distributed as $A_1 + 3E + 5T_2$. We obtained the zone-center phonon modes by diagonalizing the dynamical matrix generated via finite-difference methods. Results calculated for Si_3N_4 and Ge_3N_4 both as spinel and wII structures are listed in Tables 3 and 4, respectively. The frequencies we obtain for γ-Ge_3N_4 are almost identical to those previously reported [11,12], which in turn match the experimental spectra of γ-Ge_3N_4 very closely. The basic difference between the vibrational spectra of

Table 4
Calculated frequencies of Raman-active zone-center phonon modes of γ-Si_3N_4 and γ-Ge_3N_4 (in cm^{-1})

	A_{1g}	T_{2g}	E_g	T_{2g}	T_{2g}
γ-Si_3N_4	946	838	518	500	413
γ-Ge_3N_4	831	719	471	574	244

spinel and wII phases is the number of Raman-active modes: 5 for spinel and 9 for the wII type. Most useful for a phase characterization will be the range 600–1000 cm^{-1}, in which the wII phase has twice as much modes as spinel.

4. Summary and conclusion

The willemite-II structure type may become accessible for nitride compounds of carbon, silicon, and germanium. Within the C_3N_4 phase diagram it is more favorable than a spinel modification and constitutes the enigmatic high-pressure structure of C_3N_4, first proposed by Teter and Hemley [25]. For Si_3N_4 and Ge_3N_4, on the other side, it is the spinel type, which is accessible via standard techniques using equilibrium thermodynamics, but not the wII modification. The calculations we presented in this paper show, however, that for both phase systems the wII type has a pressure range in which it is more favorable in enthalpy than spinel, but less favorable than the phenacite ground state structure. Alloying Si_3N_4 with carbon then alters the enthalpy of spinel and wII phases. Consequently, there is a fair chance to get a wII modification of Si_2CN_4.

A pure Si_3N_4 or Ge_3N_4 phase with wII structure, nevertheless, is within experimental reach. The structures of spinel and wII are related by a mechanism similar to the Bain correspondence, which plays a significant role in martensitic and other diffusionless phase transformations [30]. This mechanism can be utilized to obtain the metastable wII modification from spinel by a kinetically activated process. At zero pressure, where the wII modification is energetically more favorable than spinel for both Si_3N_4 and Ge_3N_4, the activation barrier for a spinel → wII transformation is 0.92 and 0.56 eV/f.u., for Si_3N_4 and Ge_3N_4, respectively. Therefore, at temperatures of 1500 and 930 K this transformation will play a significant role in the decomposition of γ-Si_3N_4 and γ-Ge_3N_4, respectively. A recovery of the wII modification will require high experimental skills and propitious conditions, since the excess energy of the transformation needs to be dissipated to avoid deterioration. While the spinel modification of Si_3N_4 is meanwhile available in high quantities through shock synthesis, appropriate amounts of γ-Si_3N_4 may be used as solid state precursor for a synthesis of wII-Si_3N_4. If this transformation is indeed observed, it would be a pioneering example in ceramic materials.

References

[1] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueß, P. Kroll, R. Boehler, Nature (London) 400 (1999) 340–342.
[2] M. Schwarz, G. Miehe, A. Zerr, E. Kroke, B. Poe, H. Fuess, R. Riedel, Adv. Mater. 12 (2000) 883–887.
[3] E. Soignard, M. Somayazulu, J.J. Dong, O.F. Sankey, P.F. McMillan, J. Phys. Condens. Matter 13 (2001) 557–563.
[4] G. Serghiou, O. Tschauner, A. Zerr, R. Böhler, J. Chem. Phys. 111 (1999) 4659–4662.
[5] K. Leinenweber, M. O'Keeffe, M. Somayazulu, H. Hubert, P.F. McMillan, G.H. Wolf, Chem. Eur. J. 5 (1999) 3076–3078.
[6] W.Y. Ching, S.-D. Mo, I. Tanaka, M. Yoshiya, Phys. Rev. B 63 (2001) 064102.
[7] W.Y. Ching, S.-D. Mo, L. Oyuang, Phys. Rev. B 63 (2001) 245110.
[8] P. Kroll, J. von Appen, Phys. Stat. Sol. B 226 (2001) R6–R7.
[9] W.Y. Ching, S.-D. Mo, L. Z. Oyuang, P. Rulis, I. Tanaka, M. Yoshiya, J. Am. Ceram. Soc. 85 (2002) 75–80.
[10] K. Tatsumi, I. Tanaka, H. Adachi, F. Oba, T. Sekine, J. Am. Ceram. Soc. 85 (2002) 7–10.
[11] S.K. Deb, J.J. Dong, H. Hubert, P.F. McMillan, O.F. Sankey, Solid State Comm. 114 (2000) 137–142.
[12] J.J. Dong, O.F. Sankey, S.K. Deb, G. Wolf, P.F. McMillan, Phys. Rev. B 61 (2000) 11979–11992.
[13] T. Sekine, J. Am. Ceram. Soc. 85 (2002) 113–116.
[14] H.L. He, T. Sekine, T. Kobayashi, K. Kimoto, J. Appl. Phys. 90 (2001) 4403–4406.
[15] T. Sekine, private communication.
[16] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558–561.
[17] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251–14269.
[18] G. Kresse, J. Furthmüller, Comput. Mat. Sci. 6 (1996) 15–50.
[19] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169–11186.
[20] J.P. Perdew, in: P. Ziesche, H. Eschrig (Eds.), Electronic Structure of Solids '91, Akademie Verlag, Berlin, 1991, p. 11.
[21] D.M. Teter, R.J. Hemley, G. Kresse, J. Hafner, Phys. Rev. Lett. 80 (1998) 2145–2148.
[22] Th. Demuth, Y. Jeanvoine, J. Hafner, J.G. Angyan, J. Phys.: Condens. Matter 11 (1999) 3833–3874.
[23] P. Kroll, Z. Allg. Anorg. Chem, in press.
[24] P. Kroll, W. Schnick, Chem. Eur. J. 8 (2002) 3530–3537.
[25] D.M. Teter, R.J. Hemley, Science 271 (1996) 53–55.
[26] S.-D. Mo, L. Ouyang, W.-Y. Ching, I. Tanaka, Y. Koyama, R. Riedel, Phys. Rev. Lett. 83 (1999) 5046–5049.

[27] T. Hughbanks, Y.C. Tian, Solid State Commun. 96 (1995) 321–325.

[28] P. Kroll, R. Riedel, R. Hoffmann, Phys. Rev. B 60 (1999) 3126–3139.

[29] E.C. Bain, Trans. Am. Inst. Min. Met. Eng. 70 (1924) 25.

[30] L. Delaey, R.W. Cahn, P. Haasen, E.J. Kramer, in: P. Haasen (Ed.), Materials Science and Technology Volume 5: Phase Transformations in Solids, Wiley-VCH, Weinheim, Germany, 1990, p. 339.