

# First-Principles Lattice Dynamics Calculations of the Phase Boundary Between $\beta$ -Si<sub>3</sub>N<sub>4</sub> and $\gamma$ -Si<sub>3</sub>N<sub>4</sub> at Elevated Temperatures and Pressures

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**Abstract:** The phase boundary between  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> is investigated at high pressure and high temperature using first-principles lattice dynamics calculations within the quasi-harmonic approximation. We find a positive slope of the phase boundary, hence, at higher temperatures it requires higher pressures to synthesize the high-pressure polymorph of silicon nitride. It turns out that the thermal expansion of the spinel-type  $\gamma$ -phase is larger than that of the phenacite-type  $\beta$ -phase. On the other side, pressure affects more the volume of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> than of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, reflected in the higher bulk modulus of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> up to about 40 GPa. The origin of the different temperature behavior of these phases, consequently, is rooted in a larger volume dependence of the zero point energy in  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> in comparison to  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

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**Key words:** silicon nitride; phase transitions; lattice dynamics; thermal expansion; density functional calculations

## Introduction

About a decade ago, a new polymorph of silicon nitride,  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> with spinel-type structure, has been realized by high-temperature/high-pressure chemical synthesis.<sup>1</sup> The first report gave a pressure of 15 GPa and a temperature of 2000 K needed to favor the formation of the  $\gamma$ -phase over the  $\beta$ -phase. Additional enthalpy-pressure computations that went along with the experiment indicated a transition pressure of 12.1 GPa. Subsequent experimental studies using amorphous silicon and nitrogen-containing precursors instead of elemental silicon and nitrogen located the phase boundary between 10 and 13 GPa at temperatures between 1600 and 2000 K.<sup>2</sup> No account for a conversion or back-transformation from the  $\gamma$ -phase to the  $\beta$ -phase has been given.

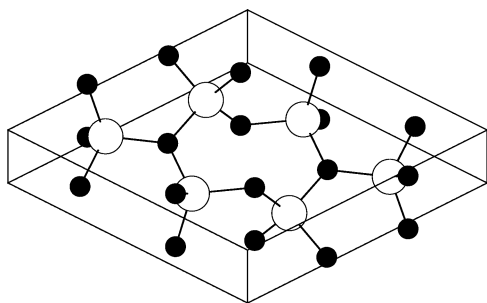
At high temperatures and high pressures it is usually difficult to determine correctly the phase boundaries of solids due to the sluggish kinetics involved, especially if the transformation is reconstructive. Consequently, computations can be employed as a supporting tool to study such problems, although they may idealize the true experimental conditions to a certain extent. Studying the phase boundary at high pressures and high temperatures then requires an assessment of the thermal properties as a function of pressure. Several studies addressed thermal properties of the polymorphs of silicon nitride at ambient pressure. Focussing on

the spinel-type modification, Jiang et al. reported a linear expansion coefficient  $\alpha_{\text{lin}}$  of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> of  $3.9 \times 10^{-6} \text{ K}^{-1}$  at 300 K.<sup>3</sup> The thermal expansion increases with increasing temperature up to  $7.0 \times 10^{-6} \text{ K}^{-1}$  at 1100 K. Further investigations are in reasonable agreement to these results, given the different syntheses of the investigated samples and experimental uncertainties.<sup>4,5</sup> In all three experimental studies, additional computations have been employed to substantiate the respective findings. Overall, it was revealed that the thermal expansion coefficient of spinel-type silicon nitride is significantly larger than that of the phenacite-type polymorph  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, for which an  $\alpha_{\text{lin}}$  of  $1.2 \times 10^{-6} \text{ K}^{-1}$  at 300 K up to  $3.6 \times 10^{-6} \text{ K}^{-1}$  at 1300 K has been determined.<sup>6</sup>

In this study, we address the pressure–temperature phase diagram of silicon nitride and, explicitly, compute the thermal properties of  $\beta$ - and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> as a function of pressure using first-principles lattice dynamics calculations. Our focus is the phase boundary between  $\beta$ -Si<sub>3</sub>N<sub>4</sub>- and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> and its temperature dependence as the pressure increases. The crystal structures of  $\beta$ - and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> that provide the base for our investigations are shown in Figures 1

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**Figure 1.** Crystal structure of  $\beta$ - $\text{Si}_3\text{N}_4$  ( $P6_3/m$ ). Open and filled spheres denote silicon and nitrogen atoms, respectively.

and 2, respectively. Si atoms in the phenacite-type  $\beta$ -structure are four fold approximately tetrahedrally coordinated. As a substantial difference, the spinel-type  $\gamma$ -structure comprises two-thirds of the Si atoms octahedrally coordinated, the remaining Si are tetrahedrally coordinated. As a consequence of this higher average coordination, the density of  $\gamma$ - $\text{Si}_3\text{N}_4$  is about 26% larger than that of  $\beta$ - $\text{Si}_3\text{N}_4$ .

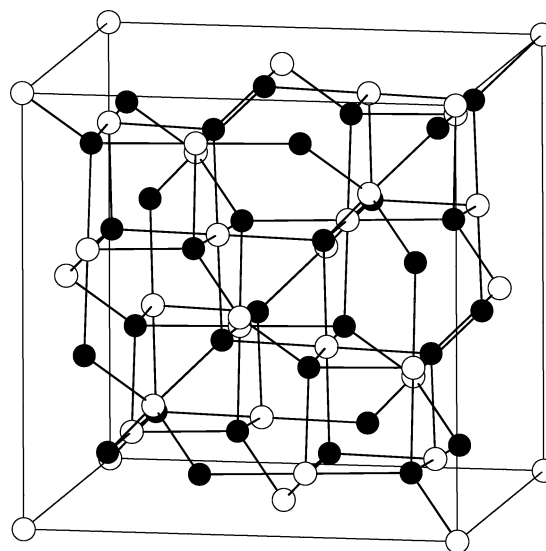
## Methods

Our first-principles calculation were carried out with the Vienna ab-initio simulation package (VASP).<sup>7–9</sup> We used the projector augmented wave (PAW) method<sup>10</sup> in the framework of density functional theory within the generalized gradient approximation according to Perdew-Burke-Ernzerhof (PBE)<sup>11</sup> together with a cut-off energy of 500 eV for the expansion of the wave function into a plane wave basis set. For a given volume, the structure is optimized and its phonon spectrum is computed. Furthermore, the free enthalpy-like function  $G(p, T)$  is computed according to<sup>12</sup>

$$G[p, T] = \min_V \{U(V) + F_{\text{phonon}}(V; T) + pV\}, \quad (1)$$

Herein,  $p$ ,  $T$ , and  $V$  denote pressure, temperature, and volume, respectively.  $U$  is the internal energy and  $F_{\text{phonon}}$  is the phonon free energy calculated within the quasi-harmonic approximation (QHA) (e.g., 13). The phonon contributions to the free enthalpies were calculated using the frozen phonon method as implemented in the *fropho* code.<sup>14</sup> The procedure is repeated for several volumes and if the investigated phase is a stable phase, then  $G(p, T)$  corresponds to its free enthalpy. Finally, Murnaghan's equation of state<sup>15</sup> was used to fit the calculated values and to derive a bulk modulus.

To allow for an accurate assessment of the free energy, some severe convergence criteria have to be employed to avoid the appearance of imaginary frequencies within the Brillouin zone. The energy was considered to be converged when differences in consecutive steps were lower than  $10^{-9}$  eV. Forces and stresses were converged until they became less than  $10^{-6}$  eV/Å and  $10^{-4}$  GPa, respectively. The Brillouin zones were sampled by a  $4 \times 4 \times 8$  ( $\beta$ - $\text{Si}_3\text{N}_4$ ) and by a  $4 \times 4 \times 4$  of ( $\gamma$ - $\text{Si}_3\text{N}_4$ , primitive unit cell)  $k$ -point mesh generated according to the Monkhorst-Pack scheme. We then built supercells for the frozen phonon calculations, both a  $2 \times 2 \times 2$  supercell for  $\beta$ - $\text{Si}_3\text{N}_4$  and for  $\gamma$ - $\text{Si}_3\text{N}_4$ . A finite atomic displacement of 0.01 Å was used. Overall, the frozen phonon calculations were carried out at 41 different volumes for both phases. We used a  $8 \times 8 \times 20$  and

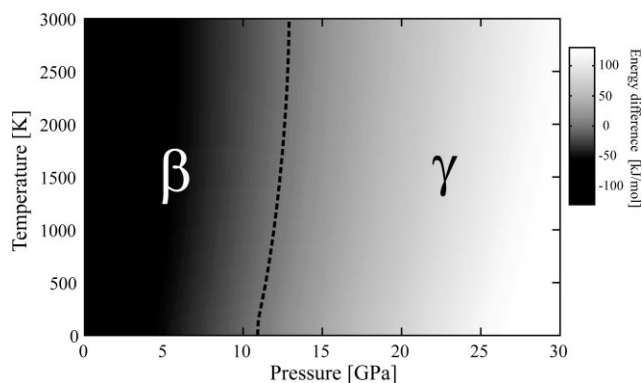


**Figure 2.** Crystal structure of  $\gamma$ - $\text{Si}_3\text{N}_4$  ( $Fd\bar{3}m$ ). Open and filled spheres denote silicon and nitrogen atoms, respectively.

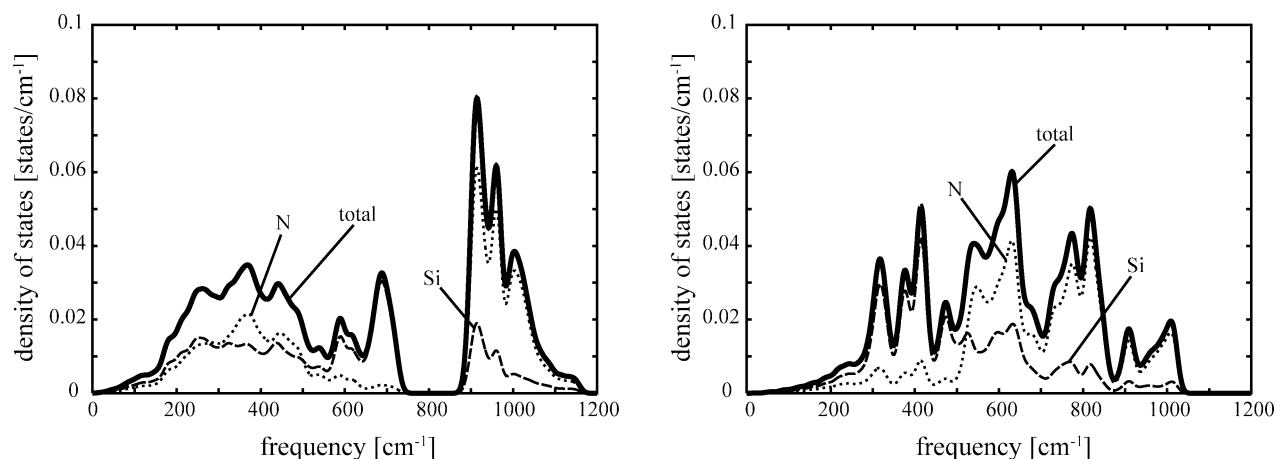
a  $12 \times 12 \times 12$  mesh for the Brillouin zone sampling of  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\gamma$ - $\text{Si}_3\text{N}_4$ , respectively. Addressing the relevance of  $\alpha$ - $\text{Si}_3\text{N}_4$ , we could not find a significant difference ( $>0.002$  eV/atom) in enthalpy up to 20 GPa between the two polymorphs  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  in our calculations. Further (preliminary) calculations also show an almost matching entropy contribution to the free enthalpy. This renders the two polymorphs virtually identical in free enthalpy. Consequently, we decided to concentrate on  $\beta$ - $\text{Si}_3\text{N}_4$  with its smaller unit cell to facilitate the computations.

## Results

In Figure 3, we show the calculated pressure–temperature ( $P$ – $T$ ) phase diagram of silicon nitride including the two phases  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\gamma$ - $\text{Si}_3\text{N}_4$ . The difference in the free enthalpy-like functions between the two phases, hence the value of  $\Delta G$ , is represented by the intensity of the gray scale. The phase boundary corresponds to the line drawn; here the difference in  $\Delta G = 0$ . Accordingly, while  $\beta$ - $\text{Si}_3\text{N}_4$  is stable at low pressure and  $\gamma$ - $\text{Si}_3\text{N}_4$  at high pressure, the



**Figure 3.**  $P$ - $T$  phase diagram. The energies are given per formula unit.



**Figure 4.** Phonon DOSs of the  $\beta$ -phase (left) and the  $\gamma$ -phase (right).

slope of the phase boundary between the two phases is found to be positive. Consequently, higher temperatures will require some higher pressures for inducing the  $\beta$  to  $\gamma$ -phase transition.

We show the phonon density of states (phonon-DOS) as a function of phonon frequencies of both phases in Figure 4. The phonon-DOS of  $\beta$ - $\text{Si}_3\text{N}_4$  is split into two regions. The occurrence of a gap is attributed to the anisotropic crystal structure. Although N is twice as light as Si, even in the low-frequency regime nitrogen contributes to the phonon-DOS. This is due to some soft vibrations that occur at the Brillouin zone boundary, which are localized within the  $a$ - $b$  plane. For  $\gamma$ - $\text{Si}_3\text{N}_4$  on the other side we do not observe a gap, although a separation into N-dominated high-frequency vibrations and Si-dominated low-frequency vibrations is visible. The compact structure, therefore, drives both regions to overlap considerably.

To study the thermal expansion of a solid structure, the volume dependence of its phonon-DOS is a necessary ingredient, since volume and temperature are implicitly related within the QHA. In principle, the phonon free energy also depends directly on temperature. However, investigating the volume dependence of the phonon-DOS only is usually enough to derive a trend of the phonon free energy with temperature and volume. The zero-point energy of a phonon system is indicative of how its phonon-DOS changes with volume, because the zero-point energy  $E_{\text{zero}}$  is related to the phonon-DOS via

$$E_{\text{zero}} \propto \frac{1}{2} \sum_{\mathbf{k}, \nu} \hbar \omega(\mathbf{k}, \nu) \quad (2)$$

Herein,  $\mathbf{k}$  is a wave vector, and  $\nu$  a phonon frequency. In Figure 5, we then plot the frequency depending part of the zero-point energies of  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\gamma$ - $\text{Si}_3\text{N}_4$  as a function of volume. A negative slope indicates that a volume increase decreases the phonon free energy at 0 K, which is generally expected to be true at finite temperature. However, the data also shows a steeper slope for the curve of  $\gamma$ - $\text{Si}_3\text{N}_4$  than for  $\beta$ - $\text{Si}_3\text{N}_4$ . Consequently, the  $\gamma$ -phase will tend to exhibit a larger thermal expansion than the  $\beta$ -phase.

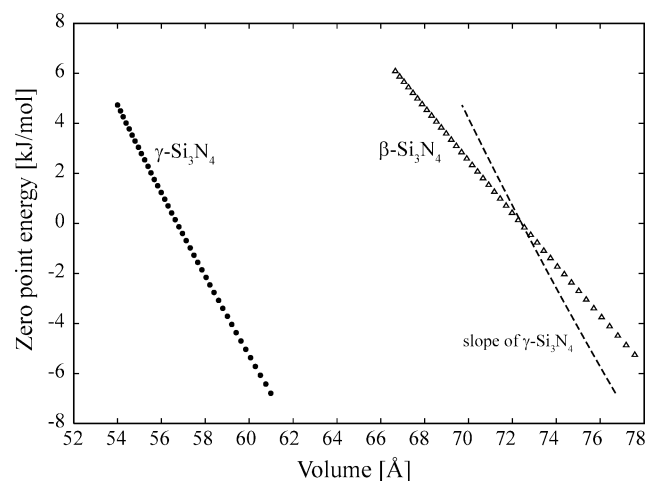
The computed volumes of the enthalpy confirm this trend, derived through inspection of the zero-point energies. Note, that the

free enthalpy in turn was accessed as the minimum value found for computations at several volumes. In Figure 6, we show the overall volume changes of both the  $\beta$ - and the  $\gamma$ -phase in the pressure-temperature space. The thermal expansion of  $\gamma$ - $\text{Si}_3\text{N}_4$  is indeed larger than that of  $\beta$ - $\text{Si}_3\text{N}_4$ . However, at the same time,  $\gamma$ - $\text{Si}_3\text{N}_4$  is also less compressible than  $\beta$ - $\text{Si}_3\text{N}_4$ .

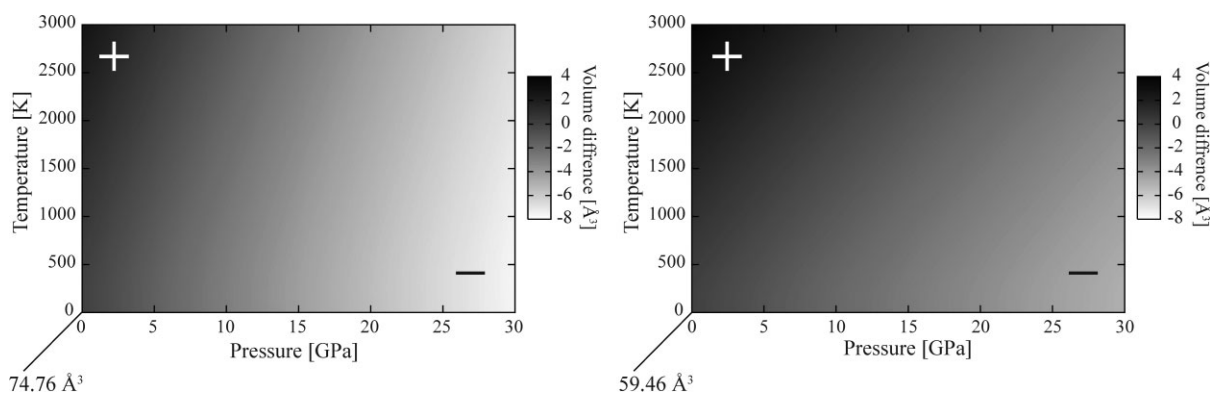
We present the temperature- and pressure-dependent bulk modulus, the inverse of compressibility, for  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\gamma$ - $\text{Si}_3\text{N}_4$  in Figure 7. As it is well known,  $\gamma$ - $\text{Si}_3\text{N}_4$  has a larger bulk modulus than  $\beta$ - $\text{Si}_3\text{N}_4$ . As it turns out, however, temperature affects the bulk modulus of  $\gamma$ - $\text{Si}_3\text{N}_4$  more than that of  $\beta$ - $\text{Si}_3\text{N}_4$ .

## Discussion

As in preceding studies of Jiang<sup>3,5</sup> and Hintzen,<sup>4,6</sup> we find that the thermal properties of  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\gamma$ - $\text{Si}_3\text{N}_4$  at ambient pressures are



**Figure 5.** Zero point energies of the  $\beta$ -phase (red points) and the  $\gamma$ -phase (blue points) as a function of volume. To compare their slopes, a copy of  $\gamma$ -phase is placed near that of  $\beta$ -phase. The energies are given per formula unit.



**Figure 6.** Volume changes of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> (left) and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> (right) in the pressure–temperature phase diagram. The change (per formula unit) is indicated relative to their volumes at 0 K and 0 GPa.

quite different: while  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> is less compressible than  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, it displays the larger expansion upon heating.  $\beta$ -Si<sub>3</sub>N<sub>4</sub> on the other side is more susceptible for volume change under pressure than at elevated temperatures. In this study, we show that the trend in thermal properties lasts even at high pressures. The direct implication of this is a positive slope for the phase boundary between  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>. Hence, with increasing temperature it requires a higher pressure to favor the spinel-type structure over the ground-state structure of the phenacite-type. Consequently, the transition pressure  $p_t$  as calculated in the initial report<sup>1</sup> provides only a lower estimate of the experimental transition pressure. It has to be noted, however, that the slope of the computed phase boundary is quite steep: there is only a difference of about 2 GPa when comparing  $p_t$  at zero and 2000 K. Impurities as well as crystal morphology can account for a similar effect on the transition pressure. For a discussion of the effect of oxygen on  $p_t$  see ref. 16.

Another consequence of the opposite properties is that at about 40 GPa the compressibility of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> equals that of  $\gamma$ -Si<sub>3</sub>N<sub>4</sub>, see Figure 7 for the bulk moduli of the two polymorphs. Of course, at such pressures  $\beta$ -Si<sub>3</sub>N<sub>4</sub> is only metastable. Nevertheless, once a volume reduction of about 12% (corresponding to 35 GPa) is reached, there is no difference in compressibility of tetrahedral and octahedral sites in Si<sub>3</sub>N<sub>4</sub>. These results imply a different bond strength versus bond length behavior for these environments in silicon nitride. Supplementing the reasoning in ref. 5, this relation

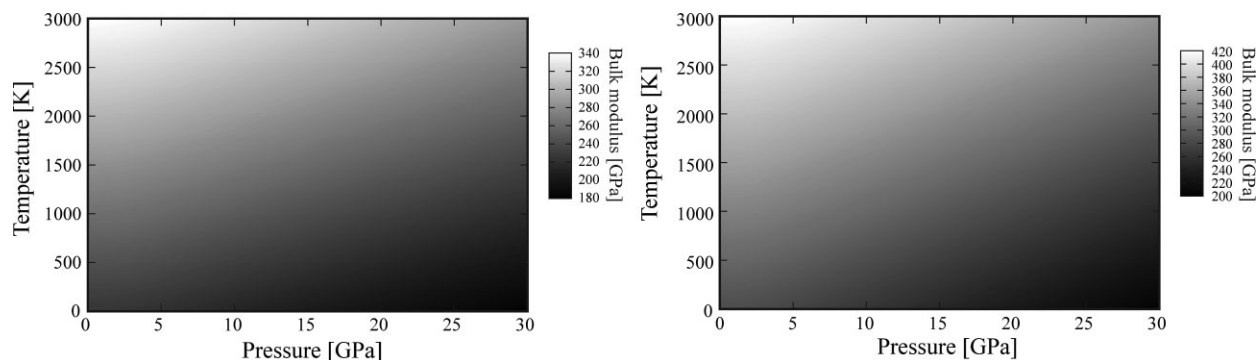
is severely impacted by the applied pressure and not only by the temperature.

### Summary

Using first-principles lattice dynamics calculations to investigate the vibronic contributions to the free enthalpies of phenacite- and spinel-type silicon nitride, we find a positive slope of the phase boundary between  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> in the pressure–temperature phase diagram. Although the spinel-phase has a larger bulk modulus than the phenacite-phase, its thermal expansion is also larger. The roots of this behavior are in a larger volume dependence of the zero-point energy in  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> in comparison to  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. Overall, the work of pressure,  $p \cdot V$ , dominates the transition pressure of the  $\beta$  to  $\gamma$  transition. The precise slope of the phase boundary, however, is governed by small energy differences, which depend on the explicit phonon structure.

### Acknowledgments

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**Figure 7.** Bulk moduli of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> (left) and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> (right) as a function of temperature and pressure.

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