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Phonon spectrum and thermal properties of cubic Si$_3$N$_4$
from first-principles calculations

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The phonon spectrum of cubic Si$_3$N$_4$ was calculated by first-principles techniques. The results permit an assessment of important mechanical and thermo-dynamical properties such as the bulk modulus, lattice specific heat, vibration energy, thermal expansion coefficient, and thermal Gruneisen parameter for this compound. The calculated phonon spectrum shows a gapless spectrum extending to a cutoff energy of $\sim 1030$ cm$^{-1}$. The calculated Raman- and infrared-active phonon frequencies are compared with measured data in the literature. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566473]

I. INTRODUCTION

A third modification of silicon nitride in the form of a cubic spinel-type structure ($\gamma$-Si$_3$N$_4$) was discovered in 1999 by Zerr et al.1–3 This new form of silicon nitride has attracted much attention for several reasons. First, in $\gamma$-Si$_3$N$_4$ the Si atoms are positioned at both the tetrahedral and octahedral sites, i.e., some Si are sixfold coordinated, which is very rare in binary compounds. Second, $\gamma$-Si$_3$N$_4$ is a semiconductor with an energy gap of about $3.5$ eV4–7 and has potential applications in electronics.8,9 Furthermore, both first-principles calculations and experiments indicate that $\gamma$-Si$_3$N$_4$ has a hardness comparable to the hardest known oxide (Stishovite, a high-pressure phase of SiO$_2$),1,10–13 and significantly greater than the hardness of the two well-known hexagonal polymorphs.14 The $\gamma$-Si$_3$N$_4$ has also a very high resistance in air to oxidation (up to 1600 K).15,16 Therefore, $\gamma$-Si$_3$N$_4$ has the potential to be used as hard materials, next to the two widely used $\alpha$ and $\beta$ forms. Different preparation methods have also been developed. Recently, Sekine et al.15,17 have prepared $\gamma$-Si$_3$N$_4$ by shock-induced transformation of $\beta$-Si$_3$N$_4$ powder, which may produce $\gamma$-Si$_3$N$_4$ in large scale.

A full characterization of the physical properties of $\gamma$-Si$_3$N$_4$ is important for applications. Due to the difficulties in the preparation of pure $\gamma$-Si$_3$N$_4$ samples,13,18 theoretical methods, especially first-principles techniques, can help. For example, Mo et al. have calculated the band structure and dielectric properties.4 In this article we report first-principles calculations of the phonon spectrum for $\gamma$-Si$_3$N$_4$. The dispersion curve and the partial phonon densities of states (PDOS) for both tetrahedral and octahedral Si atoms as well as the N atoms are reported. The Raman and infrared (IR) active modes, which can be used for characterization, are included. Using the quasiharmonic approximation (QHA), the thermal properties, including the thermal expansion coefficient, of $\gamma$-Si$_3$N$_4$ are calculated. We hope that this information will help to further an understanding of the relationship between the crystal structure on one hand and mechanical and thermal properties of $\gamma$-Si$_3$N$_4$ and related materials on the other hand, and is expected to benefit the developments of new materials for industry.

II. DETAILS OF THEORETICAL CALCULATIONS

The calculations were carried out using the first-principles molecular-dynamics computer code vasp (Vienna ab initio simulation program).19–21 This program first calculates the electronic structure from first-principles, and then the interatomic forces via the Hellmann–Feynman theorem. The phonon frequencies and eigenvectors were obtained by diagonalization of the dynamical matrix. Details of the methods can be found in Refs. 22 and 23. Calculations were applied to a conventional unit cell (1 $\times$ 1 $\times$ 1), which consists of four primitive unit cells. Periodic boundary conditions were imposed. All internal coordinates of the atoms have been fully relaxed. Selected atoms were displaced slightly (about 0.01 Å) away from their equilibrium positions, and the corresponding interatomic forces were calculated. From the calculated forces and the displacements the interatomic force constants were obtained. Using these force constants, the phonon frequencies were determined. Long-range effects on the force constants have been neglected. These long-range effects have no effect on the modes at $\Gamma$, as well as a few
other high-symmetry points in the Brillouin zone, which are exact. In a related study (on MgAl₂O₄ spinel, Ref. 23) we found only a minor influence of this approximation on the PDOS. In principle, the phonon spectrum of Fig. 1 should be most severely affected (except for the exact, high-symmetry points Γ and X). In our checks on elongated cells (these included the long-range effects, see below) we, however, found that the deviations from the converged values are small (typically 5 cm⁻¹).

This method does not account for the effect of the macroscopic electrostatic field that arises for certain longitudinal optic (LO) modes in the long-wavelength limit (k→Γ). This field lifts the longitudinal optic and transverse optic (LO-TO) degeneracy of the IR-active modes. Following Refs. 24 and 25 we corrected for the effect of the macroscopic field and the calculated frequency shifts of the LO modes. For the determination of the LO frequencies the interplanar force constants were calculated using a 3×1×1 cell (containing 12 primitive cells), which has a long a axis (about 23 Å). The phonon dispersion curves were calculated along several high-symmetry directions in the Brillouin zone (BZ). The phonon density of states (PDOS) was obtained by linear tetrahedron integration of the phonon frequencies over a 10 ×10×10 k-point mesh. The symmetry representation of the zone-center modes was examined following White and De Angelis.²⁶

The electronic structure calculations were carried out in both the local density approximation (LDA) and the generalized gradient approximation (GGA), using the projector-augmented wave method.²⁷²⁸ The electronic wave functions were sampled on a 2×2×2 k-point mesh in the BZ of the conventional unit cell. Additional calculations were carried out for an elongated cell using a consistent k-point mesh as far as possible. The kinetic energy cutoff on the wave functions was 945 eV (69 Ry). Convergence of the total energy as well as of frequencies with the number of k points and the plane-wave cutoff has been checked.

Calculations were carried out for a fixed volume with relaxation of the atomic positions. This procedure was repeated for several volumes in order to obtain a set of total energies as a function of the cell volume. From these data the equilibrium volume and bulk modulus were obtained by a fit to a second order Murnaghan equation of state.²⁹

### III. CALCULATED RESULTS FOR γ-Si₃N₄

#### A. Bulk properties

The crystal structure of γ-Si₃N₄ is isostructural with the mineral spinel MgAl₂O₄ ³⁰ i.e., it is cubic with space group Fd3m. There are eight formula units per conventional unit cell, which consists of 32 anions (N ions) and 24 cations (Si ions). The Bravais lattice of an ideal spinel structure consists of a fcc sublattice of N with the Si ions occupying both one eighth of the interstitial tetrahedral sites and one half of the octahedral sites. The crystal structure of spinel is completely defined by the lattice parameter a and the anions’ positional parameter x.

There are several calculations on the crystal structure and bulk modulus of γ-Si₃N₄, as summarized in Table I. Experimental results are also included in the table for comparison.¹,⁴⁻⁶,¹⁵,¹⁷,¹₈,³¹⁻⁴⁰ It is apparent that the experimental values are generally in good agreement with each other. As shown in Table I, the calculated lattice parameters from different methods are also in good agreement with the experimental values. The differences of our calculated data (7.696 Å for LDA and 7.789 Å for GGA) from the experimental values (about 7.74 Å) are small and typical for the

<table>
<thead>
<tr>
<th>Method</th>
<th>a (Å)</th>
<th>x</th>
<th>B (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical</td>
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<td>0.3824</td>
<td>321</td>
</tr>
<tr>
<td>LDA (this work)</td>
<td>7.737</td>
<td>0.3836</td>
<td>280</td>
</tr>
<tr>
<td>LDA-OLCA</td>
<td>7.8372</td>
<td>0.3844</td>
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<tr>
<td>LDA</td>
<td>7.687</td>
<td>0.3823</td>
<td>283</td>
</tr>
<tr>
<td>GGA (this work)</td>
<td>7.789</td>
<td>0.3823</td>
<td>285</td>
</tr>
<tr>
<td>GGA</td>
<td>7.7925</td>
<td>0.3823</td>
<td>284</td>
</tr>
<tr>
<td>GGA</td>
<td>7.419</td>
<td>0.3754</td>
<td>407</td>
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<td>Force field</td>
<td>7.692</td>
<td>0.3819</td>
<td>411.9</td>
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<tr>
<td>Experimental</td>
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<td></td>
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<tr>
<td>Electron diff.</td>
<td>7.80(8)</td>
<td>0.3819</td>
<td>411.9</td>
</tr>
<tr>
<td>XRD</td>
<td>7.744</td>
<td>0.3846</td>
<td>286</td>
</tr>
<tr>
<td>Electron diff.</td>
<td>7.75</td>
<td>0.3846</td>
<td>286</td>
</tr>
<tr>
<td>EDXD</td>
<td>7.737(6)</td>
<td>0.3846</td>
<td>286</td>
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<tr>
<td></td>
<td></td>
<td>290(5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>302(6)²⁸</td>
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</tr>
<tr>
<td>XRD</td>
<td>7.738(2)</td>
<td>0.3846</td>
<td>286</td>
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<tr>
<td>XRD</td>
<td>7.744(11)</td>
<td>0.3846</td>
<td>286</td>
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<tr>
<td>XRD</td>
<td>7.74(3)</td>
<td>309(3)³⁰</td>
<td>308</td>
</tr>
<tr>
<td>XRD</td>
<td>7.7339</td>
<td>0.3833</td>
<td></td>
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<table>
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<tr>
<th>Method</th>
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<th>x</th>
<th>B (GPa)</th>
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<tbody>
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<td>Reference 4</td>
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<td>Reference 15</td>
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</table>

TABLE I. The lattice parameter (a), coordinates of nitrogen atoms (x) and bulk modulus (B) for cubic Si₃N₄ from our calculations compared with those from literature (prediction vs experiments).

FIG. 1. Calculated phonon dispersion curves along high-symmetry directions in BZ for γ-Si₃N₄.
density functional theory (DFT). The only exception is the value (7.419 Å) by Mori-Sánchez et al. using the ab initio Hartree–Fock aiPI code.

However, the values of the bulk modulus calculated by the ab initio Hartree–Fock aiPI code as well as that from classic pair-potential methods (~410 GPa) are much larger, as compared with those from experiments (~300 GPa) and DFT methods. Our value of the bulk modulus calculated from the LDA (~321 GPa) is slightly larger than that predicted by Ching et al. using the LDA-orthogonalized linear combination of atomic orbitals (OLCA) approach. However, our value is close to that obtained by Soignard et al. Our value of the bulk modulus calculated using the LDA is slightly larger than the experimental data, which were measured at room temperature, while the value (285 GPa) from the GGA is slightly smaller.

In all subsequent calculations, the optimized calculated values of \( a \) and \( x \) using the LDA were used. The bulk modulus of \( \gamma\text{-Si}_3\text{N}_4 \) [about 321 GPa (LDA) or 285 GPa (GGA)] is much larger than that for \( \beta\text{-Si}_3\text{N}_4 \) (about 235 GPa) calculated using the same method.

### B. Phonon spectrum

Figure 1 shows the dispersion curves along the high-symmetry lines in the Brillouin zone (BZ). The primitive cell of \( \gamma\text{-Si}_3\text{N}_4 \) contains two formula units (total 14 ions) giving rise to a total of 42 phonon branches. The 42 phonon branches fill the entire energy range, leaving no gap in the PDOS. Figure 2 shows the calculated partial and total PDOS of \( \gamma\text{-Si}_3\text{N}_4 \). The total PDOS spans up to about 1030 cm\(^{-1}\), which is about 10% smaller than the maximum frequency (1119 cm\(^{-1}\)) obtained by Marian et al. using the pair-potential approach.

The low energy vibrations (<500 cm\(^{-1}\)) originate dominantly from the Si atoms. The N ions are involved in vibrational modes over the high energy range (>500 cm\(^{-1}\)). The modes in the high energy part are dominated by N character.

Different vibrational contributions from the two different Si atoms are apparent as shown in Fig. 2. In the very low energy range (between 200 and 400 cm\(^{-1}\)) the vibrations are mainly due to the octahedral Si atoms. The tetrahedral Si atoms contribute to the vibrations over the whole energy range with a peak at about 415 cm\(^{-1}\).

### C. Vibrations at \( \Gamma' \)

The phonon modes at \( \Gamma' \) for \( \gamma\text{-Si}_3\text{N}_4 \) are classified following White and De Angelis as

\[
\Gamma(k=0) = A_{1g}(R) + E_{1g}(R) + 3T_{2g}(R) + 4T_{1u}(IR) + T_{1g} + 2A_{2u} + 2E_u + 2T_{2g},
\]

where R and IR correspond to Raman- and infrared-active, respectively. The calculated frequencies at \( \Gamma' \) and the dominant contributions from the ion species are listed in Table II. The crystal symmetry implies five Raman- and four IR-active modes.

In Table III the experimental Raman values by Zerr et al. and by Jiang et al. are compared with our theoretical results. Four of the experimental modes agree well with our calculated values (Table III). However, the assignment of the symmetry is different. The calculations show that the mode near 979.5 cm\(^{-1}\) is \( A_{1g} \) and the mode at 845 cm\(^{-1}\) is \( T_{2g} \), that is, an interchange of species, as compared to the assign-

### Table II. Calculated frequencies \( f \) of the optical modes of \( \gamma\text{-Si}_3\text{N}_4 \) at the \( \Gamma \) point of the primitive cell. The LO modes of the infrared-active species are between brackets.

<table>
<thead>
<tr>
<th>Species</th>
<th>( f ) (cm(^{-1}))</th>
<th>Dominant eigen characters(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{2u} )</td>
<td>317</td>
<td>( \text{Si}_1+N )</td>
</tr>
<tr>
<td>( T_{1u}(\text{IR}) )</td>
<td>406(410)</td>
<td>( \text{Si}_1+\text{Si}_3+N )</td>
</tr>
<tr>
<td>( T_{2e}(R) )</td>
<td>415</td>
<td>( \text{Si}_1+N )</td>
</tr>
<tr>
<td>( E_u )</td>
<td>455</td>
<td>( \text{Si}_2 )</td>
</tr>
<tr>
<td>( T_{1g} )</td>
<td>504</td>
<td>( N )</td>
</tr>
<tr>
<td>( E_{1u}(R) )</td>
<td>522</td>
<td>( N )</td>
</tr>
<tr>
<td>( T_{1u}(\text{IR}) )</td>
<td>619(718)</td>
<td>( N+\text{Si}_2 )</td>
</tr>
<tr>
<td>( T_{2u} )</td>
<td>631</td>
<td>( N+\text{Si}_2 )</td>
</tr>
<tr>
<td>( T_{2g}(R) )</td>
<td>726</td>
<td>( N+\text{Si}_1 )</td>
</tr>
<tr>
<td>( T_{1u}(\text{IR}) )</td>
<td>729(764)</td>
<td>( \text{Si}_1+\text{Si}_2 )</td>
</tr>
<tr>
<td>( E_{1u} )</td>
<td>775</td>
<td>( N )</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>782</td>
<td>( \text{Si}_2 )</td>
</tr>
<tr>
<td>( T_{1u}(\text{IR}) )</td>
<td>819(1030)</td>
<td>( N+\text{Si}_1+\text{Si}_2 )</td>
</tr>
<tr>
<td>( T_{2g}(R) )</td>
<td>840</td>
<td>( N+\text{Si}_1 )</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>946</td>
<td>( N )</td>
</tr>
<tr>
<td>( A_{1g}(R) )</td>
<td>972</td>
<td>( N )</td>
</tr>
</tbody>
</table>

\(^a\text{Si}_1\) represents tetrahedral Si atoms and \( \text{Si}_2 \) octahedral Si.
ment by Jiang et al.\textsuperscript{32} The peak at 1331 cm\(^{-1}\) is far away from any of our calculations. It originates, we speculate, from an impurity or defect in the sample. Instead of this peak we find that the calculated fifth frequency at 415 cm\(^{-1}\) is very close to one (420 cm\(^{-1}\)) of the many weak peaks observed by Jiang et al.\textsuperscript{32}

The experimental results on IR active modes for \(\gamma\)-Si\(_3\)N\(_4\) are very unclear. Schwarz et al.\textsuperscript{18} reported IR absorption bands at 1094, 872, 702, and 465 cm\(^{-1}\), which are completely different from the corresponding absorption bands for \(\alpha\)- and \(\beta\)-Si\(_3\)N\(_4\). It seems obvious that the bands at 610 and 702 cm\(^{-1}\) correspond to the calculated TO modes at 619 and 729 cm\(^{-1}\), although there is a small discrepancy. However, assignment of the other bands is problematic. The measured band at 465 cm\(^{-1}\) is in between the calculated LO mode at 410 cm\(^{-1}\) and the TO mode at 619 cm\(^{-1}\). Therefore it is unlikely that it pertains to spinel \(\gamma\)-Si\(_3\)N\(_4\). In the energy range above 800 cm\(^{-1}\) there are too many bands as our data suggest only one in that range. For good comparison, a careful measurement on a pure, stoichiometric sample with Kramers–Kronig analysis of frequency dependent reflectivity data is needed.

D. Thermal properties

In the quasiharmonic approximation (QHA), the Helmholtz free energy \(F\) is given by

\[
F(V, T) = U_o(V) + \frac{1}{2} \sum_{q,j} \hbar \omega_j(q, V) + k_B T \sum_{q,j} \ln[1 - \exp(\hbar \omega_j(q, V)/k_B T)],
\]

where the first, second, and third terms are the total lattice energy, zero point, and vibrational contributions, respectively. \(U_o(V)\) denotes the total energy, \(\omega_j(q, V)\) the phonon frequency of branch \(j\) at wave vector \(q\) for lattice volume \(V\). The values of \(U_o(V)\) and \(\omega_j(q, V)\) are calculated for several volumes and \(F(V, T)\) is interpolated to obtain the zero-pressure volume \(V_o(T)\). The summation (integration) runs over the Brillouin zone (BZ). In general, the QHA gives reliable results for temperatures well below the melting point, which is confirmed in several studies.\textsuperscript{42} From Eq. (2) and standard thermodynamics, the thermal properties, including vibrational energy, entropy, and specific heat, thermal expansion coefficient, etc., can be obtained.

The calculated zero-point energy for the zero-pressure volume of \(\gamma\)-Si\(_3\)N\(_4\) is 0.7896 eV/f.u. (f.u. represents a Si\(_3\)N\(_4\) formula unit), which is slightly larger than that (0.76 eV/f.u.) reported by Marian et al.\textsuperscript{40}

Figure 3 shows the relationship between the calculated entropy \(S\) as well as the free energy \(F\) of vibration of the optimized volume \(V_o\) with temperature. The value of the free energy decreases fast from about 60 K, while the absolute value of the vibrational entropy also increases rapidly from about 120 K. The calculated values of free energy \(F\) over the Brillouin zone (BZ). In general, the QHA gives reliable results for temperatures well below the melting point, which is confirmed in several studies.\textsuperscript{42} From Eq. (2) and standard thermodynamics, the thermal properties, including vibrational energy, entropy, and specific heat, thermal expansion coefficient, etc., can be obtained.

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and entropy $S$ for $\gamma$-Si$_3$N$_4$ are about $-5.13$ kJ/mol and $92.39$ J/mol K, and $-106.40$ kJ/mol and $216.72$ J/mol K at 300 and 1000 K, respectively.

Figure 4 shows the relationship between the calculated specific heat $C_V$ and temperature. The $C_V$ at 300 and 1000 K is about 92.39 and 162.99 J/mol K, respectively. The $C_V$ value at room temperature is slightly smaller than that (98.2 J/mol K) of $\beta$-Si$_3$N$_4$.\textsuperscript{15}

The result for the linear lattice thermal expansion coefficient $\alpha(T) = (da(T)/dT)/a(T) = (dV(T)/dT)/(3V(T))$ of $\gamma$-Si$_3$N$_4$ is shown in Fig. 5. The coefficient $\alpha(T)$ has very low values in the low temperature range (<50 K). After an initial steep increase (50–400 K), the slope changes and $\alpha(T)$ increases gradually with temperature again, but slower, above 600 K. Experimental measurements for the linear thermal expansion coefficient of $\gamma$-Si$_3$N$_4$ have been performed by Jiang et al.,\textsuperscript{31} and Hintzen et al.\textsuperscript{33} (who also took the boundary condition $\alpha(T) = 0$ as $T = 0$ K) into account. The shape of the calculated curve is slightly different from the experimental results (also plotted).\textsuperscript{31,33} However, the difference between the two experimental curves is of the same order of magnitude as the difference between the experiments and theory. If the experimental uncertainty is taken into account, the agreement between the theoretical calculation and the experiments is good. The scatter between various experiments may, in our opinion, be explained by impurities in the samples, as shown by Jiang et al.\textsuperscript{31}

The calculated linear thermal expansion coefficient for $\gamma$-Si$_3$N$_4$ is $3.3 \times 10^{-6}$ and $6.5 \times 10^{-6}$ K$^{-1}$ at 300 and 1000 K, respectively. These values are much larger than the corresponding data for $\beta$-Si$_3$N$_4$ (1.19 $\times 10^{-6}$ and 3.47 $\times 10^{-6}$ K$^{-1}$ at 300 and 1000 K, respectively).\textsuperscript{44}

The thermal Grüneisen parameter, which is very important in materials science, is defined as $\gamma_{th} = (V\alpha V/B/C_V)$, where $V$ is the molar volume, $B$ is the isothermal bulk modulus, $\alpha_V$ the volume thermal expansion coefficient, $C_V$ the heat capacity. At zero pressure, the calculated value is $\gamma_{th} = 1.194$ and 1.346 for 300 and 1000 K, respectively. These values are much larger than the corresponding data for $\beta$-Si$_3$N$_4$ (about 0.40 and 0.63 at 300 and 1000 K, respectively).\textsuperscript{44}

A measure of lattice anharmonicity can be obtained by the difference between the specific heat $C_V$ at constant volume and the specific heat $C_p$ at constant pressure. The value of the specific heat (at constant pressure) $C_p = (1 + 2\gamma_{th}T)C_V$, which is calculated to be 92.72 and 166.95 J/mol K at 300 and 1000 K, respectively.

As shown above, the cubic silicon nitride shows a much larger thermal expansion coefficient and thermal Grüneisen parameter as compared with that of the $\beta$ form. That indicates larger lattice anharmonicity of the $\gamma$-Si$_3$N$_4$ than $\beta$-Si$_3$N$_4$, which is probably due to the particular SiN$_6$ and NSi$_4$ coordinations in the cubic form.

IV. CONCLUSIONS

First-principles calculations have been performed for the phonon spectrum of $\gamma$-Si$_3$N$_4$. The calculations show that the PDOS has a cutoff energy of 1030 cm$^{-1}$ with the contributions from Si atoms all over the energy range, while the contributions from the N atoms are mainly in the high energy range (500–1030 cm$^{-1}$).

The interpretation of Raman experiments needs to be qualified. A weak low frequency mode (415 cm$^{-1}$) is characteristic of bulk $\gamma$-Si$_3$N$_4$ instead of a strong high frequency mode.

Thermal properties have been obtained using the QHA. At 300 K the specific heat, linear thermal expansion coefficient and thermal Grüneisen parameter are calculated to be 92.39 J/K mol, 3.47 $\times 10^{-6}$ K$^{-1}$ and 1.194, respectively. We hope the obtained information will be useful in characterization of $\gamma$-Si$_3$N$_4$ and for the appraisal of applications.

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