

Lattice dynamical, elastic properties and sound velocities of γ -Si₃N₄

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Lattice dynamical, elastic properties and sound velocities of γ -Si₃N₄ have been calculated by using a proposed six parameter bond-bending force constant model. In this model, the potential energy of the compound γ -Si₃N₄ is expanded by using the Taylor's expansion in the harmonic approximation. The proposed theoretical model is used to calculate the zone-centre phonon frequencies, elastic properties, sound velocities and Debye characteristic temperature for γ -Si₃N₄ and compared our results with experimental and previously calculated results available in the literature. It is found to be in good agreement with the experimental results. The significant outcome of the present work is that the octahedral bonding is stronger than that of the tetrahedral bonding.

Keywords: γ -Si₃N₄, Octahedral, Tetrahedral, Zone-centre, Phonon

1 Introduction

Silicon nitride (Si₃N₄) is an important structural and ceramic material with many applications such as in micro-electronics, optoelectronics, mechanics, automobile, solar cells and tools for ceramic cutting and processing¹ due to its outstanding high temperature and oxidation resistant properties. Silicon nitride has been described at least in four different crystalline polymorphs as α -, β -, γ - and δ -Si₃N₄. In which α - and β -Si₃N₄ have hexagonal structure² with almost the same density of 3.2g/cm³. The third polymorph of Si₃N₄ has cubic structure (γ -Si₃N₄ = c-Si₃N₄) which is discovered by Zerr *et al*³. at high pressure. High pressure experiments on β -Si₃N₄ at room temperature led to the formation of fourth polymorph of Si₃N₄, i.e., δ -Si₃N₄ with tetragonal symmetry⁴ in 2001. δ -Si₃N₄ is most likely a metastable intermediate between β - and γ -Si₃N₄.

In recent years, γ -Si₃N₄ has much attraction due to several reasons. The α - and β -phases of Si₃N₄ have hexagonal structure in which the N-atoms are tetrahedrally coordinated with the Si-atoms but in the γ -Si₃N₄ the N-atoms are tetrahedrally as well as the octahedrally coordinated with the Si-atoms, which is very rare in binary compounds. This introduces some different physical properties of γ -Si₃N₄ from other polymorphs of Si₃N₄. Therefore, the nature of bonding in the compound γ -Si₃N₄ is very important. The γ -Si₃N₄ is a semiconductor with direct band gap⁵⁻⁸ of about 3.45 eV and hence, it has potential

applications in optical and electronic devices in addition to the structural applications⁹⁻¹¹.

A full characterization of the physical properties of γ -Si₃N₄ is important for applications. The lattice dynamical calculations are one of the important tools in understanding the thermodynamical, structural, bonding and numerous other solid state properties. Phonons, being one of the elementary excitations of solids, provide complete information about the interatomic forces in solids. The interatomic forces are of paramount importance as their study leads to study an understanding of bonding and the structural properties of compounds. All the properties depend upon the constituent atoms of the crystal and can be obtained with the help of lattice dynamical calculations. Recently, Fang *et al*¹². have done the lattice dynamical calculations for γ -Si₃N₄ using the first principles molecular dynamics¹³⁻¹⁵ computer code VASP (Vienna *ab initio* simulation program).

Wang *et al*¹⁶. have investigated the bulk modulus and some thermodynamic properties of γ -Si₃N₄ using the analytic mean field method. Kuwabara *et al*¹⁷. have obtained the phonon dispersion curves, phonon DOSs, bulk moduli, thermal expansion coefficients, and heat capacities of γ -Si₃N₄ using density functional theory (DFT) calculations¹⁸ were performed using VASP code^{14,15}. Electron-ion interaction was represented by the projector augmented wave (PAW) method¹⁹ and the local density approximation²⁰ (LDA).

Dong *et al*²¹. have optimized the ground state γ -Si₃N₄ in the framework of the first-principles method based on the Kohn–Sham equation¹⁸. The self-consistent total energy calculations are performed with the plane-wave pseudo-potential (PW-PP) method²². The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof²³ is used for the exchange–correlation function.

2 Crystal Structure and Potential Model

The crystal structure of γ -Si₃N₄ is classified as HI₁ space group O_h^7 (Fd3m), is cubic and consist of a slightly distorted cubic close-packed arrangement of N-atoms with the Si-atoms occupy 1/8 of the tetrahedral and 1/2 of the octahedral interstices, respectively²⁴ (normal spinel). The crystal structure of γ -Si₃N₄ is shown in Fig. 1. The bond length between (Si-N)_{tet}, (Si-N)_{oct} and N-N is 1.778, 1.871 and 2.558 Å, respectively and the angle between (Si-N)_{tet}, and (Si-N)_{oct} is 109.47° and 86.58°, respectively²⁵. Group theoretical treatment of the optical zone-centre ($\Gamma=0$) phonon modes are known to be resolved into 17 fundamental lattice vibration modes^{26–28}. The representation of these modes at zero wave-vectors is expressed as:

$$\Gamma = A_{1g} + E_g + 2E_u + 2A_{2u} + F_{1g} + 3F_{2g} + 5F_{1u} + 2F_{2u} \quad \dots(1)$$

where A_{1g} , E_g and $3F_{2g}$ modes are Raman-active and F_{1u} modes are infrared-active modes. In the $5F_{1u}$ modes, one mode with frequency zero is translation mode, and the other four modes are observed in the infrared region. There is one Raman-inactive mode, F_{1g} , while $2A_{2u}$, $2E_u$ and $2F_{2u}$ are infrared-inactive modes.

In the present paper, the potential energy ϕ of the γ -Si₃N₄ can be expanded by using Taylor's series and can be written as:

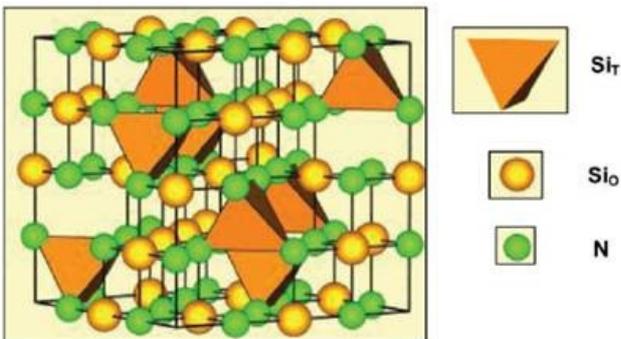


Fig. 1 — Crystal structure of γ -Si₃N₄

$$\phi = \sum_{lmn} \left[\frac{1}{r} \left(\frac{d\phi}{dr} \right) \Big|_{r=|r_k|} \left\{ r_{lmn}^o (S_{lmn} - S_o) + \frac{1}{2} |S_{lmn} - S_o|^2 \right\} + \frac{1}{2} \left\{ \frac{1}{r} \frac{d}{dr} \left(\frac{1}{r} \frac{d\phi}{dr} \right) \Big|_{r=|r_k|} \{ r_{lmn}^o (S_{lmn} - S_o) \}^2 \right\} \right] \quad \dots(2)$$

where S_0 and S_{lmn} are the displacements of the central ion and its first neighbour ions from their equilibrium position r_{lmn}^0 represent the position coordinates of neighbouring ions in equilibrium. l, m, n , represent the direction cosines of the line joining the central ion and a nearest neighbour ions. $|r_k|$ is the nearest neighbour distance.

Let A_k be the bond-stretching force constant defined by the second derivative of the potential energy ϕ :

$$\frac{e^2}{V} A_k = \frac{d^2\phi}{dr^2} \Big|_{r=|r_k|} \quad \dots(3)$$

The bond-bending force constant B_k is expressed as the first derivative of the potential energy ϕ :

$$\frac{e^2}{V} B_k = \frac{1}{r} \frac{d\phi}{dr} \Big|_{r=|r_k|} \quad \dots(4)$$

where $k = 1, 2, 3$ for first, second and third neighbours, respectively.

3 Elastic Constants and Related Properties

Elastic constants for γ -Si₃N₄ are calculated from the dynamical matrix $D_{\alpha\beta}(\mathbf{q}, \mathbf{k}\mathbf{k}')$ by expanding it as a function of \mathbf{q} in the neighbourhood²⁹ of $\mathbf{q} = 0$, the relation between the elastic constants and the coupling coefficients (force constants) can be established.

Debye temperature is an important fundamental parameter related to many other physical properties such as elastic constants, specific heat and melting temperature. The Debye temperature Θ_D can be calculated³⁰ as :

$$\Theta_D = \frac{h}{k_B} \left(\frac{3}{4\pi V_0} \right)^{1/3} v_m \quad \dots(5)$$

where h is the Planck's constant, k_B is the Boltzmann's constant, V_0 is the molar volume and v_m is the average sound velocity in the material γ -Si₃N₄.

At low temperature, the Debye temperature can be calculated from elastic constants because at low temperatures the vibrational excitations arise solely from acoustic vibrations. Average sound velocity in the polycrystalline materials can be calculated³¹ as:

$$v_m = \left[\frac{1}{3} \left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \right]^{-1/3} \quad \dots(6)$$

where v_L and v_T are the longitudinal and transverse sound velocities in an isotropic material, respectively. Longitudinal and transverse velocities can be obtained with the formula³⁰ :

$$v_L = \left[\frac{B + (4/3)G}{\rho} \right]^{1/2} \quad \dots(7)$$

$$v_T = \left(\frac{G}{\rho} \right)^{1/2} \quad \dots(8)$$

where B , G and ρ are the bulk modulus, shear modulus and molecular density of the material, respectively.

4 Results and Discussion

In the present paper, let A_1 and B_1 represent the bond-stretching and bond-bending force constants between Si-N (tetrahedral) types of ions, respectively, whereas A_2 and B_2 represent similar force constants between Si-N (octahedral) types of ions. Likewise A_3 and B_3 correspond to bond-stretching and bond-bending force constants between N-N or (Si-Si) types of ions.

The dynamical matrix of the order of (42×42) is obtained and solves it at the zone-centre, we get analytical expressions for all the different fundamental modes of γ -Si₃N₄. Using the experimental values of Raman modes³² A_{1g} , E_g and the infrared modes³³ F_{1u} , we have calculated the three bond-stretching (A_1 , A_2 and A_3) and three bond-bending (B_1 , B_2 and B_3) force constants. These force constants are listed in Table 1.

Using above force constants, we have calculated the zone-centre phonon frequencies of γ -Si₃N₄ have been calculated and listed in Table 2 along with the experimental Raman³², the infrared modes³³ and the results of Fang *et al*¹². The calculated result shows a very good agreement with the experimental results.

Table 1 — Values of force constants (kdynes/cm) for γ -Si₃N₄

Force constant	Internal coordinates	γ -Si ₃ N ₄
A_1	Si-N (tet)	40.49
B_1	Si-N (tet)	1.82
A_2	Si-N (oct)	156.55
B_2	Si-N (oct)	6.23
A_3	N-N (Si-Si)	24.79
B_3	N-N (Si-Si)	1.02

Table 2 — Observed^{32,33} and calculated zone-centre phonon frequencies for γ -Si₃N₄ along with the results of Fang *et al*¹².

Species	Frequencies (cm ⁻¹)		
	Observed	Calculated	Fang <i>et al.</i>
A_{1g}	979	978	972
E_g	522	522	522
$F_{2g}(1)$	845	846	840
$F_{2g}(2)$	727	725	726
$F_{2g}(3)$	420	419	415
$F_{1u}(1)$	1094	1097	1030
$F_{1u}(2)$	872	873	764
$F_{1u}(3)$	702	699	718
$F_{1u}(4)$	465	463	410
$A_{2u}(1)$		949	946
$A_{2u}(2)$		781	782
$E_u(1)$		782	775
$E_u(2)$		451	455
F_{1g}		502	504
$F_{2u}(1)$		634	631
$F_{2u}(2)$		313	317

From the results obtained on the basis of the above force constants model, it is concluded that the in the case of γ -Si₃N₄ the second neighbour interaction is stronger than the first neighbour interaction this means that the octahedral bonding (second neighbour interactions) is stronger than that of the tetrahedral bonding (first neighbour interactions), the reason being that the bonding between Si-N ions (octahedral bonding) is more ionic than the bonding between Si-N (tetrahedral bonding). This result shows that the bonding in γ -Si₃N₄ is partially ionic and partially covalent in nature which is very much different from the nature of bonding (covalent) in the other polymorphs of Si₃N₄ such as α -Si₃N₄ and β -Si₃N₄. Hence, the properties of γ -Si₃N₄ very much differ from α -Si₃N₄ and β -Si₃N₄.

Using the calculated force constants (Table 1), we have calculated the elastic constants C_{11} , C_{12} and C_{44} for γ -Si₃N₄ and these are listed in Table 3. Once the elastic constants is calculated, the bulk modulus B , compressibility coefficient K , shear modulus G , Young's modulus Y , Poisson's ratio σ , anisotropy factor A are also calculated by the relations given

Table 3 — Calculated elastic constants C_{11} , C_{12} and C_{44} (GPa), bulk modulus B (GPa), compressibility coefficient K (GPa^{-1}), shear modulus G (GPa), Young's modulus Y (GPa), Poisson's ratio σ , anisotropy factor and as compared to experimental data³ and other researchers^{3,12,17,36-44} of $\gamma\text{-Si}_3\text{N}_4$.

	C_{11}	C_{12}	C_{44}	B	K	G	Y	A	σ
Present	542.2	193.4	338.22	309.7	3.23	259.2	608	1.94	0.263
Others	512.1 ^a	177.3 ^a	330.9 ^a	288.9 ^a	3.46 ^a	251.7 ^a	585.2 ^a	1.94 ^a	0.162 ^a
	532.6 ^b	191.2 ^b	341.0 ^b	305.0 ^b		258.3 ^b	604.3 ^b	1.94 ^b	0.169 ^b
	550.6 ^c	191.0 ^c	349.4 ^c	310.9 ^c		264.6 ^c	618.3 ^c	1.90 ^c	0.168 ^c
				300 ^d		258 ^f	379 ⁱ		0.28 ⁱ
				335 ^e		261 ^m			
				308 ^f		148 ⁱ			
				412 ^g		205-260 ^k			
				285 ^h					
				290 ⁱ					
				321 ^j					
				290-308 ^k					
			320 ^l						

^a36, ^b37, ^c38, ^d3, ^e39, ^f40, ^g41, ^h12, ⁱ42, ^j12, ^k43, ^l17, ^m44

Table 4 — Elastic wave velocities (in km/s) for different propagation directions and Debye temperature (Θ_D in K) for the $\gamma\text{-Si}_3\text{N}_4$

Velocities	Present calculation
$v_L^{[100]}$	11746
$v_T^{[100]}$	9276
$v_l^{[110]}$	13403
$v_{tl}^{[110]}$	9276
$v_{t\perp}^{[110]}$	6661
$v_{vl}^{[111]}$	23189
$v_{vr}^{[111]}$	9543
V_L	12912
V_T	8121
V_m	10067
Θ_D	1248

elsewhere³⁴ and listed in Table 3 along with the experimental and previously calculated results.

The components of the elastic tensor have been calculated. The components of the elastic tensor for a cubic crystal are characterised by three independent elastic constants C_{11} , C_{12} and C_{44} . These components are allowed to obtain acoustic velocities along [100], [110] and [111] directions³⁴ and listed in Table 4 along with the experimental and previously calculated results. For the calculation of sound velocities, we have taken the density³ of $\gamma\text{-Si}_3\text{N}_4$ as 3.93 gm/cm^3 .

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