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Cite as: AIP Advances 9, 115311 (2019); https://doi.org/10.1063/1.5128064
Submitted: 16 September 2019. Accepted: 31 October 2019. Published Online: 20 November 2019

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AFFILIATIONS
Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China

I. INTRODUCTION

Silicon nitride (Si₃N₄) is a very important member of the class of materials known as ultrahigh temperature ceramics (UHTCs). It has superior physical and chemical properties, including high strength, excellent thermal conductivity, outstanding thermal shock resistance, temperature resistance, and oxidation resistance. With such unique properties, Si₃N₄ has the best comprehensive mechanical properties of all ceramic materials. Today, Si₃N₄ ceramics are used as cutting tools, antifriction bearings, and pump plungers in the machine industry and are considered a promising material for microelectronic applications. Moreover, Si₃N₄ ceramics are the best candidate material for heat engine parts. There are two phases of the material: α-Si₃N₄ [space group P31c (159)] and β-Si₃N₄ [space group P63/m (176)] with hexagonal structures at ambient pressure; the latter has a higher synthesis temperature than the former. In these two phases, one Si atom is linked to four N atoms, and the structural units are tetrahedral. c-Si₃N₄ [space group Fd3m (227)], also called γ-Si₃N₄, is stable under high pressure, with a spinel structure, where 2/3 of the Si atoms are linked to six N atoms and the remaining 1/3 to four N atoms. Thus, tetrahedral and octahedral structural units coexist in c-Si₃N₄.

In previous studies, Xu et al. performed first-principles calculations with a quasiharmonic approximation and discovered that α-Si₃N₄ remained in a metastable phase at high pressure (10 GPa) and temperature (2000 K). Nishiyama et al. carried out high-temperature and high-pressure experiments and found that an α → γ transformation occurred at 15.6 GPa and 1600°C. The quasihydrostatic equation of state (EOS), compressibility, and stability of α-Si₃N₄ were studied by Kruger using a diamond anvil cell (DAC). The crystal structure and electron density of α-Si₃N₄ were researched by Toraya through synchrotron radiation powder diffraction experiments. In 2005, the high-pressure and high-temperature yield strength of α-Si₃N₄ was investigated by Qian et al. by analyzing the related diffraction peak broadening, and they observed that no significant strain saturation
occurred at pressures of up to 9.2 GPa, while heating at 9 GPa the yield behavior was observed at 400°C. Unfortunately, there is a lack of experimental studies on the strength and deformation behavior of α-Si₃N₄ under high-pressure and ambient-temperature conditions, conditions critical for both the preparation of high-performance Si₃N₄ ceramics and the evaluation of the potential of applications under extreme conditions. In this article, the deformation properties and high-pressure strength of polycrystalline α-Si₃N₄ at pressures of up to 60 GPa are examined using synchrotron radiation angle-dispersive axial diffraction. To further supplement the experimental results, we also performed density functional theory calculations.

II. EXPERIMENTAL AND THEORETICAL DETAILS

α-Si₃N₄ powder (99.9% purity, average grain size 1 μm) was obtained from Macklin. Its crystal structure, purity, and surface morphology were analyzed using x-ray diffraction (XRD: DX-2700, Dandong, China) (λ = 1.5404 Å) and field emission scanning electron microscopy (SEM: S-4800 II, Hitachi, Japan). The XRD pattern and SEM image of the initial material are presented in Fig. 1. As seen in the image, a small amount of β-Si₃N₄ exists in the initial sample, which has no effect on the experimental results.

Synchrotron radiation powder diffraction experiments were carried out in a diamond anvil cell (DAC) with 300 μm cuvets. The α-Si₃N₄ sample was placed in a T301 stainless steel gasket (center hole diameter 100 μm), which was prepressed to ∼40 μm thickness. Pressure in the experiment was calibrated using a 5 μm ruby sphere. In situ experiments were carried out without any pressure transmitting medium to obtain the maximum nonhydrostatic stresses. Synchrotron radiation at beamline 4W2 of the Beijing Synchrotron Radiation Facility (BSRF) (λ = 0.6199 Å) was used for the XRD experiments. Two-dimensional (2D) diffraction patterns were recorded with image plate detectors (Pilatus) and transformed for analysis into one-dimensional (1D) patterns using software FIT2D. Unit-cell parameters of α-Si₃N₄ were acquired by analyzing the diffraction peaks of (101), (110), (200), (201), (202), and (301). However, the (002), (102), (210), (211), (112), and (300) peaks were not selected due to their extremely low intensity and overlapping.

α-Si₃N₄ crystals have a hexagonal lattice structure [space group P31c (159)], as shown in Fig. 2. The atomic space occupation for Si and N atoms was obtained from previous experimental results (Si₁: 0.081, 0.512, 0.653; Si₂: 0.253, 0.167, 0.446; N₁: 0.656, 0.612, 0.430; N₂: 0.312, 0.317, 0.698; N₃: 1/3, 2/3, 0.599; and N₄: 0, 0, 0.447). In theoretical studies, we performed structural optimization and electronic structure calculations using the Perdew-Burke-Ernzerhof (PBE) functional within the framework of VASP code and employed the frozen-core, all-electron projector-augmented wave (PAW) method to determine the electron-ion interaction with 3s²3p² and 2s²2p³ valence electrons for Si and N, respectively. Tests revealed a cutoff energy of 600 eV and that a 10 × 10 × 8 Monkhorst-Pack k mesh can handle these systems well, ensuring that all enthalpy calculations converge to less than 1 meV/atom. In order to explore the dynamic stability of our structures, we adopted the finite displacement approach to execute phonon calculation with

![FIG. 2 Crystal structure of α-Si₃N₄. Large red spheres represent Si atoms and small green spheres N atoms.](image-url)
56 atoms in a $1 \times 1 \times 2$ supercell, as implemented in the Phonopy code. All structures were relaxed and fully optimized until the Hellmann-Feynman force and the total energy were less than $1 \times 10^{-2}$ eV/Å and $5 \times 10^{-6}$ eV/atom, respectively.

### III. RESULTS AND DISCUSSION

#### A. Compression properties and structural stability

The typical diffraction patterns of $\alpha$-Si$_3$N$_4$ at high pressure are displayed in Fig. 3. As expected, the hexagonal structure of $\alpha$-Si$_3$N$_4$ remains stable over the range of experimental pressure. The diffraction peaks of $\alpha$-Si$_3$N$_4$ are broadened monotonically and slightly shifted to higher angles, indicating that the pressure causes a decrease in $d$-spacing and unit-cell volume. The unit-cell parameters from diffraction peaks at ambient conditions are $a = 7.752$ Å and $c = 5.619$ Å, generating a unit-cell volume $V = 292.430$ Å$^3$. These data are almost consistent with previously reported results. However, our theoretical calculation (GGA) results are slightly larger than in other studies, as shown in Table I. Figure 4(a) represents the plot of unit-cell volume changes against pressure for $\alpha$-Si$_3$N$_4$. The bulk modulus is evaluated through fitting the P–V data with a third-order Birch-Murnaghan equation of state (EOS),

$$P(V) = 1.5K_0 \times \left[ \left( \frac{V}{V_0} \right)^{-\frac{3}{2}} - \left( \frac{V}{V_0} \right)^{-\frac{1}{2}} \right] \times \left[ 1 - 0.75(4 - K'_0) \times \left( \left( \frac{V}{V_0} \right)^{-\frac{1}{2}} - 1 \right) \right],$$

(1)

where $K_0$, $K'_0$, $V$, and $V_0$ represent the bulk modulus under ambient conditions, the pressure derivative of $K_0$, and the unit-cell volumes under pressures $P$ and zero (ambient), respectively. The compression data generate a bulk modulus of $K_0 = 256.3(4)$ GPa, and the corresponding pressure derivative ($K'_0$) is 5.6, which are slightly higher than the values gained from first-principles calculation results: $K_0 = 232.5(2)$ GPa and $K'_0 = 2.5$. Additionally, our experimental values are larger than those of nano-$\alpha$-Si$_3$N$_4$ found by Kruger et al., who used a quasihydrostatic medium in the XRD measurements. This discrepancy might be explained by their sample and our sample possessing different particle sizes. The present results and those of other studies are summarized in Table I for comparison.

![Figure 3. XRD images ($\lambda = 0.6199$ Å) of $\alpha$-Si$_3$N$_4$ under various pressures at room temperature.](image)

**Figure 4(b)** displays the compression behavior along unit cell axes, where $a$ ($c$) and $a_0$ ($c_0$) are the cell parameters at pressures $P$ and zero, respectively. In the present results, the anisotropic compressibility of the $a$-axis and $c$-axis is not prominent in the low-pressure segment. With increasing pressure, the anisotropic property of $\alpha$-Si$_3$N$_4$ becomes increasingly obvious, and the $a$-axis is easier to compress than the $c$-axis. However, the theoretical calculations show weak anisotropy running between the $a$-axis and $c$-axis, consistent with the results of Kruger et al. Experimental values were recorded under nonhydrostatic conditions, and the sample generally suffered from inhomogeneous stresses during compression at ambient temperature. These phenomena may lead to inconsistency between experimental and theoretical results.

To verify the dynamical stability of structures, we calculated the phonon spectrum of $\alpha$-Si$_3$N$_4$ at 0 and 60 GPa by employing a finite-displacement approach. The absence of the imaginary

#### TABLE I. Measured and calculated unit-cell parameters $a$, $b$, $c$ (Å), unit-cell volume $V$ (Å$^3$), bulk modulus $K_0$ (GPa), the first-order pressure derivative $K'_0$, and those from other studies. LDA: local density approximation. OLCAO: orthogonalized linear combination of atomic orbitals.

| Method                  | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $K_0$ (GPa) | $K'_0$ | References |
|-------------------------|---------|---------|---------|------------|-------------|--------|------------|
| Nonhydrostatic compression | 7.752   | 7.808   | 5.619   | 292.430    | 5.6         | 256.3 (±4) | This work |
| GGA                     | 7.752   | 7.808   | 5.619   | 292.430    | 5.6         | 256.3 (±4) | This work |
| Quasihydrostatic compression | 7.757(1)| 7.722   | 5.623(1)| 293.030(7)| 4.5 (±1.3)  | 223.4 (±15)| 11         |
| Ultrasonic              | 7.752   | 7.722   | 5.619   | 295.190    | 4.0 (fixed) | 240.1 (±4) | 21         |
| LDA                     | 7.752   | 7.722   | 5.619   | 295.190    | 257.0       | 22     | 11         |
| LDA                     | 7.752   | 7.722   | 5.619   | 295.190    | 257.0       | 22     | 11         |
| OLCAO                   | 7.792   | 7.722   | 5.598   | 289.099    | 4.0 (fixed) | 240.0  | 21         |
phonon frequencies in the entire Brillouin zone of $\alpha$-Si$_3$N$_4$ at both pressures indicates that the structures are dynamically stable, as shown in Fig. 5, which is consistent with our experimental results. Furthermore, we adopted the band structures and density of states (DOS) to analyze the electronic properties for $\alpha$-Si$_3$N$_4$ at 0 and 60 GPa; see Fig. 6. In the present calculations, the bandgaps can be determined to be about 4.6 eV and 4.7 eV at 0 and 60 GPa, which agrees well with previous studies.\textsuperscript{1,4} Hence, the band structures and DOS of $\alpha$-Si$_3$N$_4$ possess similar metallicity bonding features at 0 and 60 GPa. The lowest valence band, 4–5 eV wide, originates from the N-2s orbitals, and the upper valence band, about 10 eV wide, mainly originates from N-2p and Si-3p orbitals. The conduction band DOS consists predominantly of Si-3p orbitals mixed with Si-3s, N-2s, and N-2p orbitals. The calculated results show that hybridization occurs between the Si-3p, N-2s, and N-2p orbitals and that pressure has a little effect on the electron distribution of $\alpha$-Si$_3$N$_4$ systems.

**B. Yield stress and strength**

The yield strength of $\alpha$-Si$_3$N$_4$ is deduced from full width at half maximum (FWHM) analysis which is well documented elsewhere.\textsuperscript{14,23,24} Peak broadening has two origins: the existence of microscopic deviatoric strain $\epsilon$ and the reduction in grain size.\textsuperscript{25} Diffraction peak broadening theory of metal deformation is applied to the analysis of experimental data.\textsuperscript{26} Once $\epsilon$ is determined, microscopic deviatoric stress, $\psi$, can be derived from $\epsilon^*E$; $E$ denotes the aggregate Young’s modulus, 315 GPa.\textsuperscript{11} Under uniaxial loading, deviatoric stress at the beginning of plastic deformation is considered as the yield strength of the sample.\textsuperscript{25} The relationship is as follows:

$$\psi = \epsilon^*E = Y.$$  

(2)

The aggregate Young’s modulus, $E$, can be estimated using the following relationship:

![FIG. 4. (a) Experimental and theoretical P–V data of $\alpha$-Si$_3$N$_4$ with pressures of up to 60 GPa. (b) Experimental and theoretical cell parameter ratio ($a/a_0$ and $c/c_0$) vs pressure for $\alpha$-Si$_3$N$_4$.](image)

![FIG. 5. The phonon dispersion curves of $\alpha$-Si$_3$N$_4$ at (a) 0 GPa and (b) 60 GPa.](image)
The microscopic deviatoric strain, $\varepsilon$, can be obtained from the grain size and diffraction peak width, using

$$\left(2\omega_{hkl}\cos\theta_{hkl}\right)^2 = \left(\frac{\lambda}{d}\right)^2 + \eta_{hkl}^2 \sin^2 \theta_{hkl},$$

where $2\omega_{hkl}$ represents the FWHM and $\theta_{hkl}$, $\lambda$, and $d$ denote the Bragg angle, the x-ray wavelength, and the grain size of the crystal-lites, respectively. $\eta_{hkl}$ is the microscopic deviatoric strain, $\varepsilon$. Here, $\varepsilon$ is the average value of $\eta_{hkl}$ derived from all recorded diffraction peaks.

The microscopic deviatoric strain, $\varepsilon$, can be obtained from the grain size and diffraction peak width, using

$$E = \frac{9KG}{(3K + G)}.$$

where $2\omega_{hkl}$ represents the FWHM and $\theta_{hkl}$, $\lambda$, and $d$ denote the Bragg angle, the x-ray wavelength, and the grain size of the crystal-lites, respectively. $\eta_{hkl}$ is the microscopic deviatoric strain, $\varepsilon$. Here, $\varepsilon$ is the average value of $\eta_{hkl}$ derived from all recorded diffraction peaks.

Peak broadening analysis results are shown in Fig. 7. As pressure increases from zero to 20 GPa, stress and pressure show a linear relationship, indicating that the grains squeeze each other in the initial stages of compression—stress is produced at points of contact, increasing with increasing external loading, that is, elastic deformation mainly occurs. From Fig. 7, a distinct relaxation in stress is discovered above 20 GPa, implying that $\alpha$-Si$_3$N$_4$ begins to experience an elastic-plastic transition and macroyield, and supporting a stress of up to 21 GPa. Subsequently, the stress of $\alpha$-Si$_3$N$_4$ increases slowly with increasing pressure, which may be due to work hardening of the sample. Stress reaches a maximum of 23 GPa at 43 GPa. Hence, the yield strength, $Y$, of $\alpha$-Si$_3$N$_4$ is 21 GPa at high pressure, which is also equal to the macroscopic differential stress.

Furthermore, Fig. 7 compares the stresses for MgO, WB$_3$, c-BC$_2$N, and $\alpha$-Si$_3$N$_4$ obtained from reference studies with results from the present experiments. The stress of MgO reaches a maximum value of 7 GPa at 10 GPa, WB$_3$ has a maximum stress of $\sim$30 GPa, with a non-hydrostatic compression of $\sim$77 GPa, and c-BC$_2$N has a limited stress of $\sim$38 GPa at $\sim$66 GPa. The yield stress of $\alpha$-Si$_3$N$_4$ is larger than that of MgO but lower than that of WB$_3$ and c-BC$_2$N.
discrepancy may be related to the hardness of the material. The Vickers hardness of MgO (∼4 GPa), WB$_3$ (∼43.1 GPa), c-BC$_2$N (∼70 GPa), and a-Si$_3$N$_4$ (20–30 GPa) has been reported in detail elsewhere.\textsuperscript{17,29}

\textbf{IV. CONCLUSIONS}

The compressibility and high-pressure strength of a-Si$_3$N$_4$ were examined experimentally using synchrotron radiation powder diffraction data and theoretically using first-principles calculations. Diffraction experiments and first-principles calculations indicate that there is no isostuctural phase transition during compression up to 60 GPa. The compression curve of a-Si$_3$N$_4$ is derived from powder diffraction data, generating a bulk modulus of $K_0 = 256.3 \pm 4$ GPa and $K_0’ = 5.6$. The bulk modulus is 10% higher in the experimental results than in the theoretical calculations. Diffraction peak broadening analysis indicates that a-Si$_3$N$_4$ begins to yield at 20 GPa (at ambient temperature) with a yield strength of ∼21 GPa. The present experimental and theoretical studies will be extremely helpful in the preparation of high-performance Si$_3$N$_4$ ceramics.

\textbf{ACKNOWLEDGMENTS}

High pressure synchrotron radiation XRD experiments were carried out at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF). This work was supported by the National Natural Science Foundation of China (Grant No. 51872189) and the Fundamental Research Funds for the Central Universities (Grant No. 2018SCUH0022).

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