ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

Compression behavior and phase transition of β-Si_3N_4 under high pressure

Hong-xia Gong(龚红霞), Zi-li Kou(寇自力), Cong Fan(樊聪), Hao Liang(梁浩), Qi-ming Wang(王齐明), Lei-lei Zhang(张雷雷), Fang Peng(彭放), Ming Yang(杨鸣), Xiao-lin Ni(倪小林), Jing Liu(刘景)
Citation: Chin. Phys. B . 2018, 27(5): 056101. **doi:** 10.1088/1674-1056/27/5/056101

Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Structural phase transition, strength, and texture in vanadium at high pressure under nonhydrostatic compression

Lun Xiong(熊伦), Jing Liu(刘景)
Chin. Phys. B . 2018, 27(3): 036101. **doi:** 10.1088/1674-1056/27/3/036101

Behaviors of Zn_2GeO_4 under high pressure and high temperature

Shu-Wen Yang(杨淑雯), Fang Peng(彭放), Wen-Tao Li(李文涛), Qi-Wei Hu(胡启威), Xiao-Zhi Yan(晏小智), Li Lei(雷力), Xiao-Dong Li(李晓东), Duan-Wei He(贺端威)
Chin. Phys. B . 2016, 25(7): 076101. **doi:** 10.1088/1674-1056/25/7/076101

High pressure structural phase transitions of TiO_2 nanomaterials

Quan-Jun Li(李全军), Bing-Bing Liu(刘冰冰)
Chin. Phys. B . 2016, 25(7): 076107. **doi:** 10.1088/1674-1056/25/7/076107

Phase transition and chemical decomposition of liquid carbon dioxide and nitrogen mixture under extreme conditions

Xiao-Xu Jiang(姜晓旭), Guan-Yu Chen(陈冠宇), Yu-Tong Li(李玉同), Xin-Lu Cheng(程新路), Cui-Ming Tang(唐翠明)
Chin. Phys. B . 2016, 25(2): 026102. **doi:** 10.1088/1674-1056/25/2/026102

Li-ion batteries: Phase transition

Peiyu Hou(侯配玉), Geng Chu(褚赓), Jian Gao(高健), Yantao Zhang(张彦涛), Lianqi Zhang(张联齐)
Chin. Phys. B . 2016, 25(1): 016104. **doi:** 10.1088/1674-1056/25/1/016104

Compression behavior and phase transition of β-Si_3N_4 under high pressure

Hong-xia Gong(龚红霞)[1], Zi-li Kou(寇自力)[1,†], Cong Fan(樊聪)[1], Hao Liang(梁浩)[1], Qi-ming Wang(王齐明)[1], Lei-lei Zhang(张雷雷)[1], Fang Peng(彭放)[1], Ming Yang(杨鸣)[1], Xiao-lin Ni(倪小林)[1], and Jing Liu(刘景)[2]

[1] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*

[2] *Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*

(Received 25 November 2017; revised manuscript received 2 February 2018; published online 26 April 2018)

The compressibility and pressure-induced phase transition of β-Si_3N_4 were investigated by using an angle dispersive x-ray diffraction technique in a diamond anvil cell at room temperature. Rietveld refinements of the x-ray powder diffraction data verified that the hexagonal structure (with space group $P63/m$, $Z = 2$ formulas per unit cell) β-Si_3N_4 remained stable under high pressure up to 37 GPa. Upon increasing pressure, β-Si_3N_4 transformed to δ-Si_3N_4 at about 41 GPa. The initial β-Si_3N_4 was recovered as the pressure was released to ambient pressure, implying that the observed pressure-induced phase transformation was reversible. The pressure–volume data of β-Si_3N_4 was fitted by the third-order Birch–Murnaghan equation of state, which yielded a bulk modulus $K_0 = 273(2)$ GPa with its pressure derivative $K_0' = 4$ (fixed) and $K_0 = 278(2)$ GPa with $K_0' = 5$. Furthermore, the compressibility of the unit cell axes (a and c-axes) for the β-Si_3N_4 demonstrated an anisotropic property with increasing pressure.

Keywords: phase transition, bulk modulus, β-Si_3N_4, high pressure *in situ* x-ray diffraction

PACS: 61.05.cp, 31.15.ae, 81.05.Je, 64.70.K– **DOI:** 10.1088/1674-1056/27/5/056101

1. Introduction

Ceramic silicon nitride (Si_3N_4) has a broad range of applications (cutting tools, antifriction bearings and etch masks in microelectronics) in various industries because of its superior properties such as excellent mechanical strength, high thermal stability and relatively low mass density.[1–4] Studying the influence of pressure on the structural stability and possible phase transition of β-Si_3N_4 will provide us with insight into its potential applications under extreme conditions. The two known polymorphs of silicon nitride are α-Si_3N_4 and β-Si_3N_4. Both have a hexagonal lattice with different stacking sequences of the layered atoms perpendicular to the c-axis. A third cubic form (c-Si_3N_4) with a spinel structure has been found recently and studied at pressures above 15 GPa and temperatures over 2000 K.[5–11] This phase, c-Si_3N_4, is expected to be a hard material. In 2016, Nishiyama *et al*. reported the synthesis of the hardest transparent spinel ceramic, i.e., polycrystalline cubic silicon nitride (c-Si_3N_4). It is believed to be the third-hardest material after diamond and cubic boron nitride (cBN).[12–14] So it is of great importance to study the high-pressure behavior of silicon nitride.

In 2001, Zerr *et al.* found the fourth form of Si_3N_4 (labeled the δ phase) by energy dispersive x-ray diffraction (EDXD) measurements, which were derived from a pressure-induced phase transition of the β-Si_3N_4 at 42.6 GPa.[15] However, the obtained data (only one pattern) was not enough to determine the structure of δ-Si_3N_4.[15] After that, although some people predicted the structure of the δ-Si_3N_4 (Table 1),[16,17] the structure of the δ-Si_3N_4 has not been determined yet. According to the crystallographic data predicted in some literatures, we also spent a lot of time refining the structure of δ-Si_3N_4. However, the identify the structure of δ-Si_3N_4 has not yet been identified. We believe that high-quality x-ray diffraction (XRD) patterns and more measurements are necessary to identify the structure of δ-Si_3N_4. In 2011, Xu *et al.* reported that the β-Si_3N_4 transforms to the δ-Si_3N_4 at about 34.0 GPa, while there was no visible δ-Si_3N_4 peaks at 34.0 GPa.[16] In addition, many researchers have devoted their studies to the compressibility and bulk modulus of β-Si_3N_4 based on first-principles calculations. Xu *et al.* reported the bulk modulus of β-Si_3N_4, $K_0 = 241$ GPa.[17] Kuwabara *et al.* obtained 252 GPa for the bulk modulus of β-Si_3N_4.[18] Ogata acquired the average bulk modulus of β-Si_3N_4, which was 225 GPa, by using the generalized gradient approximation (GGA) and the local density approximation (LDA).[19] Until now, few experiments have been conducted to obtain the compressibility and bulk modulus of β-Si_3N_4 by means of *in situ* angle dispersive x-ray diffraction (ADXRD) in a diamond anvil cell (DAC). Li *et al.* experimentally determined the bulk modulus of β-Si_3N_4, $K_0 = 270(5)$ GPa with $K_0' = 4.0(1.8)$ by using ADXRD techniques.[20] However, the data were too limited to permit reliable analysis. In addition, Cartz *et al.* obtained the bulk modulus of β-Si_3N_4, 256 GPa, by neutron diffraction methods, as shown in Table 2.[21]

†Corresponding author. E-mail: kouzili@scu.edu.cn

© 2018 Chinese Physical Society and IOP Publishing Ltd

Table 1. The predicted lattice parameters, Wyckoff positions, and space group of δ-Si_3N_4.

Space group	$P3$	$P\bar{6}$	$C2/m$	$cmcm$	$pnma$	Ref.
N1	1*b* (1/3,2/3,0.300)	1*c* (1/3,2/3,0)				
	1*c* (2/3,1/3,0.333)	1*f* (2/3,1/3,1/2)				
N2	1*c* (2/3,1/3,0.333)	3*j*(0.269,0.013,0)				[15]
	3*d* (0.625,0.021,0.795)	3*k*(0.630,0.994,1/2)				
Si	3*d* (0.136,0.733,0.293)	3*j*(0.148,0.741,0)				
	3d(0.860,0.294,0.773)	3*k* (0.853,0.257,1/2)				
a/Å			9.85	2.66	8.70	
b/Å			2.80	8.91	2.75	[32]
c/Å			2.80	9.18	9.57	

Table 2. Comparison of compressibility and phase transition pressure: bulk modulus K_0, its pressure derivative K_0' and phase transition pressure P of β-Si_3N_4.

K_0/GPa	K_0'	Techniques	P/GPa	Ref.
252	4.0	LDA		[18]
237.2		GGA		[35]
225		LDA		[19]
270(5)	4(1.8)	ADXRD		[20]
256		neutron diffraction		[21]
241	3.4	LDA		[17]
273(2)	4(fixed)	ADXRD		this work
278(2)	5	ADXRD		this work
			42.6	[15]
			34	[17]
			41	this work

In this work, we investigated the compression behavior of β-Si_3N_4 at room temperature using ADXRD measurement and determined the equation of state (EOS) of β-Si_3N_4 under high pressure of up to 37 GPa. The pressure-induced reversible phase transformation process from β-Si_3N_4 to δ-Si_3N_4 was observed at ambient temperature.

2. Experimental procedures

The initial silicon nitride (β-Si_3N_4) powder (99.9% purity, 2.5 μm average particle size) was purchased commercially from Alfa Aesar. The sample was baked at 800 °C for 60 min to remove any possible hydroxide and moisture before loading into the DAC. Characterizations of the starting material were carried out by using both XRD and scanning electron microscopy (SEM) techniques. The XRD pattern (Fig. 1(a)) confirmed that the initial powder had a pure hexagonal structure ($P63/m$ space group, $Z = 2$ formula units per unit cell). The average particle size of the sample was estimated to be about 2.5 μm from the SEM micrograph (Fig. 1(b)).

High pressure was generated using a symmetric-type DAC with the culet size of 300 μm. The stainless steel (T301) gasket with an initial thickness of 250 μm was pre-indented to about 35 μm and a sample chamber with a diameter of about 100 μm was drilled in the center. The initial powder (β-Si_3N_4) was pre-compressed to a thickness of less than 35 μm with a pair of tungsten carbide (WC) cubes and loaded into the sample chamber.[22] A tiny ruby sphere was placed near the sample in the chamber as the pressure standard,[23] which can decrease the error of the measured pressure. The pressures were determined by the ruby fluorescence method.[23] The methanol–ethanol (4:1) mixture was used as the pressure-transmitting medium for quasihydrostatic conditions.[24]

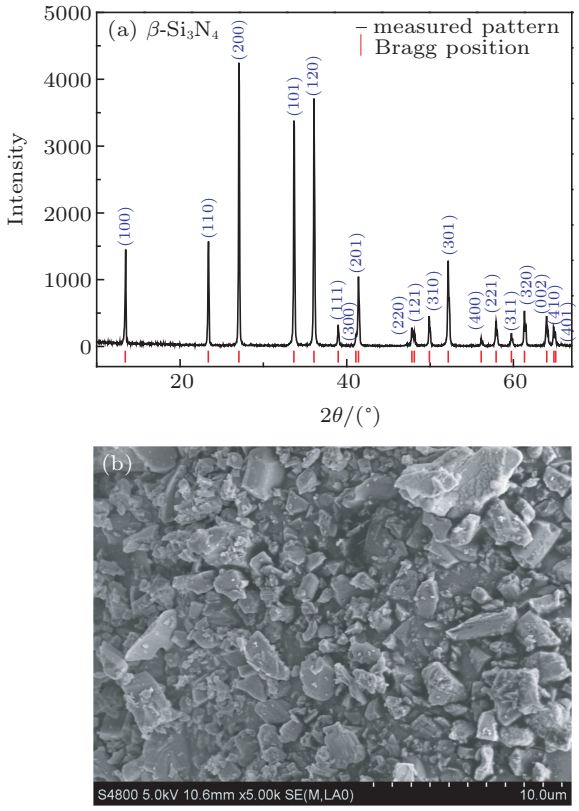


Fig. 1. (color online) (a) The XRD pattern of the initial β-Si_3N_4 powder under normal pressure and room temperature. Black solid line: measured pattern, red short vertical lines: all possible Bragg positions. (b) The SEM image of the initial β-Si_3N_4 powder.

In situ high pressure ADXRD experiments were performed at room temperature at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF, China), Chinese Academy of Sciences. In all experiments, the synchrotron source with a wavelength of 0.6199 Å was tuned by a Si (111) monochromator. The incident x-ray beam was focused to approximately 38 μm (vertical)×16 μm (horizontal) full width at half-maximum (FWHM) by a pair of Kirkpatrick–Baez

mirrors. The two-dimensional diffraction patterns at various pressures were collected using a Mar345 image plate detector. The collected two-dimensional diffraction patterns were integrated into one-dimensional diffraction profiles with the software FIT2D.[25] High-purity CeO_2 powder was used to calibrate the distance and orientation of the detector.[26] Rietveld analysis was performed using the general structure analysis system (GSAS) program as implemented in the EXPGUI package.[27–29]

3. Results and discussion

Figure 2 shows the XRD spectra of β-Si_3N_4 during compression and decompression to atmosphere. The hexagonal structure β-Si_3N_4 remains stable up to 37.0 GPa. New diffraction peaks marked with asterisks emerge at the pressure of 41.0 GPa, clearly indicating that the phase transition begins. The phase transition pressure (PTP) is in excellent agreement with that in the previous study.[15] However, this PTP is about 7 GPa higher than that confirmed by Xu *et al.* and the phase transition confirmed by Xu *et al.* was not obvious.[17] The deviation of the PTP could be ascribed to the different grain sizes or impurities of the starting sample being used, the different pressure calibration methods and different assemblies. In addition, the PTP is also influenced by the experimental conditions, such as non-hydrostaticity of pressure.[16,30] Zerr and Xu *et al.* did not elaborate upon the grain size, purity of the initial powder and experimental assembly. Upon further compression, the (100), (200) and (101) planes in the initial β-Si_3N_4 phase disappear gradually with the rapidly enhancement of the three new diffraction peaks. Finally, three original peaks are replaced by three new diffraction peaks, suggesting the accomplishment of the phase transition at the pressure of 43.2 GPa. The phase transition can also be confirmed by the collected Debye rings from β-Si_3N_4 at pressures of 33.8 GPa (Fig. 3(a)), 37.0 GPa (Fig. 3(b)) and 41.0 GPa (Fig. 3(c)). At 41.0 GPa, the Debye ring changes obviously. In addition, the typical XRD pattern at 5.6 GPa by Rietveld refinements is presented in Fig. 4, which confirms that the crystal structure of β-Si_3N_4 is stable under high pressure up to 37.0 GPa. Upon releasing pressure to ambient pressure, all the diffraction peaks of β-Si_3N_4 are retained, suggesting that the pressure-induced phase transition is reversible.

Figure 5 shows the pressure-dependent volume measurements. The third-order Birch–Murnaghan EOS is given as[31,32]

$$P(V) = \frac{3}{2}K_0\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right] \times \left\{1 + \frac{3}{4}(K_0' - 4)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\},$$

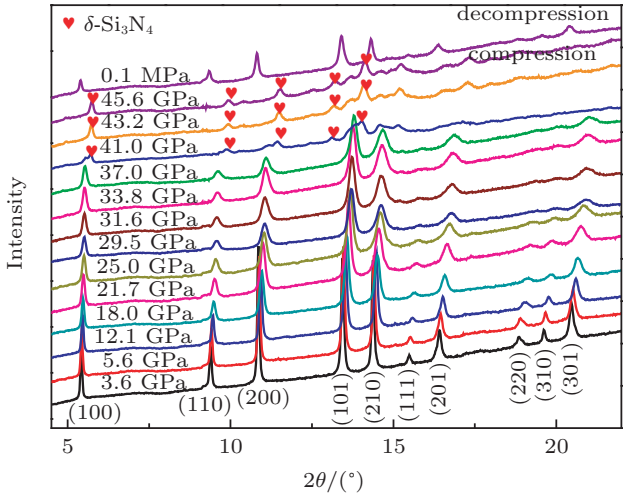


Fig. 2. (color online) Representative high-pressure synchrotron radiation XRD patterns of β-Si_3N_4 at various pressures.

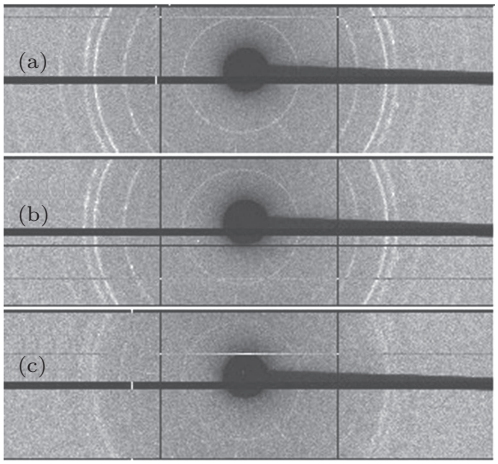


Fig. 3. Typical two-dimensional ADXRD patterns obtained from β-Si_3N_4 under different pressures: (a) $P = 33.8$ GPa, (b) $P = 37.0$ GPa, (c) $P = 41.0$ GPa.

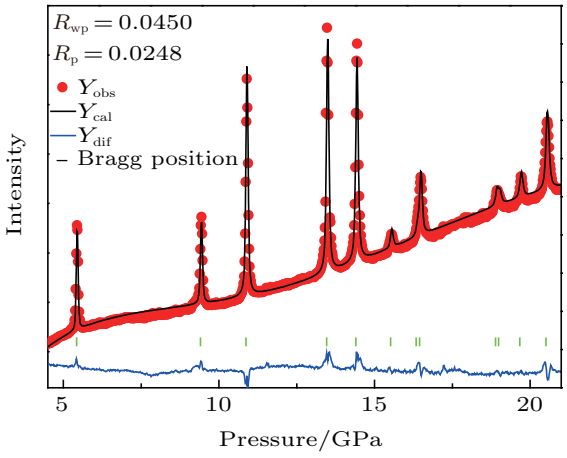


Fig. 4. (color online) Powder XRD structure refinement pattern of β-Si_3N_4 at 5.6 GPa. Red dotted line: measured pattern, black solid line: calculated curve, green short vertical lines: all possible Bragg positions, bottom line: difference curve.

where V_0, K_0 and K_0' are the volume at zero pressure, the zero pressure bulk modulus and the bulk modulus pressure derivative, respectively. By the least-squares fit to our data obtained at BSRF using the Birch–Murnaghan EOS, we ob-

tain bulk modulus $K_0 = 273(2)$ GPa with its pressure derivative $K_0' = 4$ (fixed) and $K_0 = 278(2)$ GPa with $K_0' = 5$. Our results are well consistent with the experimental bulk modulus, $K_0 = 270(5)$ GPa.[20] Nevertheless, the bulk modulus of our experiment is much higher than the results of theoretical calculations, 225 GPa and 237.2 GPa (Table 2).[19,35] This can be attributed to the larger non-hydrostatic compression caused by solidification of the pressure media methanol–ethanol (4:1) mixture.[33] To better understand the compression behavior of the unit cell axes, we plot the pressure dependence of the normalized lattice parameters a/a_0 and c/c_0 (Fig. 6), where a_0 and c_0 are the equilibrium structural parameters under ambient conditions. Obviously, the compression behaviors of β-Si_3N_4 are anisotropic between the a-axis and c-axis under high pressure up to 37.0 GPa. The compression of the a-axis is more obvious than that of the c-axis. Among the elastic constants, C_{11} and C_{33} represent the incompressibility of the a and c directions, respectively. Previous studies reported the calculated elastic constants C_{ij} (GPa) of β-Si_3N_4 under pressures up to 35.0 GPa (Table 3).[34] In our work, the anisotropic compressibility of the a-axis and c-axis is not obvious in the low pressure section. With increasing pressure, the anisotropic property of β-Si_3N_4 becomes more and more distinct (Fig. 6). Our experimental results are in agreement with the theoretical calculations (Table 3). In order to understand the anisotropic behavior, it is necessary to investigate the crystal structure of β-Si_3N_4. Figure 7 displays the crystal structure of hexagonal β-Si_3N_4, which consists of SiN_4 tetrahedrons connected by three coordinated N atoms within the plane. Six SiN_4 tetrahedrons round a ring stacking structure along the c-axis. However, the ring-type structure does not lie in the a–b plane, but has an angle relative to the a–b plane. Thus, the specially puckered ring structure layers and SiN4 tetrahedrons may enhance the incompressibility along the c-axis.

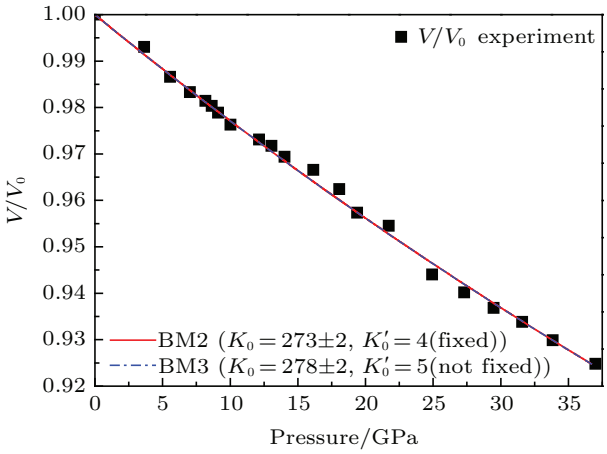


Fig. 5. (color online) Pressure dependence of the normalized unit-cell volumes in β-Si_3N_4 measured from 0 to 37.0 GPa at room temperature. The black solid squares represent the experimental data. The red solid and blue dashed lines correspond to the fitting results generated via second- and third-order Birch–Murnaghan EOSs, respectively.

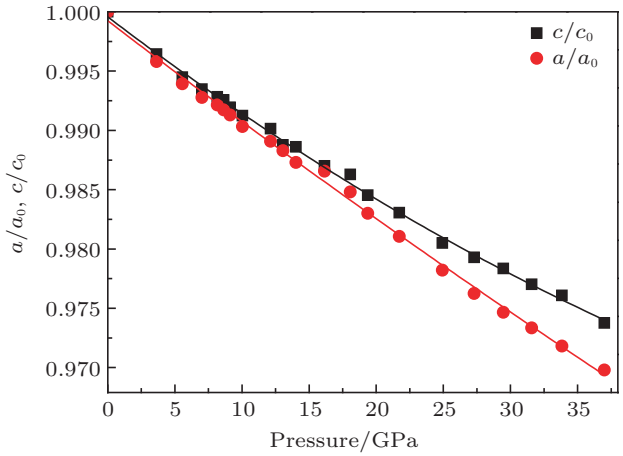


Fig. 6. (color online) Compressibility of the normalized lattice parameters of β-Si_3N_4. As the pressure increases the anisotropy of β-Si_3N_4 becomes more and more distinct.

Table 3. Calculated elastic constants C_{ij} (GPa) of β-Si_3N_4 under pressures up to 35 GPa from Ref. [30].

Pressure/GPa	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
0	444.96	186.35	119.65	583.27	109.84
5	459.77	204.83	135.70	606.49	108.18
10	473.88	227.17	151.49	628.41	102.84
15	490.82	246.87	168.50	651.76	100.10
20	508.44	264.53	182.49	680.26	96.67
25	517.41	283.41	198.90	704.70	92.17
30	537.12	292.64	216.10	724.21	93.95
35	541.81	318.40	232.16	743.49	85.25

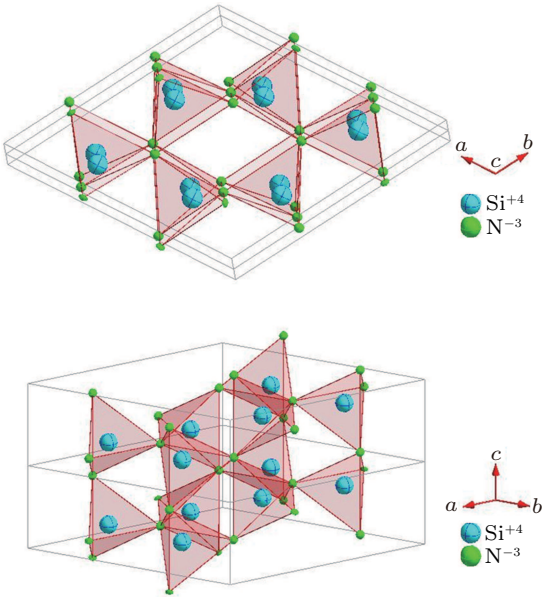


Fig. 7. (color online) Crystal structure of β-Si_3N_4. Large blue spheres represent Si atoms and small green spheres are N atoms.

4. Conclusion

In summary, the phase transition and compressibility of β-Si_3N_4 were investigated at pressure up to 45.6 GPa by synchrotron ADXRD at room temperature. A pressure-induced reversible phase transition was observed at 41 GPa. The compression curve of β-Si_3N_4 yielded a bulk modulus $K_0 =$

273(2) GPa with $K_0' = 4$ (fixed) and $K_0 = 278(2)$ GPa with its pressure derivative $K_0' = 5$. We also plotted the pressure dependence of the normalized lattice parameters a/a_0 and c/c_0, indicating that the compression behavior of the a-axis and c-axis of β-Si_3N_4 under high pressure up to 37.0 GPa is anisotropic.

Acknowledgment

The high pressure *in situ* synchrotron radiation angle dispersive x-ray diffraction (ADXRD) experiments were carried out at beam line 4W2 of the Beijing Synchrotron Radiation Facility (BSRF), which is supported by Chinese Academy of Sciences (Grant Nos. KJCX2-SW-N03 and KJCX2-SW-N20).

References

[1] Clarke D R, Lange F F and Schnittgrund G D 1982 *J. Am. Ceram. Soc.* **65** c51
[2] He H, Sekine T, Kobayashi T, Hirosaki H and Suzuki I 2000 *Phys. Rev. B* **62** 11412
[3] Jack K H 1976 *J. Mater. Sci.* **11** 1135
[4] Zhang C, Shun J X, Tian R G and Zhou S Y 2007 *Acta Phys. Sin.* **56** 5969 (in Chinese)
[5] Jiang J Z, Lindelov H, Gerward L, Ståhl K, Recio J M, Morisanchez P, Carlson S, Mezouar M, Dooryhee E and Fitch A 2002 *Phys. Rev. B* **65** 161202
[6] Jiang J Z, Ståhl K, Berg R W, Frost D J, Zhou T J and Shi P X 2000 *Europhys. Lett.* **51** 62
[7] Paszkowicz W, Minikayev R, Piszora P, Knapp M, Bähtz C, Recio J M, Marqués M, Morisánchez P, Gerward L and Jiang J Z 2004 *Phys. Rev. B* **69** 052103
[8] Soignard E, Somayazulu M, Dong J, Sankey O F and Mcmillan P F 2001 *J. Phys.: Condens. Matter* **13** 557
[9] Togo A and Kroll P 2008 *J. Comput. Chem.* **29** 2255
[10] Wang W, He D, Tang M, Li F, Liu L and Bi Y 2012 *Diamond Relat. Mater.* **27** 49
[11] Zerr A, Miehe G, Serghiou G, Schwarz M, Kroke E, Riedel R, Fueß H, Kroll P and Boehler R 1999 *Nature* **400** 340
[12] Nishiyama N, Ishikawa R, Ohfuji H, Marquardt H, Kurnosov A, Taniguchi T, Kim B N, Yoshida H, Masuno A and Bednarcik J 2017 *Sci. Rep.* **7** 44755
[13] Tanaka I, Oba F, Sekine T, Ito E, Kubo A, Tatsumi K, Adachi H and Yamamoto T 2002 *J. Mater. Res.* **17** 731
[14] Zerr A, Kempf, Schwarz M, Kroke E, Göken M and Riedel R 2002 *J. Am. Ceram. Soc.* **85** 86
[15] Zerr A 2001 *Phys. Status Solidi B* **227** R4
[16] Kroll P and Appen J V 2001 *Phys. Status Solidi B* **226** R6
[17] Xu B, Dong J, Mcmillan P F, Shebanova O and Salamat A 2011 *Phys. Rev. B* **84** 014113
[18] Kuwabara A, Matsunaga K and Tanaka I 2008 *Phys. Rev. B* **78** 064104
[19] Ogata S, Hirosaki N, Kocer C and Shibutani Y 2004 *Acta Mater.* **52** 233
[20] Li Y M, Kruger M B and Nguyen J H 1997 *Solid State Commun.* **103** 107
[21] Cartz L and Jorgensen J D 1981 *J. Appl. Phys.* **52** 236
[22] Liang H, Peng F, Fan C, Zhang Q, Liu J and Guan S X 2017 *Chin. Phys. B* **26** 053101
[23] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673
[24] Kaner R B, Gilman J J and Tolbert S H 2005 *Science* **308** 1268
[25] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 14
[26] Yang S W, Peng F, Li W T, Hu Q W, Yan X Z, Lei L, Li X D and He D W 2016 *Chin. Phys. B* **25** 076101
[27] Larson A C and Dreele R B V 1994 *Los Alamos National Laboratory Report No LAUR* **86**
[28] Rietveld H M 1969 *J. Appl. Cryst.* **2** 65
[29] Toby B H 2001 *J. Appl. Cryst.* **34** 210
[30] Qian Z, Xiang W and Shan Q 2017 *Chin. Phys. B* **26** 090703
[31] Birch F 1978 *J. Geophys. Res.* **83** 1257
[32] Murnaghan F D 1944 *Proc. Natl. Acad. Sci. USA* **30** 244
[33] Angel R J, Bujak M, Zhao J, Gatta G D and Jacobsen S D 2007 *J. Appl.Cryst.* **40** 26
[34] Hou H J, Zhu H J, Lao C W, Li S P, Guan H and Xie L H 2016 *Braz. J. Phys.* **46** 393
[35] Zhang R F, Sheng S H and Veprek S 2007 *Appl. Phys. Lett.* **90** 191903