Silicon pernitride, SiN$_2$, was synthesized from the elements at 140 GPa in a laser-heated diamond anvil cell. Its crystal structure was solved and refined by means of synchrotron-based single-crystal X-ray diffraction data. The title compound crystallizes in the pyrite structure type (space group $P$a$_3$, No. 205). The Si atom occupies a site with multiplicity 4 (Wyckoff letter b, site symmetry .3.), while the N atom is located on a site with multiplicity 8 (Wyckoff letter c, site symmetry .3.). The crystal structure of SiN$_2$ is comprised of slightly distorted [SiN$_6$] octahedra interconnected with each other by sharing vertices. Crystal chemical analysis of bond lengths suggests that Si has a formal oxidation state of +IV, while nitrogen forms pernitride anions (N—N)$^{4–}$.

1. Chemical context

Nitrogen-rich materials have gained a lot of attention due to their diverse properties such as high hardness, incompressibility (Young et al., 2006; Bykov et al. 2019a) and high energy density (Bykov et al., 2021; Wang et al., 2022). Among these, binary high-pressure nitrides of group 14 elements are of particular interest, as they exhibit remarkable elastic and electronic properties compared to their ambient-pressure counterparts. In particular, cubic silicon nitride $\gamma$-Si$_3$N$_4$, synthesized from the elements at about 15 GPa, is significantly more incompressible than the ambient-pressure $\alpha$- and $\beta$-polymorphs (Zerr et al., 1999). Recently Niwa et al. (2017) have synthesized pernitrides of group 14 elements (SiN$_2$, SnN$_2$ and GeN$_2$) by using laser-heated diamond anvil cells at pressures above 60 GPa. The crystal structures of GeN$_2$ and SnN$_2$ were solved and refined against powder X-ray diffraction data. However, the weak X-ray powder pattern of SiN$_2$ only allowed the suggestion that SiN$_2$ crystallizes in the pyrite structure type, while no structure refinement was performed.

In this work, we synthesized SiN$_2$ from the elements at pressures of 140 GPa and examined it by means of synchrotron single-crystal X-ray diffraction in order to solve and refine its crystal structure.

2. Structural commentary

SiN$_2$ crystallizes in fact in the pyrite structure type in the space group $P$a$_3$ (No. 205). The asymmetric unit comprises two atoms, a silicon atom (multiplicity 4, Wyckoff letter b, site symmetry .3.), and a nitrogen atom (8 c, .3.). The nitrogen atoms form N—N dimers, and consequently each of the N atoms is tetrahedrally coordinated by three Si atoms and one N atom. The centers of the N—N dimers form an fcc sublat-
3. Synthesis and crystallization

A piece of silicon (10×10×5 μm³) was placed in the sample chamber of a BX90-type diamond anvil cell equipped with Bohler–Almax type diamonds using culets of 100 μm in diameter. The sample chamber was eventually created by laser-drilling a 50 μm hole in the Re gasket preindented to a thickness of 18 μm. Nitrogen, loaded using the high-pressure gas-loading system of the Bavarian Geoinstitute (Kurnosov et al., 2008), served both as a pressure-transmitting medium and as a reagent. Pressure was determined by the shift of the diamond Raman band (Akahama & Kawamura, 2006). Upon compressing to the target pressure of 140 GPa, the sample was heated using a focused Nd:YAG laser (λ = 1064 nm) to temperatures exceeding 2500 K. The heating duration was approximately 10 seconds. The reaction products consisted of multiple high-quality, single-crystalline domains.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The sample was studied by means of synchrotron single-crystal X-ray diffraction (SCXD) at the beamline ID11 (ESRF, Grenoble, France) with the following beamline setup: λ = 0.28457 Å, beamsize ~0.7×0.7 μm², Eiger CdTe 2M detector. For the SCXD measurements, samples were rotated around a vertical ω-axis in the range ±30°. The diffraction images were acquired at an angular step Δω = 0.5° and an exposure time of 5 s per frame. For analysis of the single-crystal diffraction data (indexing, data integration, frame scaling and absorption correction) we used the CrysAlis PRO software package (Rigaku OD, 2023). To calibrate an instrumental mode using CrysAlis PRO, i.e., the sample-to-detector distance, detector origin, offsets of goniometer angles, and rotation of both X-ray beam and the detector around the instrument axis, we used a single crystal of orthoenstatite [(MgSi1.93Fe0.06)(Si1.93Al0.06)O6] space group Pbcn, a = 8.8117(2), b = 5.18320(10), and c = 18.239(13) Å.

Data analysis followed several steps:

1. After collecting SCXD data sets (series of ~120 frames), a 3D peak search procedure was performed as implemented CrysAlis PRO. This search identified reflections from all crystalline phases present in the collection spot, including reaction products, initial reagents, pressure-transmitting medium, diamonds and gasket material.

2. The peak search table was processed by means of the DaFi program (Aslandukov et al., 2022), which sorts reflections into groups: if reflections fall into one group they originate from one grain of the multigrain sample.
3. The reflection groups were assessed individually by indexing the reflections within the current group using built-in procedures in CrysAlis PRO. If indexing succeeded, the group was chosen for final data integration.

4. Datasets were integrated, and data was reduced following standard procedures, taking into account the shadowing of the diamond anvil cell.

Acknowledgements

We acknowledge the European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities and we would like to thank Pierre-Olivier Autran for assistance and support in using beamline ID11. We thank Dr Alexander Kurnosov for loading the DAC with nitrogen.

Funding information

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References


Supporting information


Synthesis and crystal structure of silicon pernitride SiN$_2$ at 140 GPa

Pascal L. Jurzick, Georg Krach, Lukas Brüning, Wolfgang Schnick and Maxim Bykov

Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2023); cell refinement: *CrysAlis PRO* (Rigaku OD, 2023); data reduction: *CrysAlis PRO* (Rigaku OD, 2023); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: Olex2 (Dolomanov et al., 2009).

Silicon pernitride

**Crystal data**

SiN$_2$

$M_r = 56.11$

Cubic, $P\overline{4}3$

$a = 4.1205$ (5) Å

$V = 69.96$ (3) Å$^3$

$Z = 4$

$F(000) = 112$

$D_x = 5.327$ Mg m$^{-3}$

**Data collection**

Customized $\omega$-circle diffractometer

Radiation source: synchrotron, ESRF, beamline ID11

Synchrotron monochromator

Detector resolution: 5.0 pixels mm$^{-1}$

$\omega$ scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2023)

**Refinement**

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.071$

$wR(F^2) = 0.191$

$S = 1.07$

101 reflections

6 parameters

0 restraints

Primary atom site location: dual

$w = 1/[\sigma^2(F_o^2) + (0.109P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.08$ e Å$^{-3}$

$\Delta\rho_{min} = -1.15$ e Å$^{-3}$

Synchrotron radiation, $\lambda = 0.28457$ Å

Cell parameters from 79 reflections

$\theta = 3.4$–16.4°

$\mu = 0.21$ mm$^{-1}$

$T = 293$ K

Irregular, colourless

0.001 × 0.001 × 0.001 mm
Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

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Symmetry codes: (i) −x+1, y+1/2, −z+3/2; (ii) −x+3/2, −y+1, z−1/2; (iii) x, −y+1/2, z−1/2; (iv) −x+1, −y+1, −z+1; (v) x−1/2, y, −z+3/2; (vi) −x+1, y−1/2, −z+3/2; (vii) −x+3/2, −y+1, z+1/2; (viii) −x+1, −y+1, −z+2.