

More Than 50 Years after Its Discovery in SiO₂ Octahedral Coordination Has Also Been Established in SiS₂ at High Pressure

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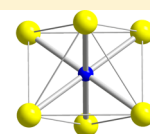
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S Supporting Information

ABSTRACT: SiO₂ exhibits a high-pressure–high-temperature polymorphism, leading to an increase in silicon coordination number and density. However, for the related compound SiS₂ such pressure-induced behavior has not been observed with tetrahedral coordination yet. All four crystal structures of SiS₂ known so far contain silicon with tetrahedral coordination. In the orthorhombic, ambient-pressure phase these tetrahedra share edges and achieve only low space filling and density. Up to 4 GPa and 1473 K, three phases can be quenched as metastable phases from high-pressure high-temperature to ambient conditions. Space occupancy and density are increased first by edge and corner sharing and then by corner sharing alone. The structural situation of SiS₂ up to the current study resembles that of SiO₂ in 1960: Then, in its polymorphs only Si–O₄ tetrahedra were known. But in 1961, a polymorph with rutile structure was discovered: octahedral Si–O₆ coordination was established. Now, 50 years later, we report here on the transition from 4-fold to 6-fold coordination in SiS₂, the sulfur analogue of silica.



HP4-SiS₂ 12.7 GPa
Si – S: 2.29(1) Å
Si – Si: 3.22(1) Å
S – S: 3.22(1), 3.24(1) Å

1. INTRODUCTION

It is very well known¹ that the most common elements in the earth's crust are oxygen (49.4 wt %) and silicon (25.4 wt %). The binary compound silica (SiO₂) incorporating these elements is the most abundant oxide on the surface of the earth.² It plays an important role in the physics and chemistry of the upper earth's crust and has a wide spectrum of technological applications.³ The compositional simplicity of this compound is accompanied by a considerable structural complexity.⁴ The ambient-pressure minerals quartz,⁵ tridymite,⁶ and cristobalite,⁷ all with a silicon coordination number (CN) of 4, exist in both low- and high-temperature forms. In 1961, a remarkable discovery was made by Stishov and Popova in Russia.⁸ They treated quartz with pressures between 10 and 18 GPa at temperatures between 1473 and 1673 K.⁹ With this, they obtained a microcrystalline high-pressure (HP) phase that could be quenched as a metastable phase to ambient conditions and indexed from the X-ray powder pattern as being the tetragonal rutile (TiO₂) structure. The density of 4.35 g·cm^{−3} represents an increase in relation to quartz of 62%.⁸ With the rutile structure, the first SiO₂ polymorph was established in which six oxygen atoms are coordinated as an octahedron around the central silicon atom, instead of the four oxygen atoms in a tetrahedron.

In 1962, Chao et al.¹⁰ investigated Coconino Sandstone of the Meteor Crater in Arizona. The most abundant phase was quartz, with small amounts of coesite¹¹ and still less of the new high-pressure SiO₂ polymorph with rutile structure. In addition, the new HP-polymorph of SiO₂ was also detected in coesite-bearing suevite of the Ries Crater in Bavaria.^{11,12} Thus, the new HP-polymorph of SiO₂ occurred naturally on the earth as a mineral. Chao et al. named it stishovite.¹⁰

Considering only valence electrons (e), SiO₂ and SiS₂ are both 16e systems. Such electron counts are observed in the symmetric linear three-atomic species CO₂, N₂O, N₃[−], OCN[−], CNO[−], NO₂⁺, CN₂^{2−}, or BN₂^{3−}. Up to 2015, however, only four crystal structures had been detected for solid SiS₂, all with a silicon CN of 4.¹³ Therefore, the structural situation in SiS₂ resembles that of SiO₂ before the discovery of Stishov and Popova in 1961.⁸

The ambient pressure (NP) phase NP-SiS₂ was first characterized in 1935 by Zintl and Loosen¹⁴ and also by Büssem et al.¹⁵ as orthorhombic.¹³ It consists of edge-sharing Si–S₄ tetrahedra running parallel to the *c*-axis. SiSe₂¹⁶ and the beryllium dihalogenides BeX₂ (X = Cl, Br, I),¹⁷ also with 16e, are isotypic to NP-SiS₂.^{13–15} The missing dihalogenide BeF₂

Received: September 22, 2016

Published: December 21, 2016



has at lower temperature a α -quartz structure and at higher temperature a β -quartz structure.¹⁸

The first HP investigations on SiSi_2 (6.0–6.5 GPa, 1148–1573 K) were performed by Silverman and Soulen in 1964¹⁹ and Prewitt and Young in 1965.²⁰ Silverman and Soulen indexed only the X-ray powder patterns with a tetragonal lattice,¹⁹ but Prewitt and Young solved via a single-crystal investigation the whole structure, here called HP3- SiSi_2 .²⁰ It consists of slightly distorted Si-Si_4 tetrahedra that share all corners and build up a three-dimensional net. Neglecting the symmetry properties, HP3- SiSi_2 can be compared with the α -quartz structure in which also all corner-sharing tetrahedra form a three-dimensional net.

The remaining two HP phases, here called HP1- and HP2- SiSi_2 , form the missing links between the two extremes of only edge-sharing (NP- SiSi_2) and only corner-sharing (HP3- SiSi_2). Both phases contain Si-Si_4 tetrahedra in which one edge and two corners are connected to neighboring tetrahedra. HP1- SiSi_2 ¹³ builds up a layer structure, and HP2- SiSi_2 forms a three-dimensional net.¹³ From packing analyses in HP1-, HP2-, and HP3- SiSi_2 it was derived in 2015 that “a large increase of the density may be possible if the applied pressure is increased up to 10–20 GPa”, changing the coordination of the silicon from tetrahedral to octahedral.¹³

In this paper, we report on the preparation and characterization by X-ray powder diffraction and also by Raman spectroscopy of HP4- SiSi_2 with the CdI_2 structure,²¹ featuring octahedral Si-Si_6 coordination.

2. RESULTS AND DISCUSSION

The X-ray diffraction pattern collected at the lowest experimental pressure of 2.6 GPa can be assigned to the NP- SiSi_2 orthorhombic *Ibam* structure with lattice parameters $a = 9.27(2)$, $b = 5.35(2)$, $c = 5.29(2)$ Å, consistent with the ambient-pressure single-crystal data.¹³ According to the X-ray diffraction patterns collected at room temperature and the isothermal compression (Figure 1), the NP- SiSi_2 phase remains stable up to approximately 7 GPa, at which pressure the appearance of the new diffraction peaks indicates the onset of the structural phase transition.

The transition to the new high-pressure phase appears to be very sluggish, with a broad pressure range in which there is a two-phase coexistence. The single-phase diffraction patterns collected at a pressure of 27.5 and 29.6 GPa (Figure 1) can be unambiguously indexed with the CdI_2 structure ($a = 3.179(5)$ Å, $c = 5.059(10)$ Å, $c/a = 1.59$, $V = 44.3(2)$ Å³; $a = 3.174(3)$ Å, $c = 5.022(8)$ Å, $c/a = 1.58$, $V = 43.8(2)$ Å³, respectively). Here, the lattice parameter c is more easily compressed than a . This leads to lowering of the axial ratio c/a with increasing high pressure, as a result of the weak van der Waals bonding in the c -direction. Despite pressure-induced line broadening, preferred orientation effects, and strong background (due to Compton electron scattering in stressed diamond anvils), Rietveld refinement of the diffraction patterns collected at the highest experimental pressure of 27.5 and of 29.6 GPa (Figure 1) provide good agreement with the suggested CdI_2 structure of the HP4- SiSi_2 phase. During the transformation, the color of the SiSi_2 sample changes from white at low pressure via yellow and brown to black at very high pressure, indicating a possible insulator–metal transition.

Raman spectroscopy studies performed at room temperature indicate the pressure-induced structural phase transition to the HP4- SiSi_2 phase also with the CdI_2 structure. The low-pressure

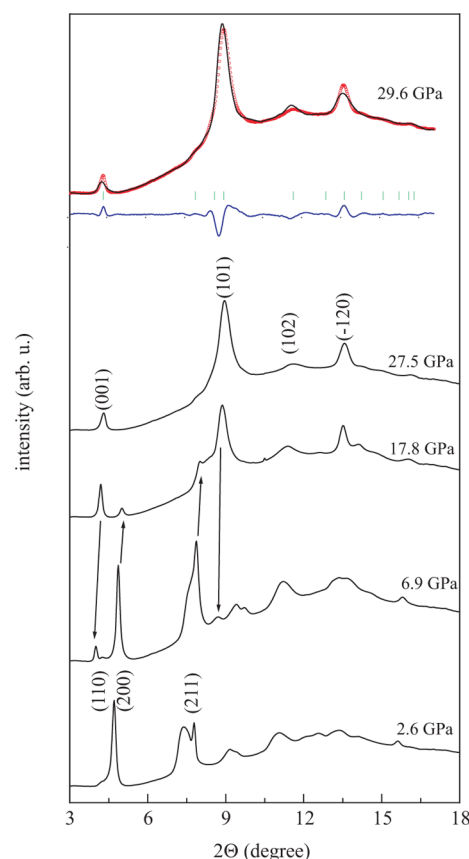


Figure 1. Diffraction patterns of SiSi_2 at different pressures collected at room temperature. Appearance of new diffraction peaks (marked with down-directed arrows) in the pattern at 6.9 GPa indicates an onset of structural phase transition to the HP4- SiSi_2 phase. The strongest reflections of the NP- SiSi_2 phase (unresolved (110) and (200) reflections and (211) peak) are seen in the pattern at 17.8 GPa as marked by up-directed arrows. The single HP4- SiSi_2 phase diffraction pattern at 27.5 GPa is indexed with the CdI_2 structure²¹ (*tP3*, $\overline{P}3m1$, $\text{Si } 1a$, (0, 0, 0), $S 2d$, (1/3, 2/3, 0.250), $a = 3.179(3)$ Å, $c = 5.059(10)$ Å, $c/a = 1.59$, $V = 44.3(2)$ Å³) by the Rietveld technique²² with $R_p = 0.0094$, $R_{wp} = 0.0141$, and $R_{Bragg} = 0.225$. At the top of the figure the Rietveld refinement of the single-phase diffraction pattern for HP4- SiSi_2 at 29.6 GPa is shown. The experimental and calculated patterns are shown as open circles and a red line, respectively. Vertical bars indicate the calculated peak positions. The difference plot (blue line) is on the same scale.

Raman spectrum recorded at 1 GPa (Figure 2) is in full agreement with ambient-pressure Raman spectra of the NP- SiSi_2 phase.¹³ At pressures up to approximately 7 GPa, all observed vibrational peaks show normal pressure-induced shift to higher frequencies. The appearance of a new peak with a frequency of approximately 414 cm^{-1} in the spectrum at 7.4 GPa indicates the onset of the phase transition to the HP4- SiSi_2 phase, similarly to our X-ray diffraction data. Raman spectroscopy data as well indicate a broad range of the phase coexistence, so that a single-phase spectrum is observed only at a pressure above 22 GPa. The Raman spectrum of HP4- SiSi_2 contains only two vibrational lines, at 294 and 453 cm^{-1} , which can be assigned to E_g and A_{1g} Raman-active vibrational modes predicted by the group theory for the $\overline{P}3m1$ space group. The observed Raman spectra of the HP4- SiSi_2 phase are very similar to those of other compounds crystallizing in the CdI_2 structure, e.g., TiSi_2 ²³ and SnSi_2 .²⁴ Thus, both X-ray diffraction and Raman

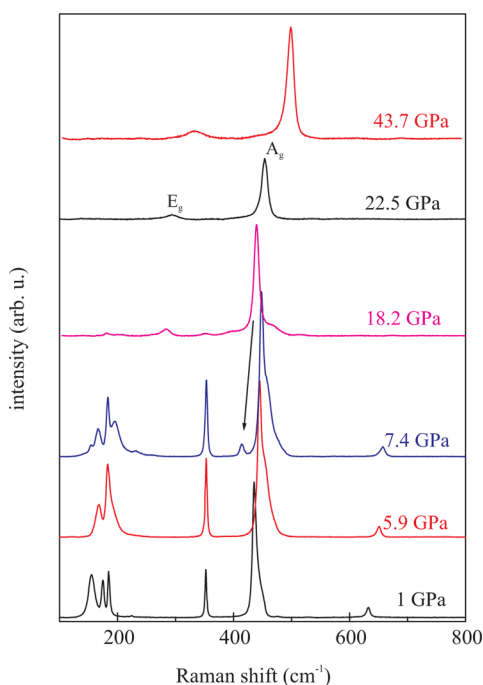


Figure 2. Raman spectra of SiS₂ at various pressures collected at room temperature. The appearance of new peaks (marked with a down-directed arrow in the spectrum at 7.4 GPa) indicates an onset of the structural phase transition to the HP4-SiS₂ phase. The single-phase spectrum of the HP4-SiS₂ phase at 22.5 GPa contains two vibrational modes, E_g and A_{1g}, as expected for the CdI₂ structure.

spectroscopy studies unambiguously indicate pressure-induced structural phase transition to the HP-4 SiS₂ phase, featuring a CdI₂ structure with an octahedral coordination of the Si atom. The CdI₂ structure of SiS₂ remains stable up to pressures well above 43.7 GPa (Figure 2). Contrary to stishovite, HP4-SiS₂ cannot be quenched to its ambient condition as a metastable phase. In Figure 3, two views of the CdI₂ structure for HP4-SiS₂ with octahedral Si-S₆ coordination are shown.

The distances Si-S, Si-S, and S-S for HP4-SiS₂ can be derived from the lattice parameters of the CdI₂ structure at 12.7 GPa ($a = 3.222(3)$ Å, $c = 5.308(5)$ Å), obtained by the Rietveld technique (Si-S 2.29(1), Si-Si 3.22(1), S-S 3.22(1), 3.24(1) Å). For NP-SiS₂, the structural data at 1 bar and 300 K (Si-S 2.130(2), Si-Si 2.776(3), S-S 3.231(4), 3.577(4), 3.615(4)

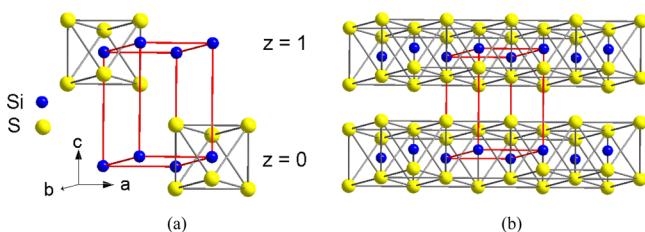


Figure 3. Crystal structure of the HP4-SiS₂ phase. (a) Diamond2²⁵ view along [110] on one unit cell of trigonal HP4-SiS₂. The sulfur atoms build up hexagonal close-packed layers with sequence A, B, ..., with silicon atoms filling half of the octahedral voids. For the ideal axial ratio $c/a = 1.633$ all 12 octahedral S-S edges are equidistant. For reasons of clarity only two Si-S₆ octahedra are shown, centered at $z = 0$ and $z = 1$. (b) Diamond2 view of the two layers of corner-shared Si-S₆ octahedra. Between the layers (A, B)...(A, B)... only weak van der Waals bonding is present, denoted by dotted lines (...).

Å), obtained from a single-crystal investigation,¹³ can be converted to 12.7 GPa. The volume $V_{\text{NP},12.7 \text{ GPa}}$ for NP-SiS₂ at 12.7 GPa with $z = 1$ is calculated from the lattice parameters of the HP diffractogram; $V_{\text{NP},12.7 \text{ GPa}} = (8.82 \times 5.09 \times 5.04)/4 = 226.26/4 = 56.6$ Å³. The volume at ambient pressure ($V_{\text{NP,ambient}}$) for NP-SiS₂ with $z = 1$ is calculated from the lattice parameters¹³ with $z = 4$: $V_{\text{NP,ambient}} = (9.6095 \times 5.61595 \times 5.5528)/4 = 299.85/4 = 74.96$ Å³. From the cubic root of the ratio of the two volumes (56.6, 74.96 Å³) one can derive a compression factor $f_{\text{com}} = (56.6/74.96)^{0.33333} = 0.911$, neglecting the different compressibilities of the lattice parameters a , b , and c in NP-SiS₂. Therefore, one can derive the distances at 12.7 GPa from that of the ambient one by multiplying them by 0.911; for example, the tetrahedral Si-S distance at 1 bar of 2.130(2) Å is converted to 0.911×2.130 Å = 1.94(1) Å at 12.7 GPa, the Si-Si distances to $0.911 \times 2.776 = 2.53(1)$ Å, and the S-S distances to 0.911×3.231 Å = 2.94 Å, to 0.911×3.577 Å = 3.26(1) Å, and to 0.911×3.615 Å = 3.29(1) Å with an average value of 3.16 Å.

In Figure 4a, a Si-S₄ tetrahedron of NP-SiS₂ is compared to a Si-S₆ octahedron of HP4-SiS₂, both at 12.7 GPa (Figure 4b).

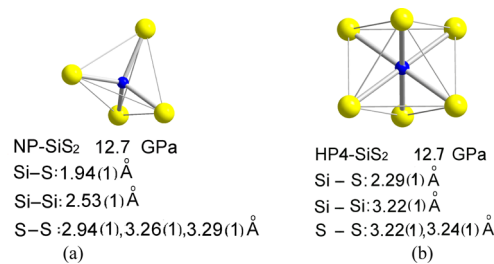


Figure 4. Coordinational units in SiS₂. (a) Diamond2 view of a Si-S₄ tetrahedron at 12.7 GPa. Distances have been estimated from the distances at ambient pressure, applying the correction factor 0.911 (see text). (b) Diamond2 view of a Si-S₆ octahedron at 12.7 GPa. Distances have been derived from the measured diffractogram.

The transformation of Si-S₄ tetrahedra in NP-SiS₂ above 12 GPa into Si-S₆ octahedra of the CdI₂ structure fulfills three principles for high-pressure chemistry: (1) The *pressure-coordination principle* derived by Neuhaus²⁶ states that application of high pressures onto a compound leads often to an increased CN. Here, Si-S₄ tetrahedra with CN 4 are transformed into Si-S₆ octahedra with CN 6. (2) The *pressure-distance paradox* derived by Kleber²⁷ states that during a high-pressure transformation distances often increase in the HP phase. Inspection of Figure 4 shows that this principle is fulfilled for the transformation of NP-SiS₂ into HP4-SiS₂.²⁸ (3) The *pressure-homologue principle* derived by Wentorf²⁹ states that often HP crystal structures resemble the structures of the analogous compound made up of heavier elements in the periodic table. A compound made of heavier elements in the periodic table is SnS₂ with CdI₂ structure at ambient pressure ($a = 3.645(1)$ Å, $c = 5.891(1)$ Å).²³

The structural change under high pressure for five SiS₂ phases (NP, HP1, HP2, HP3, HP4) is easily understood if one compares the graphs of total energy E (Ryd) as a function of decreasing volume V , bearing in mind that HP1-, HP2-, and HP3-SiS₂ were synthesized in a belt-type apparatus between 2.8 and 4.0 GPa and 1373 to 1473 K.¹³ In Figure 5, the graphs for the five SiS₂ structures, calculated with the DFT program WIEN2k,³⁰ are shown. Inspection of Figure 5 shows that NP-

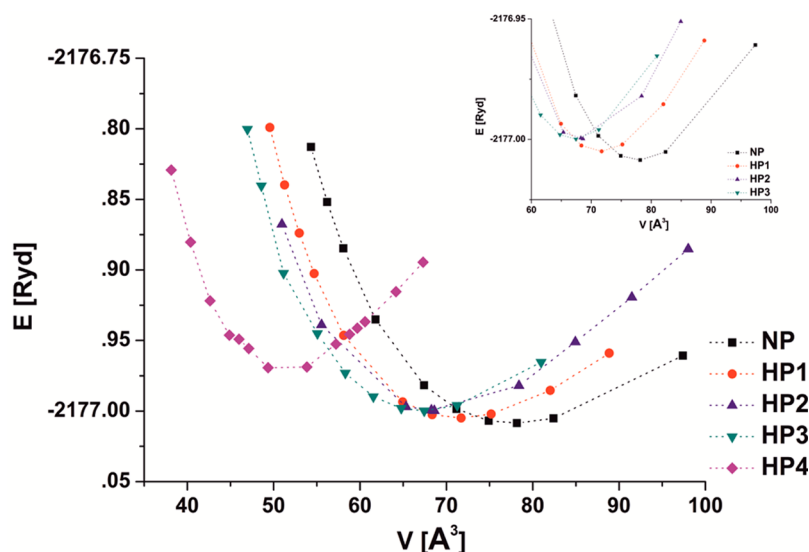


Figure 5. Total energy E (Ryd) as a function of volume V (\AA^3) for five known SiS_2 phases (NP, HP1, HP2, HP3, HP4) calculated with the DFT program WIEN2k.³⁰ The inset shows a zoom-in to distinguish NP-, HP1-, HP2-, and HP3- SiS_2 more easily.

SiS_2 has the lowest energy for the highest volume V_0 . Therefore, this phase is stable at the highest volume and lowest pressure. At nearly 70 \AA^3 the left part of the energy graph of NP- SiS_2 increases and the right part of the energy graph of HP1- SiS_2 becomes lower in energy. Therefore, HP1- SiS_2 now becomes stable. For HP2-, HP3- and HP4- SiS_2 the situation is repeated: Phases with lower volume become lower in energy.

The minima of NP, HP1, HP2, and HP3- SiS_2 , however, are in close proximity, whereas HP4- SiS_2 is shifted considerably. This is consistent with the required pressure to obtain the respective phases. NP- SiS_2 and the first three HP phases all lie in the range up about 5–6 GPa.¹³ However, HP4- SiS_2 requires pressures of at least 20 GPa. Its density ρ at ambient conditions, calculated with the DFT program WIEN2k,³⁰ is $\rho = 2.99 \text{ g cm}^{-3}$, which corresponds to an increase of 46% in relation to NP- SiS_2 , bearing in mind that the density increase in SiO_2 with rutile structure and octahedral Si-O₆ coordination is 62%. Interestingly, the rutile (TiO_2) structure for SiS_2 ⁸ (graph not shown in Figure 5) has nearly the same volume as the CdI_2 structure, but the energy is higher for the rutile structure. Up to now, the rutile structure had been established both at ambient and at high pressures only for oxides, fluorides, and hydrides, but not for sulfides.

3. CONCLUSION AND OUTLOOK

In conclusion, we were able to synthesize the first silicon sulfide with octahedral configuration and could precisely characterize the transition from 4-fold to 6-fold coordination between 18.2 and 43.7 GPa (Figure 2). It is a very convincing example for the *principles of high-pressure chemistry*. In addition, it may also be possible to further increase the CN in a new HP- SiS_2 polymorph at pressures much higher than 43.7 GPa.

Some decades ago, post-stishovite phases were identified in SiO_2 :³¹ one with CaCl_2 structure, a second with $\alpha\text{-PbO}_2$ structure, and a third with FeS_2 (pyrite) structure. Contrary to the last, the first two structures are close-packed. However, the third is even more densely packed due to the asphericity of the oxygen atoms in its structure.³¹ This phase with FeS_2 structure was synthesized in a diamond anvil cell at 102 GPa

and 2400 K and contains silicon with CN 6 + 2.³² At 271 GPa ($\text{Pa}3$, $z = 4$, $a = 3.9299(2) \text{ \AA}$) the density of this phase is $\rho = 6.59 \text{ g cm}^{-3}$, bearing in mind that stishovite has a density of $\rho = 4.35 \text{ g cm}^{-3}$ ³⁸ and α -quartz one of $\rho = 2.6495 \text{ g cm}^{-3}$ ³³ both at ambient pressure. In comparison to the smaller oxygen atoms in SiO_2 , the larger sulfur atoms in SiS_2 seem to be more easily deformed to asphericity at very high pressure. Thus, a SiS_2 polymorph with FeS_2 structure (CN 6 + 2) could probably be synthesized in a diamond anvil at less rigorous experimental conditions than for SiO_2 .

4. EXPERIMENTAL DETAILS

NP- SiS_2 was synthesized by the reaction of high-purity silicon and sulfur in a ratio of 1:2.2 in a sealed silica tube at temperatures between 770 and 1070 K. The empty silica tube was thoroughly dried before the synthesis by heating it to 1300 K under high-vacuum (HV) conditions. In a glovebox under purified argon the reactants were added to the tube and then sealed under HV. Direct contact of silicon and sulfur was avoided. A prereaction was performed at first by slowly heating the reactants for 3 days to 770 K. By this procedure an explosion was avoided since sulfur reacted from the vapor phase with silicon. Subsequently, the reaction temperature was increased within 3 days to 1070 K with a temperature gradient of 50 K between the cold and the hot end of the reaction tube, and the maximum temperature was maintained for a further 3 days. Then, the temperature of the empty side of the ampule was reduced to 970 K so that SiS_2 was sublimed within 3 days. Finally, the tube was slowly cooled to room temperature and opened in the glovebox due to the moisture sensitivity of SiS_2 . Guinier X-ray diffractograms (Huber G644, quartz monochromator) performed with Mo $K\alpha 1$ radiation ($\lambda = 0.7093 \text{ \AA}$) showed that NP- SiS_2 was obtained as single phase.

For *in situ* high-pressure synchrotron X-ray powder diffraction and Raman spectroscopy studies, sample was loaded in a diamond anvil cell equipped with diamond anvils with 500 μm culets and a tungsten gasket of 300 μm thickness preindented to $\sim 40 \mu\text{m}$. Due to the high chemical reactivity of SiS_2 , the sample was loaded without pressure-transmitting medium and loading was performed in a glovebox.

X-ray powder diffraction studies at high pressure were performed at ID27 of ESRF (Grenoble, France) with wavelength $\lambda = 0.3738 \text{ \AA}$. Raman spectroscopy studies were performed using a custom Raman optical confocal microscope system for diamond anvil cells with a single-imaging Princeton Instruments Acton SP 2500 spectrograph (focal length 500 mm) equipped with a 1200 grooves mm^{-1} diffraction

grating and a liquid nitrogen cooled charge-coupled device detector. The spectral resolution in the studied spectral range was 1 cm^{-1} . The Raman spectrometer was calibrated using Ne spectral lines with an uncertainty of 1 cm^{-1} . A Melles Griot 25-LHP-928-230 HeNe laser with a nominal power of 35 mW (accounting for losses on the optical elements, the laser power at the sample position can be estimated as $\sim 20\text{ mW}$) was used as the exciting source of the Raman spectra. The pressure was determined using the fluorescence lines of a ruby chip, which was loaded in contact with the sample.

DFT calculations (total energy as a function of unit-cell volume) were performed with the WIEN2k program³⁰ with the Generalized Gradient Approximation (GGA), potential 13, GMAX = 8, constant radii $r_{\text{MT}} = 1.80\text{ au}$, and a sufficient number of k-points (125 points for NP-SiS₂, 200 for HP1-SiS₂, 125 for HP2-SiS₂, 360 for HP3-SiS₂, 400 for HP4-SiS₂).

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02294.

For HP4-SiS₂ at 27.5 and at 29.6 GPa the CIF files and the HP4-SiS₂.out files obtained from the Rietveld fitting³⁰ with the program FullProf²² (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.E. and G.O. thank Prof. Dr. T. M. Klapötke and Prof. Dr. A. Kornath, Ludwig-Maximilian University Munich (LMU), and Dr. M. Allalen, Leibniz-Rechenzentrum (LRZ) of the Bavarian Academy of Science. L.M. thanks Prof. Dr. C. Bräuchle (LMU), O.B., S.M., and P.N. thank Prof. Dr. C. Felser (MPI-CPFS, Dresden) for encouraging support, and J.E. also thanks Prof. Dr. P. Kroll (University of Texas, Arlington) and Prof. Dr. E. Kroke and Dr. M. Schwarz (Technical University Freiberg) for critical discussions regarding the very high pressure phase of SiS₂. We acknowledge the European Synchrotron Radiation Facility for granting beam time, and we would like to thank Dr. M. Mezouar and Dr. G. Garbarino (ESRF) for assistance in using beamline ID27.

■ DEDICATION

This paper is dedicated to Prof. Sergei M. Stishov, Russian Academy of Sciences, in recognition of his outstanding contribution to high-pressure science and in honor of his 80th birthday.

■ REFERENCES

- (1) Wiberg, N. Holleman-Wiberg. *Lehrbuch der Anorganischen Chemie*; Walter de Gruyter: Berlin, 2007; p 78.
- (2) Silica, *Physical Behavior, Geochemistry and Materials Applications*, Preface and Acknowledgment; Heany, P. J., Prewitt, C. T., Gibbs, V., Eds.; *Reviews in Mineralogy*; Mineralogical Society of America: Washington, D.C., Vol. 29, 1994; p iii.
- (3) Hemley, R., Badro, J., Teter, D. M. Polymorphism in Crystalline and Amorphous Silica at High Pressures. In *Physics Meets Mineralogy, Condensed Matter Physics in the Geosciences*; Aoki, H., Syono, Y., Hemley, R., Eds.; Cambridge University Press: Cambridge, U.K., 2008; p 173.
- (4) In ref 2, p 1.
- (5) Bragg, W. H.; Gibbs, R. E. The Structure of Alpha and Beta Quartz. *Proc. R. Soc. London, Ser. A* **1925**, A109, 405–427.
- (6) Ewald, P. P.; Hermann, C. C10-Typ, β -Tridymit, SiO₂, Strukturbericht 1913–1928, Ergänzungsband; Akademische Verlaganstalt, M.B.H.: Leipzig, 1931; pp 171–174.
- (7) Wyckoff, R. W. G. The Crystal Structure of the High Temperature Form of Cristobalite (SiO₂). *Am. J. Sci.* **1925**, 9, 448–459.
- (8) Stishov, S. M.; Popova, S. V. New Dense Polymorphic Modification of Silica. *Geochimija (Russ.)* **1961**, 10, 837–839.
- (9) Today it is accepted that Stishov's experiments led to an overestimate of pressure of about 30% (10).
- (10) Chao, E. C. T.; Fahey, J. J.; Littler, J.; Milton, D. J. Stishovite, SiO₂, a Very High Pressure New Mineral from Meteor Crater, Arizona. *J. Geophys. Res.* **1962**, 67, 419–421.
- (11) Chao, E.; C. T.; Shoemaker, E. M.; Madsen, B. M. First Natural Occurrence of Coesite. *Science* **1960**, 132, 220–222.
- (12) Chao, E. C. T., Littler, J., J., Additional Evidence for the Impact Origin of the Ries Basin, Bavaria, *Geol. Soc. Am. Abstr. Germany*, **1963**, 127.
- (13) Evers, J.; Mayer, P.; Möckl, L.; Oehlinger, G.; Köppe, R.; Schnöckel, H. Two High Pressure Phases of SiS₂ as Missing Links between the Extremes of Only Edge-Sharing and Only Corner-Sharing Tetrahedra. *Inorg. Chem.* **2015**, 54, 1240–1253.
- (14) Zintl, E.; Loosen, K. Silicon disulfide, ein anorganischer Faserstoff mit Kettenmolekülen. *Z. Phys. Chem. (Leipzig)* **1935**, A174, 301–311.
- (15) Büssem, W.; Fischer, H.; Gruner, E. Die Struktur des Siliciumdisulfids. *Naturwissenschaften* **1935**, 23, 740.
- (16) Weiss, A.; Weiss, A. Die Kristallstruktur des Siliciumdiselenids. *Z. Naturforsch., B: J. Chem. Sci.* **1952**, B7, 483–484.
- (17) Troyanov, S. I. Crystal Modifications of Beryllium dihalides BeCl₂, BeBr₂, BeI₂. *Zh. Neorg. Khim.* **2000**, 45, 1619–1624.
- (18) Wright, A. F.; Fitch, A. N.; Wright, A. C. The Preparation and Structure of α - and β -Quartz-Polymorphs of Beryllium fluoride. *J. Solid State Chem.* **1988**, 73, 298–304.
- (19) Silverman, M. S.; Soulen, J. R. High Pressure Synthesis of a New Silicon Sulfide. *Inorg. Chem.* **1965**, 4, 129–130.
- (20) Prewitt, C. T.; Young, H. Germanium and Silicon Disulfides: Structure and Synthesis. *Science* **1965**, 149, 535–537.
- (21) Bozorth, R. M. The Crystal Structure of Cadmium Iodide. *J. Am. Chem. Soc.* **1922**, 44, 2232–2236.
- (22) Rodriguez-Carvajal, J. R. FullProf, A Program for Rietveld Refinement and Patter Matching Analysis, Abstracts of the Satellite Meeting on Powder Diffraction of Crystallography, Chester, U.K., 1990; p 127.
- (23) Villars, P.; Calvert, L. D. *Pearson's Handbook of Crystallographic Data for Intermetallic Compounds*; American Society for Metals: Metals Park, OH, 1991; Vol. 4, pp 5154, 5155.
- (24) In ref 23, p 5138.
- (25) Diamond2: Brandenburg, K. *Visual Crystal Structure Information System*; Crystal Impact GbR: Bonn, Germany, 1999.
- (26) Neuhaus, A. Synthese, Strukturverhalten und Valenzzustände der anorganischen Materie im Bereich hoher und höchster Drücke. *Chimia* **1964**, 18, 93–103.
- (27) Kleber, W. Das "Druck-Abstands-Paradoxon". *Krist. Tech.* **1967**, 2, 13–14.
- (28) The average S–S distance increases from 3.1₆ Å to 3.22 and 3.24 Å (Figure 4).

(29) Wentorf, R. *Chemistry at High Pressures, The Physics and Chemistry of High Pressure*; Papers read at the Symposium held at Olympia, London, June 27–29, 1962; Society of Chemical Industry: London, S.W. 1, 1963; pp 185–190.

(30) Blaha, P.; Schwarz, K.; Madsen, G. D.; Kvasnicka, D.; Luitz, J. *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*; Vienna University of Technology, Inst. of Physical and Theoretical Chemistry: Vienna, Austria, 2012.

(31) Oganov, A. R.; Gillan, M. J.; Price, G. D. Structural Stability of Silica at High Pressures and Temperatures. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *B71*, 064104-1–064104-8.

(32) Kuwayama, Y.; Hirose, K.; Sata, N.; Ohgishi, Y. The Pyrite-Type High Pressure Form of Silica. *Science* **2005**, *309*, 923–924.

(33) In ref 2, p 9.