Ultrahigh-pressure induced decomposition of silicon disulfide into silicon-sulfur compounds with high coordination numbers

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Silicon disulfide, SiS_2, is thought to occur in interstellar dust and is of fundamental interest more generally among the silicon chalcogenides as a comparator to SiO_2, an important component of terrestrial planets. However, the high-pressure behaviors of silicon sulfides are unclear. Here, using an efficient structure search method, we systematically explore the structural evolution of different Si-S stoichiometries up to 250 GPa. SiS_2 is found to be stable below 155 GPa, above which it decomposes into two compounds, SiS and SiS_3. SiS adopts a high-symmetry cubic structure consisting of eightfold-coordinated silicon in face-sharing SiS_8 polyhedra, while SiS_3 crystallizes in a rhombohedral structure containing ninefold-coordinated SiS_9 polyhedra. Analyses suggest that the Si eightfold-coordination environment could be a common feature for group IV–VI compounds under high pressure. Our findings provide insights on the nature of Si-S compounds under ultrahigh pressure.

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I. INTRODUCTION

Being one of the most abundant elements in the Solar System, silicon is also rich in Earth and other terrestrial planets such as Mars and Venus, where it typically exists in crystalline compounds [1,2]. Studies of silicon chalcogenides are dominated by those focused on silicon oxide such as quartz that forms the second most abundant mineral in Earth's crust. In contrast, silicon sulfides, which are suggested to form an important component of interstellar dust [3,4], are not yet well understood. Understanding the behavior of silicon sulfide phases under high pressure (HP) is therefore important and may shed light on the structural properties of silicon chalcogenides, more specifically the silicates, as theses phases act as analogs of other HP compounds that might be formed in the important family of group IV–VI compounds (e.g., Si-O, Ge-O) [5–13].

The coordination number of silicon is of such great importance that the layering of the bulk silicate Earth is driven by density changes controlled by increasing silicon coordination by oxygen as silicates respond to increased pressure in Earth's interior. This is evidenced by the fact that bridgmanite, $MgSiO_3$ perovskite, with silicon 6-coordinated by oxygen, is the major phase in the lower mantle [14,15], while ringwoodite, spinel Mg_2SiO_4 phase, with 4-coordinated silicon, is stable at shallower depths [16]. In silicate glasses there is evidence for the existence of even higher coordination number (CN) at sufficiently higher pressures: Energy-dispersive x-ray diffraction measurements on SiO_2 glass up to 172 GPa revealed the presence of silicon coordinated by more than 6 oxygens, with CN being 6 to 6.8 [17]. In addition, germanium, in compressed GeO_2 glass, was found to have CN larger than 6, reaching as high as 7.4 [18]. Even larger CNs (larger than 8) of silicon and germanium have also been proposed in the cotunnite-type (CN = 9), Fe_2P-type (CN = 9), and $I4/mmm$ (CN = 10) structures of SiO_2 (GeO_2) at ultrahigh pressures theoretically [19–21].

Silicon disulfide, SiS_2, being isoelectronic with SiO_2 and GeO_2, is a further key representative phase of AB_2-type compounds in the IV–VI group compounds, and may yield insights into the general behavior of silicon at high pressure. At ambient pressure, Normal Pressure (NP)-SiS_2, with a structure that has space-group symmetry $Ibam$, consists of distorted edge-sharing SiS_4 tetrahedra with fourfold-coordinated silicon, first characterized in 1935 by Zintl *et al.* [22]. Upon increasing pressure to 4 GPa, the NP-SiS_2 phase subsequently transforms into three HP phases denoted HP1-SiS_2 (2.8 GPa), HP2-SiS_2 (3.5 GPa), and HP3-SiS_2 (~4 GPa) [23–25]. These HP phases can be closely related to the NP-SiS_2 phase as they all contain fourfold-coordination silicon. Very recently, a HP $P-3m1$

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phase with Si sixfold coordination has been theoretically predicted to be stable above 4 GPa and remains so up to at least 100 GPa [26], which is similar to the HP behavior of silicates. Following this prediction, the HP $P-3m1$ phase was synthesized between 7.5 and 9 GPa [27] and is characterized by 6-coordinated silicon [28]. However, a coordination number for silicon larger than 6 remains unachieved. This raises the question: Can silicon be coordinated by more than 6 sulfur atoms in SiS_2 or more generally, in other Si-S compounds with different chemical stoichiometry?

To address these questions, we have carried out crystal-structure searches within the silicon-sulfur system, in combination with first-principles energetic calculations. Our results reveal a number of HP compounds with a range of fixed stoichiometries in the $Si_xS_{1-x}(0 < x < 1)$ system and demonstrate the existence of Si-S compounds with CN greater than 6. Our enthalpy calculations show that SiS_2 is stable below 155 GPa (with Si CN$\leqslant$6), before it decomposes into compounds with a stoichiometry of SiS and SiS_3. In these SiS and SiS_3 phases, the CN of Si (by S) can reach as high as 8 or 9.

II. COMPUTATION DETAILS

Structure searches on $Si_xS_{1-x}(x = 2/3, 1/2, 1/3, 1/4, 1/5)$ system have been conducted at varied pressures, representing conditions from Earth's surface to its core (0, 50, 100, 150, 200, and 250 GPa) using structure-prediction methods with the same name code as CALYPSO [29,30]. Such an approach has previously been successfully employed to investigate structures of various compounds under HP [31,32]. A thorough survey of the literature, moreover, as well as online databases (e.g., ICSD and MaterialProject) [33,34] for the group IV–VI AB_2 compounds, including CO_2, SiO_2, CS_2, and GeO_2, was also considered. Structure searches for each stoichiometry were performed with a unit cell containing up to four formula units. Several hundreds to a thousand structures were typically predicted, before the most stable candidates for each composition in the Si-S sytem at each pressure were identified. First-principles total-energy calculations were carried out using density-functional theory (DFT) as implemented in the VASP code [35]. In the framework of DFT, the structural optimizations were achieved using exchange-correlation functional treated with generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof density functional [36]. The electron projector-augmented wave (PAW) method [37] was employed with PAW potentials, where $2s^22p^2$ and $2s^22p^4$ were treated as valence electrons for Si and S, respectively. An energy cutoff of 800 eV for the plane-wave expansion was adopted and appropriate Monkhorst-Pack k meshes [38] of uniform spacing of $2\pi \times 0.03\,\text{Å}^{-1}$ were chosen during *ab initio* electronic-structure calculations. Phonon-dispersion relations were calculated for all equilibrium structures using the direct supercell approach as implemented in the PHONOPY code [39].

III. RESULTS AND DISCUSSION

The relative thermodynamic stabilities of Si_xS_{1-x} compounds that we identified as candidate equilibrium structures at 0 K can be assessed by convex hulls. Any structure which has an enthalpy on the convex hull is considered to be thermodynamically stable and experimentally synthesizable with respect to a mixture of end members or other intermediates. As has been discussed previously [32], a phase whose formation enthalpy lies on the local minimum of the convex hull can likely be fabricated in the laboratory. If a tie line is drawn to connect $\Delta H(\alpha)$ and $\Delta H(\beta)$, and $\Delta H(\gamma)$ falls beneath it, mixtures of α and β are expected to react to form compound γ. Otherwise, should $\Delta H(\gamma)$ fall above the tie line, compound γ will decompose into a mixture of compounds α and β. At a given pressure, a convex hull depicts the formation enthalpy per atom of the most stable phases for each stoichiometry, derived from the relation $\Delta H = H(Si_xS_{1-x})–xH(Si)–(1-x)H(S)$, where ΔH is the enthalpy of formation per atom and H represents the calculated enthalpy of the candidate structure per stoichiometric unit for each compound. Here, the experimentally and theoretically known structures of the elemental silicon ($Fd-3m$, $P6_3/mmc$, and $Fm-3m$) [40] and sulfur ($I4_1/acd$, bcm, and β-Po) [41,42] were used to compute the elemental enthalpies of Si and S at the corresponding pressures.

Convex hulls at different pressures are given in Fig. 1, which summarizes the thermodynamic stability of the Si-S compounds that emerged out of our structure searches. At low pressure, as shown in Figs. 1(a)–1(c), the SiS_2 compound has the most negative enthalpy of formation and falls on the convex hull between Si and S, indicating that SiS_2 is stable in the pressure range of 0–100 GPa. This is consistent with the results from Plašienka *et al.* [26], who reported that SiS_2 exists up to at least 100 GPa. Moreover, we successfully reproduced the known phases for the SiS_2 compound, including the $Ibam$, $P2_1/c$, $I-4_2d$, and $P-3m1$ structures and confirmed the observed sequence of phase transitions, namely $\text{NP}(Ibam) \rightarrow \text{HP1}(P2_1/c) \rightarrow \text{HP2}(P2_1/c) \rightarrow \text{HP3}(I-4_2d) \rightarrow P-3m1$ [Fig. 2(a)], as reported previously in both theoretical and experimental investigations [23–28]. This agreement validates the effectiveness of our computational scheme, in particular when applied to the Si-S system under HP.

As pressure increases, SiS_2 becomes relatively less stable when SiS and SiS_3 emerge in the convex hull at 150 GPa [Fig. 1(d)]. At 200 GPa [Fig. 1(e)], the results indicate that SiS_2 is unstable and decomposes into a mixture of SiS and SiS_3 via a reaction of $2SiS_2 \rightarrow SiS + SiS_3$. On further increase of pressure up to 250 GPa, the convex hull shows that SiS_3 decomposes into SiS and S via another reaction of $SiS_3 \rightarrow SiS + 2S$ [Fig. 1(f)], and SiS becomes the only stable compound between elemental S and Si.

To determine the detailed decomposition pressure, the formation enthalpies of the decomposition products ($SiS + SiS_3$ and $SiS + S$) relative to that of SiS_2 have been calculated as a function of pressure and are shown in Fig. 2(c). It is clear that SiS_2 starts to decompose at the pressure of 155 GPa. SiS_2 would also decompose into a mixture of $SiS + S$ around 166 GPa. Above 230 GPa, SiS_3 decomposes into SiS and S. The stable pressure ranges of the equilibrium phases for SiS, SiS_2, and SiS_3 compounds at ultrahigh pressure (50–250 GPa) are depicted in Fig. 2(d). The energetically favorable crystalline phase of SiS_2, with space group of $P-3m1$, becomes stable up to 155 GPa. SiS adopts an equilibrium cubic

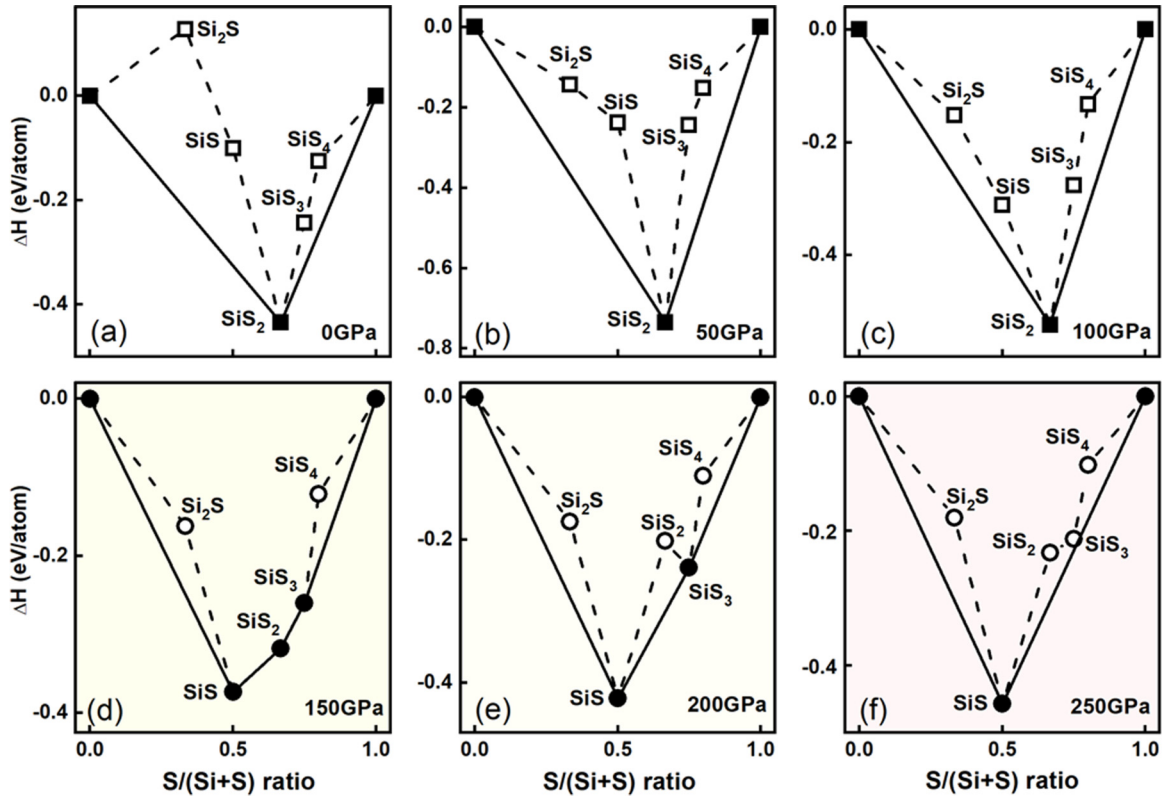

FIG. 1. Thermodynamic stability of Si-S compounds at both low and high pressures. The calculated enthalpy differences with respect to decomposition into Si and S from 0 to 250 GPa (a)–(f) are shown. Convex hulls are shown as solid lines, with stable compounds shown by solid symbols. Unstable compounds (open symbols) sit above convex hulls, with dashed lines indicating decomposition routes.

$Pm-3m$ structure at pressures of 155 to around 250 GPa, and SiS_3 forms as trigonal $R3m$ at 155 to 230 GPa. To verify our results, we also examined these predicted phase transitions and decomposition reactions using the local-density approximation functional. The pressure at which SiS_2 decomposes to $SiS + SiS_3$ was found to be ∼145 GPa, which agrees well with our GGA results.

To assess the dynamical stability of the predicted phases for the SiS and SiS_3 compounds at each desired pressure, we calculated phonon-dispersion relations using the finite-displacement method [39]. Across the Brillouin zone we found no phonon branches with imaginary frequency values in any of the predicted structures ([Figs. 3(a) and 3(b)], indicating that they are dynamically stable. The SiS compound adopts a cubic structure in $Pm-3m$ symmetry (space group 221, $Z = 1$), as shown in Fig. 3(c), with Si and S occupying the $1b$ (0.5, 0.5, 0.5) and $1a$ (0, 0, 1) positions, respectively. In this structure, Si takes the sites on the top vertex of the hexahedron and each Si atom is coordinated with 8 S atoms and forms a regular hexahedron. Figure 3(d) shows the hexagonal SiS_3 structure (space group $R3m$, $Z = 3$) with Si and S atoms occupying $3a$ (0, 0, 0.396) and $9b$ (0.523, 0.477, 0.262) positions, respectively. Here, each Si atom has 9 neighboring S atoms with Si-S distances range of 2.1–2.3 Å at 160 GPa, forming fairly regular tricapped trigonal prisms with Si ninefold-coordinated SiS_9 polyhedra. The mean nearest-neighbor Si-S distances in the SiS and SiS_3 phases are 2.23 and 2.27 Å at 160 GPa, respectively, which are close to the sum of covalent radius of Si (1.11 Å) and S (1.02 Å). Interestingly, the Si-S distances in the HP SiS and SiS_3 phases are even longer than that in the low-pressure SiS_2 phase ($P-3m1$) (∼2.17 Å at 50 GPa), which may relate to the higher CN. Moreover, the S-S distances are found to be shorter in SiS and SiS_3 than they are in SiS_2. In particular, the nearest-neighbor S-S distance decreases from 3.12 Å in the low-pressure SiS_2 ($P-3m1$) phase to 2.21 Å in the HP SiS_3 ($R3m$) structure, which is close to the sum (2.04 Å) of covalent radii of 2 S atoms. These results demonstrate that the increasing density (and hence stability) in the HP phases is achieved through the changes of polyhedral packing induced increasing of silicon CN and reduction of the nearest-neighbor S-S distances.

The discovery of eightfold Si in SiS at high pressure is quite fascinating since the CN of the group-IV atoms in the family of IV–VI AB_2 compounds (IV = C, Si, Ge; VI = O, S) is generally four-, six-, nine-, and tenfold [43–46]. Significant efforts have been devoted to searching for solids containing 8-coordinated group-IV elements but with no success. It would be interesting to check whether SiS_2 can form similar eightfold structures that may serve as the first prototype for IV–VI AB_2 compounds, regardless of its thermal stability against decomposition. Further simulations showed [Fig. 2(b)] that SiS_2 with the low-pressure $P-3m1$ phase first transforms into a $P4/mmm$ (>285 GPa) phase, then to a $Cmmm$ (>400 GPa) phase upon compression (Fig. 4). It is found that the CN of silicon by sulfur is eightfold in both structures, the same as that of Si in the $Pm-3m$

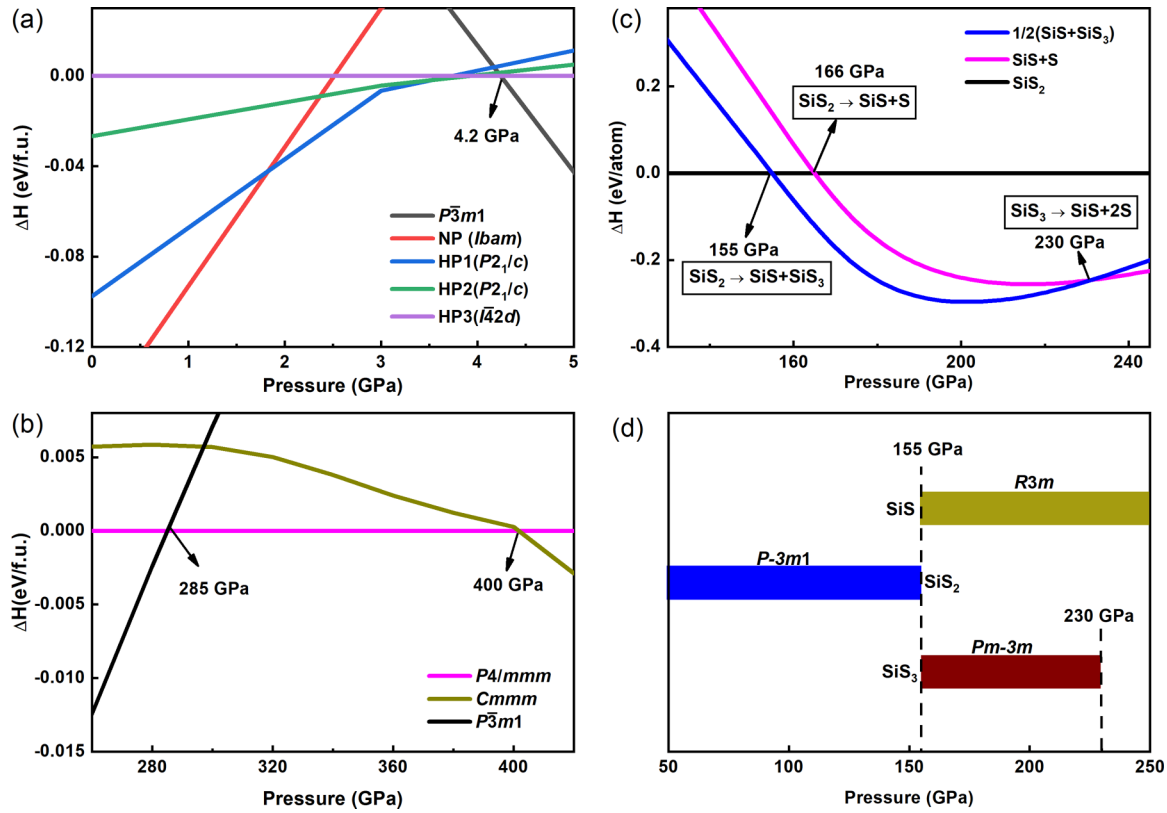

FIG. 2. Calculated enthalpy difference of HP phases for the SiS_2 compound with respect to the $P-3m1$ phase from 0 to 5 GPa (a) and from 260 to 420 GPa (b). (c) Calculated enthalpy differences (ΔH) of decomposition of SiS_2 into SiS + S and SiS + SiS_3 relative to SiS_2 as functions of pressure (50–250 GPa). (d) Schematic representation of phase diagram for stable SiS, SiS_2, and SiS_3 compounds as a function of pressure.

phase of SiS. We also examined the stability of the ninefold cotunnite- and Fe_2P-type and tenfold $I4/mmm$ structures [19–21] that have been observed in the HP phases of SiO_2 and GeO_2 for SiS_2. The results indicate that eightfold SiS_2 is stable over a wide range of pressures and ninefold is only stable above 870 GPa.

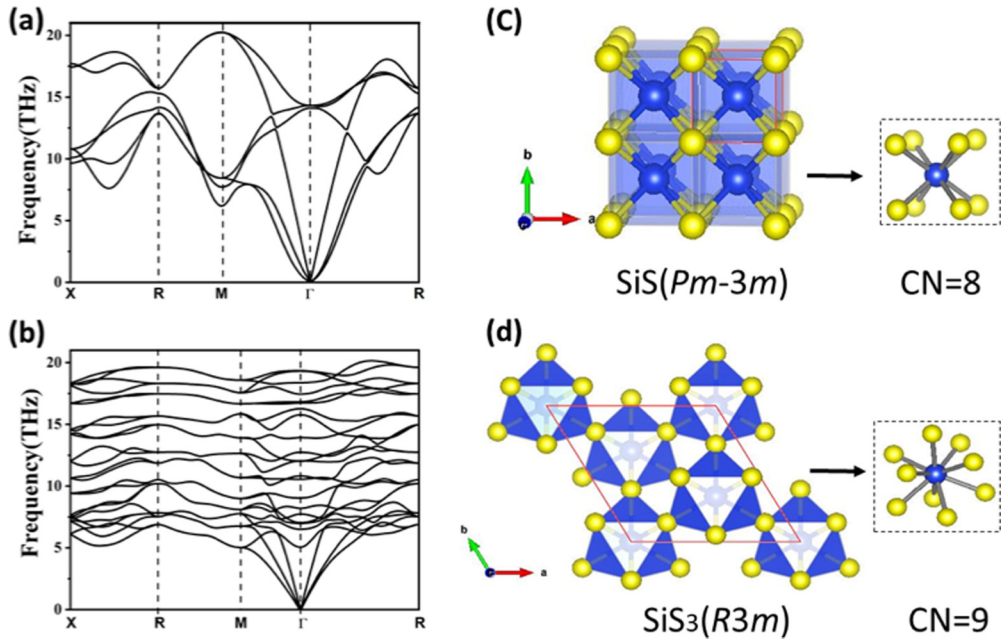

FIG. 3. Phonon-dispersion curves for the $Pm-3m$ phase of SiS at 160 GPa (a) and the $R3m$ of SiS_3 at 200 GPa (b). Stable structures of SiS in a $Pm-3m$ structure (c) and SiS_3 in an $R3m$ structure (d).

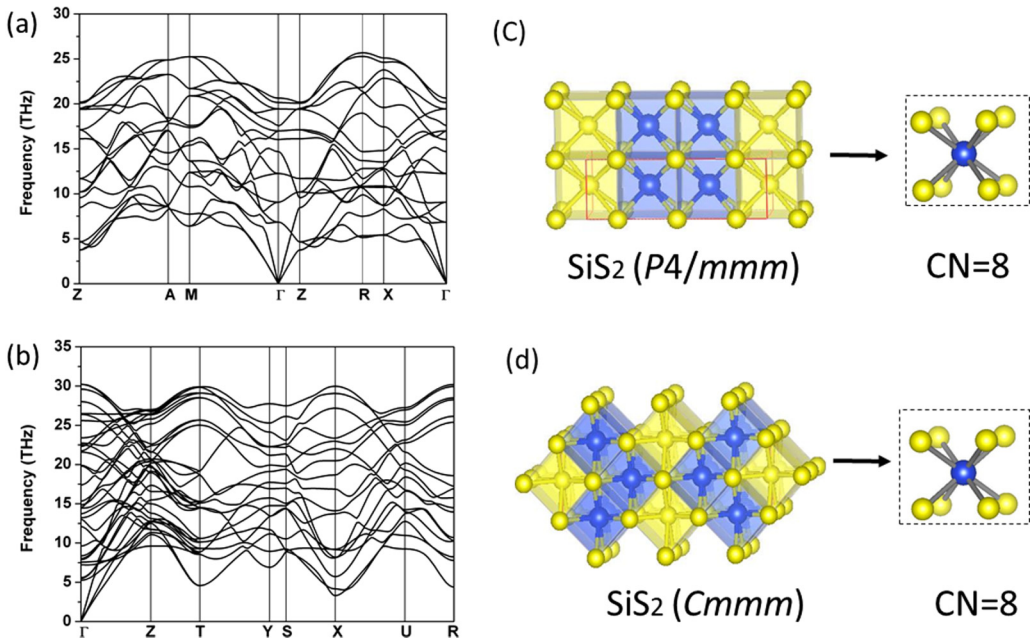

FIG. 4. Structures of the $P4/mmm$ (a) and $Cmmm$ (b) phases of SiS_2. The Si atoms are eightfold coordinated by S in both structure, forming SiS_8 polyhedra. Phonon-dispersion curves for the $P4/mmm$ phase of SiS_2 at 300 GPa (c) and the $Cmmm$ phase of SiS_2 at 450 GPa (d).

We then took the HP eightfold-coordinated phases ($P4/mmm$ and $Cmmm$) of SiS_2 as prototype structures for other IV–VI AB_2 compounds and examined their stabilities. Unfortunately, we found that both these eightfold-coordinated phases are thermodynamically unstable comparing to the known four-, six-, nine-, and tenfold-coordinated phases of AB_2. Furthermore, we have explored the other possible AB_2 structures with eightfold-coordinated A atoms at HP using CALYPSO. Our results demonstrated that four-, six-, nine-, and tenfold coordination are all favorable over eightfold coordination in all such AB_2 compounds. In other words, none of the IV–VI AB_2 compounds that we have considered form an eightfold-coordinated structure as the stable HP phase (Fig. 5).

Our predicted $Pm-3m$ phase for SiS may be among the first group IV–VI compounds to display eightfold coordination of the group-IV element. By replacing Si and S with heavier elements to consider the possibility of forming similar compounds in the IV–VI groups, the enthalpy difference of AB_2 (e.g., $GeSe_2$, $SnSe_2$) with respect to decomposition into stoichiometric AB and AB_3 was calculated at pressures up to 150 GPa. Although the relative stabilities of their different compositions were not considered, the resulting enthalpy differences ($2GeSe_2 \rightarrow GeSe + GeSe_3$) indicate that similar

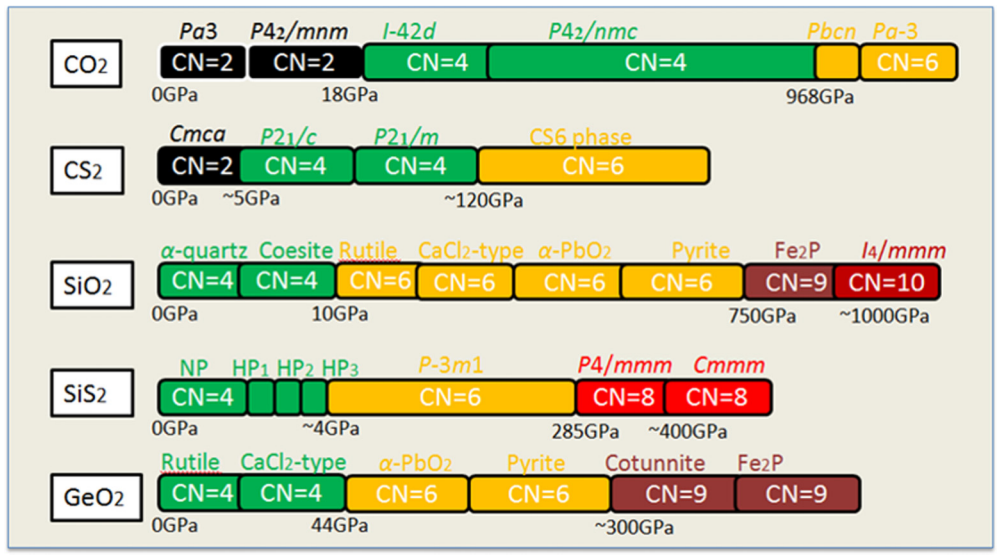

FIG. 5. Comparison of the stability ranges and the silicon coordination number of SiS_2 under pressure with those in its isovalent IV–VI AB_2 compounds, including CO_2, CS_2, SiO_2, and GeO_2.

eightfold-coordinated phase of GeSe may be formed at a lower critical pressure of ∼120 GPa. These results illustrate and highlight the fact that pressure can be deployed as a powerful tool in the search for novel materials and in the development of our understanding of the principles of chemical crystallography.

IV. CONCLUSIONS

In summary, we have systematically explored the phase stabilities and crystal structures of a range of materials with stoichiometries of Si_xS_{1-x} under HP using the CALYPSO method in combination with *ab initio* electronic band-structure framework. Our results reveal that SiS_2 is the only stable stoichiometry below 155 GPa. Remarkably, this phase becomes unstable and decomposes into a mixture of stoichiometric phases SiS and SiS_3 at higher pressure. The SiS phase adopts a high-symmetry $Pm-3m$ structure consisting of a Si in eightfold-coordinated face-sharing SiS_8 polyhedra, while SiS_3 crystallizes an $R3m$ structure consisting of ninefold-coordinated silicon in SiS_9 polyhedra. In addition, the isovalent IV–VI AB_2 compounds (CO_2, CS_2, SiO_2, and GeO_2) are all found to avoid structures with eightfold-coordinated group-IV atoms. Our predicted SiS phase is identified as among the first group IV-VI compound containing eightfold-coordinated group-IV atoms, and our predicted SiS_3 phase is a silicon sulfide material in which silicon is ninefold coordinated.

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