

Synthesis of BaSiH₆ Hydridosilicate at High Pressures—A Bridge to BaSiH₈ Polyhydride

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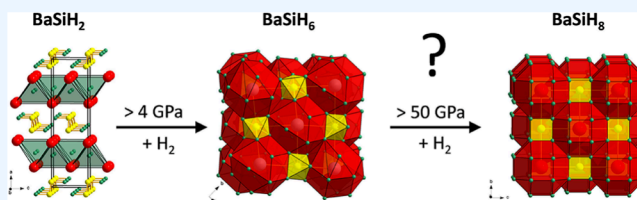


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ABSTRACT: Hydridosilicates featuring SiH₆ octahedral moieties represent a rather new class of compounds with potential properties relating to hydrogen storage and hydride ion conductivity. Here, we report on the new representative BaSiH₆ which was obtained from reacting the Zintl phase hydride BaSiH_{~1.8} with H₂ fluid at pressures above 4 GPa and subsequent decompression to ambient pressure. Its monoclinic crystal structure (C2/c, *a* = 8.5976(3) Å, *b* = 4.8548(2) Å, *c* = 8.7330(4) Å, β = 107.92(1)°, *Z* = 4) was characterized by a combination of synchrotron radiation powder X-ray diffraction, neutron powder diffraction, and DFT calculations. It consists of complex SiH₆^{2−} ions (*d*_{Si–H} ≈ 1.61 Å), which are octahedrally coordinated by Ba²⁺ counterions. The arrangement of Ba and Si atoms deviates only slightly from an ideal fcc NaCl structure with *a* ≈ 7 Å. IR and Raman spectroscopy showed SiH₆^{2−} bending and stretching modes in the ranges 800–1200 and 1400–1800 cm^{−1}, respectively, in agreement with a hypervalent Si–H bonding situation. BaSiH₆ is thermally stable up to 95 °C above which decomposition into BaH₂ and Si takes place. DFT calculations indicated a direct band gap of 2.5 eV and confirmed that at ambient pressure BaSiH₆ is a thermodynamically stable compound in the ternary Ba–Si–H system. The discovery of BaSiH₆ consolidates the compound class of hydridosilicates, accessible from hydrogenations of silicides at gigapascal pressures (<10 GPa). The structural properties of BaSiH₆ suggest that it presents an intermediate (or precursor) for further hydrogenation at considerably higher pressures to the predicted superconducting polyhydride BaSiH₈ [Lucrezi, R.; et al. *npj Comput. Mater.* 2022, 8, 119] whose structure is also based on a NaCl arrangement of Ba and Si atoms but with Si in a cubic environment of H.



INTRODUCTION

Recently, it has been shown that silicon is capable of forming hydrogen-rich hydridosilicates featuring octahedral SiH₆^{2−} complex ions. Synthesis efforts until today yielded K₂SiH₆, Rb₂SiH₆, and Na₃SiH₇.^{1–3} More potential representatives, like Na₂SiH₆, NaSiH₅, Li₂SiH₆, have been proposed from computational structure prediction.^{3–6} Hydridosilicates are salt-like compounds and their structural chemistry resembles that of well-established fluorosilicates/germanates. However, in contrast with fluorosilicates, hydridosilicates are not insulators but semiconductors. The occurrence of hypervalent SiH₆^{2−} moieties is peculiar since the polarity of the Si^{δ+}–H^{δ−} bond is rather small and hypervalence of p-elements is usually associated with electronegative ligands, such as F. It has been suggested that hydridosilicates may have interesting hydride ion conducting and/or hydrogen storage properties,⁵ yet the physical, chemical, and materials properties of these compounds remain poorly investigated because of their scarcity.

The synthesis of hydridosilicates typically requires high pressure conditions in the multi GPa range, 4–10 GPa.^{1–3} This pressure range is accessible with large-volume press (LVP) high-pressure methodology which provides sizable

sample volumes and well-controlled *p*, *T* environments for high-pressure hydrogenation reactions.^{7–9} In LVP hydrogenations, H₂ has to be delivered by an internal solid source which is integrated in the sample. Ammonia borane, BH₃NH₃, has been recognized as an ideal H-source as it possesses a high H content and decomposes neatly to inert BN and H₂ at comparatively low temperatures (200–400 °C, depending on *p*).¹⁰ Various types of precursor scenarios may be considered for high pressure hydrogenations potentially leading to hydridosilicates, such as MH_{*n*} + Si, M_{*m*}Si_{*n*}, M_{*m*}Si_{*n*}H_{*x*} (*M* = active metal), of which the latter, M_{*m*}Si_{*n*} (silicide Zintl phases) and M_{*m*}Si_{*n*}H_{*x*} (Zintl phase hydrides), have shown largely superior kinetics² thus enabling lower synthesis temperatures and potentially access to metastable products.

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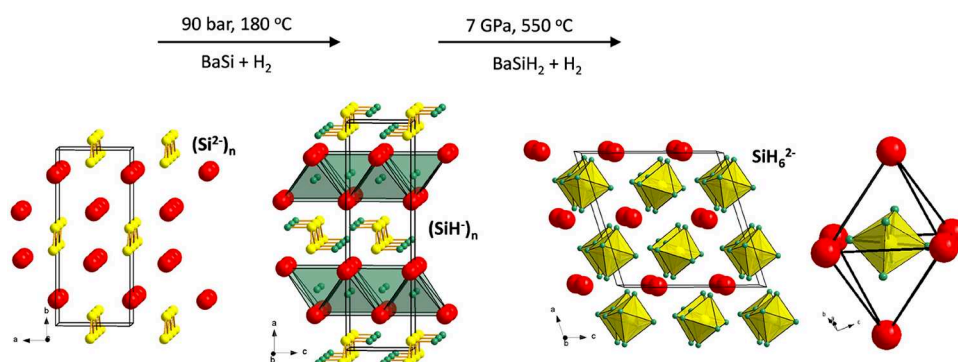


Figure 1. From left to right: low pressure hydrogenation transforms the Zintl phase BaSi (CrB structure type, *Cmcm*, *Z* = 4) into the hydride BaSiH_{2-*x*} (x ≈ 0.15; *Pnma*, *Z* = 4),¹² which in turn yields BaSiH₆ (C2/*c*, *Z* = 4) upon hydrogenation at gigapascal pressures. Ba, Si, and H atoms are depicted as red, yellow, and green circles, respectively. Far right: octahedral coordination of a SiH₆²⁻ ion by six Ba²⁺ counterions in C2/*c* BaSiH₆ (based on DFT relaxed H atom positions, see text).

We have started to explore more systematically the accessibility and compositional variety of hydridosilicates. Here we report on the synthesis of BaSiH₆ from hydrogenation of the Zintl phase hydride BaSiH_{2-*x*} at ~7 GPa which resulted in sizable bulk samples with several tens of mg quantities. We find that the structure of BaSiH₆ closely relates to that of the even more hydrogen-rich metallic and high *T_C* superconducting polyhydride BaSiH₈ which has been predicted to be thermodynamically stable at ultrahigh pressures, above 100 GPa.¹¹

METHODS

Synthesis of BaSiH_{2-*x*} (x ≈ 0.15) Precursor. The Zintl phase hydride BaSiH_{2-*x*} was prepared by sintering BaSi in a hydrogen atmosphere (H₂, Air Liquide, 99.9%) at 90 bar pressure and 180 °C for 24 h using an autoclave made from H-resistant Nicrofer 5219Nb alloy.¹² BaSi in turn was synthesized by arc-melting mixtures of the elements (Si, ChemPur, 99.9999%; Ba rod, 99.3%) with a slight (about 5%) Ba excess. The synthesis of the deuteride BaSiD_{2-*x*} is described in the [Supporting Information](#) section.

Synthesis of BaSiH₆. All steps of sample preparation for high pressure (LVP) hydrogenation experiments were performed in an Ar-filled glovebox. NaCl is considered an ideal capsule material since it provides tight seals and resists hydrogen diffusion.⁷⁻⁹ Powdered precursor BaSiH_{2-*x*} and hydrogen source BH₃NH₃ (Sigma Aldrich, 97%) were pressed into pellets with an outer diameter (OD) of 4 mm and ~3 and ~1.3 mm height, respectively. A precursor pellet was placed between two BH₃NH₃ pellets and sealed in a NaCl capsule (OD 6.1 mm, ~7.8 mm height). The molar ratio BaSiH_{2-*x*}:BH₃NH₃ corresponded roughly to 1:1 (BaSiH_{2-*x*}:H₂ = 1:3). Two synthesis runs were conducted at Arizona State University (ASU) using the COMPRES 18/12 assemblies.¹³ Samples were compressed in a 1000 tonnes press to ~7 GPa and subsequently heated to 550 °C over two hours, held at this temperature for eight hours, cooled back to room temperature over 1 h, and subsequently decompressed. The temperature was measured with a type C thermocouple. Samples were recovered in a glovebox. In situ diffraction experiments were performed at various pressures between 4 and 19 GPa at the synchrotron facility PETRA III, DESY and at 5 GPa at the neutron facility MLF, J-PARC, employing the LVP beamlines P61B¹⁴ and PLANET,¹⁵ respectively. Results from these

experiments will be reported separately. The J-PARC experiment, however, is described in more detail in the [SI section](#).

Powder X-ray Diffraction (PXRD). PXRD patterns of recovered BaSiH₆ were collected at the beamline P02.1, PETRA III, DESY¹⁶ using monochromatic synchrotron radiation (*E* ≈ 60 keV, λ = 0.20734–0.20738 Å). Samples produced at P61B were sealed (as sintered pieces without grinding) inside 1.0 mm diameter glass capillaries. For multitemperature measurements, the sample produced at ASU was finely ground and sealed in 0.3 mm diameter fused silica capillaries. Capillaries were heated with a mini hot air blower which is part of the sample environment at P02.1. For indexing of diffraction patterns, the Crysfire package¹⁷ was used. Le Bail analysis and Rietveld refinement of the PXRD data were performed in Jana2006.¹⁸ Further details are provided as [SI](#).

Spectroscopy. FTIR spectra were recorded with a “Golden Gate” micro-ATR accessory using a Varian IR-670 spectrometer with a thermostatted DTGS detector. A powdered sample of BaSiH₆ was transferred from the glovebox in an airtight vial. At the spectrometer, the vial was opened, and the powder was quickly clamped between the ATR diamond and sapphire elements. During the transfer process, moisture-sensitive BaSiH₆ may have decomposed slightly. For Raman spectroscopy, powdered samples were sealed in 0.3 mm Lindemann capillaries. Spectra were measured using a LabRAM HR 800 spectrometer. The instrument is equipped with an 800 mm focal length spectrograph and a Peltier-cooled (–70 °C), back-thinned CCD detector. Samples were excited using a double-frequency Nd:YAG laser (532 nm). A 10% filter was applied corresponding to a low power density of 5.5 × 10^{–6} mW·μm^{–2}. Raman spectra were collected with an exposure time of 150 s (100 accumulations) and using a 600 grooves/mm grating.

Theoretical Calculations. Crystal structure prediction (CSP) utilizing the USPEX code^{19–21} coupled with the Vienna Ab Initio Simulation Package (VASP)^{22,23} was employed for assisting the identification of the monoclinic BaSiH₆ structure. For the USPEX calculation, we used the numerical constraints of a fixed composition (1:1:6) and the maximum number of atoms in a candidate cell of 32 (*Z* = 4). The lowest enthalpy structure identified had C2/*c* space group symmetry and *Z* = 4. VASP calculations were based on a first-principles projector-augmented wave method²⁴ within the density functional theory (DFT).²⁵ The generalized gradient approximation for

exchange and correlation potential and energy was used in its Perdew–Burke–Ernzerhof (PBE) flavor.^{26,27} Total energy/electronic structure calculations were performed for BaH₂, BaSiH₂, Si, and BaSiH₆ on fully relaxed structures. Hydrogen was calculated as a molecule H₂. The Monkhorst–Pack²⁸ *k*-point density for integrations over the Brillouin zone was set with 0.2. The energy cutoff for plane waves was 800 eV. Phonon dispersions were calculated with PHONOPY.²⁹ The required dynamical matrix was obtained via highly accurate calculations with density functional perturbation theory as implemented in VASP, with the energies converged down to 10^{−8} eV.

RESULTS AND DISCUSSION

The Zintl phase BaSi (CrB structure type) features polyanionic zigzag chains of Si atoms (¹_∞[Si^{2−}]).³⁰ Upon hydrogenation at

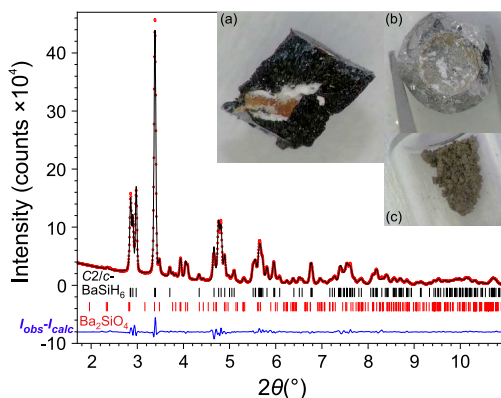


Figure 2. Rietveld fit of the BaSiH₆ structure to a synchrotron PXRD pattern ($\lambda = 0.20734$ Å). Vertical lines are reflection markers for BaSiH₆ and Ba₂SiO₄ impurity. Phase fractions: ~84(1) wt% (92 mol %) BaSiH₆ and ~16(1) wt% (8 mol %) Ba₂SiO₄. Inset (a) shows a photograph of an orange-colored BaSiH₆ sample from an in situ experiment (~8.5 GPa, 570 °C) before recovery, embedded between BN residual from decomposed BH₃NH₃ inside the NaCl capsule (which attained a black color due to X-ray irradiation). Note that the sample is largely rearranged from its original position during the reaction due to the escape of excess H₂ upon decompression. Inset (b) shows a partially recovered pellet (4 mm diameter) of BaSiH₆ from a scaled-up synthesis experiment (the NaCl capsule is partly broken off, and the surface of the pellet is not yet cleaned completely from BN residual), and inset (c) shows a part of this pellet ground into a fine powder inside a vial with a 6 mm diameter. The light brownish/gray color in (b) and (c) is attributed to a small grain size and/or the presence of Si impurity.

low-pressure autoclave conditions (90 bar (9 MPa)), the Zintl phase hydride BaSiH_{2−x} is obtained for which the basic structural features of BaSi are retained.¹² In the structure of BaSiH_{2−x}, H is located as a hydride (H[−]) anion in tetrahedral interstices formed by the Ba atoms. In addition, the zigzag chain Si atoms are decorated with covalently bonded H atoms (thus changing ¹_∞[Si^{2−}] into a ¹_∞[SiH[−]] polyanion), Figure 1. However, the site of the H coordinating Si has a slight deficiency of about 15%. Si atoms in ¹_∞[SiH[−]] obey the octet rule, and stoichiometric BaSiH₂ would correspond to an electronically balanced Zintl phase, i.e., Ba²⁺(SiH)[−](H[−]).¹²

The formation of the hydridosilicate BaSiH₆ was initially observed in in situ diffraction experiments when attempting the hydrogenation of BaSiH_{2−x} in the pressure interval 4–13 GPa, and from these experiments, it could also be shown that

Table 1. Results of the Rietveld Refinement of the BaSiH₆ Structure at Ambient Conditions

crystal system	monoclinic
space group	C2/c (no. 15)
Z	4
lattice parameters ^a	<i>a</i> = 8.5976(3) Å <i>b</i> = 4.8548(2) Å <i>c</i> = 8.7330(4) Å β = 107.918(4)°
<i>V</i> (Å ³)	346.84(2)
formula weight (g/mol)	171.46
<i>d</i> _{calc} (g/cm ³)	3.284
<i>R</i> _{obs} (%)	1.39
<i>R</i> _{all} (%)	1.39

^aPseudocubic triclinic cell: *a* = 7.040 Å, *b* = 7.008 Å, *c* = 7.040 Å, α = 89.32°, β = 87.20°, γ = 89.32°.

BaSiH₆ is retained at ambient pressure (Figure 2). Subsequently, dedicated experiments were performed at 7 GPa and 550 °C to scale up its preparation, which for the first time yielded sizable quantities (several tens of mg) of a hydridosilicate. However, although the conversion of BaSiH_{2−x} proceeded quantitatively, all samples (originating from the same batch of BaSiH_{2−x}) contained Ba₂SiO₄ (orthosilicate) as an impurity (3–8 mol%) which presumably originates from an oxide/peroxide/hydroxide contamination of the BaSiH_{2−x} precursor (cf. discussion in the SI section). BaSiH₆ displays a reddish-orange color as well sintered specimen, but when it is small-grained or as powder, it appears light brownish/gray (insets in Figure 2).

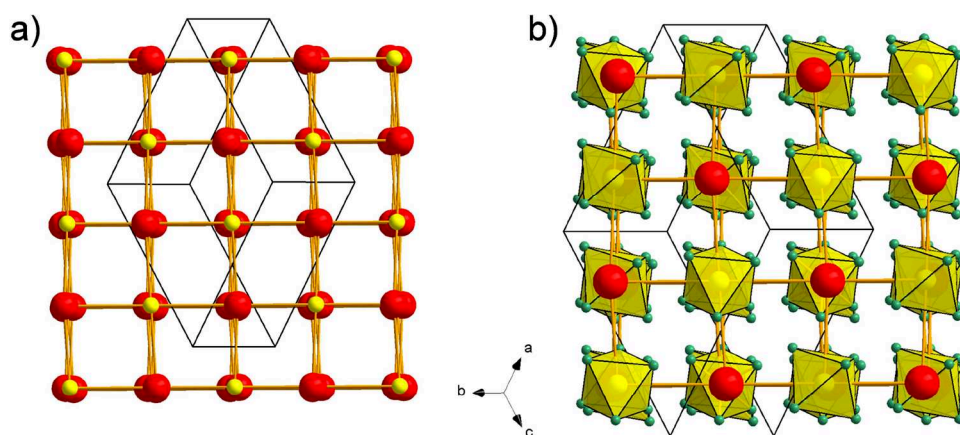
The SR-PXRD pattern of BaSiH₆ could be indexed to the monoclinic C-centered cell with *Z* = 4 that was as suggested from computational CSP (see SI for details). The refinement of the CSP model proceeded highly satisfactorily. Unambiguous confirmation of the H positions came then from an (in situ) neutron diffraction experiment, probing the formation of BaSiD₆ at around 5 GPa (see SI for details), which provided a data set at 2.5 GPa and room temperature. To arrive at the H position parameters for BaSiH₆ at ambient conditions, it was deemed most consistent to extract them from a DFT relaxation where the lattice parameters and Ba and Si atomic position parameters were constrained to the experimentally refined ones, referring to room temperature and ambient pressure. The resulting structure of BaSiH₆ after the refinement is reported in Tables 1 and 2 (see also Figure 2 and SI section). It resembles closely the unique KPF₆-III structure, which apparently was determined over 30 years ago³¹ but has come to attention only recently.³²

The monoclinic crystal structure of BaSiH₆ is built of Ba²⁺ and octahedral complex ions SiH₆^{2−} which are the characteristic constituents of hydridosilicates. The SiH₆^{2−} octahedra appear in two orientations, which are related through 2₁ symmetry axes. They are hosted within irregular octahedra of Ba²⁺ counterions (*d*_{Ba–Ba} = 4.78–5.26 Å) with their corners pointing to triangle faces and edges of the Ba₆ octahedron (Figure 1). The monoclinic unit cell blurs an almost ideal NaCl-type arrangement of cations and centers of complex anions (Figure 3), which is realized in the fcc structure of NaPF₆ (with PF₆[−] octahedra aligned in the same orientation as the Na₆ ones)³³ but from which monoclinic KPF₆ severely deviates. The parameters of the pseudocubic triclinic unit cell of BaSiH₆ are in the range 7.01–7.04 Å and 87.2–89.3° (Table

Table 2. Fractional Coordinates and Atomic Displacement Parameters (ADPs) for the BaSiH₆ Structure at Ambient Conditions^a

atom	Wyck	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} (Å ²)	<i>B</i> _{iso} (Å ²)
Ba	4e	0	0.6990(2) ^b	0	0.0198(3)	1.56(2)
Si	4d	1/4	1/4	1/2	0.0181(9)	1.43(7)
H1	8f	0.8091	0.4674	0.4394	0.038	3
H2	8f	0.4384	0.3133	0.5963	0.038	3
H3	8f	0.2327	0.0912	0.6531	0.038	3

^aHydrogen atom positions were obtained from DFT relaxation constraint to the experimental lattice, see text. The coordinates and ADPs of the H atoms remained fixed during the refinement. ^bBa is at 4e (0, 0.75, 0) for an idealized NaCl-type arrangement of Ba and Si atoms.

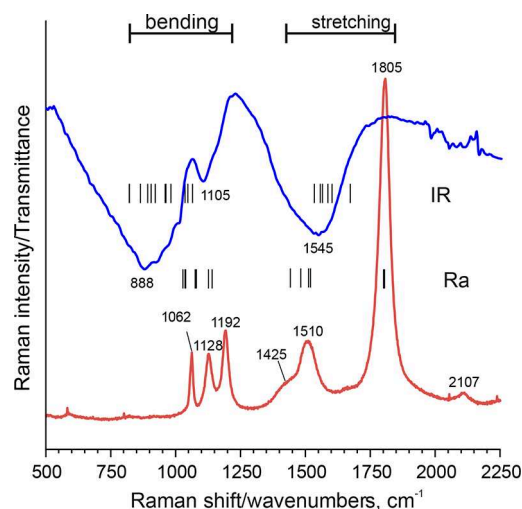
**Figure 3.** (a) Projection of the monoclinic BaSiH₆ structure showing a nearly ideal fcc NaCl structure arrangement of Ba and Si atoms (red and yellow spheres, respectively). In (b) the H atoms are added (green spheres).**Table 3. Relevant Interatomic Distances in BaSiH₆^a**

atom pair	<i>d</i> (Å)	atom pair	<i>d</i> (Å)
Si H2 ×2	1.590	Ba Ba ×2	4.775
H3 ×2	1.608	Ba Ba ×2	4.855
H1 ×2	1.609	Ba Ba ×4	4.937
Ba Si ×2	3.354	Ba Ba ×2	5.123
Si Si ×2	3.512	Ba Ba ×2	5.254
Si Si ×2	3.695	Ba H3 ×2	2.605
Si Si ×2	4.855	H3 ×2	2.607
Si Si ×4	4.937	H2 ×2	2.693
Si Si ×4	4.996	H2 ×2	2.798
Si Si ×2	5.099	H1 ×2	2.822
		H1 ×2	2.892
		H1 ×2	2.965
		H2 ×2	3.274

^aEstimated standard deviations are either smaller than 0.001 Å or not defined (when involving H atoms).

3). Nearest neighbor Ba–Si distances are between 3.35 and 3.70 Å.

The local point group symmetry of the SiH₆^{2−} ion is C_i, and there are two octahedra in the primitive unit cell. Despite the low symmetry, the Si–H distances are almost equal (*d*_{Si–H} = 1.60–1.62 Å) and angles are close to ideal (89–91°). Consequently, one would expect that the internal modes of SiH₆^{2−} follow the O_h pattern of three stretching modes (A_{1g}, E_g, T_{1u}) and three bending modes (T_{2g}, T_{1u}, T_{2u}) and that the O_h selection rules are largely obeyed.^{35,34} The IR and Raman spectra of BaSiH₆, shown in Figure 4, reveal the location of bending and stretching modes between 800–1250 and 1400–1810 cm^{−1}, respectively, which is also seen in the DFT calculated zone center optical modes. The Raman spectrum

**Figure 4.** Raman (lower curve) and IR spectrum (upper curve) of BaSiH₆. The bars represent the position of DFT calculated Si–H stretching and bending modes. The unassigned band at 2107 cm^{−1} in the Raman spectrum may correspond to an overtone. Note that Si–O bands from Ba₂SiO₄ orthosilicate impurity are expected to be below 1000 cm^{−1} and will not interfere with BaSiH₆ Si–H bands in the Raman spectrum.³⁶ In contrast, in the IR spectrum, Si–O stretching and Si–O–H bending bands from partial decomposition of the sample may be present.

shows six vibrational bands, three in the stretching and three in the bending mode regions, which implies that the O_h-degenerate modes E_g (stretch) and T_{1g} (bend) all appear considerably split by several tens of cm^{−1}. The removal of the O_h degeneracy is not visible in the IR spectrum, which only shows two broad bands, one in the stretching region

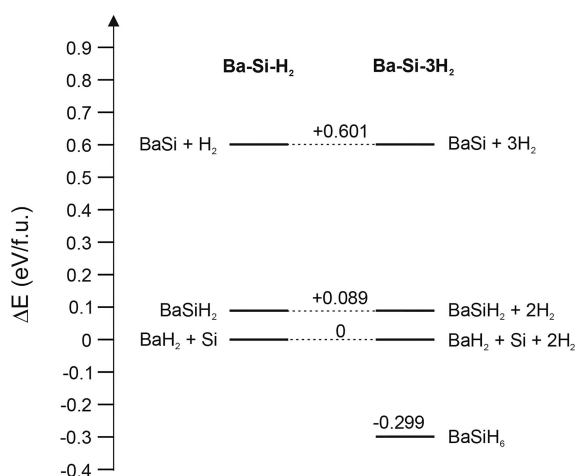


Figure 5. DFT calculated energy differences for the pseudobinary compositions BaSi–H₂ and BaSi–3H₂.

(accounting for T_{1u}) and one in the bending region (accounting for T_{1u} and the O_h -forbidden T_{2g}). An additional IR signal may come from Fermi resonance,³³ but this is not clear. The symmetric stretch is at the highest wavenumber, around 1800 cm^{−1}, which relates well to K₂SiH₆ and Rb₂SiH₆ (which are also built of separated SiH₆^{2−} octahedra but with local point group symmetry O_h).¹ The associated Si–H stretching force constant is thus considered similar (~ 1.3 N/cm),³⁵ confirming that SiH₆^{2−} is a weakly bonded moiety compared to regular-valent silicon hydride species.²

The electronic band structure of BaSiH₆ shows considerable dispersion of the occupied bands (1–3 eV), as depicted in Figure S7. Yet these bands reflect clearly the molecular orbital energy levels of octahedral SiH₆^{2−} (i.e., a_{1g} , t_{1u} , e_g) which confirms the ionic character of this compound. The highest lying e_g -type band is nonbonding and primarily composed of H states. The band gap appears to be direct with a size of about 2.5 eV. Typically, DFT calculated band gaps are underestimated when using the PBE functional. Here, however, the reddish appearance of a sintered bulk sample (cf. Figure 2, inset) suggests quite good agreement.

Multitemperature PXRD measurements revealed a limited thermal stability of BaSiH₆. At about 95 °C, decomposition onset to BaH₂ and Si is observed (Figure S4). Nevertheless,

according to DFT calculations, BaSiH₆ is a thermodynamically stable compound (with respect to the most stable component mixture BaH₂ + Si + H₂). In fact, at ambient pressure, BaSiH₆ represents the only stable ternary compound in the Ba–Si–H system, whereas the (stoichiometric) Zintl phase hydride BaSiH₂ is not (Figure 5). This follows earlier observations that hydrosilicates appear generally thermodynamically stable at ambient pressure, albeit high pressure is needed for their synthesis for raising thermal stability beyond required reaction temperatures. In this respect, and as mentioned earlier, silicide Zintl phases (or also Zintl phase hydrides) can favorably act as reactive precursors with low kinetic barriers for hydrogenation.

Recently, Lucrezi et al. reported a computational study of the even more hydrogen-rich polyhydride BaSiH₈.¹¹ BaSiH₈ was predicted to be thermodynamically stable at pressures above 130 GPa. However, minimum pressures for dynamic and kinetic stability (which are the important parameters for retaining a high-pressure material toward ambient pressure) were found to be considerably lower, at around 25 and 30 GPa, respectively.^{11,37} BaSiH₈ is potentially a promising superconducting material with a critical temperature T_C around 80 K (rather independent of pressure). The existence of BaSiH₆ was not known to these authors and also their results were based on zero Kelvin calculations. In light of our findings, it would be interesting and also important to reassess thermodynamic, kinetic, and dynamic stabilities for BaSiH₈, considering both the presence of BaSiH₆ in the ternary system Ba–Si–H and elevated temperatures of >400 °C necessary for inducing reactions.

Here, we infer that BaSiH₆ represents a precursor, or intermediate, to the higher hydride BaSiH₈, potentially accessible at pressures by far exceeding 10 GPa, and motivate this by their close structural relationship. In cubic BaSiH₈ (space group $Fm\bar{3}m$), Ba and Si atoms form an ideal NaCl-type structure arrangement. H atoms are situated on the $32f(x,x,x)$ position) and surround the Si atoms cubically. Interestingly, the calculated lattice parameter of BaSiH₈ at ambient pressure (where BaSiH₈ would be both dynamically and kinetically unstable) is close to 7 Å,^{11,37} implying an almost equal dimension of the NaCl lattice hosting SiH₆ octahedra in BaSiH₆ and SiH₈ cubes in BaSiH₈ (Figure 6). Obviously, the “insertion” of additional 2 H atoms per formula unit into the BaSiH₆ structure will change the Ba–H coordination

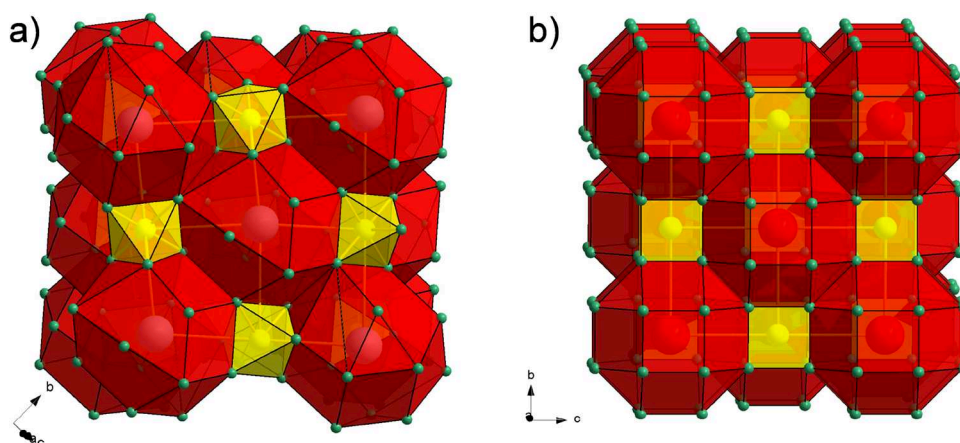


Figure 6. Comparison of the crystal structures of monoclinic BaSiH₆ (a) and cubic BaSiH₈ (b). Ba and Si coordination by H are depicted as red and yellow polyhedra, respectively.

drastically. In BaSiH_8 , Ba is coordinated by 24 H atoms, forming a rhombicuboctahedron at a distance 2.87 Å, whereas in BaSiH_6 , Ba is coordinated rather irregularly by 14 H atoms in a distance range 2.61–2.97 Å.

CONCLUSIONS

The hydridosilicate BaSiH_6 can be synthesized when reacting the Zintl phase hydride BaSiH_{2-x} with H_2 fluid at pressures above 4 GPa and subsequent decompression to ambient pressure. The monoclinic crystal structure consists of Ba^{2+} and hypervalent complex SiH_6^{2-} ions. Their mutual arrangement corresponds closely to an ideal fcc NaCl structure. BaSiH_6 is the first hydridosilicate with an alkaline earth metal and its discovery suggests a broader compositional variability in the cationic constituents of this relatively new class of compounds. Like the previously described alkali metal hydridosilicates, BaSiH_6 is a thermodynamically stable compound at ambient pressure, albeit with a rather low thermal stability. Its synthesis via BaSiH_{2-x} can be upscaled which eventually, with pure samples, will allow for detailed physical property characterization/measurements, including heat capacity, dynamic properties from inelastic/quasielastic neutron scattering spectroscopy, semiconductor properties, and H^- ion conductivity (probably only seen at pressure upon increased thermal stability). The structural properties of BaSiH_6 suggest that it represents a bridge to the predicted superconducting polyhydride BaSiH_8 ¹¹ which can be expected from hydrogenations at ultrahigh pressures of about 100 GPa and for which BaSiH_6 may serve as a most suitable precursor.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c10502>.

Detailed description of synthesis and sample preparations; details of the PXRD characterization of products; detailed description of the high-pressure neutron diffraction experiment and the refinement of neutron diffraction data; structure parameters for BaSiD_6 at 2.5 GPa; detailed description of the multitemperature synchrotron powder diffraction experiment and evaluation of data; DFT relaxed structure parameters of for C2/c BaSiH_6 ; and electronic band structure and density of states for C2/c BaSiH_6 (PDF)

Accession Codes

Deposition Numbers 2420757 and 2420758 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the joint Cambridge Crystallographic Data Centre (CCDC) and Fachinformationszentrum Karlsruhe Access Structures service.

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Notes

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