Structure and Properties of Hydrogenated Ca, Sr, Ba, and Eu Silicides

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Dedicated to Professor Martin Jansen on the Occasion of His 65th Birthday

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Abstract. The binary metal silicides CaSi, BaSi, SrSi, and EuSi that crystallize in the CrB type absorb reversibly hydrogen. Hydrogen contents of the products were measured by the carrier gas hot extraction method (CaSiH_x: 1.56 wt %, $x \approx 1.06$; SrSiH_x: 1.35 wt %, $x \approx 1.6$; BaSiH_x: 2.08 wt %, $x \approx 3.4$; EuSiH_x: 0.99 wt %, $x \approx 1.8$). According to simultaneous thermogravimetric, DTA and mass-spectroscopic analyses, the dehydrogenation for the different hydrides starts at 610 K for BaSiH_x, at 675 K for CaSiH_x and SrSiH_x, and at 640 K for EuSiH_x. BaSiH_x at 760 K. Fundamental morphological and structural changes caused by the hydrogenation of the silicides were detected and comprehensively characterized by SEM and X-ray diffraction. According to XRD results, the crystal structures of the phases *M*SiH_x (*M* = Ca, Ba, Sr, Eu) are all orthorhombic (space group *Pnma*). The lattice parame

Introduction

Reversible hydrogenation reactions are currently in the focus of intensive applied research because of the increasing demand for new hydrogen-storage materials that might enable a hydrogen-based technology, e.g. as a carbon-free alternative for powering automobiles by fuel cells [1]. Hydrogen can be stored in a variety of different materials like nanotubes, zeolithes, clathrates and metal-organic frameworks, in favorable cases already at ambient pressure and temperature [2, 3]. For the evaluation of such reactions, reversibility at low pressures and low temperatures, low weight and a high amount of hydrogen uptake represent the most important criteria. Consequently, many low-weight metals and alloys are promising candidates for use as hydrogen storage materials [4–6].

Triggered by this quest, some rather old results have reclaimed wide-spread attention recently. Since 50 years, it is known that the alloy ZrNi absorbs hydrogen while forming ZrNiH₃ [7]. In the following decades, the structure [8–11] and the thermodynamic behavior [12–15] of the hydride were studied in detail. The starting phase ZrNi crystallizes in the ortho-

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ters change from a = 4.559(1) Å, b = 10.731(1) Å, c = 3.890(1) Å (space group *Cmcm*, Z = 1) in CaSi to a = 14.4884(9) Å, b = 3.8247(1) Å, c = 11.2509(5) Å (Z = 3) in CaSiH_x caused by the hydrogen uptake that induces the formation of a threefold superstructure along the *a* axis. In CaSiH_x, the planes of the $[Si_n]^{2-}$ zigzag chains are tilted and inter-chain Si–Si contacts are formed formally corresponding to an oxidation to Si⁻. The hydrogen desorption process was investigated by in situ X-ray diffraction studies which revealed the presence of two different hydrogen species in CaSiH_x. The new phase SrSiH_x crystallizes in a related structure comprising tilted $[Si_n]^{2-}$ chains (a =15.1051(5) Å, b = 3.95400(8) Å, c = 12.3431(3) Å, space group *Pnma*). The lattice parameters of BaSiH_x are a = 15.7(2) Å, b =4.13(3) Å, c = 13.43(8); that of EuSiH_x a = 15.17 Å, b = 3.95 Å, c =11.56 Å (Z = 3).

rhombic CrB structure (space group *Cmcm*) [16]. This structure contains sheets of Cr_6 prisms which are filled with planar B chains in all-trans-configuration. The chains are stacked in an ecliptic arrangement along the *a* axis. The isostructural CaSi can be described as $(Ca^{2+})(Si^{2-})$ according to the *Zintl-Klemm* concept [17–20]. The hydride ZrNiH₃ is structurally closely related to the starting ZrNi phase. Whereas positions of the metal atoms in the hydride phase are similar to those in the original structure, the hydrogen atoms occupy mainly tetrahedrally coordinated sites [11]. Furthermore, hydrides of this type are formed by the CrB-type intermetallic phases HfNi, HfCo and ZrCo [21].

Several Zintl phases are hydrogen absorbers as well, e.g. the alkaline earth compounds AeE_2 (Ae = Ca, Sr, Ba; E = Al, Ga, In). In these systems, the structures of SrAl₂H₂ [22], SrGa₂H₂ [23] and BaGa₂H₂ [23] are well-characterized. In the crystal structure of Sr₂AlD₇, determined by neutron diffraction, isolated AlD₆ octahedra and infinite one-dimensional chains of edge-sharing DSr₄ tetrahedra appear [24]. Recently, polyanionic hydrides of AlB₂-type gallium phases AeGaE (Ae = Ca, Sr, Ba; E = Si, Ge, Sn) were reported [25, 26].

Considering these findings and having the low-weight and low-cost element silicon in focus, we turned our attention to the alkaline-earth silicides. CaSi, SrSi and BaSi are Zintl phases that crystallize in the structure type of CrB as well [27, 28]. First experimental evidence for the hydrogen uptake by CaSi was obtained by a japanese team [29–31] in parallel to

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our investigations [32, 33]. It is interesting to note that also Ca_2Si [34] and Ca_5Si_3 [35] do take up hydrogen. As no reports on other silicides with CrB structure existed so far, we have expanded our research on SrSi and BaSi. To get addditional systematic information about the behavior of CrB-type silicides in general, rare earth metal silicides like EuSi are included in our studies. To the best of our knowledge, the hydrogenation products of SrSi, BaSi and EuSi are described here for the first time.

Results and Discussion

Sorption and Desorption of Hydrogen

The hydrogenation of all *M*Si (M = Ca, Ba, Sr, Eu) phases was achieved at relatively moderate conditions in an autoclave ($T \approx 450$ K, $p(H_2) \approx 90$ bar, 1d). After hydrogenation, the obtained MSiH_x hydride phases were characterized by XRD measurements. The hydrogen content of each phase was determined by the carrier gas hot extraction method (Table 1). The percentage of uptaken hydrogen is in the range of 1–2 weight % resulting in the approximate formula CaSiH_{1.06} (1.56 wt% H), SrSiH_{1.6} (1.35 wt% H), BaSiH_{3.4} (2.08 wt% H), and EuSiH_{1.8} (0.99 wt% H), respectively. For CaSi, a maximal uptake of 1.9 wt% H corresponding to CaSiH_{1.3} was reported in the literature [29, 31]. Furthermore, the reaction of CaSi with deuterium leads to a phase CaSiD_{1.2} from which a part of the D content can be removed in a controlled way resulting in CaSiD₁ [36].

Table 1. Hydrogen content of $MSiH_x$ (M = Ca, Sr, Ba, Eu) as measured by the carrier gas hot extraction method and hydrogen release temperatures T_x .

Silicide hydrogen content /wt-%	x approx.	T_1 / \mathbf{K}	T_2/K	T_3 /K
$CaSiH_x$ 1.56 ± 0.04 $SrSiH_x$ 1.35 ± 0.04 $BaSiH_x$ 2.08 ± 0.15 $EuSiH_x$ 0.99	1.06 1.6 3.4 1.8	675 675 610 640	760 765	1000

The hydrogenation of these silicides occurs readily at quite moderate conditions, in particular that of EuSi. Compared to the earth-alkaline silicides which need reaction temperatures of about 450 K and a hydrogen pressure of 90 bar, the rare earth silicide EuSi reacts with hydrogen at the same pressure already at room temperature. It should be emphasized that crystals of all four hydrogenated silicides show a similar typical morphology and obviously have closely related structures as discussed below. Interestingly, the pure silicides and the hydrogenated ones show a similar behavior towards oxygenation. Whereas BaSi, BaSiH_x, SrSi and SrSiH_x react immediately with air, CaSi, CaSiH_x, EuSi and EuSiH_x are inert.

Subsequently, the thermal dehydrogenation of the hydrides was investigated by simultaneous TG, DTA and MS measurements (Table 1). The dehydrogenation for the different hydrides occurs in a single step for SrSiH_x (onset at $T \approx 675$ K) and EuSiH_x ($T \approx 640$ K). The investigation of CaSiH_x ($T \approx$ 675 K) and BaSiH_x ($T \approx 610$ K) reveals a hydrogen release at similar temperatures. However, the dehydrogenation is not complete in these cases since further hydrogen desorption is detected at starting temperatures of 766 K and 1000 K for BaSiH_x and of about 760 K for CaSiH_x, respectively (Table 1, Figure 1 and Figure 2a). The temperature ranges of hydrogen desorption measured for the $MSiH_x$ phases are similar to those of other hydrides of intermetallic compounds with CrB structure type (e.g. ZrNiH_x: 490–730 K [37]).



Figure 1. TG (half-dotted line), DTA (drawn-through line), and MS (dotted line) diagram of $CaSiH_x$. The first dehydrogenation step starts at 675 K and is finished at 750 K, the second starts from 760 K and is finished at 830 K. An in-situ X-ray-diffraction experiment of the dehydrogenation process is shown in Figure 3.



Figure 2. DTA (drawn-through line) and MS (dotted lines) diagrams of $BaSiH_x$ (a) and of BaH_2 (b). The dehydrogenation of $BaSiH_x$ occurs in three steps starting at 610 K, 765 K and about 1000 K, respectively, while that of BaH_2 appears in one step with an onset at about 1000 K.

Remarkably, these sorption/desorption steps can be repeated several times. Consequently, it can be concluded that CrB-type

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alkaline-earth silicides CaSi, SrSi, BaSi as well as the rare earth silicide EuSi do react reversibly with hydrogen.

The observation of hydrogen desorption at two different temperatures in the case of CaSiH_x, (Figure 1) and at three different ones in case of $BaSiH_x$ (Figure 2a), respectively, indicates that the hydrogen atoms are bound to two, respectively three energetically different sites. For getting additional information about the type of hydrogen bonding in $CaSiH_r$ and $BaSiH_r$, we performed reference TG/DTA/MS experiments with CaH2 and BaH₂. The hydrogen desorption of BaH₂ takes place in a single step at around 1000 K (Figure 2b). This temperature corresponds to that of the third hydrogen release of $BaSiH_x$ (Figure 2a). This finding indicates that a part of hydrogen in $BaSiH_x$ is in a bonding situation similar to that in BaH_2 , where H⁻ ions are coordinated by Ba²⁺ cations. However, it cannot be completely excluded that traces of possibly amorphous BaH₂ cause this effect although no evidence for its presence was found. In case of CaH2 and CaSiHx, a similar analogy of the desorption temperatures was not observed. CaH₂ dehydrogenates at 535 K and 1010 K whereas CaSiH_x does at 675 K and 760 K, respectively. Possibly the first dehydrogenation step is caused by the presence of Ca(OH)₂ [38].

YbSi and HoSi_{0.98} are further CrB-type rare earth silicides, which were tested under the same conditions but no hydrogen uptake was observed. Therefore, EuSi seems to be an exception among the CrB-type rare earth silicides. This effect may be caused by its preferred valency of two. In contrast to that, Ytterbium in YbSi is trivalent showing a lower unit cell vol-



Figure 3. In-situ X-ray diffraction analysis of the hydrogen desorption of $CaSiH_x$ with increasing temperature. Indices of the strongest reflections the room temperature patterns of CaSi (top) and CaSiH (bottom) are given. A prominent structural change takes part between 623 and 673 K, with the evolution of reflections of CaSi. The shifts of the reflection positions between 673 K and 773 K are mainly due to thermal expansion of the lattice constants. The visible separation of the reflections. The reflections in different directions. The reflections with a component along the *c*-direction (303, 113) show a strong shift towards lower diffraction angles, whereas the reflections 210 and 410 remain at the same angle.

ume [39]. In addition, the hydrogenation of the isotypic CaGe was also tested under the same conditions but without success.

To assemble further information about the mechanism of the hydrogen desorption in case of $CaSiH_x$, we performed an insitu X-ray diffraction analysis with results given in Figure 3. It can be clearly seen that a structural change takes place above 623 K and CaSi is formed. Thus, these results are in good agreement with the TG/DTA/MS measurements described above (Figure 1), showing the first dehydrogenation step at 675 K. The second step of the hydrogen loss at around 760 K is obviously not associated with larger structural changes, since the X-ray diffraction pattern is unchanged. The small shifts towards smaller diffraction angles are mainly due to thermal expansion of the unit cell.

Changes of Morphology

The hydrogenation of the silicides gives rise to significant changes of morphology as exemplified in typical SEM images of CaSi and CaSiH_x (Figure 4). The as-synthesized crystals of CaSi are several hundreds of micrometers large and show smooth, although sometimes faceted surfaces (Figure 4a-c). After hydrogenation, the crystals are broken into parallel slabs and pillars. The cracks between the individual fragments are of different width and run mostly parallel to each other (Figure 4d-f). These morphology changes, which have similarly been observed for the other silicides MSi and MSiH_x with M = Ba, Sr, Eu as well, give evidence for the difficulty of gaining reasonably good data for X-ray single crystal and Rietveld refinements (see below).



Figure 4. SEM images of CaSi before (a–c) and CaSiH_x (d–f) after hydrogenation. CaSi yields well-developed crystals (a) that sometimes shows facets and surface steps (b, c). By hydrogenation, the crystals are split into plate-like fragments (d–f) that are arranged in parallel stacks along the crystallographic *c* axis of CaSiH_x (e).

A breakage of the crystals proceeds with subsequent hydrogenations, resulting in further fragmentation. This decrease of crystallinity and crystal size by the hydrogenation process also sets the limit for the number of hydrogenation/dehydrogena-



tion cycles. After three cycles further hydrogenation cannot be observed any more.

Remarkably, the rather large crystal size of the starting compounds appears to be a prerequisite for a successful hydrogenation. Samples of *M*Si (M = Ca, Ba, Sr, Eu), which were ballmilled for some hours and contained small crystallites besides a large amount of amorphous *M*Si as proven by XRD powder investigations, did not undergo hydrogenation any more. Obviously, the increased surface area is not of significant importance here and a physical surface absorption of the hydrogen can be excluded. In contrast to that finding, the hydrogenation of Ca₂Si was exclusively observed for ball-milled samples [34]. This size effect is not fully understood yet although it is general knowledge that a decrease of crystal size may lead to a degradation of the hydrogen sorption properties and to poor cycle stability [40].

Structural Characterization of the Hydrides

The uptake of hydrogen by the silicides CaSi, SrSi, BaSi and EuSi leads to structural modifications that are indicated by differences in the XRD patterns of the hydrides. From those, lattice parameters were derived that differ significantly from that of the starting compounds (Table 2). Due to the structural modifications, the space group symmetry is reduced during hydrogenation from Cmcm (No. 63) to Pnma (No. 62) in all cases. For comparison with the cell of the starting MSi phases, the lattice parameters b and c of $MSiH_x$ are interchanged in Table 2. The cell parameters b and c of $MSiH_x$ are similar to those of the respective MSi phases: while the c axis of MSIH_x shrinks by a small amount compared to the b axis of MSI, the b axis increases significantly compared to the c axis. The most drastic change concerns the length of the *a* axis (Table 2): the parameter a is approximately tripled, indicating the formation of a threefold superstructure in this direction (see below). As

an overall effect, the volume of a formula unit in the unit cells increases caused by the space required for the inserted hydrogen atoms and the reorganizations of the silicon substructure. In Table 2, this additional volume is listed in percent per formula unit Z. The close metrical relationship between the lattice parameters of the parent silicides on the one hand and the hydrides on the other indicates topochemical reactions that involves partial changes of the starting CrB-type structures only and that leads to an obviously close relationship between the structures of all hydride phases studied here.

CaSiH_x

The unit cell parameters of CaSiH_x were refined to a =14.4884(9) Å, b = 3.8247(1) Å and c = 11.2509(5) Å (Table 2). These parameters agree with those reported for CaSiH_{1.3} and CaSiD₁ (Table 2). Because of the fragmentation of the crystals during the hydrogenation process, there are no large single crystals present in the reaction product. However, the plate- and pillar-like fragments of a former single crystal are still oriented nearly in parallel (cf. Figure 4e). This enabled us to use such crystallite assemblies as pseudo single crystals for the determination of the lattice constants and for obtaining an initial structural model by direct methods [41]. The refinement of the structure was then done on X-ray powder data. The final Rietveld refinement in the space group Pnma (No. 62) converged to $R_{wp} = 11.04$ %, $R_P = 8.33$ %, $R_F = 9.55$ %, and $\chi^2 = 2.465$ for 21 variables (Figure 5). The structure of CaSi (Figure 6a), like those of the isostructural CrB-type silicides BaSi, SrSi and EuSi, contains sheets of Ca₆ trigonal prisms that are filled with planar silicon chains in all-trans configuration (Figure 6a). The chains are stacked in an ecliptic arrangement along the *a* axis. The structure can be described according to the Zintl-Klemm concept as (M²⁺)(Si²⁻). By reac-

Table 2. Lattice constants and cell volumes of MSi and $MSiH_x$ (M = Ca, Sr, Ba, Eu).

Silicide	Spgr.	Lattice parameters			Cell volume $/\text{Å}^3$ Excess volume $/\%$ Z		me /% Z
	10	a / Å	$b_{ m MSi}$ /Å $c_{ m MSiH}$ /Å	c _{MSi} /Å b _{MSiH} /Å			
CaSi [28] CaSiH _{1.06} % change / Z CaSiH _{1.3} [30] CaSiD _{1.0} [36]	Cmcm Pnma	4.5594(9) 14.4884(9) 5.9 14.545(3) 14.5685(1)	$\begin{array}{c} 10.731(1)\\ 11.2509(5)^{a)}\\ 4.8\\ 11.226(2)^{a)}\\ 11.2092(1)^{a)} \end{array}$	$\begin{array}{c} 3.8900(7)\\ 3.8247(1)^{a)}\\ -1.7\\ 3.8198(7)^{a)}\\ 3.8203(2)^{a)} \end{array}$	190.3 623.45(5) 9.2 623.71 623.86	2.3	4 12
SrSi [28] SrSiH _{1.6} % change / Z	Cmcm Pnma	4.8162(4) 15.1051(5) 4.5	11.303(1) 12.3431(3) ^{a)} 9.2	4.0388(4) 3.95400(8) ^{a)} -2.1	219.9 737.20(3) 11.8	2.95	4 12
BaSi [28] BaSiH _{3.4} % change / Z	Cmcm Pnma	5.0430(8) 15.73(15) 4	11.933(2) 13.43(8) ^{a)} 12.5	4.1395(8) 4.13(3) ^{a)} -0.22	249.1 872.5 16.8	4.2	4 12
EuSi [39] EuSiH _{1.8} % change / Z	Cmcm Pnma	4.694(5) 15.17 7.7	11.14(1) 11.56 ^{a)} 3.8	3.981(2) 3.95 ^{a)} -0.8	208.2 692.7 10.9	2.72	4 12

a) For a better comparability of the corresponding directions in the hydrogenated and the original structure, the lattice constants are listed in the order a,c,b for $MSiH_x$ here.

tion with hydrogen, an oxidation of the chains ${}^{1}_{\infty}[Si^{2-}]$ partly takes place.



Figure 5. Rietveld refinement of $CaSiH_x$. Experimental (red), calculated (green), and difference (purple) powder pattern profiles. The reflection positions of $CaSiH_x$ and CaSi (traces) are marked in black and red, respectively. The final fit is impaired by the poor crystallinity, anisotropic peak profiles, high background, and absorption effects.



Figure 6. Structures of CaSi (a) and of CaSiH_x (b) projected along the short axis. In CaSi, the silicon atoms form zigzag chains along the direction of view. The unit cell of CaSiH_x comprises three unit cell of CaSi, leading to an approximately tripled lattice constant *a*. The directions of the shifts of some silicon atoms during hydrogenation are indicated by arrows. During the formation of CaSiH_x, the Si–Si chains are tilted and connected in such a way that 6 silicon atoms wide bands appear. Some significant distances of Si–Si bonds are given.

The Ca^{2+} substructure in $CaSiH_x$ is quite similar to that of the starting material CaSi. A threefold superstructure along the

a axis has evolved as a remarkable feature of the CaSiH_x structure (Figure 6b). This is caused by a reorganization of the silicon substructure: the planes of the silicon zigzag chains are tilted and as a result additional Si–Si bonds occur between the chains. Consequently, there are three different bond lengths Si–Si in CaSiH_x: the two short ones [2.349(6) and 2.366(9) Å] are smaller than in CaSi (2.455 Å [28]) whereas the new bond is considerably larger with 2.622(10) Å (Table 3, Table 4, Figure 6b). In the CaSiH_x structure, novel silicon slabs appear that are 6 silicon atoms wide. Whereas the silicon atoms at the rim of the slabs have two bonds to adjacent ones, those inside the slabs form three bonds (Figure 6b). Thus, the hydrogenation reaction can be formulated as:

6 (2b)Si²⁻ + 2H₂ \rightarrow 4 (3b)Si⁻ + 2 (2b)Si²⁻ + 4H⁻. Where (nb) denotes the number of single bonds.

This means that only 2/3 of the two bonded Si²⁻ are reduced to three bonded Si⁻ resulting in a ratio Si:H = 3:2. Since the actual ratio Si:H is close to 1:1, a part of the hydrogen could be incorporated (formally) in neutral form [26].

Table 3. Atomic coordinates (standard uncertainties) and isotropic displacement factors for $CaSiH_x$. All positions are fully occupied. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} .

atom	site	a)x / a	y / b	^{a)} z / c	$U_{ m iso}$ /Å 2
Ca1	4 <i>c</i>	0.3391(4)	1/4	0.8447(6)	0.0153(6)
Ca2	4c	0.3093(3)	1/4	0.1597(6)	U(Ca1)
Ca3	4c	0.3602(3)	1/4	0.4793(5)	U(Ca1)
Si4	4c	0.0418(6)	1/4	0.1862(6)	0.0261(11)
Si5	4c	0.0417(6)	1/4	0.7578(6)	U(Si4)
Si5	4c	0.0441(5)	1/4	0.5248(8)	U(Si4)

a) Standard uncertainties determined by powder diffraction are based on statistical calculations and neglect all systematic errors. Therefore more realistic uncertainties may be higher.

Table 4. Selected interatomic distances in $CaSiH_x$ given in Å.

Cal	-Si1	3.132(8) 2x	
	-Si2	3.154(10)	
	-Si3	3.260(8) 2x	
	-Si3	3.313(10)	
Ca2	-Si2	3.088(8) 2x	
	-Si3	3.236(8) 2x	
Ca3	-Si1	3.224(10)	
	-Si1	3.330(8) 2x	
	-Si2	3.448(8) 2x	
Si1	-Si2	2.349(6) 2x	
Si2	-Si3	2.622(10) 2x	
Si3	-Si3	2.366(9) 2x	

From neutron powder diffraction experiments, Wu et al. determined the deuterium positions in the phases CaSiD₁ and CaSiD_{1.2} [36]. In CaSiD₁, all Ca₄ tetrahedra are occupied by hydrogen atoms. In CaSiD_{1.2}, the additional hydrogen gives rise to D-centered Ca₃Si tetrahedra. Since in our case a hydrogen content in the intermediate range was found for CaSiH_x, ($x \approx 1.06$), some additional Ca₃Si tetrahedra are evidently filled with hydrogen besides all Ca₄ tetrahedra. Independent experimental proof for this is provided by the observation of the

hydrogen desorption in two steps (Figure 1, Figure 3) that indicate two energetically different hydrogen sites.

A tripling of the *a* axis is evident from the XRD results (Table 2). The measured length of the *a* axis in CaSiH_x is 14.4884(9) Å. This value is significantly larger than that of the tripled *a* axis of CaSi (4.56 Å × 3 = 13.68 Å), corresponding to an increase of 5.9 % (Table 2). The length of the *b* axis in CaSi with ca. 10.73 Å is smaller than the interrelated *c* axis in CaSiH_x (11.2509(5) Å] corresponding to an expansion of 4.8 % along this direction. In contrast to that, the short crystallographic axis shrinks from 3.89 Å in CaSi to 3.8247(1) Å in CaSiH_x. The tilting of the Si–Si chains and their subsequent connection with each other obviously leads to cracks in the direction of the *c* axis (referring to the standard setting of *Pnma*) which are visible by SEM (Figure 4d–f). In total, the volume per formula unit increases by 2.3 % during hydrogenation.

SrSiH_x

The hydrogenation of SrSi is possible under similar conditions as reported for the isostructural CaSi (see above), resulting in the new phase SrSiH_x. To determine the structure of SrSiH_x, X-ray powder diffraction data were used. The powder pattern was indexed based on an orthorhombic structure isotypic to CaSiH_x. The atomic parameters of CaSiH_x were used as a starting model for the refinement in the space group *Pnma* (No. 62) as well (Table 5). The final Rietveld refinement converged to $R_{wp} = 6.51$ %, $R_P = 4.95$ %, $R_F = 12.82$ %, and $\chi^2 =$ 2.137 for 19 variables. The observed and calculated X-ray powder diffraction patterns and the corresponding difference profile are shown in Figure 7.

Table 5. Atomic coordinates (standard deviations) and isotropic displacement parameters obtained from the Rietveld refinement for $SrSiH_x$. All positions are fully occupied.

atom	site	$a^{a}x / a$	y / b	$a)_{z} / c$	$U_{ m iso}$ /Å 2
Sr1	4 <i>c</i>	0.3407(3)	1/4	0.8537(4)	0.0317(4)
Sr2	4c	0.3253(3)	1/4	0.1631(5)	U(Sr1)
Sr3	4c	0.3606(2)	1/4	0.4933(6)	U(Sr1)
Si4	4c	0.0444(12)	1/4	0.7934(12)	0.0191(14)
Si5	4c	0.0441(11)	1/4	0.1896(11)	U(Si4)
Si6	4c	0.0419(8)	1/4	0.5340(9)	U(Si4)

a) Standard uncertainties determined by powder diffraction are based on statistical calculations and neglect all systematic errors. Therefore more realistic uncertainties may be higher.

The structural model derived from these data is represented in Figure 8. In this model, hypothetical but reasonable hydrogen positions are shown. As in CaSiH₁, all Sr₄ tetrahedra are occupied by hydrogen atoms. Since the composition derived from TG/MS measurements is SrSiH_{1.6} (Table 1), further hydrogen positions must exist, possibly in the centers of Sr₃Si tetrahedra as observed for CaSiH_{1.2} [36]. It is difficult to elaborate on the change of oxidation state of silicon, here, because the tilting of chains and the mutual approach of chains may lead to a higher net bond order at silicon and consequently to a partial oxidation. This may well remain at an intermediate of



Figure 7. Rietveld refinement of $SrSiH_x$. Experimental (red), calculated (green), and difference (purple) powder pattern profiles. The reflection positions of $SrSiH_x$ and SrO (traces) are marked in black and red, respectively. The high background points to a high content of an amorphous material in the sample. The final fit is impaired by the poor crystallinity, anisotropic peak profiles, high background and absorption effects.

depopulation of the π^* states of the planar chains thus leading to a net π bonding inside the chains and a σ interaction between chains. Such subtle interactions have been described before for many tetrel Zintl phases [42].



Figure 8. Structural model of $SrSiH_x$. The Si-chains in $SrSiH_x$ are tilted compared to the silicon chains in SrSi. Possible hydrogen positions are the centers of Sr_4 tetrahedra. Some Si–Si distances are given.

The cell volume increases from ca. 660 Å³ (\equiv 3 × 220 Å³) for SrSi to 737 Å³ for SrSiH_x which corresponds to an increase of about 3 % per formula unit (Table 2). A tilting of the plane of some silicon chains is observed here as well but the overall structural reorganization is small compared to that in CaSiH_x (Figure 6b). The most eye-catching difference of the two structures is that no interchain Si–Si bonds are formed in SrSiH_x. Within the chains, the Si–Si bonds are 2.395(8) and 2.493(14) Å, respectively (Table 6). The first value is significantly shorter than in the starting phase SrSi (2.492 Å [28]). The interchain distance remains rather long with ca. 3.20 Å and the resulting change of bonding is difficult to quantify (Figure 8). It should be noted that, the distances between the

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silicon chains in $CaSiH_x$ are much smaller (2.62 Å (Table 4). As mentioned above, no (formal) oxidation of the silicon chains takes place here. Concerning the silicon arrangement, the $SrSiH_x$ structure can be regarded as a kind of intermediate state between the unhydrogenated CaSi phase with isolated silicon chains and the hydrogenated $CaSiH_x$ with tilted and interconnected silicon chains.

Table 6. Selected interatomic distances in $SrSiH_x$ given in Å.

Sr1	-Si1	3.573(17)	
	-Si2	3.323(13) 2x	
	-Si3	3.340(12)	
	-Si3	3.466(11) 2x	
Sr2	-Si1	3.772(16)	
	-Si2	3.220(14) 2x	
	-Si3	3.236(11) 2x	
Sr3	-Si1	3.825(17	
	-Si1	3.472(15) 2x	
	-Si2	3.442(14) 2x	
Si1	-Si2	2.395(8) 2x	
Si3	-Si3	2.493(14) 2x	

$BaSiH_x$ and $EuSiH_x$

For both phases, which have been observed and characterized here for the first time, no single crystals were available. Moreover, a structure determination and Rietveld refinement has been impossible in consequence of the bad quality of the X-ray powder diffractograms that is caused by poor crystallinity, absorption and also fluorescence (in the case of Eu and Cu- K_{α} -radiation). However, we were able to index the powder patterns on the basis of an orthorhombic structure in the space group *Pnma* (No. 62) isotypic to $CaSiH_x$ (Table 2). The changes of the lattice constants show a similar tendency like that of hydrogenated CaSi and SrSi in conjunction with a lattice expansion (Table 2). In both cases, the *a* axis is larger than the tripled a axis of the hydrogen-free phases. Moreover, the caxis is larger than the corresponding b axes of MSi whereas the b axis is slightly smaller than c_{MSi} This observation evidences structural modifications by hydrogenation of BaSi and EuSi that are comparable to those of CaSi and SrSi: the cation sublattice of BaSiH_x and EuSiH_x remain mostly unchanged whereas the silicon positions shift such that the formation of the threefold superstructure appears. The powder diffraction patterns of the starting silicide phase and of the hydride $BaSiH_x$ are shown in Figure 9. Besides the high background, the presence of unreacted BaSi impeded a further evaluation of the $BaSiH_x$ structure. Interestingly, $BaSiH_x$ represents the silicide that incorporates by far the highest amount of hydrogen per formula unit ($x \approx 3.4$, Table 1). Therefore, additional positions must be occupied by hydrogen besides the Ba₄ tetrahedra. This assumption is also supported by the observed hydrogen release at three different temperatures pointing to the existence of three energetically different hydrogen sites. Figure 9: BaSi (a) and BaSiH_r (b). Only few residual of unhydrogenated BaSi is present in the product (marked with * in b).



Figure 9. BaSi (a) and $BaSiH_x$ (b). Few residual amounts of unhydrogenated BaSi are present in the product (marked with * in b).

Conclusions

Just like the CrB-type alloys ZrNi and LaNi, the isostructural silicides CaSi, SrSi, BaSi and EuSi can take up considerable amounts of hydrogen (up to 2 wt % for BaSiH_{3.4}). In all cases, the hydrogenation is combined with an increase of the unit cell volumes. Whereas the positions of the metal atoms remain basically the same as in the original non-hydrogenated structures, the structural reorganization during hydrogenation as observed in case of CaSiH_x and SrSiH_x significantly affects the silicon substructure. This reorganization can partly be interpreted as an oxidation process of the Zintl anions leading to a higher linking of the silicon atoms, accordingly, and to the formation of H⁻ anions. However, in the structure of SrSiH_x, the silicon chains are isolated as in the parent CrB-type structure of SrSi. Therefore, the Zintl-Klemm concept does not offer an explanation for the hydrogen uptake here.

It is not yet clear whether the morphology changes of the crystals are due to diffusion of hydrogen into the structure that occurs along well-defined crystal directions or if they are caused just by anisotropic volume work. Another open question is why well-developed crystals of MSi can be hydrogenated while ball-milled samples do not take up any hydrogen. An explanation for these findings would be an inert, possibly oxidic layer, generated either by quenching or by milling that prevents the hydrogen from diffusing into the material. Interestingly, the solid state reaction of CaH₂ (and CaD₂) with silicon in a ball-mill leads to the formation of CaSiH_x in microcrystalline form [34, 35]. It is important to further investigate the localization and bonding state of silicon and hydrogen in these *M*SiH_x phases to get a deeper understanding of the mechanism of their formation and to unravel further candidates



among CrB-type and other (Zintl) compounds for successful hydrogenation reactions.

Experimental Section

Synthesis

CaSi, SrSi, BaSi, and EuSi were prepared by reacting the redistilled metals in stoichiometric amounts (Ca: Alfa Aesar, 99.9 %; Sr: Fluka, 99 %; Ba: Aldrich, 99 %; Eu: ABCR, 99 %) with silicon (Fluka, 99.999 %) in closed tantalum ampoules running the following temperature program: heating up from 298 to 1400 K in 10 h; heating at 1500 K for 1 h and at 1350 K for 10 h; quenching the products finally in cold water. Hereby, the well-crystallized silicides were obtained in pure form according to XRD investigations. The samples were placed into an autoclave (about 200 mg). The reactor was heated up to 450 K jacket temperature and a hydrogen pressure (H₂: PanGas, 99.999 99 %) of about 90 bar was applied for one day. To avoid any reaction of starting materials and products with air, the samples were always handled in a glove-box under argon atmosphere. In particular, the reactor for hydrogenation was filled, closed and opened under the same inert conditions.

Structural Characterization

For X-ray diffraction (XRD) investigation, the samples were filled into glass capillaries (Hilgenberg, diameter: 0.1-0.3 mm) under argon and sealed to avoid contact with air. In the case of CaSiH_x, a data set of a pseudo-single crystal was collected with a SMART platform diffractometer (Bruker) equipped with a CCD detector. Structure determination and refinements of the initial model were performed with the program package SHELXTL [43].An empirical absorption correction (program SADABS) was employed. This initial model was used as a starting model for the final refinements of the powder diffraction data (Stoe, STADI-P2, Ge-monochromator, λ (Cu- $K_{\alpha 1}$) = 1.54056 Å; linear PSD; step size $\Delta 2\theta = 0.01^{\circ}$; total data collecting time = 60 h). The Rietveld refinement was done with the program-package GSAS [44-46]. Since in the case of $SrSiH_x$ no single-crystals could be obtained, the structure analysis was solely performed on the basis of powder diffraction data (measurement parameters as given above). In-situ Xray-diffraction of CaSiH_x was performed on the diffractometer described above using a capillary furnace (Stoe). Further details of the crystal structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http:// www.fiz-karlsruhe.de/request for deposited data.html) on quoting the CSD numbers 380316 for CaSiH_{1.06} and 380317 for SrSiH_{1.2}. Scanning electron microscopy (SEM) was performed with a Gemini 1530 field emission microscope (Zeiss). Samples were fixed on carbon pads and investigated as-obtained at 1 kV.

Measurements of Thermal Behavior and of the Hydrogen Content

Thermogravimetric (TG) and difference thermometric analysis (DTA) were performed with a Netzsch STA 409 under a dynamic dry argon with a heating rate of 10 K·min⁻¹ in corundum crucibles ($T_{\text{max}} =$ 1773 K). For mass spectrometric (MS) measurements, a Balzers QMS 220 was used. The amount of hydrogen was determined via the carrier gas hot extraction method using a LECO RH 404 hydrogen analyzer at room temperature and 1013 mbar (furnace EF 400; heat conductivity detector) [47].

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