



	Experiment title: Exploration of Novel Hydrogen-rich Hydrides at GPa Pressures in Na–Si–H System using NaSi as Reactive Precursor	Experiment number: CH-6290
Beamline: ID06-LVP	Date of experiment: from: 5/04/22 to: 10/04/22	Date of report: 12/09/2022
Shifts: 15	Local contact(s): Dr. Dmitrii Druzbin	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): M.Sc. Doreen S. Beyer* (University of Leipzig, Institute of Inorganic Chemistry, 04103 Leipzig, Germany) Dr. Kristina Spektor* (University of Leipzig, Institute of Inorganic Chemistry, 04103 Leipzig, Germany/DESY, PETRA III, 22607 Hamburg, Germany) Prof. Dr. Holger Kohlmann (University of Leipzig, Institute of Inorganic Chemistry, 04103 Leipzig, Germany) Prof. Dr. Ulrich Häussermann* (Stockholm University, Dept. of Environmental and Materials Chemistry, Svante Arrhenius vag. 21, 10691 Stockholm, Sweden)		

Report:

Aim of the study

Recent studies have shown that hydrogenation reactions at 4–10 GPa pressures afford unique hypervalent $[\text{SiH}_6]^{2-}$ complexes in the crystalline hydridosilicates A_2SiH_6 (A = K, Rb).¹ This suggests that a broader diversity of hypervalent silicon hydride species should be attainable, especially with application of gigapascal pressures. At the same time, the bonding properties of such species closely resemble those of high temperature superconducting binary phases PH_2 and H_3S , with the latter displaying remarkable T_C of 203 K.^{2,3} These binary phases, however, are only stable at pressures above 100 GPa and cannot be retained and studied at ambient conditions. Switching to ternary systems can lower the synthesis pressures down to several GPa and even afford recoverable products, which makes exploration of systems such as Na–Si–H in a large volume press particularly promising. In 2021 during the experiment CH-5986 at ID06-LVP, ESRF, we have studied reactions $\text{NaH} + \text{Si} + \text{H}_2$ at pressures up to 9 GPa and temperatures up to 700 °C. Indeed, a new ternary compound Na_3SiH_7 displaying remarkably complex polymorphism was discovered. The goal of the experiment CH-6290 was to extend the search for $\text{Na}_x\text{Si}_y\text{H}_z$ phases by in situ PXRD investigations at ID06-LVP using Zintl phase NaSi as reactive precursor in gigapascal hydrogenations.

Performing hydrogenations at GPa pressures using large volume devices has already shown strong potential for accessing novel ternary hydrides.^{1,4,5} Combining LVP technique with in situ diffraction is particularly

beneficial, as it allows for efficient mapping of p,T space to not only search for new materials, but also to study their phase behaviour and recovery pathways as well as to optimize synthesis conditions for large scale production and ex-situ characterization. ID06-LVP offers a unique opportunity to collect time-resolved angle-dispersive in situ PXRD during the reactions in multicomponent systems at GPa pressures while providing stable heating over a wide range of temperatures and sufficiently large sample volumes.⁶ During experiment CH-6290 we have explored reactions $\text{NaSi} + m \text{NaH} + n \text{H}_2$ ($m = 0,1$) in p,T range of 7 – 11 GPa and 300-700 °C using large volume press at ID06, ESRF. Experimental details and results of the study are discussed in the next sections.

Technical aspects

Sample preparation for CH-6290 was performed in advance at DESY and handled entirely in an Ar-filled glovebox due to air and moisture sensitivity of the starting materials. Powdered sodium silicide (NaSi) in a pure form or mixed with NaH in 1:1 molar ratio was pressed into pellets of either 1.5 or 2 mm outer diameter (OD) and 0.8–1 mm height. Along with two pellets of the hydrogen source ammonia borane (NH_3BH_3) the samples were enclosed into sodium chloride (NaCl) capsules of either 2.5 or 3 mm OD and 2.5–3.5 mm height. Smaller and larger sample/capsule sizes were used for 10/5 and 14/8 multianvil assemblies, respectively. The amount of NH_3BH_3 per sample corresponded to $\sim 6 \times$ molar excess of H_2 with respect to Si, while the complete decomposition of the hydrogen source at target pressures was expected at ~ 300 °C.⁷ NaCl (dried under vacuum) was used as sample capsule material due to its ability to form air-tight seal for sensitive materials and resist hydrogen diffusion. In addition, NaCl EOS is well-studied,⁸ and can be used for in situ p,T evaluation.

The experiments at ID06-LVP were performed with 10/5 and 14/8 multianvil assemblies depending on the target pressure. Sample capsules along with MgO plugs of the same OD were loaded into graphite heaters (3.2 or 4 mm OD for 10/5 and 14/8 setup, respectively). The graphite heaters and the two outer ZrO_2 plugs (3.2 or 4 mm OD) were then enclosed inside 10 or 14 mm OEL Cr-doped MgO octahedra. The passage of the current was ensured by topping the heaters with molybdenum (Mo) foils with respective OD, which, in turn, were in contact with Mo leads (1 mm OD, 1.6 mm height) inserted into the ZrO_2 plugs. The octahedra were positioned between eight gasketed 32 mm tungsten carbide (WC) anvils (5 or 8 mm TEL). To minimize the contribution of assembly materials to PXRD data, X-ray transparent SiBCN cylinders as well as MgO or BCN rectangles were inserted along the beam direction into the octahedra and the gaskets, respectively. The outer side of WC cubes was insulated with epoxy sheets, except the copper foil contacts at the cubes adjacent to the Mo leads.

Samples were brought to target pressure in 7–11 GPa range and heated using Delta Elektronika SM6000 power supply by regulating the power. AD-XRD data ($\lambda=0.234375$ Å) were collected continuously during compression, decompression (30-60 sec/pattern) and heating (1-2 sec/pattern) using a customized DECTRIS PILATUS3 X CdTe 900K-W-ESRF detector. The new detector system was highly advantageous for our experiments as it allowed to acquire the data with very good signal-to-noise ratio at extremely high time resolution and thus detect the slightest changes in the patterns on heating, while accessing wide 2θ range (~ 1.8 – 16°) essential for structural characterization. The heating rate and duration were adjusted depending on the observed changes in the diffraction and lasted up to 8 hours in order to drive the reactions to completion and study phase transition behaviour of the products. Temperatures were estimated based on power – temperature calibrations of the assemblies performed earlier at DESY, P61B, using type C thermocouple. Heating was terminated either by temperature quenching or slow cooling, and the samples were further decompressed and recovered at ambient conditions.

Results

During 15 shifts allocated for CH-6290 a total of 6 experiments were performed, including 2 runs for the hydrogenation of pure NaSi and 3 runs for the 1NaSi:1NaH mixture. An additional experiment targeted formation and phase transformations of ternary hydrides in Ba–Si–H system at ~ 8 GPa. Four of the experiments (3 performed using 14/8 assembly at 7 and 11 GPa, one using 10/5 assembly at 8 GPa) were successful. Other two runs performed with 10/5 cell at ~ 11 – 12 GPa terminated in blowouts during compression and heating. Exact reason for this was not clear, however, it may be related to the pressure-induced phase transition of NaSi and/or possible instability of X-ray transparent gasket insertions.

Both pure NaSi and 1NaSi:1NaH mixture were first reacted with hydrogen at the starting pressure of ~ 7 GPa. Strong similarities were observed in both experiments. H_2 release was expected to be complete by ~ 300 °C, however, no significant changes were observed in the patterns until above ~ 370 °C. Interestingly, during the further temperature increase several sets of reflections emerged sequentially in the PXRD patterns. The final set of peaks appeared at ~ 400 °C and remained unchanged upon slow cooling for the run employing pure NaSi.

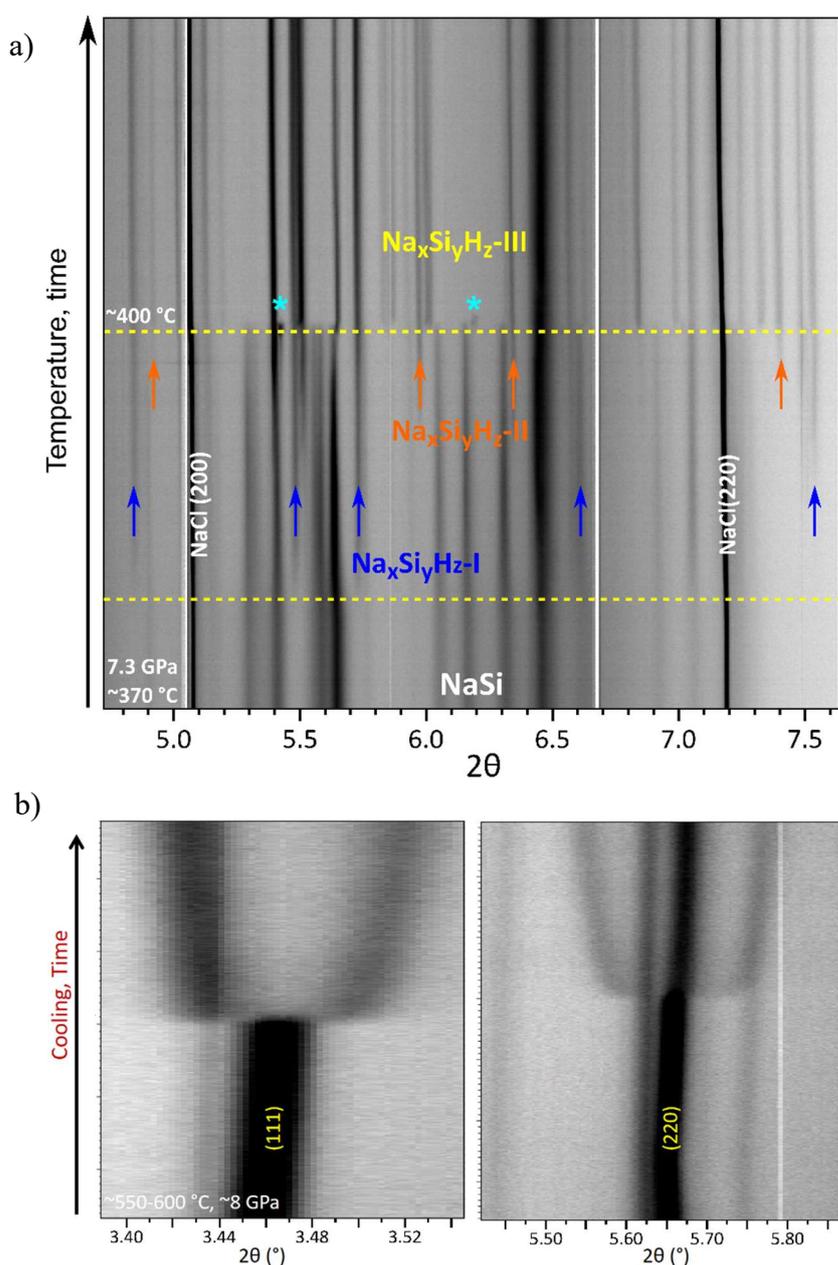


Figure 1. (a) PXR data collected during CH-6290 at ID06-LVP during hydrogenation of NaSi at ~ 7 GPa. Arrows and asterisks mark various $\text{Na}_x\text{Si}_y\text{H}_z$ phases. (b) Peak splitting observed during the transformation of cubic high temperature BaSiH_x phase to low temperature monoclinic form on cooling; data collected at ~ 8 GPa at a rate of 2 sec/pattern.

The time resolution of 1 sec/pattern allowed us to single out at least four phases in the observed sequence (Fig. 1(a)). The 1NaSi:1NaH sample was heated further (>550 °C), which resulted in partial decomposition. NaH, however, did not seem to actively participate the reaction. Similar sequence of phases, however, displaying different sets of reflections appeared during the 1NaSi:1NaH hydrogenation at ~ 11 GPa. Overall, we observed what looked like a remarkably complex interplay of reactions and resulting ternary $\text{Na}_x\text{Si}_y\text{H}_z$ phases in the Na–Si–H system when NaSi was used as a hydrogenation precursor. At the same time, the results were very different from those obtained in CH-5986, where NaH:Si mixtures were used as a starting material. In the latter case formation of tetragonal HT-HP Na_3SiH_7 phase was detected, while reaction rate was comparatively sluggish due to poor reactivity of elemental Si (see the report for CH-5986). During CH-6290 only trace amounts of Na_3SiH_7 phase were observed, while majority of the phases displayed low symmetry unit cells, possibly triclinic or monoclinic, according to preliminary indexing results. At the same time, no matching compounds were found in the available databases. Further data evaluation is in progress.

The study of ternary compounds in the system Ba–Si–H was performed in a 10/5 assembly at ~ 8 GPa using Zintl phase hydride $\text{BaSiH}_{-1.8}$ ⁹ as a hydrogenation precursor. ED-XRD data obtained for this system earlier at ~ 8.5 GPa at the beamline P61B, PETRA III, DESY suggested formation of a novel hydride (BaSiH_x) containing hypervalently coordinated silicon. The hydride was found to undergo reversible temperature-dependent phase transition. By repeating the experiment

in AD mode at ID06-LVP we have obtained valuable data for structural evaluation of BaSiH_x , which was not possible with with ED-XRD. At the same time, we could follow the temperature-induced phase transition at very high time resolution (2 sec/pattern; see Fig. 1(b)). The acquired data allowed us to confirm the monoclinic crystal system for the low temperature form of BaSiH_x and in the end aided in resolving its crystal structure. In addition, the secondary phase forming during the reaction could be identified from ID06 data. Overall, during CH-6290 we have confirmed that Zintl phases such as NaSi can act as much more reactive hydrogenation precursors compared to the mixtures containing elemental silicon. At the same time, they display very different behaviour upon hydrogenation and can give access to further novel ternary phases $\text{Na}_x\text{Si}_y\text{H}_z$. To unravel the interplay of the observed compounds in Na–Si–H system, we plan to combine analysis of the ID06-LVP data with further theoretical calculations, in particular structure prediction studies.

References

- (1) Puhakainen, K.; Benson, D.; Nylén, J.; Konar, S.; Stoyanov, E.; Leinenweber, K.; Häussermann, U. *Angew. Chem. Int. Ed.* **2012**, *51* (13), 3156–3160.
- (2) Shamp, A.; Terpstra, T.; Bi, T.; Falls, Z.; Avery, P.; Zurek, E. *J. Am. Chem. Soc.* **2016**, *138* (6), 1884–1892.
- (3) Drozdov, A. P.; Eremets, M. I.; Troyan, I. A.; Ksenofontov, V.; Shylin, S. I. *Nature* **2015**, *525* (7567), 73–76.
- (4) Spektor, K.; Crichton, W. A.; Filippov, S.; Klarbring, J.; Simak, S. I.; Fischer, A.; Häussermann, U. *ACS Omega* **2020**, *5* (15), 8730–8743.
- (5) Spektor, K.; Crichton, W. A.; Filippov, S.; Simak, S. I.; Fischer, A.; Häussermann, U. *Inorg. Chem.* **2020**, *59* (22), 16467–16473.
- (6) Guignard, J.; Crichton, W. A. *Rev. Sci. Instrum.* **2015**, *86* (8), 085112.
- (7) Nylén, J.; Sato, T.; Soignard, E.; Yarger, J. L.; Stoyanov, E.; Häussermann, U. *J. Chem. Phys.* **2009**, *131* (10), 104506.
- (8) Birch, F. *J. Geophys. Res.: Solid Earth* **1986**, *91* (B5), 4949–4954.
- (9) Auer, H.; Schlegel, R.; Oeckler, O.; Kohlmann, H. *Angew. Chem. Int. Ed.* **2017**, *56* (40), 12344–47.