	Experiment title: Mapping formation conditions and phase relations of hydrogen-rich phases in the ternary systems A-Si-H (A = Li, Na)	**Experiment number**: CH-5986
Beamline: ID06-LVP	**Date of experiment**: from: 5/05/21 to: 10/05/21	**Date of report**: 10/09/2021
Shifts: 15	**Local contact(s)**: Dr. Dmitrii Druzhbin	*Received at ESRF:*

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Report:

Aim of the study

The goal of experiment CH-5986 was to explore formation conditions and phase transition behaviour of possible new ternary hydrides in systems A-Si-H (A = Na; Li) at high pressures and temperatures. Recent studies have shown that hydrogenation reactions at 4–10 GPa pressures afford unique hypervalent $[SiH_6]^{2-}$ 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 A-Si-H systems in a large volume press particularly promising.

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-5986 we have aimed to produce ternary hydrides $A_mSi_nH_o$ containing novel hypervalent $Si_nH_o^{m-}$ species by studying reactions AH + Si + H_2 (A = Li, Na) in p,T range of 5 – 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-5986 was performed in advance at DESY and handled entirely in an Ar-filled glovebox due to air and moisture sensitivity of the starting materials. Powders of alkali metal hydrides (LiH, NaH) and silicon were mixed in either 1:1 or 2:1 AH:Si molar ratio and pressed into pellets of ~2 mm OD, 1 mm height. Along with two pellets of ammonia borane hydrogen source (NH_3BH_3) the samples were enclosed into sodium chloride (NaCl) capsules of 3 mm OD, ~3.5 mm height. The amount of NH_3BH_3 per sample corresponded to ≥8 × molar excess of hydrogen 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 being impermeable to hydrogen. Additional advantage of using NaCl is its well-studied equation of state,[8] which aided in estimating pressure and temperature during the experiments from *in situ* PXRD data.

The experiments at ID06-LVP were performed with 14/7 multianvil assemblies. The sample capsules along with two 3 mm OD MgO cylinders were loaded into graphite heaters (4 mm OD, 3mm ID, 8 mm height). The graphite heaters and the two 4 mm OD ZrO_2 outer plugs were then enclosed inside 14 mm OEL Cr-doped MgO octahedra. The passage of the current was ensured by topping the heaters with molybdenum (Mo) foils (4mm OD), which, in turn, were in contact with Mo leads (1 mm OD) inserted into the outer ZrO_2 plugs. The octahedra were then positioned between eight 7 mm TEL gasketed tungsten carbide anvils. 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 the tungsten carbide cubes was insulated with epoxy sheets, apart from the copper foil contacts at the cubes adjacent to the Mo leads.

Samples were brought to target pressure in 5–11 GPa range and heated using Delta Elektronika SM6000 power supply by regulating the power. Angle-dispersive PXRD data (λ=0.23393 Å) were collected continuously during compression, decompression (30-60 sec/pattern) and heating (1 sec/pattern) using a customized DECTRIS PILATUS3 X CdTe 900K-W-ESRF detector placed at an azimuth angle of 270°. 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 (~1.5–15°) 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 14/7 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-5986 a total of 6 experiments were performed: 3 runs were dedicated to each A-Si-H system with both 2:1 and 1:1 AH:Si compositions being examined. Five of the experiments were run successfully, while one terminated in a blowout during heating. Exact reason for the blowout was not clear, but possibly related to a collapse of the X-ray transparent gasket insertion.

In case of Na-Si-H system samples employing 2NaH:1Si molar ratio were first studied at starting pressure of 9 GPa (Fig. 1(a)). Above ~300 °C, when hydrogen release from NH_3BH_3 was expected to be complete, a set of broad, low intensity reflections appeared in PXRD patterns (blue arrows in Fig. 1(a)). The visible peaks were indexed to a hexagonal unit cell, and the parameters could not be matched to any known structure, suggesting a ternary Na-Si-H phase. Upon further heating (>450 °C) these peaks were quickly replaced by a different set of reflections, which were indexed to a tetragonal unit cell with a≈6.54 Å, c≈4.75 Å. Again, no match was found in the available databases, and reflections were assigned to a ternary high temperature, high pressure Na-Si-H phase which was not described previously (further noted as HTHP). Our preliminary data evaluations backed by theoretical calculations strongly suggest that HTHP phase has Na_3SiH_7 stoichiometry and is closely related to K_3SiH_7 structure type.[9] Interestingly, despite prolonged heating and increasing temperature to 700 °C, growth of HTHP phase proceeded very slowly, which was attributed to "inertness" of elemental silicon. On cooling below 100 °C a (possibly) second order transformation of HTHP to a low temperature, high pressure (LTHP) polymorph was observed, manifesting in continuous splitting of the peaks (see Fig. 1(a), upper part). LTHP phase unit cell represents a monoclinic distortion of the tetragonal HTHP structure. Furthermore, on decompression below 4.5 GPa LTHP phase underwent another phase transition to a low pressure (LP) polymorph. Its details were, however, obscured by a simultaneous pressure drop, which likely occurred due to release of unreacted hydrogen from the capsule.

To explore the effect of pressure on the formation kinetics of Na_3SiH_7, 2:1 NaH:Si composition was further tested at 5 GPa. Unlike in the previous run, after reaching 400 °C and keeping the temperature constant for 1 hour no formation of ternary compounds was detected. Afterwards the pressure was increased to ~6.8 GPa while T was still fixed at 400 °C. Remarkably, only a slight pressure change (by ~0.7 GPa) triggered the growth of HTHP-Na_3SiH_7, while no preceding phase was detected. Further observations closely resembled 9 GPa run, including slow formation kinetics of HTHP phase even at T>700 °C as well as continuous transition to monoclinic LTHP polymorph below 100 °C. Transformation of LTHP on decompression occurred once again at ~4.5 GPa and could be followed much better than in the 9 GPa run (details shown in Figure 1 (b)). The arising set of LP phase reflections matches closely those of tetragonal HTHP, however, additional low intensity peaks may suggest superstructuring. Further data analysis and theoretical calculations aimed at revealing observed Na_3SiH_7 structures are ongoing. In addition, the 5 GPa run was repeated using 1:1 NaH:Si starting ratio, and the results described above were reproduced closely.

Li-Si-H system was tested at starting pressures of 9 and 11 GPa. Despite increasing target pressure and heating times up to 5 hours at T reaching 700 °C, no growth of additional phases was conclusively detected for both 1:1 and 2:1 LiH:Si compositions.

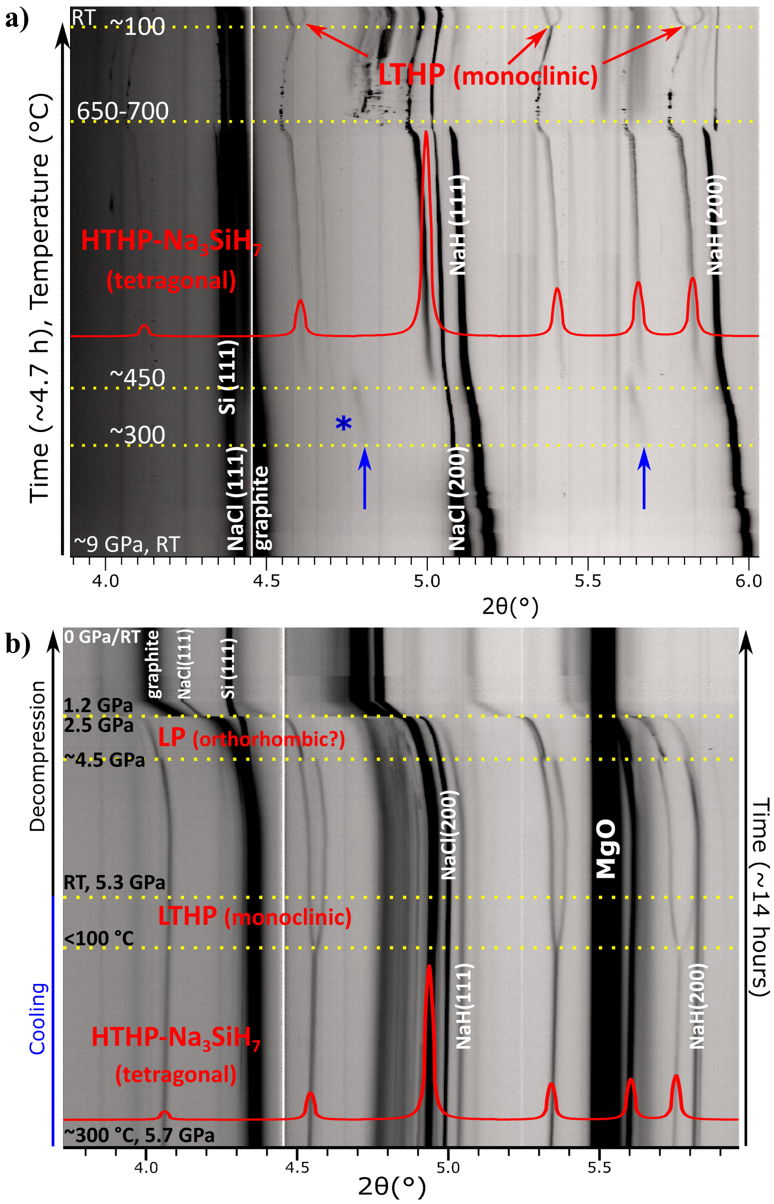

Figure 1. (a) PXRD data collected during CH-5986 at ID06-LVP for Na-Si-H system. Calculated patterns for predicted HTHP-Na_3SiH_7 are shown in red. (a) Formation of HTHP phase and its transition to LTHP during 9 GPa experiment. Blue arrows mark unknown hexagonal precursor phase. (b) Phase transformations of Na_3SiH_7 polymorphs on cooling and decompression during 5 GPa run. Calculated intensities in the overlayed pattern are not matching the observed ones since the latter are affected by texture due to prior melting/recrystallization.

Overall, during CH-5986 we have observed a formation of at least one novel ternary phase in proposed A-Si-H systems (A=Na, Li). We plan to extend studies of these systems using binary A-Si Zintl phases (instead of AH-Si mixtures) as more reactive precursors to unlock other theoretically predicted metastable ternary phases as well as to improve their formation kintetics. Further experiments at ID06-LVP would be extremely beneficial for this project. First publication based on CH-5986 results is currently being prepared.

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