ESRF	**Experiment title:** *High-pressure synthesis of new strategic clathrate(s) in the K-Si system*	**Experiment number:** CH/5431
Beamline: ID06-LVP	**Date of experiment:** from: 06/06/2018 to: 12/06/2018	**Date of report:** 13/09/2023
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Report:

Introduction:

The main scope of this experiment is to develop and optimize the synthesis procedure for new silicon (Si) materials with enhanced properties for applications, in particular photovoltaic. The possibility of engineering physical properties by means of structural modifications has already been demonstrated, in particular some metastable Si allotropes have been predicted to show a direct-bandgap [1-3]. Our previous experiments on Si transformations at high-pressure and high-temperature (HP-HT) have provided the first synthesis of hexagonal Si-4H, which exhibit an enhanced absorption of visible light compared to its cubic counterpart [4].

Here, we focus on the synthesis of binary clathrate precursors at HP-HT. This approach has demonstrated to be very efficient with the recent discovery of a new Na-Si zeolite-like clathrate, $NaSi_6$ [5], that has been successfully employed for soft chemistry synthesis of the new Si_{24} allotrope [6]. Our previous studies at the ESRF [7] have highlighted that the synthesis of $NaSi_6$ precursor occurs in a very narrow region of parameters. This has lead us to adopt a new approach, employing **potassium (K) instead of Na, with the aim of improve the synthesis efficiency**. K should simplify the Metal-Si phase diagram with respect to the strong non-stoichiometry observed in the case of Na-Si rendering thus possible the synthesis of pure clathrate samples.

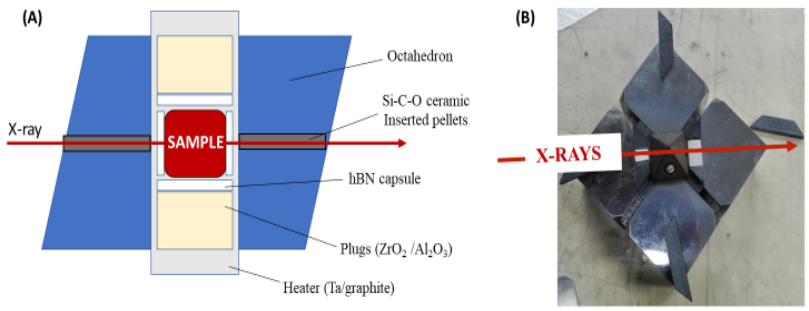


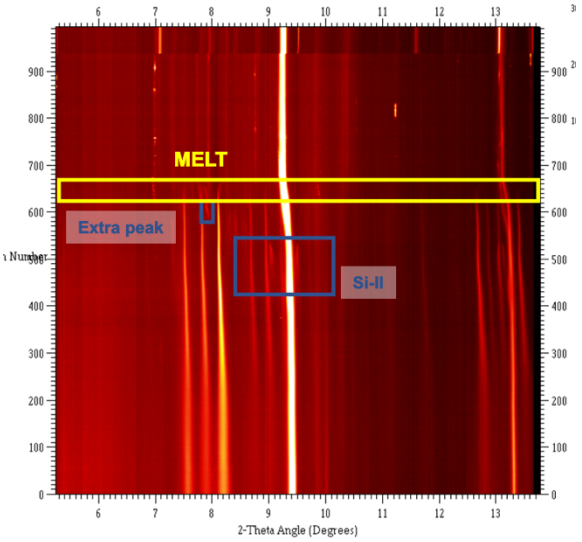
Figure 1: (A) schematic view of the octahedron and the assembly; (B) photo showing the MgO inserts in the gaskets that constitute high-transparency windows for the X-ray beam.

Setup:
We performed systematic studies of HP-HT transformations in the large volume multi-anvil press with angle dispersive diffraction (1-D detector) for fast observation of phase transformations
For our experiments, we employed 32 mm WC second-stage anvils with different octahedron edge length (OEL) to truncation edge length (TEL) ratios. Pressure cells are made of a pyrophyllite octahedron and an assembly composed of a heater (tantalum, Ta), plugs (ZrO_2 or Al_2O_3) and hBN capsule in which sample powder was loaded. Fig. 1 (A) shows a schematic view of the assembly.
In order to collect time-resolved X-ray diffraction patterns, the beam passed between the second-stage anvils; boron epoxy or MgO inserts in the gaskets and amorphous Si-C-O ceramic inserts in the octahedron facilitate the transmission of X-ray because of their low absorption as shown in Fig. 1 (B).

Results:
Table 1 shows for each of the experimetal runs performed: the system studied, assembly main features and the P-T range explored.

Run	Sample	Assembly	P [GPa]	T [K]	Data
---	K+Si	25/17	---	--	Synthesis
1	Si	10/5	10-12	~1200	EOS
2	Si	10/5	11-13	~1050	EOS
3	K-Si	10/5	10-12	~1200	Phase transition
4	K-Si	10/5	12-13	~1100	Phase transition
5	K-Si	10/5	10	blowout	Phase transition

Table 1: main features of the assembly employed during CH/5431 beamtime.



A preliminary run in a large assembly was performed to synthesize a solid K-Si starting material for the following experiments. This approach allowed us to obtain high-quality volumetric data for construction of the phase diagram and equation of state of the K-Si clathrate; in our previous experiment (CH/4896), we had noticed that the formation of K-Si compounds from elemental reactants was affecting the conditions in the assembly, preventing us from reaching the desired points in the P-T space. Two runs were also dedicated to precise EOS measurements of Si alone, data needed to complete the previous work (published in [4], plus Pandolfi et al., *in preparation*). Fig. 2 shows representative data from Run 4 acquired at upon heating at ~12 GPa.

Figure 2: representative *in situ* XRD data obtained at HP-HT: the colormap shows the evolution of the XRD peaks' intensity as a function of time (from bottom to top).

References:

[1] M. Amsler, et al., "Low-density silicon allotropes for photovoltaic applications", *Physical Review B* **92**, 014101 (2015).
[2] I. Lee, et al., "Computational search for direct bandgap silicon crystals", Physical *review B* **90**, 115209 (2014)
[3] Q. Wang, et al., "Direct band gap silicon allotropes", *Journal of the American Chemical Society* **136**, 9826-9829 (2014)
[4] S. Pandolfi et al., "Nature of hexagonal silicon forming via high-pressure synthesis: Nanostructured hexagonal 4H polytype", *Nano Letters* **18** 5989-5995 (2018)
[5] O. O. Kurakevych, et al., "Na-Si clathrates are high-pressure phases: a melt-based route to control stoichiometry and properties", *Crystal Growth & Design* **13**, 303-307 (2013)
[6] D. Y. Kim, et al., "Synthesis of an open-framework allotrope of silicon", *Nature Materials* **14** 169-173 (2015)
[7] Z. Jouini, et al., "Phase boundary between Na-Si clathrates of structures I and II at high pressure and high temperatures.", *Journal of Superhard Materials* **38** (2016)