ESRF	**Experiment title:** ***High-pressure synthesis of new strategic clathrate(s) in the K-Si system***	**Experiment number**: CH/4896
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Introduction

The importance of the search for new forms of silicon (Si) stands also in the incredible opportunities for the future development of technology and industry, as right now further improvement of current devices is strictly limited by diamond Si (d-Si) electronic properties and its indirect bandgap.
The **discovery of new Si allotropes** would not only be a fundamental goal in the study of the incredibly rich Si phase diagram, but it could lead us towards the synthesis of new advanced functional materials suitable for applications. The possibility of engineering physical properties by means of structural modifications has already been proved, in particular some metastable Si allotropes have been predicted to show a direct-bandgap [1-3].
One efficient way to obtain new Si structures is to employ clathrates as precursor for the synthesis of guest-free cage-like Si allotropes. This approach has demonstrated to be very efficient with the recent discovery of a new Na-Si zeolite-like clathrate, $NaSi_6$ [4], that has been successfully employed for soft chemistry synthesis of the new Si_{24} allotrope [5]. The new allotrope has a zeolite structure and a quasi-direct bandgap around 1.3 eV that makes it a very suitable candidate for photovoltaic applications.

The recent discovery of Si_{24} has renewed the interest for Si-based new materials, in particular for the binary Na-Si phase diagram; our previous studies at the ESRF [6] have evidenced 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 for the current study **potassium (K) instead of Si, 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.
In this study, we have observed through angle-dispersive X-ray diffraction phase transformation of K-Si systems in a pressure range 9.5-13 GPa and temperatures 300-1200 K in a large volume multi-anvil press at beamline ID06.

Experimental

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.

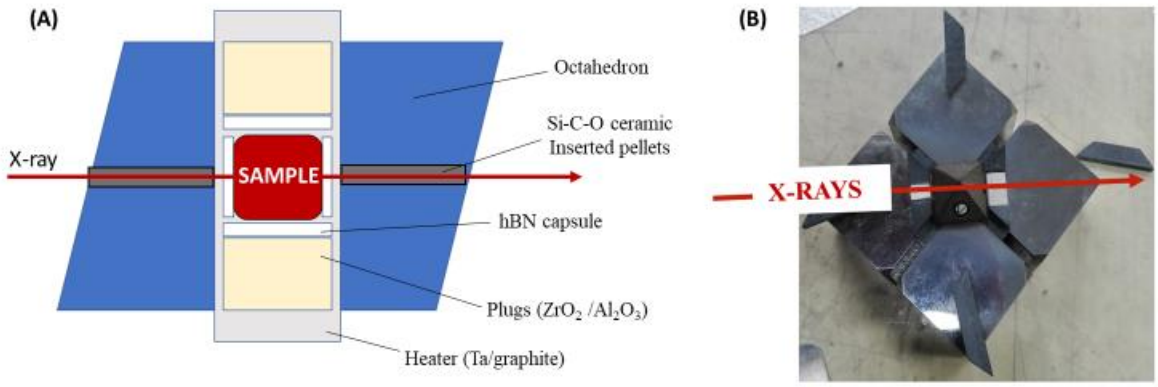

Figure 1: (A) schematic view of the octahedron and the assembly; (B) photo showing the MgO inserts in the gaskets that constitute high-transparency windows for the X-ray beam.

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).

Table 1 shows for each of the 6 K-Si runs performed the system studied and assembly main features.

Sample	Assembly	Gasket inserts	Plugs	Heater
K-Si-1	14/8	MgO	ZrO_2	Ta
K-Si-2	10/5	MgO	ZrO_2	Ta
K-Si-3	10/5	Si-C-O	ZrO_2	Ta
K-Si-4	10/5	B epoxy	ZrO_2	Ta
K-Si-5	10/4	B epoxy	Al_2O_3	Ta
K-Si-6	10/4	MgO (whole gasket)	Al_2O_3	Ta

Table 1: main features of the assembly employed during CH/4896 beamtime.

Results and Discussion

In this section, the main results we obtained will be presented; blowouts (Samples 2-3-5) will be discussed separately at the end of the section

K-Si (1:6) sample:

Successful runs were

- K-Si-1 (14/8 assembly): p_{max}= 9.5 GPa $Power_{max}$= 1100 W

In this run we observed, as shown in Fig. 2, the appearance of a triplet of XRD peaks that correspond to the formation of K-Si clathrate I structure. This kind of compound, so far, has been observed only for Na-Si system, and up to date this is the first evidence of HP-HT clathrate formation in the binary K-Si system.
The clathrate structure is formed at 650 W; the peaks start to appear after a certain time spent at this temperature and remain stable upon increasing temperature up to 1000 W.
This experiment has thus allowed us not only to observe for the first time the clathrate formation, but also to test its stability at this given pressure.

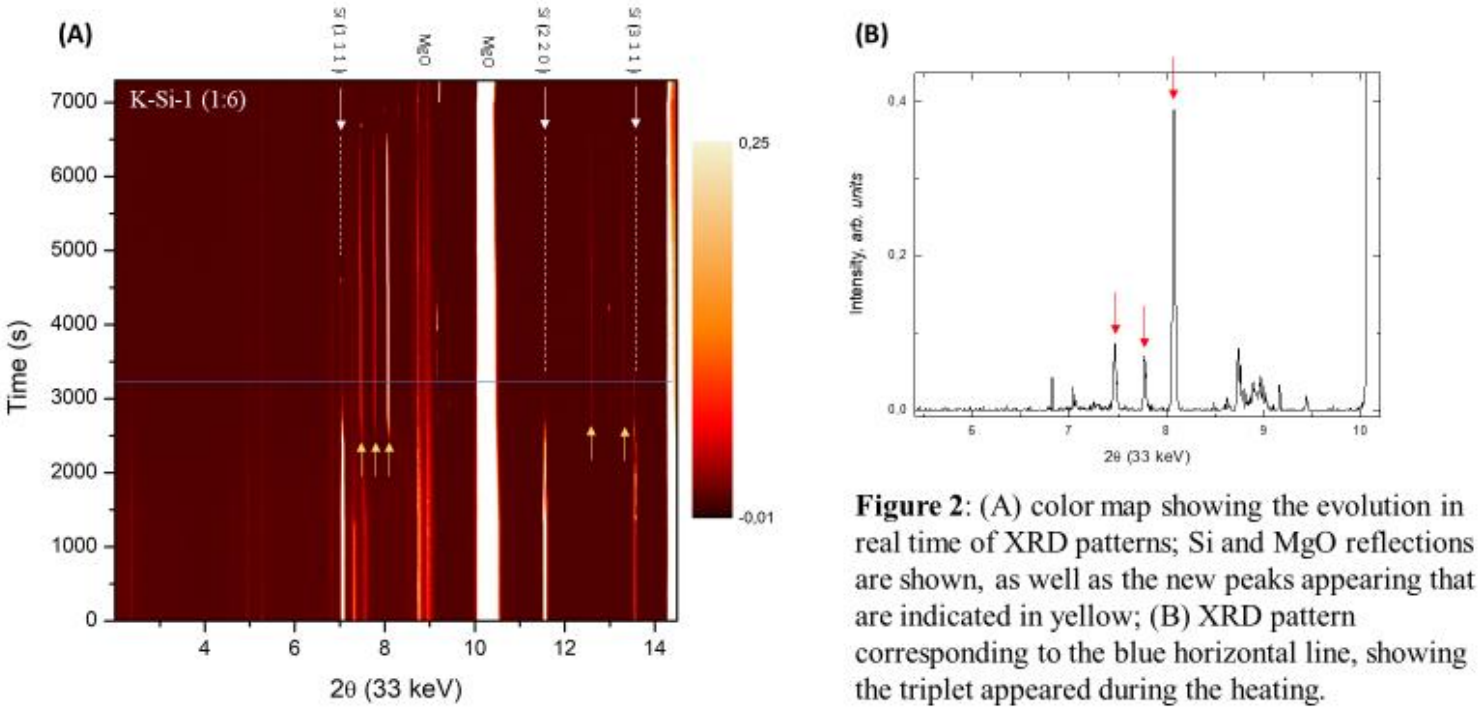

Figure 2: (A) color map showing the evolution in real time of XRD patterns; Si and MgO reflections are shown, as well as the new peaks appearing that are indicated in yellow; (B) XRD pattern corresponding to the blue horizontal line, showing the triplet appeared during the heating.

- K-Si-4 (10/5 assembly): p_{max}= 12.5 GPa $Power_{max}$= 550 V

In this second study we used a smaller assembly, the 10/5, in order to easily get to higher pressure and study the synthesis conditions.
The clathrate peaks appear around 350 W and remain stable up to 450-500 W; after the disappearance of the peaks we have tried to go back to lower temperature, but no recrystallization was observed.

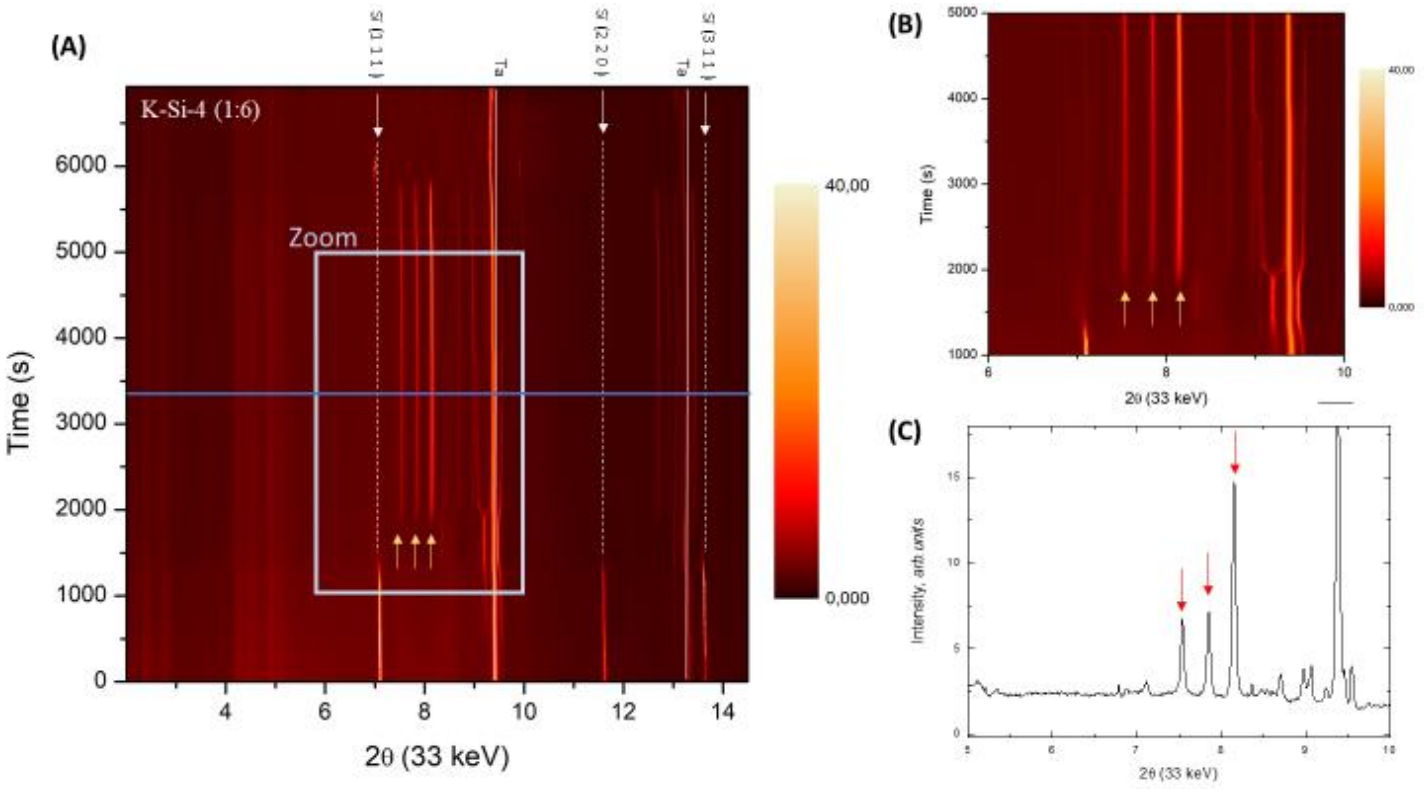

Figure 3: (A) evolution of XRD pattern during the heating performed ad P_{max}; (B) zoom corresponding to the light rectangle, from which it is possible to see the continuous transition of Si-II; (C) XRD pattern corresponding to the blue horizontal line in which we see that the triplet formed around 350 V is compatible with the clathrate I structure and with the one already observed in K-Si-1 run.

In Fig. 3 the evolution of the system during the heating at $p=p_{max}$ is shown; not only we have determined the stability region of clathrate I structure at this pressure, but we have also observed an interesting phase transition that appears to be continuous, visible in the zoom Fig. 2 (B).

A deeper analysis and further investigations, possibly with other *in situ* observations, is surely needed to fully understand these results, and eventually enlarge or correct Si HP-HT phase diagram.
It is also important to notice how in this run the use of B epoxy inserts in the gasket has allowed us to get a clearer picture of the evolution, reducing the peaks of the assembly in the region of interest.

- K-Si-6 (10/4 assembly): p_{max}= 13.5 GPa $Power_{max}$= 400 W

During this run no clathrate peaks was observed during heating; it is possible to conclude that this pressure is too high for clathrate formation, and that we have determined an upper limit for the p-T stability region of these compounds in the K-Si system.

Blowouts:

K-Si 2, K-Si-3 and K-Si-5 ended up with a blowout during compression, always around 120 bars.

For K-Si-2, the problem encountered was thought to be linked with MgO inserts; during compression, a misalignment with respect to the gasket caused their collapse, with a consequent loss of pressure.
During K-Si-3 run, we substituted MgO inserts in the gaskets with Si-C-O ceramics ones. The aim was to obtain a higher transparency and to have cleaner data during collection thanks to the amorphous structure of the ceramic; furthermore, we hoped that the behaviour of the ceramic under pressure would have helped avoiding the pressure blowout seen with MgO in K-Si-2 run.
We observed anyway a blowout during compression around the same load that had caused the MgO inserts collapse. We conclude that the use of Si-C-O ceramic insert is not an advantage in our case because not only it is a more expensive and time-demanding solution, but the inserts cannot guarantee a higher stability.

During K-Si-5 run we were using boron epoxy inserts in the gaskets; this material allows us to have cleaner data because its XRD peaks are very weak.
This time we managed to individuate the real reason of pressure blowouts during compression: the collapse was not caused by the inserts in the gaskets, but rather by the Si-C-O ceramic inserts in the octahedron. These inserts are, in fact, made up of compressed powder pellet that fills a cylindric hole on both sides of the assembly; this kind of elements are more sensible to the applied pressure because, as soon as the holes are not perfectly filled, the cylindric pellets are expelled upon octahedron compression.
We have seen in our last experiments that a careful placement of the ceramic pellets and the eventual use of glue can prevent the pellets expulsion and assure the stability of the pressure cell during experiments, allowing to avoid blowouts (as in the case of K-Si-6, where we maintained good stability at 13.5 GPa).

For future experiments we will use boron epoxy gaskets inserts to guarantee good transparency to X-ray beam and enhance data quality for *in situ* XRD pattern collection. Particular care will be given to both the preparation and the placement of Si-C-O ceramic pellets in the octahedron; glue will be eventually employed to guarantee the stability of the inserts during compression.
We believe that this experimental procedure will allow us to avoid pressure blowouts in future experiments.

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