

In order to *in situ* observe the synthesis of NaSi₆ under high pressures and high temperatures, the mixtures (1) Na+Si, (2) NaSi+Si and (3) Na+Si+Ag have been tested. Mixtures at 4-6.8 GPa (the limit of Paris-Edinburgh, PE, cells) were probed by X-ray diffraction during heating. The sequence of XRD patterns has been obtained at ID27 beamline of ESRF, with *p-T* estimation using the *p-V-T* equations of state of Si and Na.

The formation of NaSi₆ (together with phases stable) has been observed only at the pressure limit accessible by PE cells, together with low-pressure phases, which rendered impossible to accomplish the proposal at ID27, and the large-volume press of ID06 is strongly required. However, at lower pressures a number of interesting observations of high impact has been made.

First, we have established the sequences of phase transformations in silicon clathrates, e.g. at 4 GPa and 15 at% of Na in the Na-Si system the following chemical reactions occur: $\text{Na} + \text{Si} \rightarrow \text{Na}_4\text{Si}_4 + \text{Si} \rightarrow \text{Na}_{24+x}\text{Si}_{136} (\text{sII}) \rightarrow \text{Na}_8\text{Si}_{46} (\text{sI})$.

Moreover, for the first time we have observed the congruent melting of Na_{24+x}Si₁₃₆, the important information for the topology of high-pressure Na-Si phase diagram. *The in situ* probing (combined with previous *ex situ* data) at various *p-T* conditions allowed us to construct the transformations diagram (Figure) in the Na-Si system.

We have also confirmed our principal suggestion as for the Ag-Na-Si system on the absence of stable compounds above 900 K in this ternary system at least up to 6 GPa, which render our main idea on the possibility the single crystal growth of NaSi₆ in the Ag-Na-Si system credible and promising.

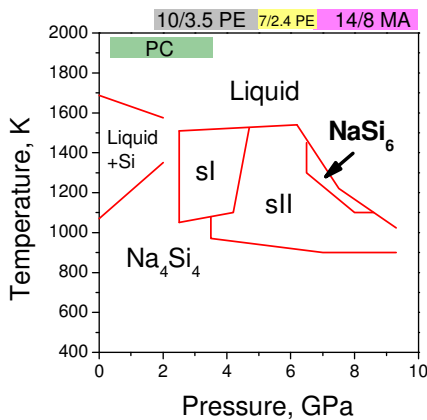


Figure. Transformation diagram in the Na-Si system.