



	Experiment title: Synthesis and investigation of new superhard silicon borides at HPHT	Experiment number: MA-2565
Beamline: ID06-LVP (C05)	Date of experiment: from: 09.06.2015 to: 12.06.2015	Date of report: 18.05.2017
Shifts: 9	Local contact(s): Wilson A. Crichton	<i>Received at ESRF:</i>
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Introduction

Silicon borides (B_3Si , B_4Si , B_6Si , etc.) attract considerable attention due to superior thermal stability, excellent chemical resistance, promising mechanical and electronic properties that offers potential for their use as advanced engineering [1] and smart functional [2] materials. Interest to the B-Si system under high pressure is determined by synthesis of new advanced compounds, e.g. superhard boron-rich solids [3], thermoelectric and superconducting clathrate with B-Si cages [4], etc. Recent *ab initio* simulations using USPEX code have shown the high-pressure stability of new superhard semiconductor $B_{12}Si$ [private communication]. The data on the HP evolution of melting diagram of the B-Si system are also required for growth of single-crystal silicon borides. Thus, systematic experimental study of silicon borides at high pressure (HP) is of outmost importance. The boron-silicon phase diagram at ambient pressure was suggested in 1984 [5]. The diagram is rather complicated and includes a number of peritectic reactions and intermediate phases of different stoichiometries (B_nSi ; $n = 3, 4, 6$, etc.). However, up to now the HP-HT phase relations in the system have not been studied at all. No experimental or theoretical data on compressibility and thermal expansion of B_nSi phases are available in the literature.

In our previous work the solid-state phase transformations and melting of B_6Si and its mixtures with hBN, cBN, C and Ge were systematically studied up to 19 GPa and temperatures up to 2400 K using quenching technique. These experiments revealed low chemical stability of B_6Si in presence of other chemical compounds as well as formation of new unknown phases. B_6Si phase was found to be stable up 4.5GPa and 1800 K during *in situ* HPHT XRD measurements. Also, a few attempts to synthesize a new $B_{12}Si$ phase in *ex situ* experiments were undertaken. However they clearly showed the necessity of *in situ* synchrotron measurements.

In the current study we have tried to observe the silicon melting followed by chemical reaction with elemental boron at pressures above 10 GPa at very high temperatures using a large volume multi-anvil press (MAP) at beamline ID06 and angle-dispersive X-ray diffraction.

Experimental

Fig. 1 presents the schematic view of the 2nd stage of 8 tungsten carbide (WC) anvils and octahedral assembly (with truncation edge length (TEL) to octahedron edge length (OEL) 14/8) that were used in our experiments.

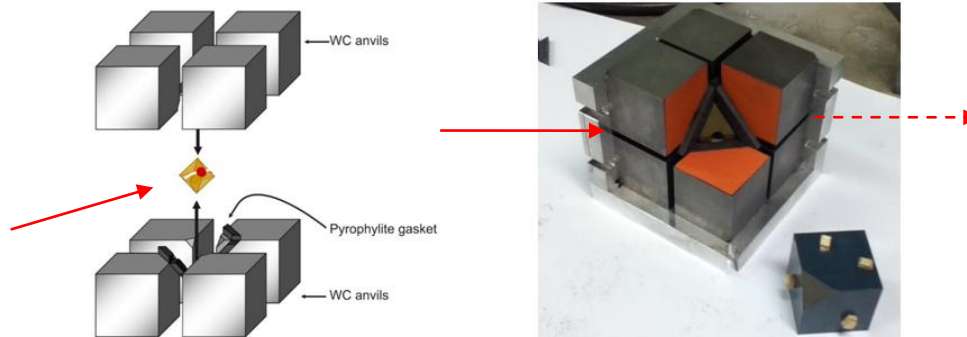


FIG.1. The second stage of the MAP. The direction of X-ray beam is shown by the red arrow.

The synchrotron X-ray beam passed between the anvils as it shown in Fig. 1. Low absorption boron epoxy inserts in the gaskets and highly transparent amorphous Si/B/C/N ceramic [6] inserts in the pressure cell in beam direction were used to achieve high transmission, leading to short acquisition times and an high signal-to-noise ratio of the collected X-ray patterns, without interfering reflections from the sample environment.

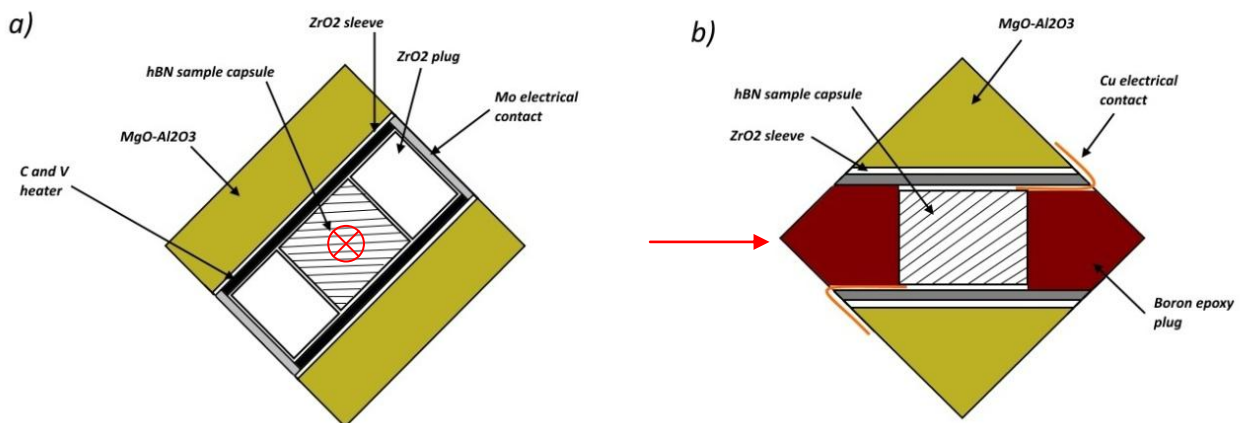


FIG.2. Cell geometries: “vertical” (a) and “horizontal” (b). X-ray beam direction is shown by the red arrow.

Fig. 2 presents two types of pressure cells used in our experiments. Graphite and vanadium furnaces (relatively “transparent” to X-rays) were used in the “vertical” geometry, while LaCrO₃ heater has been used in the “horizontal” one. High-pressure cell parts composed of hBN and MgO served as pressure and/or temperature markers. The mixtures of boron and silicon powders were loaded in hBN capsules.

Three experimental runs have been done:

run01. The sample: 12B : Si; “horizontal” cell geometry; furnace: LaCrO₃; $P_{\max} \sim 4.5$ GPa; $T_{\max}=1510$ K.

run02. The sample: 6B : Si; “vertical” cell geometry; furnace: graphite; $P_{\max} = 4.2$ GPa; $T_{\max}= 1530$ K.

run03. The sample: 12B : Si; “vertical” cell geometry; furnace: vanadium foil; $P_{\max} = 6.3$ GPa; $T_{\max}=2000$ K.

During each run, X-ray patterns were routinely collected every 20 seconds. At specific stages of experiment, patterns with longer exposure times have been recorded. All experiments were terminated by the blowouts. In two of them the blowouts occurred in a few minutes after silicon melting. Decompression was performed at room temperature within 340 min.

Results and Discussion

In Figs. 3-5, X-ray diffraction patterns of 6B:Si and 12B:Si mixtures under compression at room temperature and upon heating at a constant ram load are presented. Use of the low-absorption boron epoxy gaskets and transparent amorphous Si/B/C/N ceramic inserts made possible to reveal the reflections of such weak scatter as elemental boron. The most intense peaks of B, Si, and capsule are marked by the arrows.

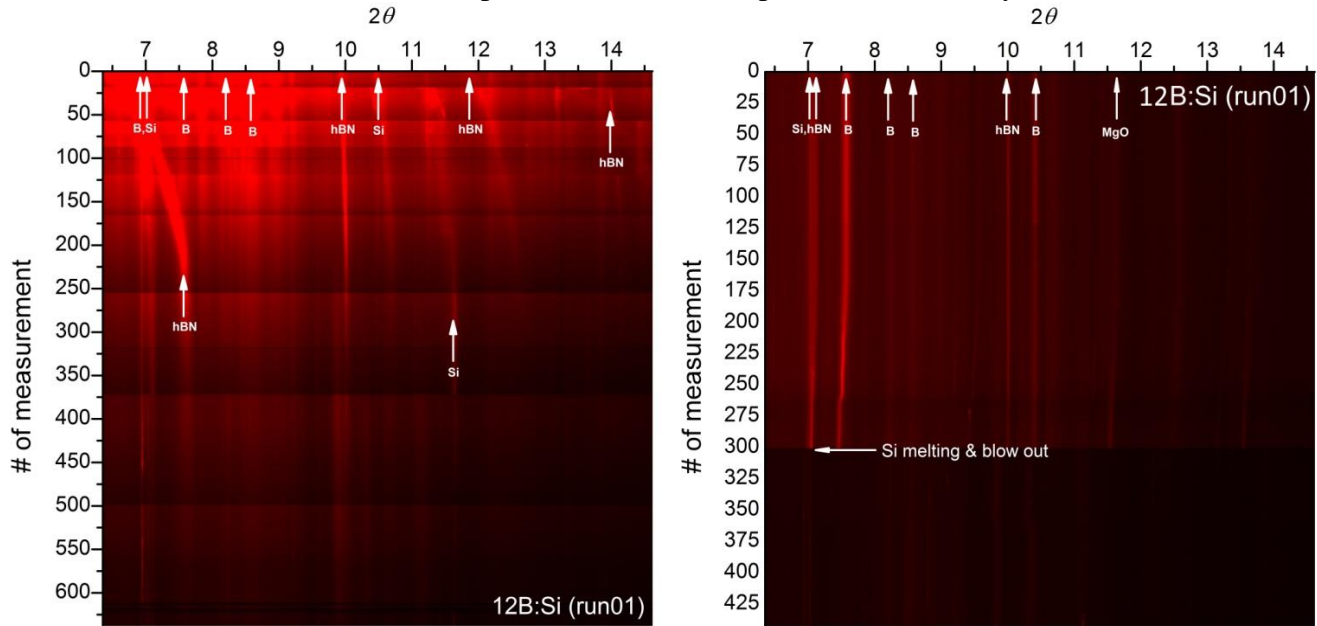


FIG. 3. Sequences of X-ray diffraction patterns taken in run01 during compression (left) and heating (right).

As one can see from Fig. 3, during compression in run01 all diffraction lines monotonously shifted towards higher 2θ angles and general intensity of the patterns significantly decreased under compression. As it was expected, upon heating all diffraction lines shifted towards lower 2θ angle values. No new phase(s) formation has been observed up to silicon melting at 1500 K (Fig. 3, right). Unfortunately, the experiment was interrupted by the blow out right after Si melting. We assume that the possible reason might be the geometry of the “horizontal” assembly: the boron epoxy insert in the gasket placed in front of boron epoxy plugs in octahedron was not properly supported by a WC anvil. Apparently, the leakage of the melted Si from hBN capsule and overheating of the boron epoxy plug and gasket led to the blow out.

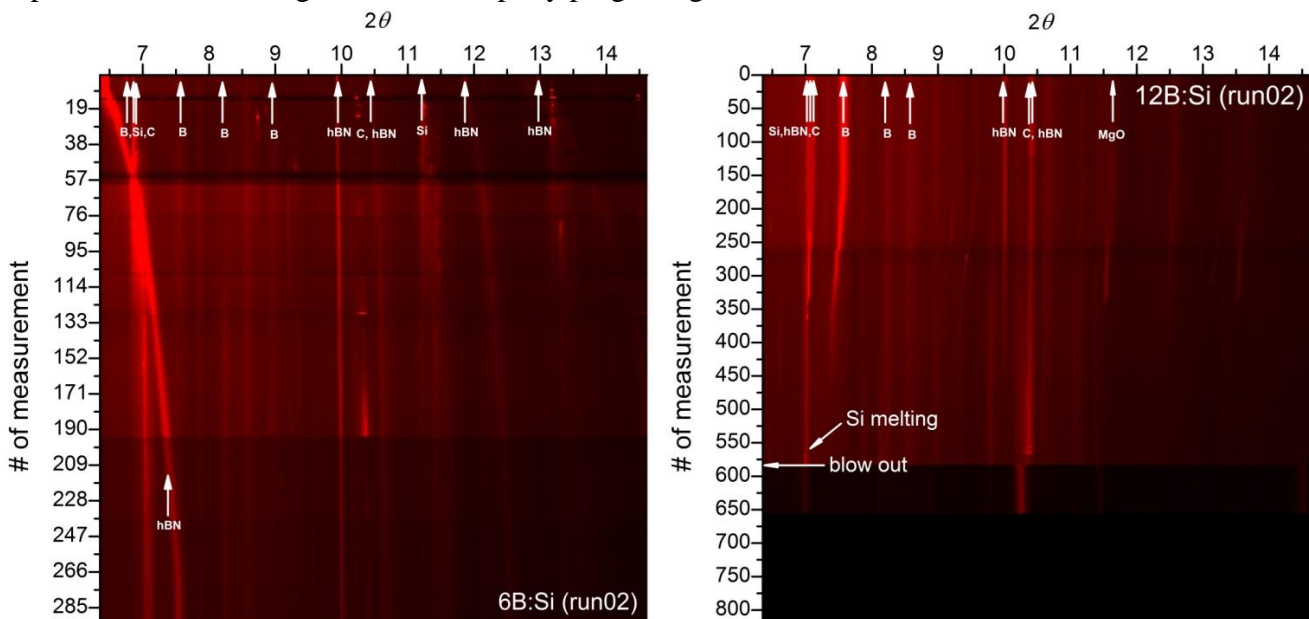


FIG. 4. Sequences of X-ray diffraction patterns taken in run02 during compression (left) and heating (right).

In run02 we refused the “horizontal” design of the cell and employed the classic “vertical” cell with graphite heater. The sequences of X-ray diffraction patterns taken upon compression (Fig. 4) reveals the shift of the

diffraction lines of B, Si, graphite and hBN towards higher 2θ angles. Similar to run01 no new phase(s) appeared up to the Si melting that has resulted in blow out. Based on run01 and run02 we can conclude that at ~ 4 GPa there is no chemical interaction between elemental boron and silicon up to the melting of the latter.

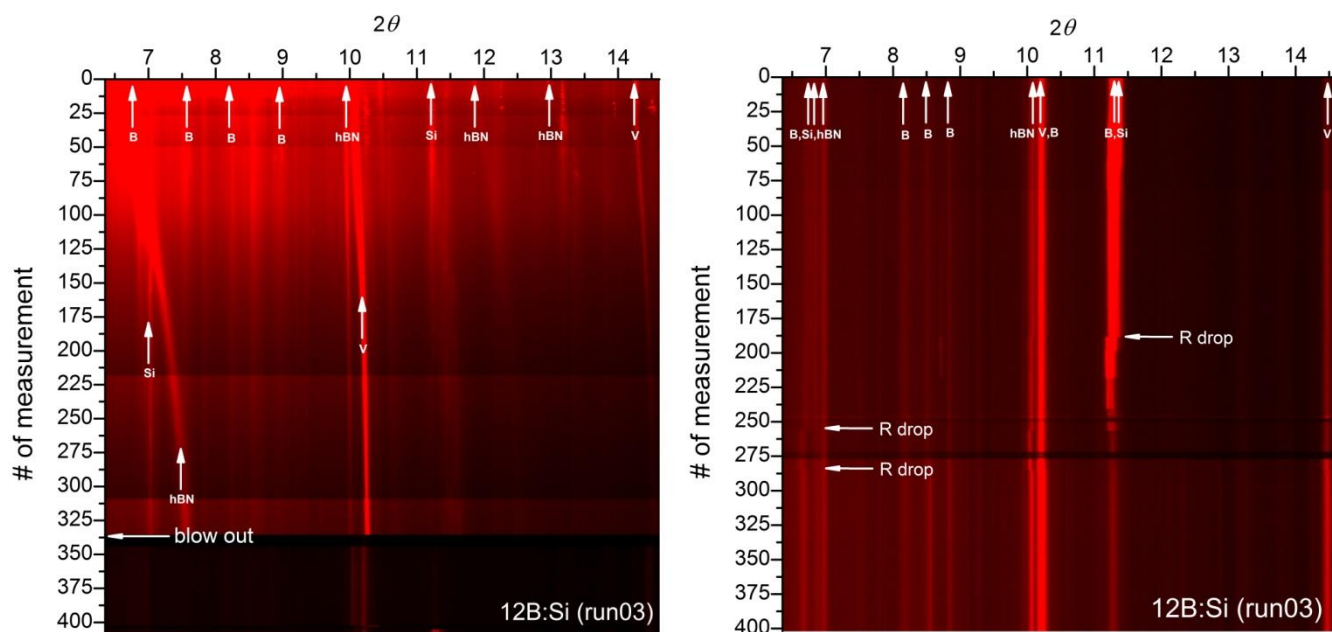


FIG. 5. Sequences of X-ray diffraction patterns taken in run03 during compression (left) and heating (right).

In run03 we used vanadium foil furnace that is relatively “transparent” to X-rays. In Fig. 5 reflections of V, Si, B and hBN can be observed. Again all lines monotonously moved towards higher 2θ values under compression, and in the opposite way under heating. It should be noted that during compression the blow out took place (see Fig. 5), and according to EOS of hBN pressure dropped from 9.4 down to 6.3 GPa. After blow out the cell was realigned, and heating was performed. No chemical interaction between B and Si was observed during heating up to 2000 K. It should be noted that in the last run we used the entire boron-epoxy gasket which allowed us to perform successful heating.

Thus, the absence of chemical interaction between B and Si at pressures to 6 GPa and temperatures to 2000 K in time scale of our experiments has been unambiguously established. Now it is obvious that higher temperatures and/or much longer interaction times are required for high-pressure synthesis of new superhard silicon borides.

- [1] S. Tanaka, N. Fukushima, J. Matsushita, T. Akatsu, K. Niihara, E. Yasuda, *Proc. SPIE* **4234** (2001) 346-354.
- [2] N. Takashima, Y. Azuma, J. Matsushita, *Mater. Res. Soc. Symp. Proc.* **604** (2000) 233-238.
- [3] V.A. Mukhanov, O.O. Kurakevych, V.L. Solozhenko, *J. Superhard Mater.* **32** (2010) 167-176.
- [4] W. Jung, J. Lörincz, R. Ramlau, H. Borrmann, Y. Prots, F. Haarmann, W. Schnelle, U. Burkhardt, M. Baitinger, Y. Grin. *Angew. Chem. Int Edit* **46** (2007) 6725-6728.
- [5] R.W. Olesinski, G.J. Abbaschian, *Bull. Alloy Phase Diagrams* **5** (1984) 478-484.
- [6] H. Baldus, M. Jansen, *Angew. Chem. Int. Ed.* **36** (1997) 329-343.