In situ studies of the Ca$_3$BN$_3$- and Ca$_3$B$_2$N$_4$-formation under HPHT-conditions

S. Schmitz, J. von der Gönna, G. Nover, and C. Lathe

Steinmann Institut Universität Bonn, Poppelsdorfer Schloß, 53115 Bonn, Germany

DESY-HASYLAB in der Helmholtz-Gemeinschaft, Notkestr. 85, 22607 Hamburg, Germany

Cubic boron nitride (cBN) is an important superhard material for technical purposes like grinding, cutting etc.. Its technical fabrication is carried out with the aid of catalysts. Metal-nitride systems like Li$_3$N-BN, Mg$_3$N$_2$-BN and Ca$_3$N$_2$-BN are favoured to reduce the pressure and temperature conditions required for the transformation of the hexagonal modification (hBN) into the cubic one [1]. While transformation conditions and phase relations in the systems Li$_3$N-BN and Mg$_3$N$_2$-BN have been studied under in situ conditions, no such information is available on the system Ca$_3$N$_2$-BN.

We have studied the system Ca$_3$N$_2$-BN with Ca$_3$B$_2$N$_4$ and Ca$_3$BN$_3$ as intermediate phases, where the boron rich Calcium Nitridoborate (Ca$_3$B$_2$N$_4$) is attributed to be the catalytical active phase in the transformation process of hBN/cBN.

In a series of experiments using energy-dispersive-X-ray diffraction technique ($2\theta$=8,12(1)$^\circ$) at the high pressure high temperature multi-anvil device MAX80 (Beamline F2/1 at HASYLAB) the formation of Ca$_3$BN$_3$ and Ca$_3$B$_2$N$_4$ was monitored for the first time under in situ pT-conditions.

The formation of Ca$_3$BN$_3$ was observed at mixing rates of Ca$_3$N$_2$:BN = 1:1 and 2:1 in a temperature range between 600 and 1000°C. Melting of Ca$_3$BN$_3$ starts at temperatures higher than 1225°C ($p = 2.7$ GPa). $\beta$-Ca$_3$B$_2$N$_4$ is evolving from hBN - Ca$_3$N$_2$ mixtures at much lower temperatures, starting from 200°C. At mixing rates of Ca$_3$N$_2$:BN = 1:5 and 1:8 only Ca$_3$B$_2$N$_4$ evolves from hBN and Ca$_3$N$_2$ prior to the formation of cBN (Fig. 1).

Figure 1: Energy-dispersive spectra of a mixture of Ca$_3$N$_2$:BN = 1:5 at 3.9 GPa in the temperature range of 22-1050°C showing the formation of $\beta$-Ca$_3$B$_2$N$_4$
No other phases were found within the pressure range 0.5-6.3 GPa and up to temperatures of 1400°C. From the experimental results there is evidence that \( \text{Ca}_3\text{B}_2\text{N}_4 \) is the catalyst for the hBN/cBN transformation.

In contrast to the systems \( \text{Mg}_3\text{N}_2\)-BN and \( \text{Li}_3\text{N}-\text{BN} \), the hBN-cBN transformation could not be observed \textit{in situ} at a pressure of 6.3 GPa and 1300 °C, but scanning of the quenched sample revealed a narrow region with high yield of cBN. This finding coincides with the results of quenching experiments in a belt type apparatus, where we found an intermediate region of low cBN transformation rates in the pressure range 5.5 – 6.5 GPa at a temperature of 1300 °C.

At a pressure of 3.9 GPa melting of \( \beta-\text{Ca}_3\text{B}_2\text{N}_4 \) starts at 1300 °C with a slight temperature increase of 20-30 °C at a maximum pressure of 6.3 GPa. The low temperature modification \( \text{Ca}_3\text{B}_2\text{N}_4(\alpha-\text{Ca}_3\text{B}_2\text{N}_4) \) proposed by Wörle et.al [2] could not be observed, although it was present in synthesis experiments at standard pressure conditions.

References