

# In-situ synchrotron radiation study of bulk BN nanocomposites during HP/HT conversion at MAX200x using improved pressure cell design

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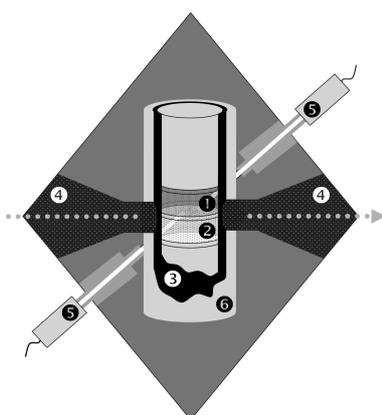
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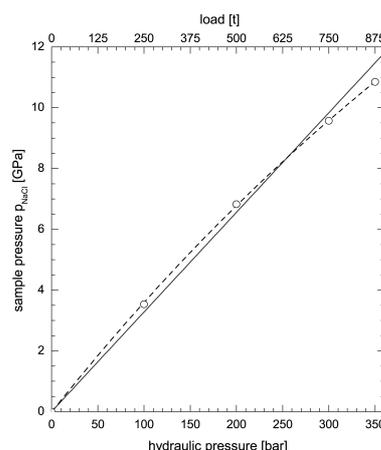
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Formation of superhard boron nitride nanocomposites via high pressure-high temperature (HP/HT) conversion was investigated using *in situ* synchrotron XRD at the MAX200x multianvil press (MAP) of the Geoforschungszentrum Potsdam (beamline W2 (HARWII 2)). Direct conversion of very pure pyrolytic *h*-BN (*p*BN) at HP/HT leads to superhard *c*-BN/*w*-BN/*h*-BN nanocomposites. It has been shown that the required pressure and temperature of the transformation from graphite-like hexagonal *h*-BN to superhard *c*-BN as well as the microstructure of the resulting composites strongly depend on the microstructure of the initial *h*-BN and especially the kind and density of defects [1]. Various types of defects promote the formation of the cubic phase directly from the graphitic modification and suppress the occurrence of the intermediate metastable wurtzitic *w*-BN [2]. The *p*BN contains a high degree of puckering type defects, i.e. stacking faults on basal planes [3].

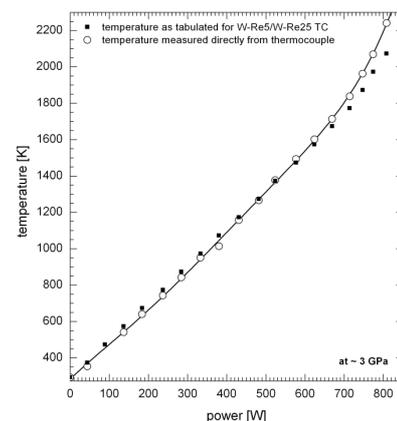
The improved pressure cell assembly is shown in Fig. 1. Graphite could be used as a robust tube-shaped heater material (Fig. 1, pt. 3). However, it had to be perforated in the beam direction in order to avoid the overlap of the diffraction lines  $000l$  from *h*-BN and graphite. The ZrO<sub>2</sub> tube (Fig. 1, pt. 6) used for thermal insulation around the furnace assembly had to be perforated in the same manner [4]. Further, the pressure cell base material MgO is disadvantageous in the beam path in the vicinity of the sample (possible overlap with *c*-BN reflections). Hence, ‘beam guides’ (Fig. 1, pt. 4) with low X-ray scattering and low thermal conductivity to compensate for the perforated ZrO<sub>2</sub> had to be introduced. An amorphous, precursor-derived Si-B-C-N-(O) ceramic [4] with a temperature stability up to 1800°C (at ambient pressure) was tested in several runs and showed a good performance with respect to low scattered intensity and heat loss. A thin Mo foil and a NaCl pellet were used as pressure calibrants (Fig. 1, pt.1) and the temperature near the *p*-BN pellets was recorded using a W-Re3%/W-Re25% thermocouple (Fig. 1, pt 5).



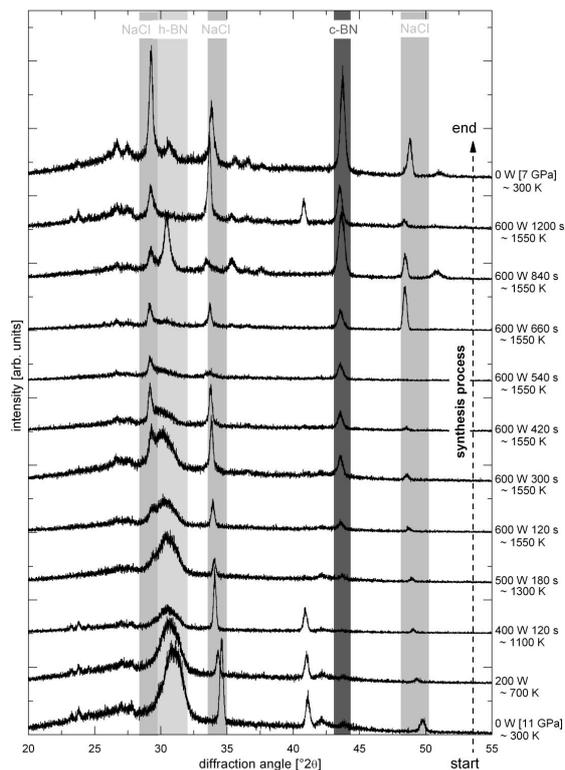
**Fig. 1:** Improved pressure cell, based on a MgO:Cr octahedron of 10 mm edge length. Components are described in the text. The arrow represents the beam.



**Fig. 2:** Pressure calibration curve of MAX200x MAP with the new pressure cell at ambient temperature up to 350 bar hydraulic pressure (~ 875 t).



**Fig. 3:** Heating characteristics for the new pressure cell at 3 GPa (open circles) and the conventional setup, (solid boxes), both recorded with a W-Re3/W-Re26 thermocouple.



**Fig. 4: Diffractograms obtained *in-situ* at beamline W2 (HARWII 2) recalculated in an angular scale ( $\lambda = 0.15418$  nm).**

due to absence of overlap of individual diffraction lines and absorption edges in the selected energy range. According to Fig. 4, the onset of transformation of *p*-BN to cubic boron nitride lies at 11 GPa between 1300 K and 1550 K. Direct conversion is indicated by the absence of *w*-BN which usually forms as an intermediate from highly ordered *h*-BN [2]. The conversion was found to be completed after approximately 10 - 15 min and was maybe retarded by a certain incubation for the activation of the motion of microstructure defects. After conversion, remnants of the *h*-BN were found in the sample, a known phenomenon in direct conversion experiments starting from *h*-BN [2]. A possible explanation is that upon nucleation of *c*-BN and subsequent conversion, the moving *c*-BN/*h*-BN interface pushes and thereby accumulates certain defects at its front until some interfaces meet and the defects are trapped in a small volume of highly distorted *h*-BN, which apparently stabilises its hexagonal graphite-like form.

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## References

- [1] D. Rafaja, V. Klemm, M. Motylenko, M. Schwarz, T. Barsukova, E. Kroke, D. Frost, L. Dubrovinsky, N. Dubrovinskaia, *J. Mater. Res.* 23 (2008) 981
- [2] F.R. Corrigan, F.P. Bundy, *J. Chem. Phys.* 63 (1975) 3811
- [3] J.Y. Huang, H. Yasuda, H. Mori, *J. Am. Ceram. Soc.* 83 (2000) 403; A.V. Kurdyumov, V.F. Britun, I.A. Petrusha, *Diamond Relat. Mater.* 5 (1996) 1229
- [4] K. Leinenweber, T. Mosenfelder, T. Diedrich, E. Soignard, T.G. Sharp, J.A., Tyburczy, Y. Wang, *High Pressure Res.* 26 (2006) 283
- [5] Polyborosilazan, Bayer AG / Belsil PMS MK Powder, Wacker AG
- [6] D.L. Decker, *J. Appl. Phys.* 42 (1971) 3239

The compression and heating characteristics of the assembly are shown in Figs. 2 and 3, respectively. The internal pressure was extracted from the reduction of the interplanar spacing of NaCl upon compression at ambient temperature [6]. The pressure was found to increase nearly linear with the applied load (i.e. hydraulic pressure) (Fig. 2). The electric power vs. temperature relation of the furnace (Fig. 3, open circles & solid line) in the new assembly was measured at 3 GPa. Solid boxes resemble the calibration curve of a conventional pressure cell.

The new pressure cell setup was used to synthesize BN nanocomposites from *p*-BN. The in-situ measurements were performed both during the heating of the sample from  $\sim 300$  K to  $\sim 1550$  K at 11 GPa and in certain time intervals as soon as the desired transformation temperature was reached. A final in-situ measurement was carried out after cooling the sample to  $\sim 300$  K at 7 GPa. The pressure drop (the applied hydraulic pressure was constant at 350 bar, i.e.  $\sim 875$  t over the whole process) can be associated with the reduction in volume during conversion of *h*-BN to *c*-BN, densification of the pressure cell and enhanced gasket flow during heating. The recorded energy dispersive spectra have been recalculated into the angular scale ( $\lambda = 0.15418$  nm) for means of comparison (Fig. 4). The diffraction maxima from individual phases can be distinguished very well using the current setup of the pressure cell