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

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Formation of superhard boron nitride nanocomposites via high pressure-high temperature (HP/HT) conversion was investigated using \textit{in situ} synchrotron XRD at the MAX200x multianvil press (MAP) of the Geoforschungszentrum Potsdam (beamline W2 (HARWII 2)). Direct conversion of very pure pyrolytic \textit{h}-BN (pBN) at HP/HT leads to superhard \textit{c}-BN/\textit{w}-BN/\textit{h}-BN nanocomposites. It has been shown that the required pressure and temperature of the transformation from graphite-like hexagonal \textit{h}-BN to superhard \textit{c}-BN as well as the microstructure of the resulting composites strongly depend on the microstructure of the initial \textit{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 \textit{w}-BN [2]. The \textit{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 000\textit{l} from \textit{h}-BN and graphite. The \textit{ZrO}_2 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 \textit{c}-BN reflections). Hence, ‘beam guides’ (Fig. 1, pt. 4) with low X-ray scattering and low thermal conductivity to compensate for the perforated \textit{ZrO}_2 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 calibrats (Fig. 1, pt.1) and the temperature near the \textit{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.](image)

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

![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.](image)
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 pBN. The in-situ measurements were performed both during the heating of the sample from \(\sim 300 \text{ K}\) to \(\sim 1550 \text{ K}\) 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 \(\sim 300 \text{ K}\) at 7 GPa. The pressure drop (the applied hydraulic pressure was constant at 350 bar, i.e. \(\sim 875 \text{ t}\) 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 \((\lambda = 0.15418 \text{ nm})\) 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 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