



# High-temperature stability of microstructure defects in graphitic boron nitride subjected to the field assisted sintering



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## ABSTRACT

Graphitic boron nitride is extremely relevant material for technical and technological applications. It is mainly used as high-temperature isolator and chemically inert material. However, its properties are strongly affected by the presence and stability of microstructure defects. In this study, the amount of microstructure defects in the graphitic boron nitride was manipulated by annealing turbostratic and pyrolytic BN up to 2573 K. For annealing, the field-assisted sintering technique was employed. The X-ray diffraction analysis confirmed that the turbostratic disorder and basal plane corrugations are the dominant microstructure defects, which are complemented by the stacking faults and dislocations. In the as-received samples, the kind of the dominant microstructure defects was found to depend on the concentration of chemical impurities like oxygen and hydrogen. After the thermal treatment, the basal plane corrugations remained stable to much higher temperatures than the turbostratic disorder. Large basal plane corrugations impeded the thermal-activated grain growth.

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## 1. Introduction

The hexagonal boron nitride with the graphite-like crystal structure (h-BN) is widely applied for different high-temperature applications [1], which make use of its high temperature resistance and chemical inertness, e.g., against many metallic liquids. Another important application of h-BN is its use as precursor for high pressure and high temperature (HP/HT) conversion to superhard cubic boron nitride.

Virgin h-BN is known to contain a large variety of microstructure defects [2,3], which are formed during the fabrication process [4,5] or during the mechanical loading [6]. Together with foreign phases, these microstructure defects were identified to have a significant impact on the electrical and dielectric properties [7,8] and on the HP/HT conversion process [9,10]. In the HP/HT conversion process, a high density of turbostratic faults or a high extent of basal plane corrugations in h-BN favour the formation of c-BN directly from h-BN, while a nearly defect-free h-BN transforms first into wurtzitic BN (w-BN) under otherwise identical conditions. Consequently, BN nanocomposites with tailored phase composition [9] can be produced if the phase formation during the HP/HT conversion process

can be controlled via microstructure defects in the h-BN precursor. Similarly, the electrical conductivity and the dielectric properties of h-BN can be adjusted via systematic manipulation of the microstructure defects during a field-assisted sintering process as illustrated by Steinborn et al. in Refs. [7,8], respectively.

Individual microstructure defects in h-BN are typically related to the specific production process. Hot-pressed h-BN is known to contain much less microstructure defects than the h-BN produced in a chemical vapour deposition (CVD) process [2]. The microstructure of the CVD h-BN is mostly affected by the temperature of the CVD process. Especially the low-temperature CVD process ( $T \leq 1173$  K) yields h-BN with turbostratic disorder [4,5]. A higher temperature during the CVD process [11] reduces turbostratic disorder but increases the propensity to form basal plane corrugations in pyrolytic BN [2]. The high-temperature densification of the h-BN powders via hot pressing or field-assisted sintering technique (FAST) modifies the defect structure of the starting powders, which can be seen immediately on the growth of the h-BN grains [7]. However, the effect of the high-temperature treatment of h-BN on the annealing of the crystal structure defects was not investigated in detail yet.

In this study, the high-temperature stability of the microstructure defects (mainly turbostratic disorder and basal plane corrugations) in h-BN subjected to FAST was investigated. The microstructure defects in h-BN were identified and quantified by

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analysing the anisotropic (*hkl*-dependent) broadening of all accessible X-ray diffraction lines and the shape of the diffraction lines 00*l* from the basal planes as described in [2] and [10]. The presence of the individual microstructure defects is related to the incorporation of chemical impurities like oxygen and hydrogen into h-BN. The foreign elements are located between basal planes [12], at the rim of h-BN sheets, where they compensate non-saturated bonds [5], and/or they form additional phases.

## 2. Experimental details

Graphitic boron nitride containing mainly turbostratic defects (tBN) was supplied in powder form by 3M Technical Ceramics (Kempton, Germany). This powder had a large surface area (50 m<sup>2</sup>/g) and relatively high oxygen content [7]. Pyrolytic h-BN (pBN) produced by CVD was available in form of 2 mm thick sheets, which were cut off from melt crucibles (Morgan Advanced Materials). The chemical composition of the samples and in particular the oxygen and hydrogen contents before and after the FAST treatment were analysed by the carrier hot gas extraction method (CHGE) using a LECO ONH836 analyser.

All samples were heat-treated by FAST by using the HP 25/2 and HHP D25 devices from FCT Systeme GmbH (Rauenstein, Germany). The FAST runs covered the temperature range between 1773 K and 2573 K; the desired temperature was held for 15 min. Longer dwelling times (60 min) did not lead to any further modification of the microstructure defects. In order to examine the effect of the applied pressure on the annihilation of the microstructure defects in powder material, tBN was FAST treated at 16, 25 and 50 MPa. Compact pBN was annealed at 50 MPa. The heat-treatment was carried out in graphite die in inert atmosphere in order to avoid additional oxidation of the samples during the thermal treatment. The heat-treated samples had the diameter of 20 mm and the height of approximately 2 mm. The rims of the samples, which were in contact with the graphite die, were removed prior to further analyses.

The microstructure of the samples was analysed by using scanning electron microscopy (SEM) and X-ray diffraction (XRD). SEM revealed primarily the size and shape of the h-BN grains, XRD the kind and density of the microstructure defects in h-BN and the phase composition of the samples. SEM was carried out with the scanning electron microscope NVision40 (Carl Zeiss SMT GmbH) that was equipped with a field emission cathode. The XRD patterns were recorded in symmetrical Bragg–Brentano geometry using a Seifert FPM URD6 diffractometer, which was equipped with a sealed X-ray tube with Cu anode operated at 40 kV and 30 mA and a secondary graphite monochromator. The diffraction patterns were measured in the range of the diffraction angles between 20° and 150°. The instrumental broadening of the X-ray diffraction lines was determined with the aid of the LaB<sub>6</sub> standard purchased from the National Institute of Standards and Technology (NIST, USA).

## 3. Results

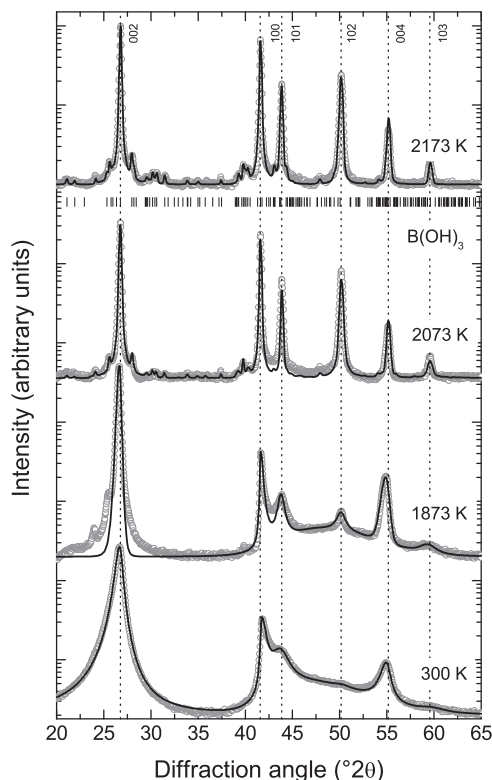
### 3.1. Chemical and phase analysis

The concentrations of impurities in tBN and pBN, which were determined using CHGE in the starting materials and for tBN also after sintering, are summarised in Table 1. Turbostratic BN contains significant amounts of oxygen and hydrogen as expected. Brožek and Hubáček [5] have shown that these elements are able to saturate dangling bonds at the rim of tBN crystallites by attaching the hydroxyl groups. The analysed [O]/[H] ratio, which is nearly 1:1 (Table 1), verifies the validity of this model also for tBN. The oxygen content in tBN did not change significantly after the FAST sintering

**Table 1**

Content of oxygen and hydrogen in tBN and pBN as determined by using carrier hot gas extraction.

	Sample	Oxygen [at%]	Hydrogen [at%]
tBN	Starting powder	4.9 ± 0.1	5.4 ± 0.1
tBN	After FAST (T = 2073 K)	6.4 ± 0.1	6.1 ± 0.1
pBN	Starting powder	< detection limit (0.01)	0.10 ± 0.05



**Fig. 1.** Low-angle segments of the XRD patterns measured in starting tBN and tBN after the thermal treatment. Open circles represent measured data, the solid lines the fits using the Pearson VII functions (in starting tBN and in tBN annealed at 1873 K) and the result of the Rietveld refinement (2073 K and 2173 K). The positions of the diffraction lines from h-BN are marked by vertical dashed lines; the corresponding diffraction indices are displayed at the top of the figure. The positions of the diffraction lines from triclinic B(OH)<sub>3</sub> are labelled by the short bars, which are located below the uppermost diffraction pattern.

(Table 1), which is in agreement with earlier results [7]. Also the [O]/[H] ratio remained nearly 1:1 also after the FAST sintering.

In heat-treated tBN, XRD (Fig. 1) detected triclinic B(OH)<sub>3</sub> as an additional crystalline phase. The amount of crystalline B(OH)<sub>3</sub> estimated by using the Rietveld method [13] in the samples annealed at 2073 K and 2173 K was approximately 2 wt%. This amount corresponds to approximately 0.8 mol% B(OH)<sub>3</sub> in the annealed composite. If all oxygen and hydrogen atoms analysed by CHGE in tBN (Table 1) would react to B(OH)<sub>3</sub> during the poly-condensation reaction [5] upon the thermal treatment, the amount of B(OH)<sub>3</sub> would reach 1.6 mol%. Usually, boric acid and also B<sub>2</sub>O<sub>3</sub> are present in amorphous state, as they form during the hydrolysis of boron nitride. In both, as received and annealed pBN, no measurable amount of crystalline B(OH)<sub>3</sub> was found by XRD. This finding is consistent with the results of chemical analysis in this sample, which revealed the oxygen content below the detection limit of CHGE (0.01 at%) and a very low hydrogen content.

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