



# EFFECT OF MOISTURE ON THE BORON NITRIDE FORMATION FROM ELEMENTS IN A XENON HIGH FLUX OPTICAL FURNACE

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The results of direct synthesis of boron nitride from boron powders of mean sizes of 0.05, 0.20, and 2.00  $\mu\text{m}$  in nitrogen flow with impurity of  $\text{H}_2\text{O}$  in a xenon high-flux optical furnace are presented. Formation of equiaxed, plate-like powders and film-like structures of different sizes was observed. The presence of moisture contributes to the formation of large film-like structures in BN powders from nanosized boron. Carbon impurity in boron powder of mean size of 0.20  $\mu\text{m}$  facilitates formation equiaxed nanosized powders of the smallest mean size. High-temperature gradients in a xenon high-flux optical furnace results in the appearance of vibrations of w-BN at  $1097\text{--}1107\text{ cm}^{-1}$  in the FTIR spectra besides the h-BN vibrations of BN powders produced. The presence of moisture in nitrogen flow promotes formation of new BN structures and other compounds as well. Vibrations belong to B-O-H bonds ( $1184\text{--}1193\text{ cm}^{-1}$ ), N-B-O and B-O-B linkages ( $1107\text{--}924$  and  $\sim 700\text{ cm}^{-1}$ , respectively), and tetrahedral  $\text{BO}_4$  units in  $\text{B}_2\text{O}_3$  could be detected in the FT-IR spectra of BN powders produced and XRD studies confirmed that the produced BN powders contains significant amount of sassolite ( $\text{H}_3\text{BO}_3$ , boric acid) as well.

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For boron nitride synthesis, various approaches have been investigated and significant achievements have been obtained in terms of quantity, structure quality and variety. The processes used for formation and growth of nanostructured BN materials should be divided on high-temperature ( $\geq 2000\text{ }^\circ\text{C}$ , arc discharge, plasma-based techniques and laser ablation)<sup>2</sup> and low-temperature ( $\leq 1500\text{ }^\circ\text{C}$ , carbothermal reduction, high-pressure techniques, template-assisted processes, ball milling and CVD) methods.<sup>12-23</sup> All high-temperature methods involve a surface vaporization in a reducing or inert atmosphere and condensing the resulting vapour with high temperature gradient. The difference in various processes is the method used for the vaporization, and of the promising way is using the so-called xenon high flux optical furnace method. Since this method has a number of advantages, e.g. versatility, rapid heating and cooling rates, ability to adjust temperature profile along each axes, high operating temperature and environmental adaptability, evaporating elemental boron in an  $\text{N}_2$  atmosphere,<sup>24-27</sup> especially in a moisture containing  $\text{N}_2$  atmosphere using xenon high-flux optical furnace is an interesting task.

## Introduction

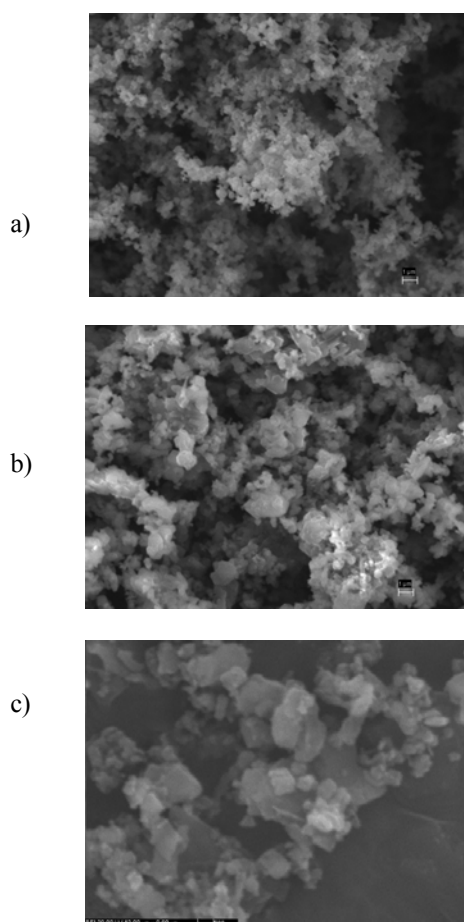
Since boron nitride is known to possess a similar layer-structure and almost identical cell dimensions to that of graphite,<sup>1</sup> studies on BN have been of great interest due to discovery of isoelectronic carbon-related nanostructures, such as nanotubes, nanofibers, graphene, etc. Boron nitride nanotubes (BNNTs), nanowires, nanoribbons, nanofibers, nanorods,<sup>2-6</sup> and 0D nested and single-layered octahedral BN fullerenes were successfully synthesized.<sup>7-8</sup> Freestanding 2D BN flakes, which were peeled off from a BN crystal were also synthesized,<sup>9</sup> however, so-called BN nanomeshes on metallic substrates had been reported only a year earlier.<sup>10</sup>

Based on similarities between isoelectronic C and BN materials, many research efforts have been directed to B-N nanostructures. We focus on the properties of nanostructured BN, in order to obtain further insight into the relationship between the structures and properties of carbon-related materials.

Bulk h-BN has been a matter of interest for a long time due to its low density, high thermal conductivity, electrical insulation, excellent inertness (i.e., passivity to reactions with acids, alkalis, and melts), and low friction coefficient.<sup>2</sup> BNNTs and nanosheets, as inheritors of h-BN, also possess these advantageous properties.<sup>11</sup>

## Experimental

Heating of initial boron powders has been performed in a xenon high-flux optical furnace in nitrogen flow. A small amount of moisture was available in  $\text{N}_2$ . A compacted sample of initial boron powder (diameter 8 mm and height 5 mm) was placed on the surface of a compacted h-boron nitride sample which was stacked on a copper water-cooling screen of a quartz chamber. The chamber was positioned in the centre of a focal zone of three xenon emitters. Synthesis of BN was carried out at the low density of energy in focal zone of set-up  $\sim 0.7 \cdot 10^4\text{ kW m}^{-2}$ . Time of the experiment was 30 min. Temperature was varied between  $1400\text{--}1700\text{ }^\circ\text{C}$ . Produced BN powders were deposited on the water cooled copper screens and partly on the surface of the quartz chamber.



**Figure 1.** SEM images of initial boron powders of mean sizes: a – 0.05  $\mu\text{m}$ , b – 0.20  $\mu\text{m}$  and c – 2.00  $\mu\text{m}$ .

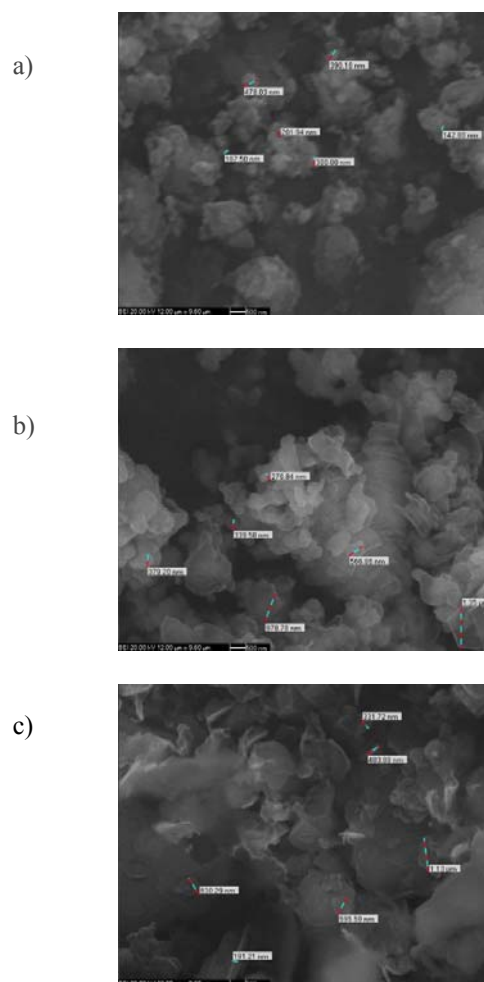
Initial boron materials and the produced BN powders were examined by scanning electron microscopy (SEM) and powder X-ray diffraction (XRD), with using microscopy “Superprobe 733” (“JEOL”, Japan) and a DRON-3.0 type ( $\text{CuK}\alpha$  radiation) diffractometer, respectively. Fourier Transform Infrared (FTIR) absorption spectra were recorded by Nicolet 6700 – FT-IR Fourier Spectrometer (Thermo Scientific).

Three boron (B) powders with different grain sizes of 0.05  $\mu\text{m}$ , 0.20  $\mu\text{m}$ , and 2.00  $\mu\text{m}$  (Fig. 1 and Supplementary material) were used as starting materials. The commercial boron with negligible content of  $\beta$ -rhombohedral phase, the boron powder with a mean grain size of 0.20  $\mu\text{m}$  contains  $\beta$ -tetragonal boron phase due to stabilization effect of the tetragonal  $\alpha\text{-B}_{49.94}\text{C}_{1.82}$  impurity, and the boron powder with mean grain size of 2.00  $\mu\text{m}$  is a  $\beta$ -rhombohedral boron with negligible quantity of the amorphous boron phase.

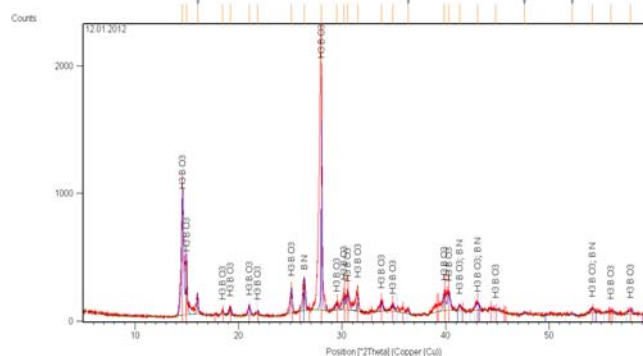
## Results and discussion

Previous investigations unambiguously demonstrated that the structure and the properties of BN powders produced in a xenon high-flux optical furnace strongly depends on the synthesis conditions.<sup>28</sup> Direct synthesis of BN using initial boron powders with mean sizes of 0.05  $\mu\text{m}$ , 0.20  $\mu\text{m}$ , and

2.00  $\mu\text{m}$  (Fig. 1) in flow of nitrogen containing  $\text{H}_2\text{O}$  as impurity resulted a plate-like, equiaxed and film-like structures of different sizes (Fig. 2). Boron powders of mean size of 0.05  $\mu\text{m}$  and 2.00  $\mu\text{m}$  formed a mostly plate-like BN with 0.50, 0.50, and 0.60  $\mu\text{m}$  (Fig. 2a, 2c) mean sizes, respectively. However, the most active boron powder with 0.05  $\mu\text{m}$  mean size stimulates a film-like structure formation about 4.00  $\mu\text{m}^2$  area as well (Fig. 2a).



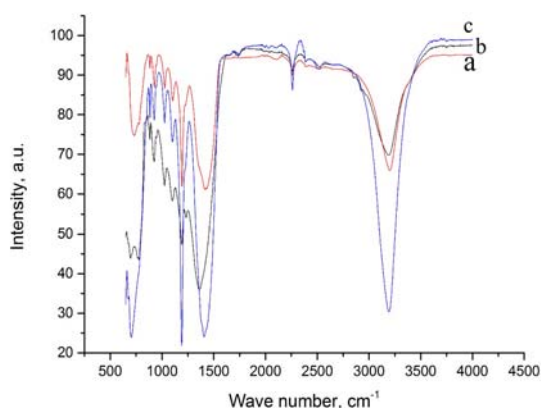
**Figure 2.** SEM images of BN, produced from initial boron powders of mean sizes: a – 0.05  $\mu\text{m}$ , b – 0.20  $\mu\text{m}$  and c – 2.00  $\mu\text{m}$  in the presence of  $\text{H}_2\text{O}$  impurity in nitrogen.



**Figure 3.** Phase composition of BN powder produced from boron of mean sizes of 0.05  $\mu\text{m}$  in presence of  $\text{H}_2\text{O}$ .

The presence of carbon impurity in boron powder with mean size of 0.20  $\mu\text{m}$  resulted an equiaxed nanosize powder formation with the smallest mean size of 0.30  $\mu\text{m}$ . XRD study of BN samples produced from boron powder of mean size 0.05  $\mu\text{m}$  confirmed formation of a powder which main components were sassolite ( $\text{H}_3\text{BO}_3$ , boric acid, 76%) and BN (33 %) (Fig. 3).

There are important differences between FTIR spectra of the commercially available nanostructured h-BN (Chempur, CH070802) and nanostructured BN powders produced by us in the xenon high-flux optical furnace in flow of nitrogen (Fig. 4). FTIR spectrum of commercially available h-BN consists only two bands located at 805 and 1381  $\text{cm}^{-1}$  which belong to the out-of-plane B-N (TO model of the  $\text{sp}^2$ -bonded h-BN) and B-N-B in-plane vibrations, respectively.<sup>25</sup>



**Figure 4.** FTIR spectra of BN powders produced from initial boron powders of mean sizes: a – 0.05  $\mu\text{m}$ , b – 0.20  $\mu\text{m}$  and c – 2.00  $\mu\text{m}$  in the presence of  $\text{H}_2\text{O}$  impurity in nitrogen.

FTIR results suggest that mostly  $\text{sp}^2$  hybridized BN is formed from elementary boron and  $\text{N}_2$  in the xenon high-flux optical furnace. The peaks of BN produced from boron powder with mean size of 2.00  $\mu\text{m}$  observed at 1361  $\text{cm}^{-1}$  and 781  $\text{cm}^{-1}$  could be attributed to the strong in-plane stretching and weak out-of-plane bending vibrations of  $\text{sp}^2$  hybridized BN. The typical feature of the presence of  $\text{sp}^3$  hybridized BN, the B-N-B bending vibration was reported to be at 1050  $\text{cm}^{-1}$ .<sup>29</sup>

The peaks at 1097-1104  $\text{cm}^{-1}$  are shifted in the case of BN samples produced in the presence of  $\text{H}_2\text{O}$  impurity in the nitrogen flow. It is a typical feature for the samples prepared from all three initial boron powders and suggests formation of hexagonal BN (wurtzite BN, w-BN).<sup>29</sup> The very strong O-H (N-H) stretching bands at 3184-3197  $\text{cm}^{-1}$  and the combination bands of  $\text{H}_3\text{BO}_3$  at 2510-2517  $\text{cm}^{-1}$  ( $\square_{17} + \square_{18}$  and  $\square_{21} + \square_{18}$ ) for all produced BN powders can be attributed to the presence of  $\text{H}_3\text{BO}_3$  and its ammonium salts.<sup>30-32</sup> Some similar features of the IR spectra could be observed in the case of hydrolyzed BN powders.<sup>30</sup> The absorption peaks found at 1097-1107, 1020-1024, 916-922, and 677-694  $\text{cm}^{-1}$  were assigned to the ammonium derivatives of boric acid.<sup>30,31</sup>

This tentative explanation of peaks, however, is not completely consistent with our findings. First of all, the boric acid is a very weak acid and its ammonium salts might not be stable enough. Based on previous experiences,<sup>25-28</sup> however, during the synthesis of BN powders in the xenon high-flux optical furnace in flow of nitrogen there was no ammonia smell and XRD of the samples does not show the presence of other crystalline phases as BN and  $\text{H}_3\text{BO}_3$ . Therefore, the complete hydrolysis with ammonia formation seems to be improbable, and the bands centered at 1107–924  $\text{cm}^{-1}$  for all produced powders may be assigned to N-B-O stretching regions,<sup>33</sup> the vibrations at 881-887  $\text{cm}^{-1}$  may correspond to the stretching vibrations of tetrahedral  $\text{BO}_4$  units in  $\text{B}_2\text{O}_3$ ,<sup>33</sup> and the bands in the region around 700  $\text{cm}^{-1}$  belong due to the bending vibrations of the B-O-B linkages<sup>34-35</sup> of the amorphous intermediates contains hydrogen as well.

## Conclusion

Synthesis of BN in a xenon high-flux optical furnace has a number of positive features and benefits. High-temperature gradients in a xenon high-flux optical furnace promote formation of w-BN in all produced powders besides of the h-BN. Using initial boron powders with mean sizes of 0.05  $\mu\text{m}$ , 0.20  $\mu\text{m}$ , and 2.00  $\mu\text{m}$  stimulates formation of equiaxed, plate-like powders or film-like structures of different sizes depending on initial powders.

In the presence of moisture in the nitrogen flow during the BN synthesis resulted appearance of the vibration bands belonging to the N-B-O, B-O-B, N-H, and OH bonds and contributes to the formation of large film-like structures. Carbon impurity in boron powder with mean size of 0.20  $\mu\text{m}$  promotes formation of equiaxed nanosized BN powders. According to XRD, the produced powders mainly composed of sassolite  $\text{H}_3\text{BO}_3$  (boric acid) and BN.

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