



# GRADIENT AND LAYERED BORON NITRIDE FORMATION UNDER EFFECT OF CONCENTRATED LIGHT IN A FLOW OF NITROGEN

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Results of the effect of concentrated light energy in a xenon high-flux optical furnace on transformation of boron nitride (BN) and boron (B) powders in a flow of nitrogen are presented. Raman, Auger Electron (AES), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning and transmission electron microscopes (SEM and TEM), and the measurement of band gap using transmittance technique have been employed for investigation of the properties of produced nanostructures. According Raman, AES and FTIR study the surface of all prepared nano powders is composed of BN. XRD disclosed pure amorphous boron inside particle. Gradient transformation pure boron to BN in the framework of one particle as well as layered nanostructure was observed by TEM study. Dependence of a square of the optical absorption coefficient for a deposited BN film versus the photon energy of incident light has confirmed a gradient and layered nature of the prepared BN nanostructures.

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## Introduction

Boron nitride (BN) is a structural equivalent to carbon because of close polymorphism. Hexagonal and rhombohedral boron nitrides (h-BN and r-BN) are structurally similar to hexagonal and rhombohedral graphite. They are extremely soft, electrical insulators with poor thermal conductivities. Cubic and Wurtzite boron nitride (c-BN and w-BN) are structurally similar to diamond and lonsdalite. Consequently, c-BN is an extremely hard, electrical insulator with an excellent thermal conductivity. Another very common modification of BN is a quasi-amorphous phase called turbostratic boron nitride (t-BN) which often co-exist with c-BN.<sup>1</sup> One minor difference between BN and carbon is in their layer stacking. In h-BN, the layers are arranged so that boron atoms in one layer are located directly on top of nitrogen atoms in neighboring layers, and vice versa.<sup>2</sup>

All these modifications of BN can be considered as three-dimensional (3D) bulk substances. However, effect of architecture and grain size of BN result in different properties of powder materials because surface effect of nanostructure defines application. Therefore, a new class of material with reduced dimensionality, i.e., with one or more physical dimension(s) constrained to the nanometer scale should be recognized. Two-dimensional (2D) nanosheets, one-dimensional (1D) nanotubes, and zero-dimensional

(0D) fullerenes represent typical examples of such materials. When compared to three-dimensional (3D) bulk substances, low-dimensional structures are anticipated to exhibit new properties due to quantum confinement and/or surface and interfacial effects.<sup>3</sup> Their unusual physical and chemical properties<sup>4-6</sup> can promote novel applications in engineering. Boron nitride low-dimensional materials are among the most promising inorganic nanosystems explored so far.

For boron nitride various approaches have been investigated, synthesis methods have been intensively studied, and significant achievements have been obtained in terms of quantity, structure quality and variety.<sup>7</sup> In order to prepare BN nanostructures, high and low temperature routes have been developed, for example, high temperature and high pressure (HTHP) method, chemical vapor deposition (CVD) method, physical vapor deposition (PVD) method, hydrothermal and solvothermal synthesis routes.<sup>8</sup> A comprehensive overview of the current status of the different synthesis processes for BN has demonstrated formation of different properties for BN powders highlighting the advantages of every synthetic methods.<sup>9-20</sup>

Solar heating is a promising alternative energy source for nanotechnology. A xenon high-flux optical simulator (also artificial sun) that provides illumination approximating natural sunlight in controllable indoor tests under laboratory conditions is a good model of this source. Optical simulator has numerous advantages. Its versatility, rapid heating and cooling rates, ability to adjust temperature profile along each axes, maximum operating temperatures and environmental adaptability stand out among others. Moreover, this technique can also be suitable for both conducting and non-conducting materials and is one of cleanest energy sources available. Since hard conditions of this furnace, can cause a new structure formation with new architecture, morphology, elemental and phase composition in the prepared boron nitride powder, it would be important to define the most valuable features, which may open a new opportunity for better BN powder application.

## Experimental

Plate-like fine powder of h-BN (Chempur, CH070802) with thickness 0.001  $\mu\text{m}$  and mean grain size  $\sim 0.3 \mu\text{m}$  and boron powder with particle size  $\leq 0.05 \mu\text{m}$  have been used as a starting material. These powders exhibit uniform size and structure and high surface area.<sup>21</sup> Initially BN powder was annealed at 800  $^{\circ}\text{C}$  for 1 h in order to increase its chemical stability. Detailed description of the initial powders can be found in a number of previous papers.<sup>21–23</sup>

A quartz chamber was chosen for the process of heating. Surface of BN initial powder was treated in a xenon high-flux optical furnace in a flow of nitrogen at the density of energy in focal zone of set-up  $\sim 1.4 \times 10^4 \text{ kW m}^{-2}$  and  $\sim 0.7 \text{ n} \times 10^4 \text{ kW m}^{-2}$ . Prepared BN powders precipitated on copper water-cooling screens and on a quartz surface of the chamber. Detailed description of the experiments was presented in the earlier papers.<sup>4–28</sup>

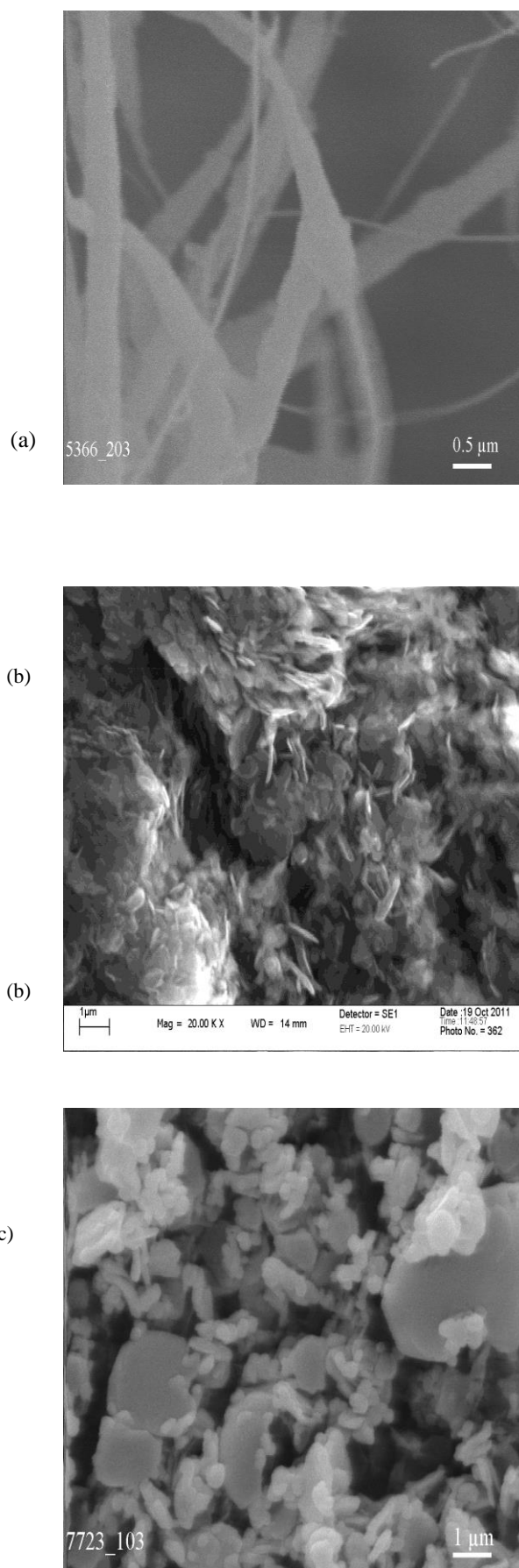
Dilor XY-800 Spectrometer in micro configuration recorded Raman spectra of prepared BN powders. As the excitation beam Ar<sup>+</sup> ion and Kr<sup>+</sup> ion lasers were used. 514.5 nm and 488 nm wavelengths of the Ar<sup>+</sup> laser and a 647 nm line of the Kr<sup>+</sup> laser were applied. Auger process was initiated by creation of a core hole carried out by exposing a sample to a beam of high energy electrons 3 keV (beam current – 120, 180, 200  $\mu\text{mA}$ , modulation – 1–2 eV, time constant – 3 s, sensitivity – 50–100  $\mu\text{mV}$ , scanning time – 1000 sec, energy rate – 500 eV). A process in an Auger spectrometer chamber was initiated by exposing a sample to a beam of high-energy electrons (3 keV), which has a sufficient energy to ionize proper levels of the researched elements.

IR spectra were examined with Nicolet 6700 FTIR spectrometer equipped with a Thermo Nicole Continuum microscope. Resulting structures were examined by transmission electron microscope JEM-2100F (ability to separate 0.1 nm) and scanning electron microscopy Superprobe-733 (electron beam diameter of 0.7 nm). Powders were analyzed using X-ray diffraction (diffractometer “DRON-3.0”, radiation of K $\alpha$  – Cu) and were examined microstructurally using optical microscopy. A detailed spectrophotometric study of spectral dependence of optical absorption was performed using a spectrophotometer “Specord UV-Vis”.

## Results and Discussion

White, glassy powder precipitated in a chamber during initial powders heating under concentrated light in flow of nitrogen. White thread-like and dark fullerene-like structures were found on a surface of the compacted h-BN sample around a crater (Fig. 1a). It is known that boron exists as a dark brown to black powder. BN, boron oxides and other boron compounds are mostly white and glassy powder. Therefore, dark fullerene-like structures were composed of boron with negligible amount of the boron oxides.<sup>23</sup>

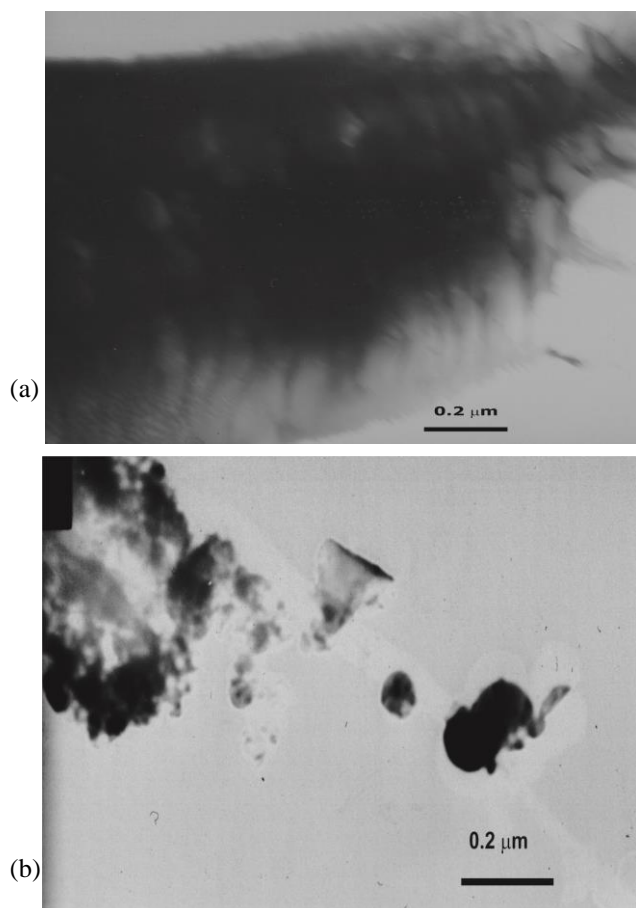
SEM and TEM study disclosed complicated BN structures of significant diversity (Figures 1, 2). SEM images of 1D (Figure 1a), 2D (Figure 1b) and 3D (Figure 1c) structures of BN are typical for powders prepared under concentrated light at different conditions.



**Figure 1.** SEM image of 1D (a), 2D (b) and 3D (c) structures for BN powders prepared under concentrated light under different conditions.

0D nanostructures of BN were not found. TEM images of nanostructures have underlined the existence of gradient (Figure 3a) and layered (Figure 3b) nature for the low-dimensional structures of different architecture (Figure 2).

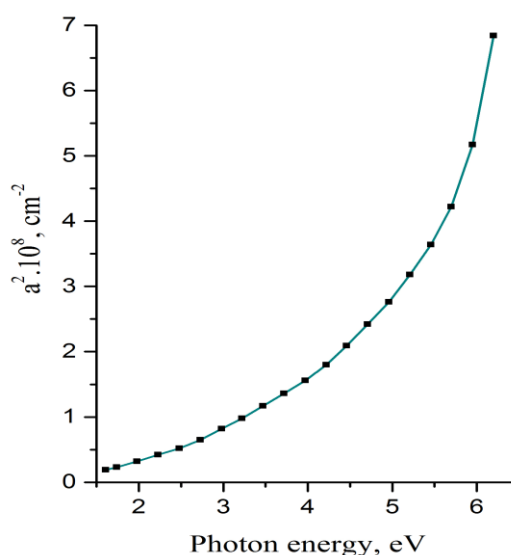
BN powder was characterized by a high transparency in a visible area of spectrum during exploration of an optical absorption. Dependence of a square of the optical absorption coefficient for a deposited BN film versus the photon energy of incident light can be a pure parabolic (Figure 3a) or with linear sections (Figure 3b).



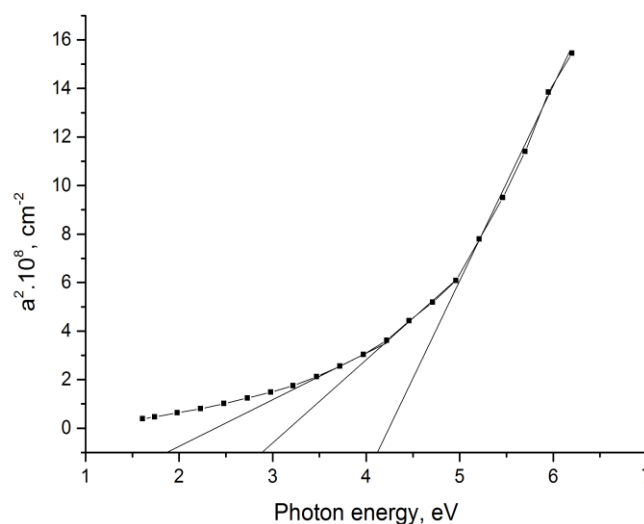
**Figure 2.** TEM image of gradient (a) and layered (b) nanostructures of BN powder of different architecture.

It is known that band gap for boron from different sources is 1.08<sup>29</sup>, 1.42<sup>30</sup>, 1.58<sup>31,32</sup> eV in depend on purification. Boron of 99.9999% purity has been produced and is available commercially with band gap of 1.50 to 1.56 eV<sup>32</sup>. The band gap of h-BN remains in dispute, but recent reports seem to be converging close to 6 eV<sup>33</sup>. BN band gap for graphene-like structures was estimated to be 5.6–5.8 eV<sup>34</sup> according to the optical absorption spectrum. For BNNTs can be 5.0 eV<sup>35</sup>; 5.5 – 5.8 eV<sup>36,37</sup> and higher – 6.0 eV<sup>38</sup>. Therefore, the peaks at ~5.5 eV are probably defect-induced and those at lower energies brought about by impurities<sup>33</sup>.

Since BN was produced in conditions of a xenon high-flux optical furnace without any catalysts (impurities), therefore, a pure parabolic dependence (Figure 4a) has disclosed gradient nature of prepared powder (Figure 3a) from pure boron inside with band gap of 1.8 eV to BN with band gap of 5.1 eV



(a)

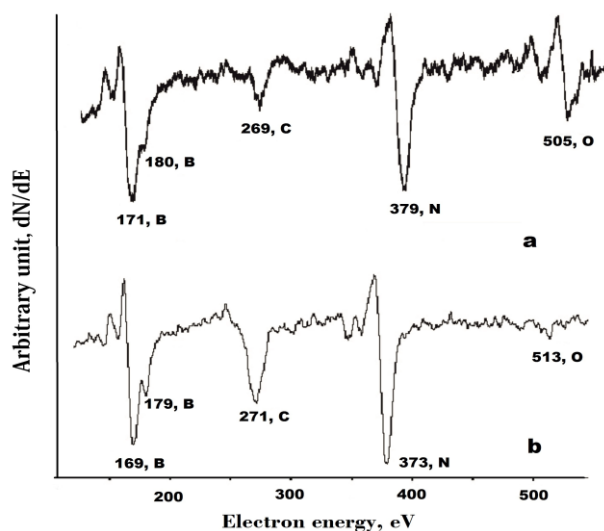


**Figure 3.** Square of the optical absorption coefficient,  $\alpha$ , versus photon energy for the gradient (a) and layered (b) low-dimensional structures of BN powder.

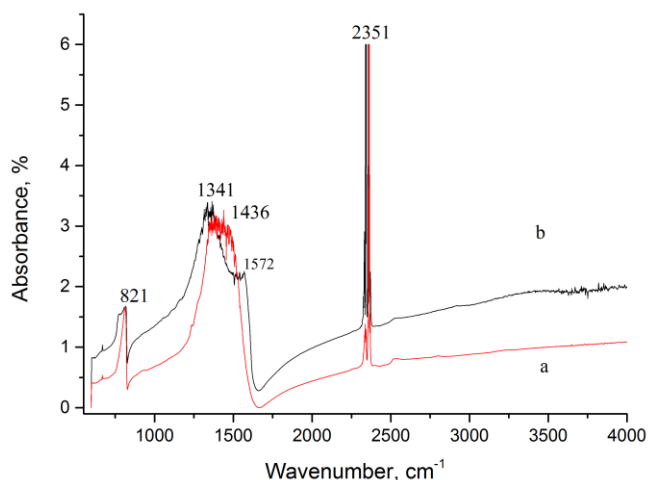
Linear sections (Figure 4b) of the band gap, 2.4, 3.2 and 4.3 eV, accordingly, indicate the layered nature of structure of a prepared powder (Figure 3b). First-principles local-density calculations have shown that the lowest band gap (4.07 eV) is indirect, located near the Brillouin-zone edges. However, due to the quasi-two dimensional nature of the hexagonal structure, the lowest direct band gap is predicted to be close by 4.2 eV.<sup>39</sup> Therefore, band gap of 4.3 eV can be ascribed to BN layer with a deficit of nitrogen, that of 3.2 eV to the layer of tetragonal boron-enriched phase B<sub>51.2</sub>N and 2.4 eV to the layer of tetragonal and rhombohedral phases boron enriched nitrogen.<sup>24</sup> Lowest gap energies, such as 3.8 eV and 4.3 eV for BN have been reported by old experimental studies using various techniques.<sup>39</sup>

In contrast to SEM, which has a typical analysis depth of 1–3 μm, Auger electron spectroscopy (AES) is a surface analysis technique with an analysis depth of less than 5 nm and is therefore better suited for the compositional analysis of the features of ultra-thin layers and nanoscale samples.

Surface AES study of boron and BN powders has underlined these features.<sup>40</sup> Nitrogen implantation to boron results in splitting boron AES peak according preliminary studies.<sup>40</sup> This splitting was always observed for surfaces of all gradient and layered structures of prepared BN powders regardless of morphology difference (Figure 4). A curvature of a surface of 1D BN (Figure 2a) can explain just a negligible shifting peak at 171 eV for initial powder to lower values of the graph (Figure 1b). Low depth of nitrogen penetration in boron during heating can effect on surface structure, its activity and, as a result, on the quantity of absorbed carbon and oxygen (Figure 4).



**Figure 4.** Differential Auger spectrum of the upper layer of the surface (a) 2D structure of initial h-BN powder,<sup>1</sup> (b) 1D thread-like structure of BN (Figure. 1a) prepared under concentrated light.

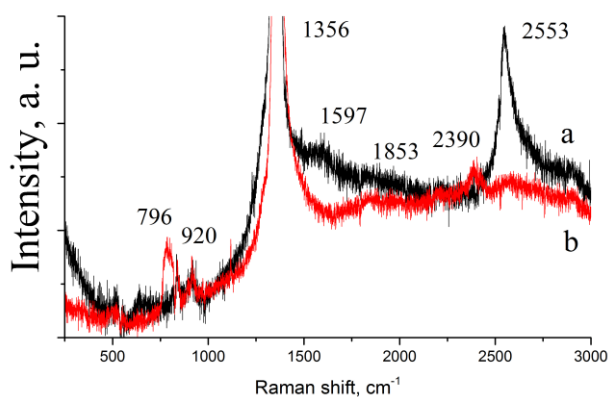


**Figure 5.** ATR-FTIR spectra (mid IR) with specific bands assignments for (a) an initial h-BN powder (2D structure) (b) prepared BN of 1D structure (Figure 2a).

In the mid-IR spectrum, the penetration depth typically is between 0.5 and 2 μm with the exact value being determined by the wavelength of light, the angle of incidence and the indices of refraction for the medium being probed.<sup>41</sup> Two peaks at wave number of 821 and 2351 cm<sup>-1</sup> of FT-IR spectra for initial h-BN and 1D BN (Figure 1a) are the same (Figure 6). The broadening, splitting and shift of the peak at 1436 cm<sup>-1</sup> for initial h-BN into 2 peaks at 1341 and 1572

cm<sup>-1</sup> for 1D BN was observed. Shift and broadening can be explained by the curvature of a surface of 1D BN, but look-like appearance of splitting may be ascribed to a new structure formation.

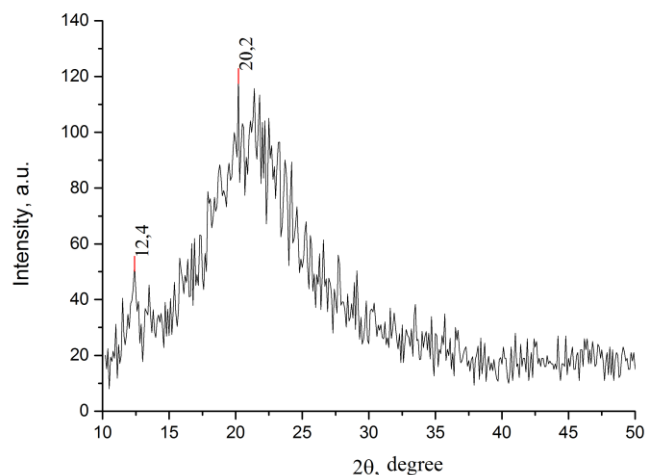
Raman spectroscopy is a valuable non-destructive analytical tool in detecting the different phases in mixed compounds. Depth of penetration for 514.5 nm and 488 nm wavelengths of the Ar<sup>+</sup> laser and a 647 nm line of the Kr<sup>+</sup> laser goes from 300 nm and higher for the best quantitatively studied silicon under effect of these lasers.<sup>42</sup> For initial h-BN and 1D BN (Figure 1a) Raman spectroscopy has disclosed that their spectra are very close (Figure 6). It is well known that bulk BN has an intrinsic E<sub>2g</sub> vibration at 1367 cm<sup>-1</sup>.<sup>43,44</sup> In our research, the main peak, which corresponds to this E<sub>2g</sub> vibration mode of h-BN was found at 1356 cm<sup>-1</sup> because of laser wavelength of Dilor XY-800 Spectrometer. For prepared 1D BN (Figure 1a) broadening of its main peak occurs with a negligible shift at 1356 cm<sup>-1</sup> (Figure 6). The shift and broadening in the Raman cross section for scattering from nanocrystals indicates that smaller crystal grain size because of the wave-vector uncertainty of the phonons. Preliminary research also has disclosed that an outer shell of 1D structures of BN (Figure 1b, Figure 2a) consists of polycrystalline nanosized h-BN. Some separate single crystals h-BN and B<sub>51,2</sub>N were also observed depending on the experimental conditions.<sup>23</sup> Therefore, Raman spectroscopy (Figure 6) also confirms the presence of BN bonds on the surface of 1D structures prepared under concentrated light up to the depth up to 300 nm and higher.



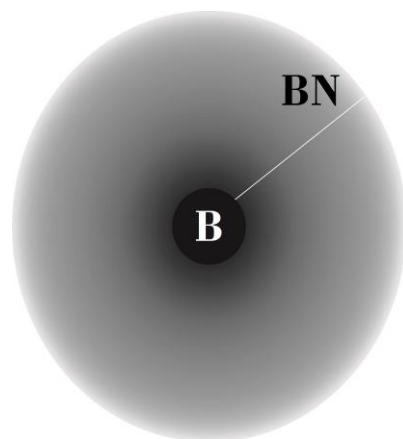
**Figure 6.** Raman spectra of (a) an initial h-BN powder (2D structure) and (b) prepared BN of 1D structure.

The depth of penetration for XRD study is much higher. Mass absorption coefficient of the BN sample and the incident angle of the X-ray beam effect on its spectra and penetration. Therefore, it is not unexpected that X-Ray diffractions pattern measured for prepared BN powder with pure parabolic dependence of a square of the optical absorption coefficient (Figure 3a) has disclosed only amorphous boron according to<sup>44-47</sup> with a small quantity of B<sub>2</sub>O<sub>3</sub> (Figure 7).<sup>45</sup>

Based on all facts the structure of prepared BN nanopowders can be represented schematically as a boron particle with increase of nitrogen content from center to periphery occurring in a gradient (Figure 9).



**Figure 7.** X-Ray diffractions pattern measured for BN of gradient nanostructure.



**Figure 8.** Schematic picture of the gradient structure of prepared BN nanoparticle.

X-Ray diffractions patterns for prepared BN powder of layered (Figure 2b) nature with linear sections of dependence of a square for the optical absorption coefficient were described before<sup>21,24</sup> and have demonstrated phases, as follows: h-BN, tetragonal boron-enriched phases B<sub>51,2</sub>N and B<sub>25</sub>N; tetragonal and rhombohedral phases of pure boron and negligible amorphous boron content. Difference in heating condition under concentrated light may cause crystalline nanostructure formation on the surface in depend on a weight of the boron particle, its deposition velocity and velocity of nitrogen.

This conclusion does not conflict our previous “gaseous” model for 1D and 2D BN structures formation.<sup>23,25</sup> Heating h-BN or boron under concentrated light results in a melt of boron, boiling process and spattering melt boron drops or grow 1D nanostructure around a crater of the melt in flow of nitrogen.<sup>21,23,25</sup> SEM and TEM study has demonstrated diversity in BN particle size, its architecture and morphology (Figure 2, 3) caused impurity content, weight of the spattered boron particle, its deposition velocity and velocity of nitrogen.

## Conclusion

Heating of boron and boron nitride powders under concentrated light, in a xenon high-flux optical furnace, in a flow of nitrogen, results in the formation of a BN powder with a new structure. Since rapid heating and cooling rate does not permit full penetration of nitrogen to boron grain, formed particle has gradient structure. Local annealing of such structure in the process of heating causes crystallization and transformation with a gradient distribution of nitrogen in boron particle to layered structure.

Thus, most of characterization challenges can be met by different research techniques of different analytical depth, which will permit one to understand the real picture of a structure of prepared powder as well as process of the formation of a new structure formation.

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