

LOW-TEMPERATURE 450 nm LUMINESCENCE  
OF HEXAGONAL BORON NITRIDE

V. Korsaks, B. Berzina, L. Trinklere

Institute of Solid State Physics, University of Latvia,  
8 Kengaraga Str., LV-1063, Riga, LATVIA  
e-mail: valdis.korsaks@inbox.lv

The low-temperature luminescence of bulk hexagonal boron nitride (hBN) powder and boron nitride multiwall nanotubes (BNNTs) was investigated. It was found that, apart from the well-known luminescence at 300 nm and 400 nm, a broad luminescence band at 450 nm appears under low temperatures (8 K), and that heating the sample results in its quenching – at 190 K the luminescence intensity becomes negligible. The 450 nm luminescence is characterized with its own excitation band at 240 nm and is excited also at 270 nm and 350 nm. Besides, this luminescence can be excited through excitonic processes with light around 205 nm. The same features of 450 nm luminescence are observed in both the hBN and BNNTs.

**Key words:** *hBN powder, BN multiwall nanotubes; photoluminescence, luminescence excitation spectra.*

## 1. INTRODUCTION

Hexagonal boron nitride (hBN) is a promising wide-band gap material. Recently, its application was proposed in the field of lasing materials and light emitters for a spectral region of deep UV light around 200 nm [1–3]. Various modifications of hBN are possible; besides the bulk material (powder, single crystals) the nanostructured forms (single and multiwall nanotubes) are also synthesized.

Spectral characterization of this material allows revealing its optical properties, and various groups from different laboratories worldwide are currently working on this problem (see [4–13] and refs. therein). Our research group is also involved in this process and conducts research into the luminescence of bulk hBN powder and multiwall BN nanotubes (BNNTs) [14–16].

The present paper contains results of the low-temperature photoluminescence research of the bulk material (hBN powder) and the nanostructured material (multiwall BN nanotubes). A special attention is focused on the 450 nm luminescence observed solely at low temperatures.

## 2. EXPERIMENTAL

Commercial hexagonal boron nitride (hBN) powder as a bulk material with the grain size of  $\sim 30\mu\text{m}$  (Aldrich Corp.) and hexagonal boron nitride multiwall nanotubes (NanoAmor Corp) with the outside diameter 40–100 nm were investigated. The photoluminescence (PL) spectra and photoluminescence excita-

tion (PLE) spectra were measured within the temperature range from 8 K to 300 K. The sample was put into a low-temperature cryostat (CCS-100/204, Janis Research Co.). Traditional equipment for registration of PL and PLE spectra was used, including a deuterium lamp (400 W) as the excitation light source, a photomultiplier tube (H7468-03, Hamamatsu Cor.) for luminescence registration, and two monochromators: a grating monochromator MDR2 for filtering the exciting light and a prism monochromator SPM2 for filtering luminescent light.

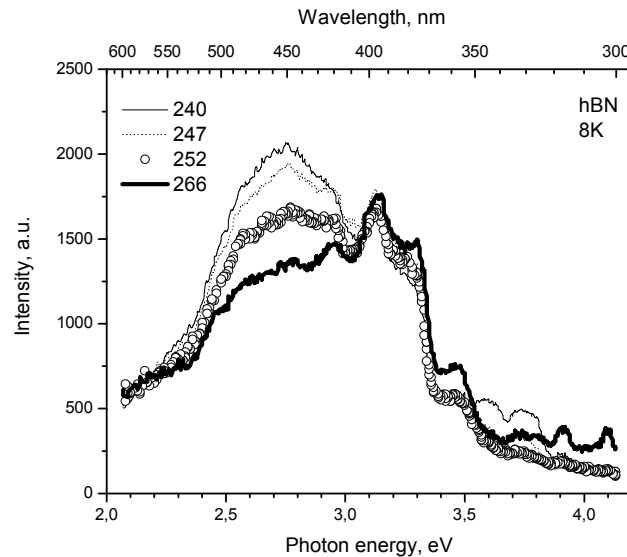
All PL spectra depicted in Figs. 1, 3 and 5 are related to a constant number of exciting light quanta. Besides, all corrections necessary for the PL and PLE spectra due to equipment characteristics have been applied.

Before measurements, the sample was preheated (for one hour at 420 °C) to remove water vapours and other sediments. All the measurements were done when the sample was in a vacuum of  $4.1 \cdot 10^{-4}$  mbar.

### 3. RESULTS AND DISCUSSION

Photoluminescence spectra were measured within the spectral region from 300 nm to 600 nm.

In Fig. 1 the photoluminescence spectra of bulk hBN at 8 K measured at different excitation wavelengths (240–266 nm) are shown. The spectra are complex, with two spectral regions distinguished under the excitation conditions, containing broad PL bands with a more or less pronounced fine structure. These PL bands are located around 400 nm and 450 nm. The 400 nm PL band exhibits a well resolved sub-band structure, whereas for the 450 nm band this substructure is resolved only weakly. The former (400 nm) PL band is analysed in our previous studies carried out at room temperature [15, 16], whereas the latter (the 450 nm PL band) appears solely at low temperature and, therefore, in this study a special interest is mainly devoted to this band.



*Fig. 1.* Photoluminescence spectra of bulk hBN powder at 8K under excitation at different wavelengths (spectral region 240–266 nm).

Figure 2 shows the PLE spectra of bulk hBN powder at 8 K with a heavy curve for the 450 nm PL band. Three short spectral intervals ( $\sim 20$  nm) from the broad 450 nm luminescence band (Fig. 1) were distinguished – one of them around its maximum at 450 nm and two others around 420 nm and 480 nm; the excitation spectra for these luminescence intervals were measured. The shapes of the mentioned three spectra are similar. As is seen in the figure, these are complex – consisting of several sub-bands. The main band for the 450 nm luminescence excitation is located at 240 nm (5.16 eV), with its energy fits in the band gap being  $\sim 1$  eV lower than that necessary for band-to-band transitions. Besides the 240 nm PLE band there are some other bands with lower intensity at 270 nm (4.59 eV) and 350 nm (3.54 eV). This luminescence can be excited also through excitonic processes with light around 200 nm.

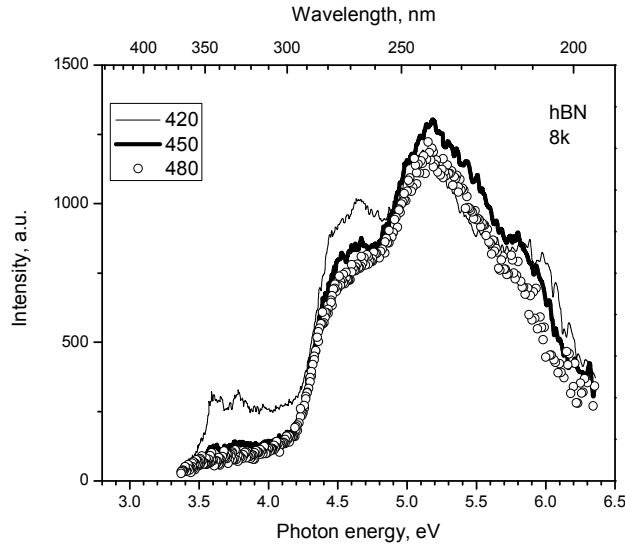


Fig. 2. Photoluminescence excitation spectra of the bulk hBN at 8K. Short intervals ( $\sim 20$  nm) from luminescence spectra (Fig. 1) are selected for the wavelengths shown on the insert.

The PL spectra of nanomaterial (the BNNTs) were examined under the same experimental conditions as in the case of the bulk hBN material. These spectra were measured at 8K using different wavelengths of exciting light from the spectral interval of 240–266 nm (Fig. 3). The wavelengths of exciting light are labelled in the picture. The shapes of all spectra are similar. Besides, these spectra are similar to the PL spectra of bulk hBN shown in Fig. 1 only in the case of the nanomaterial luminescence intensity reduced comparing with that of the bulk hBN. For BNNTs, the 450 nm PL band appears together with the 400 nm band, and the ratio of their intensities depends on the wavelength of exciting light.

The 450 nm PLE spectra of BNNTs were studied under the same conditions as in the case of bulk hBN (Fig. 2). These spectra are seen in Fig. 4. The same bands located at 240 nm, 270 nm and 350 nm responsible for the 450 nm PL excitation are observed like in the case of hBN. Only in the case of nanomaterial a strong excitation band fitting in the spectral region of exciton absorption at 205 nm is also observed, thus providing evidence that the 450 nm luminescence can be effectively excited through excitonic processes.

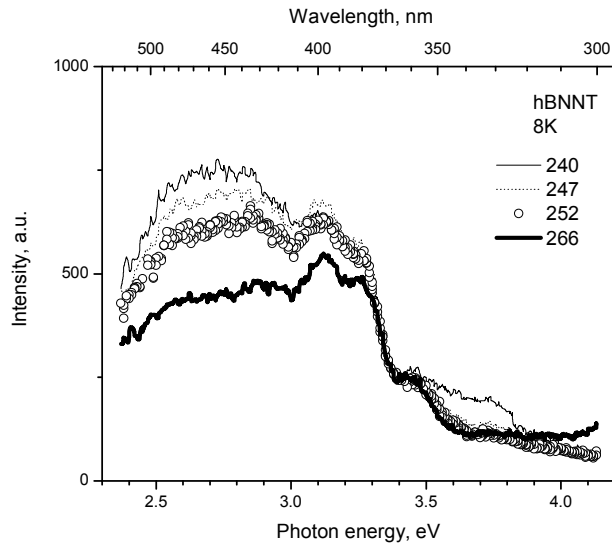


Fig. 3. Photoluminescence spectra of BNNTs at 8 K under different exciting wavelengths, nm (shown on the right).

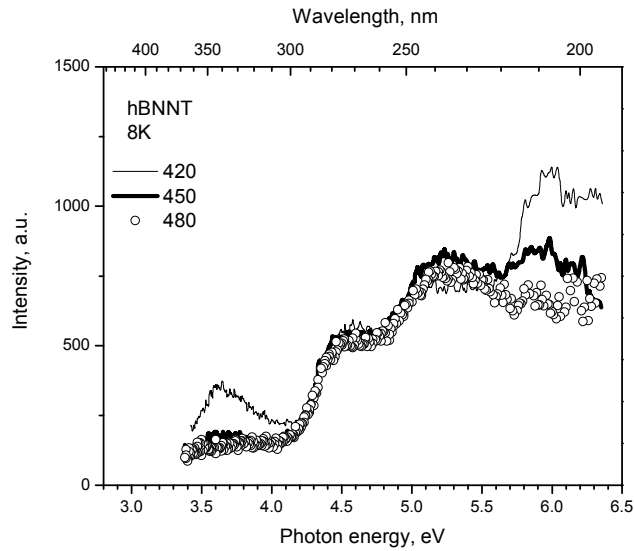


Fig. 4. Excitation spectra of the 450 nm photoluminescence of BNNTs at 8 K. Wavelengths of the selected luminescence intervals ( $\sim 20$  nm) are shown on the left.

The temperature dependence of 450 nm luminescence for bulk hBN was examined in the range from 8 K to 270 K. The sample was excited with 240 nm light from the main excitation band of 450 nm PL (Fig. 2), and the luminescence spectra were recorded at different temperatures maintaining the same experimental conditions. The results are shown in Fig. 5, where thermal quenching of the 450 nm luminescence is observed. It is seen that the intensity of this luminescence decreases when the temperature of the sample increases, and at 190 K the 450 nm luminescence practically disappears. At RT this luminescence seems to be completely quenched or its intensity is very low and cannot therefore be distinguished on the PL spectra. The same results as demonstrated above are obtained for the BNNT nanomaterial.

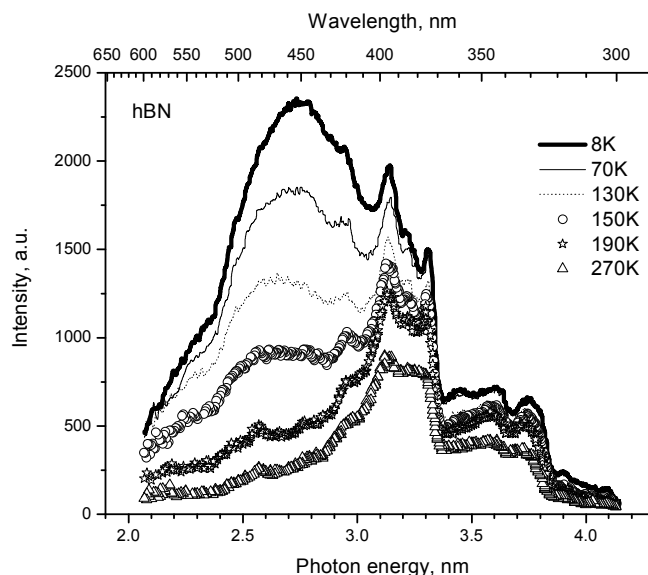


Fig. 5. The temperature dependence of 450 nm photoluminescence spectra for hBN under 240 nm excitation.

The above results confirm that the 450 nm luminescence appears in both the bulk material (hBN powder) and the nanostructured material (multiwall BNNTs), being independent of reduction in the material size, and is characteristic of the hBN crystalline lattice. The main 240 nm excitation band of the 450 nm luminescence is located far away from the exciton absorption region (200 nm) at the long wavelength side of spectra (Figs. 2 and 4). This testifies that the luminescence is caused by the crystalline lattice defects forming their energy levels within the band gap. At the same time, the 450 nm luminescence can be excited through excitonic processes, which provides evidence for the energy transfer from excitons to the luminescence centres. Unfortunately, the defect types responsible for the 450 nm luminescence are so far unknown. The 450 nm luminescence appears at low temperatures (8 K), and at higher temperatures (190 K) it is quenched. Such a phenomenon is observable in the case if the luminescence has a recombination character and when one of the recombination components is formed by a shallow trap for a charge carrier. From the other side the thermal quenching could be observed also in the case of intrinsic luminescence; however, the former version seems to be more probable.

## 5. CONCLUSIONS

A new luminescence band at 450 nm has been revealed in both the bulk material (hBN powder) and the nanostructured material (multiwall BNNTs). The 450 nm luminescence appears only at low temperatures, and at 190 K it is practically quenched. The 450 nm luminescence can be excited either in its main excitation band at 240 nm (and some other smaller bands) or by the energy transfer from excitons.

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## REFERENCES

1. Watanabe, K., Taniguchi, T., & Kanda, H. (2004). Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal. *Nat. Mat.*, (3), 404–409. DOI:10.1038/nmat1134.
2. Watanabe, K., Taniguchi, T., & Kanda, H. (2004). Ultraviolet luminescence spectra of boron nitride single crystals grown under high pressure and high temperature. *Phys. Stat. Sol. (a)*, 201(11), 2561–2565. DOI: 10.1002/pssa.200405188.
3. Taniguchi, T., & Watanabe, K. (2007). Synthesis of high-purity boron nitride single crystals under high pressure by using Ba–BN solvent. *J. of Crystal Growth*, 303, 525–529. DOI:10.1016/j.jcrysgro.2006.12.061.
4. Wu, J., Han, W-Q., Walukiewicz, W., Ager, J. W., Shan, W., Haller, E.E., & Zettl, A. (2004). Raman spectroscopy and time-resolved photoluminescence of BN and  $B_xC_yN_z$  nanotubes. *Nanoletters*, 4 (4), 647–650. DOI: 10.1021/nl049862
5. Solozhenko, V.I., Lazarenko, A.G., Petitet, J.P., & Kanaev, A.B. (2001). Bandgap energy of graphite-like hexagonal boron nitride. *J. Phys. Chem. Solids*, 62, 1331–1334. DOI:10.1016/S0022-3697(01)00030-0.
6. Serrano, J., Bosak, A., Arenal, R., Krisch, M., Watanabe, K., Taniguchi, T., Kanda, H., Rubio, A., & Wirtz, A. (2007). Vibrational properties of hexagonal boron nitride: inelastic X-Ray scattering and *ab initio* calculations. *Phys. Rev. Lett.*, 98, 095503. DOI:10.1103/PhysRevLett.98.095503.
7. Museur, L., Anglos, D., Petitet, J.-P., Michel, J.-P., & Kanajev, A.V. (2007). Photoluminescence of hexagonal boron nitride: effect of surface oxidation under UV-laser irradiation. *J. Luminescence*, 127, 595. DOI: 10.1016/j.jlumin.2007.01.24.
8. Silly, M.G., Jaffrennou, P., Barjon, J., Lauret, J.S., Ducastelle, F., Loiseau, A., Obratsova, E.D., Attal-Trétout, B., & Rosencher, E. (2007). Luminescence properties of hexagonal boron nitride: Cathodoluminescence and photoluminescence spectroscopy measurements. *Phys. Rev. B* 75, 085205, DOI: 10.1103/PhysRevB.75.085205
9. Jaffrennou, P., Barjon, J., Schmid, T., Museur, L., Kanaev, A., Lauret, J.-S., Zhi, C.Y., Tang, C., Bando, Y., Golberg, D., Attal-Tretout, B., Ducastelle, F., & Loiseau, A. (2008). Near-band-edge recombinations in multiwalled boron nitride nanotubes: cathodoluminescence and photoluminescence spectroscopy measurements. *Phys. Rev. B* 77, 235422, DOI: 10.1103/PhysRevB.77.235422.
10. Jaffrennou, P., Donatini, F., Barjon, J., Lauret, J.-S., Maguer, A., Attal-Tretout, B., Ducastelle, F., & Loiseau, A. (2007). Cathodoluminescence imaging and spectroscopy on a single multiwall boron nitride nanotube. *Chemical Phys. Lett.*, 442, 372–375, DOI: 10.1016/j.cplett.2007.06.001
11. Jaffrennou, P., Barjon, J., Lauret, J.-S., Attal-Trétout, B., Ducastelle, F., & Loiseau, A. (2007). Origin of the excitonic recombinations in hexagonal boron nitride by spatially resolved cathodoluminescence spectroscopy. *J. Appl. Phys.*, 102, 116102; DOI: 10.1063/1.2821413.
12. Jaffrennou, P., Barjon, J., Lauret, J.-S., Maguer, A., Golberg, D., Attal-Trétout, B., Ducastelle, F., & Loiseau A. (2007). Optical properties of multiwall boron nitride nanotubes. *Phys. Stat. Sol.(b)*, 224, (11), 4147–4151. DOI: 10.1002/pssb.200776109.
13. Hua Chen, Ying Chen, Yun Liu, Chao-Nan Xu, & Jim S. Williams. (2007). Light emission and excitonic effect of boron nitride nanotubes observed by photoluminescent spectra. *Optical Materials*, 29, 1295–1298. DOI:10.1016/j.optmat.2006.05.006
14. Berzina, B., Trinkler, L., Krut'khovostov, R., Williams, R.T, Carroll, D.L., Czerw, R., & Shishonok, E.. (2005). Photoluminescence excitation spectroscopy in boron nitride nanotubes compared to microcrystalline h-BN and c-BN. *Phys. Stat. Sol. (c)* 2, (1), 318–321. DOI: 10.1002/pssc.200460174.

15. Berzina, B., Trinkler, L., Korsaks, V., Krutohvostov, R., Carrol, D.L., Ucer, K.B., & Williams, R.T. (2006). Exciton luminescence of boron nitride nanotubes and nanoarches. *Phys. Stat. Sol.(b)*, 243 (14), 3840, DOI: 10.1002/pssb.200672108.
16. Williams, R.T., Ucer, K.B., Carroll, D.L., Berzina, B., Trinkler, L., Korsak, V., & Krutohvostov, R. (2008). Photoluminescence of self-trapped excitons in boron nitride nanotubes. *J. Nanosci. Nanotechnol.*, (8), 6504–6508. DOI: 10.1166/jnn.2008.005.

## HEKSAGONĀLĀ BORA NITRĪDA 450 nm LUMINISCENCE PIE ZEMĀM TEMPERATŪRĀM

V. Korsaks, B. Bērziņa, L. Trinklere

### K o p s a v i l k u m s

Tika pētīta defektu radīta luminiscence heksagonālā bora nitrīdā (hBN) un bora nitrīda daudzsienu nanocaurulēs (BNNTs) pie zemām temperatūrām. Tika atklāts, ka pie zemām temperatūrām (8 K) bez labi zināmām luminiscences joslām pie 300 nm un 400 nm parādās arī plata josla pie 450 nm, kas, paraugu sildot, dziest – pie 190 K, tās intensitāte kļūst niecīga. 450 nm luminiscenci raksturo ierosināšanas josla pie 240 nm, bez tam tā ierosinās arī 270 nm un 350 nm joslās. Šo luminiscenci var ierosināt arī eksitonu procesi, ko izraisa 205 nm gaisma. 450 nm luminiscence tika novērota gan hBN gan arī BNNTs.

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