



## Defect-induced blue luminescence of hexagonal boron nitride



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### ABSTRACT

Native defect-induced photoluminescence around 400 nm (blue luminescence - BL) was studied in hBN materials with different size and various origins. The following spectral characterizations were used: spectra of luminescence and its excitation, luminescence dependence on temperature, luminescence kinetics, optically stimulated luminescence and infrared absorption. It was found, that the BL is characteristic for all these materials, which were studied. The BL forms a wide, asymmetric and phonon-assisted emission band at 380 nm. This luminescence can be excited either through the exciton processes, or with light from two defect-induced excitation bands at 340 nm and 265 nm. It was found that the BL is caused by two luminescence mechanisms. One of them is intra-center luminescence mechanism (340 nm excitation), but the other one is recombination mechanism (265 nm excitation). It was considered that the most probable candidates for the defects, which cause the BL in hBN can be related to the nitrogen vacancy type-centers. It was certainly confirmed, that presence of oxygen gas is partly quenching the BL intensity, thus ranking the hBN material among the materials prospective for development of oxygen gas optical sensors.

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### 1. Introduction

Hexagonal boron nitride (hBN) is one of prospective wide band gap ( $E_g = 6.4$  eV) materials [1], and during the last decades it is attracting interest of many investigators around the world due to its promising optical properties. It was found that a strong exciton luminescence from the far ultraviolet (UV) spectral region is characteristic for this material making it prospective for application as emitter of far UV light [2].

Exciton luminescence of hBN material was extensively studied both theoretically [1,3] and experimentally [4–10]. As a result of these studies existence of small size Frenkel type excitons in hBN was confirmed [11]. Phonon-structured luminescence spectra of free excitons was observed at 215 nm (5.77 eV) [6], whereas, emission of the bound excitons, which are located at defects of the crystalline lattice, appears at 220 nm (5.64 eV) and 227 nm (5.46 eV) [12].

Defect-induced luminescence of hBN caused either by native defects or specially doped impurities is not so particularly studied. In hBN there are possible different kinds of native defects, which can be incorporated into a crystalline lattice of the host material during its synthesis thus forming the luminescence centers. Between them the small size native defects such as oxygen ( $O_N$ ) or carbon ( $C_N$ ) atoms substituted for the nitrogen, varieties of the host material vacancies ( $v_N$ ,  $v_B$ ), Stone Wall defects etc. are usually present in hBN.

A large part of native defects of hBN are luminescent and can be characterized by their luminescence spectra. Photoluminescence (PL) spectra caused by native defects of hBN under UV light excitation exhibit a complex structure covering a large spectral range beginning at ~300 nm and extending with decreasing intensity into a visible light region as it is shown by Wu et al. [13]. It demonstrates coexistence of different types of luminescent defects, where each of them has its own spectral characteristics. The phonon-structured UV luminescence at 320 nm (further named UVL) is the most intensive among the native defect caused spectra, and it has been observed in the PL spectra as well as in the cathode luminescence (CL) spectra for hBN materials with different origin. The UVL is comparatively well-studied [12–18], and carbon or oxygen impurities are mainly referred as possible luminescent defects, however, a direct proof of this suggestion is still absent.

Luminescence of hBN, which appears at longer wavelengths above the UVL spectrum (named LWL), is also complex and fine-structured, but its intensity is considerably lower compared to the UVL [13]. The LWL is observed in PL and CL spectra of hBN materials with different origin by many authors [9,10,13,17–23]. More detailed the LWL was studied by Musuer et al. [23, and Refs. therein] using powerful 248 nm laser excitation resulting in a fine structured luminescence around 340 nm, and its origin has been related to various types of nitrogen vacancies such as mono vacancies ( $v_N$ ) and multiple ones.

Our recent spectral investigation of hBN materials has shown [24], that intensity of a weak luminescence from the spectral region around 400 nm increases considerably, when sample is put into vacuum, compared to sample in air. As a result the hBN presents properties for

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oxygen gas optical sensing, thus motivating the spectral investigation of this luminescence.

The present work is devoted to studies of spectral characteristics of native defect-induced photoluminescence, which appears around the 400 nm (further named blue luminescence - BL) for hBN materials in order to reveal the luminescence processes and mechanisms together with estimation of possible candidates from different native defect types responsible for this luminescence.

## 2. Materials and experiment

The following hBN materials were used for spectral investigation: i) hBN powder with average grain diameter 3  $\mu\text{m}$  and purity of 99.5% synthesized by Aldrich Corporation (M1), ii) hBN powder with grain diameter 5  $\mu\text{m}$  and 98% purity obtained from NanoAmor Corporation (M2), iii) hBN powder with grain diameter 10  $\mu\text{m}$  and purity 99%, made by KOJUNDO Chemical Laboratory Co. LTD (M3), and iv) hBN nanomaterial consisting of multiwall nanotubes (MWBN) (M4) used in our previous investigation [17,18].

In the case of the hBN powders pellets with diameter of 13 mm and thickness of 1–1.5 mm were pressed and used for the experiments. Before each measurement pellets were annealed at 800 °C and then cooled down to the room temperature (RT) in order to purify the material surface. In the case of nanomaterial its pressing into a pellet was problematic and powder type material was used for measurements.

Self-made experimental set-up was used for measuring of luminescence and its excitation spectra consisting of the following main parts: i) a sample holder mounted on the cold finger inside of the sample chamber of a close cycle refrigerator (CCS-100/204, Janis Research Corporation) ensuring different fixed temperatures of sample within a range from 8 K up to room temperature (RT). At RT this sample chamber allows to keep the sample in different environments including vacuum and different gases such as technical air, oxygen, nitrogen etc.; ii) a light source for luminescence excitation consisting either of a solid state laser emitting 263 nm light or of a deuterium lamp (DL-400 W), which is used together with a grating monochromator (MDR-2, LOMO) for filtration of exciting light; iii) a luminescence recording system comprising the grating monochromator (Andor Shamrock SR-303i-B) together with the CCD camera (Andor DV 420A-BU2) or photomultiplier (Hamamatsu H7468-03). All necessary spectral corrections related to different parts of the setup are taken into account.

The following spectral characteristics were studied.

- i. Photoluminescence spectra within a spectral range 250 nm–600 nm at various fixed temperatures within the range from 8 K up to RT.
- ii. Photoluminescence spectra at RT when sample is put in different environments such as vacuum, synthetic air, nitrogen and oxygen gases.
- iii. Photoluminescence excitation (PLE) spectra within a spectral range from 190 nm up to ~400 nm and different fixed temperatures.
- iv. Luminescence kinetics at RT, which was studied using either light pulses from the forth harmonic of YAG laser RQSS266 (CryLas GmbH) with 5 ns duration emitting 266 nm or the wavelength tunable pulsed solid state laser from Ekspla NT342/3UV (pulse duration ~4 ns).
- v. Infrared (IR) absorption spectra of hBN material, which were measured on standard equipment at INFN Frascati National Laboratories, Frascati, Italy.
- vi. Spectra of optically stimulated luminescence.

## 3. Results and discussion

### 3.1. Blue luminescence spectral characterization

The PL and its excitation spectra were measured for hBN samples with different structure and origin (samples M1–M4) under condition, when the sample is in vacuum (with order of  $10^{-5}$  mbar).

The photoluminescence and its excitation spectra of the hBN powder (M1) measured at RT and 8 K, are seen in Fig. 1. A set of the PL spectra (Fig. 1a and c) is obtained exciting material with light of various wavelengths, which are shown on the right side of the pictures. It is seen that the PL spectra at RT are complex and consist of four rather well resolved sub-bands marked with dashed lines on Fig. 1a, which are situated at 361 nm (3.43 eV), 382 nm (3.25 eV, further named 380 nm band), 399 nm (3.11 eV, further named 400 nm band) and 420 nm (2.95 eV). The most intensive are the bands at 380 nm and 400 nm. At low temperatures (Fig. 1c) the same PL sub-bands are seen, which are observed at RT, but, in addition, at temperatures below 200 K a broad sub-structured luminescence around 450 nm also appears (Fig. 1c) with growing intensity, when temperature of the sample is decreased. The 450 nm luminescence of hBN has been studied more detailed in our previous work [25].

The excitation spectra for different luminescence sub-bands measured at RT and 8 K are shown in Fig. 1b and d, correspondingly. For measuring the PLE spectra the short intervals ( $\Delta\lambda \approx 15$  nm) of luminescent light were selected, which are shown at the right side of the picture. The PLE spectra are complex consisting of several sub-bands, which form three different groups located within three spectral regions labeled as I, II and III on Fig. 1b. The first group (I) forms a broad band around 205 nm, which could be related to the exciton processes [7,8] demonstrating an energy transfer from the excitons to the luminescent defects. The second group (II) of the PLE is presented by a wide band covering a spectral range from 240 nm to 290 nm, probably consisting of three individual sub-bands. The third group (III) of the PLE consists of two overlapping bands at 327 nm (3.79 eV) and 341 nm (3.64 eV). The last two groups of the PLE spectra could be related to the direct defect excitation.

From Fig. 1b and d it is seen that the structure of excitation spectra is quite similar for the luminescence sub-bands at 380 nm, 400 nm and 420 nm, whereas for the 361 nm luminescence it is different. The first three luminescence sub-bands can be excited at 327 nm and 342 nm bands belonging to the III spectral region of exciting light, whereas, the appropriate excitation bands for 361 nm luminescence are situated at 290 nm and 300 nm (Fig. 1b). It allows conclusion that the origin of the first three luminescence sub-bands can be related to one and the same type of luminescent defects, which is different from that responsible for the 361 nm luminescence. In further studies the main attention will be paid to the 380 nm, 400 nm and 420 nm PL bands, which are forming together the BL spectra.

Luminescence and its excitation spectra measured for the samples M2–M4 are found to be similar to that measured for sample M1 and demonstrated in Fig. 1. It allows conclusion, that the BL is characteristic for all of used hBN materials.

### 3.2. Phonon-assisted character of the blue luminescence

The sub-band structure of the BL spectrum (Fig. 1a, c) could be related either to phonon-induced processes or it could be caused by electronic level structure of luminescent defect. As it is known in hBN the phonon-related sub-band structure of luminescence appears in the case of exciton luminescence [2] and native defect-induced UVL around 300 nm [17,18]. It allows suggestion that the phonon-structured spectra are characteristic for this material in general. Therefore, a potential phonon-induced nature of the BL, consisting of three sub-bands at 380 nm, 400 nm and 420 nm, was considered.

As it is known, in phonon-structured luminescence spectra phonon energy is characterized by energy difference between the peak positions of two neighbor luminescence sub-bands. Therefore, from the PL spectra (Fig. 1a, c) of hBN an energy difference between peaks of two neighbor luminescence sub-bands forming the pairs at 380 nm–400 nm and 400 nm–420 nm was determined, and the average value of that energy is estimated as ~140 MeV. In the same time, an energy difference between two sub-bands from the PLE spectra peaking at 3.79 eV and

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