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## Color centers with reproducible spectral characteristics in hexagonal boron nitride (hBN) irradiated with protons

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The possibility of reproducible creation of optically active centers in hexagonal boron nitride (hBN) in the visible and near infrared ranges by irradiating hBN with high-energy protons (15 MeV) was investigated. It was shown that such irradiation leads to the appearance of a set of narrow zero-phonon lines (ZPL) with wavelengths  $\lambda_{ZPL1} = 533.3$  nm,  $\lambda_{ZPL2} = 542.6$  nm,  $\lambda_{ZPL3} = 542.6$  nm in the visible range of the micro-photoluminescence spectrum upon excitation by a laser with  $\lambda = 514$  nm and a temperature  $T = 12$  K. In this case, the zero-phonon line  $\lambda_{ZPL1}$  is also observed at room temperature with a maximum intensity at a wavelength of  $\lambda_{ZPL1} = 534.9$  nm. Along with these lines, the photoluminescence spectrum contains a band in the near IR range, corresponding to a negatively charged boron vacancy ( $V_B^-$ ).

**Keywords:** hexagonal boron nitride, color centers, micro-photoluminescence.

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### 1. Introduction

The spin and optical properties of defects in the crystal structure of hexagonal boron nitride (hBN) have recently become the object of intensive studies. This is due to the demonstration of the potential of such defects for use as sources of single photons [1–3], qubits active at room temperature [2–5], as well as quantum sensors of magnetic fields, temperature and pressure [6–9]. The recent discovery of spin-dependent luminescence of some centers in hBN is of particular interest, which provides the possibility of detecting their quantum states by optically detected magnetic resonance (ODMR) [2,3,5,9]. The latter is the basis of their applicability to qubits and quantum sensors.

One of the main tasks for the further successful development of this field is the development of methods for reproducible generation of fluorescent defects, which is necessary for their unambiguous identification, study and further use. It is also necessary to accumulate a set of data allowing for a correlation between the type of created defect and the impurity that generates it. This fact is well illustrated in Ref. [10,11], which demonstrated a direct correlation between the presence of a number of optically active defects in the visible and near-infrared ranges in hBN and impurity carbon. The need for reproducibility of the creation of one or another type of centers with specified optical and spin characteristics is well illustrated in Ref. [2,3,5,9]. Single defects based on carbon impurity in hBN samples grown by organometallic gas-phase epitaxy were studied in Ref. [2]. Changing of the impurity carbon

concentration during growth made it possible to create a set of single defects with a distribution of a phononless luminescence line (PL) in the spectral range from 2.05 to 2.17 eV, the authors of the article associate this fact with the presence of carbon clusters or carbon-oxygen clusters. The spin-dependency of the PL of these defects is their important characteristic which made it possible to observe ODMR spectra at room temperature. The latter opens up opportunities for their use for spin-photon interfaces and quantum sensors. However, it is necessary to be able to create them in a controlled manner for exploiting these defects and determining their real structure. This statement is well illustrated in Ref. [3,5]. In particular, the authors of article [5], studied nanoscale ( $\approx 70$  nm) flakes of hBN annealed at  $T = 1000^\circ\text{C}$  in vacuum for 1 h. As a result, the authors observed a number of single defects with spin-dependent PL and phononless lines in the range of  $540 \pm 10$  nm. Obviously, it is difficult to use such a method to create optically active defects with reproducible characteristics.

Currently, it is possible to determine unambiguously the structure and spin properties of only one optically active defect, which is a negatively charged boron vacancy ( $V_B^-$ ) in hBN [9,12,13]. This made it possible to create methods for reproducible generation of this type of center by irradiating hBN crystals with high-energy particles and short laser pulses [6,12,14–16], which allowed for conducting further detailed studies of the properties of  $V_B^-$  centers and use them to create quantum sensors, qubits [4,6–8,17]. It follows from the above that the task of finding methods

for reproducible creation of fluorescent defects in hBN is relevant.

## 2. Experimental part

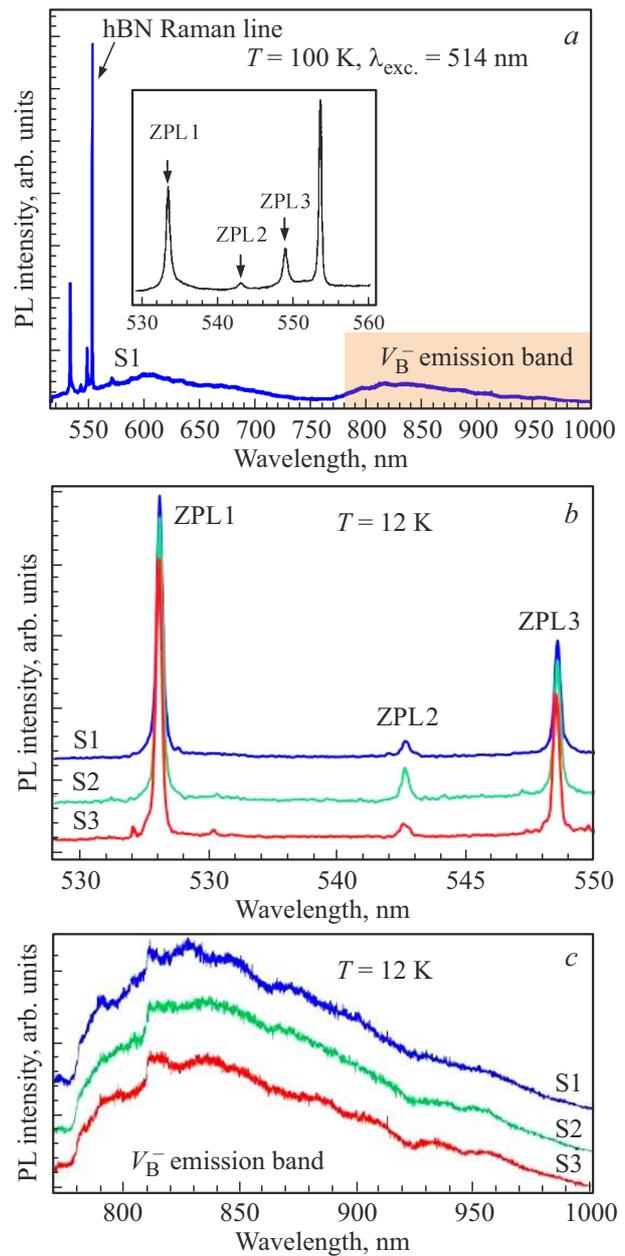
Three samples of single-crystal hBN (S1, S2, S3) fabricated by „hq Graphene“ with the size of  $\approx 1.5 \times 1.5 \times 0.1$  mm, irradiated by protons with energy  $E_p = 15$  MeV and a total dose of  $1 \cdot 10^{16} \text{ cm}^{-2}$  were investigated. After irradiation samples S1, S2 and S3 were studied by micro-photoluminescence ( $\mu$ -PL) method for detection of defects created as a result of radiation exposure. The  $\mu$ -PL experiments were conducted using T64000 spectrometer (Horiba Jobin-Yvon, Lille, France) with a confocal microscope and a silicon CCD matrix cooled to the liquid nitrogen temperature. The line  $\lambda = 514$  nm (2.4124 eV) was used to excite the PL. The PL spectra were recorded using 600 grooves/mm diffraction grating. RC-102 closed-cycle cryostatic system (Cryo Inc., USA) was used to study the temperature dependence of the PL spectra.

## 3. Results and discussion

Figure 1, *a* shows the low-temperature  $\mu$ -PL spectrum of the hBN S1 sample after proton irradiation. Except for the intense Raman line, indicated in Figure 1 as the hBN Raman line, the spectrum contains a number of phononless lines designated as ZPL1, ZPL2 and ZPL3. In addition to these spectral lines, a wide band is observed in the near-infrared range (770–1000 nm) corresponding to the boron vacancy PL in the negative charge state ( $V_B^-$ ), as it was established in Ref. [9,14,16,18] using correlated photoluminescence, electron paramagnetic resonance and ODMR data.

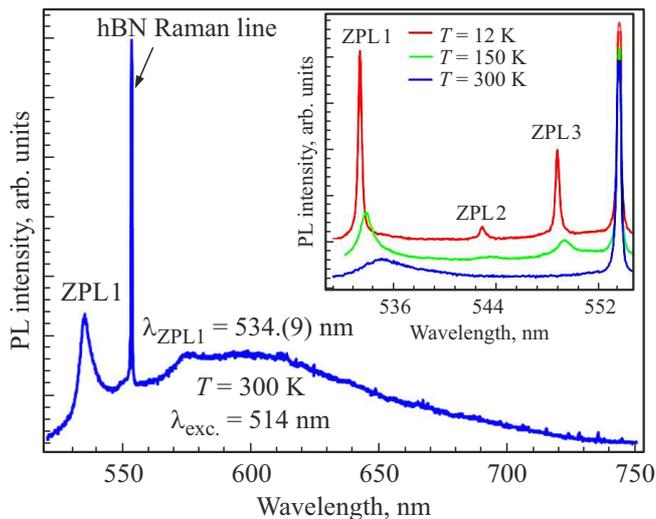
It is important to note that phononless lines from the ZPL1–ZPL3 family were presumably observed in Ref. [5,19]. As it was shown in Ref. [5], defects with these intracenter transitions can be isolated at the level of single defects demonstrating ODMR at room temperature. However, it is not possible to establish an unambiguous correspondence of the spectra between the ones we observed and those given in Ref. [5,19], since the results of experiments performed at room temperature are presented in Ref. [5,19]. It is worth noting that the nature and structure of these defects have not been reliably established. It was suggested in Ref. [19] that localized excitons trapped on isoelectronic defects are sources of this PL, however, there is no unambiguous identification of the nature of these centers yet.

We studied a series of commercially available hBN samples irradiated by protons under the same conditions for studying the reproducibility of the creation of these defects (samples S1, S2, S3). So,  $\mu$ -PL spectra recorded at a temperature of 12 K are shown in Figures 1, *b* and 1, *c*. It can be seen from the spectra that both the set of phononless lines ZPL1–ZPL3 and the presence of a band from boron



**Figure 1.** (a)  $\mu$ -PL spectrum of the proton-irradiated sample S1 in a wide wavelength range. The spectrum was recorded with excitation by laser  $\lambda = 514$  nm and at temperature of  $T = 100$  K. The insert shows the phononless lines ZPL1, ZPL2, ZPL3 at an enlarged scale. The inset on the right shows a part of the spectrum in the near-infrared range on an enlarged scale, corresponding to the fluorescence of  $V_B^-$  centers. (b, c) The  $\mu$ -PL spectra of samples S1, S2, S3, recorded with excitation by laser  $\lambda = 514$  nm and at temperature  $T = 12$  K. Wavelengths corresponding to the maxima of phononless lines:  $\lambda_{ZPL1} = 533.3$  nm,  $\lambda_{ZPL2} = 542.6$  nm,  $\lambda_{ZPL3} = 548.5$  nm. The spectra are shifted vertically for clarity.

vacancies are preserved from sample to sample. This suggests that proton irradiation makes it possible to create defects belonging to the ZPL1–ZPL3 and  $k V_B^-$  family in a reproducible manner.



**Figure 2.**  $\mu$ -PL spectrum of the hBN S1 sample, recorded at a temperature of  $T = 300$  K, excited by laser  $\lambda = 514$  nm. The insert shows the dependence of the intensities and positions of the ZPL1–ZPL3 lines on temperature.

Next, the dependences of the position and intensity of the ZPL1–ZPL3 lines on temperature were studied for determining the possibility of their observation at room temperature and for detecting the presence of a temperature shift in the positions of the lines. Figure 2 shows the  $\mu$ -PL spectrum recorded at  $T = 300$  K. It can be seen that the spectrum consists of a temperature-widened ZPL1 line and a wide wing of phonon repeats of low intensity. The temperature dependence shown in the box in Figure 2 clearly demonstrates that the entire three lines undergo a shift and broadening with increasing temperature. The lines ZPL2 and ZPL3 are practically not observed already at a temperature of 150 K, and only the ZPL1 line is observed up to room temperature with a maximum shifted by the wavelength of  $\lambda_{\text{ZPL1}} = 534.9$  nm. This type of spectrum, which demonstrates a phononless line at room temperature, is of considerable interest for further study, as it opens up the opportunity for recording ODMR at room temperature and for further use in quantum sensors and as a qubit.

## 4. Conclusion

The study found that irradiation of hexagonal boron nitride with high-energy protons (15 meV) makes possible the reproducible creation of optically active defects in both the visible and near infrared ranges. Three narrow phononless lines (ZPL1–ZPL3) with wavelengths in the visible spectral region were observed. The position and intensity of these ZPLs depend on temperature, namely: an increase in temperature results in a broadening and shift of all three ZPLs. Nevertheless, one phononless line with a maximum at 534.9 nm is clearly observed even at room temperature. The results published earlier

in Ref. [5] suggest the potential possibility of registering ODMR on a defect with a phononless ZPL1 line. Thus, the created color centers can be used in various quantum technologies. The obtained results confirm the stability of the spectral characteristics of the created centers and open up prospects for the use of such defects in quantum sensors and single photon sources. Moreover, a band corresponding to a negatively charged boron vacancy is reproducibly observed in the near-infrared range. Boron vacancies are considered to be one of the key defects in hBN that have special spin and optical properties, which makes them promising for use in quantum sensors and other quantum devices. This highlights the importance and applicability of the proton irradiation method for creating specified color centers in hBN.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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