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# Application of hexagonal boron nitride micropowder for thermoluminescent dosimetry of UV radiation

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## HIGHLIGHTS

- Thermoluminescence (TL) response of h-BN micropowder after ultraviolet irradiation was studied.
- TL excitation spectra within the 200–380-nm range were analyzed.
- Participation of $V_N$, $O_N$, and $C_N$ centers in the TL mechanisms was assumed.
- Linear behavior of TL response of h-BN in the suberythemal UV dose range was shown.

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## ABSTRACT

Thermoluminescence (TL) response of h-BN micropowder, characterized by two peaks near 337 and 584 K, was studied in the 380-nm band after excitation with monochromatic ultraviolet radiation (UVR). On the basis of the obtained results and independent data analysis, assumptions were made on the mechanisms of donor–acceptor recombination with the participation of 1B, $O_N$, and $C_N$ centers, responsible for the observed thermally activated emission. TL excitation spectra in the 200–380-nm range were analyzed. It was observed that the resolved maxima correspond quite to the characteristic wavelengths of 260 nm (maximum bactericidal efficiency) and 297 nm (maximum skin erythema). It is found that the dose dependence for an integral intensity of high-temperature peak is linear in the suberythemal range of 0.01–0.35 mJ/cm$^2$.



## 1. Introduction

Detection of ultraviolet radiation (UVR) is an actual task due to its increasing use in different fields, including modern human activity and health care such as therapy and disinfection (Eischeid et al., 2009; Hijnen et al., 2006; Honigsmann, 2013). Biological effects of UVR vary enormously with wavelength. For example, the absorbance of DNA reaches a maximum at around 260 nm and then decreases. It increases again below 230 nm, which corresponds to the UVC radiation (100–280 nm) (Eischeid et al., 2009; Hijnen et al., 2006). At the same time, the value of relative spectral effectiveness for erythema has a maximum at 297 nm corresponding to the UVB range (290–320 nm) (Diffey and McKinlay, 1983). It is known that UVA radiation (320–400 nm) can penetrate deeper into the skin and reach the dermis and hypodermis layers, thus releasing free radicals and causing mutations in the DNA. Hence, it is necessary to develop compact, radiation-resistant, low-cost narrowband dosimeters of high sensitivity and storage capacity.

The non-toxic nature, high temperature and chemical stability, and wide band gap ($E_g \geq 5.5$ eV) of hexagonal boron nitride (h-BN) enhance its potential application in UVR solid-state dosimetry (Katzir et al., 1975; Weinstein et al., 2013). We had previously shown that thermoluminescence (TL) response above room temperature (RT) of UV-irradiated h-BN is characterized by multiple temperature peaks in different emission bands such as 330, 380, and 425 nm (Vokhmintsev et al., 2015). In addition, it was demonstrated that the stand-alone peak at 575 K in the 380-nm band shows the maximum intensity and could be used for dosimetric purposes (Vokhmintsev et al., 2015; Weinstein et al., 2013). Therefore, the goal of the study is to analyze dose dependencies for thermally stimulated luminescence characteristics in h-BN micropowder under monochromatic UV irradiation.

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## 2. Samples and technique

The h-BN under study was synthesized using the modified O'Conner technique (Nechepurenko et al., 2005) and was provided by FSUC « UNICHIM & EP». The powder had an average particle size of 7 ± 3 μm (see Fig. 1 inset). According to the manufacturer's datasheet, the carbon concentration in the samples under study did not exceed 0.38 wt.% (Nechepurenko et al., 2005).

To confirm the hexagonal structure of powder under study the Raman spectra were measured using a Leica DM/LM optical microscope (Leica Microsystems, Germany/Switzerland) and Renishaw U1000 (Renishaw plc, UK). A laser with a mean power of 150 mW at a wavelength of 532 nm served as the excitation source. The laser beam spot diameter on the sample surface was 1 μm. Fig. 1 shows Raman spectrum of h-BN in the wavenumber range of interest. The observed peak near 1366 $cm^{-1}$ with full width at half maximum FWHM = 9 $cm^{-1}$ is attributed to the B–N vibrational mode ($E_{2g}$) within the h-BN layers (Bergman and Nemanich, 1996; Wu et al., 2004).

TL experiments were performed using a Perkin–Elmer LS 55 spectrometer equipped with a developed high-temperature accessory in the temperature range of RT to 750 K (Vokhmintsev et al., 2014). The TL excitation spectrum was recorded in the 380-nm band after monochromatic UV irradiation using a Xe lamp for 5 min in $\lambda_{ex}$ = 200–380 nm range at 10-nm slit and with 5-nm step. Under the given irradiation conditions the emission spectrum intensity of Xe source changes slightly when $\lambda_{ex} \geq 225$ nm (5.51 eV). In this regard the obtained TL excitation spectrum was not normalized to the emission spectrum of the Xe lamp. The heating rate during the measurements was 2 K/s.

Dose dependencies of the TL response were analyzed in the 380-nm emission band after monochromatic UV irradiation at 260 nm (maximum bactericidal efficiency) (Eischeid et al., 2009) and 297 nm (maximum skin erythema) (Diffey and McKinlay, 1983). The experimental TL response glow curves were estimated in the 430–700 K temperature range. The UV dose was measured using an Optronics Ophir Vega power meter with a PD300UV photodiode sensor and it varied in the dose range $D$ = 0.003–22.4 mJ/$cm^2$. It was altered by changing the irradiation time of the sample from 5 s to 10 min.

## 3. Results and discussion

Fig. 2 shows the experimental TL curves for the samples under study. It is observed that the glow curves comprise two TL peaks. Low-temperature peak (P1) with halfwidth of $\omega_T$ = 29 K shows maximum intensity at $T_{max}$ = 337 K and under irradiation of $\lambda_{ex}$ = 230 nm. High-temperature TL peak (P2) has $\omega_T$ = 73 K at $T_{max}$ = 584 K and $\lambda_{ex}$ = 260 nm, respectively. So P2 peak is ≈ 3 times more intensive and ≈2.5 times wider. It is worth to mention that under the increment of $\lambda_{ex}$ peak P1 position rests stable – $T_{max}$ = 339 ± 3 K, while for peak P2 a high temperature shift within the 582–600 K band is registered. In this case, it is possible to discuss the presence of at least two types of the traps with discrete and quasi-simultaneous level distribution responsible for the formation of P1 and P2 peaks, respectively. Besides that, P1 and P2 peaks are also recorded at $\lambda_{ex}$ = 200 nm.

It is worth mentioning that the presence of TL response under irradiation with photons with $E_{ex} \geq E_g$ indicates the mechanism of filling of traps (both electron and hole types) following charge carrier separation upon interband excitation. Conversely, more intense TL at P2 upon excitation with $E_{ex} < E_g$ indicates effective mechanisms of direct redistribution of localized carriers between the levels within the forbidden gap.

In previous studies (Weinstein et al., 2013), P1 peak in the 380-nm band was not observed under the irradiation of h-BN micropowder with unfiltered UVR from the Xe source. Apparently, this fact indicates emptying of shallow traps, responsible for P1 peak, directly during the exposure. In this connection, P1 peak is supposed to be very unstable at ambient temperatures and demonstrate high fading. According to independent studies (Katzir et al., 1975; Ohtani et al., 2013), the observed P1 peak can be attributed to the presence of $O_N$ trapping centers, which are formed by oxygen impurities in the vacant nitrogen sites and have a depth of 0.3–0.5 eV. Conversely, the presence of anion vacancy-based $V_N$ traps – the so-called 1B-centers with 0.7-eV depth – is responsible for the appearance of P2 peak (Katzir et al., 1975; Zhang et al., 2014). At the same time, TL recorded in the 380-nm (3.26 eV) band is attributed to the donor–acceptor recombination between 1B and $C_N$ centers (carbon impurities in nitrogen sites), responsible for thermally activated emission. The $C_N$ centers actively accept holes and demonstrate energy levels of 4.1 eV, relatively less than the reference level in the bottom of conduction band (Du et al., 2015;

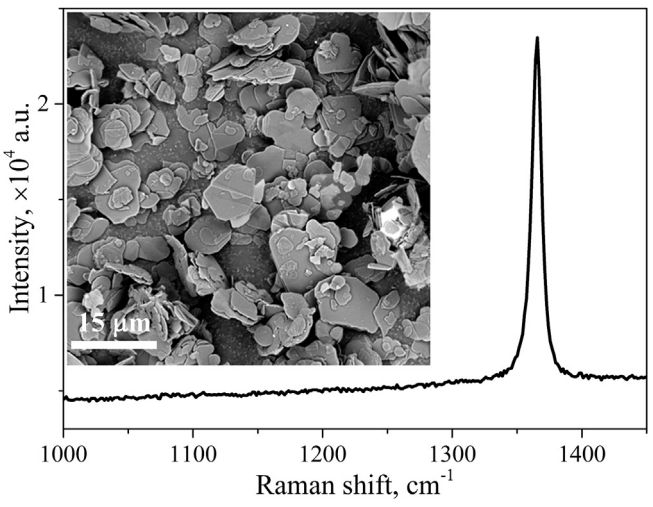


**Fig. 1.** Raman spectrum and SEM image (inset) of h-BN micropowder.

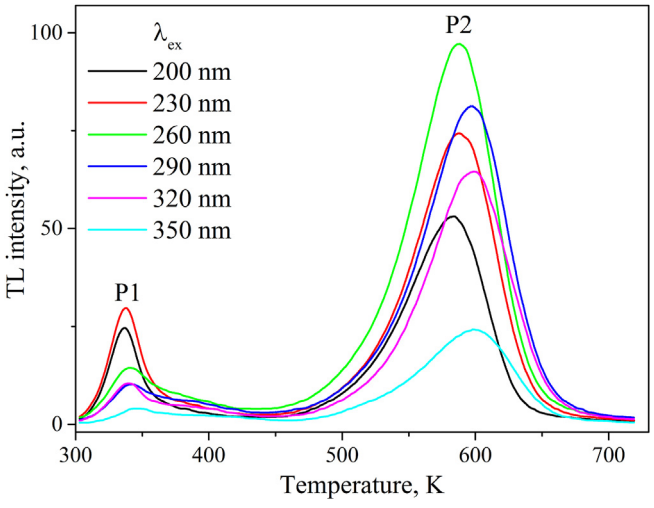


**Fig. 2.** Experimental TL curves of h-BN micropowder irradiated by monochromatic UVR at different wavelengths.