Detection and study of polarized pulsed photoluminescence of diamonds for mapping of natural diamond

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Abstract. The bulk mapping of natural diamond poses problems where it is required to characterize various defects and measure their optical properties in volume. The combination of photoluminescence spectroscopy methods and methods for detecting the state of polarization in the volume will expand the functionality for mapping natural and artificial diamonds. The implemented methods will be an effective tool for the structural description of diamond optical centers.

1. Introduction
In the development of spectroscopy of solid media, the transition from studying only the scalar characteristics of radiation – phase and intensity – to studying them together with the vector properties of radiation, which find their expression in the state of polarization of radiation, is quite natural. Existing methods allow measuring only the final state of polarization at the output from the medium under study. At the same time, when the conditions of the problem require measuring the state of polarization not only at the output, but also inside the medium \cite{1, 2}, one can use the apparatus of the intensity transfer equation taking into account the state of polarization. This direction has been developing over the past several decades and allows one to calculate not only the amplitude and phase of radiation, at any point in space, but also to take into account the state of polarization \cite{3, 4}. Several techniques were developed for numerical simulation of radiation transfer in an inhomogeneous flat layer of finite thickness containing a single or multicomponent mixture of substances \cite{5}. Also, research was carried out on the solution of the inverse problem for the stationary vector equation of the transfer of polarized radiation in an isotropic medium. The proposed approach has demonstrated the advantages of the algorithm when using a vector equation over a method corresponding to the scalar model \cite{6}.

The disadvantage of these works is that they considered isotropic media or an inhomogeneous mixture of isotropic substances. A separate scientific interest is the mapping of natural diamond defects, where the definite knowledge of the state of polarization at each point in space will allow to describe the complete picture of the defects or in other words to do the mapping of the crystal.
At the same time, luminescence is a widely known and applied method for detecting various defects and numerous optically active impurities in diamonds [7]. Typically, such methods are highly efficient x-ray luminescence or photoluminescence (PL) are used. The latter provides excitation with a wide tuning spectrum, with Stokes radiation shifter into the red part of the spectrum with width of 200‒300 nm [8]. In the PL spectra, the zero-phonon line is usually the most noticeable (intensity wise), while the following Stokes phonon repetitions have a much lower intensity [9]. The form and positions in spectra of the zero-phonon line and phonon repetitions allow one to determine the nature of the various defects and optical centers in diamond.

Thus, the combination of these two methods: polarization measurements and luminescence, will expand and complement the already existing methods for mapping natural and artificial diamonds. This article proposes a method for measuring the polarized luminescence spectra of optical cents in a diamond for the purpose of its bulk three-dimensional mapping.

2. Experimental studies and discussion
The study of the dependence of the luminescence spectrum of natural diamond on the state of polarization was carried out on an optical stand, which included a laser with ultrashort laser pulses (figure 1).

As monochromatic source of laser radiation to excite the photoluminescence a diode-pumped femtosecond laser was used. It provides radiation at two harmonics with the main line $\lambda_1 = 1050$ nm and second harmonics at $\lambda_2 = 525$ nm. The duration of the pulses was 150 fs with a repetition rate of 80 MHz. A micro objective with numerical aperture NA = 0.25 was used to focus the ultrashort pulses into the bulk of the diamond. The waist at an energy $1/e^2$ level was $\sim 4.4$ μm. The PL image was visualized perpendicular to the ultra short pulse propagation axis using a quartz/fluorite micro objective with a numerical aperture NA = 0.2 and a monochrome camera CS2100M-USB (CMOS camera with pixel size of 5.04 μm and dynamic range up to 87 dB). The PL analysis was performed using an ASP-150F broadband spectrometer. The image of the luminescent region of the diamond was projected on to the entrance slit of the spectrometer. For polarization analysis, a linear polarizer (with effective band at 360‒700 nm with extinction ratio > 1000:1) was installed between the quartz/fluorite micro objective and the spectrometer on a motorized circular translator of displacements.

The dependence of the PL intensity spectrum on the pump radiation power is shown in figure 2(a). Figure 2(b) shows the cross-section of the PL intensity spectra at 440 nm. This dependence can be approximated by two polynomials of the first degree (linear function) in two sections with the power of the slopes equal 1 and 3, respectively. The discrepancy between experimental data and the approximation is less than 1%. Such dependences show that the process of the carrier generation
changes from one photon to multiphoton with an increase in pulse power [10]. The values of the PL intensity spectrum in figure 2 are measured without a linear radiation polarizer in the scheme.

![Figure 2](image.png)

**Figure 2.** PL intensity spectrum on the pump radiation (a), cross-section of the PL intensity spectra at 440 nm (b).

In view of the specific features of the selected linear polarizer, namely, the radiation transmittance and extinction coefficient at the selected wavelengths, the study of the PL intensity from the state of polarization was carried out at a maximum achievable energy of ~ 0.069 µJ. In each measurement of the PL spectrum, the linear polarizer was rotated at an angle of 30°±0.1°. Figure 3 shows two-dimensional PL intensity images obtained with a CMOS camera with an objective. Figure 3(a) shows an isometric projection of the PL intensity, and figure 3(b) shows a top view of the PL intensity.

![Figure 3](image.png)

**Figure 3.** 2D dimensional PL intensity images: isometric view of the PL intensity (a), top view of the PL intensity (b), the cross sections of the PL intensity maxima along the x (c), y axes for several polarization states, respectively (d).
Figures 3(c) and 3(d) show cross sections of the PL intensity maxima along the x and y axes for several polarization states, respectively. It can be seen from the figures that, depending on the state of polarization, insignificant changes in the PL intensity occur, as well as the shape of the PL itself. The PL intensity spectra depending on the polarization state are shown in figure 4(a).

![Figure 4](image)

**Figure 4.** The dependence of the PL intensity spectrum on the polarization state (a), the dependence of the PL intensity maxima on the azimuth of polarization (b).

From figure 4(a) it can be seen that the shape of the PL intensity spectrum after introducing the linear polarizer into installation in the observation scheme changed greatly (in comparison to figure 2(a)). The polarizer “smoothed” the spectrum, as a result of which the local maxima of the PL spectrum disappeared, while the global maximum remained. At the same time, the position of the global maximum remained unchanged. This change is associated with the transmittance of the radiation of the polarizer itself, which is ~ 30%. As a result of a series of 12 experiments, the dependence of the PL spectrum on the polarization azimuth was obtained, the form of which is shown in figure 4(b). From the figure 4(b) one can see that the function describing the dependence has a harmonic form (sin), which corresponds to the cyclic nature of the change in the state of polarization. In this case, the change in the PL intensity spectrum at antiphase points is ~ 7%. Also we can say that the PL is partially polarized from figure 4(b). More thorough study of the polarization resolved PL spectrum will allow more precise mapping of the various defects and optical active centers in diamond and other crystals.

### 3. Conclusion
Optical methods, such as photoluminescence, IR spectroscopy, Raman spectroscopy, remain as the most effective tools for characterization of the diamonds. Polarization resolved photoluminescence can become a powerful tool that will help and expand already existing diamond mapping methods. Ultra short pulses, which can be tuned not only in wavelength, duration and energy, but also in the state of the polarization will allow fine mapping of the crystals inner structure and its full characterization.

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