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Temperature features of ultraviolet photoluminescence of Gd^{3+} ions in a quartz glass matrix used for the synthesis of optical fibers

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The article presents the results of the study of the temperature behavior of the ultraviolet photoluminescence (PL) band at 315 nm for Gd^{3+} ions in the matrix of quartz glass preforms synthesized by plasma chemistry, which are used for drawing optic fibers. It is shown how the shape and intensity of the PL band change when the glass sample is heated in the temperature range of 5−500 K. The mechanism of temperature change in the PL decay kinetics in the range of 83−500 K is presented. A hypothesis explaining the PL quenching mechanism is put forward.

Keywords: quartz glass workpieces, optical fibers, UV luminescence band, Gd^{3+} ions, PL decay time, temperature behavior of the band, activation energy.

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Recently the quartz glasses doped with Gd^{3+} ions and optical fibers on their basis attract more and more attention of the researchers in connection with the discovered opportunities of using short-wave photoluminescence (PL) of these ions to develop new UV-laser sources (see paper [1] and references therein), sensor devices to record synchrotron, X-ray and proton radiation in various setups used in the current approaches in material science, bio- and chemical technology and in space and nuclear industry [2–6]. In most cases it is the emerging effect of radio luminescence [7] with an emission band at 312−315 nm in such matrices is the foundation for development of such sensor devices. Since monitoring using light guides based on quartz glass with Gd^{3+} ions may occur in various conditions, such as the highly radioactive area of a nuclear reactor or outer space, the need to do temperature research for this PL band in these matrices becomes evident. Moreover, recent experiments on the crystalline structures with Gd^{3+} ions within their use for thermometry [8] indicated the feasibility of doing such measurements of UV-band intensity in other matrices as well.

The specimens of preforms to draw optical fibers were synthesized in Institute of Radio Technologies and Electronics of the Russian Academy of Science by the modified plasma-chemical method (so called SPCVD-method [9]). The doped quartz glass of the fiberoptic core was synthesized from a mix of silicon and gadolinium chloride vapors in the oxygen atmosphere at pressure of 1 Torr. The fluorine-doped quartz glass of the light-reflecting shell was synthesized from the silicon tetrachloride vapors in O_2 atmosphere with addition of CF_4. The preforms produced in this manner contained around 0.12 at.% gadolinium [1]. Note that this method of synthesis seems to be more progressive compared to the sol-gel-method, which was earlier used mostly to synthesize such preforms with gadolinium (see for example [5,7]).

PL spectra measurements in UV-area and kinetic measurements of its decay in a wide temperature range from 5 to 500 K were carried out in a specialized setup located in the Institute of Physics of the University of Tartu (Estonia). PL spectra excited in VUV-range were measured using deuterium discharge lamp Hamamatsu L11798 as a source of excitation and vacuum monochromator McPherson 234/302 at spectral bandwidth of the slit 16 nm. The specimen was installed in the closed cycle helium cryostat by ARS. Luminescence spectra were recorded using secondary monochromator-spectrograph Shamrock 303i (Andor Technology), equipped with a head to count photons Hamamatsu H8259, and with a CCD-detector.

Kinetics of PL decay were also measured at 315 nm using a specialized setup, which included a pulse xenon lamp as a source of PL excitation and prism monochromator DMR-4. The specimen was placed into vacuum optical nitrogen cryostat Janis VPF-800, temperature monitoring and control were done using controller LakeShore 335. PL kinetics was recorded by photon count head Hamamatsu H8259, connected to multi-channel time counter Ortec MCS-PCI Card with resolution of 2 μs.

In PL spectra of preforms measured in the temperature range of 5−300 K, a PL band was observed with maximum at 315 nm (fig. 1), related to the intracenter transition $^6P_{7/2}$−$^8S_{7/2}$ in Gd^{3+} ions[10]. Besides, additional bands are seen at the short-wave side from the main peak, and their intensity increases as temperature rises. This is probably due to thermal filling of the above sublevels of gadolinium $^6P_{7/2}$ term, arising as a result of term splitting by the electric field of the short-range order. Similar effect is described in [8] for a case of certain crystalline structures doped with Gd^{3+} ions. As specimen temperature decreases from 300 to 5 K, the intensity in the maximum of the main peak increases approximately 5 times, and additional higher energy components of the spectrum disappear when this happens. Integral intensity of PL, as specimen temperature rises from 5 to 50 K, decreases by 40 %, and is then stabilized up to 200 K, and as temperature increases further from 200 to 300 K, a drop of another 10 % is observed (fig. 2).

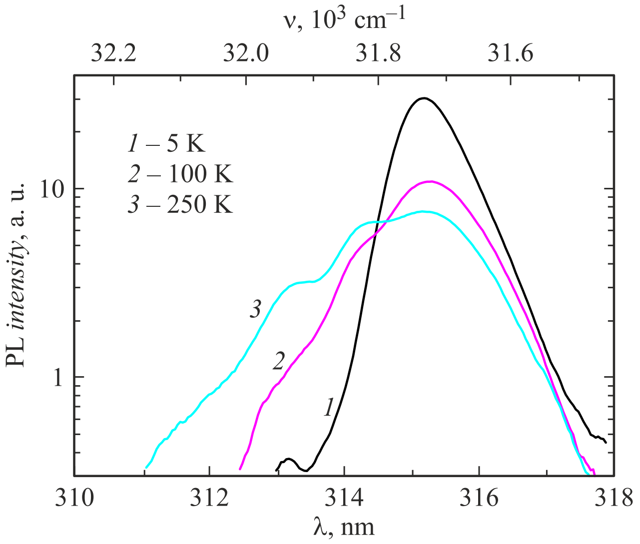

Figure 1. PL spectra at three specimen temperatures. Spectral bandwidth of the slit is 0.13 nm. Excitation wavelength is 150 nm.

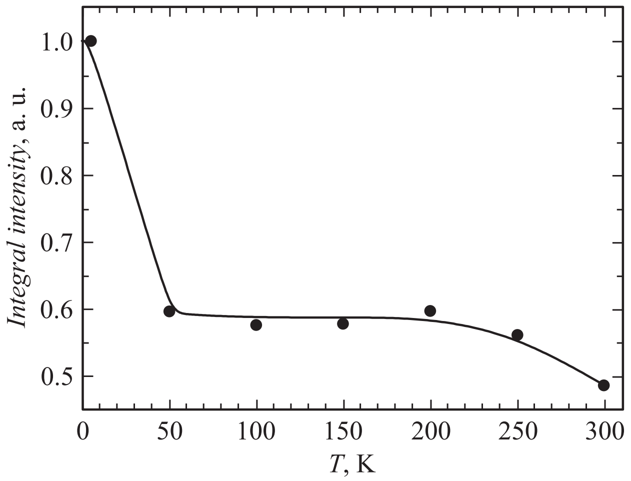

Figure 2. Temperature dependence of integral intensity of PL band of Gd^{3+} ions in preform for optical fibers. Excitation wavelength is 150 nm.

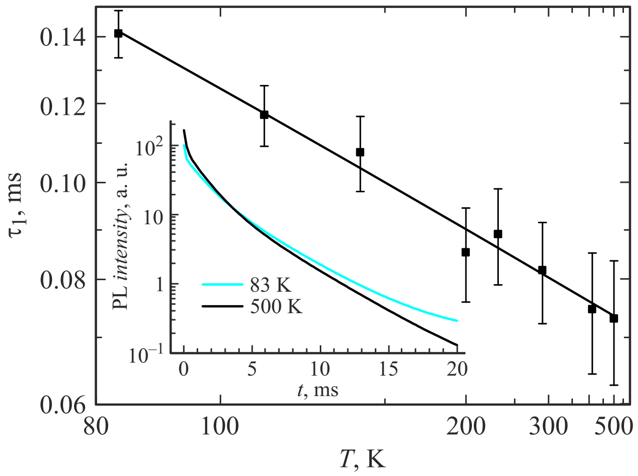

Figure 3. Temperature dependence of time constant for one of components of PL kinetics of Gd^{3+} ions at wavelength of 315 nm. The insert presents PL kinetics for two temperatures.

Fig. 3 presents the results of analysis of the temperature behavior of luminescence kinetics for 315 nm band in the temperature range from 83 to 500 K as transition Gd^{3+} $^8S_{7/2}$–^6I_J is excited at wavelength of 274 nm. The insert to the figure for two temperatures shows kinetics of PL band 315 nm of Gd^{3+} ions. All measured kinetics for the temperature range of 83–500 K were approximated by superposition of three exponents:

$$y = y_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3).$$

At room temperature the components have times constant of 3.4, 1.2 and 0.077 ms. Two components with the times constant of 3.4 and 1.2 ms are present in the kinetics for all temperature points, and the time constant for the third component (the fastest one) varies from 0.077 to 0.138 ms as temperature decreases from 500 to 83 K (points in fig. 3). Note that previously the kinetics of PL decay in 315 nm band for the optical fibers synthesized from such preforms by authors [1] was approximated by Kohlrausch function with time constant of 1.2 ms. Kohlrausch function [11] makes it possible to model a kinetic curve for the systems with a distributed parameter, such as glasses, however, it will not allow analysis of which part of this distribution is most subjected to temperature changes. In our case due to the above model of superposition of three exponents it was possible to demonstrate that the shortest-lived part of this superposition was most subjected to temperature changes. The temperature dependence of the specific relaxation time of this short-lived component in the assumption that the quenching process may be described by the Mott formula $1/\tau_1(T) = 1/\tau_1(0) + \exp(-E_A/kT)/\tau_1(\infty)$ served as the basis to generate the activation energy of E_A process of 6.1 meV. Such process is most probably compliant with the transmission of energy from the excited gadolinium ion to the quenching centers in the core glass, the nature of which is not yet finalized. One of the possible candidates for the role of such quenching centers may be the clusters of Gd^{3+} ions in the lattice of the preform core glass, which may be formed in the process of plasma-chemical synthesis [9]. The presence of such cluster formations in the preform glass is indirectly indicated by a blue tint observed visually when it is viewed. Such tint may be caused by the formation of the submicron-scale scattering centers in process of plasmachemical synthesis of the glass. Such cluster formations with the increased local concentration of rare-earth ions may well demonstrate the quenching effects [12].

Temperature dependence of the integral intensity of PL (fig. 2) may not be analyzed as simply as it was done for kinetic parameters, since it reflects both the processes of deactivation (quenching) excited state $^6P_{7/2}$ and the processes that impact the filling of the level by photoexcitation Gd^{3+}. Activation dependence compliant with the specific relaxation time of the short-lived component in the PL kinetics contributes somewhat to the intensity of the entire PL band, since the share of the short-lived component in the kinetics (product of the amplitude and time constant for this component vs. the integral of the entire curve) is from 6 to 1.5 % for temperatures of 83 and 500 K.

Therefore, we found that the PL intensity with 315 nm band for Gd^{3+} ions in the preforms decreased as temperature increased in the range from 80 to 500 K by not more than 20 %, and these changes are not related to the quenching of level $^6P_{7/2}$ Gd^{3+}.

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Conflict of interest

The authors declare that they have no conflict of interest.

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