Investigation of the Cr^{3+} impurity luminescence in proton-irradiated β-Ga$_2$O$_3$

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Proton irradiation of β-Ga$_2$O$_3$ crystals has been established to lead to a significant increase in the amount of Cr^{3+} ions being active in luminescence. Using angle-resolved luminescence, the features of the spectra of Cr^{3+} ions were studied. The high sensitivity of photoluminescence spectra and the related selection rules to the local symmetry of Cr^{3+} ions in the β-Ga$_2$O$_3$ matrix has been found. The results obtained indicate the potential possibility of using β-Ga$_2$O$_3$ crystals as optical dosimeters of proton irradiation.

Keywords: β-Ga$_2$O$_3$, α-Ga$_2$O$_3$, proton irradiation, photoluminescence, symmetry analysis.

Polytype β-Ga$_2$O$_3$ with a band gap width of ~ 4.9 eV possesses electronic and electrophysical properties that are promising for use in UV detectors, high-temperature gas sensors, nanophotonic switches, etc. e.There is quite a considerable amount of research devoted to studying the effects of radiation exposure on β-Ga$_2$O$_3$ oxide-based devices (see, for example, the review [1] and references therein). However, many questions related to the influence of radiation exposure on the nature of impurity states and structural defects in this material have not been sufficiently studied. The aim of the present study was to obtain new information on the possibility of using electron and proton irradiation for controlled change of the charge state of impurities in hboxβ-Ga$_2$O$_3$ in order to identify them by optical methods.

Initially undoped and chromium-doped bulk crystals β-Ga$_2$O$_3$, grown by the Czochralsky [2] method and epitaxial layers α-Ga$_2$O$_3$: Cr, grown on Al$_2$O$_3$ (0001) substrate by chloride-hydride epitaxy were studied. Unalloyed β-Ga$_2$O$_3$ crystals were irradiated with electrons at energies of 0. 9 MeV doses $2.0 \cdot 10^{16}$ and $5.0 \cdot 10^{16}$ cm^{-2} at the electron accelerator RTE-1V and protons with energy 15 MeV dose $1.0 \cdot 10^{16}$ cm^{-2} at the isochron cyclotron MGC-20 in SPbPU named after Peter the Great. The vibrational and electronic characteristics of crystals by micro-combination light scattering (μ-RS) and micro-photoluminescence (μ-PL) were measured using a LabRAM HREvo UV-VIS-NIR-Open spectrometer (Horiba, France). $\lambda = 532$ nm (2.33 eV) Nd : YAG-laser line was used to excite the μ-RS spectra. Angle-resolved μ-PL spectra over a temperature range

(80−300 K) were measured using a wide range of excitation radiation energies (2.33−5.82 eV).

μ-QW studies confirmed that bulk unalloyed and Cr of samples Ga$_2$O$_3$ samples belong to the β- polytype, and epitaxial layers of Ga$_2$O$_3$: Cr/Al$_2$O$_3$ — to α-E polytype. No noticeable changes were found in the μ-RS spectra of samples irradiated with electrons or protons compared to the spectra of the original samples. Also, no noticeable changes were found in the μ-PL spectra of the electron-irradiated samples. However, the μ-PL spectrum of the proton-irradiated sample β-Ga$_2$O$_3$ was significantly different from that of the non-irradiated sample.

The μ-PL spectra of unirradiated, proton-irradiated and chromium-doped samples β-Ga$_2$O$_3$, measured at room temperature and $T = 80$ K are shown in Figure 1. In all spectra, a broad band with a maximum at ~ 3.25 eV is observed in the UV band, the parameters of which depend weakly on the type of the investigated sample. This feature has been reported in works related to studies of the PL spectra of β-Ga$_2$O$_3$, crystals grown by different methods [3–5]. In most cases, this band is decomposed into three components: ultraviolet (UV), blue (BL), and green (GR). The UV component is generally independent of impurities and is attributed to the recombination of free electrons and autolocalized holes. The GR component was attributed to donor-acceptor pair transitions involving deep donors and deep acceptors. As for the GR component, the nature of its origin needs further research.

As can be seen in Figure 1, the spectrum of the proton-irradiated β-Ga$_2$O$_3$, in addition to the band in the UV,
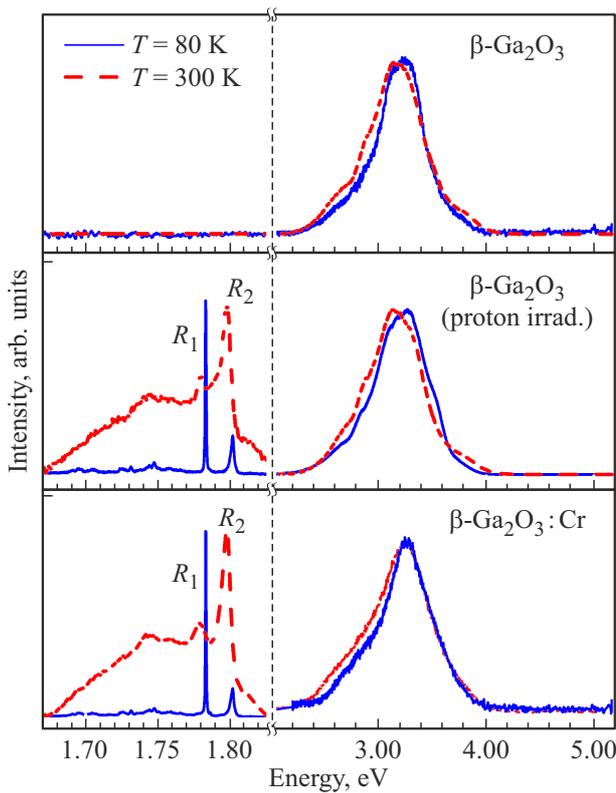
Figure 1. PL spectra of unirradiated, proton-irradiated and chromium-doped bulk samples β-Ga$_2$O$_3$, measured at room temperature and $T = 80$ K. Spectra in the UV band were obtained using excitation radiation of 4.66 eV, and in the visible band — using excitation radiation of 2.33 eV.

shows a broad band in the red range with a maximum around 1.75 eV (710 nm) and two narrow lines that have energies of 1.782 and 1.801 eV at $T = 80$ K. This spectrum has a small intensity, but it is completely similar to the μ-PL spectrum of the sample β-Ga$_2$O$_3$:Cr, in which the narrow features recorded in the spectrum are attributed $^2E_g \rightarrow {}^4A_{2g}$ to internal transitions Cr^{3+}. A broad band with a maximum around 1.75 eV (710 nm), which has significant intensity in the PL spectrum of the sample β-Ga$_2$O$_3$:Cr at $T = 300$ K, is attributed $^4T_{2g} \rightarrow {}^4A_{2g}$ to the internal Cr^{3+} transitions (with the lower indices g omitted in most works) [6–8].

With decreasing temperature, the population of $^4T_{2g}$ states decreases and the broad band at $T = 80$ K is practically not observed. In literature, the narrow singularities have been designated as R_1 (1.78 eV) and R_2(1.80 eV) lines, the temperature behavior of which will be discussed below. Thus, it can be concluded that the proton irradiation of β-Ga$_2$O$_3$results in a change in the charge state of the background impurity Cr^{2+}, which is inactive in PL, leading to a significant increase in the number of Cr^{3+} ions active in PL. To the best of our knowledge, there is only one work in the literature where the effect of a strong increase in red PL in samples β-Ga$_2$O$_3$:Cr under proton irradiation [9] was found. However, in contrast to our studies, the samples

already doped with Cr were studied in this work, and the PL spectra were recorded only at $T = 300$ K.

In articles [10,11], the classification of states of the ion Cr^{3+} in the β-Ga$_2$O$_3$ is given based on the irreducible representations of the local cubic group O_h. Thus the symmetry of states taking into account the spin-orbit interaction (on the basis of irreducible representations of double groups) is absent at all. In result, correct selection rules for PL spectra cannot be obtained. To determine the selection rules in the PL spectra of the ion Cr^{3+} in the β-Ga$_2$O$_3$, the crystal structure (i.e., its spatial symmetry group and the placement of atoms at symmetry positions) and the local symmetry group of the ion Cr^{3+} were set in the present work. The β-phase of crystal Ga$_2$O$_3$ that we study belongs to the monoclinic system and its symmetry is described by the space group $C12/m1 = C_{2h}^3$ (No 12) with the symmetry axis 2nd order directed along the translation vector **b** [010] (axis y). The translation vectors **a** (axis x) and **c** (axis z) are directed along the crystallographic directions [100] and [001], respectively. In the β-phase there are two non-equivalent orbits of 4 Ga 4i ($x\,O\,z$), atoms having the same local symmetry described by the point group $C_s(m)$. One of the orbitals of the Ga atom has an octahedral environment of oxygen atoms, and the other — tetrahedral. The impurity ions Cr^{3+} occupy an orbital with an octahedral environment [12]. The results of our symmetry analysis are presented in Figure 2, which shows the evolution of the electronic states from the free ion Cr^{3+} (through the intermediate cubic local symmetry O_h) to its position with local symmetry C_s in the β-Ga$_2$O$_3$. The same figure shows the PL polarizations of the Cr^{3+} ion allowed by the selection rules both without and with the spin-orbit interaction taken into account. We performed a similar analysis for α-Ga$_2$O$_3$, in which the local symmetry of the Cr^{3+} ion is described by the group C_3.

Figure 3, a shows the low-temperature PL spectra of the proton-irradiated β-Ga$_2$O$_3$ and epitaxial layer α-Ga$_2$O$_3$:Cr in the band of manifestation R_1 and R_2 lines. Since the epitaxial layer α-Ga$_2$O$_3$:Cr was grown on an Al$_2$O$_3$ substrate, the PL spectrum of the sample also clearly shows lines related to the substrate spectrum. They are labelled R_1^{Sp}(1.788 eV) and R_2^{Sp}(1.792 eV); the energy distance between them is 3.65 meV (~ 30 cm^{-1}). Undoubtedly, these lines are associated with internal ($^2E_g \rightarrow {}^4A_{2g}$) transitions of Cr^{3+}, impurity of which is mostly contained
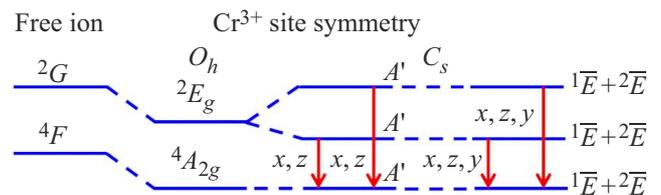
Figure 2. Evolution of the electronic states of the Cr^{3+} ion in the β-Ga$_2$O$_3$ matrix. The same figure shows the PL polarizations of the ion Cr^{3+} allowed by the selection rules.
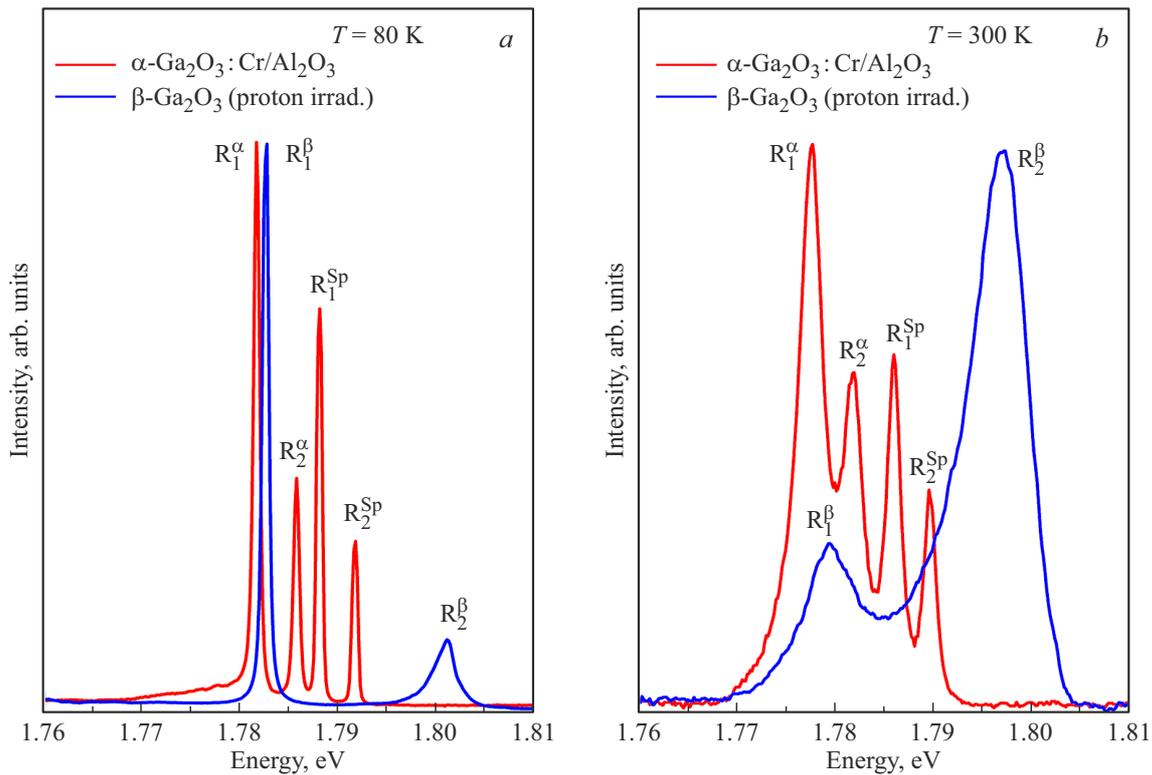
Figure 3. Spectra of μ-PL at $T = 80$ and 300 K for α-Ga$_2$O$_3$: Cr/Al$_2$O$_3$ and proton-irradiated β-Ga$_2$O$_3$ in the manifestation band R_1 and R_2 lines. The spectra were obtained using excitation radiation of 2.33 eV. (The colored version of the figure is available on-line).

in sapphire substrates. In the spectrum of the sample α-Ga$_2$O$_3$: Cr/Al$_2$O$_3$ another doublet of lines R_1^α (1.781 eV) and R_2^α (1.785 eV) is registered, the energy distance between which is 3.65 meV(~ 30 cm^{-1}). With high probability, these are lines also associated with internal $(^2E_g \rightarrow {}^4A_{2g})$ transitions in Cr^{3+}, but already in the matrix α-Ga$_2$O$_3$.

The PL spectrum of the proton-irradiated sample β-Ga$_2$O$_3$ is also represented by two lines labelled R_1^β (1.782 eV) and R_2^β (1.801 eV), but the energy distance between them is 18.5 meV (~ 149 cm^{-1}). It is known that the energy of internal transitions in transition metals, such as Cr^{3+}, depends on the local crystal field formed by the atoms of the nearest neighborhood. In literature there are statements that the increase in the energy distance between the lines $R_{1,2}$ β-Ga$_2$O$_3$ compared to their distance in Al$_2$O$_3$ is the result of a change in the value of the local crystal field. However, the work [13] argues that for Cr^{3+} only the transition energies of $^4A_{2g} \rightarrow {}^4T_{1g}$ and $^4A_{2g} \rightarrow {}^4T_{2g}$ depend significantly on the magnitude of the local crystal field, while the transition energy of $^2E_g \rightarrow {}^4A_{2g}$ is independent of this parameter. Thus, the explanations proposed in the literature for the increased energy distance between lines $R_{1,2}$ in β-Ga$_2$O$_3$ do not seem unambiguous and need further verification.

We also note significant differences in the $R_{1,2}$ line widths recorded in the PL spectra of α-Ga$_2$O$_3$: Cr and

proton-irradiated β-Ga$_2$O$_3$. The narrow lines R_1 and R_2 (their FWHM $\sim 0.6 - 0.7$ meV at $T = 80$ K) in Al$_2$O$_3$ and α-Ga$_2$O$_3$: Cr are typical of PL due to internal transitions in ions. However, for the proton-irradiated β-Ga$_2$O$_3$ at $T = 80$ K, only the line R_1 has a small width (FWHM$_{R1} \sim 0.8$ meV), while the FWHM$_{R2} \sim 2.7$ meV. It should also be noted that the widths of the lines R_1 and R_2 in the spectrum of proton-irradiated β-Ga$_2$O$_3$, in contrast to their widths in the spectrum of α-Ga$_2$O$_3$: Cr, increase very strongly with increasing temperature. Another difference is the difference in the temperature dependence of the line intensities I_{R1} and I_{R2} in α-Ga$_2$O$_3$: Cr and proton-irradiated β-Ga$_2$O$_3$. From the spectra shown in Figure 3, a and b, it can be seen that for Al$_2$O$_3$ and α-Ga$_2$O$_3$: Cr the intensity ratio $k = I_{R1}/I_{R2} > 1$ at both $T = 80$ K and room temperature. This is consistent with the transition pattern of $^2E_g \rightarrow {}^4A_{2g}$, where the R_2 line arises from a transition from an upper, less populated level E_g, to a lower level A_{2g}. However, for the proton-irradiated sample β-Ga$_2$O$_3$ the condition $k > 1$ occurs only at $T = 80$ K, while for $T = 300$ K the parameter $k < 1$. Moreover, as follows from our measurements of the angular dependence of the k parameter for the (100) plane of the proton-irradiated sample β-Ga$_2$O$_3$, its magnitude at the same temperature depends on the relationship between the crystallographic directions and the polarization vector of the linearly polarized PL.

Summarizing the results obtained, we should note the high sensitivity of PL spectra and selection rules for them to the local symmetry of Cr^{3+} ions in the β-Ga_2O_3 matrix. It is found that proton irradiation of β-Ga_2O_3 results in a change in the charge state of the background impurity Cr^{2+}, which is inactive in PL, leading to a significant increase in the number of ions Cr^{3+} active in PL. The results also indicate that the behavior of the R_1 and R_2 lines observed in the β-Ga_2O_3, spectra is not fully understood, which requires further investigations into the nature of their origin.

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Conflict of interest

The authors declare that they have no conflict of interest.

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