

Luminescence properties of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals

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The spectral and kinetic luminescence characteristics of undoped $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ single crystals have been studied using synchrotron irradiation with 4–30 eV energy, X-ray and optical irradiation (N_2 laser) in 10–300 K temperature range. It is established that the undoped crystals show an intrinsic luminescence consisting of three elementary emission bands peaked at 355, 400, and near 500 nm. The UV emission bands (355 and 400 nm) are effectively excited in exciton absorption and band-to-band regions while the 500 nm emission can be excited in the crystal transparency region. Possible nature of intrinsic luminescence bands in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals is discussed.

Исследованы спектрально-люминесцентные и кинетические характеристики неактивированных монокристаллов $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ при возбуждении синхротронным излучением с энергией 4–30 эВ, рентгеновскими лучами и оптическим излучением (N_2 -лазер) в температурном диапазоне 10–300 К. Показано, что исследованные кристаллы характеризуются собственной люминесценцией, которая состоит из трех элементарных полос с максимумами при 355, 400 и 500 нм. Полосы 355, 400 нм эффективно возбуждаются в области экситонного поглощения и зона-зонных переходов, а свечение 500 нм – в области прозрачности кристалла. Обсуждается возможная природа полос собственного свечения в кристаллах $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$.

Crystals of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ with trigonal Ca-gallogermanate structure (space group $D_3^2\text{-P}321$) show a unique combination of physical properties: luminescence, laser, resilient, piezoelectric, and acoustic. The disordered trigonal compounds $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ activated with RE ions and transition elements are known as effective materials of quantum electronics combining the functions of generation and frequency transformation of laser radiation. This fact has stimulated the study of spectral and luminescence properties of transitional and RE metals impurity ions in these materials [1, 2]. However, the centers of intrinsic luminescence in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals, which provide information about electron transitions in the matrix, have not been sufficiently studied. In this work, we report the studies of intrinsic luminescence in

$\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals under excitation with X-rays, N_2 laser, and synchrotron radiation (SR).

The crystals were grown by Czochralski technique in argon atmosphere with oxygen additive using platinum crucible. The initial materials CaCO_3 , Ga_2O_3 , GeO_2 of at least 99.99 % purity were used as starting materials. The samples were prepared as plates of 0.1–0.9 mm thickness, cut in a (0001) plane. The optical absorption and luminescence spectra were investigated in unpolarized light, in the 10–300 K temperature range. The optical absorption spectra were measured using a "Specord-M40" spectrophotometer. The luminescence investigations were carried under X-ray excitation, optical excitation (N_2 laser, $\lambda_m = 337.1$ nm) and SR excitation. To study the X-ray luminescence spectra (RL) at 80–295 K tempera-

tures, a microfocused X-ray tube with a copper anticathode was used, operated at 45 kV, 0.3 mA. The RL spectra were analyzed using a home-made spectral setup including a SF-4A quartz monochromator and FEU-51 photomultiplier. Measuring of photoluminescence (PL) spectra under excitation with synchrotron radiation (SR) of 4–30 eV energy at 10 K temperature were performed using a SUPERLUMI station at HASILAB (DESY, Hamburg). The emission spectra were registered in the 200–900 nm range using an ARS SpectraPro SP-308i monochromator (0.3 nm) with CCD detector. The PL excitation spectra were measured both in the integral regime and in the 0–50 ns and 150–200 ns time gates within limits of pulse repetition. The PL excitation spectra were normalized to an equal number of photons incident the sample. The decay kinetics was measured in 150–200 ns time gate at 10 K.

The $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ single crystals are transparent in UV and visible ranges (Fig. 1, curve 1). The fundamental absorption edge of undoped crystals at 300 K starts from $\lambda \sim 245$ nm. A spectrum of RL at all undoped nominally pure $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ single crystals at 80 K is a wide asymmetric band in the 300–600 nm spectral region with a maximum at 420–430 nm (Fig. 1). Temperature dependence of the RL band intensity is presented as an inset in Fig. 1. As is seen from Fig. 1, luminescence is quenched in the temperature range of 120–240 K. The luminescence spectrum under laser excitation (N_2 laser) presents a weak radiation in the 400–700 nm region with a maximum near 500 nm (Fig. 1, curve 3). The luminescence near 500 nm was observed in all undoped nominally pure crystals, the 500 nm band intensity being considerably increased in crystals annealed in vacuum. The asymmetry of 500 nm luminescence band in the undoped crystals, as well as its maximum shift towards long-wave region under N_2 laser excitation, demonstrates that it is not elementary. To understand the nature of luminescence centers in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals, the PL spectra at various excitation quantum energies of synchrotron radiation were investigated.

The PL spectra recorded at 10 K under SR excitation in the range of 4.6–7.8 eV are shown in Fig. 2. The spectral composition of emission is presented by a wide asymmetric band with the main maximum near 400 nm. Fig. 2 illustrates that the highest luminescence efficiency is observed

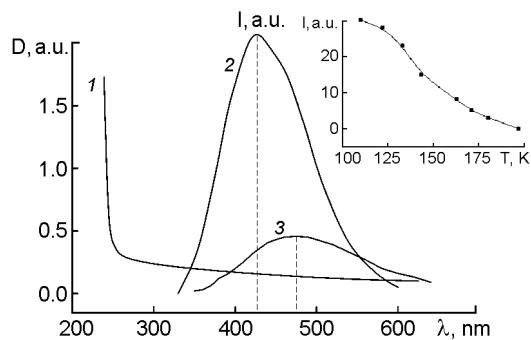


Fig. 1. Optical absorption (1) and luminescence spectra of undoped $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals under the X-ray excitation (2) and optical excitation (N_2 -laser) (3). Inset: temperature dependence of X-ray luminescence.

under excitation at 220 nm (5.63 eV). The increase of SR energy (>5.9 eV) results in a decrease of luminescence approximately twice and in the shift of the 400 nm band maximum towards short-wave region ($\lambda_m = 389$ nm). In that case, a shoulder at 340–360 nm is observed in the short-wave wing of this band. At a lowered SR energy ($\lambda_{exc} = 252$ nm, 4.92 eV), the emission decreases more than by 5 times. In the luminescence spectrum, a wide band is observed with a maximum at 500 nm having an inflection in the asymmetrically extended long-wave wing at $\lambda_m \sim 540$ nm and narrow bands at $\lambda_m \sim 610$ and $\lambda_m \sim 700$ nm. Diminishing of spectral recording width resulted in appearance of line structure of narrow bands associated with $f-f$ transitions (${}^5D_0-{}^7F_j$ channels) of Eu^{3+} background impurity. Similar characteristic lines of the Eu^{3+} ions luminescence in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ were observed before in [4]. The consideration of PL spectrum composition shows that experimental curves can be fitted by three strongly overlapped bands with maxima at $\lambda_m = 355$ nm, $\lambda_m = 400$ nm, and $\lambda_m = 495$ nm, while the intensity ratios depend on the exciting SR quantum energy. The extension of PL band into elementary components was carried out using the Alencev-Fock method [5].

Fig. 3 presents the luminescence excitation spectra. An intensive exciton absorption band ($\lambda_m = 218$ nm, 5.68 eV) and weakly expressed bands at 160 and 180 nm in band-to-band absorption region are observed in the excitation spectra of $\lambda_m = 400$ and 355 nm emission bands. A reduction in the relative intensity of the exciton absorption band, a shift of its peak towards higher

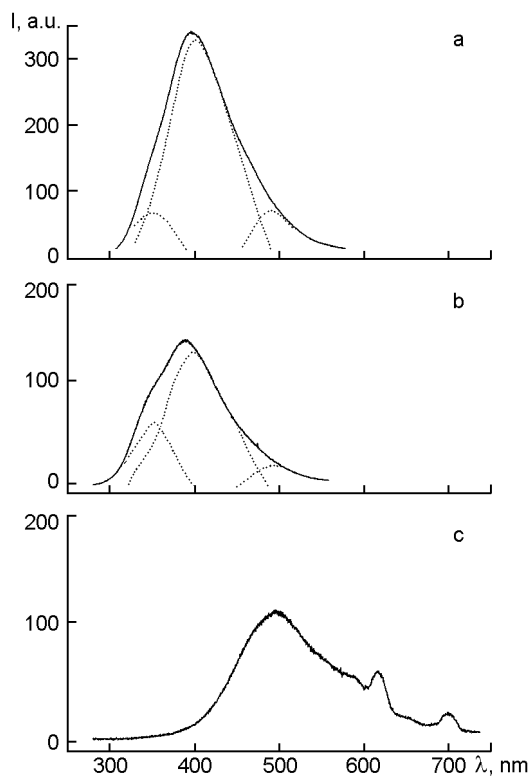


Fig. 2. Luminescence spectra of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals under SR excitation at $\lambda_m = 220$ (a), 160 (b), 252 (c) nm at 10 K. Dashed line shows the elementary components of luminescence band.

energies compared with the corresponding excitation peak of 400 nm luminescence is observed for the 355 nm band. However, the character of the excitation spectra for 355 and 400 nm luminescence bands is almost the same and does not change at the measurement in "fast" and "slow" time windows, the slow component contribution being prevailing. According to Fig. 3, the excitation spectrum of emission in the 500 nm region, in contrast to the PL bands in the UV region, is characterized by two maxima: in the transparency region of crystal peaked at 4.92 eV ($\lambda_m = 252$ nm) and in region of exciton absorption peaked at 5.52 eV ($\lambda_m = 224$ nm).

The luminescence decay curves of inactivated $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals in the case of excitation SR quanta at $T = 10$ K are presented in the Figure 4. The decay time parameters were determined by exponential approximation. The decay kinetics of 355 and 400 nm PL bands are described by superposition of fast (ns) and slower exponential components (tens ns), the contribution of the latter being dominant. The kinetic

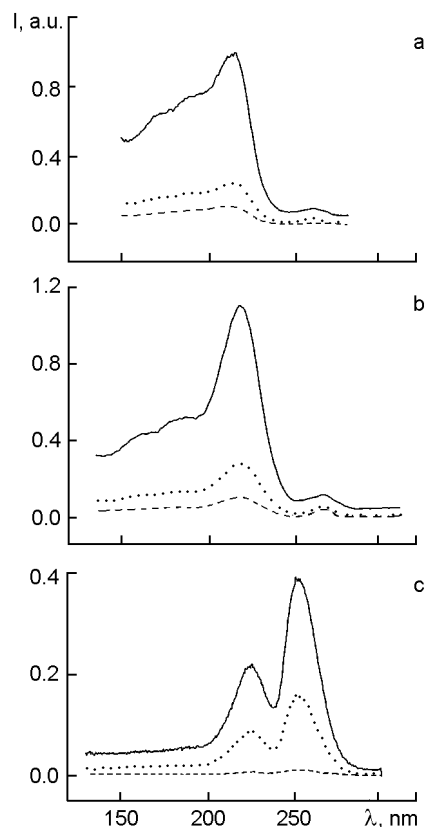


Fig. 3. Luminescence excitation spectra of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals at $\lambda_m = 340$, 400, 510 nm. Spectra are measured in integral regime (points), "fast" (solid line) and "slow" (dotted line) time intervals.

curve of 355 nm luminescence is formed by components of $\tau_1 \sim 6.72$ ns and a slower one with $\tau_2 \sim 64$ ns, while the decay kinetics of 400 nm luminescence can be approximated by two components with life times $\tau_1 \sim 12.38$ ns and $\tau_2 = 160$ ns. In the kinetics of PL band peaked near 500 nm, obtained by excitation at any SR energy, a pronounced "pedestal" indicating the existence of slow dominant component in microsecond range is present besides of low intensity fast component ($\tau_1 = 1.86$ ns).

It should be noted that both PL bands in the UV region ($\lambda_m = 355$ and 400 nm) are excited in the region of the band-to-band transition and exciton absorption, and exciton narrow band dominates in the excitation spectra (Fig. 3). The excitation spectrum of luminescence bands near 500 nm together with a band in exciton absorption range at 5.52 eV is characterized by intense band in the transparency region with a maximum at 4.92 eV. The 500 nm luminescence band is weakly excited by photons with energies

that match the band-to-band transitions. Decay kinetics of 355 and 400 nm PL bands are described by fast times (few ns and tens ns), while a dominant slow component with μs decay time is present in the decay kinetics of 500 nm PL.

The above results indicate that low-temperature emission bands in the ultraviolet region with maxima at 360 and 400 nm, being similar in many important properties (kinetic constant, almost identical character of the excitation spectra, quenching temperature) can be attributed to the luminescence centers of similar structure. The emission band peaked near 500 nm, differing in excitation spectrum and decay kinetics from the UV region bands, can be attributed to another luminescence center kind. Thus, the experimental results indicate that two types of intrinsic luminescence are shown in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals.

The bands peaked near 340 and 400 nm can be regarded as the emission of self-trapped exciton and localized exciton emission, respectively. It is known that the low-temperature luminescence bands are typical of the complex oxide crystals where oxygen ions occupy low symmetry sites. As to their nature, there is no single point of view in literature (see, e.g. [6, 7]). These intrinsic luminescence bands are interpreted often as radiative decay of self-trapped excitons formed by the relaxation of large-radius excitons or by recombination of electrons with holes localized at intrinsic or impurity defects of crystal lattice. The hole component of exciton for many oxides is genetically different. Some intrinsic luminescence bands in oxides are referred to emission of antistructural defects or luminescence-active structure defects such as vacancies. Note that the appearance of excitation spectra for $\lambda_m = 355$ and 400 nm PL is typical of the spectra associated with the formation of electron excitations in a crystal. In our opinion, the most reasonable interpretation of 355 nm emission is radiative decay of self-trapped excitons. The hole component could be the O^- center studied by EPR [8] in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals irradiated with ultraviolet and X-ray quanta. A wide excitation spectrum of the 335 nm PL band shows that self-trapped excitons in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ may arise due to relaxation of both free excitons and electron-hole pairs, which appear under excitation with photons at energies exceeding E_g . The longer-wavelength and more intense intrinsic emission band ($\lambda_m = 400$ nm) can be con-

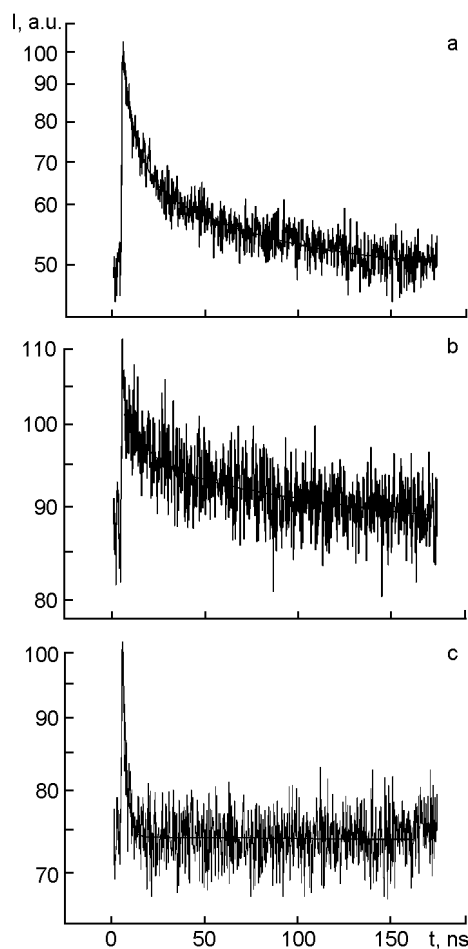


Fig. 4. Luminescence decay curves in the bands $\lambda_m = 340$ (a), 400 (b), 510 (c) nm in $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals at $T = 10$ K under excitation by SR with $\lambda_m = 160, 220, 252$ nm, respectively.

nected with radiative annihilation of excitons located near the lattice cationic positions statistically populated with atoms Ga^{3+} , Ge^{4+} differing in size and charge. Ga^{3+} ions in $3f$ tetra positions or Ge^{4+} in $1a$ octa ones may be attracted to one of other electron-hole pair components followed by trapping of the second charge carrier. Thus, a "localized exciton state" is formed. The luminescence occurs as a result of radiative annihilation of these excitons. The existence of fast and slow components in the UV luminescence bands decay kinetics can be explained by two exciton radiation levels characterized by different transition probabilities.

The luminescence at $\lambda_m \sim 500$ nm, which is effectively excited in transparency range, seems to be related to the structure defects. Taking into account the fact that the oxide

compounds may contain a noticeable concentration of anion vacancies [9], the crystal under study can be considered to include the F type luminescence centers. This assumption is consistent with the fact that the 500 nm band intensity increases in the vacuum annealed crystals, where a high concentration of anion vacancies is formed. The wavelength positions of this band and its exciting band in the crystal transparency region at $\lambda_m = 252$ nm (4.92 eV) agree rather well with the spectral characteristics of F -centers identified in thermochemically colored crystals $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ and with experimental studies of F -centers in other complex oxide crystals [10, 11].

Luminescence at about 500 nm occurs also under excitation in exciton region in the band with $\lambda_m = 224$ nm. This indicates a possibility of F -center excitation due to energy transfer from excitons localized at these centers. The presence of an intense slow exponential stage and weak fast one in the decay kinetics of the 500 nm band may be due to the contribution from singlet-singlet transitions and forbidden singlet-triplet ones, which are provided by the F -center electron structure. Asymmetrical long-wavelength edge of the F band with inflection at 540 nm suggests the existence of an additional band. The lack of separation of F band even at 10 K and its considerable width can be explained by structural peculiarities of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals. The $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystal matrix is characterized by disordered cationic sublattice, which is due to $3f$ tetra and $1a$ octa structural positions randomly occupied by Ga^{3+} and Ge^{4+} ions. As a result, a statistical set of centers appears coupled with anion vacancy in the $6g$ oxygen positions, which have different local surroundings. This pro-

vides the significant broadening of the F center band and the lack of its structure in the studied crystals.

Thus, new experimental results are presented evidencing that the undoped $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ crystals are characterized by low-temperature intrinsic luminescence which consists of three components. Based on the consideration of the results and literature data, it can be concluded that the emission bands in the UV region (355 and 400 nm) are connected with exciton radiative annihilation, while the band at about 500 nm can be ascribed to luminescence of F type centers.

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Люмінесцентні властивості кристалів $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$

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Досліджено спектрально-люмінесцентні та кінетичні характеристики неактивованих монокристалів $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ при збудженні синхротронним випромінюванням з енергією 4–30 eV, рентгенівськими променями та оптичним випромінюванням (N_2 -лазер) у температурному діапазоні 10–300 К. Показано, що кристали, які досліджуються, характеризуються власною люмінесценцією, яка складається з трьох елементарних смуг з максимумами при 355, 400 та 500 нм. Смуги 355, 400 нм ефективно збуджуються в області екситонного поглинання та зона-зонних переходів, а свічення 500 нм – в області прозорості кристала. Обговорюється можлива природа смуг власного свічення у кристалах $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$.