Time-resolved spectroscopy of intrinsic luminescence of $Y_3Ga_5O_{12}$ and $(LaLu)_3Lu_2Ga_3O_{12}$ single crystals

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**Abstract**

The nature of intrinsic luminescence of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) single crystals grown from a melt was determined. In the case of a YGG single crystal containing YGa antisite defects with a concentration of 0.25–0.275 at.% the intrinsic luminescence was considered as a superposition of luminescence of self-trapped excitons (STE), luminescence of excitons localized near antisite defects (LE(AD) centers) and luminescence caused by a recombination of an electron with a hole captured at YGa antisite defects. Due to a large (2–3%) concentration of LuLa antisite defects in LLGG single crystals the intrinsic luminescence was a superposition mainly of the LE(AD) center emission and the recombination luminescence of LuLa antisite defects. The energy structure of the mentioned centers in YGG and LLGG hosts was determined from the excitation spectra of their luminescence under excitation by synchrotron radiation in the range of the fundamental absorption edge of these garnets.

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**1. Introduction**

A peculiarity of the structural disorder of single crystals (SC) of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) garnets that appears during their crystallization from a melt at high temperatures is a formation of antisite defects (AD); specifically, the $Y^{3+}$ cations in the octahedral sites of $Ga^{3+}$ cations (YGa) in the YGG SC and the $Lu^{3+}$ cations in the dodecahedral sites of the $La^{3+}$ cations (LuLa) in LLGG SC [1–5]. The concentration of AD of such type in YGG and LLGG SC reaches 0.2–0.275 at.% [1–3] and 2–3 at.% [4,5], respectively. The AD is an analogue of cation isoelectronic impurities and significantly contributes to the intrinsic UV luminescence of single crystals of garnet compounds [6].

The intrinsic luminescence of Ga-garnets, in particular the YGG and LLGG SC, has been recently studied in the papers [6–8] by conventional spectroscopic methods. It has been found that intrinsic luminescence of SC of these garnets is represented by broad complex bands in the UV spectral range which are a superposition of several components. The position and intensity of these components depend on the AD concentrations and temperature of measurements [6–8].

This work is devoted to further detailed investigation of the nature of the intrinsic luminescence of YGG and LLGG SC using the time-resolved luminescent spectroscopy under excitation in the range of fundamental absorption edge of these garnets.

**2. Samples and experimental technique**

The YGG and LLGG SC were grown by the Czochralsky method in Ir crucibles in Ar + 1.5% O₂ atmosphere at the National University of Lviv and the Institute of Technology of Electronic Materials in Warsaw, respectively. The $Y_2O_3$, $Lu_2O_3$, $La_2O_3$ and $Ga_2O_3$ oxides of 4 N purity were used as a charge. The crystal content was determined by atomic emission spectroscopy. Plates cut from the upper part of crystals with (1 1 1) orientation of the growth axis that had $La_{2.6}Lu_{2.4}Ga_{3}O_{12}$ and $Y_{3.055}Ga_{4.945}O_{12}$ contents were used for investigating the luminescence properties.

The time-resolved intrinsic luminescence of YGG and LLGG SC was measured at 9–10 K under excitation by pulsed (0.127 ns with a repetition time of 200 ns) synchrotron radiation (SR), with an energy of 3.7–25 eV at the Superlumi experimental station (HASYLAB...
at DESY). The emission and excitation spectra were measured in the integral regime over 1.2–10 ns and 150–200 ns time intervals, for fast and slow components, respectively. The luminescence decay was measured in the time range of 0–200 ns at 10 K.

3. Results and discussion

The intrinsic luminescence spectra of the YGG SC obtained under excitation by SR with two different excitation energies at 9 K are presented in Fig. 1. Similarly to the well-known Y₃Al₅O₁₂ (YAG) SC [9], the spectra of YGG SC are a superposition of the luminescence of self-trapped excitons (STE) with the band peaked at $E_{\text{max}} = 4.13 \text{ eV}$, the luminescence of excitons perturbed at AD defects (LE(AD) centers) with the band peaked at $E_{\text{max}} = 3.75 \text{ eV}$ and the luminescence of YGa AD with the band peaked at $E_{\text{max}} = 3.27 \text{ eV}$ originate from a radiative recombination of electrons of a conduction band with holes previously localized at these AD [6].

The intrinsic luminescence spectra of LLGG SC (the fast and slow components as well as the integrated spectrum) under excitation by SR with an energy of 6.45 eV in the range of LLGG fundamental absorption edge are presented in Fig. 2. LLGG SC is characterized by a substantially larger (by one order of magnitude) concentration of the LuAl AD with respect to YGG SC, and therefore the intrinsic spectrum practically does not contain any STE luminescence even at 10 K (see also [8]). The luminescence of LLGG SC (Fig. 2) is a superposition of the emission band peaked at $E_{\text{max}} = 3.59 \text{ eV}$ related to the LE(AD) centers and the band peaked at $E_{\text{max}} = 3.08 \text{ eV}$ related to the recombination of the hole and the electron at Lu₃Al AD (see also [8]). The spectra presented in Fig. 2 are very close to those for the LuAG SC with a significantly large concentration of Lu₃Al AD with respect to YAG SC [9].

The excitation spectra of the luminescence of YGG SC monitored at energies of 4.13 eV and 3.39 eV are shown in Fig. 3. Actually, the mentioned spectra are a superposition mainly of two different components of the intrinsic emission. Specifically, curve 1 presents a superposition of the excitation spectra of LE(AD) and the STE luminescence, whereas curve 2 presents a superposition of the excitation spectra mainly of LE(AD) and YGa AD emission. In turn, the excitation spectra of all these components of the intrinsic emission show double structures with two peaks (Fig. 3). This phenomenon is typical for the excitation spectra of components of the intrinsic luminescence of Al-garnets [9] and caused by the transition from the ground state to singlet and triplet excited states of excitons related to the above mentioned centers.

Thus, the excitation spectrum of YGG SC (Fig. 3) allows the energies of STE formation to be estimated as equal to 6.69 eV and determines the energies of creation of the LE(AD) states (equal to 5.9 and 6.675 eV) (curves 1), as well as the energies of formation of excitons bound with the YGa AD (equal to 5.855 and 6.22 eV) (curves 2). It is worth noting that due to a strong overlap of the excitation spectra of the emission of STE, LE(AD) and the YGa AD centers, the positions of the excitation levels of STE must be defined more precociously. Specifically, this can be done by studying the STE luminescence in YGG single crystalline films where the AD and related luminescence centers are completely absent and the STE emission is a dominant component of the intrinsic luminescence [6,9].

The excitation spectra of LE(AD) and AD Lu₃Al emission components (the luminescence monitored at 3.695 eV and 2.88 eV, respectively) in LLGG SC are shown in Fig. 4. Both spectra are the superposition of the LE(AD) and AD Lu₃Al centers luminescence with the dominating content of one of them. The excitation spectra of both components of the intrinsic luminescence consist of two
characteristic peaks caused by the transition to the singlet and triplet excited states of excitons related to the LE(AD) and AD LuLa centers [9]. From these excitation spectra we determined the energies of formation of the LE(AD) states in LLGG (equal to 5.64 and 5.36 eV, Fig. 4, curve 1) and the energies of formation of the excitons bound with the AD LuLa (equal to 5.31 and 5.935 eV, Fig. 4, curve 2).

The decay kinetics of different components of the intrinsic luminescence of YGG and LLGG SC is shown in Figs. 5 and 6, respectively. All the decay curves have a similar shape. Generally, the decay curves of the intrinsic luminescence of YGG SC can be presented as a superposition of three components caused by the transition from the excited states of the STE, LE(AD) and excitons bound with the YGa AD in YGG. In the case of LLGG SC the decay curves of the intrinsic luminescence can be represented by a superposition of two components related to the LE(AD) and excitons bound with the LuLa AD. At the same time, using the appropriate energies of excitation and luminescence at the maxima of excitation and emission bands for different components of the intrinsic luminescence, it is possible to separate their dominant emission decay (Figs. 5 and 6). The parameters of fitting of the corresponding decay curves (shown in Figs. 5 and 6 by solid lines) are summarized in Table 1.

As can be seen from Table 1, the complex decay kinetics of all components of the intrinsic luminescence of YGG and LLGG SC with the decay times of components in the ns, ten ns and hundred ns ranges, respectively suggests a radiative relaxation of different types of triplet excitons related to the above mentioned centers. This result matches well with the data for the decay of different emission components of the intrinsic luminescence in YAG and LuAG SC [9].

4. Conclusions

The nature of centers of the intrinsic UV luminescence of single crystals of $Y_3Ga_5O_{12}$ (YGG) and $(LaLu)_3Lu_2Ga_3O_{12}$ (LLGG) garnets obtained from melt has been considered. The intrinsic luminescence of YGG single crystals with a concentration of YCa antisite defects (AD) of 0.25–0.275 at.% is a superposition of luminescence of self-trapped excitons (STE), luminescence of excitons localized near antisite defects (AD) (LE(AD)) centers and recombination luminescence of centers formed by YCa AD. Due to a large (2–3%) concentration of LuLa AD in LLGG single crystals, the STE luminescence in these crystals is strongly diminished and the intrinsic luminescence presents a superposition mainly of the LE(AD) emission and the recombination luminescence of centers formed by LuLa AD.

The energy structure of the mentioned centers in YGG and LGGG garnet hosts is determined. The presence of two peaks in the excitation spectra, as well as the complex kinetics of the luminescence decay with the decay time of components respectively in the ns, ten ns and hundred ns ranges suggests the
radiative relaxation of triplet excitons related to different components of intrinsic luminescence in the investigated materials.

The obtained results are consistent in the whole with the results of studying the nature of the intrinsic luminescence of single crystals of Al-garnets [9]. This indicates the universality of a model approach to the role of AD in a structure of intrinsic luminescence of oxides with a garnet structure [6,8,9].

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