



# Article Decay Kinetics of Gd<sub>3</sub>Al<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Ce<sup>3+</sup> Luminescence under Dense Laser Irradiation

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**Abstract:** The decay kinetics of  $Gd_3Al_2Ga_3O_{12}:Ce^{3+}$  single crystal luminescence were studied under dense laser excitation. It was shown that the decay times as well as the intensity of  $Ce^{3+}$  luminescence depend on the excitation density. The observed effects were ascribed to the interaction between excitons as well as to the features of energy transfer from the excitons to  $Ce^{3+}$ . The numerical simulation of the experimental results was performed for justification of the proposed model.

Keywords: GAGG:Ce; decay kinetics; Z-scan; excitons interaction; non-linear density effects



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# 1. Introduction

 $Gd_3Al_2Ga_3O_{12}$ :Ce<sup>3+</sup> (GAGG:Ce) scintillator is a high-density chemically stable compound with a high scintillation yield (~60,000 ph/MeV), which is used in medicine and high-energy physics [1]. The scintillation of GAGG:Ce is due to 5d–4f Ce<sup>3+</sup> transitions, which give rise to emission band peaking at ~550 nm. Ce<sup>3+</sup> decay time under 4f–5d(1) intracenter excitation is 40–60 ns [2,3]. Additional slow decay components usually arise at high-energy transfer from the host to the activator. In particular, intermediate localization of charge carriers at shallow traps as well as energy transfer via Gd<sup>3+</sup> states slow down the energy transfer processes [4,5].

Interaction of excitations is another effect which influences the scintillation response. When a scintillator absorbs high-energy particles, it converts their energy into electronic excitations, for which spatial distribution depends on the particles' type and energy as well as the stopping power of scintillator. A high concentration of excitations in the local volume usually occurs at the end of the particles' tracks and their interaction results in the non-proportional scintillation response to the energy of the ionizing particles and changes in scintillation decay kinetics [6,7]. The interaction between two excitations (e.g., excitons) can be described as an Auger-like dipole–dipole interaction, when one exciton annihilates while its energy is transferred to another one. The distance between excitons should be as small as the value of the radius of the dipole–dipole interaction ( $R_{d-d}$ ), which is of the order of few nanometers.

In most cases, the non-exponential fast component(s) appears in the decay kinetics of compounds with intrinsic emission (e.g., self-trapped excitons (STEs) emission) while its intensity is suppressed due to the decrease in the number of excitations as a result of their interaction [8–11]. However, for CsI, it was shown that the luminescence intensity of 4.1 eV band increases quadratically with the increase the in excitation density which was connected with a new type of localized state of singlet exciton created through the "fusion" of self-trapped exciton and free exciton [12].

The influence of high-density excitation on the emission of Ce<sup>3+</sup> was studied for CeF<sub>3</sub> and Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> in [13–15]. It was shown that the interaction between excited Ce<sup>3+</sup> ions, which are located in the neighboring sites of the CeF<sub>3</sub> crystal lattice, results in the acceleration of decay kinetics in its initial part and in the suppression of the light yield, i.e., the behavior is similar to that observed in the case of the interaction of STEs. In contrast to CeF<sub>3</sub>, the high density excitation does not influence the  $Ce^{3+}$  decay time in the Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce crystal as it contains cerium as an activator in concentrations much lower than those required for the interaction of neighboring Ce<sup>3+</sup> ions. Non-linear dependence of Ce<sup>3+</sup> luminescence intensity on excitation density has been detected for Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>:Ce with the emission saturation at the excitation level of  $\sim 2.0 \times 10^{20} \text{ eV/cm}^3$  and it has been explained by mutual quenching of excitons created at high densities, preceding the stage of energy transfer to the  $Ce^{3+}$  ions. The influence of the high-density laser excitation of the activator emission has been also studied for CsI:Tl and NaI:Tl in [16]. Again, the decay time do not depend on the excitation density because the interaction occurs between STEs and only after interaction is the energy transferred to activator centers, which demonstrates luminescence with characteristic for Tl ions' decay times.

In contrast to  $Y_3Al_5O_{12}$ :Ce and alkali halides, the presence of a gadolinium sublattice in gadolinium-containing crystals allows for the formation of additional pass-ways of energy transfer from the host to the emission centers. This will result in the appearance of delayed components in the emission decay, as was shown for cerium-doped gadolinium orthosilicates in [5]. One can expect redistributions between different pass-ways of energy transfer with the excitation density under interband excitation. Previously, the decay kinetics of GAGG:Ce were widely studied using high-energy sources such as X-ray, gamma, and electron beams and usually several decay components (corresponding to intracenter  $5d-4f Ce^{3+}$  transitions as well as delayed ones) were detected [4,17–21]. However, in case of high energy excitation, a variety of excitations are created, whose energy and spatial distribution changes throughout the track of the high-energy particle (or quanta) absorbed in the GAGG:Ce. As a result, the distribution between different pass-ways to Ce<sup>3+</sup> emission centers is averaged and the manifestation of density effects in decay kinetics is smeared.

The effect of the interaction of electronic excitations requires a high excitation density (>10<sup>17</sup> cm<sup>-3</sup>) and can be studied using intense laser sources. Excitation with the 4th harmonic of a Ti:Saphire laser (6.2 eV) allows selective excitation in the energy region, which corresponds to the direct excitons' creation in GAGG:Ce [18]. The selected energy as well as high excitation densities, which can be controlled and tuned up to  $10^{21}$  cm<sup>-3</sup>, are distinctive properties of laser excitation sources, which allows for information on the excitations' interaction and modification of energy transfer process with the excitation density to be obtained.

Here, we present a study of the interaction of electronic excitations in GAGG:Ce crystals under intense laser irradiation. The influence of high-density excitation on the decay characteristics of GAGG:Ce luminescence will be in the focus of the study.

### 2. Experimental Details

### 2.1. Crystal Growth

A single crystal with the composition in the melt  $Gd_{2.97}Ce_{0.03}Al_2Ga_3O_{12}$  (GAGG:Ce) was grown by the Czochralski method. The growth was performed in Ir crucibles in Ar atmosphere with 1–2 vol.% and additional amounts of  $O_2$ . An optically polished crystal with a size of approximately  $5 \times 8 \times 1$  mm was cut perpendicular to the growth axis.

#### 2.2. XRD Studies

Synchrotron XRD data for GAGG:Ce were measured in a large Debye–Scherrer camera at the BL15XU beamline of SPring-8 [22,23]. The intensity data were collected between  $3.042^{\circ}$  and  $27.842^{\circ}$  at  $0.003^{\circ}$  intervals in  $2\Theta$ ; the incident beam was monochromatized at  $\lambda = 0.65298$  Å. The sample was packed into a Lindemann glass capillary (inner diameter 0.1 mm), which was rotated during the measurement. The Rietveld analysis was performed using JANA2006 [24].

### 2.3. Luminescence Spectroscopy

The study of luminescence spectra and decay curves were performed at the CELIA laser center using a Ti:sapphire laser system, which generated 25 fs pulses at 800 nm with a frequency 1 of kHz. The luminescence was excited by the 4th harmonic (6.2 eV) of laser radiation. The collinear scheme was used for the harmonic generation. The filtering of the laser beam was achieved using the combination of dichroic mirrors and prisms. The density of created excitations in the laser spot center was controlled by the translation of the focusing lens and by the variation of laser beam energy. The lens with a 50 cm focal length was moved along the Z-axis which resulted in variation of the spot size (full width at half maximum) on the sample surface from 20 to 450  $\mu$ m. The energy in the pulse was varied from 2 to 30 nJ in the 4th harmonic.

The peak density of electronic excitations was calculated using the following formula:

$$N_0^{max} = 1.34 * 10^9 \mathrm{E}\left(\frac{\alpha\sigma}{\pi a^2}\right) \tag{1}$$

where E—beam energy (up to 30 nJ),  $\sigma$ —1 (number of excitations created by one photon),  $\alpha$ —absorption coefficient, and a—beam waist. Measurement of the beam profile gives the 21 µm waist (full width at half maximum) of the beam with an M<sup>2</sup> better than 2 (see Figure S1 of Supporting Information).

The energy of the 4th harmonic—6.2 eV—corresponds to the fundamental absorption edge of GAGG:Ce. The value of absorption coefficient  $\alpha$  was obtained from the Urbach fit of absorption spectrum previously performed for GAGG in [18]. The fit was performed for undoped GAGG because in a Ce-doped crystal, the fundamental absorption edge is distorted due to superposition with the Ce-related broad absorption band near the fundamental absorption edge. As a result, the  $\alpha$  value at 6.2 eV was determined as 3000 cm<sup>-1</sup> (see Figure S2 of Supporting Information).

Considering all of the parameters, the variation in the density of excitations was determined using (1) as from  $\sim 10^{15}$  to  $\sim 10^{19}$  cm<sup>-3</sup>. The dependence of excitation density on the position of focusing lens is presented in Figure 1.

The samples were placed into a helium closed-cycle cryostat from ARS. All of the measurements were performed at 300 K. The luminescence was detected using the registration system, which consists of the TRIAX secondary monochromator from HORIBA Scientific (Kyoto, Japan) equipped with Hamamatsu MCP R3809U52 (Shizuoka, Japan) and intensified CCD camera Andor iStar (Belfast, UK). The luminescence spectra were not corrected on the registration sensitivity function.

The decay curves were measured using the MCP with 100 picosecond temporal resolution at the maximum of the Ce<sup>3+</sup> emission band (525 nm). The luminescence spectra were measured using CCD in the whole temporal region 0–20,000 ns as well as in the time gating mode with time windows 0–50 ns (fast tw) and 200–5000 ns (slow tw), which were used to separate the influence of density effects on the "fast" emission which were characteristic for Ce<sup>3+</sup> decay times and "slow" emission, which arise due to the delayed energy transfer to Ce<sup>3+</sup>. The measured dependences of Ce<sup>3+</sup> emission intensity on the translation of the focusing lens along the Z-axis (Z-scans) are presented as intensity dependence on the excitation density using the data from Figure 1.



**Figure 1.** Dependence of maximal density of excitations on the translation of the focusing lens along the Z-axis of the laser beam, E = 20 nJ.

## 3. Results and Discussion

3.1. XRD Studies

It is well known that GAGG is a representative of the garnet-type structure  $(Ca_3Al_2(SiO_4)_3 [25])$  described as  $A_3B_2(CO_4)_3$ . The structure is made up of  $AO_8$  polyhedra,  $BO_6$  octahedra, and  $CO_4$  tetrahedra. The Gd<sup>3+</sup> cations occupy the *A*-positions of GAGG while the Ga<sup>3+</sup> and Al<sup>3+</sup> cations are located in the octahedral and tetrahedral sites. A synchrotron XRD study of GAGG:Ce was performed on the same sample as the one that was studied by powder XRD [18] to compare the structure refinement results from two datasets. Site occupation and the fractional atomic coordinates of GAGG:Ce from structure refinement using powder XRD data were used as an initial model. Occupancy of Ga<sup>3+</sup> and Al<sup>3+</sup> over the *B* and *C* positions was refined considering their multiplicities ( $B = mGa^{3+} + (1 - m)Al^{3+}$ ,  $C = nGa^{3+} + (1 - n)Al^{3+}$ ). As a result, the composition was determined to be Gd<sub>3</sub>Al<sub>2.23</sub>Ga<sub>2.77</sub>O<sub>12</sub>, which is slightly different from the powder XRD results (Gd<sub>3</sub>Al<sub>2.3</sub>Ga<sub>2.7</sub>O<sub>12</sub>).

The reliability factors (*R*-factors) show a good agreement between the calculated and the experimental XRD patterns. Figure 2 shows a portion of the observed, calculated, and difference XRD patterns for GAGG:Ce. The crystallographic data and refinement results for GAGG:Ce are presented in Table 1. The site occupation, fractional atomic coordinates, isotropic displacement atomic parameters ( $U_{iso}$ ), and anisotropic atomic displacement parameters for GAGG:Ce are listed in Table S1 of the Supporting Information. The main relevant interatomic distances are shown in Table S2 of the Supporting Information.

**Table 1.** Crystallographic data and refinement results for the  $Gd_3Al_{2.23}Ga_{2.77}O_{12}$ :Ce structure (SG  $Ia\overline{3}d$ , Z = 8).

Composition	$Gd_{3}Al_{2,23}Ga_{2.77}O_{12}$
Lattice parameters: <i>a</i> , Å	12.26005(1)
Unit cell volume, Å <sup>3</sup>	1842.794(3)
Calculated density, g/cm <sup>3</sup>	6.61(9)
R and $R_w$ (%) for Bragg reflections ( $R_{all}/R_{obs}$ )	1.45/1.34 and 2.26/2.24

Table 1. Cont.

Composition	$Gd_{3}Al_{2.23}Ga_{2.77}O_{12}$	
$2\theta$ range (°)	3.042–27.841	
Step scan $(2\theta)$	0.003	
I <sub>max</sub>	211,632	
№ reflec. (All/Obs.)	34/32	
$R_P$ and $R_{wP}$ ; $R_{exp}$ (%)	3.18, 4.93, 1.75	
Goodness of fit (ChiQ)	2.82	
Max./min. res. density ( $e \times Å^{-3}$ )	0.23/-0.26	



**Figure 2.** Fragments of the observed, calculated, and difference XRD patterns for Gd<sub>3</sub>Al<sub>2.22</sub>Ga<sub>2.78</sub>O<sub>12</sub>:Ce. Tick marks denote the peak positions of possible Bragg reflections.

#### 3.2. Influence of Excitation Density on the Decay Curves of GAGG:Ce

A broad non-elementary band peaking at 525 nm was observed in the luminescence spectra of GAGG:Ce (Figure 3). The band arose due to 5d(1)–4f transitions within Ce<sup>3+</sup> ions. The band profile does not depend on the excitation density as well as on the time windows used for the experiment.

A set of decay curves obtained for the excitation densities from  $N_0^{max} = 6.1 \times 10^{16} \text{ cm}^{-3}$  (lens out of focus) to  $N_0^{max} = 1.2 \times 10^{19} \text{ cm}^{-3}$  (lens in focus) are presented in Figure 4. From the figure, the initial part of the decay curve is supressed while it increases for the  $\tau > 200$  ns with an increase in excitation density. The fit of the decay curves with the sum of four exponential components has been performed (Figure S3 of Supporting Information). The curves can be fitted by the same set of decay components, two fast ( $\tau_{f1}$ ,  $\tau_{f2}$ ) and two slow ( $\tau_{s1}$ ,  $\tau_{s2}$ ), regardless of the excitation density. The characteristic decay times were  $\tau_{f1} = 16.4 \pm 2.4$ ,  $\tau_{f2} = 61.1 \pm 13.5$ ,  $\tau_{s1} = 138 \pm 12$ , and  $\tau_{s2} = 517 \pm 22$  ns, Figure 5a. The fastest component  $\tau_{f1}$  is artificial and arises due to the electronic distortion of the decay curve, namely pulse miscounts during the dead time after pulse registration. Another fast decay component  $\tau_{f2} \sim 60$  ns corresponds to the characteristics of 5d–4f intracenter electronic transitions in Ce<sup>3+</sup> ions. In contrast to the decay times, their amplitudes depend on the excitation density (Figure 5b). The amplitudes of two fast components decrease while those of slow ones increase with the increase in excitation density.



**Figure 3.** Luminescence spectra of GAGG:Ce measured at  $E_{ex} = 6.2$  eV in fast (0–50 ns) and slow (200–5000 ns) time windows.



**Figure 4.** Decay curves of GAGG:Ce measured at the excitation density in the range from  $N_0^{max} = 3.6 \times 10^{16} \text{ cm}^{-3}$  to  $7 \times 10^{18} \text{ cm}^{-3}$ ,  $E_{ex} = 6.2 \text{ eV}$ .



**Figure 5.** The dependence of the decay curves fitting parameters—decay times (**a**) and amplitudes (**b**) on the excitation density.

It is worth noting that the increase in the excitation density does not result in the acceleration of the initial part of the decay curve as was reported for CeF<sub>3</sub> [13]. This indicates that cerium ions are not directly involved in the interaction processes and the interaction occurs between excitons directly created under 6.2 eV laser excitation and the energy is transferred to Ce<sup>3+</sup> only after the interaction.

### 3.3. Z-Scans of GAGG:Ce

The dependence of the  $Ce^{3+}$  emission intensity measured in the whole temporal region (0–20,000 ns) on the density of excitations (Z-scan) is presented in Figure 6a. The

luminescence intensity decreases with the excitation density increase that is related to exciton–exciton interaction. The threshold excitation density needed for the luminescence suppression is only  $N_0^{max} = 2 \times 10^{17}$  cm<sup>-3</sup>. Such a value implies a relatively low concentration of excitations. The mean distance between the excitations for this excitation can be estimated as  $\frac{1}{\sqrt[3]{N_0^{max}}} \sim 17$  nm. The calculated value exceeds the typical values of dipole–dipole interaction distances (R<sub>d-d</sub> < 5 nm) by several times [8–11]. Therefore, we suppose that the interaction occurs between mobile excitons in the case of GAGG:Ce.



**Figure 6.** Dependence of GAGG:Ce emission intensity on the excitation density (Z-scan) measured in the whole temporal region (**a**) and in the fast (1) and slow (2) time windows (**b**). The curve (**c**) presents the ratio of dependences measured in slow and fast time windows. The ratio between the amplitudes of fast and slow components of the decay curve fit are given by asterisks.

Time-resolved Z-scans measured in the fast (0–50 ns) and slow (200–5000 ns) time windows are presented in Figure 6b. For the fast time window, the curve is similar to that obtained for the whole temporal region (Figure 6a). In contrast, for the slow time window, an increase in intensity is observed for the densities up to ~10<sup>18</sup> cm<sup>-3</sup>. The effect is saturated at  $N_0^{max} \sim 2 \times 10^{18}$  cm<sup>-3</sup> which can be deduced from the constant in the ratio between fast and slow time windows (Figure 6c). The ratio between delayed and prompt decay components was also determined from the fit of decay components presented in Figure 5 as  $(\tau_{s1}A_{s1} + \tau_{s2}A_{s2})/(\tau_{f1}A_{f1} + \tau_{f2}A_{f2})$ . The corresponding data are presented by asterisks in Figure 6c and they coincide with the curve obtained from the time-resolved Z-scan experiment.

### 3.4. Discussion

According to the presented data, the decay kinetics of Ce<sup>3+</sup> emission in GAGG:Ce depend on the excitation density. The decay becomes slower with the increase in the excitation density. No additional decay components arise according to the presented fit but the redistribution between the amplitudes of fast and delayed decay components takes place. This means that no additional channels of energy relaxation are created under excitation density increase but the redistribution between the existing energy channels occurs. There are several channels of the energy transfer from the host to Ce<sup>3+</sup> emission centres in GAGG. The scheme of the energy transfer pass-ways is presented in Figure 7. The excitation energy 6.2 eV corresponds to the region of the direct exciton creation. The most probably Gd charge transfer (GdCT) excitons are created on the electron transition from 2p states of oxygen, which form the valence band top, to 5d states of Gd, which probably form the bottom of the conduction band similarly to  $Gd_3Ga_5O_{12}$  and  $Gd_3Al_5O_{12}$  [26]. Energy transfer from the GdCT exciton to cerium may occur in two ways: (1) directly from GdCT (it is a prompt excitation) and (2) via self-trapping of the GdCT exciton (STE) with further slow energy transfer to Ce<sup>3+</sup> via 4f states of Gd<sup>3+</sup>. The former channel of energy transfer dominates under the excitation with a low density of laser irradiation. The low electron mass at the conduction band bottom in Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub> and Gd<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> [26] implies high mobility of GdCT and low probability of their self-trapping.



**Figure 7.** Scheme of the energy transfer pass-ways from the excitons to Ce<sup>3+</sup> emission centers in GAGG:Ce in case of low (at **left**) and high (at **right**) excitation densities. GdCT—Gd charge transfer exciton; STE—self-trapped exciton; STH—self-trapped hole, Ce<sup>3+</sup>\*-excited cerium ion.

The energy transfer via the second channel will result in the appearance of delayed decay component(s). As was shown in [5] for cerium-doped gadolinium oxyorthosilicate, there are two delayed components with decay times up to 194 and 736 ns, which arise due to the energy transfer via  ${}^{6}I_{J}$  and  ${}^{6}P_{J}$  states of gadolinium. Two delayed components with similar decay times—150 and 600 ns—were also obtained by the fit of experimental decays for GAGG:Ce. Their origin is ascribed to the energy transfer from the exciton to Ce<sup>3+</sup> via  ${}^{6}I_{J}$  and  ${}^{6}P_{I}$  Gd<sup>3+</sup> states as well.

In the case of high excitation density, two mobile excitons may interact with the annihilation of the first one and disintegration of the second one into a separated electron and a hole. Such interaction takes place in GAGG:Ce which was proven by the Ce<sup>3+</sup> intensity decrease in Z-scan experiments (Figure 6). The appearance of separated e-h pairs redistributes the contributions of the prompt and delayed energy transfer channels. We suppose that the hole can be self-trapped (formation of STH in Figure 7), as has previously been shown for garnets [27]. The electrons will be bound with STHs with the formation of self-trapped excitons. According to the model, self-trapped excitons transfer their energy via the Gd<sup>3+</sup> subsystem, i.e., via delayed transfer. The number of excitations which are subjected to the process of exciton-exciton interaction quadratically increases with the excitation density while the number of excitations linearly grows with the density. This is a reason of redistribution between the amplitudes of slow and fast decay components with the increase in excitation density (Figure 5). As a result, the increased contribution of delayed components in the decay curves of Ce<sup>3+</sup> emissions is obtained. The increase in the ratio is saturated at  $N_0^{max} > 2 \times 10^{18}$  cm<sup>-3</sup> which is related to the reaching of a balance between the delayed and prompt energy transfer channels.

In order to demonstrate the described excitation density effect, we can write the simplified set of rate equations for concentrations of gadolinium charge transfer excitons  $n_{GdCT}(t)$ , Gd ions with excitation at 4f subsystem  $n_{Gd4f}(t)$ , STEs  $n_{STE}(t)$ , and excited cerium ions  $n_{Ce}(t)$ :

$$\frac{dn_{Ce}(t)}{dt} = -\frac{1}{\tau_{Ce}}n_{Ce}(t) + \beta_{GdCT \to Ce}n_{Ce}^{0}n_{GdCT}(t) + \beta_{Gd4f \to Ce}n_{Ce}^{0}n_{Gd4f}(t),$$

$$\frac{dn_{GdCT}(t)}{dt} = -\beta_{GdCT \to Ce}n_{Ce}^{0}n_{GdCT}(t) - w_{GdCT \to Gd4f}n_{GdCT}(t) - 2\beta_{GdCT + GdCT \to STE}n_{GdCT}^{2}(t),$$

$$\frac{dn_{Gd4f}(t)}{dt} = -\beta_{Gd4f \to Ce}n_{Ce}^{0}n_{Gd4f}(t) - \frac{1}{\tau_{Gd4f}}n_{Ce}(t) + w_{GdCT \to Gd4f}n_{GdCT}(t) + w_{STE \to Gd4f}n_{STE}(t),$$

$$\frac{dn_{STE}(t)}{dt} = -w_{STE \to Gd4f}n_{STE}(t) + \beta_{GdCT + GdCT \to STE}n_{GdCT}^{2}(t)$$
(2)

with initial conditions

$$n_{\text{GdCT}}(0) = n_0, \ n_{\text{Gd4f}}(0) = 0, \ n_{\text{STE}}(0) = 0, \ n_{\text{Ce}}(0) = 0$$

Here,  $\tau_{Ce}$  and  $\tau_{Gd4f}$ —radiation time of excited cerium and gadolinium,  $\beta_{i\rightarrow j}$ —bimolecular rates of the process  $i \rightarrow j$ ,  $n_{Ce}^0$ —concentration of cerium in a non-excited state,  $w_{i\rightarrow j}$ —monomolecular rates of conversion of GdCT and STE into 4f excitation of gadolinium. Please note that in reaction GdCT + GdCT  $\rightarrow$  STE, two excitations disappear and only one is created (pay attention to factor 2 in the last term of the second equation). This set of equations was solved for the set of parameters  $\tau_{Ce} = 60 \text{ ns}$ ,  $\tau_{Gd4f} = 100 \text{ µs}$ ,  $\beta_{Gd4f} \rightarrow Ce n_{Ce}^0 = 1/(200 \text{ ns})$ ,  $\beta_{GdCT} \rightarrow Ce n_{Ce}^0 = 1 \text{ ns}^{-1}$ ,  $w_{GdCT} \rightarrow Gd4f = 0.1 \text{ ns}^{-1}$ ,  $w_{STE} \rightarrow Gd4f = 1 \text{ ns}^{-1}$ , and  $\beta_{GdCT} \rightarrow STE = 10^{-17} \text{ cm}^3/\text{s}$ . The results of the solutions for the initial concentration of excitations  $n_0$  from  $10^{16}$  to  $10^{19} \text{ cm}^{-3}$  are presented in Figure 8a (decay kinetics for different initial concentrations) and Figure 8b (dependence of total integral of cerium emissions and partial integrals for 0–50 ns and 200–5000 ns intervals). Decay curves are normalized to the initial concentration of excitations. The results of the numerical simulation qualitatively reproduce the experimental results thus justifying the proposed model of energy relaxation in GAGG:Ce.



**Figure 8.** Results of numerical simulation using Equation (2) of the dependencies of decay kinetics (**a**) and emission intensity (**b**), total (1) and time-resolved in time windows 0–50 ns (2) and 200–5000 ns (3) on the initial concentrations of excitations.

### 4. Conclusions

The luminescence properties of GAGG:Ce single crystals were studied using the 4th harmonic of a Ti:saphire laser. It was shown that the emission intensity and decay

characteristics of  $Ce^{3+}$  luminescence depend on the excitation density. The intensity of luminescence decreases with the excitation density that is related to exciton–exciton interaction. It is estimated that the exciton–exciton interaction starts when the average distance between excitations is 16 nm thus implying interaction between mobile (not self-trapped) excitons. The redistribution between the decay components of the  $Ce^{3+}$  emission occurs with the excitation density. In particular, the contribution of prompt components in the decay of the  $Ce^{3+}$  emission decreases and that of delayed components increases with the excitation density. The observed redistribution between decay components is connected with the increase in the probability of delayed energy transfer to  $Ce^{3+}$  via 4f levels of the  $Gd^{3+}$  sublattice when the interaction between excitations is realized. Numerical simulation of the modification of the energy transfer process with an excitation density has been performed, which qualitatively reproduces the experimental results and justifies the proposed model

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma16030971/s1.

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