Temperature-dependent nonradiative energy transfer from Gd\(^{3+}\) to Ce\(^{3+}\) ions in co-doped LuAG:Ce,Gd garnet scintillators

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1. Introduction

Scintillator materials are widely used for detection of X-rays, gamma rays or high energy particles. In last decades particular emphasis was put on yttrium and lutetium aluminum garnets doped by trivalent Ce\(^{3+}\) ions, Y\(_3\)Al\(_5\)O\(_{12}\):Ce (YAG:Ce) and Lu\(_3\)Al\(_5\)O\(_{12}:\)Ce (LuAG:Ce), respectively, due to their fast allowed 5d\(\rightarrow\)4f emission and relatively high light yield (LY) of 20 kPh/MeV for YAG:Ce [1] and 26 kPh/MeV for LuAG:Ce [2]. However, due to complexity of garnet structure, many kinds of defects such as cation antisites, vacancies, or vacancy complexes are formed [3–7]. As a consequence, energy levels related to shallow or deep traps appear in the energy gap which may result in delayed radiative recombination at the Ce\(^{3+}\) centers and negatively influence the scintillation response. In order to diminish such defects a new concept of Gd\(_3\)Ga\(_5\)Al\(_5\)O\(_{12}:\)Ce (GGAG:Ce) multicomponent garnet has been recently designed [8]. In these garnets with optimized Gd and Ga composition the light yield increases up to 50–60 kPh/MeV [9,10].

In our recent work we have shown that in Ce,Gd co-doped LuAG garnets there should exist nonradiative energy transfer (ET) from Gd\(^{3+}\) to Ce\(^{3+}\) ions which is effective even at low Gd and Ce concentrations when D–D (donor–donor) or D–A (donor–acceptor) distances are large [11,12]. Gd to Ce energy transfer was also reported for Gd\(_5\)Si\(_2\)O\(_{12}:\)Ce [13]. Based on photoluminescence decay kinetics it was demonstrated that Gd\(^{3+}\) ions serve as sensitizers in aluminum garnets and the excitation energy captured by these ions is transferred to the Ce\(^{3+}\) acceptor ions. In fact, high efficiency of GGAG:Ce garnet scintillators should profit just from the effective Gd\(^{3+}\)–Ce\(^{3+}\) energy transfer. The heavy gadolinium ions are more easily excited by high energy radiation or particles as compared to lighter yttrium ions. Therefore, efficient energy transfer from a Gd\(^{3+}\) donor (sensitizer) to an acceptor (activator) Ce\(^{3+}\) emission center is important mechanism for high sensitive scintillators or phosphors.

However, some questions related to the mechanism of the Gd\(^{3+}\)–Ce\(^{3+}\) ET still remain unanswered. In view of the fact, that the overlap between Gd\(^{3+}\) emission at 314 nm and 5d\(_2\) (Ce\(^{3+}\)) absorption band centered at 340 nm is rather small, the direct radiative ET has smaller efficiency. It was suggested that lattice phonons should participate in the mechanism of the ET [11]. Furthermore, in many oxide or fluoride compounds the Gd\(^{3+}\) sublattice plays the role of a transport system for the excitation energy where both \(^{5l}\) and \(^{4P}\) (Gd\(^{3+}\)) energy states can contribute to this process [14,15].

The aim of this work is to shed more light on the underlying mechanism of the Gd\(^{3+}\)–Ce\(^{3+}\) energy transfer. We concentrated here on low doped LuAG:Ce,Gd garnet systems where migration of the excitation energy over the Gd sublattice is substantially reduced as was experimentally confirmed in this work. One can get insight into the nature of the Gd–Ce interaction by examining the response of the system to the pulse excitation since both Gd\(^{3+}\) and Ce\(^{3+}\) ions exhibit intensive photoluminescence in these diluted systems. Therefore, particular attention was focused on the...
study of the Gd\(^{3+}\) photoluminescence decay and its dependence on content of Ce co-dopant and temperature.

For this work a set of Ce and Gd co-doped LuAG samples was prepared with Gd content fixed to \(-5\%\) while the concentration of Ce varied from 0% to 0.5% (both values relate to ratio of respective ions to Lu in the dodecahedral sites). The photoluminescence (PL) decay kinetics was studied in the temperature range from 77 to 480 K. The results are discussed using the Forster–Dexter theory [16, 17] of the nonradiative ET using a single step ET approach developed by Inokuti and Hirayama [18] and diffusion limited approach developed by Yokota and Tanimoto [19], which considers also migration of the excitation energy over the Gd subsystem. In both these approaches the ET was observed to occur via long range multipolar interaction.

2. Experimental

2.1. Samples

Thin single crystalline garnet films of nominal composition \((\text{Ce},\text{Gd},\text{Lu}_{1-x-y})_3\text{Al}_5\text{O}_{12}\) were grown by liquid phase epitaxy (LPE). Starting raw materials of 5 N purity were used. A set of samples with constant Gd content of \((4.8 \pm 0.3)\%\) and variable Ce content which changed in several steps from 0% to 0.5% (values apply to proportion of ions in the dodecahedral rare earth sites in the garnet lattice) was prepared. All garnet films reported here were grown by the standard isothermal dipping technique from the lead-free BaO–B₂O₃–BaF₂ flux (referred here as BaO-flux), the growth details were published elsewhere [20, 21]. The main advantage of the BaO-flux is high purity of films, negligible concentration of solvent ions in the garnet lattice (content of divalent \(\text{Ba}^{2+} < 5\) ppm according to the GDMS analysis). Its negligible chemical reactivity with platinum crucible and incorporation of flux species (e.g. \(\text{Pb}^{2+}, \text{Pt}^{4+}\) ions from standard PbO flux) into the crystal is eliminated. The films were grown from supercooled melt solution onto \((111)\) oriented LuAG substrates of 20 mm in diameter. The growth temperatures were in the range of 1000–1070 °C and the growth rates 0.10–0.17 \(\mu\)m/min.

2.2. Film characterization and experiment

Thickness and concentration of Gd and Ce dopants in samples are summarized in Table 1. Thickness of epitaxial films was measured by weighting; the composition was determined by the electron probe X-ray microanalysis (EPMA). The segregation coefficients were typically \(k_{\text{Ce}} \sim 0.03–0.1\) and \(k_{\text{Gd}} \sim 0.5\) for Ce and Gd ions, respectively. The crystallographic properties of films were studied using the X-ray diffraction. Absorption spectra were measured by Shimadzu 3101PC spectrometer in the spectral range from 190 to 800 nm at various temperatures (77–400 K). Photoluminescence decay kinetics was measured using the custom made spectrofluorometer 5000M Horiba Jobin Yvon. The nanoLED pulse (\(\lambda = 339\) nm) and microsecond xenon flash lamp were used as excitation sources for fast and slow decay kinetics, respectively. The PL decays were measured in the submicrosecond (time correlated single photon counting) and millisecond (multichannel scaling) time ranges. Photon counting TIX-04 detection and single grating excitation/emission monochromator were used. An Oxford Instrument Optistat cryostat was used to obtain temperature dependencies of the PL and absorption within the temperature range 77–480 K. In all measured decay curves the convolution procedure is applied to extract the true decay time values.

3. Experimental results

3.1. Photoluminescence (PL) spectra

The Ce\(^{3+}\)-related photoluminescence spectra of two LuAG:Ce, Gd films which differ in Gd content are shown in Fig. 1a. Observed broad emission band between 500 and 700 nm is typical for \(5d_{\text{Gd}^{3+}} \rightarrow 4f^2\text{P}_{2(2S)}\) emission in Ce\(^{3+}\) ions. In the excitation spectra, measured at 520 nm of cerium emission, the \(5d_{\text{Gd}^{3+}}\text{Ce}^{3+}\) broadbands at 340 and 450 nm dominate, however, sharp 4f–4f (\(6\)\(^{1}S\)) Gd absorption lines are also observed in these spectra at around 274 nm. Therefore, the Ce\(^{3+}\) emission is excited also by means of excitation of \(6\)\(^{1}S\) multiplet states of Gd\(^{3+}\). These observations support the concept of energy transfer from Gd\(^{3+}\) to Ce\(^{3+}\) ions as discussed in Refs. [11, 12]. The ET away from Gd ions is also evident in Fig. 1b. Table 1

<table>
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<th>Sample</th>
<th>Thickness ((\mu)m)</th>
<th>Ce content, x (\times 10^2)</th>
<th>Gd content, y (\times 10^2)</th>
<th>(\tau_{\text{as}}) (ms)</th>
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<td>3.51</td>
</tr>
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</table>

Table 1

Thickness and concentration of Gd and Ce ions in \((\text{Ce},\text{Gd},\text{Lu}_{1-x-y})_3\text{Al}_5\text{O}_{12}\) epitaxial garnet films determined by EPMA. \(\tau_{\text{as}}\) is asymptotic decay time of \(5d_{\text{Gd}^{3+}} \rightarrow 5f\text{S}\) emission, for details see text.

Fig. 1. (a) Photoluminescence excitation (left) and emission (right) spectra of two \((\text{Gd},\text{Lu}_{1-x-y})_3\text{Al}_5\text{O}_{12}:\text{Ce}\) epitaxial films with different Gd contents; (b) 4f–4f photoluminescence \(5d_{\text{Gd}^{3+}} \rightarrow 5f\text{S}\) emission peak of Gd\(^{3+}\) (solid lines) for samples with different Ce contents and 5d\(_2\) excitation spectral band of Ce\(^{3+}\) (dashed line) of co-doped (GdLu\(_3\))\text{Al}_5\text{O}_{12}:\text{Ce} epitaxial films at \(T = 300\) K. Concentrations of Ce and Gd are given in the legend.
3.2. PL decay kinetics of Gd in (a) calculated using Eq.

The decay is accelerated especially in the initial part, i.e. at short times after the excitation, where the decay curves noticeably deviate from one-exponential form, which is most apparent in samples with the highest Ce content. This nonexponentiality at early times after excitation is a signpost of the nonradiative ET from Gd$^{3+}$ ions. This suggests that higher Ce concentration enhances energy transfer probability. Namely, the non-radiative energy transfer from donors to acceptors reduces the population of donor Gd$^{3+}$ excited states and causes the life-time and their own emission to decline. However, the ET is only important when the transfer rate is higher than the radiative rate of the donor Gd$^{3+}$ ion. When the acceptor Ce$^{3+}$ ions are randomly distributed in the crystal, those excited donor ions, which are close enough to the acceptors, decay rapidly, so that the decay rates at short time after excitation are large. The donor Gd$^{3+}$ ions which are distant from Ce acceptors remain excited and their decay approaches to the radiative rate. This is reflected in the shape of the Gd$^{3+}$ decay curves which become mostly parallel at longer times. The asymptotic values of decay times $\tau_{AS}$ for long times obtained by fitting of the decay curves at 300 K are summarized in Table 1. Summarizing, the ET in the absence of energy migration among the donor subsystem is characterized by a nonexponential emission decay at short times and by a decay approaching the purely radiative rate at long times after pulse excitation. This is just the case we observe in Fig. 2, see also Figs. 5 and 6 for low temperatures.

4. Discussion

The theory of nonradiative energy transfer in inorganic solids was developed by Forster [16] and by Dexter who extended this concept to exchange interaction [17]. Energy transfer process can occur provided the following conditions are fulfilled: (a) resonance – the energy differences between the ground and excited states of donor and acceptor are equal, (b) suitable interaction between both systems exists – multipolar long range or, provided the wave function overlap exists, exchange short range interaction. When the resonance condition is not fully satisfied, but the energy gap is not too large, the energy transfer may take place with the assistance of lattice phonons. For donor–acceptor interaction, which arises from multipolar coupling between Gd and Ce, the transfer rate can be expressed as an inverse power of the Gd–Ce distance [22,23]

$$W(R) = \frac{\beta_s}{R^s},$$

where $\beta_s$ is the interaction parameter and $s = 6, 8, 10$ for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The exchange mechanism, which requires the spatial overlap of wavefunctions of involves ions, is ineffective in the studied garnet samples due to large Gd–Ce distance, which is well above 10 Å.

In the next sections two approaches are reviewed and discussed: (a) single step ET from a donor to an acceptor when energy migration over the donor system is insignificant and (b) “migration limited” ET when energy migration within the donor Gd$^{3+}$ system is slow but still comparable to intrinsic radiative decay rate.

The fast migration limit, when the migration rate is much higher than the donor–acceptor transfer rate and donor radiation rate, is not considered here. In such case the migration leads to spatial equilibrium of excitation within the donor system and the donors exhibit fast exponential decay with decay time determined by migration, e.g. [22,24,25]. Fast migration was observed in high Gd$^{3+}$ concentrated system when D–D separation is small [14,15].

![Graphical representation of theoretical fit and experimental decay curves](image)
4.1. Energy transfer without migration

The solution for time dependence of the signal after the pulse excitation and for multipolar coupling was derived by Inokuti and Hirayama (IH) [18]. Their approach takes into account the following assumptions: (i) the energy is transferred from donors (Gd$^{3+}$) to acceptors (Ce$^{3+}$), the latter are randomly distributed in the material and their concentration is much lower than that of donors, so that the distance between donors is much greater than between acceptors. (ii) Concentration of donors is low enough to disable migration of the excitation energy over the Gd-sublattice and (iii) there is one-way and one-step energy transfer, only from the donors to acceptors, back transfer Ce→Gd is impossible. For electric multipolar interaction, the intensity $I(t)$ is given by [18]

$$I(t) = I(0)\exp\left(-\frac{t}{\tau_{Gd}} - \alpha(C \frac{t}{\tau_{Gd}})^{3/5}\right)$$

(3)

where

$$\alpha(C) = I\left(1 - \frac{3}{4\pi a}\right)C$$

(4)

$I(0)$ is initial excitation, $\tau_{Gd}$ is the intrinsic lifetime of the donor Gd$^{3+}$ ions in the absence of Ce$^{3+}$ acceptors, $I$ is the gamma function, $C$ is the concentration of acceptor Ce$^{3+}$ centers, and $C_0$ is the critical concentration of acceptors which is related to the critical transfer distance $R_0$ of donor (Gd$^{3+}$) and acceptor (Ce$^{3+}$) pairs defined as $R_0 = (3/4\pi C_0)^{1/3}$. The quantity $R_0$ represents the Gd–Ce separation at which the probability of energy transfer from Gd to Ce is equal to the intrinsic probability of radiative decay of the donor

$$\frac{1}{\tau_{Gd}} = \frac{\beta_j}{R_0^3}.$$ 

(5)

The Gd decay depends on concentration $C$ of acceptors and the type of multipolar interaction, Eq. (3). Immediately after excitation, energy is nonradiatively transferred to the acceptors randomly distributed around the donors. Increase of acceptor concentration reduces the average donor–acceptor distance and results in acceleration of the energy transfer rate. Using Eqs. (3) and (4) the dominant interaction mechanism responsible for the nonradiative ET and critical concentration of acceptors, $C_0$, can be determined from the experimental decay data.

Studied garnets meet all requirements for using the IH model which adequately describes time evolution of Gd$^{3+}$ decays in the presence of Ce$^{3+}$ ions at short times after excitation. The results of the fit using Eq. (3) are displayed for room temperature decays in Fig. 2b. We used unperturbed Gd$^{3+}$ lifetime $\tau_{Gd} = 4.25$ ms (i.e. in the absence of acceptor Ce ions) and the parameter $s$ was varied in order to obtain the best fit to the experimental data. The best agreement was obtained for $s = 6$, corresponding to the dipole–dipole interaction, while $s = 8$ and 10 do not provide reasonable consent with the experimental data as demonstrated in Fig. 3. This indicates that the dipole–dipole interaction is the most appropriate mechanism governing the nonradiative energy transfer from Gd$^{3+}$ to Ce$^{3+}$ states.

The quantity $\alpha(C)$, Eq. (4) was determined simultaneously during the fitting procedure, dependence of $\alpha(C)$ vs Ce concentration is shown in Fig. 4. Subsequently, from this linear dependence the critical concentration, $C_0 = 9.4 \times 10^{19}$ cm$^{-3}$, was obtained. Corresponding critical transfer distance of donor (Gd$^{3+}$)-acceptor (Ce$^{3+}$) pair, is $R_0 \sim 14$ Å at RT, which indicates that the energy transfer occurs over rather long distances. This result is in agreement with the assumption that electric dipole–dipole interactions are dominant in the ET transfer process since the transitions in donor (Gd$^{3+}$) and acceptor (Ce$^{3+}$) are both of electric dipole character.

It is interesting to compare the obtained values with literature data. Tb$^{3+}$→Ce$^{3+}$ energy transfer was reported for YAG:Ce,Tb garnets prepared either by LPE [26,27] or by solid-state reaction [28]. Results were discussed based on the single-step ET approach and dipole–dipole dominant interaction was found most probable. Obtained $R_0$ values ~15–18 Å correlate with reported results here. Detailed study of energy transfer between unlike trivalent rare earths, Tb$^{3+}$→RE$^{3+}$ and Eu$^{3+}$→RE$^{3+}$, in phosphate glasses Ca (PO$_4$)$_2$:RE, where RE stands for ten various rare earths, were made by Nakazawa et al. [29]. He found critical diameter in the range from 4 to 12 Å and the ET is predominantly governed by dipole–quadrupole interaction.

4.2. PL decay kinetics of Gd$^{3+}$ – temperature measurements

The Gd$^{3+}$ decays measured at temperatures from 77 K to 480 K in samples with different concentrations of Ce=0%, 0.22%, 0.40% and 0.50% are displayed in Figs. 5 and 6. The sample LuAG:Gd without Ce co-doping, shows one exponential Gd$^{3+}$ decay at all temperatures. The Gd$^{3+}$ decay times $\tau_{Gd}$ are virtually independent on temperature and any temperature quenching was not observed up to 480 K. The intrinsic values $\tau_{Gd}$ for various temperatures are summarized in Table 2. All other samples containing Ce$^{3+}$ co-dopant show nonexponential Gd$^{3+}$ decays similarly to the PL decays measured at RT.

Significant nonexponential decay was observed especially at higher temperatures. As observed in Fig. 5, the initial nonlinearity, i.e. faster initial decay, noticeably increases both at higher temperatures and also at higher Ce content, which implies faster
energy transfer by direct relaxation to nearby ions. The effect of Ce concentration on the Gd decay is demonstrated in Fig. 6 for two specific temperatures of 77 and 430 K (results at 300 K are shown in Fig. 2). Evident deviation from single exponential dependence at short times is observed at higher Ce concentration. At long times the decay rates are close to intrinsic Gd radiative rate, Fig. 5 and 6. All these observations support presumed nonradiative energy transfer from Gd$^{3+}$ to Ce$^{3+}$ ions.

Similarly to the PL decay measurement at RT, we applied the IH model to all decays measured between 77 and 480 K and fitted the experimental data using Eq. (3). For each particular temperature the relevant $\tau_{cd}$ from Table 2 was used. The best fit of the experimental data was obtained for dipole-dipole interaction, $s=6$, at all temperatures. The decay curves in Figs. 5 and 6 are results of the fit, the experimental data are not shown for clarity.

Comparing the dependencies in Figs. 5 and 6, we see rather moderate effect of temperature on the ET process. The parameters calculated from the experimental decay curves measured at various temperatures, i.e. critical concentration, $C_0$, and critical transfer distance, $R_0$, are summarized in Table 2. Parameter $R_0$ increases only by 18% when temperature raises from 77 to 480 K presumably due to increased number of excited phonons. Dependence of the critical distance $R_0$ on temperature is shown in Fig. 7. The ratio

$$\eta = \frac{\int_0^\infty \Phi(t)dt}{\tau_{cd}}$$

represents the relative yield of the donor Gd$^{3+}$ emission in the presence of acceptor ions. The integral intensities of Gd$^{3+}$ PL decays measured at various temperatures are shown in Fig. 8. We see that integral intensity of the sample without Ce doping is basically constant up to the highest temperatures. At increasing both Ce activator content and/or temperature this yield decreases, Fig. 8. This figure demonstrates that the ET towards Ce$^{3+}$ acceptors is more efficient at higher Ce$^{3+}$ concentrations and at higher temperatures.

### 4.3. Migration limited energy transfer

Detailed examination of the experimental curves prompts, that decay at long times (i.e. their asymptotic values) are somewhat lower than the intrinsic values $\tau_{cd}$ in Table 1 and Figs. 5 and 6. This suggests some contribution from migration to the Gd–Ce energy transfer process. In fact, in many real systems energy migration among donors cannot be neglected since this transfer is resonant and, in principle, rapid. Excitation energy migrating over Gd$^{3+}$ sublattice, before passing to a Ce$^{3+}$ acceptor, decreases the effective Gd–Ce distance. The migration of energy may be treated as a diffusion process [19,25]. General formula describing decay function at dipole–dipole interaction, when both single step ET and diffusion are active, however, the diffusion is not fast enough to
maintain the initial distribution of excitation, was derived by Yokota and Tanimoto [19]

\[ I(t) = I(0) \exp \left( -\frac{t}{\tau_{\text{Gd}}} - \alpha(t_t) \left( \frac{1 + 10.87x + 15.5x^2}{1 + 8.743x} \right)^{3/4} \right) \]  

(7)

where \( x = D\beta^{-1/3}t^{2/3} \) and \( D \) is the diffusion coefficient. Generalization of this formula for any kind of multipole interaction was reported in Ref. [30].

When diffusion coefficient \( D \) is small and/or at short times after excitation, then \( x \ll 1 \), and Eq. (7) reduces to the IH Eq. (3) and nonexponential decay is predicted as discussed above. The decay is governed by those donors, which have the shortest distance to activators. In the other limit at enough long times, the decay given by Eq. (7) becomes nearly exponential, \( I(t) \sim \exp(-t/\tau_t) \), with a rate approximated by

\[ \frac{1}{\tau_t} = \frac{1}{\tau_{\text{Gd}}} + \frac{1}{\tau_M} \]  

(8)

where \( 1/\tau_M \) is the decay rate correction due to migration (diffusion), which is given in Refs. [25,31]

\[ \frac{1}{\tau_M} = 8.5C\beta^{1/4}D^{3/4} \]  

(9)

Analysis of decay curves measured for various acceptor concentrations and in a wide temperature range, Figs. 5 and 6 enable us to estimate the role of energy migration in the energy transfer process. The radiative rates of \( \text{Gd}^{3+} \), \( 1/\tau_{\text{Gd}} \), determined in LuAG:Gd sample without acceptor Ce ions, are summarized in Table 2. The transfer rate \( 1/\tau_t \) was estimated from asymptotic values of decays. The calculated diffusion rates using Eq. (8), \( 1/\tau_M \), are very low in the entire temperature range 77–480 K, about 5–10 times lower as compared to the \( \text{Gd} \) radiative rates. The parameter \( \beta \) was determined using Eq. (2). In the cited temperature range it yields \( \beta \sim 1.1 \times 10^{-39} \text{ cm}^6 \text{ s}^{-1} \) at temperatures 77–480 K. The calculated diffusion coefficient is very small, \( D \sim 4 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \) at 300 K. Furthermore, the diffusion rate and diffusion coefficient depend on temperature only slightly – they change by a factor of only \( \sim 1.5 \) when temperature increases from 77 to 480 K. This weak dependence on temperature is likely due to great \( \text{Gd} \)–\( \text{Gd} \) distance in studied samples. For comparison we refer the results of Eu\(^{3+} \)–Cr\(^{3+} \) energy transfer in Eu(Po\(_3\)\(_3\)Cr\(_{2}\)) glass (i.e. at high donor Eu concentrations), where the Eu\(^{3+} \) decay rate, migration rate, and diffusion constant were observed to change an order of magnitude in the temperature range 77–600 K [31].

These results justify the application of the IH approach to our low doped LuAG:Ce,Gd samples, Eq. (3), where the ET is treated as a single step process which dominates and migration of the excitation energy was neglected to the first approximation. In fact, the asymptotic values \( \tau_{\text{AS}} \) for long times, cf. Figs. 2, 5 and 6, differ only little from intrinsic decay \( \tau_{\text{Gd}} \). In studied samples, the \( \text{Gd}–\text{Gd} \) separation is large enough. Therefore only a small number of excited donors are within the critical distance \( R_0 \) of an acceptor. In such a case the migration is significantly limited as was experimentally observed.

It is worth mentioning that significant energy migration, resulting in quenching of \( \text{Gd}^{3+} \) emission, was observed in heavily concentrated \( \text{Gd} \) oxides and fluorides when \( \text{Gd}–\text{Gd} \) separation is small [14,15,32]. The critical distance for efficient energy migration between \( \text{Gd}^{3+} \) ions was found to be 5 and 6.5 Å in fluorides and oxides, respectively, in \( \text{Gd} \) garnets with center of symmetry this was 5 Å [14] which corresponds to 50% \( \text{Gd} \) occupation of dodecahedral sites. Above this distance the migration is significantly limited.

Setlur et al. [33] studied \( \text{Tb} \rightarrow \text{Ce} \) energy transfer in \( \text{TiB}_{2} \text{Lu}_{1-x} \text{Al}_{3} \text{O}_{5} \text{Ce} \) as a function of \( \text{Tb} \) concentration. It was shown that the mechanism for nonradiative energy transfer can switch from a longer-range dipole–dipole mechanism to a short-range exchange mechanism through energy migration between donors in heavily \( \text{Tb} \) substituted samples with \( \sim 65\% \) of \( \text{Tb} \) ions in the dodecahedral site.

4.4. Optical absorption

The spectral overlap of donor emission and acceptor absorption bands is important assumption for efficient energy transfer [34,35]. Fig. 1b displays \( 3\text{P}_{2,1} \rightarrow 3\text{G}_{7/2} \) emission of \( \text{Gd}^{3+} \) and \( 4\text{F}_{5/2} \rightarrow 4\text{I}_{11/2} \) excitation band of \( \text{Ce}^{3+} \). The narrow \( \text{Gd}^{3+} \) emission peak is situated just at the edge of broad allowed absorption band of the activator \( \text{Ce}^{3+} \) ions. However, if weak transitions (such as parity forbidden \( f-f \) transitions in \( \text{Gd}^{3+} \)) have sufficiently long life times of excited states, significantly longer as compared to life times of \( \text{Ce}^{3+} \) acceptors, they may also effectively contribute to the ET. Energy transfer may then substantially increase the population of excited \( \text{Ce}^{3+} \) states as compared with direct absorption of light. Effective sensitization requires that the \( \text{Gd}^{3+} \rightarrow \text{Ce}^{3+} \) energy transfer has much higher rate than the radiative rate of the \( \text{Gd}^{3+} \) ions.

Efficiency of the ET depends on the spectral overlap of \( \text{Gd}^{3+} \) emission at 314 nm and \( \text{Ce}^{3+} \)–\( \text{Ce}^{3+} \) broad-band absorption with maximum at 340 nm. This overlap and its temperature development can be assessed from absorption spectra shown in Fig. 9. The \( \text{Gd}^{3+} \) lines are practically temperature independent, while the cerium \( 5d_{2} \) absorption considerably increases with temperature due to rising population of the higher crystal field split state \( 2\text{F}_{5/2} \) (\( \text{Ce}^{3+} \)) of ground multiplet [36]. Since the weak parity forbidden \( 4f-4f \) (Gd) absorption is not discernible in thin epitaxial films, absorbance of heavily Gd doped 1 mm thick single crystal garnet \( \text{Gd}_{3}\text{Ga}_{5}\text{Al}_{12} \text{O}_{37}: \text{Ce} \) is displayed in Fig. 9. This single crystal has its \( 5d_{2} \) absorption band located almost exactly at the same energy as in studied epitaxial films, cf. Fig. 1b. Hence this material can be used as a model system, which enabled us to evaluate reliably the temperature dependence of the spectral overlap of \( \text{Gd}^{3+} \) line emitter and \( \text{Ce}^{3+} \)–\( \text{Ce}^{3+} \) broad-band absorber. The results are shown in Fig. 9b. Increasing spectral overlap, mainly due to inhomogenous broadening of the Ce absorption band at 340 nm, supports conclusions declared above, that the ET is more efficient at elevated temperatures in \( \text{Gd},\text{Ce} \) co-doped garnets due to participation of phonons in the ET process. The development in Fig. 9b well correlates with that shown in Fig. 8 supporting proposed suggestion that \( \text{Gd}^{3+} \rightarrow \text{Ce}^{3+} \) ET increases with temperature.
4.5. PL decay of trivalent cerium

The 5d–4f PL decays of Ce$^{3+}$ were obtained under excitation at 339 nm and emission at 510 nm. As an example, the Ce$^{3+}$ decay curves at three temperatures 77, 280 and 480 K of three samples with different Ce content are shown in Fig. 10. The Ce$^{3+}$ decay times, $\tau_{\text{Ce}}$, for all samples were between 53 and 56 ns in the temperature range from 77 to 480 K. These values correspond to the decay time in LuAG:Ce single crystals without Gd co-doping [21,37]. Decay curves of samples with lower Ce concentration <0.4% are strictly one exponential with $\tau_{\text{Ce}} \sim 53$ ns. Only sample with the highest Ce content of 0.5% exhibits 2-exponential decay at the highest temperature: $\sim 56$ ns (96%) and weak fast component $\sim 11$ ns (4%). This can be a sign of Ce concentration quenching onset and/or thermal ionization of excited states at high temperatures. Negligible temperature dependence of the Ce$^{3+}$ decay time shown in Fig. 11 suggests that temperature quenching of Ce$^{3+}$ emission is well above 600 K.

5. Conclusion

The decay kinetics of Gd$^{3+}$ (4f–4f) and Ce$^{3+}$ (5d–4f) emissions, measured in a wide temperature range, provided a firm evidence of non-radiative energy transfer from donor $^6P_J$(Gd$^{3+}$) to acceptor $^5D_J$(Ce$^{3+}$) states ions in co-doped LuAG:Ce,Gd garnets. This ET is effective even at low Gd and Ce concentrations. Analysis of the experimental data using the single-step ET and diffusion limited approaches demonstrated that the energy transfer is virtually single step process with dominating long range dipole–dipole interaction while the contribution from diffusion within the donor Gd$^{3+}$ subsystem is minimal. The critical concentration and critical transfer distance of donor (Gd$^{3+}$) and acceptor (Ce$^{3+}$) ions was found $C_0=9.4 \times 10^{16}$ cm$^{-3}$, $R_0=14$ Å at room temperature. The mechanism of non-radiative energy transfer based on the dipole–dipole interaction consists in the simultaneous non-radiative deexcitation of the donor (Gd$^{3+}$) center and excitation of the acceptor (Ce$^{3+}$) center. This mechanism is enabled by the partial resonance of the donor emission and acceptor absorption transitions (the overlap integral is nonzero). As the resonance is not perfect, i.e. the maximum of emission line of Gd$^{3+}$ is not centered at the maximum of absorption of Ce$^{3+}$ acceptor, the phonon assistance can enhance the energy transfer probability. The hole at the ground state of Ce$^{3+}$ is arising merely due to the excitation of 4f electron to the 5d excited state, i.e. without any further interaction with the host lattice valence band. The reported results suggest that this energy transfer is beneficial also for significant increase of scintillation efficiency in heavily Gd doped GAGG:Ce scintillators when the excitation energy migrating over the Gd sublattice is efficiently transferred to Ce$^{3+}$ activators.
Acknowledgments

This work was supported by the Czech Science Foundation, Grant no. P204/12/0805.

References