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LETTER TO THE EDITOR

Study of Yb^{3+}–Yb^{3+} and Yb^{3+}–Ce^{3+} energy transfer in Yb,Ce:$CaGd_4Si_3O_{13}$ (Yb,Ce:CGS) crystals

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Abstract. The Yb radiative lifetime of 923 μs has been determined by the extrapolation to the zero concentration of Yb. Quenching of the Yb luminescence is observed in the Yb^{3+},Ce^{3+}:$CaGd_4Si_3O_{13}$ (Yb,Ce:CGS) crystals due to their intrinsic defects and Ce^{3+} ions. The main quenching mechanism is the energy migration through Yb ions to the defects with a micro-parameter $C_{DD}(\text{Yb–Yb}) = 1.0 \times 10^{-38}$ cm^6 s^{-1}, and the $Yb^{3+} \rightarrow Ce^{3+}$ energy transfer with a micro-parameter $C_{DA} = 5.5 \times 10^{-44}$ cm^6 s^{-1}.

1. Introduction

Crystals with Yb^{3+} ions offer prospects for use as laser materials [1]. Extremal efficiency of laser generation in such crystals is higher than in crystals with Nd^{3+}. Yb^{3+} ions are traditionally used as a sensitizer of Er^{3+} ions. In crystals of $CaGd_4Si_3O_{13}$:Yb^{3+},Er^{3+} (CGS:Yb^{3+},Er^{2+}), the effectiveness of sensitization Yb–Er increases when the crystal is co-doped with Ce^{3+} ions [2]. An analogous situation takes place in the crystals of $Ca_2Al_2SiO_7$:Yb,Er,Ce [3]. Such crystals are interesting for obtaining 1.5 μm generation. Ce ions quench luminescence rather effectively not only of the $^4I_{11/2}$ erbium level and other higher levels characterized by a small energy split, but also of the $^4I_{13/2}$ erbium level. Such data were obtained from the luminescence, kinetic study of different crystals with Er and Ce. Quenching of ytterbium luminescence is also quite appreciable in Yb,Ce:CGS. The present work represents attempt of an experimental research of strongly unresonant Yb to Ce interaction in CGS crystals.

2. Crystal samples and experimental procedure

Single crystals of $CaGd_{4-x-y}Yb_xCe_ySi_3O_{13}$ were grown by the Czochralsky method. The melting temperature of crystals was 1900–1950 °C. Crystals of $Ca_2Ln_8(SiO_4)_6O_2$ had the appatite structure and belonged to the space group $P6_3/m$ [4]. Optically pure crystals were used for measurements. The segregation coefficients for Yb^{3+}, Er^{3+} and Ce^{3+} were determined by the study of absorption coefficient along the crystal. Their values were close to each other and were 0.55–0.65. Using hydrostatics weighing, the density of $Yb_{0.3}$:CGS was determined to be 6.18 g cm^{-3}. The CGS concentration was about 3.9×10^{21} cm^{-3}. Taking the distribution coefficient to be 0.6, the activators concentrations in our crystals were determined by the following expression: $N = 0.6\alpha 3.9 \times 10^{21}$ (cm^{-3}), where α is a stoichiometric coefficient.

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The absorbtion and luminescence spectra were measured by standard methods using a monochromator MDR-23 (reverse linear dispersion 2.6 nm mm^{-1}) with a slit width of 0.1–0.15 mm. Luminescence decay kinetics were measured after excitation with the first harmonic of a Q-switched YAG:Nd laser with a mono-pulse duration of 15 ns, using an analyser with a time resolution of 0.4 μs/channel. The luminescence spectral region was selected by a spectrophotometer, SDL-1, with a double grating. The decay curves were analysed using the expression $I = I_0 \exp(-t/\tau_{Yb} - \gamma\sqrt{t})$, where $1/\tau_{Yb} = 1/\tau_r + W$, τ_{Yb} is the luminescence lifetime of ytterbium, τ_r is the ytterbium radiative lifetime, W is the energy migration probability, γ is a macro-parameter of the energy transfer. We determined the luminescence rate parameters by fitting the theoretical curve to the experimental one. The absolute error for γ does not surpass ± 1.5, the relative error for W is not more than 30 s^{-1}. The systematic and random errors in the definition of the activator concentrations did not exceed 10% and 0.3%, respectively.

3. Experimental results and discussion

The lowest-energy transition of Yb in CGS is observed near 1064 nm [5]; it links the highest level of the lower multiplet with the lowest level of the upper multiplet. So the luminescence from the $^2\mathrm{F}_{5/2}$ multiplet can be excited by the main harmonic of YAG:Nd laser. We have determined that the time of the luminescence decay of ytterbium decreases when the Yb concentration increases. The introduction of the Ce ions into the crystals leads to the additional lifetime reduction. Kinetic parameters of the luminescence decay curves (see figure 1 for example) are shown in the table 1.

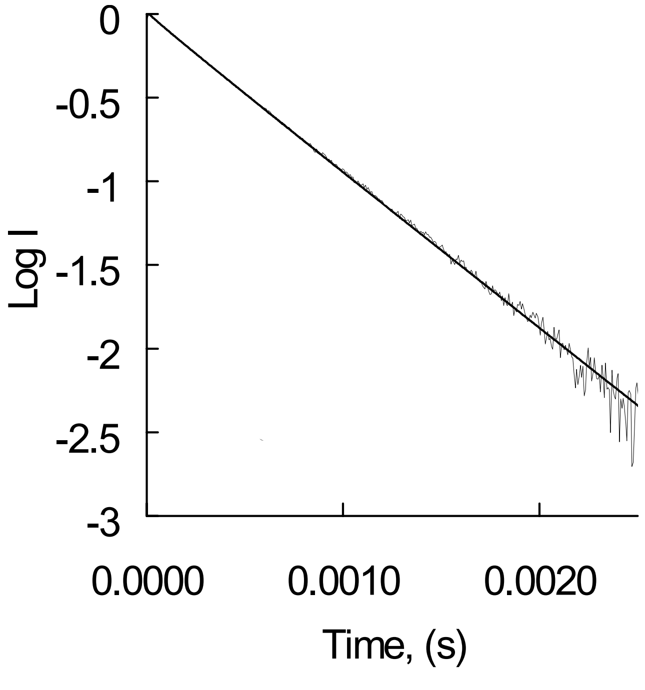

Figure 1. Decay curve of the 980 nm luminescence of $\mathrm{Yb}_{0.22}\mathrm{Ce}_{0.4}$:CGS crystal after a 1064 nm laser pulse.

Table 1. Kinetic parameters of the Yb_xCe_y:CGS crystals. W_{def} is calculated by equation (1).

Crystal	N_{Yb} (10^{19} cm^{-3})	N_{Ce} (10^{19} cm^{-3})	τ_{Yb} (μs)	$W = 1/\tau_{Yb} - 1/\tau_r$ $(1/\tau_{Yb} - W_{def} - 1/\tau_r)$ (s^{-1})	γ (s$^{-1/2}$)
$Yb_{0.03}$:CGS	7.0	—	847	97.5 (−7.75)	6.27
$Yb_{0.23}$:CGS	53.8	—	522	832 (31.4)	6.68
$Yb_{0.3}$:CGS	70.2	—	475	1021 (−22.6)	5.45
$Yb_{0.22}$,$Ce_{0.4}$:CGS	51.5	93.6	499	920 (155)	6.72
$Yb_{0.21}$,$Ce_{0.8}$:CGS	49.1	187.2	459	1095 (365)	6.38

Macro-parameters of the energy transfer from Yb to the defect centres of unknown nature are small and remain permanent (the average value in the three first samples $\gamma = 6.15$ s$^{-1/2}$), while the lifetime essentially decreases with the increase of the ytterbium concentration. Hence the reason for the luminescence quenching is energy migration through the excited levels of Yb to the defects. The dependence of $1/\tau_{Yb}$ on the concentration of Yb is linear and the approximation of this dependence to zero concentration of Yb^{3+} makes it possible to define the Yb radiative lifetime (see figure 2) as 923 μs. The study of the line slope gives us the following correlation:

$$W_{def} = N_{Yb} 1.658 \times 10^{-18} \tag{1}$$

where $W_{def} = 1/\tau_{Yb} - 1/\tau_r$ the probability of energy migration through the $^2F_{5/2}$ states of Yb^{3+}. The energy migration probability in the case of dipole–dipole interactions and migration process with energy jumps can be described as

$$W = \pi(2\pi/3)^{3/2}(C_{DA}C_{DD})^{1/2}N_DN_A = 19.91(C_{DA}C_{DD})^{1/2}N_DN_A \tag{2}$$

or

$$W = 2.68\gamma N_D(C_{DD})^{1/2} \tag{3}$$

where

$$\gamma = \tfrac{4}{3}\pi^{3/2}N_A(C_{DA})^{1/2} = 7.42N_A(C_{DA})^{1/2} \tag{4}$$

and subscript A denotes acceptors (Ce or intrinsic defects), subscript D denotes donors (Yb).

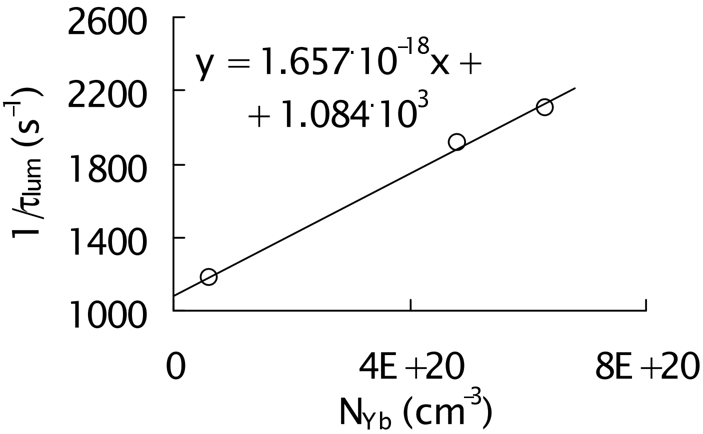

Figure 2. The dependence of ytterbium reverse lifetime against ytterbium concentration.

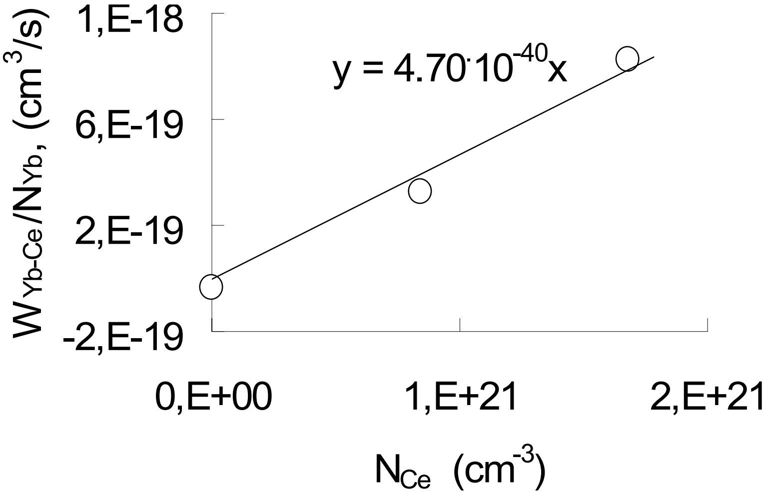

Figure 3. The dependence of the energy migration probability (from the ytterbium to the cerium ions) against the cerium concentration.

Using the average value of the energy transfer macro-parameters $\gamma = 6.15$ s$^{-1/2}$, we have defined from (1) and (3) the micro-parameter of the energy migration of C_{DD}(Yb–Yb) $= 1.01 \times 10^{-38}$ s^{-1} cm^6. It should be noted, that the size of γ in the crystals with Ce does not appreciably vary in comparison with the crystals without Ce (see table 1). Hence, the size of γ (Yb–Ce) does not exceed a random error of measurements. In reality, the estimation of γ by (3) for $y = 0.8$ and $W = 365$ s^{-1} gives approximately 2.8, i.e. it is within the limits of the possible error of measurements. Nevertheless it is possible to estimate the energy transfer parameters from the ytterbium to the cerium ions as follows. Assuming that two channels of quenching—by defects and by Ce^{3+} ions—are independent from each other, we can write:

$$W(\text{Yb–Ce}_y) = 1/\tau_{Yb(Yb_xCe_y)} - W_{def} - 1/\tau_r \qquad (5)$$

where $W(\text{Yb–Ce}_y)$ is the probability of the energy migration from Yb^{3+} to Ce^{3+}. In conformity with (2) the probability $W(\text{Yb–Ce}_y)$ increases proportionally with the Ce^{3+} concentration. The maximum disorder of our measurements is 31.4 s^{-1} (see table 1, the first three values in brackets of the 5th column should be ideally equal to zero). Taking errors into account, the probability of the energy migration to the Ce ions can be well approximated by a linear function of the Ce concentration (figure 3) in accordance with equation (2). From the linear function and from (2) we have calculated a micro-parameter C_{DA} (Yb–Ce) $= 5.5 \times 10^{-44}$ s^{-1} cm^6. The small value of the parameter C_{DA}(Yb–Ce) is caused by the unresonant character of the Yb–Ce interaction. It should be noted, that according to our data the Ce ions in Er,Ce:CGS crystals may quench luminescence not only of $^4S_{3/2}$ and $^4I_{11/2}$ erbium levels and other levels with a small power split, but also of the $^4I_{13/2}$ level with the transition energy (about 6000 cm^{-1}) much more than that for the Ce^{3+} ion (about 2000 cm^{-1}). The measurements carried out on the same crystals by the same technology show that the concentration dependence of Er–Ce energy transfer parameters for the resonant interaction (with $^4\text{I}_{11/2}$–$^4\text{I}_{13/2}$) is linear; as for the unresonant interaction (with $^4\text{I}_{13/2}$–$^4\text{I}_{15/2}$), it is not less than quadratic. It shows, as we think, the cooperative character of quenching for the $^4\text{I}_{13/2}$ erbium level in the Er,Ce:CGS crystals. Therefore the linear connection of the quenching parameters for ytterbium with the cerium concentration in the Yb,Ce:CGS crystals is unexpected. So the necessary conclusion is that the ytterbium luminescence quenching occurs in single Ce^{3+} ions. Based on the small value of C_{DA}(Yb–Ce)$= 5.5 \times 10^{-44}$ s^{-1} cm^{6} we have concluded that cerium ions are poorly effective acceptors. So, rather strong Yb luminescence quenching in the Yb,Ce:CGS crystals occurs mainly due to the developed energy migration through the Yb ions with the rather high value of C_{DD}(Yb–Yb) $= 1.01 \times 10^{-38}$ s^{-1} cm^{6}.

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