Energy transfer processes in YAG:Er$^{3+}$-Ce$^{3+}$ crystal

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Abstract. In the work results of research of nonradiative energy transfer processes taking place in the impurity subsystem of the YAG: Er$^{3+}$-Ce$^{3+}$ crystal under optical excitations of Er$^{3+}$ and Ce$^{3+}$ ions are presented at room temperatures. By means of time-resolved fluorescence spectroscopy, some kinetic characteristics of fluorescence responses of the crystal under optical excitations at 405 and 808 nm wavelengths are investigated. Comparison of the measured characteristics of fluorescence signals at 860, 980 and 1555 nm wavelengths with the theoretical values numerically calculated from appropriate sets of rate equations allowed to estimate the positive contributions of energy transfer processes into population dynamics of energy levels responsible for generation near 1.5 μm of Er$^{3+}$ active ions in the YAG matrix.

1. Introduction
Laser radiation in eye-save spectral region around 1.5 μm has very high importance for applications in multi-kilometers optical communication systems, remote sensing, laser range finding, etc [1-4]. Thanks to the combination of good optical, thermal and mechanical properties, the yttrium aluminum garnet Y$_3$Al$_5$O$_{12}$ (YAG) crystals doped with Er$^{3+}$ active ions are currently one of the most perspective activated medium for lasing in the mentioned spectral region.

Intensive spectroscopic studies have shown that, for improvement of optical excitation energy efficiency usage, it is very fruitful codoping of this crystal with sensitizer ions of trivalent cerium (Ce$^{3+}$), which have very intensive absorption bands in the blue and ultraviolet wavelengths regions, as well as have channels for effective nonradiative transfer of absorbed excitation energy (NTAEE) to active Er$^{3+}$ ions in YAG matrix [5-19]. Our previous investigations on the influence of Ce$^{3+}$ ions on the spectral characteristics and intensity of the luminescent bands of the YAG:Er$^{3+}$-Ce$^{3+}$ crystal revealed significant increase in the efficiency of the fluorescence excitation near 1.5 μm on the $^4$I$_{13.2} \rightarrow ^4$I$_{15.2}$ transition of the Er$^{3+}$ ions under pumping of this material at 457 nm wavelength (about an order of magnitude compared with the YAG:Er$^{3+}$ crystal when pumped near 980 nm) [18, 19].

Such kind of improvement is due to the fact that in this crystal excitation at 457 nm wavelength corresponds to the very strong absorption peak of the Ce$^{3+}$ ion via interconfigurational $4f \rightarrow 5d$ spin-allowed transition, as well as the fact that there is good spectral overlap between broad and intensive fluorescence band of the Ce$^{3+}$ donor ions with the absorption bands of the acceptor Er$^{3+}$ ions, corresponding to $4f \rightarrow 4f$ transitions from the ground level to excited.

For quantitative estimations of probabilities of NTAEE processes it is also necessary information about kinetic characteristics of fluorescent transitions in impurity subsystem of the material under study, which is absent in the literature.

The present paper is devoted to the kinetic investigations of fluorescence response of the YAG:Er$^{3+}$-Ce$^{3+}$ crystal using time-resolved luminescence spectroscopy technique with optical
excitations at 405, 457 and 808 nm wavelengths, allowing realization of selective excitation of either sensitiser ($\lambda_{\text{pump}}=457$ nm) or activator ions ($\lambda_{\text{pump}}=808$ nm) and simultaneous excitation of both impurity ions ($\lambda_{\text{pump}}=405$ nm).

To determine the degree of influence of the Ce$^{3+}$ ion on the kinetic characteristics of the luminescent signal of Er$^{3+}$ ions, similar investigations carried out on garnet crystals doped separately with Er$^{3+}$ and Ce$^{3+}$ impurity ions.

Comparison of measured kinetic characteristics with the theoretical values obtained by numerical solution of rate equations allowed us to estimate the contributions of certain NTAEE processes in the $^4I_{13/2}$ upper laser level population formation of the Er$^{3+}$ ions in the matrix of YAG.

2. Samples and experimental technique

Studies of optical properties were performed at room temperatures on polished plates made from YAG crystal, doped with Er$^{3+}$ (5% atomic), Ce$^{3+}$ (0.15 atomic %) ions and codoped with Er$^{3+}$ (5% atomic) + Ce$^{3+}$ (0.15 atomic %) ions. More detailed information about the growth of these crystals has been published previously [19, 20].

Kinetic measurements were carried out with time-resolved luminescence spectroscopy method using short laser pulses (a few microseconds) at 457 (second harmonic of a pulsed YVO4:Nd$^{3+}$ laser crystal, working at 914 nm wavelength), 405 and 808 nm (pulsed laser diode) wavelengths.

Selection of a fluorescence wavelength of crystals under study was carried out by a diffraction monochromator, at the exit slit of which depending on a spectral region corresponding high-speed radiation detector (photomultiplier or photodiode) was placed. The time constant of the registration system was about 1-2 microseconds. Electrical signals from the detectors delivered to the high-speed dual channel digital storage oscilloscope from which digital data transmitted to the on line personal computer for subsequent mathematical processing.

In the present work among kinetic characteristics of fluorescence responses the delay time between excitation pulse and the peak of the signal ($\Delta t$) and the decay time of the responses ($\tau_d$) were chosen for detailed study.

3. Results

It is known that energy levels’ population formation of the Er$^{3+}$ ions in various matrixes is strongly dependent on dynamics of the processes associated with the $^4S_{3/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ levels [6-19, 21-24], and, therefore, study of kinetic characteristics of their fluorescence was in the center of our attention. However, despite of numerous works, devoted to the study of kinetics of green fluorescence (near 550 nm, correspondent to the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition) [10-16, 20-23], the present work the fluorescence at 860 nm wavelength ($^4S_{3/2} \rightarrow ^4I_{13/2}$ transition) was chosen as a test subject for our investigations. Such alternative choice seems convenient and useful for YAG:Er$^{3+}$-Ce$^{3+}$ crystal study, since kinetic characteristics of fluorescence at both wavelengths are the same (because of initial level is the same) and it is not overlapped by the intense and wideband fluorescence of the Ce$^{3+}$ ions (peaked near the 590 nm in the YAG host), which could result in considerable distortion of the green fluorescence dynamics. The 980 and 1555 nm wavelengths are correspondent to the well-known $^4I_{13/2} \rightarrow ^4I_{15/2}$ and $^4I_{13/2} \rightarrow ^4I_{15/2}$ transitions of Er$^{3+}$ ions in the YAG crystal.

Results of room temperature measurements of above mentioned kinetic characteristics from fluorescence responses, registered at 860, 980, 1555 nm wavelengths of the YAG:Er$^{3+}$ and YAG:Er$^{3+}$-Ce$^{3+}$ crystals under short optical excitations, are presented in the table 1. It will be noted that studies of kinetic parameters of YAG:Er$^{3+}$ and YAG:Er$^{3+}$-Ce$^{3+}$ crystals fluorescence under 457 nm wavelength pumping did not give additional useful information and they are not included in the table, since the duration of the laser’s optical excitation we used (about 10 $\mu$s) was much longer than the excitation energy transfer “duration” from Ce$^{3+}$ donor to the Er$^{3+}$ acceptor ions.
Table 1. Kinetic characteristics of fluorescence responses of the investigated crystals depending on optical excitations at 405 and 808 nm wavelengths.

| Lumin., nm | YAG:Er⁺³ pump at 405 nm | YAG: Er⁺³ pump at 808 nm | YAG:Er⁺³-Ce⁺³ pump at 405 nm | YAG:Er⁺³-Ce⁺³ pump at 808 nm |
|------------|--------------------------|--------------------------|-------------------------------|-------------------------------|
|            | 860                      | 980                      | 1555                          |                               |
| τ_d/Δt, μs | 14/4                     | 97/22                    | 6060/350                      |                               |
|            |                           |                          |                               | 7460/700                      |
| τ_d/Δt, μs | -                        | 94/4                     | 6000/280                      | 6081/600                      |
|            | -                        |                          |                               |                               |

Figure 1 shows a simplified energy level diagram of Er⁺³⁺ and Ce⁺³⁺ ions in the matrix of YAG, which was used for compiling of corresponding systems of rate equations for the populations of the energy levels of impurity ions under different excitation conditions.

Figure 1. Energy levels of Er⁺³⁺ and Ce⁺³⁺ ions in YAG.

Here the N_i symbols denote the populations of the levels, solid and dashed lines correspond to the optical excitations and observed fluorescent transitions, respectively, and curly curves point the non-radiative transitions. The well-known process of excitation transfer from Ce⁺³⁺ donor to Er⁺³⁺ acceptor ions (5d→4f [Ce⁺³⁺]:4^1I_{15/2}→4^1I_{13/2} [Er⁺³⁺]) is labeled by symbol 1 in the circle and possible cross-relaxation back-transfer process (4^1I_{13/2}→4^1I_{11/2} [Er⁺³⁺]:2^2F_{5/2}→2^2F_{7/2} [Ce⁺³⁺]) is marked by symbol 2 in the circle.

Dynamics of the processes taking place in the impurity subsystem of the YAG:Er⁺³⁺-Ce⁺³⁺ crystal under optical excitations can be described by the following set of rate equations:
\[ \dot{N}_1 = A_{21} N_2 + A_{31} N_3 + A_{41} N_4 + A_{51} N_5 + A_{61} N_6 + A_{71} N_7 - C_{11}^c N_{10} N_1 \]
\[ \dot{N}_2 = A_{12} N_1 + A_{42} N_4 + A_{52} N_5 + A_{62} N_6 + A_{22} N_2 + w_{32} N_3 - A_{21} N_2 + C_{21}^c N_3 N_8 \]
\[ \dot{N}_3 = A_{43} N_4 + A_{53} N_5 + A_{63} N_6 + A_{33} N_3 + w_{43} N_4 - A_{31} N_3 - A_{32} N_3 - w_{32} N_3 - C_{22}^c N_3 N_8 \]
\[ \dot{N}_4 = A_{54} N_5 + A_{64} N_6 + A_{44} N_4 + w_{44} N_5 - A_{42} N_4 - A_{43} N_4 - w_{43} N_4 \]
\[ \dot{N}_5 = A_{65} N_6 + A_{55} N_5 + w_{55} N_5 - A_{25} N_5 - A_{35} N_5 - A_{45} N_5 - w_{45} N_5 \]
\[ \dot{N}_6 = A_{76} N_7 + w_{76} N_7 - A_{66} N_6 - A_{65} N_6 - A_{64} N_6 - A_{63} N_6 - w_{65} N_6 \]
\[ \dot{N}_7 = -A_{17} N_7 - A_{27} N_7 - A_{37} N_7 - A_{47} N_7 - A_{57} N_7 - A_{16} N_7 - w_{76} N_7 + C_{16}^c N_{10} N_1 \]
\[ \dot{N}_8 = A_{98} N_8 + w_{98} N_9 + A_{410} N_{10} - C_{28}^c N_8 N_8 + C_{48}^c N_{10} N_1 \]
\[ \dot{N}_9 = -A_{99} N_9 - w_{98} N_9 + A_{109} N_{10} + C_{29}^c N_9 N_8 \]
\[ \dot{N}_{10} = -A_{108} N_{10} - A_{109} N_{10} - C_{110}^c N_{10} N_1 \]

Here \( A_{ij} \) and \( w_{ij} \) are probabilities of radiative and nonradiative transitions between \( i \) and \( j \) energy levels, correspondingly, \( C_{ij}^c \) are macroscopic transfer coefficients of appropriate cross-relaxation processes.

Taking into account that the nonradiative transitions dominate in the transitions between adjacent energy levels for multiplets above \( ^4H_{9/2} \), the system of rate equations (1) in case of excitation at 808 nm for YAG:Er\(^{3+}\)-Ce\(^{3+}\) crystal can be simplified to the following form

\[ \dot{N}_1 = A_{21} N_2 + A_{31} N_3 \]
\[ \dot{N}_2 = A_{12} N_1 + w_{32} N_3 - A_{21} N_2 + C_{21}^c N_3 N_8 \]
\[ \dot{N}_3 = w_{43} N_4 - A_{33} N_3 - A_{32} N_3 - w_{32} N_3 - C_{22}^c N_3 N_8 \]
\[ \dot{N}_4 = -w_{44} N_4 \]
\[ \dot{N}_8 = w_{98} N_9 - C_{28}^c N_8 N_8 \]
\[ \dot{N}_9 = -w_{99} N_9 + C_{29}^c N_9 N_8 \]

\[ N_i(0) = N_{E_i}; \quad N_j(0) = N_{3}(0) = 0; \quad N_j(0) = N_{4}^0; \]
\[ N_j(0) = N_{Ce}; \quad N_j(0) = 0 \]
\[ N_1 + N_2 + N_3 + N_4 = N_{E_5}; \quad N_8 + N_9 = N_{Ce} \]

In the Figure 2 the measured response (points) and the theoretical curve (solid) calculated with system of rate equations (2) by use of the Wolfram Mathematica 8 software are shown for the luminescence response at 980 nm of the YAG:Er\(^{3+}\)-Ce\(^{3+}\) crystal under optical excitation at 808 nm. In the numerical calculations the following data were used: \( A_{21}=156.2 \text{s}^{-1}, A_{31}=131.7 \text{s}^{-1}, A_{52}=29.4 \text{s}^{-1}, w_{32}=9838.9 \text{s}^{-1}, w_{43}=2.10^8 \text{s}^{-1}, A_{33}=1449.5 \text{s}^{-1}, A_{32}=56.6 \text{s}^{-1}, A_{53}=73.2 \text{s}^{-1}, A_{54}=5.2 \text{s}^{-1}, w_{34}=8.3.10^8 \text{s}^{-1}, A_{61}=814.3 \text{s}^{-1}, A_{62}=548.4 \text{s}^{-1}, w_{63}=39.1 \text{s}^{-1}, A_{63}=7.3.8 \text{s}^{-1}, A_{64}=0.8 \text{s}^{-1}, w_{65}=5.9.10^8 \text{s}^{-1}, A_{41}=A_{42}=A_{43}=A_{71}=A_{72}=A_{33}=A_{34}=A_{73}=A_{75}=A_{76}=0. \) The initial conditions are \( N_{E_5}=6.7.10^{10} \text{cm}^{-3}, N_{Ce}=1.667.10^{10} \text{cm}^{-3}, N_4^0=2.10^{18} \text{cm}^{-3}. \) By use of known technique of the root-mean-square best possible fit was achieved when the value of \( C_{28}^c \) cross-relaxation transition rate was equal to \( 4.10^{-17} \text{s}^{-1} \text{cm}^3 \).
Figure 2. Comparison between measured (points) and calculated (solid curve) decay of fluorescence at 980 nm for the YAG:Er-Ce crystal under excitation at 808 nm.

4. Discussion
Analysis of measured kinetic characteristics gathered in Table 1 shows that the decay time of the fluorescence from $^4I_{11/2}$ energy level of Er$^{3+}$ ions in the YAG crystal is reduced in the presence of Ce$^{3+}$ ions under optical excitation at both 405 and 808 nm. Such behaviour can be explained by taking into consideration processes resulted in depletion of this level. It seems to us, that such de-excitation can be induced by the back-transfer cross-relaxation process taking place according to the following mechanism:

$$^4I_{11/2} \rightarrow ^4I_{13/2} \ [\text{Er}^{3+}]; ^2F_{5/2} \rightarrow ^2F_{7/2} \ [\text{Ce}^{3+}]$$

This effect is somewhat interesting and unexpected since concentrations of the impurity ions in our crystals are rather small and it was observed in other materials at considerably larger content of impurity ions [6, 11, 14]. Such reduction is probably due to better spectral overlap between the luminescence band of Er$^{3+}$ donor ions at the $^4I_{11/2} \rightarrow ^4I_{13/2}$ transition with the absorption band of Ce$^{3+}$ acceptor ions at the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition in the YAG host than in other matrices. It will be noted that this process should have a positive influence to achieve lasing near 1.5 μs, since it suppresses the radiative transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ and enhances nonradiative transition of $^4I_{11/2} \rightarrow ^4I_{13/2}$ and hence promotes more rapid establishment of population inversion between initial and final laser levels with smaller losses of excitation energy.

From the same Table 1 one can see that delay times of the peaks of fluorescence responses relative to the end of excitation pulses have strong dependence on the excitation wavelength. This behavior is apparently due to the involvement of different mechanisms of optical excitation energy redistribution in the impurity subsystem of the crystal under study and thus can serve as a sensitive indicator of presence of various cooperative processes. Unfortunately, we were not able to deduce an analytical expression describing the dependence of this parameter on probabilities of various cooperative processes.

5. Conclusion
Kinetic characteristics of the fluorescent responses from the $^4S_{3/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ energy levels of Er$^{3+}$ ions in YAG:Er$^{3+}$ and YAG:Er$^{3+}$-Ce$^{3+}$ crystals under optical excitation at wavelengths of 405, 457 and 808 nm are studied. For the first time a marked shortening of the $^4I_{11/2}$ level decay time due to the presence of cerium ions in the YAG matrix is revealed. The possible mechanism of back-transfer
cross-relaxation process $^4I_{11/2} \rightarrow ^4I_{13/2} \ [\text{Er}^{3+}]; ^2F_{5/2} \rightarrow ^2F_{7/2} \ [\text{Ce}^{3+}]$ is suggested, which satisfactorily explains the observed reduction of the decay time of the fluorescence signal at 980 nm. Comparison of experimental data with theoretical model numerically calculated by use of rate equation formalism allows to estimate the probability of such process.

The high sensitivity of the delay times to the involvement of various cooperative mechanisms in impurity subsystem of doped crystals is pointed out.

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