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Interaction of Er^{3+} ions in Er-doped calcium – niobium – gallium garnet crystals

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***Abstract*. The processes of nonradiative energy transfer in calcium – niobium – gallium garnet (CNGG) crystals doped with Er^{3+} ions are studied. It is found that the energy of erbium ions in the Er : CNGG crystal with the erbium atomic concentrations $C_{Er} = 6\,\%$ and 11 % is transferred via the nonradiative co-operative processes $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4F_{7/2}$; $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4F_{9/2}$; and $^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{9/2}$, whose efficiency increases with increasing intensity of exciting radiation. It is shown that the cross-relaxation processes $^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$, whose intensity depends on the concentration of Er^{3+} ions, are characteristic for Er : CNGG crystals with the Er atomic concentration above 1 %.**

Keywords: *calcium – niobium – gallium garnet crystals, Er^{3+} ions, cross-relaxation, co-operative nonradiative energy transfer.*

1. Introduction

The calcium – niobium – gallium garnet (CNGG) crystals are characterised by a disordered crystal structure, because of which the absorption and luminescence bands of dopant ions (Nd^{3+}, Tm^{3+}, Yb^{3+}, Er^{3+}) in these crystals are strongly inhomogeneously broadened. This fact makes these crystals interesting due to a better coincidence of the absorption bands of dopant ions with the emission spectra of diode pump sources, as well as due to the possibility of obtaining tunable and mode-locked operation.

Today there is a large number of works devoted to investigations of spectral, luminescent, and lasing properties of Nd : CNGG, Tm : CNGG, and Yb : CNGG crystals, as well as to nonradiative energy transfer in these crystals [1 – 6]. Publications [7 – 11] present the results of investigation of the Er : CNGG crystal structure and provide the determined spectroscopic characteristics, which can be used for estimating the lasing properties of this crystal. However, it is known that the parameters of lasing on the transitions $^4I_{11/2} \rightarrow {}^4I_{13/2}$ ($\lambda \sim 3$ μm) and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ ($\lambda \sim 1.5$ μm) of Er^{3+} ions in crystal matrices strongly depend on the nonradiative energy transfer between these ions. The authors of works published in [12] have shown that efficient lasing on the self-restricted transition $^4I_{11/2} \rightarrow {}^4I_{13/2}$ in Er : YAG crystals under lamp pumping can be obtained only at high ($C_{Er} = 30\,\%$) atomic concentrations of Er^{3+}, at which the up-conversion processes depopulating the lower laser level $^4I_{13/2}$ are efficient. Works published in [12] present the result of detailed investigations of nonradiative energy transfer between Er^{3+} ions in $(Y_{1-x}Er_x)_3Al_5O_{12}$ crystals and consider the effect of this transfer on the creation of inversion population and lasing on the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions in these crystals.

The processes on nonradiative energy transfer of electronic excitation of Er^{3+} ions in Er : CNGG crystals have not been studied to date. In this paper, we present the results of investigation of nonradiative energy transfer between Er^{3+} ions in Er : CNGG crystals, which were obtained from the analysis of the spectra of the green and red luminescence from the $^4S_{3/2}$ and $^4F_{9/2}$ levels and from the decay curves of the luminescence from the $^4I_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels upon excitation into the $^4I_{9/2}$ level of Er^{3+} ions.

2. Results and discussion

The Er : CNGG crystals with Er atomic concentrations of 0.1 %, 1 %, 6 %, and 11 % were grown by the Czochralski method from melt. The concentration was controlled using a Camebax X-ray microanalyser.

The luminescence spectra of Er : CNGG crystals with the erbium concentration $C_{Er} = 6\,\%$ for the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions at $T = 300$ K were measured with an automated setup based on an SP-558 grating monochromator. As a radiation detector, we used an R-928 photomultiplier. The luminescence spectra were excited by the second harmonic of a Nd : YAG laser ($\lambda_{ex} = 532$ nm) and by a laser diode ($\lambda_{ex} = 813$ nm). The decay curves of the luminescence from the $^4I_{11/2}$ ($\lambda_{mes} = 970$ nm), $^4S_{3/2}$ ($\lambda_{mes} = 560$ nm), and $^4F_{9/2}$ ($\lambda_{mes} = 670$ nm) levels of Er^{3+} ions were recorded upon excitation into the $^4I_{9/2}$ level by 15-ns pulses of a $Ti^{3+}:Al_2O_3$ laser ($\lambda_{ex} = 791$ nm). As detectors, we used cooled PMT-83 and PMT-136 depending on the spectral region.

Figure 1 shows the luminescence spectra of Er^{3+} ions in Er : CNGG crystals ($C_{Er} = 6\,\%$) corresponding to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions upon excitation into the $^4S_{3/2}$ level of Er^{3+} ions by the second harmonic of an Nd : YAG laser ($\lambda_{ex} = 532$ nm). Figure 2 presents the luminescence spectra corresponding to the same transitions in the same crystals upon excitation into the $^4I_{9/2}$ level of Er^{3+} ions by a laser diode at $\lambda_{ex} = 813$ nm.

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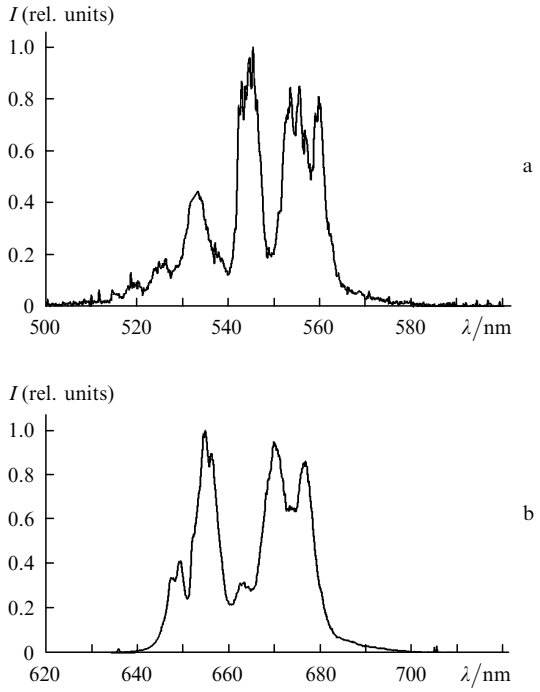

Figure 1. Luminescence spectra of Er^{3+} ions on the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (a) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (b) transitions in Er : CNGG crystals ($C_{Er} = 6\,\%$) at $T = 300$ K and $\lambda_{ex} = 532$ nm.

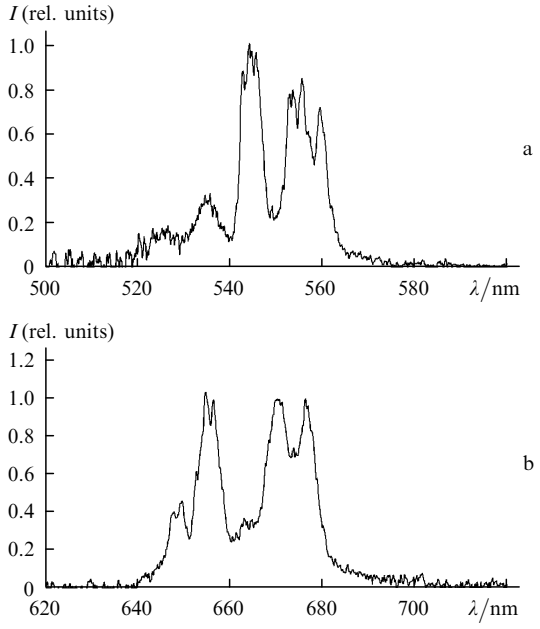

Figure 2. Luminescence spectra of Er^{3+} ions on the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (a) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (b) transitions in Er : CNGG crystals ($C_{Er} = 6\,\%$) at $T = 300$ K and $\lambda_{ex} = 813$ nm.

To clarify the mechanism of population of the $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} ions in the second case of excitation, we studied the decay kinetics of the luminescence from the $^4I_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels of Er^{3+} ions in Er : CNGG crystals with concentrations of 0.1 %, 1 %, 6 %, and 11 % upon excitation into the $^4I_{9/2}$ level of Er^{3+} ions by radiation of a $Ti^{3+} : Al_2O_3$ laser ($\lambda_{ex} = 791$ nm). The excitation energy density was changed by focusing the laser beam.

Figure 3 shows the decay curves of the luminescence from the $^4I_{11/2}$ ($\lambda_{mes} = 970$ nm) level in these crystals upon excitation by unfocused (Fig. 3a) and focused (the incident beam was focused on the surface of a sample, which was placed in the focal plane of a collimator positioned in front of the input slit of a monochromator) radiation of a $Ti^{3+} : Al_2O_3$ laser ($\lambda_{ex} = 791$ nm) into the $^4I_{9/2}$ level of Er^{3+} ions. One can see that the luminescence decay curves for Er : CNGG crystals with erbium concentrations of 0.1 % and 1 % for both unfocused and focused beams are close to exponential with the characteristic lifetimes $\tau = 663$ and 641 μs, respectively (the lifetime of the $^4I_{11/2}$ level of Er^{3+} ions in Er : YAG crystals is 100 μs [12]). The decay curves of the luminescence from the $^4I_{11/2}$ level for the Er : CNGG crystals with erbium atomic concentrations of 6 % and 11 % are nonexponential in both cases. The decay curves for these concentrations have two typical stages in contrast to the curves for concentrations of 0.1 and 1 %. In the case of unfocused excitation (Fig. 3a), the luminescence from the $^4I_{11/2}$ level of the Er : CNGG crystal with the erbium concentration $C_{Er} = 6\,\%$ decays faster than $\exp(-t/\tau)$ at the first decay stage corresponding to the time interval 0 – 3.6 μs. At the second stage, this curve decays more slowly than $\exp(-t/\tau)$, which is characteristic of Er : CNGG crystals with small Er^{3+} concentrations. As one can also see from Figure 3a, the range corresponding to more slow luminescence decay than $\exp(-t/\tau)$ in the case of the Er : CNGG crystal with $C_{Er} = 11\,\%$ is larger than for the crystal with 6 % of erbium. In the case of the focused excitation beam (Fig. 3b), the decay curve of the luminescence form the $^4I_{11/2}$ level of Er^{3+} in Er : CNGG crystals with concentrations $C_{Er} = 6\,\%$ and 11 % are also composed

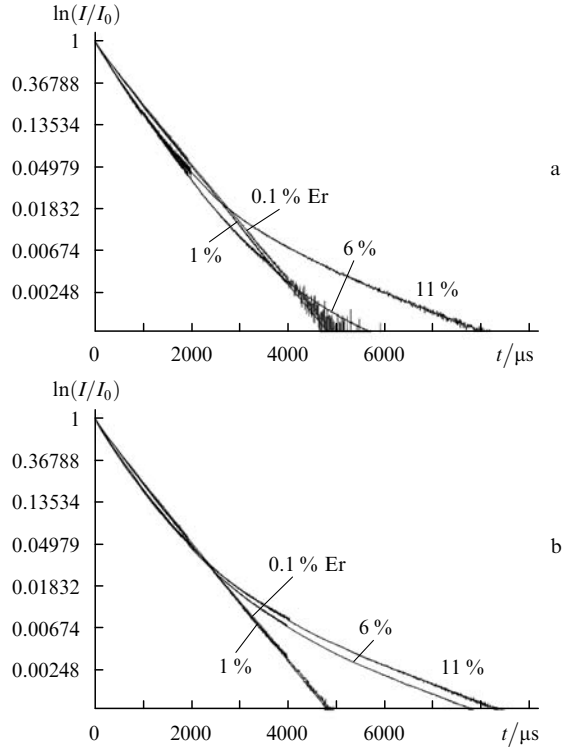

Figure 3. Normalised decay curves of the luminescence from the $^4I_{11/2}$ level ($\lambda_{mes} = 970$ nm) in Er : CNGG crystals with different concentrations of Er^{3+} ions excited into the $^4I_{9/2}$ level ($\lambda_{ex} = 791$ nm) by unfocused (a) and focused (b) radiation of a $Ti^{3+} : Al_2O_3$ laser.

of two stages. It is necessary to note that, in this case, the region of the slow luminescence decay of the Er : CNGG with $C_{Er} = 6\,\%$ is larger than in the case of unfocused excitation and begins (as well as for $C_{Er} = 11\,\%$) from 2.5 μs.

Figures 4 and 5 present the decay curves of the luminescence from the $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} in Er : CNGG crystals excited by focused radiation into the $^4I_9/2$ level. The analysis of the luminescence decay curves shows that the development times of luminescence from the $^4S_{3/2}$ (~ 3 μs) and $^4F_{9/2}$ (~ 2 μs) levels considerably exceeds the excitation pulse duration ($\tau_p \sim 15$ ns). This allows us to unambiguously conclude that the luminescence from these levels is caused by cross-relaxation transitions with summation of excitation energy rather than by multistep excitation.

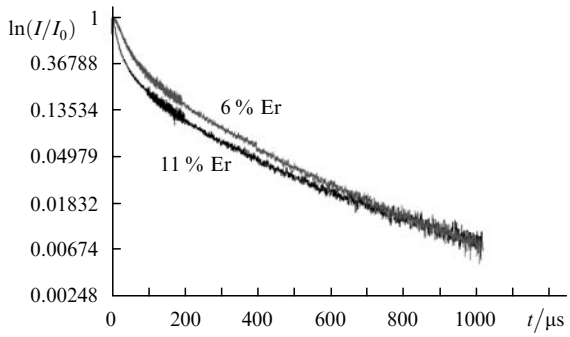

Figure 4. Normalised decay curves of the luminescence from the $^4S_{3/2}$ level ($\lambda_{mes} = 560$ nm) in Er : CNGG crystals with erbium concentrations of 6 % and 11 % upon excitation into the $^4I_{9/2}$ level ($\lambda_{ex} = 791$ nm).

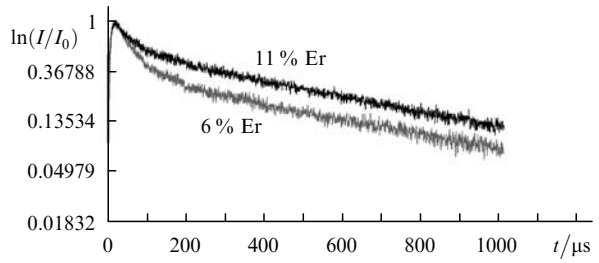

Figure 5. Normalised decay curves of the luminescence from the $^4F_{9/2}$ level ($\lambda_{mes} = 670$ nm) in Er : CNGG crystals with erbium concentrations of 6 % and 11 % upon excitation into the $^4I_{9/2}$ ($\lambda_{ex} = 791$ nm).

Based on the analysis of the energy level diagram of Er^{3+} ions (Fig. 6) and on the results of spectral and kinetic investigations described above, we can suggest that the luminescence from the $^4S_{3/2}$ and $^4F_{9/2}$ levels in Er : CNGG crystals observed upon excitation of the $^4I_{9/2}$ energy level, which lies below the $^4S_{3/2}$ and $^4F_{9/2}$ levels, occurs due to the co-operative nonradiative energy transfer $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4F_{7/2}$ (indicated by number 1 in Fig. 6). From the $^4F_{7/2}$ level, excitation nonradiatively relaxes to the $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels, from which radiative relaxation occurs to the ground $^4I_{15/2}$ level. The occurrence of the nonlinear interaction of Er^{3+} ions in Er : CNGG crystals by the scheme $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4F_{7/2}$ is evidenced by the existence of a range at which the luminescence from the $^4I_{11/2}$ decays faster than $\exp(-t/\tau)$.

The existence of the range at which the luminescence from the $^4I_{11/2}$ decays more slowly than $\exp(-t/\tau)$ is

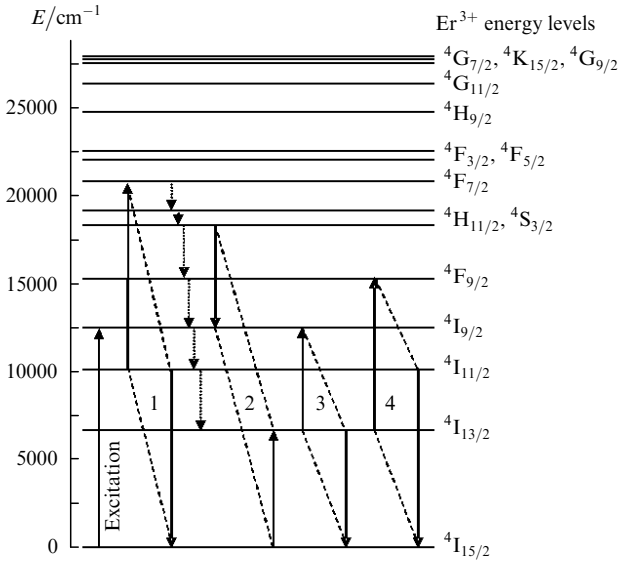

Figure 6. Main cross-relaxation transitions in Er : CNGG crystals: $^4I_{11/2} \rightarrow {}^4F_{7/2}$, $^4I_{11/2} \rightarrow {}^4I_{15/2}$ (nonlinear interaction, 1); $^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ (cross-relaxation, 2); $^4I_{13/2} \rightarrow {}^4I_{9/2}$, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (nonlinear interaction, 3); and $^4I_{13/2} \rightarrow {}^4F_{9/2}$, $^4I_{11/2} \rightarrow {}^4I_{15/2}$ (nonlinear interaction, 4).

probably caused by the cross-relaxation from the $^4S_{3/2}$ level ($^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$) (indicated by number 2 in Fig. 6), as well as by co-operative nonradiative energy transfer from the $^4I_{13/2}$ level ($^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{9/2}$) (number 3 in Fig. 6). These processes populate the $^4I_{9/2}$ level, from which excitation nonradiatively decays to the $^4I_{11/2}$ level, thus increasing its population. The efficiency of cross-relaxation from the $^4S_{3/2}$ level ($^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$) increases with increasing concentration of erbium. This is proved by the fact that the time interval of the low decay of the luminescence from the $^4I_{11/2}$ level in the case of unfocused excitation is larger for Er : CNGG crystal with $C_{Er} = 11\,\%$ than with $C_{Er} = 6\,\%$. The occurrence of cross-relaxation from the $^4S_{3/2}$ level ($^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$) and the increase in its intensity with the concentration of Er^{3+} ions can also explain the fact that the decay of the $^4S_{3/2}$ level of Er^{3+} ions excited into the $^4I_{9/2}$ occurs faster in the Er : CNGG crystals with $C_{Er} = 11\,\%$ than with $C_{Er} = 6\,\%$ under the same excitation.

The use of focused excitation of the $^4I_{9/2}$ level of Er^{3+} increases the efficiency of the co-operative nonradiative energy transfer $^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{9/2}$, which contributes to the population of the $^4I_{11/2}$ level. This is confirmed by the fact that the time interval corresponding to the low stage of the decay curve of luminescence from the $^4I_{11/2}$ level in the Er : CNGG with $C_{Er} = 6\,\%$ is larger in the case with focused than with unfocused excitation beam.

Comparative analysis of the decay curves of the luminescence from the $^4I_{11/2}$ level of Er^{3+} + ions in Er : YAG [12] and Er : CNGG crystals obtained upon focused excitation indicates that the luminescence decay curves for these crystals have a similar character both in the case of high Er^{3+} concentrations ($C_{Er} = 6\,\%$ and 12 %), when they consist of fast and slow decay regions, and in the case of small concentrations. According to [12], in the dynamic range of the intensity $I(t)$ of two orders of magnitude within the time interval of 0 – 400 μs, the ratio of the time intervals of the fast and slow luminescence decay in Er : YAG crystals

is 1 : 1. We found that this ratio for Er : CNGG crystals in the intensity dynamic range of three orders of magnitude within the interval 0 – 8 ms is 1 : 3. This fact, which testifies to an efficient population of the $^4I_{11/2}$ level of Er^{3+} ions in Er : CNGG crystals due to the interaction of excited Er^{3+} ions, as well as our previous data showing that the quantum yield of the luminescence from the $^4I_{11/2}$ level of the Er^{3+} ion in Er : CNGG is 14 % and exceeds the corresponding yield in Er : YAG crystals [9] by an order of magnitude, allows us to suggest that it is possible to achieve three-micron lasing on the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+} ions in Er : CNGG crystals.

Analysing the decay curves of luminescence from the $^4F_{9/2}$ level of Er^{3+} ions in Er : CNGG crystals with $C_{Er} =$ 6 % and 11 % excited by focused radiation into the $^4F_{9/2}$ level (Fig. 5), one can see that the $^4F_{9/2}$ level decays more slowly in the case of higher erbium concentration. This is obviously caused by the nonlinear interaction $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4F_{9/2}$ (number 4 in Fig. 6), whose efficiency increases with increasing concentration of Er^{3+} ions.

3. Conclusions

The experiments performed in this study have demonstrated the occurrence of co-operative nonradiative energy transfer $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{11/2} \rightarrow {}^4F_{7/2}$; $^4I_{11/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4F_{9/2}$; $^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{9/2}$ in Er : CNGG crystal with Er^{3+} atomic concentration exceeding 1 %. It is also found that the population of the $^4I_{11/2}$ level is affected by the cross-relaxation process $^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$, whose intensity depends on the Er^{3+} concentration.

Our investigations allow us to suggest that, to obtain lasing on the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions ($\lambda_{las} \sim$ 1.5 μm), it is reasonable to use Er : CNGG crystals with Er^{3+} concentration not exceeding 1 %. The cross-relaxation from the $^4S_{3/2}$ level ($^4S_{3/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$) and the co-operative nonradiative energy transfer from the $^4I_{13/2}$ level ($^4I_{13/2} \rightarrow {}^4I_{15/2}$, $^4I_{13/2} \rightarrow {}^4I_{9/2}$) of Er^{3+} ions in Er : CNGG crystals with an erbium concentration higher than 1 %, observed with increasing the density of excitation into the $^4I_{9/2}$ level, allows us to suggest that it is possible to obtain lasing on the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ ($\lambda_{las} \sim 3$ μm) transition of Er^{3+} in these crystals. To determine the optimum concentration or Er^{3+} ions in Er : CNGG crystals for tree-micron lasing, it is necessary to perform additional investigations, in particular, to study in detail the cross-relaxation from the $^4S_{3/2}$ level and to consider the specific features of the $^4I_{13/2}$ level relaxation at different densities of excitation into the $^4I_{11/2}$ level and at different Er^{3+} concentrations.

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