

Quantum efficiency of energy transfers in non-uniformly doped crystals of Er, Yb: LiNbO₃

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Abstract. Spatial and temporal distribution of quantum efficiency of energy transfers in crystals of lithium niobate with non-uniform concentration profiles of Er³⁺ and Yb³⁺ ions has been studied for the cases of Yb³⁺-Er³⁺ Foerster transfer and radiative decay of upper energy levels of erbium ions (green and red luminescence).

1. Introduction

Previous studies [1-4] of non-uniformly doped laser crystals, which are being grown with technique developed by authors of this work [5], shows that efficiency of energy transfers can be tuned and increased by varying concentrations of optical centers along the active medium. In this paper we report the impact of non-uniform doping on dynamics of some major energy transfers in crystals of Er, Yb: LiNbO₃ grown with concentration profiles of active ions which are depicted on Figure 1. Curves can be approximated with following equations:

$$C_{Yb}(z) = C_{1\%} \cdot (az^3 + bz^2 + cz + d) \quad (1)$$

$$C_{Er}(z) = C_{1\%} \cdot (a'z^3 + b'z^2 + c'z + d') \quad (2)$$

where: $C_{1\%}$ – concentration of dopant in LiNbO₃ lattice equal to 1 % at. ($C_{1\%}=1.88 \cdot 10^{20} \text{ cm}^{-3}$);
 $a, a', b, b', c, c', d, d'$ – numerical coefficients (Table 1).

Table 1: Coefficients for equations of concentration profiles

a	b	c	d	a'	b'	c'	d'
0.0205	-0.1118	-0.0372	1.2089	-0.0098	0.0511	0.0221	0.0205

2. Foerster resonance energy transfer in system of Yb³⁺-Er³⁺ ions

In energetic system of Yb³⁺ - Er³⁺ ions erbium generally acts as an acceptor of electron excitation energy, while ions of ytterbium provide the most of it as donors. Main channel of energy transition between these ions is a non-radiative FRET (Foerster resonance energy transfer) process between Yb: ²F_{7/2} and Er: ⁴I_{11/2} states, which is more effective for excitation of erbium ions than direct pumping at 980 nm wavelength. General scheme of energy levels of Yb³⁺ - Er³⁺ system is shown on Figure 2 where direct FRET process is marked with coefficient C₂₅. Optical pumping of crystal was provided with GaAs laser diode with 980 nm wavelength.



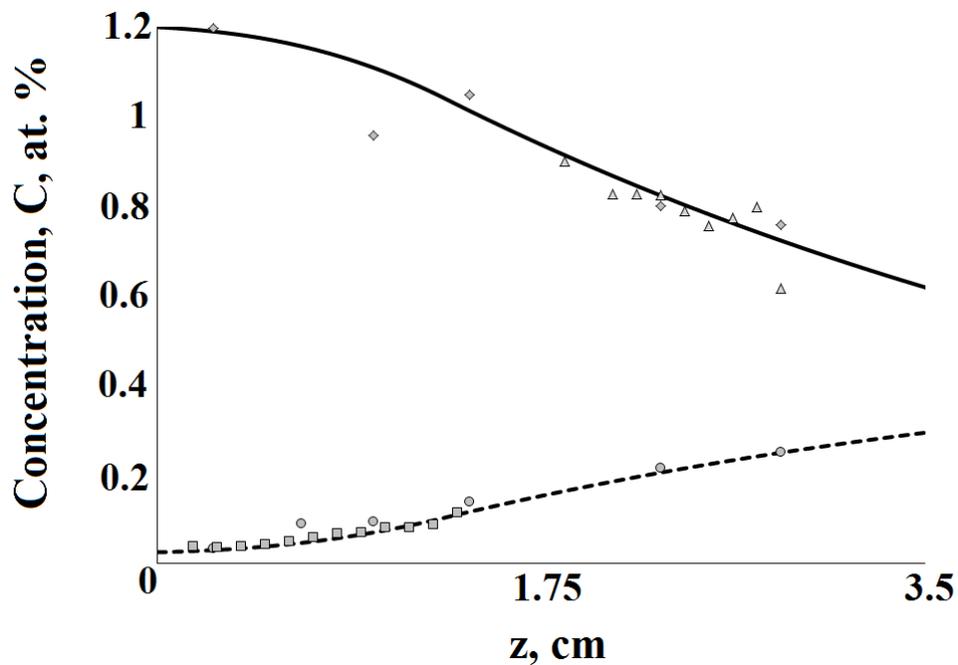


Figure 1 Concentration profiles of active ions (Yb^{3+} (solid line) and Er^{3+} (dashed line)) and their relations with absorption and emission processes: Er^{3+} absorption at 980 nm (circles), Yb^{3+} absorption at 980 nm (rhombs), Er^{3+} emission at 1.5 μm (triangles), Er^{3+} emission at 550 nm (squares).

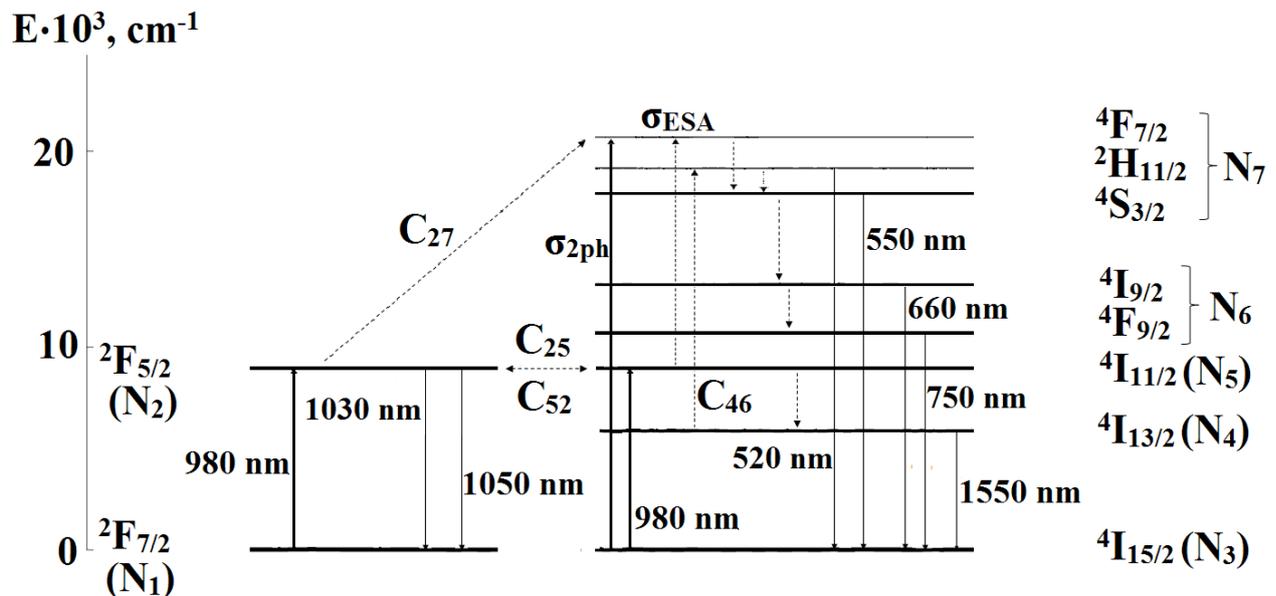


Figure 2 Scheme of energy levels in system of Er^{3+} and Yb^{3+} ions

Efficiency of FRET can be evaluated with application of mathematical formalism of rate equations. For system of Yb^{3+} - Er^{3+} ions it comes down to system of five equations [6], one for each of excited states (Figure 2 – N_2, N_4, N_5, N_6, N_7). After solving rate equations with Runge-Kutta method of fourth-order we

expanded this mathematical model with spatial inhomogeneity of concentrations of dopants [7, 8], and resulting equation for efficiency of FRET process obtained in following form:

$$\eta_{Yb-Er}(z) = \frac{\frac{A_5}{A_5 + C_{52}N_1(z)}}{\sigma_{Yb_{abs}}N_1(z) + \sigma_{Er_{abs}}N_3(z)} \cdot \left(\frac{C_{25}N_3(z)\sigma_{Yb_{abs}}N_1(z)}{\frac{C_{25}N_3(z)A_5}{A_5 + C_{52}N_1(z)} + A_2} + \sigma_{Er_{abs}}N_3(z) \right), \quad (3)$$

where: A_i – decay probability constant of i -th excited state (Figure 2), s^{-1} ;

C_{ij} – coefficient of energy transfer rate between i -th and j -th states, $cm^3 \cdot s^{-1}$;

$\sigma_{Yb_{abs}}, \sigma_{Er_{abs}}$ – absorption cross-sections of ytterbium and erbium ions at 980 nm wavelength, cm^2 ;

$N_i(z)$ – concentration of ions at i -th excited state, cm^{-3} .

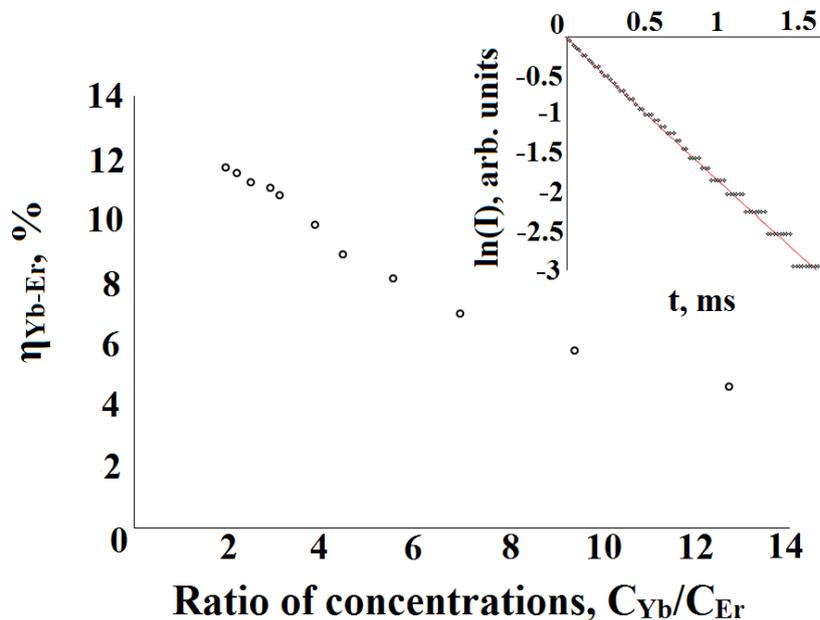


Figure 3 Efficiency of direct FRET in non-uniformly doped LiNbO₃:Yb, Er crystal and kinetics of luminescence of ytterbium ions at 970 nm (inset)

Figure 3 shows results experimental data of luminescence quenching of ytterbium ions at 970 nm wavelength and evaluated values of efficiency of FRET process in dependence of ratio of concentrations of active ions. Ytterbium ions were excited by YAG: Nd laser (1064 nm), measurements of quenching rate were conducted in several points along the crystal with different ratios of ytterbium and erbium concentrations, $C_{Yb}(z)/C_{Er}(z)$. It was obtained that the efficiency of FRET reaches higher values at the regions with low ratios of concentrations. Studies of luminescence of erbium ions at 1.5 μm wavelength showed that intensity of radiation measured along the non-uniformly doped crystal of LiNbO₃:Yb,Er correlates with the form of concentration profile of ytterbium ions (triangles on Figure 1). That proves leading role of FRET process in populating of excited states of erbium ions and shows correlation between efficiency of this energy transfer and intensity of luminescence at 1.5 μm wavelength.

3. Quantum efficiency of visible light luminescence

Solved rate equations also can be applied for evaluation of quantum efficiency of radiative transitions. For example, mathematical expressions for efficiency of green (η_g ; 520 and 550 nm) and red (η_r ; 660 and 750 nm) luminescence can be obtained as:

$$\eta_g(t, z) = \frac{A_{73}N_7(t, z)}{C_{27}N_2(t, z)N_5(t, z) + (\sigma_{ESA} + \sigma_{2ph})\varphi(t, z)N_3(t, z)} \quad (4)$$

$$\eta_r(t, z) = \frac{A_{63}N_6(t, z)}{C_{46}N_2(t, z)N_4(t, z) + (A_{76} + W_{76})N_7(t, z)} \quad (5)$$

where: A_{ij} – probability constant of radiative transition from i -th to j -th state (Figure 2), s^{-1} ;

$\varphi(t, z)$ – flux density of optical pumping, $cm^{-2}s^{-1}$;

$\sigma_{2ph}, \sigma_{ESA}$ – cross-sections of two-photon absorption (2ph) and excited-state absorption (ESA), cm^2 .

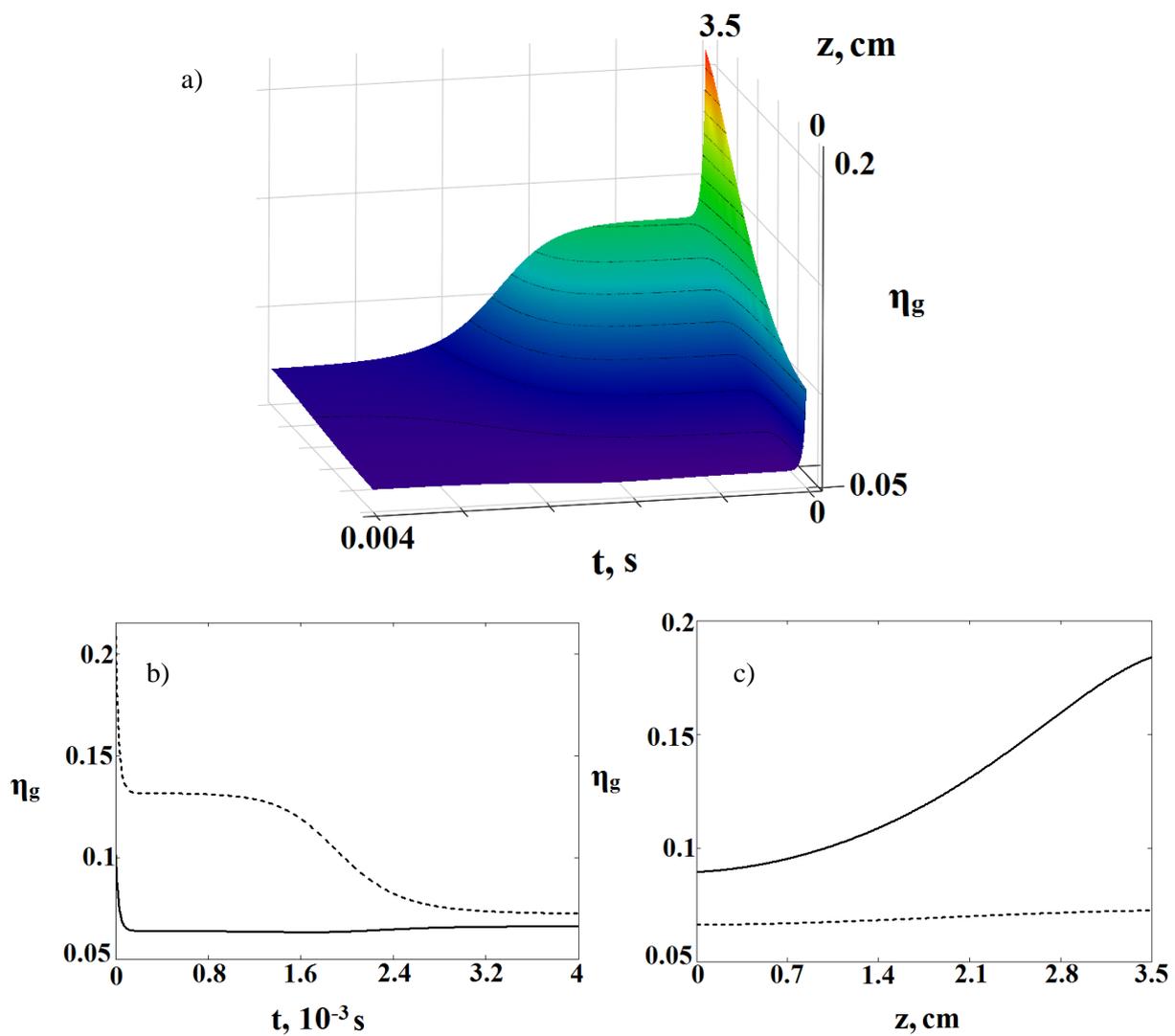


Figure 4 Quantum efficiency of green luminescence of erbium ions:

- a) spatio-temporal dynamics, $\eta_g(t, z)$;
- b) temporal dynamics, $\eta_g(t)$ (solid line – at $z=0$ cm, dashed line – at $z=3.5$ cm);
- c) spatial dynamics $\eta_g(z)$ (solid line – $t=8 \cdot 10^{-6}$ c, dashed line – $t=4 \cdot 10^{-3}$ c)

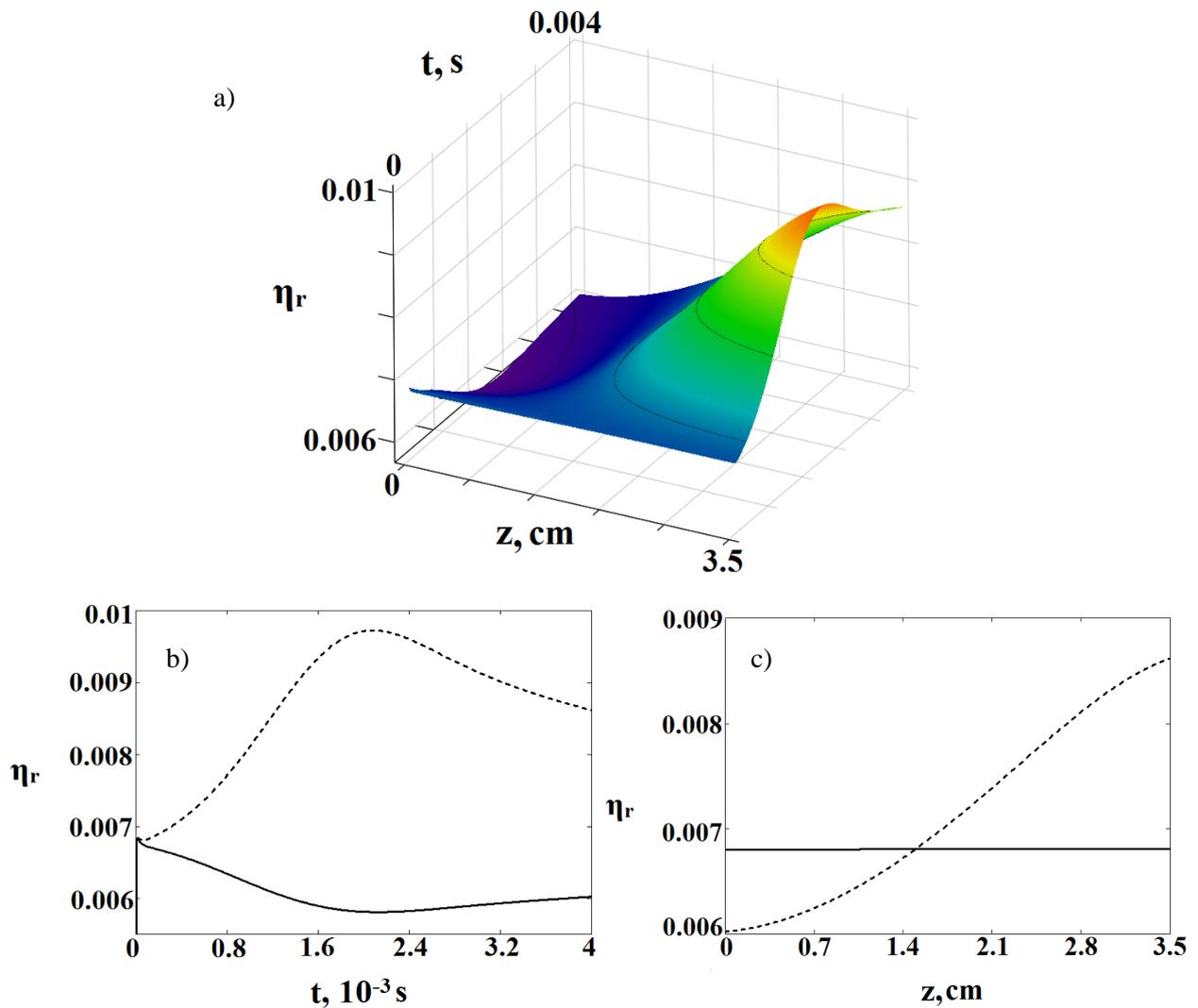


Figure 5 Quantum efficiency of red luminescence of erbium ions: a) spatio-temporal dynamics, $\eta_r(t, z)$; b) temporal dynamics, $\eta_r(t)$ (solid line – at $z=0$ cm, dashed line – at $z=3.5$ cm); c) spatial dynamics $\eta_r(z)$ (solid line – $t=8 \cdot 10^{-6}$ s, dashed line – $t=4 \cdot 10^{-3}$ s)

Equations (4-5) allow to evaluate ratio of rate of radiative decay of corresponding excited states in the volume of the crystal (numerator, $\text{cm}^{-3}\text{s}^{-1}$) to rate of population of these energy levels in the volume of the crystal (denominator, $\text{cm}^{-3}\text{s}^{-1}$). Results of evaluation for green and red luminescence are shown of Figures 4 and 5. Figure 4 (a) represents combined spatio-temporal dynamics of quantum efficiency of green luminescence in non-uniformly doped crystal. Temporal profiles $\eta_g(t)$ at both edges of the crystal ($z=0$ and $z=3.5$ cm) are shown on Figure 4 (b): from the start of optical pumping ($t=0$ s) until stationary mode of generating luminescence ($t=4 \cdot 10^{-3}$ s). Inflection points correlate with lifetimes of Yb: ${}^2F_{5/2}$ (Figure 2: N_2) and Er: ${}^4I_{11/2}$ (N_4) excited states, which are participating in transition of energy to emitting manifolds ${}^2H_{11/2}$ and ${}^4S_{3/2}$ (N_7). Figure 4 (c) depicts spatial profiles of quantum efficiency $\eta_g(z)$ in two moments of time: during transient state ($t=8 \cdot 10^{-6}$ s) and in stationary mode ($t=4 \cdot 10^{-3}$ s). In stationary mode distribution

of efficiency is almost uniform along the crystal (changes from 6.6 to 7.3 %), while in transient state populations of short-lived upper levels increase noticeably with changes of erbium and ytterbium concentrations.

Manifolds ${}^4F_{9/2}$ and ${}^4I_{9/2}$ (N_6) demonstrate a very different dynamics of quantum efficiency of luminescence (Figure 5 (a)). The main reason behind that is a mechanism of population of these energy levels: under pumping with wavelength 980 nm it can't be populated directly, only by slow non-radiative decays of upper levels, ${}^2H_{11/2}$ and ${}^4S_{3/2}$ (N_7). Secondly, both ${}^4F_{9/2}$ and ${}^4I_{9/2}$ states has lifetimes in order of 10^{-6} s which is shorter than lifetimes of all other energy levels in the system by 2-3 orders of magnitude. In result, the main factor of shaping quantum efficiency of red luminescence is not a rate of population but a concentration of erbium ions and its rate to ytterbium ions concentration. Figures 5 (b) and (c) illustrate this thesis. Efficiency of red luminescence at the low-doped end of crystal ($z=0$ cm) reacts to lifetimes of feeding energy levels, including FRET-related excited states (Figure 5 (b), solid line), but at high-doped end of crystal ($z=3.5$ cm; dashed line) up-conversion from ${}^4I_{13/2}$ state becomes a dominant factor in population of "red" levels. It leads to a formation of a significant peak close to lifetime ${}^4I_{13/2}$ ($t=2.7 \cdot 10^{-3}$ s). Spatial dynamics on Figure 5 (c) shows that distribution of efficiency is less uniform in stationary mode than in transient state. This peculiarity is also can be explained with strong dependence of efficiency to concentration of erbium ions: highest rate of decay leads to a difference of population of 7-8 orders of magnitude with adjacent excited states by the time of the start of stationary mode, so quantum efficiency of luminescence directly correlates with concentration profile of erbium ions.

4. Conclusion

We have studied relation of efficiency of FRET process between Yb^{3+} and Er^{3+} ions to ratio of their concentrations in non-uniformly doped crystal of lithium niobate. It was obtained that efficiency of luminescence at 1.5 μm wavelength also depends on this ratio and correlates with concentration profile of ytterbium ions.

Spatio-temporal dynamics of quantum efficiency of green and red luminescence of erbium ions were obtained. It was shown that these transitions demonstrate a highly different dynamics because of major distinctions in lifetimes and populating mechanisms, and it leads to different correlations with concentration profiles of erbium and ytterbium ions.

Acknowledgments

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