

# **Ce<sup>3+</sup>, Pr<sup>3+</sup>:LiY<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>4</sub> Mixed Crystal as a Perspective Upconversionally Pumped UV Active Medium**

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**Abstract.** The key parameters of processes provided up-conversion pumping of 5d-states of Ce<sup>3+</sup> ions in Ce<sup>3+</sup>, Pr<sup>3+</sup>:LiY<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>4</sub> mixed crystals were estimated for the first time. The prospects of this material as the first up-conversionally pumped UV active media were demonstrated.

## **1. Introduction**

The most effective solid-state UV lasers are based on Ce:LiCaAlF<sub>6</sub> and Ce:LiLuF<sub>4</sub> active media and operated on interconfigurational 5d-4f transitions of Ce<sup>3+</sup> ions [1]. However, UV pumping radiation of these lasers induces degradation of optical properties of solid-state media because of various photodynamic processes (PDP). One of the ways to avoid or significantly reduce harmful manifestations of PDP is to use up-conversion pumping [2].

Here we investigate an opportunity of effective pumping of 5d-states of Ce<sup>3+</sup> ions in LiY<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>4</sub> (LYLF) crystals by stepwise <sup>3</sup>H<sub>4</sub>→<sup>1</sup>D<sub>2</sub>, <sup>3</sup>P<sub>j</sub>→4f5d up-conversion excitation of states of 4f5d-configuration of Pr<sup>3+</sup> ions, followed by the energy transfer from Pr<sup>3+</sup> to Ce<sup>3+</sup> ions.

## **2. Results and discussion**

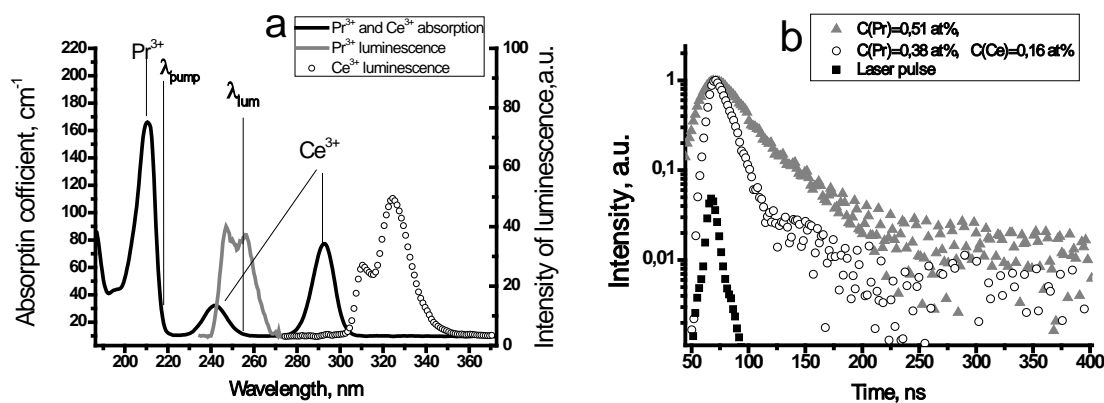
The choice motivation of Ce<sup>3+</sup>, Pr<sup>3+</sup>:LiY<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>4</sub> mixture crystals follows from the results of ref.[3], which show the necessity to increase the concentrations of the impurity ions for effective excitation energy transfer from Pr<sup>3+</sup> to Ce<sup>3+</sup> ions. Take into account that the scheelite crystal structure persists throughout the series of crystals with the formula LiY<sub>x</sub>Lu<sub>1-x</sub>F<sub>4</sub>, where x is any value from 0 to 1 and the LiY<sub>0.3</sub>Lu<sub>0.7</sub>F<sub>4</sub> (LYLF) crystals have the greatest isomorphic capacity to Pr<sup>3+</sup> and Ce<sup>3+</sup> ions [4], samples of Ce,Pr:LYLF mixture crystals were grown in Kazan University. The Pr<sup>3+</sup> ions content in the initial components was 1 at% and the concentration of Ce<sup>3+</sup> ions was varied from sample to sample from 0 to 2 at%. The real concentrations of the dopants in the samples (see Table 1) were determined by X-ray fluorescence and optical absorption spectroscopic methods described elsewhere [5].



Table 1. Absolute concentration of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions, fluorescent lifetimes of the lowest 4f5d-state of  $\text{Pr}^{3+}$  ions and the coefficients of excitation energy transfer from  $\text{Pr}^{3+}$  ions to  $\text{Ce}^{3+}$  ions in the  $\text{LiY}_{0.3}\text{Lu}_{0.7}\text{F}_4$  crystal samples

No of the sample	Concentration of $\text{Pr}^{3+}$ ions ( $C_{\text{Pr}}$ ), at%	Concentration of $\text{Ce}^{3+}$ ions ( $C_{\text{Ce}}$ ), at %	$\tau_{\text{лиом}}$ , ns	$K \cdot 10^7, \text{c}^{-1}$
1	$0.51 \pm 0.05$	0	$20 \pm 1,1$	-
2	$0.38 \pm 0.07$	$0.16 \pm 0.04$	$14,6 \pm 0,8$	1.85
3	$0.38 \pm 0.05$	$0.28 \pm 0.05$	$13,9 \pm 0,9$	2.19
4	$0.24 \pm 0.04$	$0.47 \pm 0.06$	$16,0 \pm 0,8$	1.25

Typical absorption and luminescence spectra of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions in the crystal samples are shown in Figure 1(a) and typical kinetics of 4f5d-4f<sup>2</sup> luminescence of  $\text{Pr}^{3+}$  in LYLf crystals, as well as the temporal profile of the laser excitation pulse are shown in Figure 1(b). Determination of excitation energy transfer efficiency from  $\text{Pr}^{3+}$  to  $\text{Ce}^{3+}$  ions was carried out by comparing the characteristic decay time of the luminescence of the donor ( $\text{Pr}^{3+}$ ) depending on the concentration of acceptor ions ( $\text{Ce}^{3+}$ ) [6]. The excitation of 4f5d-4f<sup>2</sup> luminescence of  $\text{Pr}^{3+}$  ions in LYLf crystals were performed at 218 nm. Fluorescence decays of  $\text{Pr}^{3+}$  ions were studied at 255 nm using the photomultiplier PMT-87 and digital oscilloscope DPO 7354 Tektronix.



**Figure 1.** Absorption and luminescence spectra of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions in  $\text{LiY}_{0.3}\text{Lu}_{0.7}\text{F}_4$  crystals (a) and typical kinetics of 4f5d-4f<sup>2</sup> luminescence of  $\text{Pr}^{3+}$  ions at 255 nm in crystals with temporal profile of the laser excitation pulse (b)

Energy transfer parameter  $k$  from 4f5d-states of  $\text{Pr}^{3+}$  ions to 5d-states of  $\text{Ce}^{3+}$  ions were estimated by formula (1):

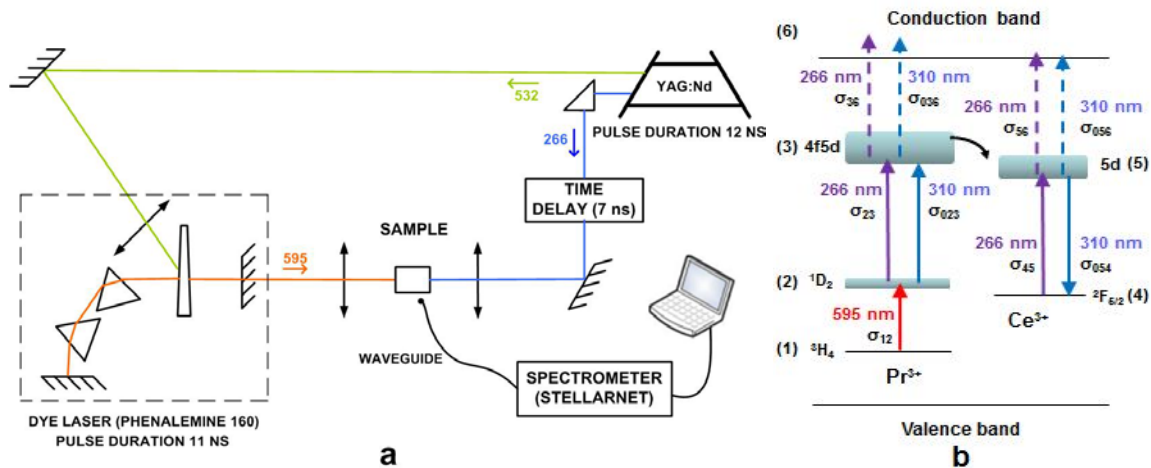
$$K = \frac{1}{\tau_{\text{codoped}}} - \frac{1}{\tau_0}, \quad (1)$$

where  $\tau_0$  – decay time of 4f5d-4f<sup>2</sup> luminescence of  $\text{Pr}^{3+}$  in  $\text{LiY}_{0.3}\text{Lu}_{0.7}\text{F}_4$  crystals without doping by  $\text{Ce}^{3+}$  ions,  $\tau_{\text{codoped}}$  – with the one, correspondently. The results are shown in Table 1. As it can be seen from the table, co-doping of the Pr:LYLF crystals by  $\text{Ce}^{3+}$  ions leads to displacement of  $\text{Pr}^{3+}$  ions and that is why the maximum of energy transfer coefficient reaches  $2.19 \cdot 10^7 \text{ c}^{-1}$  in the sample #3 with total content of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions 0.38 and 0.28 at.%, correspondently. This result exceeds the value of the energy transfer coefficient previously defined in [3] for  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ :LiLuF<sub>4</sub> crystals.

To excite the states of 5d-configuration of  $\text{Ce}^{3+}$  ions the double-stepwise up-conversion scheme using intermediate <sup>1</sup>D<sub>2</sub> manifold of  $\text{Pr}^{3+}$  ions was chosen. This scheme proposes to excite samples by

two pumping radiation beams with 595 nm and 266 nm wavelengths [3]. The reason was the fact that, in accordance with data of [7], the color centers that are induced in Ce:YLF crystal by UV pumping (YLF is the “parent crystal” for the ones studied here) are discoloring by 266 nm irradiation of the samples. The experimental setup, the up-conversion scheme and legends are shown in Fig 2.

To estimate the perspectives of Ce,Pr:LYLF crystals as up-conversionally pumped UV active media, the dependences of integral intensity of  $\text{Ce}^{3+}$  luminescence on energy density at 266 nm for fixed energy density at 595 nm were studied. The model is depicted in Figure 2.



**Figure 2.** Experimental setup (a) and model of excitation of 5d-4f luminescence of  $\text{Ce}^{3+}$  ions in  $\text{LiY}_{0.3}\text{Lu}_{0.7}\text{F}_4$  crystals (b). The solid arrows pointing upwards shows the transitions that provide excitation of 4f5d-configuration of  $\text{Pr}^{3+}$  ion for the two stepwise up-conversion pumping schemes and 5d-states of  $\text{Ce}^{3+}$  ions. Solid arrows pointing downwards show 5d-4f transitions of  $\text{Ce}^{3+}$  ion. Dashed arrows indicate the possible transitions from the 4f5d-excited states of  $\text{Pr}^{3+}$  ions and 5d-states of  $\text{Ce}^{3+}$  ions to the conduction band, arc arrow indicates energy transfer processes from  $\text{Pr}^{3+}$  to  $\text{Ce}^{3+}$  ions

Figure 2(b) was applied to interpret these dependences. Here the levels 1,4 are ground states of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions; 2, 3, 5 – excited levels of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions; 6 – conduction band of the crystal, correspondently. The  $\sigma_{12}$ ,  $\sigma_{23}$  are absorption cross-sections from ground state to  $^1\text{D}_2$  level and from  $^1\text{D}_2$  to 4f5d level of  $\text{Pr}^{3+}$  ion at 266 nm, respectively;  $\sigma_{45}$  – absorption cross-section from the ground to 5d level of  $\text{Ce}^{3+}$  ion at 266 nm;  $\sigma_{36}$ ,  $\sigma_{56}$ ,  $\sigma_{036}$ ,  $\sigma_{056}$  – absorption cross-sections from excited 4f5d and 5d levels of  $\text{Pr}^{3+}$  and  $\text{Ce}^{3+}$  ions at 266 nm;  $\sigma_{056}$  – absorption cross-sections from excited 5d level of  $\text{Ce}^{3+}$  ion at 310 nm;  $\sigma_{054}$  – stimulated 4f-5d transitions cross-sections of  $\text{Ce}^{3+}$  ions. These designations are also used in the equations (2) that describe this model:

$$\begin{aligned}
 \frac{dn_1}{dt} &= -U_1(t) \cdot \sigma_{12} \cdot n_1 + \frac{1}{\tau_2} \cdot n_2 + \frac{1}{\tau_3} \cdot n_3 + K \cdot n_3 \cdot \frac{n_4}{c_e}, \\
 \frac{dn_2}{dt} &= U_1(t) \cdot \sigma_{12} \cdot n_1 - \frac{1}{\tau_2} \cdot n_2 - U_2(t) \cdot \sigma_{23} \cdot n_2 + U_2(t) \cdot \sigma_{32} \cdot n_3, \\
 \frac{dn_3}{dt} &= U_2(t) \cdot \sigma_{23} \cdot n_2 - U_2(t) \cdot \sigma_{32} \cdot n_3 - U_2(t) \cdot \sigma_{36} \cdot n_3 - \frac{1}{\tau_3} \cdot n_3 - K \cdot n_3 \cdot \frac{n_4}{c_e} + p_{63} \cdot n_6, \\
 \frac{dn_4}{dt} &= -K \cdot n_3 \cdot \frac{n_4}{c_e} - U_2(t) \cdot \sigma_{45} \cdot n_4 + \frac{1}{\tau_5} \cdot n_5, \\
 \frac{dn_5}{dt} &= K \cdot n_3 \cdot \frac{n_4}{c_e} + U_2(t) \cdot \sigma_{45} \cdot n_4 - \frac{1}{\tau_5} \cdot n_5 - U_2(t) \cdot \sigma_{56} \cdot n_5 + p_{65} \cdot n_6, \\
 \frac{dn_6}{dt} &= U_2(t) \cdot \sigma_{36} \cdot n_3 + U_2(t) \cdot \sigma_{56} \cdot n_5 - (p_{63} + p_{65}) \cdot n_6,
 \end{aligned} \tag{2}$$

where  $n_1, n_2, n_3, n_4, n_5$  – populations of the appropriated states,  $U_1(t), U_2(t)$  – photon flux density of the pumping radiation at 595 and 266 nm, respectively;  $\tau_2, \tau_3, \tau_5$  – lifetimes of  $^1D_2, 4f5d$  states of  $Pr^{3+}$  ions and  $5d$  states of  $Ce^{3+}$  ions, respectively;  $\sigma_{ij}$  – appropriated transition cross-sections,  $p_{63}$  and  $p_{65}$  – recombination probabilities,  $K$  – energy transfer coefficient from  $Pr^{3+}$  to  $Ce^{3+}$  ions;  $C_{Ce}$  and  $C_{Pr}$  – concentration of  $Ce^{3+}$  and  $Pr^{3+}$  ions.

Parameters  $\tau_2, \sigma_{12}, \sigma_{23}$  are known from [8],  $\tau_3, \tau_5$  – [5], [9],  $\sigma_{56}$  – from [10] and  $\sigma_{036}, p_{63}$  and  $p_{65}$  are estimated in [1]. This system of equations was solved by means of MATLAB built-in algorithm based on the 4th-order Runge–Kutta method. The unknown parameters  $\sigma_{36}$  – excited-state photoionization cross-section of  $Pr^{3+}$  ions,  $\sigma_{45}$  – ground state cross-section of  $Ce^{3+}$  ions at 266 nm and  $K$  – energy transfer coefficient from the ion  $Pr^{3+}$  ions to  $Ce^{3+}$  ions were determined by means of direct Hooke–Jeeves search and equal, respectively, to  $1 \cdot 10^{-18} \text{ cm}^2$ ,  $1 \cdot 10^{-21} \text{ cm}^2$  and  $5.2 \cdot 10^7$ ,  $2.19 \cdot 10^7$ ,  $1.25 \cdot 10^7 \text{ c}^{-1}$  for crystals with concentrations  $C_{Ce} = 0.47 \text{ at\%}$ ,  $C_{Pr} = 0.24 \text{ at\%}$ ;  $C_{Ce} = 0.38 \text{ at\%}$ ,  $C_{Pr} = 0.28 \text{ at\%}$ ;  $C_{Ce} = 0.16 \text{ at\%}$ ,  $C_{Pr} = 0.38 \text{ at\%}$ , respectively. These results are in good agreement with the data of ref.[3] and above mentioned kinetic measurements.

Numerical simulation of optical gain on the  $5d$ - $4f$  transitions of  $Ce^{3+}$  ions in samples were carried out and the up-conversion pump optimal conditions for further pump-probe experiments were found. It were established that to realize optical gain coefficient more than 1.2 the all of the pumping beams should be  $\pi$  polarized and their radiation density should be more than  $0.8 \text{ J/cm}^2$ . The optimal delay between the first (595 nm) and second (266 nm) pumping pulse should be about 15 ns.

## 5. Conclusion

Here the key parameters of processes provided up-conversion pumping of  $5d$ -states of  $Ce^{3+}$  ions in  $Ce^{3+}, Pr^{3+}:\text{LiY}_{0.3}\text{Lu}_{0.7}\text{F}_4$  mixed crystals via  $^1D_2$  level of  $Pr^{3+}$  ions were estimated for the first time. The optimal up-conversion pump conditions were determined. The prospects of this material as the first up-conversionally pumped UV active media were demonstrated.

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## 6. References

- [1] Semashko V V 2012 *Active media of ultraviolet solid-state lasers. Prospects, obstacles and advances* (Saarbrücken: Palmarium Academic Publishing)
- [2] Semashko V V, Joubert M F, Descroix E, et.al. 2000 *Proc. of SPIE*. **4061** 306–316
- [3] Nicolas S, Descroix E, Joubert M F, et.al. 2003 *Opt.Mat.* **22** 139-146
- [4] Nizamutdinov A S, Semashko V V, Naumov A K, et.al. 2008 *Phys. of Solid-State* **50** 1648-1651
- [5] Gorieva V G, Semashko V V, Korableva S L, et.al. 2013 *Uchenie zapiski Kazanskogo universiteta* **155** 52 – 58
- [6] Nikolas S, Descroix E, Guyot Y, et.al. 2001 *Opt. Mat.* **16**
- [7] Lim K-S, Hamilton D S 1989 *Opt. Soc. Am. B.* **6** 1401-1406
- [8] Nicolas S, Descroix E, Guyot Y, et.al. *Opt. Mat* **16** 233-242
- [9] Nizamutdinov A S, Marisov M A, Semashko V V, et.al. 2005 *Phys. of Solid State.* **47** 1460-1462
- [10] Pavlov V V, Marisov M A, Semashko V V, at.al. 2013 *J. of Lum.* **133** 73-76