Ce$^{3+}$, Pr$^{3+}$:LiY$_{0.3}$Lu$_{0.7}$F$_4$ 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$^{3+}$ ions in Ce$^{3+}$, Pr$^{3+}$:LiY$_{0.3}$Lu$_{0.7}$F$_4$ 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$_6$ and Ce:LiLuF$_4$ active media and operated on interconfigurational 5d-4f transitions of Ce$^{3+}$ 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$^{3+}$ ions in LiY$_{0.3}$Lu$_{0.7}$F$_4$ (LYLF) crystals by stepwise $^3$H$_4$→$^1$D$_2$, $^3$P$^j$→4f5d up-conversion excitation of states of 4f5d-configuration of Pr$^{3+}$ ions, followed by the energy transfer from Pr$^{3+}$ to Ce$^{3+}$ ions.

2. Results and discussion
The choice motivation of Ce$^{3+}$,Pr$^{3+}$:LiY$_{0.3}$Lu$_{0.7}$F$_4$: 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$^{3+}$ to Ce$^{3+}$ ions. Take into account that the scheelite crystal structure persists throughout the series of crystals with the formula LiY$_x$Lu$_{1-x}$F$_4$, where x is any value from 0 to 1 and the LiY$_{0.3}$Lu$_{0.7}$F$_4$ (LYLF) crystals have the greatest isomorphic capacity to Pr$^{3+}$ and Ce$^{3+}$ ions [4], samples of Ce,Pr:LYLF mixture crystals were grown in Kazan University. The Pr$^{3+}$ ions content in the initial components was 1 at% and the concentration of Ce$^{3+}$ 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 Pr$^{3+}$ and Ce$^{3+}$ ions, fluorescent lifetimes of the lowest 4f5d-state of Pr$^{3+}$ ions and the coefficients of excitation energy transfer from Pr$^{3+}$ ions to Ce$^{3+}$ ions in the LiY$_{0.3}$Lu$_{0.7}$F$_4$ crystal samples

| № of the sample | Concentration of Pr$^{3+}$ ions (C$_{Pr}$), at% | Concentration of Ce$^{3+}$ ions (C$_{Ce}$), at% | $\tau_{\text{lum}}$, ns | $K\times10^7$, c$^{-1}$ |
|-----------------|---------------------------------------------|---------------------------------------------|-----------------|-----------------|
| 1               | 0.51 ± 0.05                                | 0                                           | 20±1,1          | -               |
| 2               | 0.38 ± 0.07                                | 0.16 ± 0.04                                | 14,6±0,8        | 1.85            |
| 3               | 0.38 ± 0.05                                | 0.28 ± 0.05                                | 13,9±0,9        | 2.19            |
| 4               | 0.24 ± 0.04                                | 0.47 ± 0.06                                | 16,0±0,8        | 1.25            |

Typical absorption and luminescence spectra of Pr$^{3+}$ and Ce$^{3+}$ ions in the crystal samples are shown in Figure 1(a) and typical kinetics of 4f5d-4f$^2$ luminescence of Pr$^{3+}$ in LYLFI 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 Pr$^{3+}$ to Ce$^{3+}$ ions was carried out by comparing the characteristic decay time of the luminescence of the donor (Pr$^{3+}$) depending on the concentration of acceptor ions (Ce$^{3+}$) [6]. The excitation of 4f5d-4f$^2$ luminescence of Pr$^{3+}$ ions in LYLFI crystals were performed at 218 nm. Fluorescence decays of 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 Pr$^{3+}$ and Ce$^{3+}$ ions in LiY$_{0.3}$Lu$_{0.7}$F$_4$ crystals (a) and typical kinetics of 4f5d-4f$^2$ luminescence of 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 Pr$^{3+}$ ions to 5d-states of Ce$^{3+}$ ions were estimated by formula (1):

$$K = \frac{1}{\tau_{\text{coped}}} - \frac{1}{\tau_0},$$

where $\tau_0$ – decay time of 4f5d-4f$^2$ luminescence of Pr$^{3+}$ in LiY$_{0.3}$Lu$_{0.7}$F$_4$ crystals without doping by Ce$^{3+}$ ions, $\tau_{\text{coped}}$ – 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 Ce$^{3+}$ ions leads to displacement of Pr$^{3+}$ ions and that is why the maximum of energy transfer coefficient reaches $2.19\times10^7$ c$^{-1}$ in the sample #3 with total content of Pr$^{3+}$ and 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 Ce$^{3+}$, Pr$^{3+}$:LiLuF$_4$ crystals.

To excite the states of 5d-configuration of Ce$^{3+}$ ions the double-stepwise up-conversion scheme using intermediate $^1D_2$ manifold of 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-convensionally pumped UV active media, the dependences of integral intensity of Ce3+ 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](image)

**Figure 2.** Experimental setup (a) and model of excitation of 5d-4f luminescence of Ce3+ ions in LiY0.3Lu0.7F4 crystals (b). The solid arrows pointing upwards shows the transitions that provide excitation of 4f5d-configuration of Pr3+ ion for the two stepwise up-conversion pumping schemes and 5d-states of Ce3+ ions. Solid arrows pointing downwards show 5d-4f transitions of Ce3+ ion. Dashed arrows indicate the possible transitions from the 4f5d-excited states of Pr3+ ions and 5d-states of Ce3+ ions to the conduction band, arc arrow indicates energy transfer processes from Pr3+ to Ce3+ ions.

The levels 1, 4 are ground states of Pr3+ and Ce3+ ions; 2, 3, 5 – excited levels of Pr3+ and Ce3+ ions; 6 – conduction band of the crystal. The σ12, σ23 are absorption cross-sections from ground state to 1D2 level and from 1D2 to 4f5d level of Pr3+ ion at 266 nm, respectively; σ45 – absorption cross-section from the ground to 5d level of Ce3+ ion at 266 nm; σ36, σ56, σ036, σ056 - absorption cross-sections from excited 4f5d and 5d levels of Pr3+ and Ce3+ ions at 266 nm; σ054 - absorption cross-sections from excited 5d level of Ce3+ ion at 310 nm; σ054 – stimulated 4f-5d transitions cross-sections of Ce3+ ions. These designations are also used in the equations (2) that describe this model:

\[
\frac{dn_1}{dt} = -U_1(t) \cdot \sigma_{12} \cdot n_1 + \frac{1}{r_2} \cdot n_2 + \frac{1}{r_3} \cdot n_3 + K \cdot n_1 \cdot \frac{n_1}{n_c},
\]

\[
\frac{dn_2}{dt} = U_1(t) \cdot \sigma_{23} \cdot n_2 - \frac{1}{r_2} \cdot n_2 - U_1(t) \cdot \sigma_{23} \cdot n_2 + U_2(t) \cdot \sigma_{12} \cdot n_1,
\]

\[
\frac{dn_3}{dt} = U_2(t) \cdot \sigma_{23} \cdot n_3 - U_2(t) \cdot \sigma_{23} \cdot n_3 - U_2(t) \cdot \sigma_{56} \cdot n_5 + \frac{1}{r_3} \cdot n_3 - K \cdot n_1 \cdot \frac{n_1}{n_c} + p_{43} \cdot n_4,
\]

\[
\frac{dn_4}{dt} = -K \cdot n_1 \cdot \frac{n_1}{n_c} - U_2(t) \cdot \sigma_{45} \cdot n_4 + \frac{1}{r_5} \cdot n_5,
\]

\[
\frac{dn_5}{dt} = K \cdot n_1 \cdot \frac{n_1}{n_c} + U_2(t) \cdot \sigma_{45} \cdot n_4 - n_5 - U_2(t) \cdot \sigma_{56} \cdot n_5 + p_{45} \cdot n_5 + p_{56} \cdot n_6,
\]

\[
\frac{dn_6}{dt} = U_2(t) \cdot \sigma_{56} \cdot n_6 + U_2(t) \cdot \sigma_{56} \cdot n_6 - (p_{45} + p_{56}) \cdot n_6,
\]
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 $^{1}D_2$, 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 $1*10^{-18}$ cm$^2$, $1*10^{-21}$ cm$^2$ and $5.2*10^{-7}$, $2.19*10^{-7}$, $1.25*10^{-7}$ cm$^{-1}$ for crystals with concentrations $C_{Ce} = 0.47$ at%, $C_{Pr} = 0.24$ at%; $C_{Ce} = 0.38$ at%, $C_{Pr} = 0.28$ at%; $C_{Ce} = 0.16$ at%, $C_{Pr} = 0.38$ 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 was 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 J/cm2. 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$^{3+}$:LiY$_{0.3}$Lu$_{0.7}$F$_4$ mixed crystals via $^{1}D_2$ 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-conventionally pumped UV active media were demonstrated.

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