Laser-like effects and upconversion fluorescence temporal 
dynamic in Tm$^{3+}$, Yb$^{3+}$ doped YF$_3$ single crystals

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Abstract. A new way of managing fluorescence features in doped bulk and nanosized materials by variation of excitation temporal characteristics is demonstrated. Random laser-like effect on $^3\text{H}_4-^3\text{F}_4$ transitions of Tm$^{3+}$ ions in Yb,Tm:YF$_3$ single crystal was revealed under rectangular pulse train excitation in 930-980 spectral domain.

1. Introduction
Modification of optical excitation conditions allows the effective managing of upconversion (UC) processes and gives an opportunity to populate or depopulate high-lying states of doped bulk and nanosized materials. This is fruitful for realization of multicolor lasers and high-effective luminophors for IT [1], biomedicine [2] and photovoltaic applications [3]. The most typical physical mechanisms determining distribution of population of active ions energetic levels under UC excitation are the processes combination: a) cross-relaxation (CR), b) excited-state absorption (ESA) of excitation and/or fluorescence radiations, c) energy transfer and energy migration between dopants, d) cooperative processes [4]. As it is generally considered, materials’ UC-fluorescence features are operated by excitation radiation wavelength and its intensity or by changing the chemical composition of samples (e.g. by dopant types and/or dopant concentrations) or by variation of sample size characteristics or ambient conditions (e.g. by sample’s temperature, pressure, additional electromagnetic fields etc.). However there is still a forgotten additional “degree of freedom”, which impacts on population evolution of excited state of active ions – it is exposure time (pulses length, their repetition rate or different types excitation pulse trains). For the first time to our knowledge here we demonstrate opportunity to manage spectral-fluorescence and kinetics properties of YF$_3$ single crystals doped by Yb$^{3+}$ (20 at.%) and Tm$^{3+}$ (1 at.%) ions (Yb,Tm:YF$_3$) by means of variation of optical excitation exposure time in $^3\text{F}_{7/2}-^3\text{F}_{5/2}$ transitions domain of Yb$^{3+}$ ions.

2. Experimental peculiarities and results
Multiple rare-earth ions doped YF$_3$ crystal host is well known as high effective phosphor due to low probability of multiphonon non-radiative processes and more close packing of the active ions in comparison with double- and triple fluoride hosts [5,6]. Orthorhombic YF$_3$ single crystals doped by Yb$^{3+}$ and Tm$^{3+}$ were grown by Bridgman-Stockbarger technique in Kazan Federal University. Yb$^{3+}$ and Tm$^{3+}$ ions contents in the crystal were 20 and 1 at.%, accordingly. Because of crystallization peculiarity, samples look as the needles extended along C axis with diameter up to 2 mm and up to 3-5 mm long.
The Yb,Tm:YF₃ samples fluorescence was excited by radiation of temperature tuned laser emitting diodes (LED) operated around 930 and 980 nm. This wavelength is correspondent to ⁴F₇/₂→⁴F₅/₂ transition of Yb³⁺ ions. Maximal LED output power was about 4 W. LED provided a sequence of rectangular laser pulses with pulse repetition rate 66.7 Hz and varied pulse duration τₑₓ = 0.08÷14.5 ms. LED radiation was collimated by spherical lens to slightly distorted circle spot about 0.25 mm in diameter. Fluorescence spectra were registered by CCD StellarNet spectrometer-radiometer or by scanning spectrometer based on prismatic ZMR-3 monochromator. Both spectrometers provided spectral resolution better than 0.5 nm [7]. Fluorescence decays were registered by means of photomultipliers FEU-39, FEU-79 and FEU-62 with temporal resolution better than 1-5 μs. Input window of photomultiplier was attached to output slit of ZMR-3 monochromator and electrical output of the photomultiplier was connected to 12-bit high-speed 4 channel A/D convertor L-Card E20-10 with 30 MHz bandwidth. The principal feature of decay measurements was to avoid data averaging and study every response of Yb,Tm:YF₃ system for IR excitation act allowing detection of new fluorescence dynamic peculiarities. All experiments were carried out at 300 K.

**Figure 1.** Typical upconversion fluorescence spectra of Tm³⁺ ions in double-doped Yb,Tm:YF₃ crystal under excitation of Yb³⁺ ions at 929 and 974 nm by CW (a) and by rectangular pulses train (b). Spectra marked by blue and red lines were registered under CW excitation by 929 nm radiation with about 90 and 8000 W/cm² power density (a) and under sequences of rectangular 1 ms and 14 ms LED pulses (pulse repetition rate 66.7 Hz, λₑₓ=974 nm, power density ~ 200 W/cm²) (b), correspondingly.

Intensive UC-fluorescence originated from ³Pₐ, ³I₆, ¹D₂, ¹G₄, ³F₃, ³H₄ states of Tm³⁺ ions were detected under excitation of Yb³⁺ ions at 920-980 nm spectral domain. The processes which lead to such UC-fluorescence features are known well [4-7] and have to be considered as dynamic. But there are neither comprehensive experimental nor theoretical studies to our knowledge aimed at demonstration of the opportunity to utilize these temporal dynamics to population managing of activator ions higher-lying manifolds. Indeed it is pronounced well in UC-fluorescence spectra of double-doped Yb,Tm:YF₃ single crystals under various excitation temporal characteristics. For instance, typical fluorescence spectra of Yb³⁺ and Tm³⁺ ions in YF₃ crystal under continuous wave (CW) (a) and under sequence of rectangular pulses (b) excitation of Yb³⁺ ions at 929 and 972 nm are shown on the fig.1. The fig.2 demonstrates dependences intensity of main upconversion fluorescence lines versus LED pumping current (it is identical to excitation power) (a) and versus laser excitation pulse length (b). Correspondent experimental conditions are shown in figures captions.

As it can be seen from the fig.1 and 2, variation of temporal characteristics of excitation (pulses length and/or pulse repetition rate) as well as a optical excitation intensity change lead to effective UC population of higher lying manifolds of Tm³⁺ ions.

At the same time population distribution features of these states under rectangular pulse train excitation are essentially different in comparison to CW or periodical short pulse excitation, because
UC processes include numerous intermediate energetic states of activator and/or sensitizer ions with the proper lifetimes. In particular, it is easy to see from the figures, that the conversion from pulse train to CW excitation demonstrates the rise of effective population of $^1P_0$ manifold of Tm$^{3+}$ ions in Yb,Tm:YF$_3$ single crystal and appearance of intensive fluorescence bands at 339 ($^1P_0-^3H_5$), ~ 683 and 702 nm ($^1P_0-^1G_4$). The same effect takes place in case of other $^1P_j$ and $^1I_6$ manifolds. Therefore, sensitivity of population to excitation prehistory in similar fluorescent materials opens additional opportunity of managing the population distribution at energy states of dopants and it appears to be extremely important from the point of view of photonics urgent problems.

\[\text{Figure 2.} \quad \text{Dependences of intensities of upconversion fluorescence lines in Yb,Tm:YF}_3\ \text{crystal versus LED pumping current (CW excitation at 929 nm) (a) and versus laser pulses length (rectangular pulse train excitation at 972 nm with the power density \sim 200 W/cm}^2\text{) (b)}\]

\[\text{Figure 3.} \quad \text{Random spike-likelasing distorted fluorescence decays at 824 nm ($^3H_4-^3H_6$ transition of Tm}^{3+}\text{ ions) (a) and the example of jump-like nature of fluorescence kinetic associated with $^3D_2-^1H_6$ transitions of Tm}^{3+}\text{ ions in Yb,Tm:YF}_3\text{ single crystals (b). Excitation pulse lengths duration was 80 }\mu\text{sec (a) and 14 ms (b), correspondingly. Pulse repetition rate is 66.7 Hz.}\]

In addition our experiments have elucidated laser-like effects which appeared in fluorescence kinetics under rectangular pulse train excitation. For instance, random spike-like lasing distorted decay of 824 nm fluorescence originating from $^3H_4$ manifold of Tm$^{3+}$ ions is shown on fig.3,a. Taking into account
that well-known $^3H_4-^3F_4$ laser transition of Tm$^{3+}$ ions is characterized by high stimulated emission cross-section [4], we propose that random lasing is appeared only at the said transition at 1.5 μm spectral domain. Despite the fact that we did not study here spectral-kinetic properties of Yb,Tm:YF$_3$ samples at wavelengths longer 1100 nm, the obvious evidences of such random lasing the spike-like features have well pronounced in fluorescence kinetics at 824 nm, and these features appeared above certain threshold (about 1.1-1.2 A of LED current). Moreover the stimulated emission driven character of fluorescence evaluation curve is proved by results of simulation of Tm$^{3+}$ ions transitions with excited-state absorption and energy transfer originated from Yb$^{3+}$ ions [8]. Jump-like modulation characteristic for $^3H_4$ manifold population is also displayed in fluorescence features at other wavelengths correspondent to transitions from higher lying manifolds of Tm$^{3+}$ ions which could be clearly seen from curve for $I_{LED}=3.6$ A excitation in fig. 3,b. This is due to cross-relaxation and ESA processes originating from $^3H_4$ term and populating the higher lying states [4-6]. Another evidence of lasing feature is dropped fluorescence at $^1D_2-^1H_6$ transitions (363 nm) when excited with excitation power $I_{LED} > 2.5$ A (fig.3,b) correspondent to the lasing threshold described above. The similar behavior has fluorescence kinetics associated with transitions from $^3P_j$, $^1I_6$, $^1G_4$ manifolds of Tm$^{3+}$ ions in Yb,Tm:YF$_3$ possesed the similar behavior. Detailed studies of these effects are in progress.

3. Conclusion
Here we have demonstrated a new way to manage fluorescence features of doped bulk and nanosized materials by variation of excitation temporal characteristics. It can be done by variation of pulse length, pulse repetition rate or implementing different types excitation pulses train. Laser-like effect was revealed in Yb,Tm:YF$_3$ single crystal under excitation by rectangular pulse train at 930-980 nm spectral domain. $^3H_4-^3F_4$ transitions of Tm$^{3+}$ ions possess stimulated emission radiation features which appear above certain threshold excitation power and characterized by jump-like evaluation of fluorescence kinetics. This was also observed for higher lying $^3P_j$, $^1I_6$, $^1D_2$, $^1G_4$ manifolds obviously populated due to excited-state transitions and up-conversion process in Yb,Tm:YF$_3$. These results open an opportunity of elaborating high effective upconversionally pumped microchip solid-state lasers.

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