Rise kinetics of up-conversion luminescence under pulsed excitation. Probabilistic model and experiment

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ABSTRACT

A probabilistic model describing the luminescence kinetics in systems of interacting rare-earth ions is proposed. The basic position of the model is that any mechanism of energy transfer between ions can be represented as a sequence of elementary processes. The duration of each elementary process of energy transfer is a random variable. An analytical expression is found for the time dependence of the radiant flux spectral density of ions for any pump modulation and its special case when the durations of elementary processes have exponential distribution laws and the excitation modulation is a rectangular or short pulse. It is shown that the initial stage of this dependence is a power function. The process of energy transfer from the pump radiation to the emitting ion consists of a number of elementary successive stages which determine the exponent. Mechanisms of up-conversion energy transfer under pulsed excitation are considered in systems consisting of ions of two types: donors interacting with pump radiation and acceptors receiving energy from donors. The number of successive elementary processes, of which these mechanisms are composed, is determined. A regression analysis of the rise kinetics of up-conversion luminescence of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} (1 at%) crystal is made using the proposed probabilistic model. The kinetics was obtained under rectangular pulsed excitation by IR radiation of a $\lambda_p = 933$ nm semiconductor laser diode. The most important mechanisms of energy transfer from Yb^{3+} ions to the Tm^{3+} ions responsible for transitions between the ground $^3H_6$ term and excited $^3F_4$, $^3H_4$, $^1G_4$, $^1D_2$, $^1I_6$ terms of the Tm^{3+} ions are established. The durations of these energy transfer processes are determined.

1. Introduction

Upconversion energy transfer in crystals, glasses, organic compounds doped with rare-earth ions is of great practical interest, since it makes it possible to convert the energy of infrared radiation into the energy of visible and ultraviolet radiation [1–6]. There are various mechanisms of up-conversion energy transfer: APTE or multistage one-quantum energy transfer (energy is transmitted in portions approximately equal to the quantum of pump radiation) [1,7], cooperative luminescence sensitization [8,9], multiquantum energy transfer due to stimulated emission or absorption of induced photon groups (a portion of the transmitted energy is equal to two or more quanta of pump radiation) [10,11], photon avalanche [2,12] and etc.

In order to fully control the processes of up-conversion energy transfer and use them for practical purposes, for example, in the optical thermometry of nanoscale structures [13–15], it is necessary to establish which mechanism is responsible for the up-conversion of the radiation energy. Despite the great achievements in understanding the

mechanisms of up-conversion luminescence, the methods of their theoretical and experimental research have practically not changed in the last 50 years. The main experimental technique for determining the mechanisms of up-conversion is to investigate the dependence of the luminescence intensity on the power of the stationary exciting radiation [16,17]. The luminescence kinetics and the dependence of the luminescence intensity on the power in the presence of these mechanisms are calculated mainly by means of systems of kinetic equations [18].

Our theoretical and experimental studies of the up-conversion luminescence of fluoride crystals activated by Yb^{3+}, Tm^{3+} and Ho^{3+} ions excited by IR radiation of a laser diode ($\lambda_p = 930$–980 nm) have shown that using traditional techniques is not always possible to accurately determine the mechanism of excitation energy transfer from Yb^{3+} ions to Tm^{3+} and Ho^{3+} ions. In particular, in [10,11] we found that the dependence on the pump power of the radiation intensity at the Tm^{3+}: $^1G_4 \rightarrow {}^3H_6$ transition in the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} crystal is nonmonotonic. The explanation of this experimental fact with the help of systems of kinetic equations was extremely difficult. Therefore, we constructed a

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theoretical model based on the theory of stationary Poisson processes and the assumption of the dominant role of stimulated emission in the excitation of the up-conversion luminescence of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} crystal. The model successfully explained this nonmonotonic dependence [10,11]. The important role of stimulated emission was confirmed by experimental studies of the luminescence kinetics of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} crystal [19,20]. This was made possible by using a rectangular modulation of the pump radiation and varying the pulse repetition period and duration [19,20]. The correlation analysis of the luminescence spectra, developed and applied by us in [21], also confirmed the important role of stimulated emission in the excitation of the up-conversion luminescence of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} crystal. Finally, using the z-scan technique and analyzing the luminescence intensity distribution in the crystal via photographs of its longitudinal cross sections, we have experimentally observed amplified spontaneous emission of Yb^{3+} ions in $LiYbF_4$ crystal [22,23].

All this variety of theoretical and experimental methods allowed us to conclude that the mechanisms for the formation of up-conversion luminescence of fluoride crystals activated by Yb^{3+}, Tm^{3+} and Ho^{3+} ions differ from the conventional mechanisms described for example in [1,16,17,24-27].

In papers [2,12,26] it was pointed out that the various mechanisms of multiquantum energy transfer should manifest themselves differently in the kinetics of the up-conversion luminescence under pulsed excitation. In particular, in the case of a short pulse (delta-pulse) excitation for the APTE mechanism this kinetics should contain a rising stage, while for absorption processes of photons from the ground and further from the excited states, the rising stage is absent: the kinetics has the form of an exponential decay [26]. This is due to the fact that the absorption of a photon by an ion is an almost instantaneous process, and the transfer of energy from an excited ion to an unexcited one is a process that takes a long time, sometimes comparable in magnitude with the time of spontaneous decay of the excited state. Another example is the rise kinetics of the up-conversion luminescence caused by a photon avalanche. This kinetics, at the initial stage, contains an extended concave region, which according to the authors of works [2,12] uniquely identifies the presence of a photon avalanche.

Our own experimental studies also show that the form of the rise kinetics of up-conversion luminescence under rectangular pulsed excitation depends significantly on the type of energy transfer processes that cause the population of excited states of rare-earth ions. For example, in the Fig. 1, the luminescence kinetics of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+} (1 at%) crystal is shown for four up-conversion luminescence transitions. It is clearly seen that curve 1 differs significantly from curves 2, 3 and 4: it does not have time to reach the steady state during the duration of the pump pulse and is characterized by a weakly expressed concave region at the initial stage. Let us assume that the dependence of the luminescence intensity on time t at $t \to +0$ ($t = 0$ is the moment of appearance of the leading edge of the pump pulse in the crystal) is a power function with a nonnegative exponent k: Intensity $\propto t^k$. Approximation by this function of the initial stages of curves 1–4 of Fig. 1 leads to the following values of the exponent k: $k = 2.04 \pm 0.06$ for curve 1, $k = 3.06 \pm 0.07$ for curve 2, $k = 3.90 \pm 0.14$ for curve 3 and $k = 4.85 \pm 0.16$ for curve 4. Apparently, exact value of this exponent for curves 1, 2, 3, 4 is two, three, four and five, respectively.

Analysis of the differences between curves 1–4 leads to the following conclusions. First, there is a temporal hierarchy of the population of the energy levels $^3H_4$, $^1G_4$, $^1D_2$, $^1I_6$ of the Tm^{3+} ions: at first the level $^3H_4$, then $^1G_4$, then $^1D_2$ and only then $^1I_6$ is populated. Second, energy transfer processes that populate the energy level $^3H_4$ differ from the corresponding processes populating the energy levels $^1G_4$, $^1D_2$ and $^1I_6$. Moreover, apparently, the processes populating the $^1D_2$, $^1I_6$ levels are the child processes, and the processes populating the level $^1G_4$ are the parent processes (see Fig. 2).

Thus, the asymptotics of the rise kinetics of the up-conversion luminescence as $t \to +0$, as well as the dependence of the intensity of this
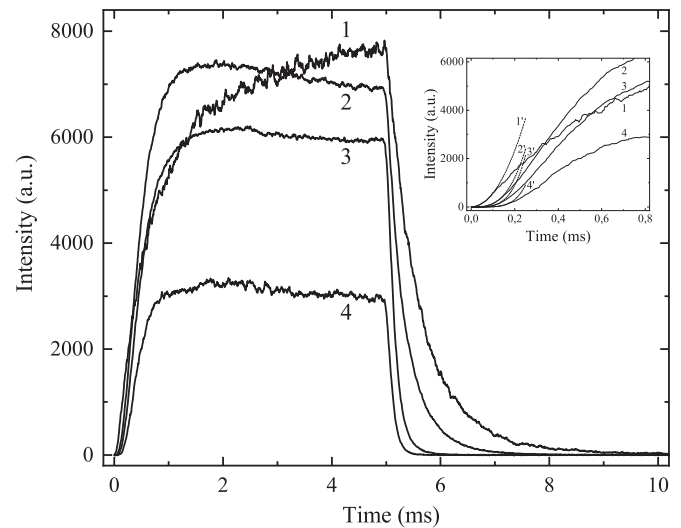
Fig. 1. Kinetics of the luminescence of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+}(1 at%) crystal under rectangular pulsed excitation with a period $T = 16.67$ ms, pulse duration $\Delta t_p = 5$ ms and wavelength $\lambda_p = 933$ nm: 1—spectral line Tm^{3+}: $^3H_4 \to {}^3H_6$, $\lambda_e = 824$ nm; 2—spectral line Tm^{3+}: $^1G_4 \to {}^3H_6$, $\lambda_e = 479$ nm; 3—spectral line Tm^{3+}: $^1D_2 \to {}^3H_6$, $\lambda_e = 363$ nm; 4—spectral line Tm^{3+}: $^1I_6 \to {}^3H_6$, $\lambda_e = 290$ nm. The inset shows the initial stage of the rise kinetics of luminescence, containing a concave region. Lines 1′, 2′, 3′ and 4′ are the approximations by the power function t^k of the initial stages of curves 1 ($k \approx 2$), 2 ($k \approx 3$), 3 ($k \approx 4$) and 4 ($k \approx 5$). The duration of the leading edge of the pulse produced by the infrared laser diode was ≈ 20 μs. This time interval, which does not contain a useful signal, was excluded from the approximation region and is not shown in the figure.
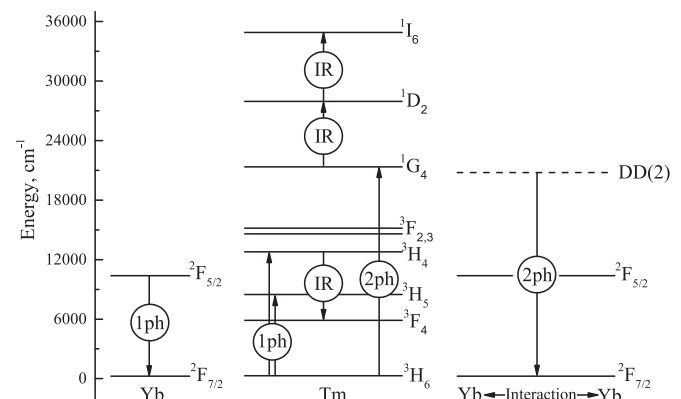
Fig. 2. Most important one-photon (1 ph), two-photon (2 ph) and IR transitions of Tm^{3+} and Yb^{3+} ions of the $Y_{0.8}Yb_{0.2}F_3$: Tm^{3+}(1 at%) crystal. $DD(2)$ is two Yb^{3+} ions (donors), bound by the interaction, that are in the two-quantum cooperative state.

luminescence on the power of continuous-wave excitation, apparently, is a power function with an exponent, depending on the number and physical nature of the processes, causing the population of energy levels, whose radiative transitions form a luminescence. The dependence of the luminescence intensity on the pumping power for different mechanisms of the up-conversion energy transfer is established [18]. At the same time, according to our information, there are no theoretical studies explaining the influence of these mechanisms on the rise kinetics of luminescence under pulsed excitation.

The purpose of this paper is to create a probabilistic model describing the dynamics of the transition of the ion system from the ground state to the excited state and containing the temporal hierarchy of the processes of populating the excited states of these ions. In particular, using this model, we will prove that the initial stage of the rise